

**ON THE PREPARATION, CHARACTERIZATION, AND
APPLICATION OF JANUS SPHERES**

By

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Abstract**ON THE PREPARATION, CHARACTERIZATION, AND APPLICATION OF
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By

JINGQIN CUI

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Surface-anisotropic Janus particles are a new class of materials with interesting properties that have attracted great attention recently. There have been many reports on the manufacture of Janus particles. However, most of them employ the traditional high-cost vapor phase deposition to obtain an asymmetric surface modification of particles.

In this thesis, a novel templating process is developed for the manufacturing of Janus spheres via the economic and mild electroless deposition (ELD) method. Templated micron- and submicron-sized polystyrene (PS) spheres are modified with a silver cap composed of 50-200 nm nanoparticles (NPs) through the ELD process. The deposits are found to be stable over time and under physical treatment. Further, the study determines that the substrate sphere curvature influences the ELD modification due to the functional group coverage and distribution as well as the size ratio of the substrate sphere to the NPs deposit. Gold, palladium and titanium oxide particles are successfully deposited onto PS spheres using the same templating process and nanoparticle synthesis methods from literatures in the electroless/wet chemical deposition.

Modifications obtained with the ELD conditions studied exhibit a rough surface compared to the vapor-phase modified surfaces. The surface roughness is controlled by varying the ELD reaction conditions to adjust the amount of deposit and the size

distribution of the NPs deposited. The assembly of Janus spheres with smooth caps produces planar 2-D structures while spheres with rougher caps tend to form 3-D cluster structures, implying that the surface morphology has an effect on the sphere-sphere interactions. The assembly of new dual-cap/mono-belt Janus particles prepared by combining the vapor phase and ELD processes confirms that the surface roughness influences the orientation of the Janus spheres during assembly.

Janus spheres are then incorporated into electroactive polymers as fillers to enhance the electromechanical performance of acrylate polymer matrixes employing the fact that Janus spheres carry large dipole moments and orient themselves in an electric field. Incorporation of the electric-field aligned Au-caped sPS spheres increase the deformation strain of the tested acrylate polymer dramatically from less than 10% to 80% and decreases the electric field required to below 20 V/ μm .

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Chapter 1 Introduction and Motivation

Research on the self-assembly of structured colloids, from the nanoscale all the way to the supra-micron scale, have grown rapidly during the past 5 years.^[1, 2] Among the many new and exciting assembly blocks of interest, the Janus particle, a particle that carries two hemispheres of different chemical composition, has attracted the greatest attention. The term “Janus” is derived from the Roman god Janus who usually is represented as a head with two faces pointing in opposite directions.^[3] Currently, the synthesis of Janus particles directly from molecular precursors is still facing great challenges and has only been achieved with limited success.^[4] A somewhat simpler approach to a Janus particle is the asymmetric surface decoration of a particle.^[1, 3, 5]

Traditional vapor phase deposition techniques are widely applied for the preparation of Janus particles by taking advantage of their essentially line-of-sight directional deposition.^[6] However expensive production costs limit the application of such technology. In contrast, liquid-phase processes such as electrodeposition, adsorption, and electroless deposition (ELD) require more moderate conditions and have been widely employed for homogeneous surface modification.^[7] Self-catalytic ELD possesses an attractive combination of high selectivity, controllable *in situ* particle growth rates onto complex structures, and low-cost equipment.^[8] However the lack of an easily controllable mask has so far hampered the broad application of ELD towards partial surface modification of micron and submicron-sized particles.^[4]

Janus particles are of great interest when their directional properties are considered for applications such as sensors, stabilizers or rheological probes.^[5, 9] It has been demonstrated that the asymmetry of a Janus particle can cause particles to spontaneously

assemble into specific 2D or 3D structures owing to asymmetric interactions.^[10] Amphiphilic Janus particles, for example, are able to assemble into superstructures and stabilize oil-in-water or water-in-oil emulsions.^[11] Orientation and assembly of Janus particles in external electric or magnetic fields (induced-assembly) have just recently appeared and show a very different behavior from symmetric particles.^[12, 13] Even real-life applications such as electronic color paper has been proposed by Suzuki based on the dispersion of particles with gold cap nanostructures of various shape and sizes.^[14]

The unique and novel properties of Janus particles and overall structural robustness rely on the composition, shape and size of the structure.^[15, 16] Recently, it has been reported that surface roughness can dominate over surface chemistry with regards to particle orientation.^[17] It has also been suggested that a difference in surface morphology affects properties such as surface plasmons.^[5] However, a detailed study of Janus particles with varying surface morphology and the effect of the surface morphology on the directional properties during assembly of Janus particles has not been discussed.

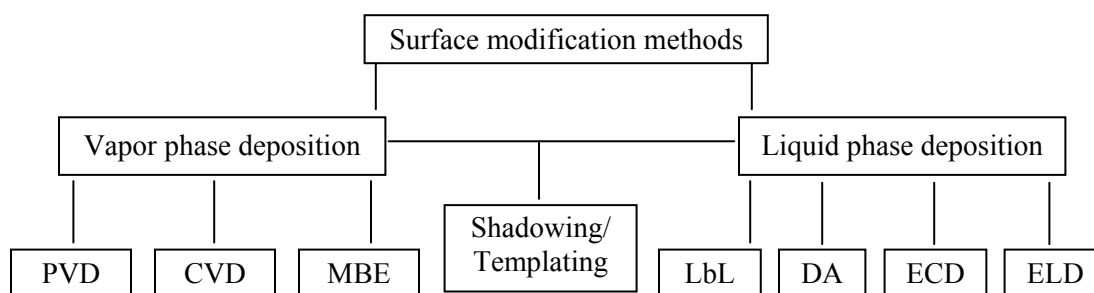
Therefore this thesis strives to develop a procedure to modify particles via asymmetric electroless deposition. A simple solid template is employed in the asymmetric ELD of several commonly used metals to manufacture Janus particles. Further, a detailed study of the effects of various deposition methods and conditions on the surface morphology of the modification is investigated. Once Janus particles of different surface morphology are prepared, the study of self- and electric field induced-assembly of these Janus particles is carried out in order to understand the effect of surface morphology on the relative orientation (interparticular forces) of Janus particles during the assembly and the resulting structure. An electrical application of Janus particles

employing their asymmetric electric property is then introduced as a more applied extension of the academic research.

In the following, a literature review on general surface modification methods will be presented in the Chapter 2 cumulating in a comparison of their applicability, advantages, and limitations as well as the principles for both isotropic and anisotropic surface modification. Chapter 3 focuses specifically on electroless deposition. In particular, commonly used chemicals are reviewed and a discussion of parameters affecting the deposition process and the deposit morphology is presented. In Chapter 4 we summarize all experimental details and procedures that are employed to manufacture and characterize Janus particles. In this project the solid template for partial coverage used is a PDMS mask. Results for partial masking of the spheres and generation of silver-capped Janus polystyrene spheres are given in Chapter 5. Chapter 6 concentrates on the ELD parameters that affect the surface topology of Janus spheres modification and sheds light on the deposition mechanism. With the successful preparation of silver-capped Janus spheres and a deeper understanding of the ELD process, we explore several other materials, i.e., gold, palladium and titania, in partial ELD on PS spheres in Chapter 7. In addition, the surface morphologies of Janus spheres prepared via physical vapor deposition (PVD) and ELD are compared and the convective assembly of the spheres is carried out to study the effect of surface roughness on interparticular forces. Further, an exciting new dual-cap particle type is created by the combination of PVD and ELD. Last but not least, an electrical application of Janus spheres as fillers in electrocative polymers leading to the enhancement of the electromechanical performance of the polymer is investigated in Chapter 8.

Chapter 2 Surface Modification Methods

Most methods currently used to modify surfaces are derived from the original manufacturing processes employed for conventional surface modification.^[18] The two main groups of processes used for the surface modification are (i) vapor phase (VP) deposition and (ii) liquid phase (LP) deposition, while solid phase deposition is rarely used and will not be discussed here. In this chapter, we will briefly review the two categories of methods and their application in surface decoration of micro- and nanoparticles both isotropically and anisotropically.



Scheme 2.1 Structure of chapter 2

As shown in Scheme 2.1, of the VP deposition methods, principles and procedures of physical vapor deposition (PVD), molecular beam epitaxy (MBE) and chemical vapor deposition (CVD) are discussed first, followed by the description of LP deposition methods including layer-by-layer (LbL), direct adsorption (DA), electrochemical deposition (ECD) and electroless deposition (ELD).

The main requirement for anisotropic surface decoration by either liquid- or vapor-phase deposition is that part of the particle surface is shielded from the depositing material, which can either be achieved by shadowing (vapor phase deposition) or by templating (liquid phase deposition). Therefore in both sections 2.1 and 2.2, the

conditions necessary for asymmetric deposition are discussed first, with special emphasis on LP deposition methods.

2.1 Vapor phase deposition

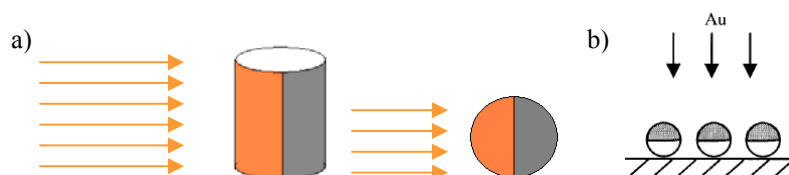
Vapor deposition processes are widely used to form coatings, which alter the mechanical, electrical, thermal, optical, and wear properties as well as corrosion resistance of the substrate. The directional nature of VP deposition extends itself to micro-scale asymmetric surface modification. In a vapor phase deposition,^[19] the to-be-deposited material in its vapor state is condensed through condensation, chemical reaction, or conversion to form a solid film on a substrate surface. Vapor deposition usually takes place within a vacuum chamber.

There are two distinguishable categories of vapor deposition: physical vapor deposition and chemical vapor deposition. In addition, molecular beam epitaxy is usually singled out as a third category owing to its very delicate control of thin film growth although target materials can be deposited both physically and chemically from the vapor phase. All three techniques are summarized following the introduction of the shadowing effect.

2.1.1 Shadowing effect in vapor phase deposition

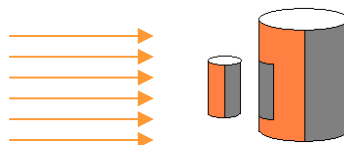
Vapor deposition methods exhibit a directional nature similar to the shadow effect observed when objects are exposed to sunlight as illustrated in Scheme 2.2a. The extension of the shadowing phenomenon to the micro- and nanoscale has been confirmed by many experiments. For example, spheres have been used as masks to produce lithographic patterns on planar substrates^[20] and even on spheres of underlying layers.^[21] One of the earliest applications of shadowing for the generation of surface anisotropic

particles was reported in 1997.^[22] In this publication, a polystyrene sphere monolayer on a polystyrene piece was placed in a high vacuum chamber of an evaporator. Gold was evaporated at a rate of $0.5 \text{ \AA/s}$ and formed a film of 100 nm only on the side of the spheres facing the evaporation source, as depicted in Scheme 2.2b.



Scheme 2.2 a) Shadowing effect; b) Gold evaporated to partial surface of spheres^[22]

Additional control of the vapor deposition process can be achieved by the introduction of a mask. The principle is illustrated in Scheme 2.3. Various masks used in nano lithography involving nanotubes or rods, sphere monolayers as well as proteins can be or have been used to produce patterns on planar or particle surfaces, which are subsequently used in optical, magnetic, and catalytic devices.^[23, 24, 25]



Scheme 2.3 Shadowing achieved by application of a mask

2.1.2 Physical vapor deposition

PVD, consisting of a group of vacuum techniques such as filament (thermal) evaporation, electron-beam evaporation and sputtering, are used for the generation of a vast number of products as diverse as medical implants, cutting tools, decorative fittings and machine components.^[26]

The coating method involves purely physical processes. In the thermal evaporation, metal sources are heated via a resistive filament to their melting point and give off a

vapor of atoms that travel in a straight line to a sample surface and condense there resulting in deposition rates on the order of 1 nm/sec. When the temperatures required are too high for thermal evaporation, thermal emission of electrons from a filament source is used to heat metal sources to higher temperatures. In the case of sputtering, atoms of a solid target material are ejected into the gas phase due to bombardment of the material by energetic ions, high-current arcs or a laser. Subsequently, the atoms condense on the solid substrate atom by atom forming a coating. External heating is often applied to the substrate to enhance the metallurgical bonding between the coating and the substrate.

More specialized PVD techniques include arc evaporation, pulsed laser deposition, ionized sputter deposition, and electron beam physical vapor deposition.^[27] Typically materials formed through PVD are predominantly carbides, nitrides, borides and silicides of a single metal or alloyed elements from groups IV, V, and VI of the periodic system of the elements formed by introducing nitrogen, hydrocarbon, or silanes during the deposition process. Multilayer and superlattices formed by alternately depositing two or more different components are also possible.^[28] One additional advantage of PVD is that some depositions can be done at temperatures as low as 500 °C since there is no melting of the material required for PVD.^[29]

2.1.3 Chemical vapor deposition^[30]

CVD is another frequently used technique for depositing thin films of various materials. Unlike PVD, CVD involves a chemical process. In a typical CVD process, the substrate is exposed to one or more volatile precursors, which react and/or decompose on the substrate surface to produce the desired deposit. Sometimes byproducts are also formed. Fortunately, they are usually volatile and can be removed by gas flow through

the reaction chamber. It is important in CVD that the reaction path converting vapor to solid happens only where and when it is desired. The approaches to achieving this selectivity typically rely on four controllable parameters: temperature, time, pressure, and surface specificity.

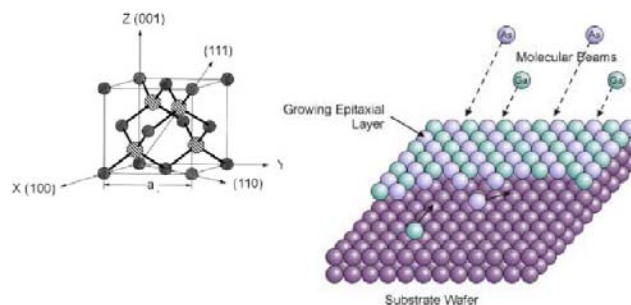
A large number of specialized forms of CVD are in wide use and are frequently cited in the literature, such as atomic layer CVD, plasma-enhanced CVD, remote plasma-enhanced CVD, and rapid thermal CVD.^[31]

With CVD, it is possible to produce films of most metals, many nonmetallic elements such as carbon and silicon as well as a large number of compounds including carbides, nitrides, oxides, intermetallics, and others. Today CVD is widely used in the semiconductor industry, as part of the semiconductor device fabrication process, to deposit various films for microelectronic devices because of its excellent control over film composition. Other important applications are manufacturing of optical devices and the traditional deposition of protective coatings. Synthetic diamonds and carbon nanotubes (CNT) have also been grown by CVD.^[32]

2.1.4 Molecular beam epitaxy (MBE) ^[33]

MBE involves the deposition of one or more pure materials onto a heated crystalline substrate under ultra-high vacuum (UHV) conditions at a controlled very low deposition rate usually on the order of a few Å (one layer of atoms) /s, thus permitting formation of a perfect crystal. The term “beam” means that evaporated atoms do not meet each other or any other gas molecules until they reach the wafer as shown in Scheme 2.4. The “molecular beams” are typically created from thermally evaporated elemental sources.

The evaporated elements or molecules condense on the wafer, where they form compounds or alloys.



Scheme 2.4 Schematic illustration of MBE ^[34]

The beams can be closed off in a fraction of a second, allowing for nearly atomically abrupt transitions from one material to another. Therefore it is possible to control the growth of the crystal layers precisely at a level of a single layer of atoms. Most MBE work has focused on the growth of compound semiconductor “III-V” (three-five) materials, which are combinations of elements from Group III of the periodic table and the Group V elements. MBE is also well suited for “II-VI” materials using the Group II elements and the Group VI elements. Besides, it has been shown that organic semiconductors materials can also be deposited by MBE. ^[35]

The application of MBE focuses on the formation of superlattices for devices used in fiber-optics, cellular phones, satellites, radar systems, displays, and high quality magnetic structures. The precise control of growth rate and real-time monitoring make MBE a powerful tool for fabricating high-quality thin films.

In *summary*, the requirements of high energy, high vacuum, clean environment and ultra purity of the depositing materials for vapor phase deposition result in complicated, delicate, and thus expensive equipment as well as limited output. Therefore vapor phase

deposition methods currently mainly serve to prepare extreme thin films like atomic layers and are used mostly for small substrates.

2.2 Liquid phase deposition (LPD)

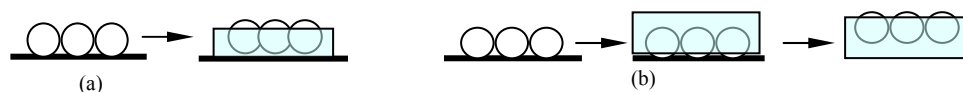
Liquid phase deposition, usually occurring under more moderate conditions, is a wet process used for the formation of metal, alloy, or other material thin films. The deposits homogeneously grow on a variety of substrates, which are in contact with the deposition solution. Therefore unlike vapor deposition, a specially designed templating process other than the monolayer used in vapor phase deposition is usually required. Frequently used liquid phase deposition techniques (Scheme 2.1) and their applications in both isotropic and anisotropic modification are discussed briefly following the discussion of the templating process.

2.2.1 Templating

The most straightforward templating idea is to cover particles partially with a solid film. De Gennes et al. first mentioned this approach in 1991.^[3] They prepared amphiphilic glass microspheres (40–50 μm in diameter) by partially covering the isotropic beads deposited on a solid substrate with a cellulose film of controllable thickness, which can be dissolved after completion of the surface treatment. Only the unprotected part of the microsphere was treated to make it hydrophobic, and the covered part remained hydrophilic. Alga gel and some polymers such as poly(dimethylsiloxane) (PDMS) have also been used as templating materials since then.^[5, 36]

There are two approaches to templating, (a) “bottom” coverage and (b) “top” coverage as depicted in Scheme 2.5. “Bottom” coverage requires the infiltration of the particle monolayer with a solidifiable liquid from the bottom, whereas “top” coverage

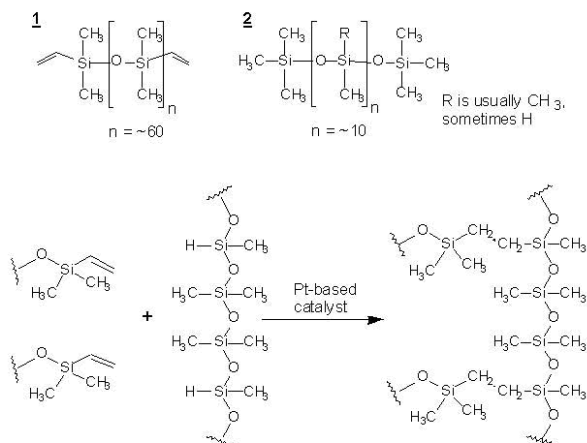
requires the application of a templating material from the top. Both procedures allow the solid template to be prepared easily and the template simplifies handling of the subsequent surface treatment. However, it is rather difficult to control the film thickness and flatness at an acceptable level suitable for nanoparticles if “bottom” coverage as shown in Scheme 2.5a is the goal. “Top” coverage (Scheme 2.5b) is the choice when the spheres strongly adhere to the substrate by electrostatic or chemical interactions, and the viscosity of the templating material is high. In the “top” case, the thickness of the film is not problematic, but rather the flatness of the film critical for uniform coverage is challenging. The “top” method has been used to partially cover particles of ~ 200 nm in diameter.^[5]



Scheme 2.5 (a) “Bottom” Solid Coverage (b) “Top” Solid Coverage

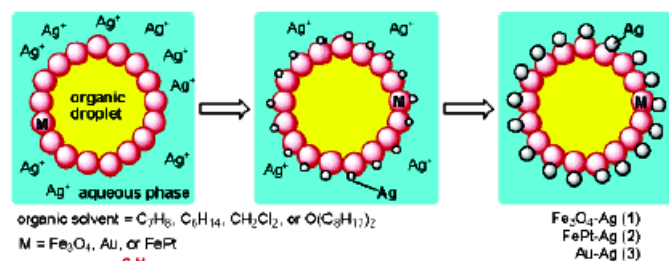
PDMS has been widely used as templating agent in lithography and recently also in biology and nanotechnology.^[37] PDMS is cured by an organometallic crosslinking reaction. The siloxane-based oligomers contain vinyl groups and the cross-linking oligomers contain at least three silicon hydride bonds each. The curing agent contains a proprietary platinum-based catalyst that catalyzes addition of the SiH bond across the vinyl groups, forming Si-CH₂-CH₂-Si linkages as shown in Figure 2.6. The multiple reaction sites on both the base and the crosslinking oligomers allow for three-dimensional crosslinking. The ratio of curing agent to base affects the cross linking and thus the hardness of the cured film. A higher ratio results in a harder, more cross-linked elastomer. Heating accelerates the cross linking reaction.^[38]

siloxane oligomers siloxane cross-linkers



Scheme 2.6 Structure of PDMS base and agent and the cross-linked structure ^[38]

Liquid templating is more easily applied to systems where the particles stabilize themselves at the gas-liquid or liquid-liquid interface. One of the advantages is that the templating portion on the sphere is pre-determined by the physical or chemical properties of the particles and the phases, for example, the contact angel of the particle and the liquid or the specific gravity of the particle.^[36, 39, 40] A stable interface is required since mixing of the phases will disturb or render partial modification impossible. A liquid-liquid interface formed by two immiscible liquids as for example found in emulsions, gives a large interfacial area formed by the numerous droplets. When tiny (diameter < 10 nm) particles can stabilize at the interface, one could imagine the modification of the particle surface exposed to one of the two liquid phases thereby producing anisotropic particles.^[41] Following this emulsion-based route, Gu et al. recently reported the *in-situ* synthesis of snowman-like particles made of two different materials (Scheme 2.7).^[4a]



Scheme 2.7 Schematic of particles stabilized at the oil-water droplet interface and formation of snowman shaped anisotropic particles ^[4a]

2.2.2 Layer by layer deposition (LbL)

The electrostatic layer-by-layer technique is based on the sequential deposition of oppositely charged species onto a charged substrate,^[42, 43] yielding thin films with highly defined structural order, composition, and thickness. First introduced in 1991 by Decher et al. for the assembly of thin polyelectrolyte multilayer films, LbL has been expanded to a wide range of different building blocks (e.g., metal nanoparticles, proteins, clay platelets, virus particles) and substrates.^[43] Some successful examples include the synthesis of colloid/polyelectrolyte core-shell composite particles with good colloidal stability; where the core consists of either sterically stabilized polymer or metal spheres while some coatings are polypyrrole or polyaniline.^[44, 45, 46] Gold nanorods have also been successfully wrapped with bovine serum albumin and polyethylenimine using the LbL technique without aggregation of nanorods.^[47]

The major advantages of LbL deposition from solution are that many different materials can be incorporated in individual layers and the complex film architectures are determined by the deposition sequence only. This technique is a rapid and experimentally very simple way to produce complex layered structures with precise control of layer composition and thickness without manipulation of functional groups on either the

polyionic species or the substrates. These properties not only widen the choice of substrate, but also make LbL the practicable process to get uniform and dense surface coverage.^[42, 48] Even with particles size as tiny as 10 nm, the coating could reach up to more than 20 layers while the resulting core/shell nanoparticles stay so stable that they can be centrifuged and re-dispersed without agitation or ultrasonication.^[49]

However, LbL suffers from the inevitability of layer interpenetration and some variability of interlayer distances. Also the concentrations typically used in the deposition solution are much higher than those required to reach the plateau of the adsorption isotherm in order to ensure that the solutions do not become depleted during fabrication. One or more washing steps are necessary after each adsorption step to avoid contamination of the next step. The adsorption time and conditions vary for different materials. For example, it takes minutes in the case of polyelectrolytes^[50, 51] and hours for gold colloids.^[52, 53]

To date LbL deposition has mostly been employed to prepare multi-layer films (even with nanostructures), deposition on particles has not been fully discussed and there are only a few reports about asymmetric LbL deposition procedures. An alternative one-layer only deposition method, e.g., electrostatic adsorption, has been modified to decorate the surface of microparticles asymmetrically with the help of a covering substrate with opposite charges.^[54]

2.2.3 Direct adsorption (DA)

With the rapid development of nanoparticle preparation techniques, there is an easy and direct way to deposit nanoparticles onto curved particle surfaces via covalent or non-covalent interaction by immersing surface-functionalized particles into the solution of

well-dispersed nanoparticles. Oldenburg and his colleagues have demonstrated that gold nanoparticles can be immobilized on functionalized silica nanoparticles and can be used as nucleation sites for the growth of a thin gold shell.^[55] In close agreement with the attachment of gold colloids on planar silica surfaces, the gold colloid coverage on the silica sphere surfaces is approximately 30%, most likely limited by inter-particle Coulomb repulsion.^[56] Thus, alternative treatments or techniques are necessary when a high percentage coverage up to the complete coverage (a “shell”) is required.

When the proper coverage template is used, particles with both spatial and chemical surface anisotropy can be produced. For example, particles of a specific gravity can spread into a Langmuir-Blodgett monolayer with each particle presenting two sides, one in contact with the gas phase, the other one in contact with the aqueous phase where nanoparticles are to be deposited.^[7a, 57] Similarly, water has been introduced into the organic phase to help particles aggregate at the immiscible water-oil interface and get partially modified with hydrophobic groups at the “outer” surface facing the organic phase.^[58, 59] A porous membrane template was introduced by the Fitzmaurice’s group to immobilize and modify nanospheres asymmetrically.^[7b]

The mono-dispersed particles to be deposited through DA are usually prepared via two wet-chemical processes (chemical solution deposition): (i) reduction-oxygenation process for metal nanoparticles, or (ii) sol-gel process for metal oxides. The former is discussed in detail in the following section, while sol-gel method is described next taking TiO_2 as an example.

Titanium dioxide (TiO_2 , titania) coated surfaces, polymer spheres and hollow shells of TiO_2 have been discussed with increasing interests in recent years for numerous

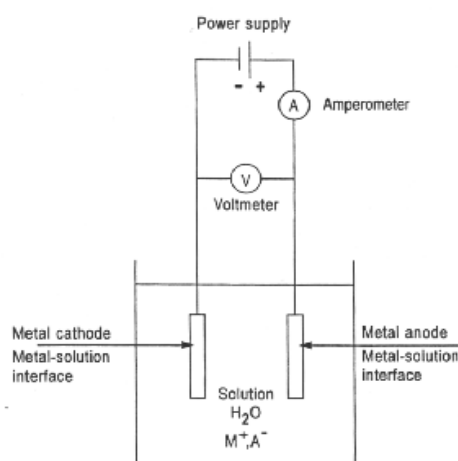
potential applications.^[60, 61] The high vacuum or high energy required for deposition of TiO₂ in vapor phase deposition methods such as CVD^[62, 63, 64] or sputtering^[65] makes liquid phase deposition (LPD)^[66] or the so-called sol-gel process a competitive alternative choice. The “precursor” for a sol-gel process is usually either a chemical solution (*sol*, short for solution) or colloidal particles (*sol* for nanoscale particle) and an integrated network (*gel*) is produced after the reaction.^[67] Typical precursors are metal alkoxides and metal chlorides, which undergo hydrolysis and polycondensation reactions to form a colloid system composed of solid particles dispersed in a solvent. The sol-gel approach is a cheap and low-temperature technique but it allows for the fine control of the product’s chemical composition.

LPD of TiO₂ thin film on indium-tin-oxide (ITO)-coated glass was first reported by Wang’s group.^[68] Coating of TiO₂ onto a substrate surface through an *in situ* sol-gel procedure have been realized such as uniform coatings of TiO₂ on monodisperse spheres of silica and polystyrene.^[60, 69] Further, crystalline silver/titania composite shells have been observed by coating of the as-prepared polymer/silver particles with an amorphous titania layer in a the sol-gel process.^[61] However, combination of a sol-gel process and the asymmetric deposition methods developed in this thesis has not been fully explored.

2.2.4 Electrochemical deposition (ECD)

Electrochemical deposition is usually shortened as electrodeposition. It indicates the coating of an electrically conductive item with a layer of metal using an electrical current. The detailed setup is shown in Scheme 2.8. The substrate to be coated is placed into a container with a solution of one or more metal salts. The substrate is connected to an electrical circuit as the so-called working electrode. A counter electrode completes the

circuit. When an external voltage is applied, metal ions in the solution are attracted to the working electrode resulting in a current flow through the plating solution. At the working electrode, electrons are either added (reduction) or removed (oxidation) from the metal ion resulting in zero-valence metal deposition. Considerable skill and knowledge of the technique are required to assure evenly-coated finished products. The process is regulated by controlling parameters such as voltage, temperature, residence times, the purity of bath solutions, and the geometry of the electrodes. ^[70]



Scheme 2.8 Schematic of an electrolytic cell for electrodepositing metal "M" from a solution of the metal salt "MA" ^[71]

The earliest use of electrodeposition can be traced back to around 1800. These days it is used in many industries for functional and/or decorative purposes. Some well known examples are chrome-plating of steel parts on automobiles, nickel electrodeposition on steel bumpers, and chromium deposition on steel camshafts to improve corrosion and wear resistance. Silver is also electroplated on copper or brass electrical connectors resulting in a more efficient electrical connection. More recently, electrodeposition has been applied in three main areas: metal deposition for the fabrication of integrated

circuits; deposition of magnetic recording devices (heads, discs); and deposition of multilayer structures.

Most commonly single metallic elements are deposited. Alloys can also be electrodeposited, most notably brass. Some metals such as titanium and aluminum can only be deposited from organic electrolytes, while other metals such as zirconium, niobium, tantalum, and tungsten can only be plated from molten salt electrolytes (at 700°C and above) because of lack of water soluble salts.^[72]

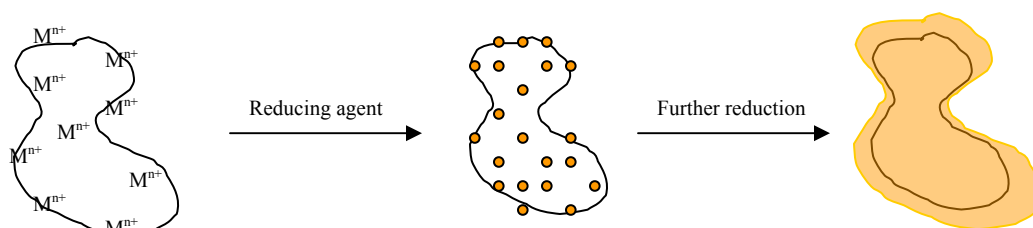
Electrochemical deposition has been attempted at the nanoscale with the aid of scanning tunneling microscopes (STM) or scanning electrochemical microscopes (SECM). Delicate silver pillars, 10-30 nm in diameter and 4-10 nm in height, were generated on a graphite surface using STM.^[73] Semiconductor ZnO nanowire arrays were fabricated by a one-step electrochemical deposition technique employing an ordered nanoporous alumina membrane^[74, 75] or without the aid of a template.^[76] Silver and copper micro- and nanostructures including nanocrystals and nanowires have also been successfully generated by electrodeposition.^[77, 78] A combination of LbL and ECD was applied to deposit gold clusters on an indium tin oxide (ITO) electrode initially modified with six bilayers of poly(diallyldimethylammonium chloride) and poly(4-styrene sulfonate) to fabricate a super-hydrophobic surface.^[79]

With the aid of a porous membrane, e.g., Nafion, and an appropriate electrode, the electrochemical deposition has been limited to occur only at the designed area.^[80] However, due to the requirement of electrodes, usually a planar and electrically conducting substrate, surface asymmetric modification of particles might require a special and complicated template, which limits the application of ECD in asymmetric

deposition. Recently, short carbon nanotubes have been selectively modified on one end with a metal using a bulk technique based on bipolar electrochemistry with the help of a capillary and a high electric field.^[81]

2.2.5 Electroless deposition (ELD)^[82]

The principle of electroless deposition, also called chemical deposition or autocatalytic deposition, is similar to that of ECD. In contrast to ECD, the electrons are not provided by an external source, but rather by a chemical reducing agent added to the metal salt solution. Metal cations are reduced to zero valent metal and deposited only on surfaces, which have been catalytically activated prior to the reaction. This non-galvanic deposition process usually involves several simultaneous reactions in the aqueous solution. The probability for deposition is essentially equal at all points of the surface as illustrated in Scheme 2.9. Thus, very uniform coatings independent of the objects shape and size can be achieved. This is particularly useful for some surfaces such as irregularly shaped objects, holes, internal surfaces, or threaded parts.^[83]



Scheme 2.9 Electroless deposition of metal on substrate. M^{n+} : metal cations, ● metal clusters

The deposition rate is usually slow and the achievable coating is less than 50 μm in practice because of the slow deposition rate. Adjustment of critical parameters such as metal precursor concentration, reducing agent concentration, pH, temperature, and

agitation enables easy control of the deposition process. Noble metals with good resistance to corrosion or oxidation, e.g., silver, gold, palladium, platinum or their alloys, have been widely deposited onto surfaces using ELD and the techniques are fully developed. Nickel, copper, and cobalt ELD have also been industrialized and realized in high-throughput processes. ELD results in a fine-grained metal deposit similar to traditional electroplating finishes. The advantage compared to ECD is that ELD can be used to deposit a conductive surface on a nonconductive object such as plastics once the surface has been activated. A more detailed discussion on fundamentals and applications of ELD will be given in Chap. 3.

The *in situ* growth of an ELD film on particles has been used very frequently and the techniques are fairly developed. Deposition of metals such as gold, silver, palladium, platinum, nickel and copper on polymer^[84, 85] or silica spheres,^[86] nanotubes,^[87] nanowires,^[88] and even viruses^[89] and studies discussing the application of the manufactured core-shell structures have been published.

Asymmetric or surface-anisotropic ELD on nanoparticles was first developed by Halas group with the introduction of a PDMS film, which partially covers the functionalized silica nanoparticles that are deposited onto an oppositely charged substrate. With the approach discussed in Scheme 2.5, they achieved silica nanoparticles with a gold cup-shaped shell and a gold cap^[5]. Gu et al.^[4a] also reported the snowman-like particles made of two different materials with the aid of an oil-water droplet interface (Scheme 2.7).

In *summary*, LP deposition methods have been widely used in the manufacturing of core-shell structures employing their characteristics that all exposed surface get a

homogeneously deposit. In the asymmetric deposition cases, a specially designed templating procedure is necessary to employ LPD compared to VPD. However, it is receiving more and more attention as an economic, moderate choice, which in addition provides access for the deposit of various materials.

2.3 Summary of surface modification methods

As a result of the methods reviewed, we chose electroless deposition as the method of choice to achieve decoration not only because of its simple equipment requirement, moderate and easy-to-control operation, high-throughput in short time and stable deposition on various kinds of materials, but also because it can be used to decorate particles both symmetrically and asymmetrically using the same equipment, chemicals, and reaction conditions while only a proper template is needed for the latter type of decoration. In addition, ELD provides access to metals, alloys and other materials as long as the proper precursor and reducing agents are provided. The template, which is necessary for anisotropic modification by a liquid-phase deposition method, is used to protect the area that should stay free of deposit. For ELD where there are many chemicals and the reaction bath is always stirred, templating based on an inert solid is the first choice. In this project, the inert solid cover for templating is a PDMS film.

Chapter 3 Electroless Deposition

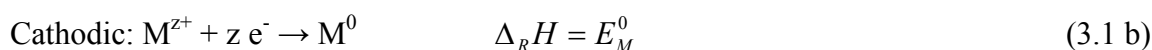
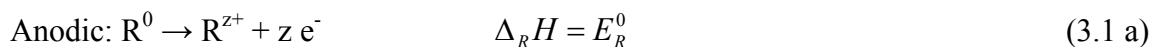
Since first presented by Brenner and Riddell in 1946,^[90, 91] electroless deposition (ELD) has been used in a number of important technological applications including the fabrication of integrated circuits and the production of new materials for electronics, medicine, and batteries as well as new wear and corrosion resistant materials. Numerous electroless-plating bath compositions containing metal precursors, reactants, and reducing agents at particular pH values have been developed over the last decades for conventional deposition. In this chapter, we will illustrate the electroless process in general and then more specifically for silver deposition. Further, we will discuss parameters controlling the deposition process. Next, we will summarize the deposition conditions for several other frequently used metals, i.e., gold and platinum group metals. We will conclude with a brief discussion of advantages and disadvantages of ELD.

3.1 General principle of ELD

ELD is defined as an autocatalytic process during which a metal is reduced and deposited in the absence of an external source of electric current. The metal ions from a metal salt solution are reduced by addition of a chemical reducing agent, which provides electrons for the reduction. As a result the reduced metal atoms deposit as a zero-valence metal coat onto a catalytically active surface. In some cases, light is employed as a reducing agent and the radiolytic process is then called photoreduction. In the ELD process, the driving force for the reduction-oxidation (red-ox) reaction is the red-ox potential, which is a measure of the electron affinity of a species relative to that of hydrogen, which is set to zero. The red-ox potential is essentially constant at all points of the surface to be coated, provided the agitation of the system is sufficient to ensure a

uniform concentration of metal ions and reducing agents. Deposits can therefore be very uniform in thickness independent of the shape and size of the coated object.^[92]

In contrast to ECD, where the two reactions happen at different electrodes, the cathodic (reduction) and anodic (oxidation) reactions occur both on the working surface in ELD as described in Equations 3.1 a and b,



A condition necessary for deposition to occur is that the equilibrium potential for the reducing agent E_R^0 is more cathodic (i.e., more negative and reducing) than the corresponding potential E_M^0 for the metal deposition reaction. Recently, electroless metal deposition processes have been identified as mixed potential systems.^[93] The theory for mixed potential systems was originally developed by Wagner and Traud for corrosion processes.^[94] It postulates that the rate of a faradaic process does not depend on other faradaic processes occurring simultaneously on the same electrode and therefore depends only on the electrode potential. As a result of this postulate one can add the polarization curves for anodic and cathodic processes to predict overall rate and potentials for such systems and *vice versa* find individual rates from the overall measured rate.

The electrode reactions can either be controlled by the rate of diffusion of the reactants to the plating surface (i.e, reaction under diffusion control) or by the rate of an electrochemical reaction step (i.e., reaction under electrochemical control). This yields four possible combinations for two electrode reactions. However, the cases where both reactions are either diffusion or electrochemical controlled are rarely observed.^[95] Diffusion and electrochemically controlled processes maybe distinguished by variation of

the reactant concentrations and the temperature of the reaction medium, i.e., increased concentrations will enhance diffusion-controlled processes, while elevated temperatures will accelerate electrochemically controlled processes.

It has been suggested that the mechanisms can be predicted from the polarization curves for the partial processes.^[95] Polarization curves are obtained when the mixed potential E_{MP} is plotted as a function of the plating rate. At equilibrium, the Wagner-Traud postulate^[94] applies and the plating rate, i_{plating} , is given by

$$i_{\text{plating}} = i_R = |i_M| \quad (3.2)$$

where i_R and i_M are the anodic and cathodic partial currents with opposite signs. The potential associated with this dynamic equilibrium condition is referred to as the mixed potential E_{MP} , which lies between E_R^0 and E_M^0 and depends on parameters such as exchange current densities (i_R^0 and i_M^0), Tafel slopes (b_R and b_M),^[96] and temperature. In the case of a large cathodic current density (i), the current as a function of overpotential (η) can be written as Equation 3.3:

$$\ln i = \ln i_0 - \frac{\alpha n F \eta}{RT} \quad (3.3)$$

where α is the cathodic electron transfer coefficient, F is Faraday's Constant, and n is the number of electrons transferred in the reaction. Solving for the over potential η gives Equation 3.4:

$$\eta = \frac{2.3RT}{\alpha n F} \log i_0 - \frac{2.3RT}{\alpha n F} \log i \quad (3.4)$$

This corresponds to an early empirical equation given by Tafel (1905), Equation 3.5

$$\eta = a - b \log i \quad (3.5)$$

where b is the Tafel slope that provides information about the mechanism of the reaction, and a is the current exchange density which provides information about the rate constant of the reaction. Plotting η over $\log(i)$ yields a and b . The relation between η and E_{MP} is given in Equation 3.6.

$$\eta_R = E_{MP} - E_R^0 \text{ and } \eta_M = E_{MP} - E_M^0 \quad (3.6)$$

However, recent investigations also indicate that the two electrode reactions are sometimes interdependent and thus the Wagner-Traud postulate needs to be applied with caution.^[95]

3.2 Parameters affecting ELD

It is evident from the description of ELD above that the choice of reducing agents and metal precursors will undoubtedly affect the deposition process and quality. Further, the metal precursor concentration and the temperature of the plating solution will certainly influence the deposition when the electrode processes are diffusion and electrochemically controlled, respectively.^[97] Another ingredient of the plating bath is the stabilizer. The primary function of stabilizers is to help maintain overall solution stability by preventing plate-out on the bath surfaces and spontaneous metal reduction in solution. During the deposition, the metal salt and reducing agent will be depleted near the to-be-plated surface because of reaction and thus the stirring rate and agitation of the plating solution may enhance mass transfer toward the depleted regions resulting in more efficient plating. The pH of the plating solution is another parameter that can be tweaked and is likely to have an effect on the red-ox potential by stabilizing or destabilizing intermediates and transition states. In addition to the properties of the plating solution, the substrate surface itself will also have an effect on the plating rate and the film quality, the

more evenly the surfaces is covered with active sites the lower the porosity and the better the coverage of the film will be. With the correct pretreatment sequence and accurate process control, good adhesion and excellent service performance can be obtained from an electroless deposit material on a multitude of metallic and non-metallic substrates.

3.2.1 Components of a plating bath and their concentration

Typically, the constituents of an electroless deposition solution are: a source of metal ions, a reducing agent, suitable complexing agents, stabilizers/inhibitors and energy (temperature).

The preferred **sources of metal cations** are various for different metals and are determined by cost of metal salts, its oxidation ability, reducing agents employed, special pH or temperature requirement, if an alloy of the metal and phosphorous or boron is desired or not, and some other factors influencing the operation, stability and deposit of ELD. Some examples are: silver nitrite or silver acetate for silver ELD; $\text{KAu}(\text{CN})_2^-$ for gold deposition, while nickel sulfate is mostly used in nickel ELD (the ideal nickel cation source is its salt of hypophosphorus acid, $\text{Ni}(\text{H}_2\text{PO}_2)_2$).

The **reducing agent** plays an important role in the ELD technique since its ability to reduce the metal ion determines the driving force for the deposition process. Riedel summarized the properties of various reducing agents used in industrial ELD (Table 3.1).^[98] Commonly used reducing agents include hypophosphite, borohydride, and alkylamine boranes of the general formula $\text{R}_3\text{N-BH}_3$. While the use of borohydride is limited to highly alkaline media because of their weak basicity, amine-boranes are used for mildly alkaline, neutral, or mildly acidic solutions.^[99] Hydrazine is a powerful reducing agent that works both in acid and alkaline media. When hypophosphite is used

as reducing agent a limited utilization efficiency of 35% is acquired because of side reactions that give elemental P and molecular hydrogen.^[82] Borohydrides are also widely applied as reducing agents where elemental boron may also form as a side product. Metal alloys of phosphorus or boron $M_x(P \text{ or } B)_y$ or amorphous deposits may form very often when there are side reactions. These P or B incorporations in the metal deposits are strictly prohibited in some applications. In such cases, the use of hydrazine as a reducing agent is required to produce 97–99% pure metal deposits with the balance consisting of nitrogen and oxygen with other trace elements.^[82]

Table 3.1 Redox Potentials of Reducing Agents versus Normal Hydrogen Electrode (NHE) ^[98]

Reducing agents (available electrons)	Red-ox potential (vs. NHE), V
Sodium hypophosphite (2)	-1.40
Hydrazine (4)	-1.16
Dimethyl amine borane (DMAB) (6)	-1.20
Diethyl amine borane (DEAB) (6)	-1.10
Sodium borohydride (8)	-1.20

The metal ion and reducing agent concentrations and their molar ratios are also important variables. Deposition on a suitable substrate was shown to occur over a quite wide range of nickel and hypophosphite concentrations, however, to achieve optimum plating conditions, a narrow, more limited concentration range for hypophosphite was required. Also the molar ratio of $Ni^{2+}/H_2PO_2^-$ was found to be within a preferred range of 0.30 to 0.45.^[82, 100] The dependence of the deposition rate on reactant concentration is limited within a small range of concentrations, which is usually pretty low and not employed in commercial deposition baths. In the case of $Ni^{2+}/H_2PO_2^-$, the deposition rate does vary as a function of $Ni^{2+}/H_2PO_2^-$ molar ratio ^[101] and the phosphorus content of the deposit also varies with the changing of nickel ion or hypophosphite concentration.

The additives referred to as **complexing agents** in ELD are mostly organic acids or their salts such as acetate, hydroxyacetate, malate or citrate. Inorganic compounds are sometime used in limited cases, e.g., pyrophosphate anion is used exclusively in alkaline Ni ELD solutions. It has been summarized by Mallory ^[82] that the three principle functions of complexing agents are: (i) to reduce the concentration of free metal ions; (ii) to prevent the precipitation of metals salts and (iii) to exert a buffering action that prevents the pH of the solution from decreasing too fast. Theoretically, all three functions are reflecting the influence of the ligand concentration on the rate of the deposition reaction.^[102] The difference in the rate of deposition between two plating solutions containing different complexing agents is also discussed and the reason is attributed to the differences in magnitude of the stability constant of the two metal complexes. In addition, the nature of the complexing agent determines whether the metal complex remains in solution or precipitates.

During the deposition, bath decomposition and the formation of precipitate of insoluble metal salts may occur to form insoluble metal alloys, basic salts or metal hydroxides that precipitate at operating pH. The precipitate, in turn, acts as a highly efficient catalyst, thus triggering a self-accelerating chain reaction in the solution instead of on the surface to be modified. Therefore, **stabilizers** are used to prevent the initial homogeneous reaction. Gutzeit ^[101] pointed out that most stabilizers (or inhibitors) are identical with the materials that prevent the hydrogenation/dehydrogenation catalysis. The most effective stabilizers include compounds of Group VI elements, compounds containing oxygen, heavy metal cations or unsaturated organic acids. Only a trace amount of stabilizer is necessary to avoid the “death” of the deposition bath. Stabilizers from the

first two classes can function effectively at concentrations as low as 0.10ppm. Actually, their concentration can be very critical: the plating reaction can be completely inhibited by adding too much stabilizer, e.g., over 2 ppm.

Catalytic reactions require **energy**, which is supplied in the form of heat, in order to proceed. The energy added to the system is also one of the most important factors affecting the kinetics and rate of the deposition reaction. Ni ELD, if any, is almost ignorable at temperatures below about 60 °C. It was proven that the rate of the deposition reaction is dependent on temperature in an exponential manner until the temperature exceeds some critical value and the relationship, interestingly, is independent of the acidity or alkalinity of the solution. The comparison of two Ni ELD solution baths containing citrate and pyrophosphate, respectively, showed a considerably higher deposition rate in the pyrophosphate bath at equivalent temperatures. But it is worth mentioning that too high temperatures may accelerate the solution plate-out or even cause solution decomposition. Also the impurity content of the deposit may be affected by temperature variations. For example, the phosphorus content of nickel deposits is decreased when the temperature of the depositing bath is increased beyond its normal operating range.^[103]

3.2.2 Effect of pH

In the plating bath, the pH of the bath solution changes with the reactions proceeding due to accumulation of hydrogen or hydroxyl ions depending on the reducing agents employed. For example, in both acidic and alkaline Ni ELD baths, the pH decreases following the accumulation of hydrogen ions. The change of pH during the deposition process affects mostly the rate of deposition. The rate change might be attributed to the

difference of the red-ox potential for reducing agents at different pH values.^[82] In an acidic Ni deposition with hypophosphite, the decrease of the solution pH resulted in a lower deposition rate. The rate changed from more than 20 $\mu\text{m/hr}$ to less than 3 $\mu\text{m/hr}$ when the pH dropped from 6.0 to 4.0 at the given reaction conditions. The deposition rates of copper and silver ELD are also affected by variation of the pH of the reaction bath. In some cases, a basic metal salt or complex precipitates as the result of a too far drop of the pH value. Sometimes a decrease in the deposition bath pH is not harmful since it helps to incorporate a higher content of phosphorus. When the content of phosphorus in Ni-P deposits is in excess of 10 percent by weight, the alloy will produce good corrosion resistance, low porosity and a non-magnetic surface.^[82] But still, it is of essential importance to maintain a relatively constant solution pH during the deposition. Fortunately, there are buffers that stabilize the solution pH value because of their ability to neutralize both acids and bases without appreciably changing the original pH. Commonly used buffers are some organic acids such as acetic and succinic acid. Addition of ammonium or other weak bases is necessary to monitor the bath pH since even the most efficient buffers will not prevent the pH from eventually dropping. Note, the concentration of metal salts and reducing agents may also affect the pH of the bath solution.

3.2.3 Effect of agitation

Agitation is not a primary factor affecting the deposition, but proper agitation allows uniform distribution of depositing chemicals and helps to eliminate localized product accumulation or overheating.^[82] It has been reported that air agitation of Ni ELD significantly enhances the stability of the plating bath, too. While agitation introduces air

to the bath, filters are used to keep dirt out of the deposition bath. In lab-scale studies, modest stirring is enough to provide sufficient solution movement.

With such a complicated system, it is predictable that the effects of each compound are not independent from each other. For example, effects of DMAB (reducing agent) concentration and bath temperature on the deposition rate in Ni ELD were found to vary in magnitude at difference pH levels. Overall, when operating the deposition bath, it is necessary to know which conditions yield deposits with the desired properties with minimum cost and difficulty as well as optimum efficiency.

3.3 ELD of sample metals

As already stated, many noble metals, e.g., silver, gold, palladium, platinum or their alloys, have been widely deposited onto surfaces using ELD and the techniques are fully developed. Nickel, copper, and cobalt ELD have also been industrialized and realized in high-throughput processes. Here we briefly introduce the deposition conditions for several metals and summarize recent developments in nano- and microscopic deposition.

3.3.1 Electroless silver deposition

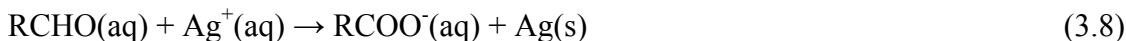
Silver has the highest electrical and thermal conductivity of any metal. These properties make silver widely applicable in electrical and electronic products. In addition, silver is employed as the reflective film for mirrors when high reflectivity is required. In the context of this thesis, we concentrate on the electroless deposition of silver onto spherical and curved surfaces, which has been widely studied in numerous labs for potential application in many areas.^[42, 86a, 104, 105, 106, 107, 108] These studies show that the coating is composed of numerous tiny grains or particles of nanometer size. In most cases, metal nanoparticles smaller than 100 nm were obtained by adjusting the

concentrations of chemicals and other reaction conditions. Xia et al.,^[109] for example, found grains in their silver films with diameters ranging from 30 to 60 nm for a silver film thicknesses of ~40 nm.

As discussed above, the two most important compounds in an ELD process are the reducing agent and the metal salt. In the case of silver, formaldehyde is typically used as a mild reducing agent in the presence of ammonia, while different silver salts such as AgNO_3 ,^[110] and $\text{Ag}(\text{CH}_3\text{COO})$ ^[104] have been employed as precursors for Ag^+ . For example, mirrors can be manufactured using the following reaction:



where R is an organic group or hydrogen. If R is hydrogen (H), the reducing agent is formaldehyde. Other reducing agents have been employed such as potassium tetrahydroborate, hydrazine, tannis, and hypophosphite under certain reaction conditions.^[104] Although a variety of procedures and reagents have been studied,^[111, 112] their fundamental mechanism can be traced back to Tollens' process, equation 3.8:^[113]



3.3.2 Electroless nickel, cobalt, and nickel alloy deposition

Brenner and Riddell first reported autocatalytic chemical deposition of cobalt and nickel films from aqueous solutions of the metal chlorides or sulfates on a catalytic surface.^[114] Over the past years, microscopic electroless nickel plating has been well commercialized because of the various applications of and the increased need for Ni coatings. Consequently, deposition of nickel might be the most developed and understood procedure. A table summarizing the primary components that make up a typical

deposition bath can be found in the literature.^[115] The balance and controlled administration of these constituents are necessary for successful operation.

Catalytic activation of the surface is required to initiate electroless nickel deposition. Palladium (Pd) is the most common choice of catalyst (for details on deposition see below).^[116] The uniformity of the palladium coverage ensures simultaneous, uniform nickel initiation across the sample.^[117] Ruthenium has also been used successfully as catalyst.^[118]

Recently, nanoscale nickel deposition has received increased attention because of the growing interest in construction of functional nanoscale materials and devices. One example is the deposition of Ni on Al₂O₃ ceramic powders to reinforce the Al₂O₃ matrix and increase its fracture toughness.^[119, 120] A successful deposition of a film with the thickness of about 20 nm from NiSO₄·6H₂O reduced by NaH₂PO₂·H₂O in the presence of NaC₂H₄O₂ as a complexing agent was reported.^[121] Tzeng et al.^[122] used sodium hypophosphite as reducing agent for nickel sulfate in the deposition of nickel onto carbon nanotubes with sodium citrate and sodium potassium tartrate as complexing agents. Pinto et al.^[123] used the same metal source and reducing agent, but different complexing agents (complexors) and got approximately 100 nm uniform metal film coatings after exposing the sample for 20 min to a 50 °C Ni bath.^[124]

3.3.3 Electroless gold deposition

Gold is the most malleable and ductile metal known to man. It is a good conductor of heat and electricity. Gold is relatively stable metal and will be little if at all affected by air, heat, moisture, oxygen or most corrosive agents. As a soft metal, it will readily form alloys with many other metals. Thin layers of gold are usually electrolytically or

electrolessly plated on the surface of electrical connectors to avoid oxidation and ensure good connection. A typical commercial electroless gold bath formulation contains KAu(CN)_2 as the source of gold ions and either potassium borohydride (KBH_4) or dimethyl aminoborane (DMAB) as the reducing agent. Other compositions include potassium cyanide (KCN) as stabilizer and aqueous potassium hydroxide (KOH) as the supporting medium. Small amounts of organic chelating agents such as citric acid, ethylenediaminetetraaminoacid (EDTA), and inorganic catalysts like Pd^{2+} and Ti^{2+} are added to complex undesirable metallic contaminants and increase the plating rate.

Electroless deposition of gold films onto spherical and curved surface has been studied in many laboratories because of the unusual catalytic, optical, and electronic properties of nanometer sized gold particles.^[55, 125, 126] Electroless deposited gold films in capillaries have been applied for high-sensitivity electrochemical detection of catechol and several nitroaromatic explosives.^[127] The 79 nm thick films inside the capillaries were analyzed to consist of gold aggregates in the range from 100 to 150 nm. Gold films have also been successfully deposited on polystyrene^[42] and silica spheres,^[126] carbon nanotubes^[108b] and even viruses.^[89] Single crystalline and polycrystalline gold particles as small as 3-4 nm were also observed.^[126]

3.3.4 Electroless deposition of platinum group metals

The platinum group metals (PGMs) are known to be good catalysts for various chemical and electrochemical reactions, thus the production of such catalytic surfaces with a range of particle sizes and surfaces are of prime importance. Electroless deposition of palladium and platinum are the two most extensively studied subjects among the platinum group metals. Palladium has many applications in electronic, magnetic, and

catalytic fields. Electroless deposited platinum films are mainly applied in the medical field because of the biological inertness of Pt.^[99]

For platinum electroless deposition, Rhoda and Vines developed a process by employing hydrazine as reducing agent and sodium hexahydroxy palatinate as precursors in late 1969.^[128] A more efficient bath proposed by Leeman et al. was based on hexachloroplatinic salts and hydrazine. There are two different processes for Pt ELD; one for the alkaline and the other for the acidic pH range.^[129] The acidic process uses hexachloroplatinic acid and hydrochloric acid at 60–70 °C and the reduction to platinum metal by hydrazine. In the alkaline process the same metal salt and reducing agent are employed, but addition of ammonium hydroxide leads to $(\text{NH}_4)_2 \text{PtCl}_6$ formation and a change in the red-ox potential.

This decade also observed the soaring interest in controllable, nanometer sized PGM particles. Wang et al. deposited 2-nm-diameter Pd seeds by anchoring of tetraaminepalladium ($\text{Pd}(\text{NH}_3)_4^{2+}$) from aqueous solution to PAA carboxylic acid functionalities in a polymer film and subsequent reduction.^[130] Johansson et al. defined the size of the nanoparticles between 6 and 11 nm by repeating the deposition process several times.^[131] They also found that a higher Pd concentration led to larger particles.

3.4 Advantages and limitations of ELD

There are many advantages to the application of electroless deposition for metal and alloy coatings; (i) electroless processes are autocatalytic and require no external current supply, (ii) ELD will plate onto any shape as long as the surface is catalytically active and in contact with the solution, (iii) ELD can deposit metal on non-conducting materials such as plastics and glass allowing its use for providing the initial metallic film needed

for any subsequent electrodeposition or electroless coating, (iv) ELD baths are simple to operate and perform over a range of moderate temperatures and concentrations, (v) the equipment is relatively simple compared to that of chemical and physical vapor deposition processes where sophisticated vacuum reactors, induction coils and other equipment are required, (vi) a uniform deposition leading to thin films with high purity is possible in ELD, e.g., silver and platinum films with 99.9 % purity can be generated.

There are also limitations to ELD. While the set up is simple, the solution composition is usually complex and tight control of the chemistry is required. A detailed study on deposition conditions is necessary before scaling up although complicated operation skills are not required to get a controlled deposit. Poor control may result in free metal particles in the plating bath, which may accumulate on the surface, or produce a rough surface finish. The control over film thickness is not as precise as in a vapor deposition processes. The chemicals used in ELD are more expensive than conventional electro-deposition chemicals and the plating bath has a shorter life span. Co-deposition of impurities is possible.

3.5 Summary

In summary, ELD is an easily controlled, cost effective, versatile, moderate process for deposition of various metals and alloys onto substrate of almost any kind of material (conducting, semiconducting, and insulating) and any shape.^[132] Deposition of metals (silver, gold, and palladium) and metal oxides (titanium oxide) has been studied in this project, with a detailed investigation of silver ELD procedure to control surface morphology.

Chapter 4 Experimental Procedures and Details

In this chapter, we present the detailed procedures used in this project starting with the symmetric silver electroless modification of microspheres, followed by sphere monolayer preparation, templating of the sphere surface with PDMS, and asymmetric modification of the partially covered spheres. Given the successful selective decoration with silver, deposition of other materials, i.e., gold, palladium, and titanium dioxide (sol-gel process), onto partially covered spheres are also described.

4.1 Symmetric electroless deposition of silver decoration onto microspheres

Research on the fabrication of polystyrene (latex) or silica micro-spheres with symmetric silver or gold metal decoration via electroless deposition has been widely published as reviewed in Chapter 2.2 and forms an excellent basis for this part of the project. We have chosen to deposit silver onto sulfate polystyrene (sPS) spheres or aliphatic amine polystyrene (aPS) spheres with diameters ranging from 2.6 μm to 0.5 μm (available from Interfacial Dynamics Corp. or Invitrogen) in our initial experiments. Very little has so far been published on the asymmetric surface decoration of sPS spheres or aPS spheres through electroless deposition. Therefore we will first test the practicability of controlled metal deposition onto the surface of the sPS or aPS micro-spheres. For this purpose we need to decide which metal precursor, reducing agent, protecting agent and which concentrations to use whereby our choice will be guided by the overall surface charge of the spheres; for sPS spheres, negative ($-\text{SO}_4^-$) and aPS spheres, positive ($-\text{NR}_x\text{H}_{4-x}^+$).

Based on the data available in the literature,^[3] silver acetate ($\text{Ag}(\text{CH}_3\text{COO})$) is chosen as the silver precursor, and formaldehyde (HCHO) is the reducing agent in the presence

of ammonia ($\text{NH}_3 \cdot \text{H}_2\text{O}$) as complexor. In a typical bulk electroless deposition reaction, a small amount, e.g., 200 μL , of a sphere suspension (used as received, 8 wt% for 2.4 μm sPS spheres and 0.99 μm sPS spheres, 2.1 wt% for 2.6 μm aPS spheres, and 6.6 wt% for 0.51 μm and 0.47 μm sPS spheres) and 200 μL 0.01 M silver acetate solution (prepared from silver acetate powder, 99%, Sigma-Aldrich) are mixed in a 20 mL glass vial, and deionized water is added to reach the total volume of 1.5 mL. It has been observed that association of silver precursor to the PS spheres surface helps the deposition,^[126] therefore the liquid mixture is stirred at a specific stirring rate (120-180 rpm) for at least 4 hours to help the anchoring of the precursor. It is necessary to keep the liquid in the dark by covering it with aluminum foil to eliminate the interaction of silver precursor with ambient light.

After the anchoring pre-treatment, 0.08 mL 1.0 N aqueous ammonium hydroxide ($\text{NH}_3 \cdot \text{H}_2\text{O}$, Acros Organics) is added into the stirred liquid mixture and stirred for additional 5 min at the same stirring rate. Then 0.04 mL of 12 wt% formaldehyde (HCHO , diluted from 20 wt%, Tousimis Research Corporation) is added and the mixture is stirred for another 5 min. During the process of the anchoring and reduction-oxidation reaction, the reaction liquid is kept at room temperature. Milli-Q water is employed for all dissolving, dilution and rinsing steps.

The spheres are collected via centrifugation with a tabletop centrifuge (Minispin, Eppendorf) after deposition. The self-settled reaction solution is placed into 2 mL centrifuging tips and centrifuged at 5000 rpm, or higher speed for smaller spheres, for 5 min. Then the supernatant is removed and the bottom sediment is rinsed once and re-suspended with DI- H_2O by 1 minute of 40 kHz ultrasonication (Branson Ultrasonic

Cleaner 1510). The centrifuging step is repeated twice. Finally the spheres are recovered with only 20 μL DI- H_2O per tube. One drop of the concentrated sphere suspension is dried on a piece of clean silicon (110) wafer with a native oxide surface (University Wafer) and analyzed with the variable-pressure scanning electron microscope.

4.2 Asymmetric electroless deposition of silver decoration onto spheres

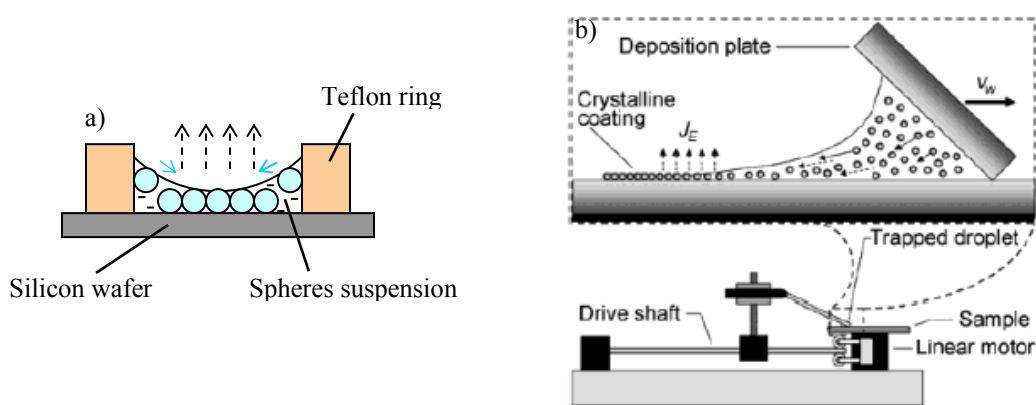
As discussed in Section 2.2.1, a templating mask is required to modify spheres asymmetrically. Because of better stability and easier processing, we use a solid film made of an elastic polymer to partially cover the micro-spheres. First, the spheres are arranged into a monolayer structure. Next, the monolayers are partially embedded into a polydimethylsiloxane (PDMS) templating mask. Last, the exposed sphere surfaces are modified via ELD.

4.2.1 Self assembled monolayer

A two-dimensional (2D) monolayer of spheres can be prepared by continuous convective assembly^[133, 134] or controlled rapid deposition^[135] on a piece of pre-treated silicon wafer as depicted in Scheme 4.1.

In the convective assembling method, a Teflon ring with an inner diameter of 1 cm and a thickness of 3 mm is clipped to the silicon wafer to form a cell for the sphere suspension. An appropriate volume (usually 20 or 30 μL) of suspension containing the number of spheres needed for covering 50%-100% of the bottom area of the cell with a monolayer is filled into the cell. The whole setup is kept in a desiccator where the solvent evaporates and the spheres assemble on the exposed silicon wafer surface. During the liquid evaporation, the spheres convectively assemble into an ordered, closely packed

monolayer due to capillary forces and the convective flow towards the center of the cell. The flow is generated by the surface tension due to the lowering of the liquid surface. The temperature, humidity and air pressure inside the desiccator, as well as the liquid volume (affecting the solid fraction), and inner diameter of the ring (together with the liquid volume it determines the initial depth of the liquid) all influence the assembly. Here, we apply the assembling conditions based on experimental results of C. Silvera.^[136]



Scheme 4.1 a) Continuous convective assembly; b) Controlled rapid deposition ^[135]

The controlled rapid deposition is used for rapid preparation of large-area monolayers. As shown in Scheme 4.1b, two pieces of pre-treated glass slides – substrate plate and deposition plate - contact each other and form a fixed angle θ . The substrate plate can be replaced by a silicon wafer. A small amount (3-10 μL) of concentrated sphere suspension (16 wt%) is injected at the end of the contact line between the two slides. The liquid spreads along the contact line immediately due to capillary forces. Upon dragging or pushing of the deposition plate across the substrate plate at room temperature, the liquid slowly evaporates and leaves a crystalline layer behind. A linear motor setup (PHD 2000 Infusion, Harvard Apparatus) is employed to control the velocity of the deposition plate, which ranges from 0.2 to 3.5 mL/min. The deposition plate, the

top part of which is placed between two pieces of flexible plastic film and secured with clips, is connected to the driving part and can move backward (dragging) or forward (pushing) axially.

Both assembly procedures use silicon wafers and glass slides thoroughly cleaned to ensure a clean hydrophilic surface, which is of critical importance in the assembly. The glass slides and wafers are immersed in fresh Nochromix powder and sulfuric acid solution for at least 3 hours and then rinsed with DI-H₂O and dried in an oven (Isotherm, Fisher Scientific) at 55-65 °C before usage.

4.2.2 Partial embedment of spheres

As mentioned in section 2.2.1, PDMS is cured by an organometallic crosslinking reaction. Taking advantage of the controllable crosslinking process of the polymer matrix, we adjust the embedment depth of the spheres by varying the viscosity of the PDMS film. PDMS viscosity is significantly affected by temperature and time or heat exposure as well as the ratio of base and curing agent. Unlike the conventional approach of pouring a freshly mixed base and curing agent liquid directly onto the sphere assembly; we can reduce the fluidity of PDMS by pre-curing the mixture of base and agent for a well-defined amount of time at a certain temperature. The pre-curing creates a PDMS film, which is viscous enough not to encapsulate the spheres completely, while it is also still viscous enough to partially embed the spheres into the film.

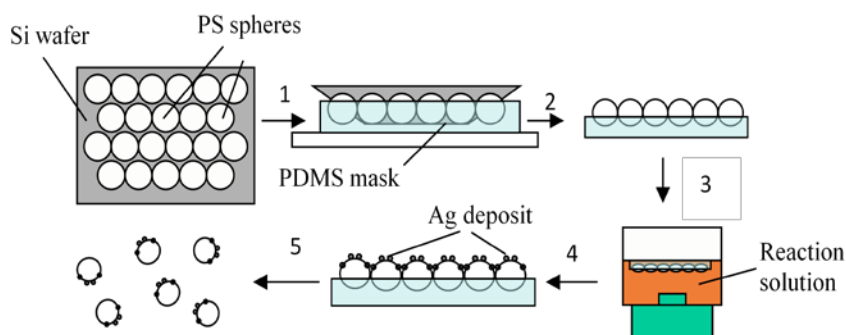
Usually a liquid mixture of base and crossing agent (mass ratio 10:1) is well stirred and carefully poured onto sufficiently cleaned glass slides. The glass slides with pre-polymer liquid are kept at room temperature in a desiccator for 1 hour to allow the liquid to spread widely and remove bubbles before the heat treatment for partial crosslinking.

Smoothed, liquid PDMS films are pre-cured at 70 °C in an oven for 10 to 13 min to give different polymer viscosities, resulting in different embedment depths of the spheres. Then the silicon wafers with the sphere monolayers are pressed gently into the pre-cured semi-viscous films and the sandwich structures are kept in a 60 °C oven for 2 hr to finish crosslinking of the PDMS surrounding the embedded spheres. Upon removing of the sandwich structures from the oven, the PDMS films can be peeled from the wafer yielding a PDMS mask with partially trapped spheres. White color can be seen in the area where spheres are embedded in the PDMS. The polymer masks with embedded spheres thus provide the templates (referred as sphere/PDMS template) for anisotropic electroless decoration of the sphere surfaces. The embedment depth of the spheres is determined using a Zeiss EVO40 scanning electron microscope (SEM).

4.2.3 Asymmetric silver electroless deposition on micro-sphere/PDMS templates

The complete experimental procedure is schematically depicted in Scheme 4.2. As described above, after detachment of the sphere/PDMS template from the silicon wafer the embedded spheres will exhibit only partially exposed surface areas. Immersion of the sphere/PDMS template into the electroless deposition bath provides the substrate for electroless deposition of silver. The exposed PS sphere surfaces have sulfate groups with which silver cations can associate. As in the isotropic deposition, anchoring of cations and negative surface groups is necessary to enhance the surface deposition. Therefore each piece of sphere/PDMS template (1cm × 1cm) is also kept in a mixture of 200 μ L 0.01 M silver acetate solution and 1.3 mL DI-H₂O in the dark for 4 hr under stirring at 180 rpm before it is exposed to the reducing agent. Note that PDMS is lighter than water. Thus, the film floats on top of the liquid, so the exposed sphere surfaces must face the

liquid in order to get deposition as indicated in Scheme 4.2, step 3. After the association, 0.08 mL 1.0 N aqueous ammonium hydroxide is added and stirred for 5 min, before 0.04 mL of 12wt% formaldehyde is added. Ammonium hydroxide is used as the complexor to form a silver-ammonia complex $[\text{Ag}(\text{NH}_3)_2]\text{OH}$ which reacts with the reducing agent formaldehyde slowly to produce zero valence silver, according to the reaction mechanism in the literature.^[82] The mixture is allowed 5 min of stirring between adding the ammonia and the formaldehyde to finish the complexing. At least 5 min of reacting time is necessary for the redox reaction to occur after formaldehyde is introduced.



Scheme 4.2 Schematic processes for asymmetric modification of polystyrene spheres. Grey surface: Silicon substrate; large spheres: Microsphere; blue: PDMS membrane; orange: Reaction solution; small dots: Metal deposit

It can be observed that the reaction liquid turns into a light yellow solution almost immediately upon adding formaldehyde and gets darker and darker until it reaches a misty brown color. Though the reaction solution color varies according to reactant concentrations and reacting conditions, it is always observed that the solution color does not vary much after about 3 min of stirring. This observation leads us to believe that 5 min of reacting time is enough to reach equilibrium. The sphere/PDMS templates are taken out after reaction and rinsed with flowing DI water for about 30 seconds and dried at room temperature in covered Petri dishes. The previously white area with the spheres

turns lightly yellow, indicating a successful silver deposition. Samples are all imaged and analyzed with SEM.

The parameters influencing the reduction of silver hence the surface morphology of the decoration include the concentration of precursor, the concentration of the reducing and protecting agent, and the reacting time as well as the stirring rate during the reduction. A detailed study of the effects of these parameters is investigated in Chap. 6 to provide a better understanding of the silver electroless deposition mechanism and adjust the surface morphology of the deposit.

4.2.4 Physical vapor deposition

Surface anisotropic spheres decorated with metal caps are also prepared directly with the monolayer of spheres described in 4.2.1 by physical vapor deposition as discussed in section 2.1. Caps of gold or silver with thicknesses of 10-40 nm are deposited in a Cressington 308R bench top vacuum coating system with a thin film of titanium (usually 3-5 nm) as adhesion layer between the metal and polystyrene spheres.

In general, the metal-loaded tungsten filament is given a current ~ 50 A from 8V (Cressington 308 evaporation supply LT750) at a vacuum of $\sim 4 \times 10^{-6}$ mbar (4×10^{-4} Pa) for degassing. A second current is employed to evaporate metal to the surface to be modified. The thickness of the film deposited is measured by a Cressington mtm10 thickness monitor and a shutter below the filament is used to block the deposition once the desired thickness is achieved. In our PVD system there are two filaments so the deposition of titanium and gold/silver can be realized subsequently without breaking the vacuum by switching the power supply from filament 1 to filament 2. This eliminates the risk of introducing dirt and impurities in between depositions.

4.3 Asymmetric electroless deposition of other metals: gold and palladium

As discussed in sections 3.3.3 and 3.3.4, gold and palladium can also be deposited with ELD. In the following, deposition of gold and palladium are discussed using (i) free spheres and (ii) the sphere/PDMS template described in the previous section.

4.3.1 Gold deposition

Our approach is based on a standard procedure used to manufacture mono-dispersed gold nanoparticle solutions with excellent particle size control.^[137] As follows, solution I containing 0.01 wt% of hydrogen tetrachloroaurate ($\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$, Sigma-Aldrich) and solution II containing 1.0 wt% sodium citrate ($\text{Na}_3\text{C}_6\text{H}_5\text{O}_7$, Sigma-Aldrich) are prepared in advance. 50 mL of solution I is heated to boiling and 0.50 mL of solution II is added. Reduction of gold precursor is practically complete after 5 min of boiling and refluxing. Varying the amount of solution II gives gold particles with different diameters from 16 nm (1.00 mL solution II) to 147 nm (0.16 mL solution II).

The symmetric deposition on the 9.6 μm SPS spheres is done without seeding of the spheres with gold colloids. 0.5 mL of 0.35 wt% sphere dispersion is added into 5 mL of solution I and kept in the dark for 6hr at room temperature with 120 rpm stirring. Upon finishing of the “incubation” period, the mixture of sphere dispersion and solution I is heated to boiling and 0.05 mL of solution II is added followed by boiling for 5 min. After about 20 s the solution turns faintly pink and changes into red after another 1-2 min. The reaction is quenched after 12 min by cooling the solution. Drops of solution with spheres are dried on a piece of silicon wafer and then checked with the SEM for deposition.

The PDMS embedded sulfate or amine polystyrene spheres are used as templates for asymmetric electroless deposition. Typically, as in the silver electroless deposition, a piece of $1\text{ cm} \times 1\text{ cm}$ PDMS with spheres partially embedded is immersed (floating on top) in 5 mL of solution I. Then the solution is kept in the dark for 6 hr under 120 rpm stirring. Although the negative gold precursors are not likely to deposit onto the exposed negative sulfate groups, it is suggested in the literatures that the incubation process helps the nucleation and the subsequent particle growth.^[126] Then solution I is heated to boiling and 0.05 mL of solution II is added under continuous refluxing for 10 min. Pink color is observed within 2 to 3 minutes and then turns into purple. The color of the transparent solution after reaction can vary from reddish yellow to purple to brilliant red depending on the size of the monodisperse gold particles, which is determined by the precursor to reducing agent molar ratio. The sphere areas on the PDMS film usually also show a faintly pink color. When amine group terminated polystyrene spheres are used, the exposed amine functional groups are believed to enhance the attachment of the gold precursor AuCl_4^- or of reduced gold seeds.

It has been reported that activation of the surface with silver helps deposition of gold onto silica spheres.^[126] In some experiments, we similarly treat our sphere/PDMS template with silver deposition as described in 4.2.2 followed by gold deposition as discussed above to test if this also applies to partially embedded sPS spheres.

4.3.2 Palladium deposition

Here, we describe the asymmetric electroless deposition on sphere/PDMS templates based on the preparation of palladium nanoparticles in aqueous solution by the reduction of its salts with a weak reductant – potassium bitartrate.^[138] All chemicals used in the

palladium deposition are purchased from Sigma-Aldrich unless noted otherwise. Palladium precursor stock solution (50 mM) is prepared from potassium tetrachloropalladium (K_2PdCl_4) and DI- H_2O resulting in a transparent liquid with brownish color. The reducing agent solution is prepared by adding 0.5 g potassium bitartrate ($\text{KC}_4\text{H}_5\text{O}_6$) powder to 100 mL DI- H_2O . Heating is necessary to dissolve the powder completely. For each batch of reaction, 0.028 g potassium hydroxide (KOH) is dissolved in 20 mL of 1 mM (diluted from 50 mM) K_2PdCl_4 solution containing 0.2 wt% polyvinylpyrrolidone (PVP, 0.04 g).

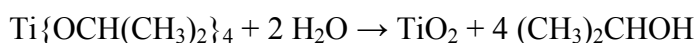
For symmetric deposition tests, 0.2 mL of sulfate-PS sphere suspension (8 wt%, 0.99 μm in diameter) is added to the solution and kept in the dark for 4 hr under stirring. Then the solution is added to a 20 mL 0.5 wt% potassium bitartrate aqueous solution which is heated to *ca.* 100 $^\circ\text{C}$ under stirring. Continuous refluxing under 180 rpm stirring for 2 hr is performed before the reaction is quenched by cooling the solution mixture. Dried droplets of solution are checked with SEM. A similar procedure is used for deposition on monodispersed amine-PS spheres (2.6 μm) or sPS or aPS sphere/PDMS templates.

4.4 Sol-gel deposition of titanium dioxide

There are few reports discussing the growth of partial TiO_2 shells and here we report tests on the first step: the asymmetric coating of polystyrene spheres with titania prepared in a sol-gel process in the presence of sphere/PDMS templates. As described in the literature,^[60] titanium isopropoxide (TIsoP, substituted for titanium tetrabutoxide used in literature), acetonitrile (CH_3CN), ammonium hydroxide ($\text{NH}_3\cdot\text{H}_2\text{O}$, 1N) and ethanol ($\text{C}_2\text{H}_5\text{OH}$, 99%) are all purchased from Sigma-Aldrich and used as received. The coating

reaction is performed in a mixture of ethanol and acetonitrile at room temperature by hydrolyzing TIsOP in the presence of ammonia.

The procedure is separated into two parts which are performed in parallel. In part 1, 50 mL solution of ethanol/acetonitrile (3:1 v/v) is mixed with 0.15 mL 1N ammonium and 0.2 mL sulfate-PS sphere (8 wt%, 2.4 μm in diameter) dispersion is added. Then, the liquid mixture is stirred at 180 rpm for 1 hr to enhance the dispersion of all reactants and substrates. In part 2, several pieces of amine-PS sphere/PDMS templates are added in 0.25 mL TIsOP mixed with 10 mL ethanol/acetonitrile (3:1 v:v) and also kept at room temperature for 1 hr with 180 rpm stirring. The amine groups carry positive charges on the PS sphere surface possibly resulting in the adsorption of negatively charged titania precursor upon exposure to ammonium. The ethanol/acetonitrile mixture has a density lower than or close to PDMS and the sphere/PDMS templates are suspended in the solution. After 1 hr, the two solutions are mixed together and the room temperature reaction starts upon mixing and is kept undisturbed for 1 hr. Titanium isopropoxide reacts with water (hydrolysis) to deposit titanium dioxide (polycondensation):



The mixed liquid appears white and milky with suspended PS spheres. There is no obvious color change after reaction despite of the formation of dispersed TiO_2 colloids. The PDMS films are taken out and rinsed several times with DI-water while the dispersed spheres and TiO_2 particles are collected through two cycles of centrifugation and ultrasonic dispersion in ethanol and subsequently analyzed with SEM.

4.5 Asymmetric silver electroless deposition on smaller spheres

The templating method discussed in section 4.2 is also used for partial modification of polystyrene spheres of smaller size. Monolayer assembly of sulfate PS spheres and amine PS spheres with diameters of 1 μm or 0.5 μm are carried out analogous to the procedure described in section 4.2.1. Templates of spheres embedded partially in PDMS are prepared thereafter from the monolayers (4.2.2) and used for silver deposition onto the exposed sphere surfaces according to the procedure described for 2.4 μm spheres in section 4.2.3.

4.6 Chemical modification and 3-D assembly of surface-anisotropic spheres

Electroless-deposited spheres are collected from the PDMS films via gentle scratching of the films with a blade. White clusters of PDMS and spheres at the blade edge are washed off via dipping the blade in DI-H₂O followed by ultrasonication.

The vapor deposited surface-anisotropic PS spheres (4.2.4) are removed from the silicon wafer by ultrasonication. The silicon wafers with metal-capped spheres are dipped into DI-H₂O and ultrasonicated for 2 min. Most spheres will fall off easily during the sonication with the empty silicon wafer left behind. The sphere suspension liquid shows a yellowish color indicating that the spheres keep their metal film deposit. The spheres are collected by two cycles of centrifugation and rinsing with DI-H₂O and kept in DI-H₂O in the fridge for future use.

Chemical modification of gold capped spheres is carried out in an ethanol solution of 1,8-octanedithiol (99%, Sigma-Aldrich). A piece of PDMS film with modified spheres is put into 1mL of 1 mM dithiol ethanol solution and kept in the dark for 24 hr to facilitate

the association of the –SH group and the gold deposit. After the treatment, the sample is taken out and rinsed thoroughly with DI-water to remove any physically adsorbed molecules. Then the FTIR spectrum of the treated metal-sphere/PDMS sample is compared to a reference metal-sphere/PDMS film to detect if there is any adsorption caused by the extended free –SH group.

Self-reassembly of surface-anisotropic spheres is carried out with the concentrated sphere suspension using the continuous convective assembling method described in section 4.2.1. Modified spheres (PVD) collected from three pieces of monolayer (round area of 1 cm diameter) are used to assemble two new monolayers assuming about 30% loss during the recovery procedure.

4.7 Variable-pressure scanning electron microscopy

The variable-pressure (VP) mode of SEM imaging is different from regular SEM in such a way that the non-conductive PS spheres can be analyzed without coating with a thin film of conductive metal or carbon. In VP mode, the electron gun chamber is maintained at high vacuum while a controlled amount of gas is allowed in to the sample chamber. A fine aperture separates the gun and sample chambers to prevent excessive gas reaching into the gun chamber. The sample surface releases secondary electrons (SEs) as it is bombed by the energetic primary electron (PE) beam, and these electrons encounter gas molecules in the sample chamber once they exit the surface. The gas molecules are struck by the SEs, produce SEs themselves and amplify the original SE signal from the sample. The rest positive gas ions are attracted to and neutralize by the negative charge accumulated on the nonconductive sample surface. Thus charging effect caused by accumulation of electrons on the non-conducting surface is eliminated. By controlling the

pressure in the sample chamber, the number of gas molecules can be balanced to both prevent charging and give detailed images.

Solid samples or a drop of sphere suspension are dried on a piece of clean silicon wafer and analyzed with variable-pressure scanning electron microscope. Typical imaging conditions are an electron beam emitted by the filament at 12-15 kV and a sample chamber pressure of 35-40 Pa.

Chapter 5 Surface Modification of Spheres with Silver via ELD

This chapter introduces a process to manufacture surface-anisotropic spheres via electroless deposition (ELD) modification. Surface anisotropic modification of a particle reduces the symmetry of the particle and provides a directionality to the particle that can be used as a tool to affect and control ordering of particles during assembly of three-dimensional (3D) shapes and structures.^[139] As reviewed in chapter 2, there are various methods available in the literature for sphere surface decoration. Among all these processes, self-catalytic electroless deposition (ELD) possesses an attractive combination of many advantages if provided with a necessary mask or template for partial coverage of the particle surface.^[8] Both solid and liquid masks have been employed to cover part of the surface of a substrate sphere followed by the partial deposition at the microscale and even at the nanoscale.^[3, 4a, 4c, 5] However, the availability of a stable, easy-to-handle and also easy-to-remove mask (without disturbing the deposit on the particle surface) is still among the most difficult practical issues.

In this chapter, we discuss the development of a flexible mask made from a PDMS polymer film and the design of a template to meet requirements like the ability to vary the modification portion or substrate sphere size as well as compatibility with different modification materials. We first report the results for the manufacturing of surface-anisotropic microspheres partially modified with silver nanoparticles generated via electroless deposition of silver onto templated sulfate-terminated polystyrene (sPS) spheres. Next, variation in the amount of surface modification is realized through adjusting the pre-treatment of the PDMS mask. The stability of the deposit is also

examined. In addition, the anisotropic decoration of sub-micron spheres is reported followed by a brief discussion of the effect of substrate curvature on the deposition.

5.1 Isotropic electroless deposition of silver onto free spheres with $d > 2\mu\text{m}$

Research on fabricating free polystyrene (latex) or silica micro-spheres with silver or gold metal decoration via electroless deposition has been widely published ^[104, 126] and forms an excellent basis for this part of the project. We have chosen to deposit silver onto sPS spheres with diameters ranging from 10 to 1 μm available from IDC as introduced in the experimental details. Since little has been published on the electroless modification of sPS spheres, we first test the practicability of controllable metal deposition onto the surface of freely dispersed sPS spheres.

This approach helps in deciding on the metal precursor, reducing agent, protecting agent and the amounts or concentrations to be used whereby our choice will be guided by the overall negative surface charge of the sPS spheres. Further, the catalytic pretreatment (if applicable), the deposition mass to substrate surface ratio, and other important parameters such as temperature, stirring rate, and reacting volume will be determined.

After the dispersed sPS spheres are modified in the ELD solution as described in section 4.1, 20 μL of the post-reaction mixture liquid is taken out and dropped on a piece of acid-cleaned silicon wafer. The dried drop is imaged with the SEM. Figure 5.1a and b below show the surfaces of spheres with diameters of 9.6 and 2.4 μm , respectively, after the ELD modification. In contrast to the untreated spheres whose surface is smooth, the spheres exposed to the ELD reaction are coated with bright spots. These bright areas are identified as the silver nanoparticle deposit. For the 9.6 μm spheres, there are big agglomerates ($\sim 0.5\ \mu\text{m}$), particles of much smaller size (100-250 nm, Fig. 5.1a inset),

and also some clusters of these smaller particles while interestingly the deposit on 2.4 μm spheres appears more uniformly distributed with respect to both particle size and distribution.

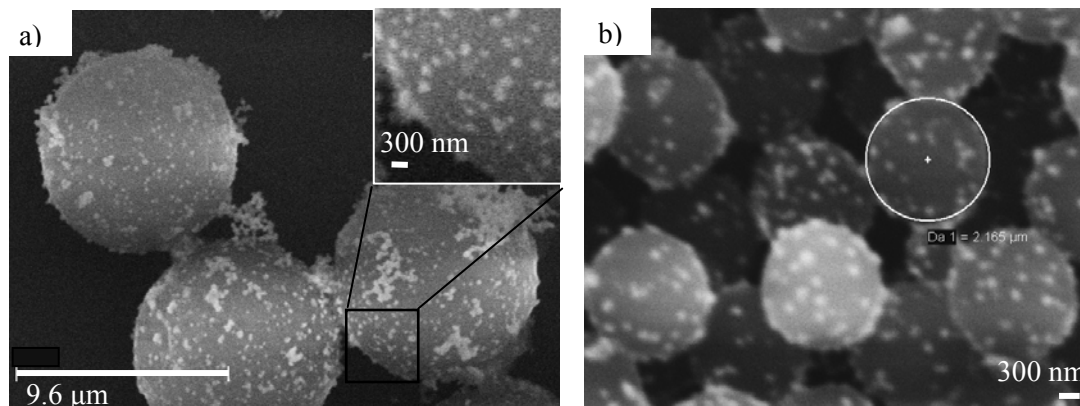


Figure 5.1 SEM images of symmetrically silver decorated sPS spheres a) 9.6 μm spheres, b) 2.4 μm spheres. Scale bars: 9.6 μm and 300 nm

There are several possible reasons for the difference in deposit morphology. First, the distribution and density of sulfate groups, as well as the surface charge density on various sizes of spheres are likely to be different. As reported previously, sulfate groups play an important role for anchoring the deposited silver nanoparticles.^[140] For 2.4 μm sPS spheres, the specific area per sulfate group is $A(\text{SO}_4) = 193 \pm 33 \text{ \AA}^2$ with $(9.2 \pm 1.8) \times 10^6$ charge groups per sphere when averaged over three batches. Unfortunately, the two numbers are not available for 9.6 μm spheres. Comparison with values for 1 μm ($A(\text{SO}_4) = 408 \text{ \AA}^2$ and $\#(\text{SO}_4) = 7.6 \times 10^5$) and 0.5 μm spheres ($A(\text{SO}_4) = 469 \pm 203 \text{ \AA}^2$ and $\#(\text{SO}_4) = (1.7 \pm 0.6) \times 10^5$), predicts a smaller specific area and a larger density of charged groups on the surface. A more even distribution of sulfate groups yields a more uniform distribution of silver particles. A larger specific area per sulfate group, results in a sparser and rougher deposit due to the greater distance between nucleation sites. In addition, at the

same stirring rate smaller spheres disperse more easily in the reaction solution due to a low gravitational force and therefore have a better chance to be more uniformly modified.

Hence 2.4 μm spheres are chosen for the anisotropic modification study. This decision is made also because of their preferable size: closer to sub-micron scale while still easy to handle as well as their more uniform and known surface properties ($A(\text{SO}_4) = 193 \pm 33 \text{ \AA}^2$ and $\#(\text{SO}_4) = (9.2 \pm 1.8) \times 10^6$). The reactant chemicals chosen are silver acetate as the metal precursor, formaldehyde as the reducing agent, and ammonia, which is added before addition of formaldehyde, as the complexor to control the red-ox reaction speed and subsequently the silver deposit size. The amount and concentration of sPS spheres and all reactants for the isotropic and anisotropic deposition are given in the standard procedure described in section 4.1 and 4.2.3, respectively.

5.2. Anisotropic electroless deposition of silver on spheres with $d = 2.4 \mu\text{m}$

The process for anisotropic modification of spheres involves two steps: (i) templating of the spheres and (ii) ELD on the exposed sphere surfaces. The template prepared from a sphere monolayer and a piece of PDMS film is discussed first followed by the results of the silver deposition on the exposed sphere surface.

5.2.1 Templating of spheres

Prior to embedding, a monolayer of spheres to be partially covered is necessary and achieved through convective assembly of microspheres as described in Chapter 4. With both continuous convective assembly^[133, 134] and controlled rapid deposition,^[135] we are able to get neighboring hexagonal domains of an average size of $(20 \times 40) \mu\text{m}^2$ containing approximately 1000-2000 close-packed spheres per domain for the first method. With optimized self-assembly conditions, larger close-packed domains are also prepared

successfully. For the rapid deposition method, a much larger and smoother monolayer area as large as $1 \times 1 \text{ cm}^2$ containing thousands of spheres can be prepared in less than one minute at the cost of a very highly concentrated sphere suspension.

The optical microscope images shown in Figure 5.2a and b are samples of $2.4 \text{ }\mu\text{m}$ sphere monolayers obtained from the convective assembling method and from the rapid deposition method, respectively.

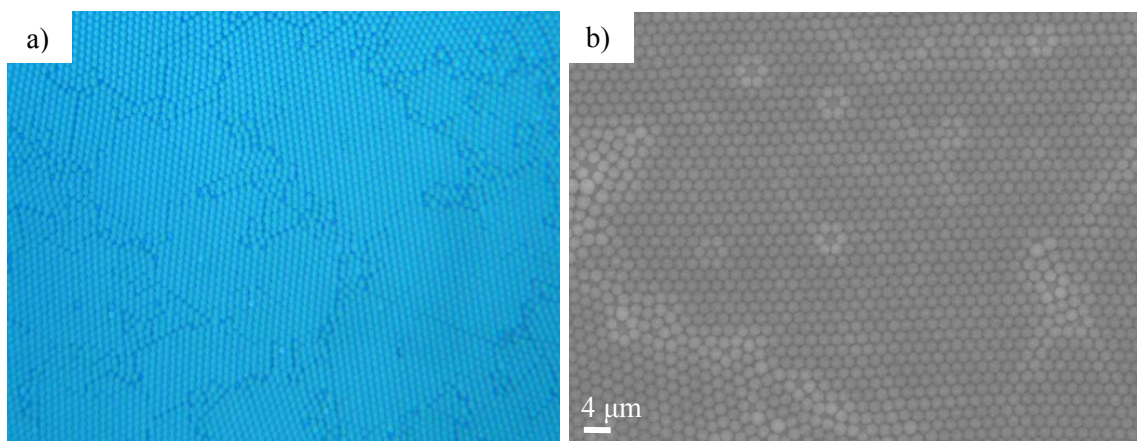


Figure 5.2 Optical and SEM images of monolayer of $2.4 \text{ }\mu\text{m}$ sPS spheres: a) convective assembling method and b) rapid deposition method. Scale bar: $4 \text{ }\mu\text{m}$

As discussed in Section 2.2.1, templating can be achieved with a solid matrix or by assembly of particles at a liquid-liquid interface. Planar solid films made of elastic poly(dimethyl siloxane) (PDMS) are proposed as substrate to partially embed the microspheres to get better stability. In contrast to the traditional approach of pouring a solidifying liquid polymer onto sphere templates assembled on a planar substrate (usually monolayer) as discussed in Chapter 2, we pre-cure the pre-polymer liquid, a mixture of siloxane oligomers and cross-linking agent, by heating the liquid at a certain temperature for a short time. The pre-heated PDMS shows increased stiffness but still remains soft and pliable enough to embrace the spheres.

A monolayer of spheres (on a piece of silicon wafer) is put onto a piece of pre-heated PDMS film upside down as sketched in Scheme 4.2. Wetting is observed immediately upon contacting of the monolayer and the PDMS template. The silicon wafer/spheres/PDMS sandwich structure is kept in a 65 °C oven for 2 hr. Then the sandwich structure is taken out and the solidified PDMS mask is separated from the silicon wafer. Most of the spheres also peel off with the mask due to their partial embedment in the PDMS film. As a result of the pre-heating, only part of the particle surface is exposed and active for the subsequent deposition reaction. Figure 5.3 shows the PDMS mask with partially embedded spheres. In this sample, more than 50% of the surface is covered as indicated by the gaps between neighboring spheres and the average size of the circular exposed areas of $1.8 \pm 0.1 \mu\text{m}$. An embedment depth of $2.0 \pm 0.1 \mu\text{m}$ (more than 50%) is determined using the actual spheres size (i.e., $2.4 \pm 0.14 \mu\text{m}$) and the exposed area.

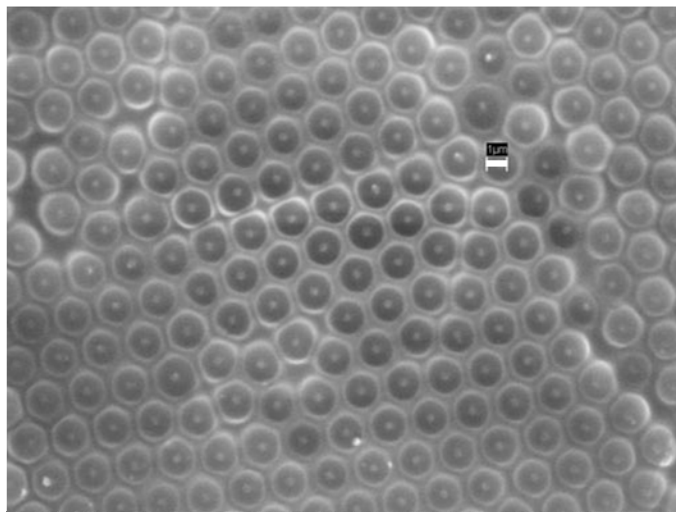


Figure 5.3 Plain 2.4 μm sPS spheres partially embedded in PDMS. Scale bar: 1 μm

The exposed areas of the spheres appear grey in the SEM image and the white points at the center of each sphere indicate the previous contact point of the spheres with the

silicon surface. The depth of embedment is highly influenced by the viscosity of the pre-cured PDMS and the interaction force between the PS spheres and the PDMS film during curing. It is interesting that some of the spheres seem to have assumed a polygonal shape instead of their spherical shape as reported in the literature.^[5, 36] As a possible reason for this deformation the cross-linking force experienced by the relatively soft polystyrene spheres during PDMS solidification combined with the very close packing of the initial monolayer is proposed. The bright rings observed around each sphere most likely result from the charging caused by the electron beam during scanning of the sample. Note, polystyrene spheres are non-conductive and require the use of variable pressure imaging, i.e., a background gas such as air is added to the chamber at 30 Pa to balance charging effects.

5.2.2 ELD on templated spheres

The partial embedment enables us to prepare surface asymmetric spheres by the reduction of silver precursor as described in the experimental section (section 4.2.3). One small piece of the sphere/PDMS template is carefully put into the reaction solution to make sure the side with the exposed spheres is in contact with the solution. Then the sample is taken out of the solution and rinsed immediately after reaction. Before exposure to the ELD bath, the side with the exposed spheres looks white in a transparent background of PDMS. Successful silver deposition onto the spheres is accompanied by a change in color of the sample from whitish to yellowish-brown. The yellowish-brown color does not fade or disappear during rinsing with DI water.

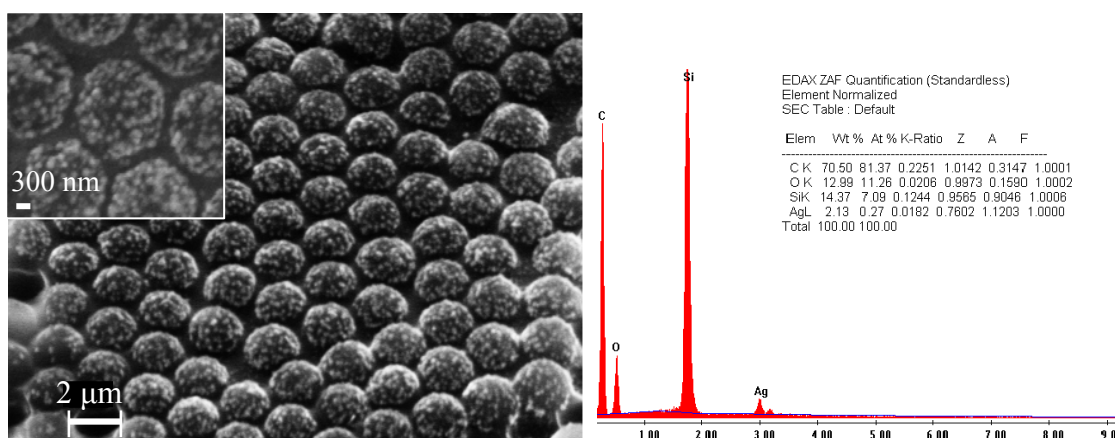


Figure 5.4 a) Ag modified 2.4 μm sPS spheres/PDMS; b) Element analysis of Ag modified sPS spheres/PDMS. Scale bars: 2 μm and 300 nm

The silver-sphere/PDMS template area is imaged with SEM and reveals silver cluster formation on the exposed sPS sphere surfaces. Figure 5.4a presents an exemplary SEM image of the sphere/PDMS template after silver deposition. Comparison of the image in Figure 5.4a to that depicted in Figure 5.3 shows that most of the spheres stay embedded in the PDMS template despite exposure to the reaction solution and agitation of the sample by stirring. The main difference between Figures 5.4 and 5.3 is that there are close-packed, circular areas with white spots visible after electroless deposition (Figure 5.4a), which coincide with the positions of the exposed sPS sphere surfaces in the PDMS mask in Figure 5.3. High-resolution SEM imaging of the white spots (Figure 5.4a inset) reveal deposited particles with diameters ranging from 50 to 150 nm. This result is in good agreement with the observation by Mayer et al. that silver nanoparticles form on the surface of free carboxylated polystyrene spheres when exposed to silver acetate and formaldehyde.^[104] An EDAX (energy disperse X-ray analysis) scan of the sample in Figure 5.4a confirms the presence of the silver on the sample. The EDAX spectrum shows peaks (Figure 5.4b) for elemental C and Ag from the silver deposited polystyrene

spheres, and elemental Si and O mostly from the PDMS film. Some of carbon is also from the PDMS mask. The EDAX spectrum confirms that silver deposition onto the sulfate-terminated PS spheres is achieved with electroless deposition.

The silver nanoparticles (AgNPs) form uniformly on all exposed sPS sphere surfaces but exhibited random patterns. Silver particle formation and agglomeration are also observed in the reaction solution, whereas deposition of silver on the PDMS mask is negligible. According to the manufacturer, the spheres have a surface charge density of $8.1 \mu\text{C}/\text{cm}^2$ equivalent to $9.1 \times 10^6 \text{SO}_4^-$ groups per sphere. Using the embedment depth of $2.0 \pm 0.1 \mu\text{m}$, we calculate the number of SO_4^- groups on the exposed surface as 1.55×10^6 . This number is much larger than the average number of 75 ± 15 silver nanoparticles found on each exposed sphere surface corresponding to $\sim 55\%$ coverage (Figure 5.4a). The rationale for the low coverage is that formaldehyde is a slow reducing agent^[104] giving rise to the formation of only a few nucleation sites. The sulfate groups acted as binding sites for Ag^+ ions, which are subsequently reduced to elemental silver. The elemental silver starts the autocatalytic reaction acting as surface nucleation site facilitating further silver reduction and Ag NP growth.^[104] The electroless deposition process is either controlled by the rate of diffusion of the reactants to the reacting surface (diffusion controlled) or by the rate of an electrochemical reaction step (kinetically controlled). A detailed study of the deposition mechanism is presented in Chapter 6.

The silver modified spheres are removed from the PDMS film with a double-sided sticky carbon tape (Structure Probe INC.). The SEM image in Figure 5.5a shows a few silver NPs on the carbon tape without sPS spheres, suggesting these AgNPs are detached from spheres that fail to be collected from the PDMS film. However, most spheres are

detached and keep their close-packed pattern, indicating good adhesion of silver deposit to the sphere surface. In apparent contrast to the “face-on” view of spheres in Figure 5.4a, the back of the spheres is imaged in Figure 5.5a and looks grey and very smooth. One the very bottom of the spheres chains of white spots from the surface modification are observed, which are visible because of the sample tilting (55°). As in Figure 5.4a, these white spots are silver NPs deposited on the surface of the spheres that is not covered by the PDMS mask, confirming partial silver deposition on the spheres.

The empty PDMS template after removal of the spheres is also imaged with SEM (Figure 5.5b). The image shows some spheres still sitting in the film as well as well packed circular holes left behind by removed spheres. Interestingly, the remaining spheres keep their silver NP decoration even after contact with the sticky carbon tape. All these observations allow the conclusion that Ag NPs are formed at and adhere to the sPS sphere surface, but do not elucidate whether the silver nanoparticles prefer to accumulate in solution or grow directly on the sphere surface under the reaction conditions employed.

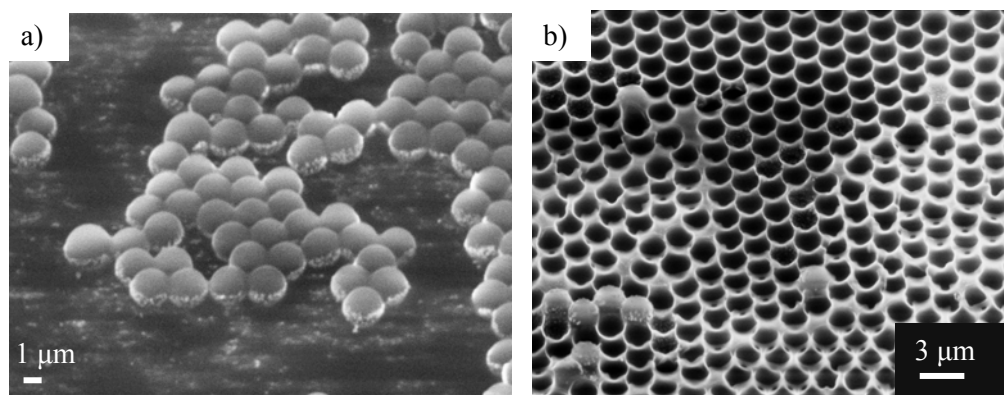


Figure 5.5 a) Silver modified sPS spheres on sticky carbon tape (55° tilt); b) Empty PDMS mask with spherical impressions from sPS spheres at 45° tilt. Scale bars: $1\ \mu\text{m}$ and $3\ \mu\text{m}$

5.2.3 Variation of embedment depth

The content of cross-linking agent, the pre-heating temperature and the curing time influence the viscosity of the pre-treated PDMS film, resulting in different depths to which the spheres are embedment. Recently, Ho et al. also reported a controllable embedding of silica submicron particles through isothermal treatment of the polymer template. Electro-spun polymer fibers of specific surface hydrophilicities determined by various composition of poly(methyl methacrylate) (PMMA) and poly(4-vinylpyridine) (P4VP), are used to adjust the elasticity of the copolymer leading to a variation of the embedment depth.^[141]

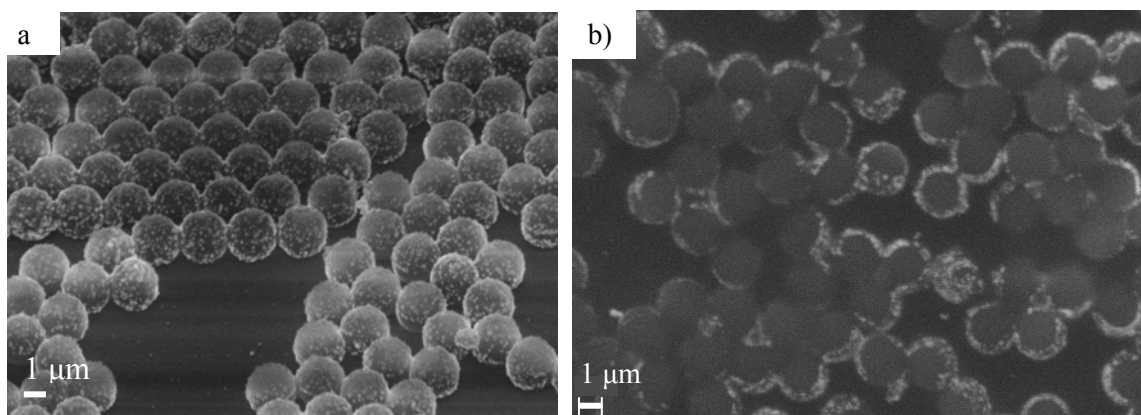


Figure 5.6 a) Ag modified 2.4 μm sPS spheres/PDMS composite - less embedded (45° tilt); b) Back side of sPS sphere removed from PDMS mask. Scale bar: 1 μm

By extending the pre-curing time of PDMS, the PS spheres are embedded less deeply, thus more portion of their surface is exposed and more silver coverage is achieved. The assembled sphere monolayer is sandwiched with a PDMS mask pre-cured for 12 min at 70 °C. The subsequent steps are kept the same. The tilted front and untilted back side views of the spheres on a sticky carbon tape from the lesser embedment are presented in Figures 5.6a and b, respectively. Both show more than 50% Ag coverage is obtained for this sample.

5.2.4 Free modified spheres and stability of deposit

To re-disperse the silver modified sPS spheres, the sphere/PDMS template is stretched and the AgNP-spheres are scratched from the PDMS mask with a metal blade according to the method reported by Paunov et al.^[36] A white residue is found on the blade's edge after the procedure. A water droplet is spread on a piece of silicon wafer and the blade is dipped into it washing off the white residue. The spheres are examined with SEM after drying in air. Large agglomerates with random orientation of surface-anisotropic spheres are found at the rim of the dried droplet. The silver modification appears unchanged by the blade collection process on most of the spheres.

The intact surface modification after removal of spheres from the PDMS mask implies that the metal nanoparticle deposit adheres strongly to the polystyrene sphere surface with the aid of surface sulfate groups. Several other procedures including ultrasonication (50 min at a frequency of 40 kHz in an aqueous solution), UV light exposure (~1 hr), and exposure to ethanol (~24 hr) are also employed to test the stability of the deposit. When the sphere/PDMS template is checked with SEM after any of these treatments, the NP deposit appears unaffected.

In addition, it is confirmed that the deposit is also chemically stable when exposed to an ambient environment for 16 months. The two SEM images shown in Figures 5.7a and b are from the same sample examined (a) immediately after preparation and (b) after 16 months in air inside a covered Petri dish. The silver NPs keep their positions on the sphere surface. Interestingly, most silver NPs appear larger even after correction for the effect of variance in image quality. One possible rationale for the observed increase in NP size is that the silver NPs get oxidized with time in air. Therefore, if oxidation is not

desired, the samples should be stored in an inert environment. In summary, the silver nanoparticle deposit on the sPS spheres is chemically and mechanically stable and enables the use and modification of these anisotropic spheres for other applications.

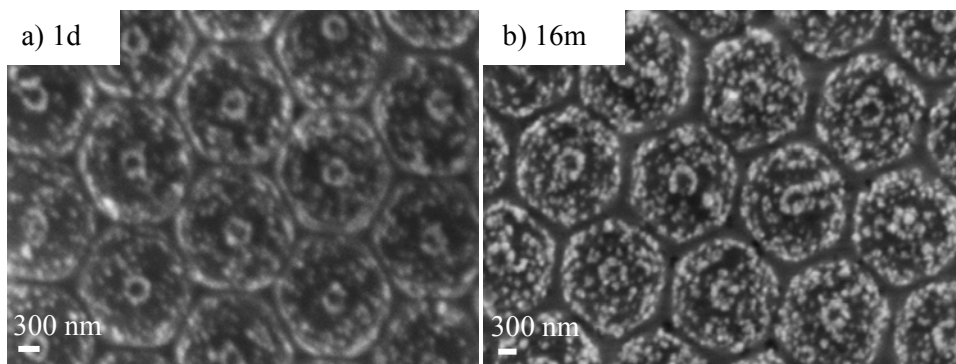


Figure 5.7 SEM images of silver deposit on spheres, a) 1 day after preparation; b) after 16 months in air. Scale bar: 300 nm

5.3 Anisotropic surface modification of spheres with $d \leq 1 \mu\text{m}$

As an attempt to move towards smaller particles, we also tested if 1 (actual size 0.99 ± 0.025) and 0.5 (0.51 ± 0.028) μm surface anisotropic sPS spheres can be modified asymmetrically with the developed silver ELD procedure. The monolayer assembly is identical to that of 2.4 μm spheres. Owing to the narrow size distribution in the 1 and 0.5 μm particle samples, larger areas of close-packed domains are observed in the monolayers from the convective and rapid assembly methods. Optical images of monolayers of 1 μm sPS spheres are shown in Figure 5.8. Interestingly, monolayers obtained from 0.5 μm PS spheres exhibit a uniform color such as green or bluish purple which is seen at a certain angle indicating highly-ordered spheres (data not shown). This optical property of a sphere monolayer forms the basis for their application as photonic band gap crystals.^[1, 142]

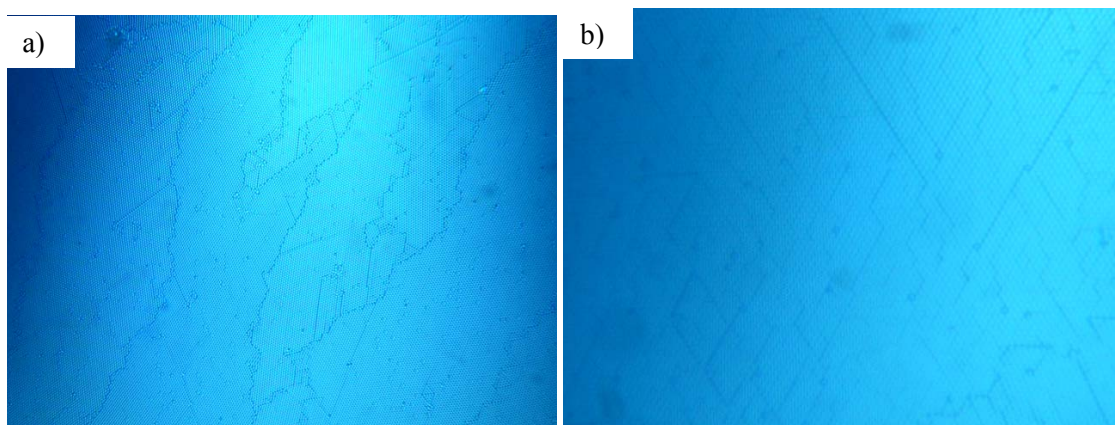
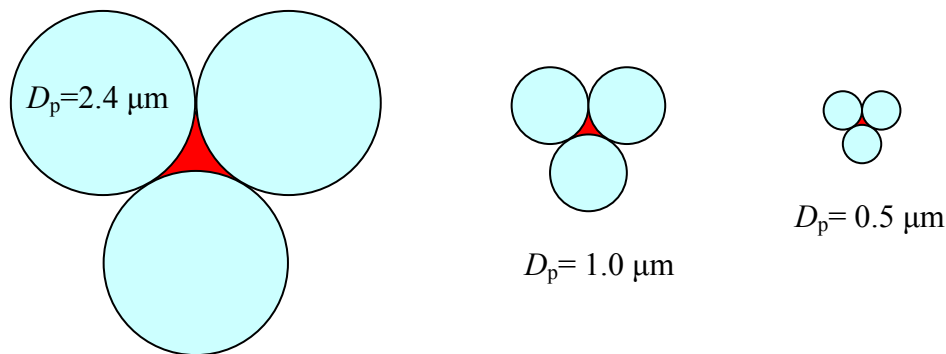


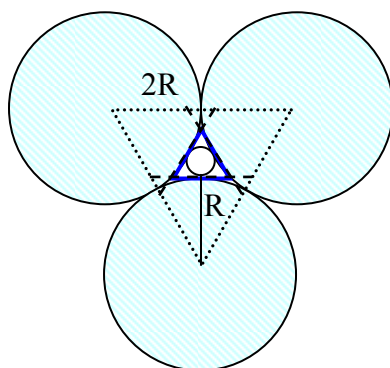
Figure 5.8 Optical microscope images of monolayer of 1 μm sPS spheres prepared through a) convective assembling method, b) rapid deposition method

The control of the embedment depth of smaller-scale spheres requires exquisite control over the flatness of the PDMS template, viscosity as well as monolayer quality. Theoretically, when particles with a smaller radius of curvature are used, a narrower “capillary neck” surrounded by three neighboring spheres forms as indicated by the dark red area in Scheme 5.1 and results in more wetting. The capillary size is dependent on the size of the surrounding spheres and one also needs to keep in mind that all capillary necks connect and form one large liquid body (but still “capillary” compared to the system) below the equatorial plane in a perfect monolayer. The area of the equatorial plane increases with decreasing distance from the silicon wafer. In a perfect monolayer, at the local center where three spheres of identical size are in contact (Scheme 5.2), the cross-section of the “capillary” can be approximated by the equilateral triangle whose inner circle touches the circumference of all surrounding spheres. The side of this equilateral triangle (where dash and solid lines overlap) in Scheme 5.2 is calculated as $(4-2\sqrt{3})R$, where R is the radius of the surrounding spheres. A smaller capillary tube (with walls composed of polystyrene) will induce higher liquid (PDMS pre-polymer) rising in the same system according to surface tension theory. Therefore a longer pre-heating time to

increase the viscosity of the PDMS - hence decrease its rising height - is required to control the embedment depth.^[143] Usually at least 11 min and 12 min of pre-heating are necessary for 1 μm and 0.5 μm spheres, respectively. The pre-heating time is also a function of ambient temperature, humidity, the composition of the pre-polymer mixture as well as the particle size.



Scheme 5.1 Cross-section capillary area formed by spheres of different sizes



Scheme 5.2 Calculation of cross-section capillary area

Images of monolayers composed of 1 and 0.5 μm spheres embedded in PDMS are shown in Figures 5.9 a (1 μm) and b (0.5 μm). The images reveal that submicron spheres have been partial embedment in the PDMS films and can be used as templates for the subsequent electroless deposition. Note the embedding process is strongly dependent on

the quality of the monolayer. For example, a monolayer with regions of multilayer will cause non-uniform particle embedment.

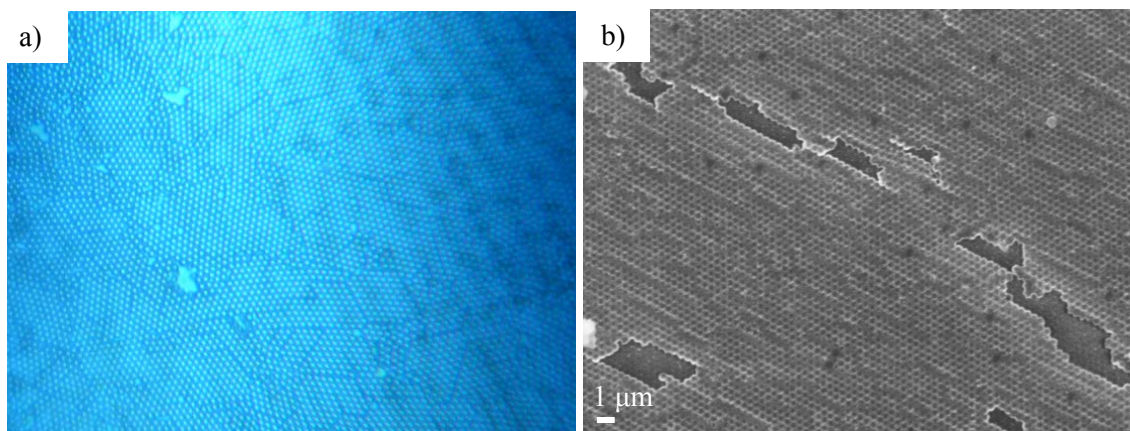


Figure 5.9 Spheres partially embedded in PDMS. a) Optical image of 1 μm sPS spheres; b) SEM image of 0.5 μm sPS spheres. Scale bar: 1 μm

5.3.1 Anisotropic deposition onto 1.0 μm spheres

Similar to the electroless deposition onto 2.4 μm spheres partially embedded in PDMS, the 1.0 μm spheres/PDMS templates are put into the reaction solution with spheres facing the solution. Reactant concentrations are adjusted according to the change in exposed surface area while the stirring rate and reacting time are kept constant. An SEM image of a sphere/PDMS template after deposition is shown in Figure 5.10a. At first sight, most spheres show deposit of silver NPs (bright dots), although only at a density of (9 ± 3) NPs per sphere, much sparser than the deposit density (75 ± 15) on partially covered 2.4 μm spheres obtained under identical reaction conditions. A more careful analysis of the image reveals that most visible silver NPs are of 30-100 nm size. There may also be NPs of smaller size but they are not detected with our SEM due to the limitation of the resolution to 30 nm in VP mode.

Upon closer inspection of Figure 5.10a at least six spheres are identified with more than the average number of particles (27 ± 4 vs. 9 ± 3 NPs/sphere). This finding indicates

that a higher coverage and more uniform deposit can be achieved on the 1 μm embedded sPS spheres. To test this hypothesis, we doubled the silver precursor concentration and the resulting deposit is shown in Fig. 5.10b. Comparison of Figures 5.10a and b confirms that an increased silver precursor concentration enhances the deposition. In both samples the spheres are ca. 50% embedded. An average of 15 ± 3 NPs/sphere are deposited on most spheres in Figure 5.10b, and there are more NPs of 50-100 nm and 100-150 nm in size. A detailed analysis shows that doubling of the Ag^+ concentration leads to a 100% increase of deposit per sphere.

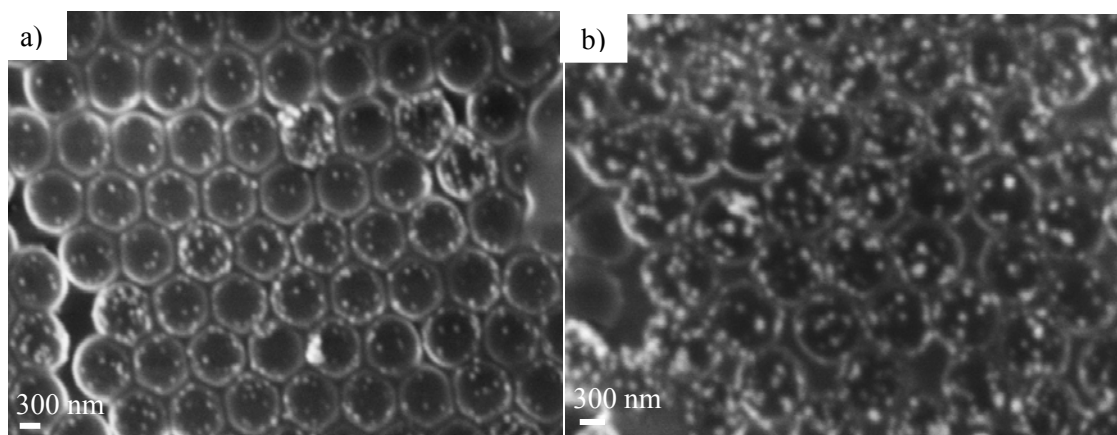


Figure 5.10 Ag modified 0.99 μm sPS spheres embedded in PDMS: a) 1 $\times$ Ag precursor b) 2 $\times$ Ag. Scale bar: 300 nm

Comparison of the silver deposit obtained with 2.4 and 1 μm spheres under identical experimental conditions indicates that the density of the NPs changes with the size of the embedded spheres. The NPs deposited on the embedded 2.4 μm spheres have a density of 75 ± 15 NPs/sphere, whereas a density of 9 ± 3 NPs/sphere is measured for the 1 μm spheres. So, why is there a dependence on the substrate particle size? Both sets of particles are made of sulfate-terminated polystyrene. However, upon inspection of the specific data sheet delivered with each set of particles, we find that the 2.4 μm sulfate terminated PS spheres are listed with a specific area per sulfate group of $222 \text{ \AA}^2$ with

7.5×10^6 charge groups per sphere, while for the 1 μm spheres, the two values are $408 \text{ \AA}^2$ and 7.6×10^5 , respectively. It is not surprising that the 1 μm spheres have an order of magnitude smaller total amount of charged groups per sphere as they have an overall smaller volume. However, the comparison of the specific area per sulfate group shows that, assuming a spherical footprint, the sulfate groups are spaced much further apart on the 1 μm spheres ($22.8 \text{ \AA}$) than on the 2.4 μm spheres ($16.8 \text{ \AA}$). Since the sulfate groups are crucial for the nucleation of the silver NPs, a change of their number and distribution will affect the amount of silver NPs formed. Fewer sulfate groups will lead to fewer silver NPs deposited in good agreement with the 88% reduction in the NPs/sphere number observed in our experiments. Last but not least, the distribution of charged groups is far from uniform and the ionic cluster-rich and ionic cluster-poor domains are randomly distributed, increasing also the surface heterogeneity of the silver deposit.^[144]

5.3.2 Anisotropic deposition onto 0.5 μm spheres

If the discussion for 1 μm spheres holds also for the 0.5 μm spheres, which are reported by Invitrogen to carry 2.1 to 1.3×10^5 charge groups per sphere with a specific area in the range of 326 to $611 \text{ \AA}^2/\text{sulfate group}$, we expect on average a decrease in silver deposition due to the wider spacing of the sulfate groups. Several samples are prepared and the SEM images of the formed deposits are summarized in Figure 5.11 and Table 5.1. The different types of deposits observed are (i) dense silver deposition forming close to a complete half-shell (Figure 5.11a), (ii) larger agglomerates bridging spheres (Figure 5.11b), (iii) sparse deposit of small silver nanoparticles (Figure 5.11c), as well as (iv) rings of silver NPs around spheres (Figure 5.11d). All surface morphologies observed and the reaction conditions under which they are prepared are summarized in Table 5.1.

Table 5.1 Silver asymmetric ELD on 0.51 μm sPS spheres/PDMS template

Monolayer	Reactants concentration	Reaction condition	Deposit morphology
1/6 piece*	0.05 ml 0.01M Ag(ac) + 0.45 ml DI-water 0.04 ml 1N $\text{NH}_3\cdot\text{H}_2\text{O}$ 0.04 ml 12% HCHO	95 rpm 5 min 5min	Uniform dense silver NPs coverage
1/4 piece	0.15 ml 0.01M Ag(ac) + 0.35 ml DI-water <u>0.08 ml</u> 1N $\text{NH}_3\cdot\text{H}_2\text{O}$ 0.04 ml 12% HCHO	95 rpm 5 min 5min	Large agglomerates
1/4 piece	0.15 ml 0.01M Ag(ac) + 0.35 ml DI-water 0.08 ml 1N $\text{NH}_3\cdot\text{H}_2\text{O}$ 0.04 ml 12% HCHO	<u>0 rpm</u> 5 min 5min	Uniform silver NPs coverage; Sparse deposit
1/8 piece	0.15 ml 0.01M Ag(ac) + 0.35 ml DI-water 0.08 ml 1N $\text{NH}_3\cdot\text{H}_2\text{O}$ 0.04 ml 12% HCHO	<u>60 rpm</u> 5 min 5min	Silver NPs rings surrounding sphere

*A whole piece is an area of 1 cm diameter with spheres monolayer.

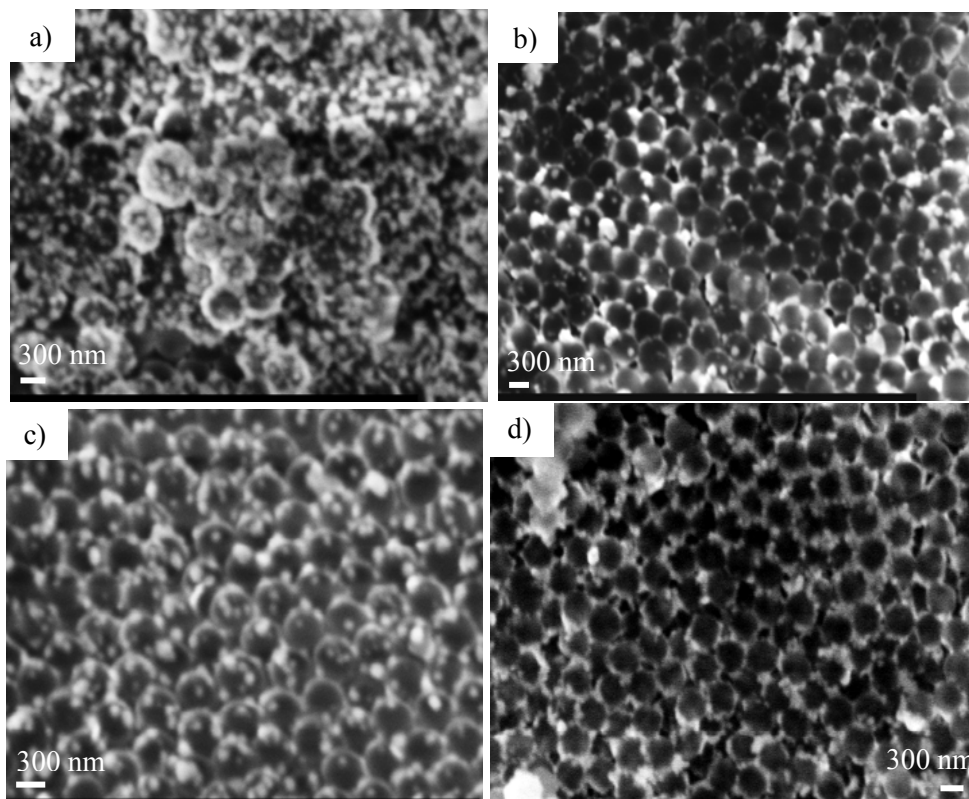


Figure 5.11 Ag modified 0.51 μm sPS spheres in PDMS. a) dense deposition close to a complete half-shell deposition, b) larger agglomerates bridging spheres, c) sparse deposit of silver NPs, d) rings of silver NPs around spheres. Scale bar: 300 nm

In some of the samples, more than one of the four types of deposits is observed. Despite careful control of the reaction conditions, it was not possible to obtain samples with uniform and reproducible silver deposition and deposit morphology. One apparent reason for the large sample-to-sample variation observed for the 0.5 μm spheres is the variation in surface group density with specific sulfate areas ranging from 326 to 611 $\text{\AA}^2$, which is likely to affect the number of nucleation sites. Another reason for the difficulty to get a uniform deposit on the smaller 0.5 μm spheres under the reaction conditions tested maybe the small size difference between the substrate spheres (e.g., ~ 500 nm) and the deposited particles (e.g., ~ 100 nm). There have been many reports discussing the control of silver NPs size or shape formed in bulk solution by careful adjustment of the reaction conditions.^[145]

A similar approach of adjusting the reaction conditions should enable us to reduce the size of silver NPs deposited on the sphere surfaces. However, a detailed study regarding all reaction variables is necessary to elucidate the reaction mechanism. We chose the 2.4 μm spheres for the study, because they are of a size that allows easy templating and also show the most uniform deposit morphology from sample to sample (Chapter 6).

5.4 Conclusion

In this chapter, we have discussed a new procedure for the preparation of a solid templating mask, which is employed for the electroless modification of sulfate-terminated polystyrene spheres with caps comprised of silver nanoparticles. The results for the 2.4 μm sPS spheres indicate that it is possible to manufacture surface-anisotropic silver-capped spheres via electroless deposition. The deposit is stable over time and unaffected by mild physical or chemical treatment. The deposit is comprised of uniformly

distributed nanoparticles, which make it rough compared the deposit prepared via physical vapor deposition. Asymmetric modification of submicron spheres (1 μm and 0.5 μm) via this procedure is also carried out successfully and the results show both the monolayer embedment and the ELD process can be scaled down. However, more work is needed to determine ideal reaction conditions for the uniform, asymmetric modification of submicron spheres embedded in PDMS.

Chapter 6 Mechanism Study of Silver Electroless Deposition

Nanoparticles have generated great interest in modern material science because of their specific size-and-shape-dependent physical, chemical and electronic properties.^[146,147] During the past years, metallic particles smaller than 200 nm have inspired interesting optical applications because of their plasmon-derived optical character such as surface plasmon resonance, which shows that light can be tuned at the nanometer scale.^[86c] Many reports on the synthesis mechanisms of metal or compound nanoparticles have focused on controlling the shape and size of particles in the bulk solution containing complexing chemicals.^[148] Various shapes of different materials, such as silver wires,^[147] disks,^[149] gold branched nanocrystals,^[150] rods,^[151] triangular, rectangular or hexagonal nanoprisms,^[152] and titania rods^[153] have been prepared by wet chemistry including electroless deposition and electrochemical methods. Besides, the introduction of templates such as DNA,^[154] nanoporous membrane^[155] or micelle structures,^[147, 156] and even nanospheres,^[146] can be used to define the shape and size of nanoparticles in a better and enhanced way. In addition, with the aid of spherical templates, core-shell and hollow shell structures have been prepared by chemical reduction of noble metals symmetrically onto silica or polymer spheres.^[86] These structures are of great interest especially for photonic applications.

Half-shells and isotropic shells, moreover, lend substrate particles different properties depending not only on their composition and size, but also on the shell orientation and surface morphology.^[157] Therefore to control the surface roughness of the deposit is of similar importance as the control of particle size and shape in the liquid phase. There have been reports discussing the procedure and deposition conditions for silver,^{[86a, 104,}

^{158]} gold ^[86b, 86c, 126] and other metals like platinum, palladium ^[84] or metal oxides ^[60] on sphere surfaces at the nanoscale. It has been found that pre-treated deposition is able to give individual, remarkably monodisperse silver nanoparticles uniformly distributed on the sphere surfaces.^[86a] On the other hand with a relatively strong reduction agent, it is possible that all seeds or nucleation sites grow simultaneously producing a smoother surface with a uniform thickness.^[86c] However, most of the research mentioned above concentrates on symmetric deposition. The control of asymmetric modification via the electroless deposition method has gained increasing attention only recently.^[4a,5]

Previously, we developed a templating procedure to manufacture surface-anisotropic, silver-modified spheres via electroless deposition (Chap. 5).^[140] Preliminary data taken at varying stirring rates indicated that the silver deposition onto the sphere surface might be diffusion-controlled. This observation prompted us to study the dependence of the cap morphology on the electroless deposition conditions. In this chapter, we investigate the effect of varying stirring rate, exposure time, and reactant concentrations on the surface morphology of the deposit. This study helps us to understand the effect of reaction parameters on the deposition process and if these parameters can be used to create a specific deposit morphology.

6.1 Experimental details

Materials process

Materials have been listed in Chap 4. Silver acetate is used as the Ag^+ precursor and two aqueous stock solutions (0.1 M and 0.01 M) are prepared and stored at 4 °C in a refrigerator for 3 months of use. 1.0 M aqueous ammonium hydroxide is used as received. 12 wt% formaldehyde is obtained by dilution of a 20 wt% aqueous solution.

Sulfate terminated polystyrene (sPS) spheres ($2.4 \pm 0.14 \mu\text{m}$, 1.10×10^{10} spheres/mL) are used for monolayer assembly and the original suspension is diluted according to the liquid volume (usually 20 or 30 μL /monolayer) and the amount of spheres needed for each monolayer. For example, a 100% monolayer covering an area of 1 cm diameter requires 1.57×10^7 spheres ($d = 2.4 \mu\text{m}$), so the concentration of spheres needed is 7.85×10^8 spheres/mL if dispersed in 20 μL deionized water or 5.23×10^8 spheres/mL for a 30 μL dispersion. Silicon (110) wafers with a native oxide surface are cleaned using a fresh NoChromix-sulfuric acid solution and subsequently rinsed with copious amounts of water. Milli-Q deionized (DI) water is used for all dilution and washing steps and as the solvent for the reaction solution during the electroless silver deposition.

The silver-capped Janus particles are prepared as described in Chap. 4.^[140] In brief, a monolayer of sPS spheres assembled on a piece of silicon wafer is placed onto a piece of polydimethylsiloxane (PDMS) film pre-cured on a glass slide. This process results in the partial templating of the spheres by the PDMS. The film with the partially embedded sPS spheres (hereafter called sphere/PDMS template) is peeled off the silicon wafer and the glass slide after complete curing at 60°C for 2 hr. The sphere/PDMS template is cut into four equal pieces and each of the four pieces is then exposed to its specific silver deposition conditions simultaneously. This helps to reduce the influence of variation in the monolayer structure and the templating procedure on the metal electroless deposition. Silver nanoparticles deposit on the exposed sphere surfaces upon addition of the complexing agent (ammonia) and the reducing agent (formaldehyde) to the silver deposition solution. After reaction, the sphere/PDMS template is rinsed thoroughly with

DI water, left to dry at room temperature in a covered Petri dish, and used for deposit characterization.

The standard electroless deposition procedure (referred to as “1.0×” concentration for all reactant concentration experiments) is as follows: The aqueous Ag^+ reaction solution is prepared in a 20-mL glass vial by mixing 1.0 mL of a 0.01 M silver acetate solution with 0.5 mL Milli-Q water. The sphere/PDMS template piece is placed upside down onto the solution such that the exposed sphere surfaces are in contact with the liquid. The solution is covered with aluminum foil and continuously stirred at room temperature for 4 hours at 120 rpm to enhance the Ag^+ - SO_4^- association. Next, 0.08 mL of 1.0 M aqueous ammonium hydroxide (NH_4OH) is added to the bottom of the stirred reaction solution using an Eppendorf pipette. The mixture is stirred for 5 min. Then 0.04 mL of aqueous formaldehyde (HCHO) solution (12 wt%, 4.0 M) is added to the bottom of the stirred mixture at room temperature and stirred for an exposure time of 5 min. The molar ratio of silver acetate, ammonium hydroxide and formaldehyde under the standard conditions is 1:8:16 ($\text{Ag}^+ : \text{NH}_3 : \text{HCHO}$). When reactant concentration effects are studied, the volume of each reactant solution is adjusted to satisfy the concentration requirement while the total reaction solution volume is kept constant at 1.62 mL. After completion of the reaction, the sphere/PDMS template is removed from the solution, rinsed thoroughly with DI water, dried in a closed container and placed into the Carl Zeiss EVO40 scanning electron microscope (SEM) for imaging.

Particle quantity and sizes distribution analysis of deposit

The number and size distribution of the silver nanoparticles deposited are determined using high magnification (25 k×) SEM images for nanoparticle counting and size

determination. The images are processed with ImageJTM to increase the image contrast and sharpen the edges of the bright dots, i.e., deposited silver NPs, on the sphere surfaces. The resolution of our SEM restricts the observable minimum particle size to ~30 nm. The average number of particles per sphere is determined by averaging the particle count for 7 to 12 spheres from different domains of the templated monolayer. Four groups of nanoparticles are categorized based on the observed particle diameter; (i) smaller than 100 nm (small NPs); (ii) between 100 nm and 150 nm (medium NPs); (iii) between 150 nm and 200 nm (large NPs), and (iv) larger than 200 nm (extra large NPs). The average number of particles in each size range is reported with the statistical error of one standard deviation. The deposit volume (per sphere) is estimated based on assuming each deposit dot is a sphere with an average diameter of 75 nm for small NPs, 125 nm for medium NPs, 175 nm for large NPs, and 200 nm for extra large NPs.

6.2 Results

Variation of stirring rate, exposure time, and reactant concentrations leads to a change in the silver nanoparticle deposit density and morphology. In the deposition study, the following parameters are varied in the standard procedure: stirring rate during reaction (0 – 270 rpm), exposure time in static liquid (5 – 30 min), silver concentration ($0.5\times$ – $2.0\times$), and agents (ammonia, formaldehyde) concentration. The agent concentration set involves varying each of the agents separately as well as varying the concentration of both simultaneously with a constant molar ratio. The concentrations employed are $0.5\times$, $2.0\times$ and $4.0\times$ compared to the standard concentration. In all experiments, the amount of ammonia and formaldehyde are theoretically enough for reacting all silver ions according

to the proposed stoichiometric reactions ($\text{Ag}^+ : \text{NH}_3 : \text{HCHO} = 2:4:1$) during the reduction process.^[82]

6.2.1 Standard deposition samples

The standard deposition condition (1.0× concentration) has been repeated frequently and deposition of silver nanoparticles is observed every time assuring the reliability of our ELD bath for silver deposition. However, despite well-controlled reaction conditions and bath composition, a large variation in total particle numbers and nanoparticle size distributions is found. Averaging of the counting obtained from the deposits found on five standard samples prepared from different monolayers over the course of the experimental study yields a total of 61 ± 39 NPs/sphere with 45 ± 39 small, 14 ± 11 medium, 0.9 ± 0.8 large, and 0.3 ± 0.3 extra-large NPs/sphere. Because of this wide variation in deposit composition obtained at standard conditions, the standard deposition condition is included in each set of experiments as the reference to minimize the effect of the sample-to-sample variation in sphere surface chemical properties, monolayer uniformity, embedment depth, and ambient conditions such as humidity and temperature.

6.2.2 Effect of the stirring rate

An increase of the stirring rate from no stirring (0 rpm) to vigorous stirring (270 rpm) increases the deposition of silver nanoparticles. Figure 6.1 summarizes the SEM images of the silver nanoparticle deposit (bright dots in the image) on the partially exposed polystyrene sphere surfaces (circular areas) obtained at four different stirring rates; no stirring (6.1a), 90 rpm (6.1b), 180 rpm (6.1c), and 270 rpm (6.1d). All other parameters are as given in the standard deposition experiment.

Analysis of Figure 6.1, results in a total number of NPs/sphere of 29.0 ± 3.0 , 62.7 ± 6.7 , 54.7 ± 8.2 , and 72.9 ± 3.1 NPs/sphere for 0, 90, 180, and 270 rpm, respectively. Under the absence of stirring (Figure 6.1a), the sphere surfaces are mainly blank with only several tiny bright nanoparticles visible on each sphere. Almost 90% of the nanoparticles per sphere are in the small-sized and medium-sized categories (≤ 150 nm in diameter) with none of the deposited nanoparticles reaching a diameter of 200 nm (extra-large). The residual 10% are large NPs (3.1 ± 3.0 NPs /sphere). A stirring rate of 90 rpm (Fig. 6.1b), results in a doubling of the number of silver nanoparticles (62.7 ± 6.7 NPs/sphere) compared to the sample with no stirring (29.0 ± 3.0 NPs/sphere).

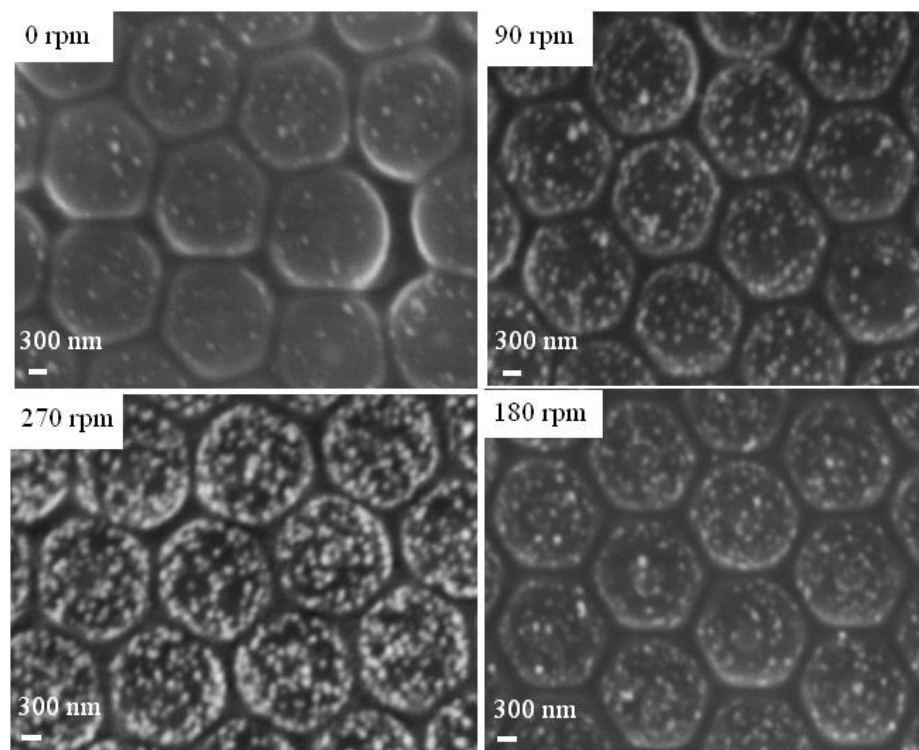


Figure 6.1 Effect of stirring rate on silver deposition. Scale bar: 300 nm

The deposit in Fig. 6.1b looks more uniformly distributed over all spheres and most NPs (97%) are also either small-sized (26.1 ± 8.9 NPs/sphere) or medium-sized ($35.1 \pm$

10.0 NPs/sphere). The average of 1.4 ± 0.8 large NPs/sphere indicates a more uniform distribution of large NPs over all spheres compared to the 0 rpm sample, which shows a large standard deviation (3.1 ± 3.0 NPs/sphere) indicating a very non-uniform distribution of large NPs.

Doubling of the stirring rate to 180 rpm shows no obvious increase of particle deposit (Figure 6.1c). Careful analysis of particle numbers and the size distribution shows that less NPs (54.7 ± 8.2 NPs/sphere) are deposited compared to the samples prepared under 90 rpm. Extra large NPs (0.14 ± 0.38 NPs/sphere) are observed occasionally at 180 rpm, while fewer medium and large NPs (17.6 ± 4.7 and 1.00 ± 1.15 NPs/sphere, respectively) are observed. But interestingly, more small NPs (36.0 ± 7.5 NPs/sphere compared to 26.1 ± 8.9 NPs/sphere for 90 rpm) are counted at 180 rpm. The highest stirring rate 270 rpm (Figure 6.1d) gives the densest and still precisely controlled deposit with an average number of 72.9 ± 3.1 NPs/sphere of which 36.0 ± 7.0 NPs/sphere are in the small and 34.4 ± 6.3 NPs/sphere are in the medium NPs category. Large and extra-large NPs are occasionally but not uniformly formed on the spheres.

6.2.3 Effect of the exposure time

Increasing the exposure time of the sphere/PDMS template to the reaction solution from 5 to 30 min at constant reactant and agents concentrations but no stirring yields more and more deposited silver particles. The images of the silver deposit obtained after 5 min (6.2a), 10 min (6.2b), 20 min (6.2c), and 30 (6.2d) min of exposure are displayed in Figure 6.2. It is apparent that the spheres in this sphere/PDMS template are less than 50% embedded because necking between particles is visible and results in a slightly different appearance from the set of samples shown in Figure 6.1. Analysis of the images in Figure

6.2 determines the average numbers of NPs/sphere as ~ 1.2 , 37.8 ± 7.0 , 49.3 ± 9.9 , and 45.5 ± 8.6 NPs/sphere for the 5, 10, 20, and 30 min samples, respectively.

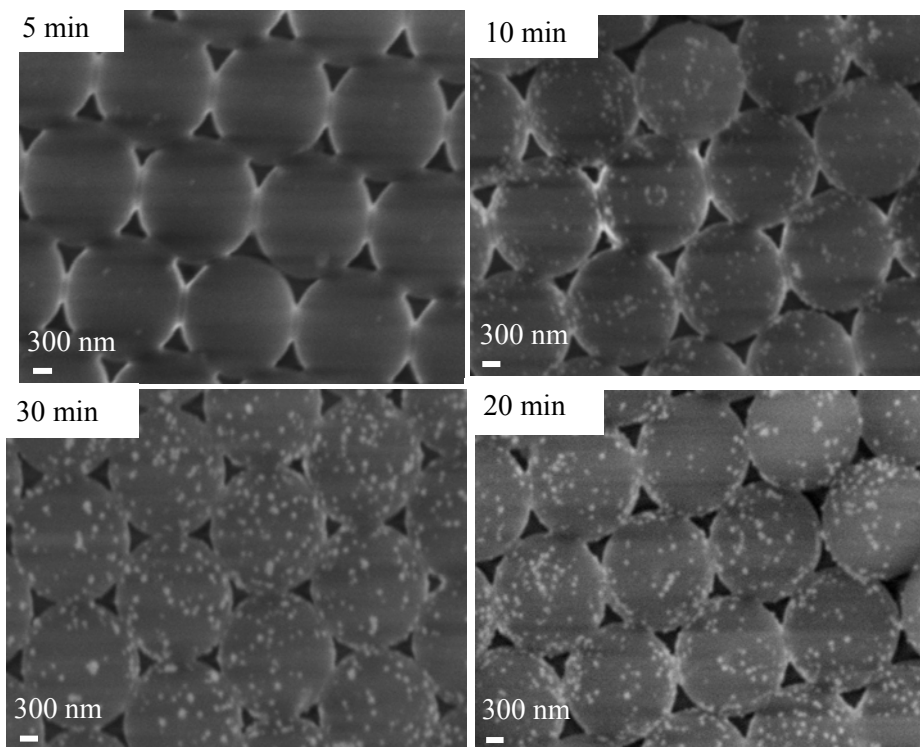


Figure 6.2 Effect of exposure time on silver deposition (0 rpm). Scale bar: 300 nm

The sample shown in Fig. 6.2a obtained after 5 min of exposure shows very sparse deposition with an average of ~ 1.2 NPs/sphere with 50% of them being small NPs. An additional 5 min of exposure results in the deposition of more particles (37.8 ± 7.0 NPs/sphere, Fig. 6.2b), while the particle size appears to remain constant with 70% in the small and medium size category. There are an average of 9.3 ± 8.0 small, 27.3 ± 5.9 medium, 1.2 ± 1.0 large, and 0.17 ± 0.39 extra large NPs/spheres counted for the 10-min sample. A 20 min exposure shows a denser deposition (49.3 ± 9.9 NPs/sphere) and the onset of short chain formation and particle aggregation into bigger clusters. The numbers for the 20-min sample are 6.9 ± 2.2 small, 38.6 ± 7.8 medium, 3.2 ± 1.8 large, and 0.6 ± 0.9 extra-large NPs/sphere. Comparison with the 10-min sample shows that the NP size

distributions of the two samples are very similar to each other. But still, evidently, more medium NPs are observed in the 20-min exposure time sample. The deposit obtained after 30 min of exposure time shows a nanoparticle density similar to the 20 min sample, with less medium NPs (decreased from 38.6 ± 7.8 to 31.8 ± 6.9 NPs/sphere) and more large (increased from 3.2 ± 1.8 to 5.3 ± 2.2 NPs/sphere) and extra large (increased from 0.6 ± 0.9 to 1.1 ± 0.9 NPs/sphere) NPs/sphere.

6.2.4 Effect of the silver precursor concentration

An increasing silver acetate concentration results in an increased silver particle deposition. Figure 6.3 summarizes the images obtained from four samples reacted at a lower (0.5×), the standard (1.0×), and two increased (1.5×, 2.0×) silver concentrations (Figure 6.3 a-d) with all other parameters kept constant.

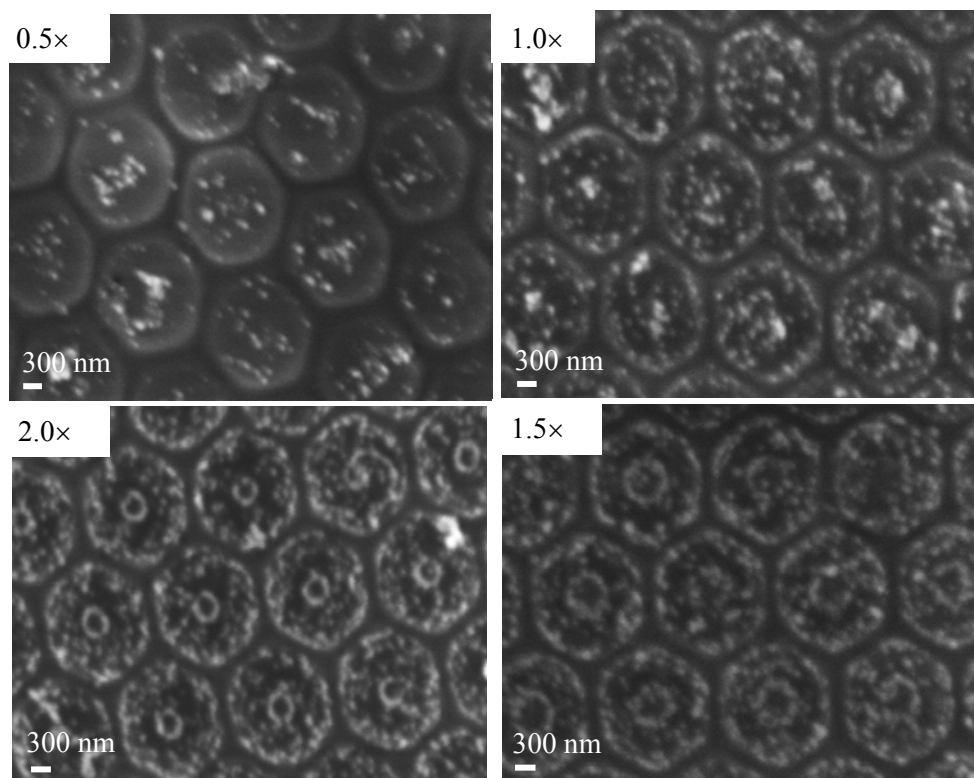


Figure 6.3 Effect of precursor concentration on silver deposition. Scale bar: 300 nm

On first inspection, the two higher silver concentration samples (Fig. 6.3c 1.5×, d 2.0×) stand out with their very uniform and dense deposits of silver NPs. For the 0.5× and 1.0× silver samples, a larger number of big agglomerates are found randomly on the sphere surfaces despite through rinsing of the samples after reaction. This may be partially due to the variation of sulfate group distribution ^[144] and non-uniform particle growth.

Analysis of Figure 6.3, yields average numbers of NPs/sphere of 23.7 ± 6.1 , 53.3 ± 6.4 , 61.1 ± 3.6 , and 61.9 ± 3.4 NPs/sphere for the 0.5, 1.0, 2.0, and 4.0× samples, respectively. The detailed counting shows that most of the NPs deposited on all silver concentration samples are small and medium NPs while there are no extra large NPs formed if the big agglomerates are excluded from the analysis. There are no large NPs deposited on the 0.5× sample (unusual agglomerates are neglected) and only about 22.4 ± 6.8 small NPs and 1.3 ± 1.5 medium NPs. For the 1.0× sample, the amount of small NPs increases to 50.7 ± 6.0 but still there are only 2.3 ± 1.1 medium NPs and 0.33 ± 0.71 large NPs. The numbers of small NPs for 1.5× and 2.0× samples both increase only by ~ 1 compared to the 1.0× sample, indicating a plateau stage for the formation of small NPs. The numbers of medium (8.9 ± 3.9 and 10.1 ± 2.5 NPs/sphere for 1.5 and 2.0× sample, respectively) and large NPs (0.71 ± 0.95 and 0.75 ± 0.46 NPs/sphere for 1.5 and 2.0× sample, respectively) in these two samples have increased by almost 200% compared to the 1.0× sample. The similarity of the NPs/sphere values for the 1.5× and 2.0× samples indicates that a plateau stages has been reached for medium and large NPs formation.

6.2.5 Effect of agents concentration

The two agents required in the deposition reaction are formaldehyde (reducing agent) and ammonia (complexing agent). We vary first the concentration of the two agents independently and then both together with a constant molar ratio.

Formaldehyde concentration variation

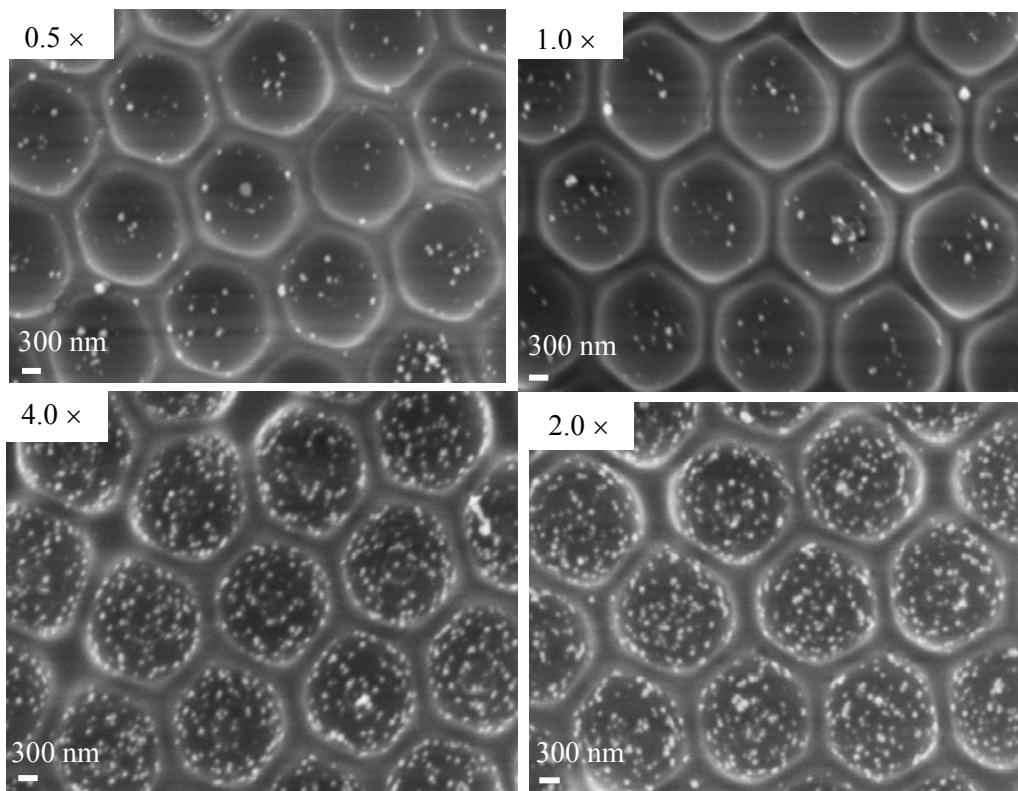


Figure 6.4 Effect of HCHO concentration on silver deposition. Scale bar: 300 nm

Figure 6.4 shows the results obtained with varying formaldehyde concentration. Inspection of the Figure 6.4 reveals that very little deposit is observed in the 0.5 $\times$ and 1.0 $\times$ samples where only several NPs (18.9 ± 5.0 and 17.3 ± 4.6 NPs/sphere, respectively) are formed with a major portion of small NPs (12.4 ± 4.4 and 14.1 ± 3.9 NPs/sphere for the 0.5 $\times$ and 1.0 $\times$ samples, respectively). In contrast, the deposits from the 2.0 $\times$ and 4.0 $\times$ formaldehyde concentration samples show a dense deposition of $74.0 \pm$

6.3 and 66.7 ± 5.5 NPs/sphere, respectively. In all four formaldehyde concentration samples (0.5×, 1.0×, 2.0×, and 4.0×), small NPs are prevalent (12.4 ± 4.4 , 14.1 ± 3.9 , 57.0 ± 8.1 , and 58.6 ± 5.3 NPs/sphere) followed by medium (4.4 ± 2.7 , 3.1 ± 1.6 , 16.7 ± 6.8 , and 7.0 ± 2.0 NPs/sphere) and large NPs (2.0 ± 1.7 , 0, 0.3 ± 0.5 , and 0.9 ± 1.1 NPs/sphere). Only the 4× sample shows a few extra large NPs with an average value of 0.3 ± 0.5 NPs/sphere.

In addition, there seems no apparent deposit concentration or morphology difference between the two samples of higher formaldehyde concentrations (2.0× and 4.0×). Both have ~70 NPs/sphere composed of about 80% small NPs/sphere. There are more medium NPs (16.7 ± 6.8 NPs/sphere) but fewer large NPs (0.3 ± 0.5 NPs/sphere) in the 2.0× sample compared to 7.0 ± 2.0 NPs/sphere and 0.9 ± 1.1 NPs/sphere, respectively, for the 4.0× sample.

Ammonia concentration variation

In Fig. 6.5 we show the deposit prepared at various ammonia concentration levels. A drastic difference in deposit morphology is observed for all four samples. Compared to Figs. 6.1-6.4, the deposited NPs are much more evenly distributed and smaller in size. A few extra-large agglomerates ($d > 200$ nm) are seen in the scanned areas, however, their distribution is non-uniform and they are excluded from analysis.

Ignoring the variation in NPs size, average particle numbers are determined as 152.7 ± 8.5 , 120.8 ± 14.6 , 88.4 ± 32.6 , and 90.1 ± 15.4 NPs/sphere for the 0.5× (Fig. 6.5a) 1.0× (Fig. 6.5b), 2.0× (Fig. 6c), and 4.0× (Fig. 6d) samples, respectively. Comparison of the numbers shows that the density of the deposit initially decreases and then plateaus as the NH_3 concentration increases.

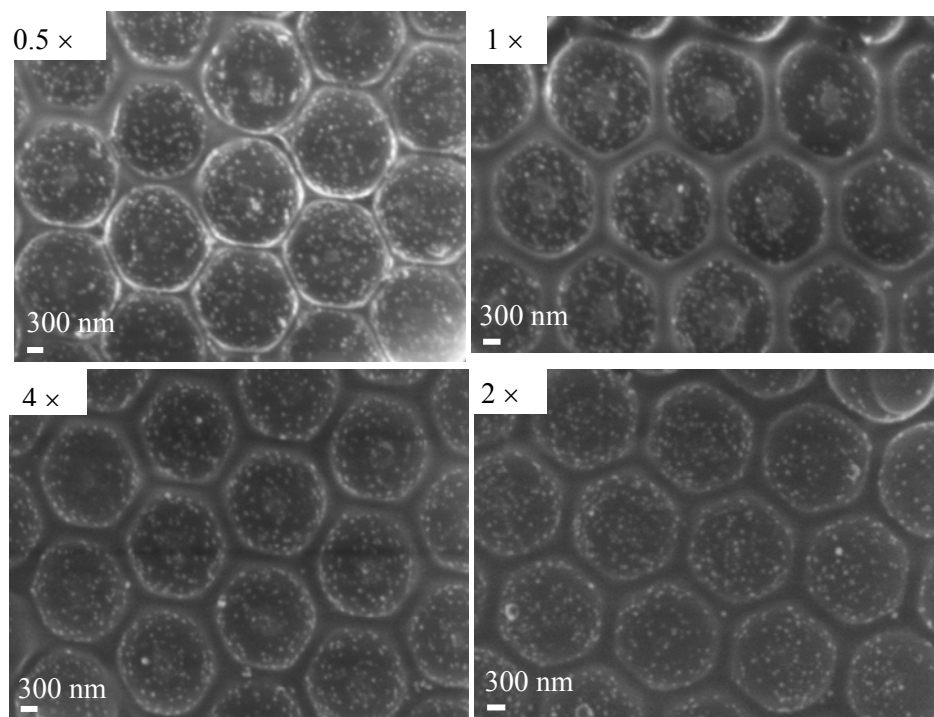


Figure 6.5 Effect of ammonia concentration on silver deposition. Scale bar: 300 nm

Careful analysis of the size distribution of the NPs in the four samples reveals that it varies only slightly. In the 0.5 $\times$ sample, most silver particles deposited are small NPs with diameters smaller than 100 nm. More specifically, on average per sphere 17.0 ± 11 NPs ($\sim 11.2\%$) are smaller than 50 nm, 130.3 ± 15.6 NPs ($\sim 85.3\%$) are between 50 and 100 nm, 5.3 ± 3.2 (3.5%) are in the 100-150 nm range and only 0.14 ± 0.4 ($<0.1\%$) are larger than 150 nm. A similar size distribution is observed in the 1.0 $\times$, 2.0 $\times$ and 4.0 $\times$ samples with the only difference that in the three higher ammonia concentration samples there are on average per sphere more 50-100 nm NPs (91-93%), fewer NPs (6-7%) smaller than 50 nm, and no NPs larger than 150 nm.

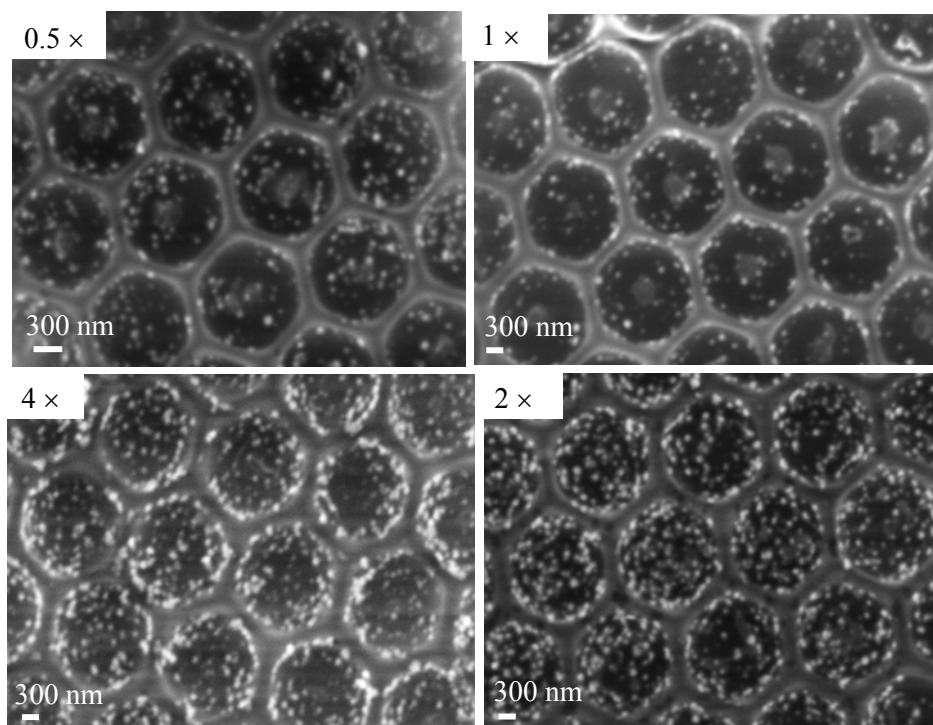


Figure 6.6 Effect of agents bound concentration (FD:AM=constant) on silver deposition. Scale bar: 300 nm

Agents bound concentration variation

Next, the effect of variation in the complexing *and* reducing agent concentration with a constant molar ratio is investigated. This study is inspired by the apparently different changes in deposit morphology observed in the formaldehyde concentration set (Fig. 6.4) and the ammonia concentration set (Fig. 6.5). The effects on the deposit morphology caused by varying the two agents at the same time while keeping their molar ratio constant (ammonia: formaldehyde = 1:2) are summarized in Figure 6.6. On first sight, the morphology of the deposit in Figure 6.6 seems similar to that found in Figures 6.1, 6.3, and 6.4 and different from that observed in Figure 6.5.

Careful analysis of the images in Figure 6.6 results in average numbers of 39.9 ± 7.2 (Fig 6.6a), 48.1 ± 5.2 (Fig 6.6b), 66.9 ± 7.2 (Fig 6.6c), and 54.3 ± 4.7 NPs/sphere (Fig

6.6d) for the 0.5×, 1.0×, 2.0×, and 4.0× samples, respectively. Initially, the amount of deposit increases as the agents-bound concentration increases. At the highest agents-bound concentration (4.0×) it decreases slightly. The majority of NPs in the deposits prepared with 0.5× and 1.0× bound concentration of ammonia and formaldehyde are of small and medium size with $d < 150$ nm. 16.1 ± 3.0 and 29.9 ± 6.1 small NPs/sphere are counted for the 0.5× and 1.0× samples, respectively, whereas values of 19.9 ± 4.3 and 16.4 ± 3.8 NPs/sphere are found for the medium size range. Much fewer ($<10\%$) large (3.7 ± 2.1 and 1.6 ± 0.5 large NPs/sphere) and more or less extra large NPs (0.1 ± 0.4 and 0.3 ± 0.5 extra large NPs/sphere) are observed in the deposit obtained with 0.5× and 1.0× bound concentration of ammonia and formaldehyde. The total number of deposited NPs/sphere increases by 40% upon increase of the agents-bound concentration from 1.0× to 2.0× and then drops by 20% upon increase to 4.0× (Figs. 6.6 c and d). Similar to the 1.0× sample, the NP size most present on the spheres is small NPs with 38.7 ± 8.6 and 27.9 ± 4.2 NPs/sphere for the 2.0× and 4.0× samples, respectively. The numbers for medium, large, and extra-large NPs/sphere in samples 2.0× and 4.0× are 24.1 ± 4.8 and 21.6 ± 3.9 , 3.0 ± 1.2 and 3.3 ± 1.4 , and 1.0 ± 1.2 and 1.6 ± 0.5 , respectively.

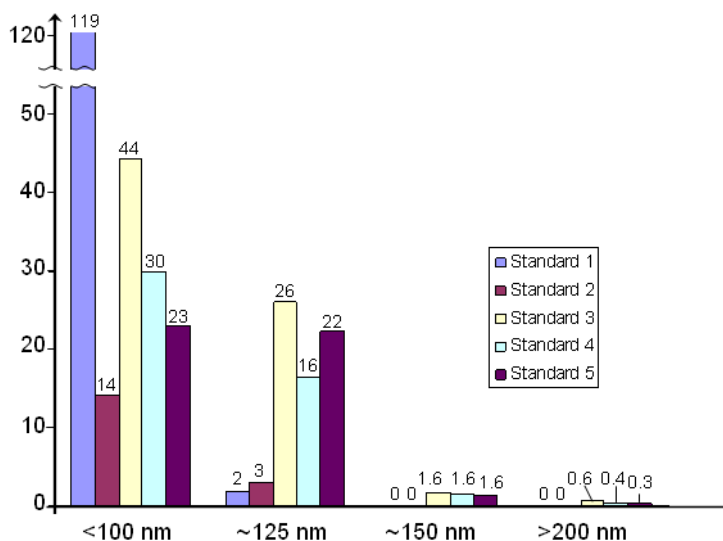
6.3 Discussion

In the following the results obtained in the deposition experiments are analyzed quantitatively and used to shed light on the deposition mechanism. The effect of each reaction parameter on the deposit morphology is discussed. In addition, reaction conditions leading to a complete deposit are presented. In our discussion, we assume that all deposited nanoparticles are spherical in shape, while their diameters fall into the small

(d = 75 nm), medium (d = 125 nm), large (d = 175 nm), or extra-large (d = 200 nm) category.

6.3.1 Variation in the standard deposition procedure

Graph 6.0 shows the nanoparticle distribution obtained for the five analyzed standard samples. It is evident from the graph that on average there is a high tendency (> 96%) for the formation of small and medium-sized nanoparticles with diameters below 150 nm at standard Ag-ELD conditions, while very few large and extra-large nano particles are formed (< 4%).



Graph 6.0 Distribution of NPs size in standard deposition (1.0×). y axis: # of NPs/sphere

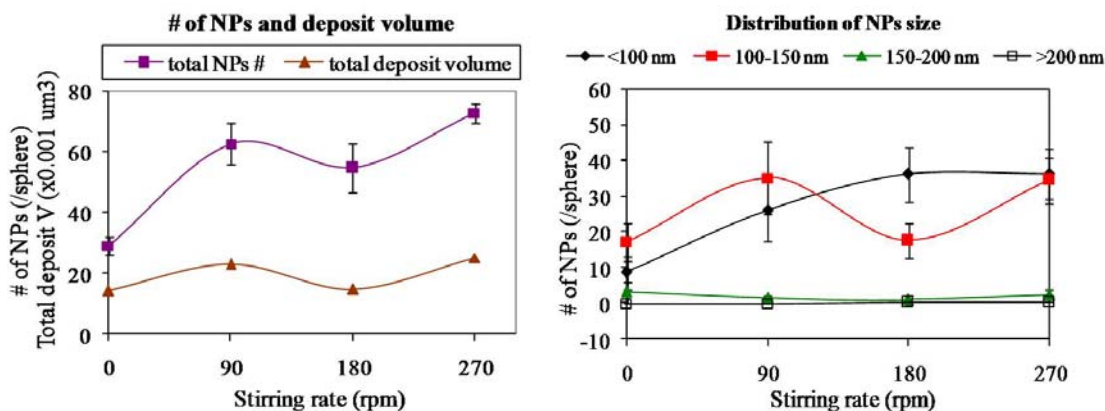
Further, it is also clear from Graph 6.0 that the deposition reaction is influenced by more than just the reaction condition and bath composition resulting in a variation of the total number of particles (61 ± 39 NPs/sphere) of more than 50% over five samples prepared under identical standard conditions. Two likely origins of this sample-to-sample deviation are the variation in surface functionality of the sulfate-terminated PS spheres

from batch to batch and a slight variation in embedment depth (10%). For example, the batches of sPS spheres used in this study varied in the specific sulfate group area and number of sulfate groups by $A(\text{SO}_4) = 193 \pm 33 \text{ \AA}^2$ ($\sim 17\%$) and $\#(\text{SO}_4) = (9.2 \pm 1.8) \times 10^6$ ($\sim 20\%$), respectively. Interestingly, the average total amount of deposit ($0.017 \pm 0.004 \mu\text{m}^3$) varies much less (30%) from standard to standard when the data for standard 2 is excluded from the calculation.

6.3.2 Effect of stirring rate

It has been reported that formaldehyde is a relatively slow reducing agent^[104] and the formaldehyde decomposition reaction is often activation-controlled.^[95] Without stirring (0 rpm), the diffusion rates of both the complexing agent ammonia and the reducing agent formaldehyde from the solution bottom ($z = 0$) where they are injected to the sphere/PDMS template floating at the top of the bulk solution ($z \sim 0.4 \text{ cm}$) where they react become comparable to the decomposition rate of formaldehyde moving the reaction into the diffusion-limited regime. Consequently, the reduction rate of silver cations and the deposit of silver NPs are affected. The total exposure time in our stirring rate experiments is short (5 min) thus limited reactant arrives at the sphere surfaces if the solution is not stirred. In addition, during the diffusion from the bottom of the vial to the sphere surfaces ammonia and formaldehyde are also consumed by the silver ions in solution leading to formation of free silver nanoparticles in solution. This occurrence is evidenced by a change of the solution color from colorless transparent to light brownish-yellow after the reaction, i.e., silver NPs are formed in solution. Further, a shiny layer of a silver mirror also forms immediately on the clean glass wall of the vial (the so-called Tollens' silver mirror reaction) upon addition of formaldehyde further lowering the silver

ion concentration and explaining the sparse deposit at 0 rpm. Introduction of stirring assures that the agents are more evenly distributed in solution and near the sphere surfaces resulting in an equal chance for all spheres in the sphere/PDMS template to have contact with the agents. As a result a stronger and more uniform deposition is observed in the 90 – 270-rpm samples.



Graph 6.1 Effect of stirring rate on (a) total # and volume ($\times 10^{-3} \mu\text{m}^3$) of NPs per sphere and (b) size distribution of NPs

Graph 6.1 shows the trends of the total amount (Gra. 1a) and size distribution (Gra. 1b) of deposited silver nanoparticles as a function of varying stirring rate. The total number of NPs deposited increases first when the stirring rate increases from 0 to 90 rpm, but slightly decreases when the stirring rate reaches 180 rpm followed by a pronounced increase at 270 rpm. Comparison of the 90 and 180 rpm values shows that they overlap within one standard deviation and could therefore be assumed to be a plateau. A similar trend is observed for the amount of NPs deposited which is calculated as the volume of nanoparticles assuming the average diameters described above. Analysis of the size distribution reveals that the number of small-sized nanoparticles increases as a function of stirring rate from 8.6 ± 4.6 to 36 ± 7 NPs/sphere where it plateaus, while the number of

large particles is small and increases only slightly from 0 to 270 rpm. The medium-sized NPs show the most interesting trend. They increase from 17 ± 5 to 35 ± 10 NPs/sphere at 90 rpm, drop to 18 ± 5 NPs/sphere at 180 rpm, and then increase again to 34 ± 6 NPs/sphere at 270 rpm.

The increase in small, medium, and large NPs at higher stirring rates is attributed to more surface-nucleation events occurring due to an abundance of reactants near the sphere surfaces provided by faster transport to the sphere surfaces. The exception is the number of medium-sized NPs formed which shows a dip at 180 rpm, while all other particles show continuously increasing trends. The unusual medium-size NP trend may be an artifact caused by the arbitrary choice of our diameter ranges. However, the fact that it also appears in the total amount of particles as a plateau means that there is indeed a reduction or leveling in nucleation in the 180-rpm sample. In an effort to explain our observations, we turn to particle nucleation and growth theory.

The number of NPs deposited is determined by the number of nucleation sites, whereas the size (and therefore detection) of the NPs is governed by both the growth rate and the particle ripening processes. In our multi-parameter and multi-process system where both homogeneous and heterogeneous nucleation/growth occurs, it is necessary to analyze the effect of the balance and competition between these two processes. One important parameter to keep in mind is that there is a resolution limit of the SEM instrument (> 30 nm) and there may be very small NPs which are too small to be seen in the SEM images.

Under mild stirring rates such as 90 rpm, fewer surface nuclei are formed in the same time interval compared to spheres exposed to 180 rpm stirring due to the slower transport

of reactants to the surface. Assuming a constant growth rate for the nuclei under both stirring conditions, more reactant would be needed to grow the larger number of initial nuclei in the 180 rpm sample to a size comparable with that in the 90 rpm sample. As a result, there should be a larger number of small particles in the 180 rpm sample which is what we observe (Graph 1b). One would also need to consider that the 180 rpm sample is more likely to have very small NPs that stay beneath the detection limit of the SEM and are thus missed during the counting, which would explain a reduced or stagnant total number of NPs/sphere.

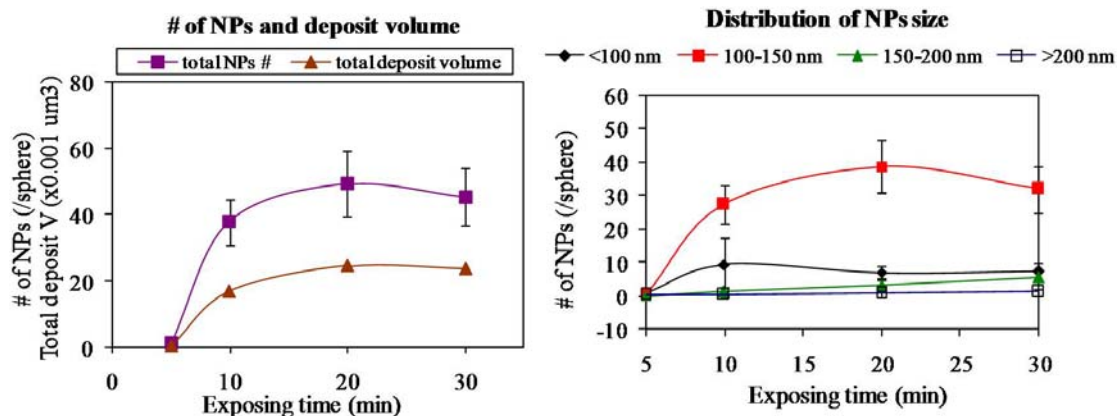
If the above holds true, more nucleation sites are expected at 270 rpm stirring and more nuclei should be able to ripen into visible NPs due to the much-improved transport. The size distribution (Graph 6.1b) shows a plateau for the number of small-sized NPs, i.e., nucleation sites have been saturated, and an increase of medium-sized NPs compared to the 180 rpm sample, which leads to an overall increase in the total number of NPs deposited on each sphere for the 270 rpm sample. The fact that the number of medium sized NPs is not substantially increased compared to the 90 rpm sample may be explained by the fact that a high stirring rate might drive away reactants from the sphere surfaces before silver ions are reduced onto the already existing nuclei thereby slowing down particle growth.

In summary, the higher stirring rate increases exposure of silver cations associated with sulfate groups on the sphere surfaces to reduction by formaldehyde and subsequent deposition of silver onto the sphere surfaces. The uniform and dense deposition also confirms that the silver ions are ubiquitously anchored on the exposed sphere surfaces

and that the sparse deposits on samples obtained at lower stirring rates are mostly due to the limited transport of agents and interaction with the precursor ions.

6.3.3 Effect of exposure time with no stirring

How are diffusion rate, electrochemical rate and exposure time related? External agitation adds convective molecular transfer that will increase the apparent transport rate.^[159] In a very short time, a uniformly mixed system with the same composition at every point is created except in the thin layer surrounding the spheres where chemicals are depleted or accumulated because of reaction. When there is no external agitation, the mass transfer from certain high-concentration areas (e.g., the center point at the solution bottom) into the bulk solution is only due to random molecular diffusion caused by the concentration gradient. The deposition rate will be affected greatly by the mass transport rate if the whole process is diffusion-controlled. Previous deposition under various stirring rates showed that the external agitation accelerates mass transfer greatly and suggest that the silver electroless deposition under our reaction conditions is diffusion-controlled. However, the enhanced flow caused by the bulk motion shortens the transport time and makes it comparable to the reaction time. Hence it is difficult to differentiate the influence of stirring on the competition and balance between the two processes of nucleation and particle growth.^[104] Here we investigate the effect of exposure time under no stirring (so there is only molecular motion driven by the concentration gradient, i.e., the diffusion rate is relatively slow) on the deposit morphology to further understand the deposition mechanism.



Graph 6.2 Effect of exposure time on (a) total # and volume ($\times 10^{-3} \mu\text{m}^3$) of NPs per sphere and (b) size distribution of NPs

The images in Figure 6.2 show that more and more silver NPs deposited on the PS spheres with increasing reaction time. In Graph 6.2a we quantify the deposit and in Graph 6.2b we present the size distribution of the deposited nanoparticles. It is clear that the total number of silver NPs deposited increases sharply from ~ 1 NP/sphere to 40 ± 7 NPs/sphere when the exposure time (time between addition of formaldehyde and quenching of the reaction by removal of the sample from the reaction solution) is extended from 5 min to 10 min. The total number of NPs deposited for 20 and 30 min is 49 ± 10 and 46 ± 9 NPs/sphere, respectively. These numbers overlap within the error bars with the 10 min sample indicating that the whole system is balanced and the silver reduction has reached equilibrium. Based on the observed plateau, it is reasonable to claim that the apparent mass transfer time from the solution bottom (injection point) to the sphere/PDMS template-liquid interface (reaction point) for the formaldehyde-induced deposition of silver onto PS spheres occurs within the order of several minutes. An approximation of formaldehyde diffusion in the aqueous liquid is calculated in Appendix A.

Very similar trends are observed for the small, medium, large, and extra-large nanoparticles (Graph 6.2b). Very little deposition is found in the 5-min sample with only a few small- and medium-sized NPs (<150 nm). The small particles size confirms that the NPs grow from nuclei formed on the sphere surface through particle ripening. It further shows that the NP size and distribution are limited by the very slow diffusion rate of formaldehyde. Interestingly, for the samples with longer exposure time the size distribution is still narrow (mainly medium sized NPs) despite the fact that the silver NPs distribution on the surface is not as even as for samples prepared with stirring. The size distribution graph shows the medium-sized NPs are the most prevalent NP size in all exposure time samples studied. In addition, the number of NPs deposited increases dramatically compared to that observed for the 5-min sample. A similar trend is observed for the small-sized NPs density, while the number of larger NPs unsurprisingly increases with increasing exposure time.

The fact that the total number of particles and the amount of deposit plateau at longer reaction times indicates a diffusion-controlled process. The formaldehyde initially reaching the sphere surface is mainly consumed to form new nuclei randomly on the sphere surfaces. Without efficient agitation or equal distribution of reducing agent to the sphere surfaces, some spots on the sphere surfaces may have a higher probability to interact with formaldehyde. The silver ions around those positions are reduced, form nuclei, and grow into nanoparticles, which then equally expand to larger particles. Thus the formation of many small crystals is kinetically favored although large crystals are thermodynamically more stable.^[160] This also explains why the distribution of NPs in exposure-time experiments is not as even as in samples for the stirring-rate study. At a

later reaction stage the seeds do not have much chance to grow larger due to the slow mass transfer, consumption of reducing agent in bulk solution, and limited reacting time. As the result, most NPs formed can at most reach medium size only.

The difference in deposit density between the stirring-rate samples (Graph 6.1) and exposure-time samples (Graph 6.2) suggests that the apparent diffusion rate is greatly decreased in the static solution compared to the stirred one and thus limits the amount of reactant transferred to the sphere surfaces in the given 5 min window. Further, it implies that the mass transfer in the no-stirring experiments is too slow compared to the slow kinetics of electron transfer provided by the weak reducing agent formaldehyde and consumption of reducing agent for nanoparticle formation in the bulk solution dominates. The silver cations in the bulk solution have a long interaction time with the formaldehyde and as a result nucleation in the bulk solution cannot be avoided with our experimental conditions leading to the formation of more free nanoparticles.^[86a]

In the exposure time experiments, medium-sized NPs present the major population of all NPs deposited, which in contrast to the stirring rate experiments where small-sized NPs are the majority at high stirring rates. Thus, in a static liquid or under low stirring rates, the slow diffusion of reducing agent limits the particle growth at the given reactant concentration conditions.

6.3.4 Effect of reactants concentration on deposit morphology

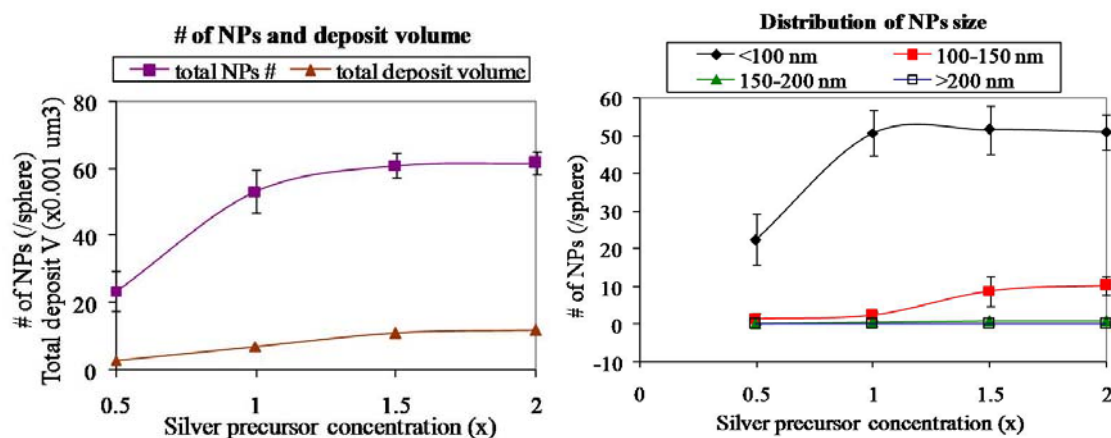
The concentration of reactants in solution not only affects mass transfer, but also the electron transfer (the reduction rate) and influences the deposit especially for a diffusion-controlled process.^[95, 97, 159] In addition, the deposit mass and morphology is determined by the amount of reactants according to mass balance and reaction equilibrium theory.^[97]

To understand the deposition process and determine the effect a variation of the reactants concentrations has on the deposit amount and morphology, we varied the Ag^+ precursor concentration and the agents concentration. The latter includes varying the formaldehyde and ammonia concentration separately as well as varying both concentrations simultaneously with a constant molar ratio.

Effect of silver acetate concentration

In Fig. 6.3, a uniform and dense deposit is seen in all samples and the deposit density increases with increasing silver concentration. A graphical representation of the deposit density and NPs size distribution are plotted in Graph 6.3. Note that irregular sized NPs are neglected. In good agreement with Fig. 6.3, the trends for the total number of NPs deposited and the total amount deposited (Graph 6.3a) increase with increasing silver precursor concentration. The total number of silver NPs deposited increases from 24 ± 6 NPs/sphere to 62 ± 3 NPs/sphere when the silver concentration increases from $0.5\times$ to $2\times$. For $1\times$ and $1.5\times$ concentrations, the NP densities are 53 ± 6 and 61 ± 4 NPs/sphere, respectively. The same increasing trend is also found for both small and medium-sized NPs.

The higher deposit density obtained with higher silver concentration is logical since we have more than enough ammonia and formaldehyde in the reaction solution to react all Ag^+ . Interestingly, the size distribution of NPs seems not to be affected dramatically by varying the silver concentration. Similar to samples in the stirring rate experiments, the small NPs take the leading position in population, indicating the NPs size is well-defined by the deposition process under the given reaction conditions.



Graph 6.3 Effect of silver precursor concentration on (a) total # and volume ($\times 10^{-3} \mu\text{m}^3$) of NPs per sphere and (b) size distribution of NPs

Reviewing Ostwald ripening theory,^[104] it seems the higher silver concentration creates abundant nucleation sites. Most NPs have an equal chance to grow into a similar size throughout the 5 min of reaction. During the incubation stage (4 hours in dark under certain stirring rate), silver cations associate with the sulfate groups on the sphere surfaces and reach an adsorption/desorption equilibrium. At higher silver concentrations, it is very likely that the sphere surfaces are covered more evenly and more densely. Then there is the complexing stage when silver ions get exposed to ammonia and form the complex $[\text{Ag}(\text{NH}_3)_2]\text{OH}$, which is subsequently reduced to silver atoms. With the help of a mild stirring (120 rpm), this reaction step reaches equilibrium soon and the complex ions $[\text{Ag}(\text{NH}_3)_2]^+$ are likely to stay in close proximity to the negative $-\text{SO}_4^{2-}$ groups. Finally, upon addition of the reducing agent formaldehyde, the silver particles start to form and attach to the exposed sphere surface nearby. The reduction rate is much slower for the silver-ammonia complex hence initially only very small nanoparticles are produced all over the sphere surfaces. A much-improved density of functional sites to which the silver complex ions are anchored is achieved by the higher silver concentration

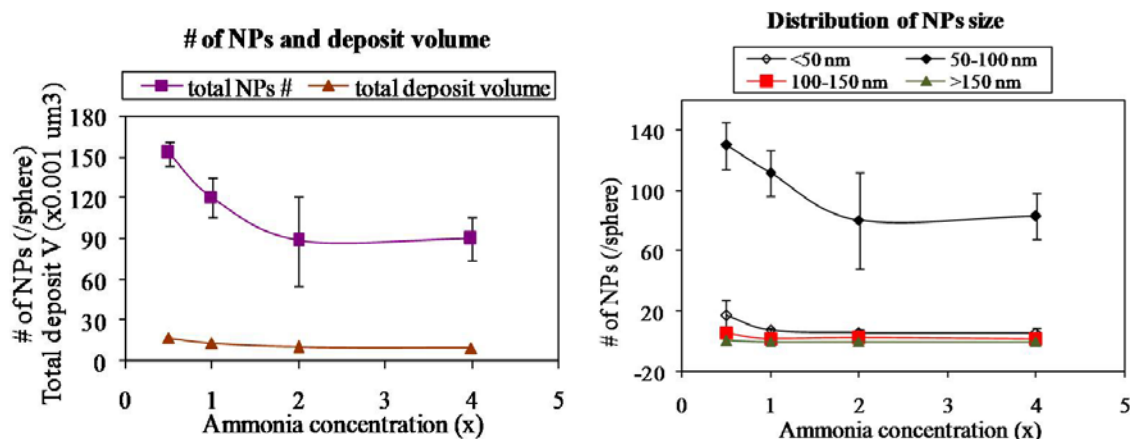
and leads to the formation of more nuclei. At a later stage during the reaction, nuclei incorporate the newly reduced atoms to mature into larger particles while very few new nuclei are formed. As a result the total number of NPs is determined by the initial nucleation event. Most silver particles grow with a similar rate to a comparable final size owing to the even distribution of the reducing agent to the reaction sites under the abundant stirring.

Ammonia concentration

Unlike formaldehyde, ammonia, as the complexing agent, plays an important role in controlling the reaction rate and avoiding of the unwanted Ag₂O precipitation in the bulk solution. Therefore knowing the effect of ammonia concentration on the final deposit quality is of great importance. The standard electrode potentials (aqueous solution, 25 °C, vs. NHE) of plain silver ions and the silver-ammonia complex are given in the following equations, respectively.^[161]



Apparently, the silver-ammonia complex ion is reduced more slowly and colloidal silver metal formation is depressed. At 1.0× ammonia concentration, the bulk solution appeared brownish and cloudy and the deposit on the PS spheres consisted of some large agglomerates. Here we increased the ammonia concentration to 2.0× and 4.0× and compared their performance to the standard sample as well as the 0.5× concentration sample.



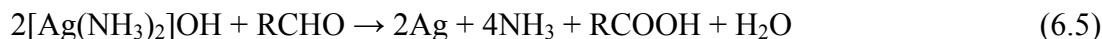
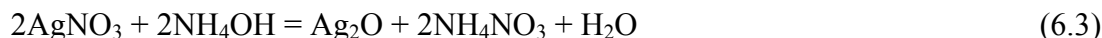
Graph 6.4 Effect of ammonia concentration on (a) total # and volume ($\times 10^{-3} \mu\text{m}^3$) of NPs per sphere and (b) size distribution of NPs

In Fig. 6.5, we see deposits quite different from the previous stirring rate, exposure time, and formaldehyde concentration experiments. Inspection of the standard condition sample and comparison with those of the other experiments, immediately reveals that the pronounced change in the deposit is due to a change in the number of nucleation sites on the sphere surfaces. However, detailed counting and comparison of the deposits obtained in the ammonia experiments allows the separation of the ammonia effect from the surface property effect. It is likely that the number of exposed sulfate groups has increased for this batch of embedded spheres leading to a larger number of nuclei and as a result an overall shift of the size distribution towards small particles. In order to adjust to this shift, the NP size groups are adjusted to extra-small (<50 nm), small (50-100 nm), medium (100-150 nm), and large (150-200 nm) NPs and the group of extra-large NPs is excluded.

Nanoparticle amounts and size distributions are depicted in Graph 6.4a and b. The plots show an exponentially decreasing trend in the total number of NPs. More interestingly, the numbers of NPs in all size groups also declined with increasing ammonia concentration. At all ammonia concentrations, no extra large-sized NPs are

observed. At the lowest ammonia concentration, there are 130 ± 16 NPs/sphere, which decreases to 112 ± 15 and 81 ± 32 NPs/sphere for the 1× and 2× concentration samples, respectively. From the 2× to 4× ammonia concentrations, there is little change in the amount of NPs indicating that the effect of ammonia concentration reached the saturation stage and further addition of ammonia has no influence on the deposition process.

The observed strong decrease in number of particles (~40%) confirms the suggested complexation function of ammonia during the reaction^[162] and is in good agreement with previous reports where the effect of concentration of chemicals with similar function was studied.^[148] The smaller numbers of NPs deposited in the samples exposed to a higher concentration of ammonia might come from the formation of fewer nuclei or slower particle growth. A poorer contact of reactants with the sphere surfaces or a slower reaction rate could serve as rationale. According to the complex formation and reduction of the ammonia complex proposed by researchers,^[162] there are several steps in the slow reduction of silver ions:



And a side reaction:



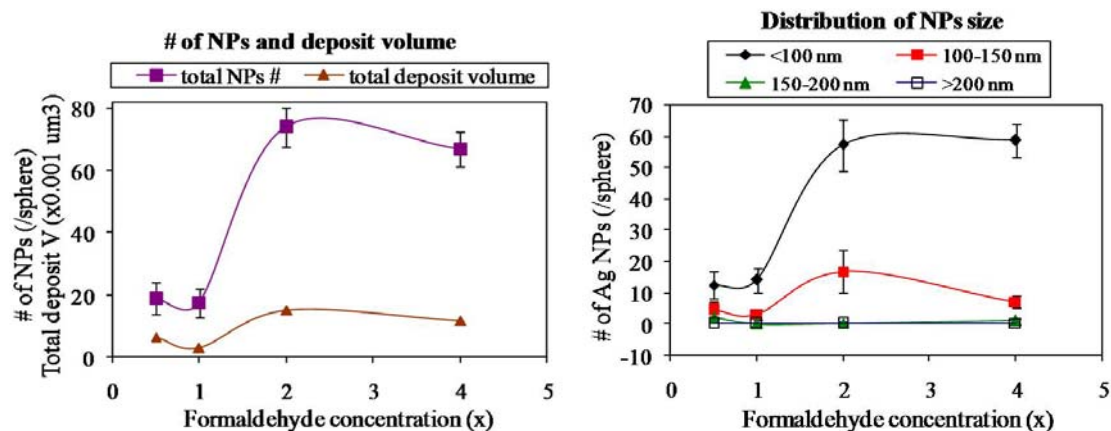
In our system, silver acetate is used instead of a nitrate salt, but it is reasonable to assume they behave similarly in the basic bulk solution. These chemical reactions indicate more silver ions (both in the bulk solution and on the exposed sphere surfaces) are complexed by the ammonia in a highly concentrated solution. As a result, the

apparent reaction rate would decrease yielding fewer nuclei within the limited reaction time. At a later reaction stage, the particle growth is slowed due to the complexation of Ag^+ and fewer nuclei can reach SEM-visible size.

In summary, all four samples show NPs size distributions with a maximum at small NPs (50-100 nm). In contrast to the previous experiments, the number of NPs of this size decreases with increasing concentration of ammonia.

Effect of formaldehyde concentration

As the images in Fig. 6.4 show, the 1.0× concentration sample in the formaldehyde concentration set is somewhat irregular hence we focus our discussion on the other three samples. When the formaldehyde concentration is increased from 0.5× to 2.0×, the amount of nanoparticles rapidly increases from 18.9 ± 5.0 to 74.0 ± 6.3 NPs/sphere, but then levels out at 66.7 ± 5.5 NPs/spheres when the FD concentration is increased to 4.0× as indicated in Graph 6.5a. The graph showing the total amount of deposit shows a similar trend with a small maximum for the 2.0× concentration sample. In addition, the size distribution of NPs shows agreement with this plateau trend. The plateau suggests that adding more reducing agent has little effect on the amount of deposit or the final NPs size distribution when a certain formaldehyde concentration is reached. However, it is necessary to point out that even the 0.5× FD concentration is high enough to reduce all silver ions in the reaction solution. The lower amount of deposit observed at the lowest FD concentration results in a decrease of reaction 6.5. This decrease leaves more of the $[\text{Ag}(\text{NH}_3)_2]\text{OH}$ complex unreacted and available for the side reaction (Eq. 6.6), which results in a slower formation of silver atoms for deposition.



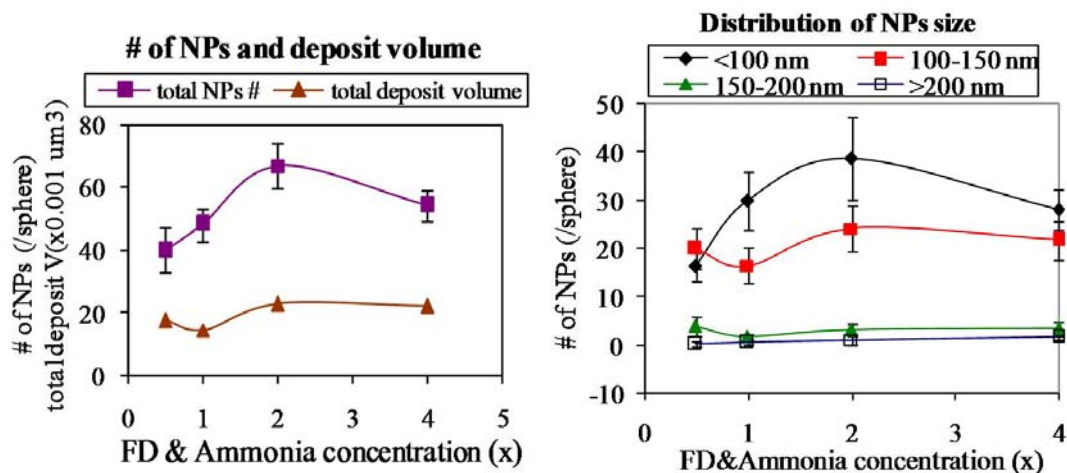
Graph 6.5 Effect of formaldehyde concentration on (a) total # and volume ($\times 10^{-3} \mu\text{m}^3$) of NPs per sphere and (b) size distribution of NPs

Again the largest population of NPs is in the 50-100 nm range of small NPs. The phenomenon is observed in all sets of experiments except the exposure time test where no stirring is applied. This particle size distribution implies that under our reaction conditions with stirring, the nucleation process and the subsequent particle growth are well-balanced and controlled. More importantly, for most conditions tested the particle ripening process is uniform for all nucleation sites and they are able to grow into similar size within the reaction time.

FD+AM bound concentration

The concentration of ammonia seems to reduce the amount of NPs deposited while the formaldehyde concentration seems to have an opposite effect, i.e., it increases the number of NPs up to a specific concentration above which the effect disappears. Keeping the molar ratio of formaldehyde and ammonia concentration constant, we investigate the effect of simultaneously increasing ammonia and formaldehyde concentrations on the resulting deposit. The fixed concentration ratio of the two agents supposedly balances the

two parallel reactions stated in Eq. 6.5 and Eq. 6.6. Both reactions consume the silver complex $[\text{Ag}(\text{NH}_3)_2]\text{OH}$.



Graph 6.6 Effect of agent bound concentration on (a) total # and volume ($\times 10^{-3} \mu\text{m}^3$) of NPs per sphere and (b) size distribution of NPs

Quick inspection of Graph 6.6 shows many similarities with Graph 6.4 (effect of formaldehyde concentration) and much fewer with Graph 6.5 (effect of ammonia concentration). The numbers of all sizes of NPs vary little at the lower two agents-bound concentrations ($0.5\times$ and $1\times$). A dramatic increase is observed going to the $2\times$ agents-bound concentration while an actual decrease occurs for the $4\times$ experiment. Comparing these trends, it is obvious that the formaldehyde concentration dominates the effects in the low concentration regime, whereas the complexing ability of ammonia becomes important in the high concentration regime leading to a decrease in nucleation and NPs despite.

Smooth and rough deposition

Using the information obtained from all deposition experiments, we tested our ability to predict conditions at which complete shells with smooth or rough surfaces should be obtained.

In a dense half-shell preparation experiment, we keep the agents concentration unchanged (both 1 $\times$) but tested various higher silver acetate concentrations: 2 $\times$, 4 $\times$, 6 $\times$, 8 $\times$. As can be seen in Figure 6.7, the deposit amount increase steeply from 2 $\times$ to 8 $\times$ precursor concentration and the highest concentration tested results in almost complete half-shells with very little unmodified area on the sphere surfaces. Interestingly, neither large agglomerates nor uneven deposit thickness are observed.

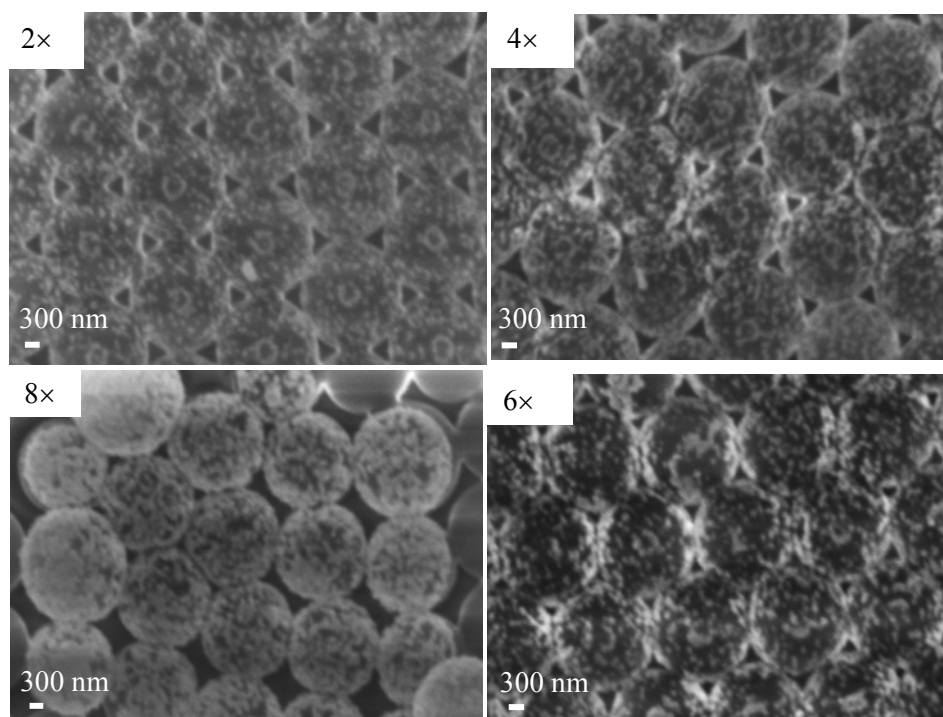


Figure 6.7 Effect of high Ag precursor concentration on deposit surface morphology

In order to obtain rougher deposits, we tested silver electroless deposition at 8 $\times$ silver concentration (stoichiometrically equal to be 1.0 $\times$ ammonia and 0.125 $\times$ formaldehyde concentration) and increased the formaldehyde concentration from 2 $\times$ to 4 $\times$ to 6 $\times$ and

finally to 8× while keeping the ammonia concentration at 1.0×. In all three experiments with very high reducing agent concentrations (much more than needed to reduce the metal ions) deposits composed of rough silver agglomerates, spikes, and even large flakes are observed (data not shown), implying a poorly controlled reduction process due to the very low ammonia concentration.

Combining the results of the individual agent concentration experiments and the bound agents concentration test, we conclude that ammonia can be used to control the number of the silver nanoparticles deposited and that a relatively high ammonia concentration can slow the reduction process kinetically to get a better well-controlled deposit. While increased formaldehyde concentration enhances the diffusion, speeds up the reduction process, and finally results in larger particles or even rough agglomerates.

6.4 Conclusion

In this chapter, we varied the macroscopic conditions, including stirring rate, exposure time, and reactant concentrations, and discussed their effect on the microscopic silver reduction as expressed by the deposit morphology of the silver nanoparticles deposited on the templated sPS spheres.

We find that in general an increasing of the stirring rate enhances the mass transfer yielding more deposit and a larger total number of NPs/sphere. At a certain point, the stirring rate benefits the nucleation process more than the particle growth process and the *apparent* NPs deposit density decreases. However, the total trend indicates that the deposition process might be diffusion-controlled under our reaction conditions and the exposure time experiments support our hypothesis. Lengthening the exposure time from 5 min to 10 min increases the NPs deposit as well as the number of NPs in all size

categories but has little effect when exposure time is further increased to 20 and 30 min. This also suggested that the diffusion time (under no external stirring but bulk consumption) is of the order of several minutes.

In addition, the effect of agent concentration on the deposit morphology shows that ammonia plays an important role in controlling the silver reduction rate and the formation of the NPs deposited. Increasing of the ammonia concentration reduces the number of silver NPs deposited. Higher silver and formaldehyde concentrations both lead to an increase of the NPs deposited while very high formaldehyde concentrations in the absence of ammonia lead to large and irregular deposits.

In all experiments carried out with stirring, the size of the majority of NPs is finely controlled to be in the small sized NPs range ($d = 100$ nm) and adjustment of the silver ion concentration results in a complete half-shell modification on the sPS spheres composed of small nanoislands.

Chapter 7 Anisotropic surface modification of spheres with other materials and a novel method for preparation of dual-cap spheres

In Chaps. 5 and 6, we successfully prepared surface-anisotropic silver-modified micron size polystyrene spheres via electroless deposition (ELD) with the aid of PDMS templating. ELD has also been widely used to modify spheres symmetrically to form core-shell composites with metals like gold, platinum and palladium as reviewed in Chap.3. However, only a few articles have reported the anisotropic decoration of polymer sphere surfaces with gold ^[5] and other metals, and even fewer on unseeded electroless deposition.^[3] Here we investigate if our templating-ELD procedure can be expanded to incorporate these industrially interesting metals. In addition, one other frequently used LPD method, the *sol-gel* process, is combined with our templating procedure to incorporate titanium oxide into the “core-cap” composite structure where polystyrene microspheres are employed as core particles.

Further, we observe (Chap. 5) that ELD produces a much rougher surface morphology compared to that prepared by PVD under our reaction conditions. We use this difference in surface roughness to study of effect of surface morphology on the orientation of spheres during assembly and report our initial results. In addition, a novel process for the preparation of dual-cap spheres is developed employing both PVD and ELD.

7.1 Anisotropic deposition of gold on microsphere/PDMS template

Many experiments have shown that spheres with positive functional groups such as amine, treated with aqueous HCl to form cationic -NH_3^+ , or carboxylic acid, treated with aqueous NaOH then poly-(allylamine hydrochloride) to become positive, show excellent

adhesion of gold colloids.^[84, 86c] Therefore 2.6 μm amine-terminated polystyrene (aPS) spheres are tested first as the core spheres to prepare surface-anisotropic structures with gold. Next, the gold electroless deposition is performed on the 2.4 μm sPS spheres employed in the Ag ELD study (Chaps. 5 and 6).

Anisotropic deposition of gold on 2.6 μm amine PS spheres

First, a monolayer of 2.6 μm aPS spheres is prepared according to both monolayer self-assembly methods discussed in Chap. 4. The monolayers obtained from the two methods show much lower quality compared to the monolayers obtained with 2.4 μm sPS spheres. The size difference between 2.6 μm and 2.4 μm is not significant enough to cause the problem. However, the surface group properties are likely to play a dominant role in the monolayer morphology. The amine groups on the sphere surface are positively charged in aqueous solution; hence the spheres easily stick to the negatively charged native oxide present on the silicon wafer surface and cannot move freely during the assembly process once they have touched the surface. Only small domains of close-packed monolayer are formed (data not shown). In analogy to the anisotropic silver deposition on sPS spheres reported in Chap. 5, the low quality monolayer structures are embedded in a PDMS mask (Chap. 4.2.2) and the procedure for gold deposition on the spheres described in section 4.3.1 is employed. After reaction, the sphere/PDMS template is removed from the reaction solution and rinsed thoroughly with DI water. The initially white sphere area on the PDMS template is pink upon removal from the reaction solution, indicating nanosized Au colloids have adsorbed on the sphere surfaces. Imaging of the sphere/PDMS template with SEM shows no visible deposit, indicating that the particles are smaller than the resolution of our VP-SEM ($d \approx 30$ nm).

Anisotropic deposition of gold on 2.4 μm sulfate PS spheres

High quality 2.4 μm sPS sphere monolayers are prepared and embedded into a PDMS mask following the process described in Chap. 4. Then the sphere/PDMS template is put into solution I (HAuCl_4 , 0.01% by weight) floating on top with the spheres exposed to the liquid. When the liquid is heated to boiling, solution II (sodium citrate, 1% by weight) is added to the bottom of the vial under stirring. Bubbles are found to sometimes form at the interface of the sphere/PDMS template and the reaction solution. To reduce bubble formation a lower stirring rate and temperature are used. The solution turns pink after about 3 min and settles into a pinkish red color. The PDMS mask with spheres is taken out and a faintly pink color is also seen on the side with spheres that has been exposed to the reaction solution. An SEM image of a representative sample is shown in Figure 7.1.

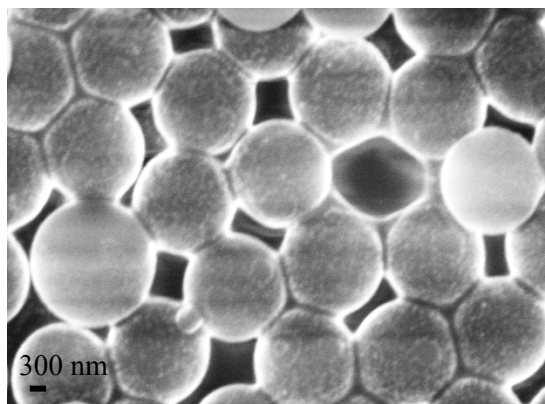


Figure 7.1 Gold-modified 2.4 μm sPS spheres partially embedded in PDMS. Scale bar: 300 nm

The solution usually boils near 100 $^{\circ}\text{C}$, which is above the glass transition temperature of PS ($T_g = 95^{\circ}\text{C}$),^[163] but most spheres still keep their shape. In the case of PS spheres studied by Dokoutchaev, et al., gold was not deposited on anionic spheres or even cationic spheres in the absence of the cationic polymer.^[84] But in our sample with sulfate-terminated PS spheres, we can see many tiny bright dots on most spheres,

indicating successful gold deposition. In contrast to the deposits obtained in the silver ELD samples, these gold NPs are much smaller in size, typically 60-100 nm and the apparent size distribution is narrower. The narrow size distribution is attributed to the strict control of the relative amounts of reactants in the deposition process. As discussed for the silver reduction mechanism (Chap.6), various ratios of reactants determine the relative rates of the two independent processes (nucleation and growth of particles) and may considerably affect the final particle size. For gold NPs obtained through reduction of gold chloride with sodium citrate in aqueous solution this process is even more controllable.^[164] More interestingly, the gold NPs shown in Fig. 7.1 appear to cover the whole sphere surface with little void space. This, other than having a surface with better distributed sulfate groups, could also be related to the balanced nucleation and growth rates during the gold reduction. Abundant nucleation sites might be formed all over the exposed sphere surface first by a fast reducing agent under our reaction conditions and later particle ripening is constrained by the limited amount of reducing agent available but occurs uniformly for all growing nuclei. Also, the image contrast in the SEM caused by the different feature sizes is improved since most NPs are of similar size resulting in a better resolution.

The pink color after reaction indicates formation of gold NPs in the solution (Figure 7.2b). However, their size may differ from that of NPs deposited on the sphere surfaces and the difference may help to determine the correct deposition process, i.e., (i) NPs nucleate and grow on the PS sphere surface directly, (ii) attach onto spheres after formation in solution, or (iii) both. The UV-vis absorbance of the solution is measured with a UV-vis spectrometer (Agilent 8453). The spectrum shows a peak (Figure 7.2a) at

519nm, which implies a particle size of ~ 20 nm.^[165] This size is smaller than the NPs (~ 60 nm) on the PS sphere surfaces observed with SEM. There may be NPs with a size of ~ 20 nm also on the sphere surfaces, but this needs to be confirmed with a high resolution SEM (HRSEM). Besides, it is possible that tiny gold NPs agglomerate into larger colloids composed of indistinguishable NPs upon adsorption onto the sulfate-terminated PS spheres.^[84] Another possibility is the reduction mechanisms are different in the liquid phase and at the liquid-solid interface. In the future, it is suggested to obtain HRSEM images as well as XRD (X-ray diffraction) data to compare the size, shape and crystallinity of the NPs on the sphere surfaces and those in solution.

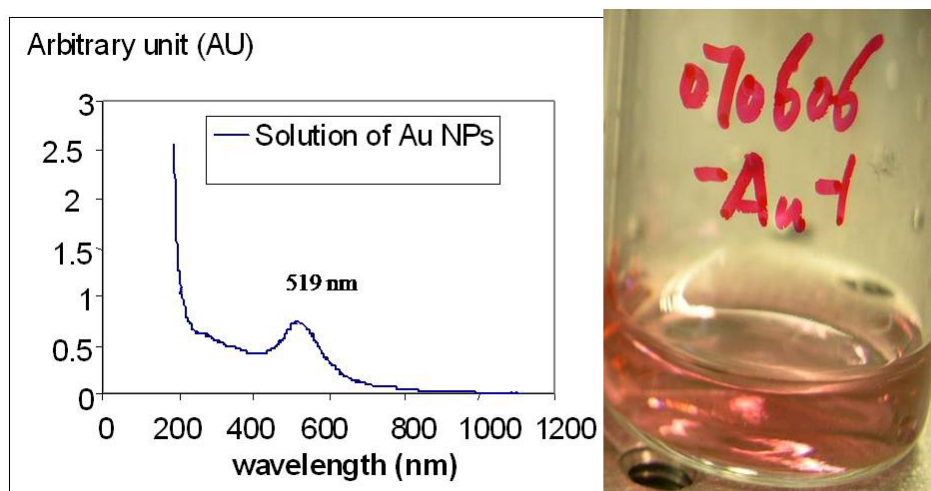


Figure 7.2 a) UV-vis absorbance spectrum of gold NP suspension (b)

Chemical modification of the gold deposit

A piece of sphere/PDMS template after gold deposition is kept in 1,8-octanedithiol ethanolic solution for 24 hours and the sample is analyzed with FTIR to determine if the second thiol functional group is still detectable as described in section 4.6. The dithiol molecule is expected to anchor to the gold deposit with one of its two thiol groups while the other one should be a free thiol in solution.

The sphere/PDMS template stays pink after removal from the thiol-ethanol solution and after several rinses with ethanol. The FTIR absorbance spectrum of a dried sphere/PDMS template shows a peak at 2500 wavenumbers, indicating the presence of a free –SH group. Hence, it seems the gold deposit is stable and further chemical modification through specific functional molecules is possible.

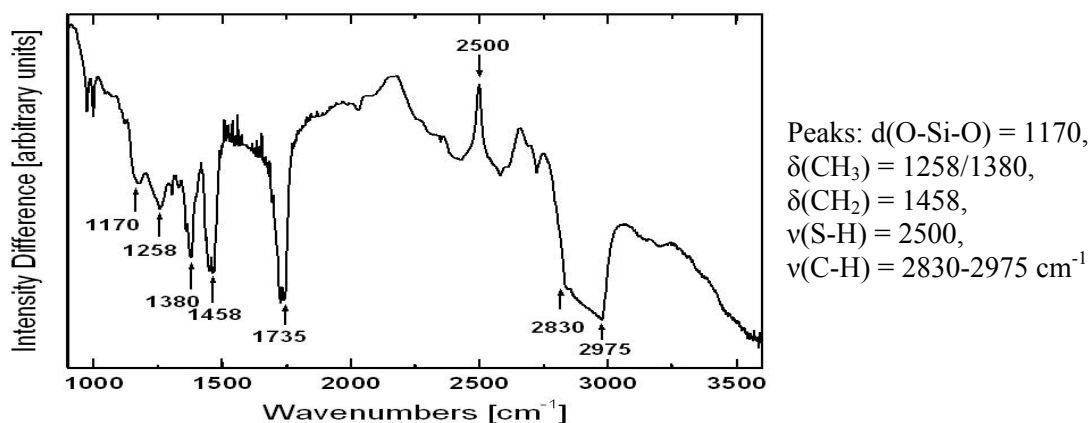
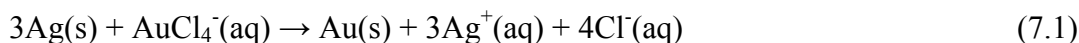


Figure 7.3 FTIR absorbance spectrum of di-thiol treated Au-modified sPS spheres

Site-activation with silver

The standard reduction potential of the $\text{AuCl}_4^-/\text{Au}$ pair (0.99 V vs standard hydrogen electrode, SHE) is higher than that of the Ag^+/Ag pair (0.80 V vs SHE), therefore silver is spontaneously oxidized into Ag^+ according to equation 7.1 when silver nanostructures and HAuCl_4 are mixed in an aqueous medium:^[166]



Sun et al. successfully manufactured hollow nanostructures via this galvanic replacement reaction using a silver nanostructure and an aqueous medium consisting of precursors of the desired metal.^[166] Deposition of gold nanocolloids on silica spheres has also been enhanced by silver pre-activation.^[126] Taking advantage of the fact that we can successfully prepare silver deposits on exposed surfaces of embedded spheres, we

introduce the idea of seeding with silver to enhance the gold deposition on sPS spheres partially embedded in a PDMS mask. Despite the fact that the gold deposition reaction should run spontaneously according to Eq. 7.1, reducing agent sodium citrate is still added to the bulk solution to control the gold deposit size.

The sphere/PDMS template appears yellowish brown after silver deposition as described in Section 5.2.2. The sample (after a small portion is cut off for future characterization of the silver deposit) is put into the mixture of 2.5 mL solution I and 2.5 mL DI-water and kept in the dark for 6 hr under no stirring. Then the solution is heated to boiling and 0.02 mL of solution II is added. The reaction is allowed to occur for 20 min at 95 rpm stirring. The sphere/PDMS template is golden in color after removal from the reaction solution and rinsing. The color covers almost the whole piece, implying deposition of a thick gold film.

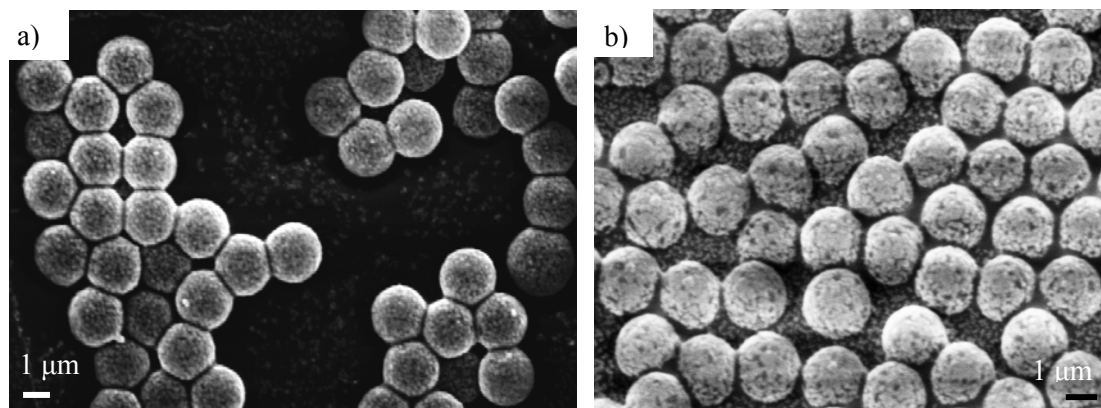


Figure 7.4 SEM images of 2.4 μm sPS sphere/PDMS a) Silver modified, b) Gold modified spheres based on silver modified samples. Scale bar: 1 μm

The solution shows a yellow color (Figure 7.5a) instead of the faintly purple color observed in the vials where the sphere/PDMS templates are only exposed to an Au ELD bulk solution. The SEM images of the small piece recovered after silver deposition and

the sample after gold electroless deposition are shown in Figure 7.4a and b, respectively.

Figure 7.5b depicts the results from EDAX analysis of the deposit in Fig. 7.4b.

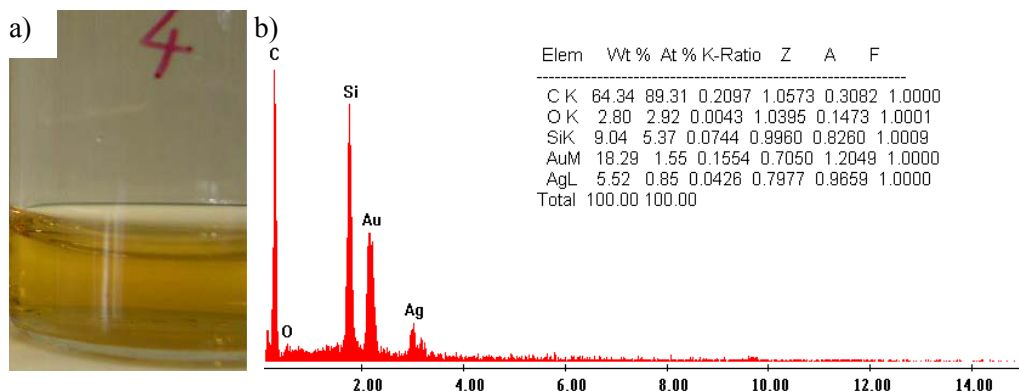


Figure 7.5 a) Solution of gold ELD over silver modified spheres, b) EDAX of Fig. 7.4b Ag-Au coated samples

The silver deposit (Fig. 7.4a) is composed of tiny silver NPs, which are uniformly distributed and almost completely cover the exposed sphere surfaces in this sample. The dense deposit is obtained due to the high concentrations of the complexing agent (ammonia) and reducing agent (formaldehyde) used. Evidently, the dense structure of the deposit is transferred to the gold deposit shown in Fig. 7.4b. This implies that gold deposition occurs on the surface of the silver deposit. Closer inspection of both images reveals dark holes in the deposit suggesting void positions where there is neither silver nor gold deposited. This indicates that the gold deposit prefers to grow on the silver surface under our reaction conditions. Finally, the EDAX elemental analysis also detects both strong gold and silver signals on the sample surface.

In the sample shown in Fig. 7.4b, spheres are more than 50% exposed (i.e. less than 50% embedded) and the freed spheres (Fig. 7.6) confirm the shallow embedment. For some spheres, area as small as ~10% are left unmodified. Interestingly, in this SEM

image of freed spheres, the hole-structure of the Ag-Au mixture modification is even more visible further supporting the gold-on-silver growth.

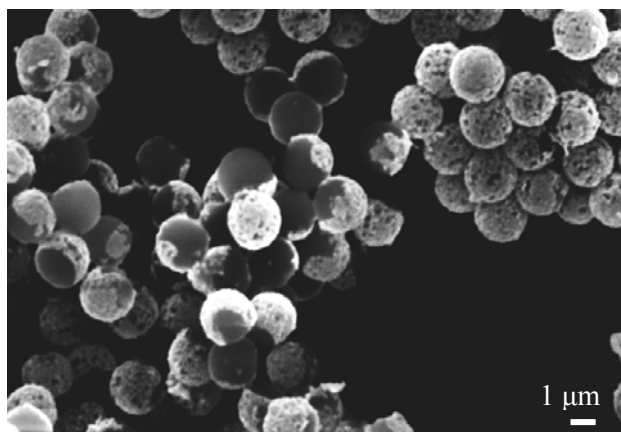


Figure 7.6 Freed 2.4 μm sPS spheres partially coated with Ag-Au. Holes on the Ag-Au caps are clearly visible. Scale bar: 1 μm

In summary, both direct deposition of gold onto sulfate-terminated PS spheres and the deposition via a silver-activation step give us successful gold-modified surface-anisotropic PS spheres. The former results in a uniform deposit composed of tiny gold NPs while the latter gives much thicker deposits composed of NPs with a size similar to the initial silver NP size.

7.2 Modification of spheres with palladium via ELD

Similarly to the silver and gold ELD processes, Pd-ELD on free spheres is tested first to determine feasibility and ELD bath composition followed by asymmetric ELD on sphere/PDMS templates.

7.2.1 Isotropic deposition of palladium on 2.6 μm aPS spheres

It has been reported that the $-\text{NH}_2$ groups on PS spheres show a large affinity for Pd nanoparticles. In the same report, direct metal deposition onto sphere surfaces through controlled hydrolysis ^[167] is studied and Pd nanoaggregates are adsorbed onto amino-

functionalized PS microspheres by adjusting the pH of the solution so that the rate of the metal hydrolysis reaction in the bulk solution is extremely slow.^[84] Here we test the isotropic direct deposition of palladium onto 2.6 μm aPS spheres with a similar chemical reaction and method of controlling the bulk solution pH value with KOH.^[138] The only difference is the amount of poly(N-vinyl-2-pyrrolidone) (PVP), responsible for adjusting the NP size and preventing NP agglomeration, is reduced or even removed completely to produce nanoparticles of a size detectable in our VPSEM and to enhance the probability of Pd NP-aPS sphere attachment.^[84] To assist the association of the $-\text{PdCl}_4^{2-}$ group to the sphere surface ($-\text{NH}_2$), the mixture is kept in the dark under stirring for at least 4 hours before adding the reducing agent potassium bitartrate. This is followed by the Pd-ELD procedure described in section 4.3.2.

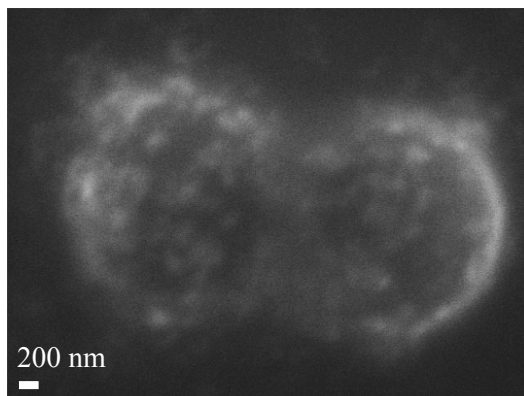


Figure 7.7 2.6 μm amine-PS spheres symmetrically, electrolessly deposited with palladium. Scale bar: 200 nm

A dried drop of solution containing 2.6 μm aPS spheres after palladium reduction is analyzed with SEM and the image of two enlarged spheres is shown in Figure 7.7. As shown in Fig.7.7, the sphere surfaces are decorated with uniform Pd nanoparticles and are very different from the originally smooth surface. The modification is observed on all spheres analyzed. NPs are also formed in the bulk solution as indicated by the presense of

bright dots (>200 nm) on the silicon wafer (data not shown). The size of the NPs on the spheres is roughly measured to be in the range of 100 to 200 nm. Increasing the amount of PVP leads to the formation of smaller sized Pd NPs (in solution), e.g., NPs as small as 6.5 nm can be achieved in the presence of 0.5 wt% PVP.^[138]

Free sulfate-terminated PS spheres with $d = 2.4$ μm are also tested for symmetric modification with Pd NPs in bulk solution. No obvious deposit is formed which can be rationalized by the repulsion between the negative precursor ions and the negative $-\text{SO}_4^-$ group. Therefore in the anisotropic Pd deposition, only amine-terminated PS spheres partially embedded in the PDMS mask are tested. As mentioned above, monolayer assembly for aPS spheres does not yield as perfect particle assembly as observed for sPS spheres due to sphere interaction with the native SiO_2 thin film on the Si wafer.

7.2.2 Anisotropic deposition of palladium on aPS sphere/PDMS template

A monolayer of 2.6 μm aPS spheres is prepared and partially embedded into a PDMS mask using the pre-curing method described in 4.2.2. The sphere/PDMS templates are then kept in an aluminum foil covered precursor solution overnight under continuous magnetic stirring (180 rpm). Then a boiling 20 mL 0.5% potassium bitartrate solution is added to the stirring mixture and reacted for 2hr with reflux. The solution turns from yellowish to brownish indicating formation of palladium colloids in the bulk solution. The sphere/PDMS template is taken out and checked with SEM after drying in air. No apparent color change is detected with the bare eye on the exposed surface of the sphere. However, deposit is indeed detected with SEM as shown in Figure 7.8a. Despite the fact that the aPS monolayer is not as nice as that observed with 2.4 μm sPS spheres, all spheres are successfully, partially embedded in the PDMS mask and keep their shape and

position even after vigorous stirring and 2 hr of boiling. More importantly, the exposed surface shows a uniform deposit – bright dots on most spheres, as dense as that observed on the free aPS spheres. Most of the visible NPs deposited are between 100-200 nm in size, in good agreement with the deposit formed in the symmetric deposition. Several large Pd-NP aggregates are also detected in Fig. 7.8a.

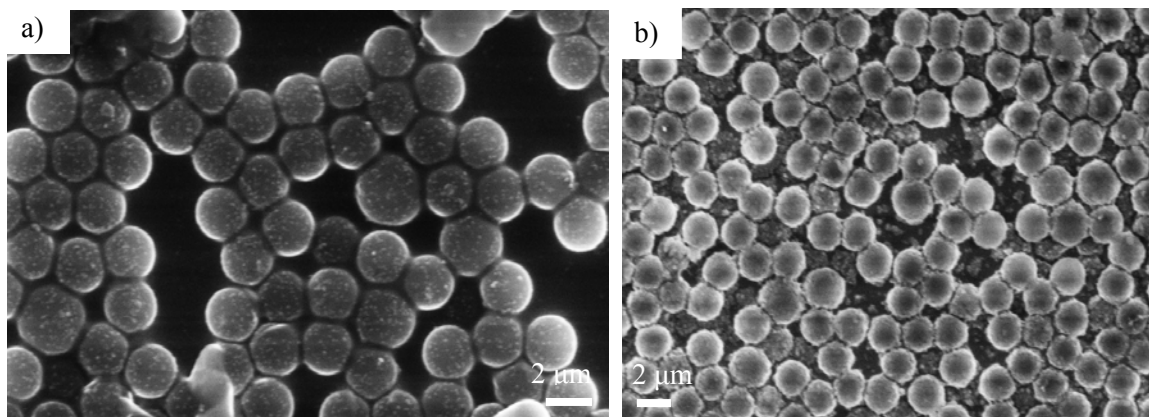


Figure 7.8 a) & b) Pd modified 2.6 μ m aPS sphere/PDMS template. Scale bars: 2 μ m

Meanwhile, on the same piece of sample but in a different area, a new type of deposit morphology is observed as shown in Fig. 7.8b. In this area, the deposit does not appear as individual NPs; instead, all spheres have a thick, smooth cap with a rough edge, implying very uniform growth of the Pd deposit on the exposed aPS sphere surfaces. Surprisingly, some metal agglomerates are also founded on the PDMS film surrounding the spheres even after abundant rinsing. A similar metal deposition on the PDMS template is also observed in the silver-activated gold deposition. PDMS is inert to many chemicals or reactions, however, when there are active catalytic sites; metal deposition on PDMS is possible. The varying deposit morphology within one sample might be due to the non-uniform contact of the sphere/PDMS template with the reaction solution. A bubble, no matter how small, can prevent the reducing agent from reaching the surface and alter the

deposition dramatically. The smooth cap modification of Fig.7.8b indicates a dense deposit of a large amount of Pd nanoaggregates evenly distributed over the entire exposed surface.

7.3 Modification with titanium oxide via sol-gel process

In this section, we explore the preparation of titania-coated surface-anisotropic polystyrene microspheres. This coating is of interest due to the broad applicability of titania coated polymer spheres in photonic band gap materials, catalysts, or nanoreactors.^[60] Two main approaches for coating polymer spheres with TiO₂ symmetrically have been used widely: (i) adhere pre-formed TiO₂ NPs to polymer spheres by direct deposition using techniques such as layer-by-layer;^[168] or (ii) form a coating through the controlled reaction of a titania precursors with the polymer sphere surface in a fashion similar to the silver, gold or palladium deposition mentioned above.^[169] Symmetric coating has been achieved on both anionic and cationic submicron PS spheres by hydrolyzing titanium tetrabutoxide (TBOT) or titanium tetraisopropoxide (TTIP) in the presence of ammonia.^[60,169] In our studies, we explore TiO₂ deposition onto both aPS spheres and sPS spheres embedded in PDMS by hydrolyzing TTIP in ethanol in the presence of ammonia.

The deposition of TiO₂ on 2.4 μm sPS sphere/PDMS template according to the procedure described in 4.4 is not successful as determined by SEM (data not shown). One example of a TiO₂ deposition on 2.6 μm aPS sphere/PDMS template is shown in Fig. 7.9. Very different from the uniform silver, gold or palladium asymmetric deposition observed in ELD, most TiO₂ particles do not sit on the exposed hemispheres but concentrate in areas where spheres are in contact with each other. Most particles are of a

size larger than ~ 200 nm. More interestingly, most titania particles appear highly spherical in shape, which is not observed in the metal ELD depositions. The observation of TiO_2 particles shows that the reaction procedure works, but the formation of spherical particles with equal size indicates that homogeneous nucleation in solution is favored over heterogeneous nucleation on the PS sphere surface under our reaction conditions.

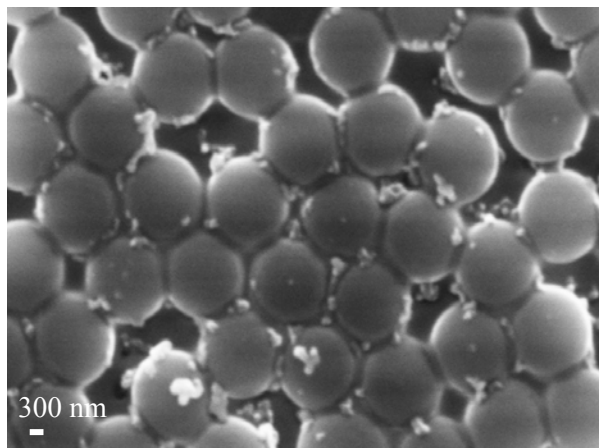


Figure 7.9 TiO_2 deposited on $2.6\ \mu\text{m}$ aPS sphere/PDMS. Scale bar: 300 nm

7.4 Surface morphology and assembly behavior of asymmetric spheres prepared via PVD and ELD

As discussed in the literature review (Chap. 2), the deposition rate in vapor phase deposition (VPD) can be accurately controlled at the cost of complicated, delicate, and expensive equipment. Most VPD methods are used to fabricate high-quality nanometer scale thin films.^[170] While electroless deposition, is more recognized as an alternative for building thick deposits of more than a few microns thickness.^[82] Moreover the deposit surface prepared from electroless deposition is frequently much rougher than that obtained from VPD processes, especially on micron-scale structures such as spheres, tubes etc.).^[5, 42, 104] Graf. et al. discussed that a simultaneous particle growth is necessary to get well-defined, uniform and closed shells when depositing materials on spheres.^[86c]

Many reports suggest that a difference in surface morphology affects properties such as the surface plasmon and the electric resistivity.^[5, 171]

In our previous experiments, we observe that isolated metal nanoparticles (50-150 nm) and amorphous deposit structures are electrolessly deposited on polystyrene spheres under the used reduction conditions while smooth metal thin films are achieved from PVD. The difference in surface morphology is partially due to a fast and non-uniform silver reduction in ELD and allows us to use ELD as a tool to study the influence of surface morphology on particle assembly properties. The surface morphologies obtained from the two asymmetric modification methods (PVD and ELD) are very distinguishable. In the following, we discuss the observed variance in the surface roughness prepared via PVD and ELD and its effect on the assembly behavior of the two types of surface-anisotropic spheres.

Surface-anisotropic spheres are freed from either the silicon wafer (PVD) or the sphere/PDMS template (ELD) via ultrasonication and the stretch-scratch method, respectively, as described in section 4.6. Recovered spheres are re-dispersed into DI-water, concentrated, and the assembly of these spheres is studied with the convective assembling method described in Chap. 4. A summary of the different structures assembled by surface-anisotropic spheres prepared from PVD and ELD are shown in Fig. 7.10 and compared with assemblies obtained by plain spheres exposed to an identical environment with the exception of the metal treatment. This discussion helps us to elucidate the effect of cap roughness on the orientation of the spheres during the continuous convective assembly. All images shown are obtained from sulfate-terminated spheres with a diameter of 2.4 μm .

Fig. 7.10a shows an ordered closed-packed monolayer formed by convective assembly of unmodified sPS spheres. Fig. 7.10b and c display less-ordered assemblies of sPS spheres which have been partially modified with an Au thin film of 20 nm and an Ag thin film of 25 nm using PVD, respectively. Fig. 7.10d is representative of the assembly observed for unmodified spheres scratched off a PDMS template and serves as a reference. Fig. 7.10e depicts the assembly found for Ag NP-capped spheres (modified with ELD method) after scratching off from the PDMS template (Section 4.6). The ELD silver caps are composed of 50 - 200 nm silver NPs. Fig. 7.10f shows a magnified image of an Au-capped sphere (left), which shows a smooth surface on both the unmodified polystyrene surface and the gold cap side. In contrast, the sphere to the right in Fig. 7.10f has a much rougher hemisphere on the silver ELD modified side.

As discussed in Section 5.2.1 and confirmed by the image in Fig. 7.10a, smooth unmodified spheres frequently form domains with close-packed hexagonal structures during convective assembly. In the case of spheres prepared by PVD with smooth gold or silver caps similar close-packed monolayers are expected if there is no interaction between the metal cap and its surrounding. Interestingly, PVD-Au-capped spheres assemble into planar 2-D structures (Fig. 7.10b), while PVD-Ag-capped spheres result in multilayer structures (Fig. 7.10c). Closer inspection of Fig. 7.10b reveals that the orientation of the PVD-Au-capped spheres in the monolayer seems random. Careful image processing, however, shows that only 25-30% of the gold surface (bright area) faces up indicating that more of the gold caps are oriented towards the substrate surface. In addition, the packing of the PVD-Au-capped spheres seems random and not closed-packed compared to the packing observed for unmodified sPS spheres, indicating that the

gold caps subtly influence the assembly behavior. Apparent from Figure 7.10c, the PVD-Ag-capped spheres form loosely packed double layers with random silver cap orientation and layer interpenetration. More careful inspection of several SEM images reveals a preference for silver cap orientation towards the substrate in the bottom layer, while more full silver caps are found face-up in the second layer. Note despite a Ti adhesion layer, dewetting of some of the silver caps is observed (upper left corner). Silver cap oxidation is the most likely origin of this dewetting phenomenon. It is unclear at this point what causes the difference in the assembly behavior. Possible rationales are: (i) higher mole fraction of particles used in the assembly, (ii) stronger Ag-Ag interaction vs. Au-Au interaction, (iii) varying metal-substrate interaction, and (iv) increased cap roughness caused by partial Ag oxidation and dewetting. More experiments varying the particle mole fraction, cap size and roughness are required to identify which of these rationales or combination of rationales causes the differences in assembly.

Figures 7.10d and e show the sPS spheres which have been in contact with the PDMS template exhibit a drastic change in their assembly behavior compared to unmodified and PVD-modified sPS spheres. Assembly of unmodified spheres after their removal from the PDMS template (Fig. 7.10d) shows that clustering of the spheres is strongly preferred over monolayer formation. The change in assembly behavior may be caused by (i) a residual thin PDMS layer on the PS hemisphere initially exposed to the PDMS template, (ii) a change in the surface charge distribution of the sPS spheres, or (iii) both. Interestingly, ELD-Ag-capped spheres do also show very strong clustering and an absence of any onset of particle layer formation (Fig. 7.10.e). Closer inspection of the silver cap orientation in Fig. 7.10 reveals more silver-silver and silver-PS contacts than

PS-PS interaction. In addition, image analysis shows that different from the assembly of PVD-cap spheres ~50% of ELD-Ag-caps face up in Fig. 7.10e.

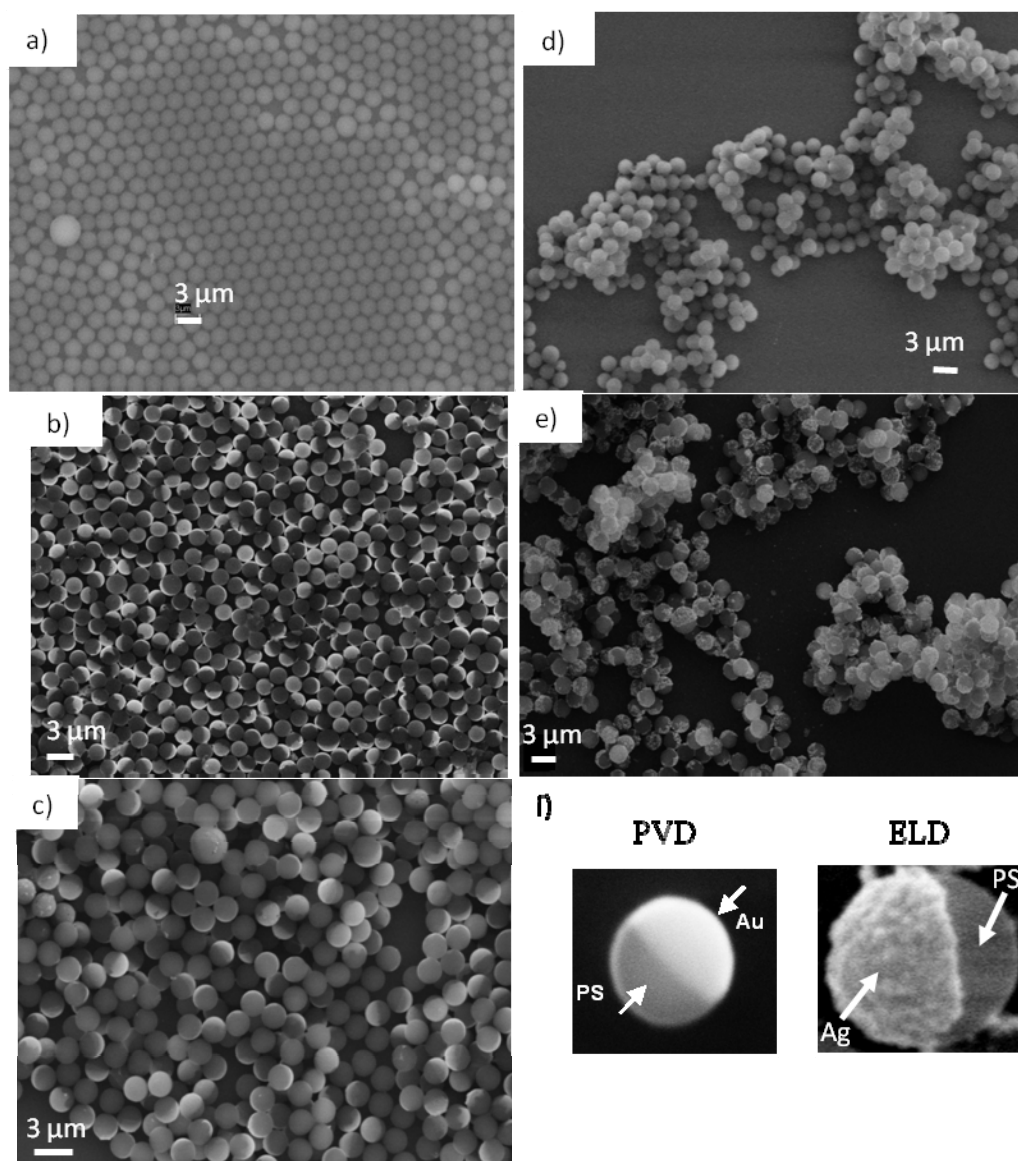


Figure 7.10 Assemblies of 2.4 μm sPS spheres; a) unmodified spheres, b) PVD modified spheres with 20 nm Au film, c) PVD modified spheres with 26 nm Ag film, d) unmodified spheres after removal from PDMS template, e) ELD modified sphere with 50-150 nm Ag NPs after removal from PDMS templated, f) high resolution image of Au-PVD (left) and Ag-ELD capped sphere (right). Scale bar: 3 μm

A calculation of the cap volume and surface area for the PVD and ELD caps shows that the surface area of modified hemisphere/deposit volume (A_S/V_D) increases by 800% from PVD to ELD. For a 20 nm thick gold cap (assuming a half shell), a deposit volume of $V_{D,PVD} = 0.18 \mu\text{m}^3$ is achieved with the total exposed surface area of $A_S = 9.05 \mu\text{m}^2$ (50% of the sphere surface area) per sphere. For the silver ELD deposit carrying a total number of 62 NPs with a composition of 51 small NPs (average diameter of $d_a = 75 \text{ nm}$), 10 medium NPs ($d_a = 125 \text{ nm}$), and 1 large NP ($d_a = 175 \text{ nm}$) per sphere, the deposit volume for one cap is calculated as $V_{D,ELD} = 0.024 \mu\text{m}^3$ (13% of $V_{D,PVD}$) with a surface area of $A_{S,ELD} = 1.47 \mu\text{m}^2$ added up per sphere. The surface area of the ELD modified hemisphere is then $10.52 \mu\text{m}^2$ ($A_{\text{hemisphere}} 9.05 + A_{S,ELD} 1.47$) per sphere, 16% more than the PVD modified hemisphere. All ELD calculations assume a spherical shape for the NPs and a point contact between the NPs and the substrate sphere. The numbers show that the ELD deposit is much sparser (~13% volume) than the PVD deposit, however, the exposed surface area is ~1.16 times of that of the PVD deposit.

The difference in surface roughness is likely to play an important role during the assembly if the weight difference of the two hemispheres is not overcome by the specific interaction force. Nie et al. and Link et al. reported an ordered orientation of Janus particles prepared via a microfluidic method (two different hemispheres without edge roughness) at the oil-water interface. They find that the hydrophobic faces are in contact with the oil phase while the hydrophilic hemispheres stay in contact with the aqueous phase.^[172, 173] On the contrary, glass spheres ($d = 31 \mu\text{m}$) covered with 30 nm gold thin film on one hemisphere did not show the expected orientation at the oil (Dodecane)/water interface despite the fact that these spheres had a size comparable to that of the spheres in

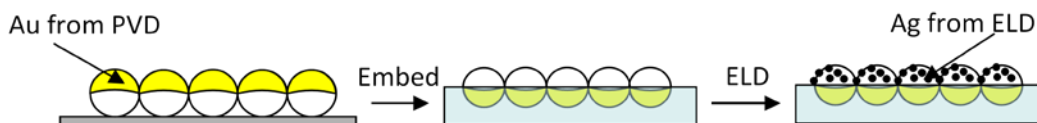
Nie et al.'s study. The researchers argue that the surface roughness of the spheres dominates over the surface chemistry effects with regard to particle orientation.^[17] For the gold- and silver-capped spheres used in our study, although the uneven charge distribution on the modified sphere surfaces (negatively charged sulfate groups on one half of the sPS spheres vs. the other half covered by a metal cap) is supposed to facilitate special orientation of spheres, the surface roughness caused by the edge of the metal cap is more pronounced than in Nie's experiments due to their smaller 2.4 μm diameter. In addition, the mass added to one hemisphere, causes a competition between orientation of spheres due to gravitational forces and orientation due to preferred metal-metal, PS-PS or PS-metal contact under our experimental conditions.

7.5 Dual-cap spheres prepared from a combination of PVD and ELD

In order to prevent above mentioned metal cap edge effects, we investigated the modification of sPS spheres with a combination of PVD and ELD. First, a metal cap is applied with PVD followed by templating of the metal cap with PDMS and subsequent ELD on the unmodified, exposed PS surface. Next, a slightly different approach is tested where the initial metal cap is tested as a template, which if successful would eliminate the PDMS templating step. Interestingly, for the latter approach we find that the ELD deposition preferentially occurs on the metal cap edge yielding a new silver belt particle.

Dual-cap spheres with PVD-Au and ELD-Ag caps are prepared when the PVD and ELD modification techniques are combined. As depicted in Scheme 7.1, a monolayer of PVD-Au capped spheres is embedded into a PDMS template after controlled gold PVD deposition yielding partially modified spheres. The gold modified hemispheres (14 nm Au with 4 nm Ti adhesion layer) are embedded into PDMS while the exposed sulfate-PS

surface are in contact with the silver reduction solutions during the ELD silver deposition step.



Scheme 7.1 Preparation of dual-cap spheres from PVD and PDMS-aided ELD

Figures 7.11a and b show SEM images of silver-capped spheres in the PDMS template after ELD modification (silver facing up) and the spheres after extraction from the PDMS template with the double-sided sticky carbon tape (gold facing up), respectively. Fig. 7.11a clearly shows successful silver deposition composed of nanoparticles on the exposed PS sphere surfaces. The spheres in Figure 7.11b after removal from the PDMS template show evident asymmetric modification on both hemispheres; (i) the top halves appear smooth and bright due to the PVD gold film while a rough, thick ELD silver deposit is seen on the bottom halves (arrows). The image is taken at a 60° tilt to enable imaging of the bottom halves. Interestingly, there is belt-shape gap with a width of 140 to 300 nm between the gold and the silver caps, which is likely the result of more than 50% embedment of spheres into the PDMS template (see section 5.2.3). This experiment also confirms the strong adhesion of the PVD gold film to the sPS spheres due to the titanium adhesion layer.

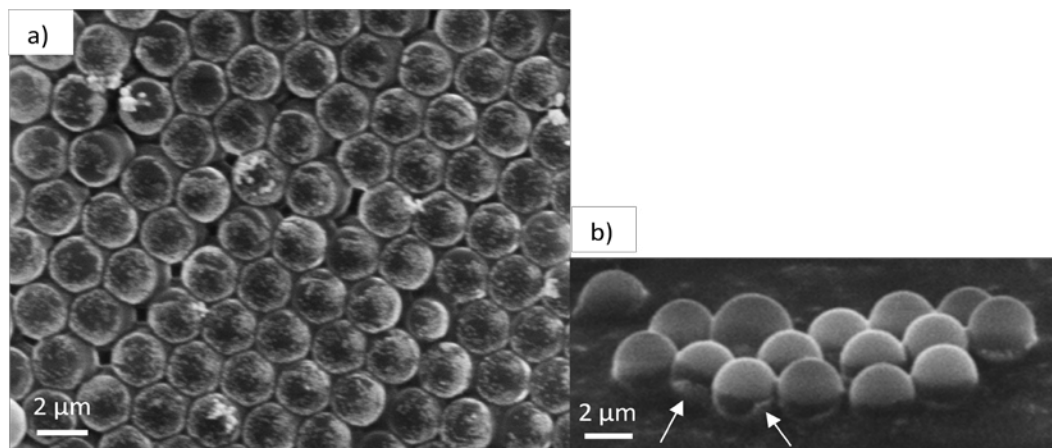
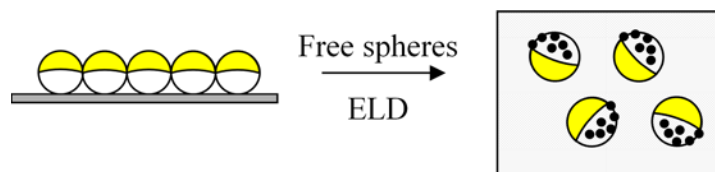


Figure 7.11 a) Ag deposited 2.4 μm spheres embedded in PDMS with Au thin film deposit at back, b) Spheres on carbon tape with Au cap facing up and Ag NPs at bottom (60° tilt). Scale bar; 2 μm



Scheme 7.2 Preparation of dual-cap spheres from PVD and free ELD

The stability of the PVD-gold modification inspired us to use the thin film as a templating mask instead of the elaborate PDMS templating procedure. Scheme 7.2 depicts the modification process involving PVD-Au caps as templates followed by the decoration of the exposed hemisphere with silver NPs via ELD.

The PVD-Au modified spheres are collected from the silicon wafer after PVD by ultrasonication in DI-water for 2-4 min. The spheres are then dispersed into a silver precursor solution. Next, complexing (ammonia) and reducing agents (formaldehyde) are added into the solution analogous to the procedure reported in Section 4.1 for the symmetric deposition experiments on free sPS spheres. The spheres are recovered from

the reaction solution after silver deposition by centrifugation and a drop of solution is dried on a piece of clean silicon wafer and imaged with SEM.

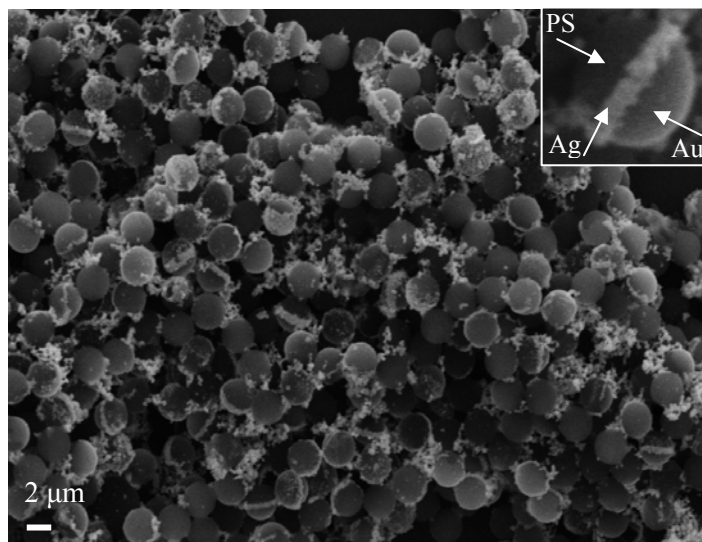


Figure 7.12 Freed spheres with Au cap from PVD after Ag ELD

To our initial surprise the particles show a new and unexpected silver deposit morphology (Fig. 7.12), i.e., silver deposition is not only found on the exposed sphere surfaces but also on the gold cap and more importantly as a thick belt along the edge of the PVD-Au cap. The preference of the silver nanoparticles to accumulate at the cap edge can be rationalized by nucleation theory. In nucleation theory, step edges and surface defects present highly reactive nucleation sites due to so-called “dangling bonds”, i.e., atoms at those sites are under-coordinated and therefore much more reactive than atoms in a smooth surface.^[174, 175] Comparison of the particle assembly in Figure 7.12 with those presented in Figure 7.10, shows that these new silver-belt/Au-cap particles assemble into clusters analogous to the particles that were in contact with the PDMS template. This observation highlights the importance of deposit roughness and indicates

that the clustering observed for the ELD-Ag-capped spheres may not only result from the PDMS templating.

In future studies, the edge nucleation effect can be applied in the synthesis of interesting particles when, for example, the patch size is decreased as well as serve as visualization tool of smaller patches.

7.6 Conclusion

Our procedure developed for surface anisotropic electroless/wet chemical deposition on spherical surfaces has been realized for two new metals (gold and palladium) and one metal oxide (titania). The results show Au NPs can be successfully deposited onto sulfate-terminated PS spheres with and without the silver-activation step. A dense, uniform, and stable deposit topography is obtained and the deposited NPs can be further modified with molecules containing chemical functional groups such as $-SH$. The anisotropic deposition of Pd NPs on amine-terminated PS spheres is also accomplished and various surface morphologies are observed. The anisotropic deposition of TiO_2 while observed is not uniform on the sphere surfaces and thus requires a more detailed study of the experimental conditions.

Surface morphology of the deposit affects the assembly of the asymmetrically modified spheres and can be varied by employing physical vapor deposition or electroless deposition. The assembly of surface-anisotropic spheres with smooth and rough caps indicates that surface morphology changes particle packing and affects the cap orientation. For example, spheres with smooth gold caps from PVD arrange themselves into a 2-D planar structure of random-packed and randomly oriented spheres whereas spheres with a rough silver cap from ELD agglomerate into 3-D clusters.

In addition, we tested two new approaches to the fabrication of dual-cap spheres by combining the PVD and ELD procedures. In method 1, we obtained sPS spheres with smooth gold deposition (PVD) on one side and rough silver deposition (ELD) on the other side. In method 2, a new and interesting type of particle with a smooth gold cap and a rough silver belt is discovered.

Chapter 8 Application of Surface-anisotropic Spheres: Nanostructure/poly(acrylate) Elastomer Composite Actuators

Over the last five years there have been several reports discussing the synthesis and manufacturing of surface-anisotropic particles (Janus particles), as well as the characteristics properties of these Janus particles.^[3, 176] However, many applications of Janus particles that employ their specific properties are far from fully developed^[176] and most of them concentrated mainly on the self-assembly of Janus particles taking advantage of the particle's directional properties.^[177, 178] Recently, the assembly behavior of Janus particles in an external field, e.g., an electric or magnetic field, has intrigued great interest^[22, 179] and possible applications based on the electric asymmetry of Janus particles have also been reported.^[14]

In this chapter, we explore the application of Janus spheres as fillers in electroactive polymers, i.e., electric-stimulus responsive polymer materials. In this study, we make use of the giant dipole moment and the ability of Janus particles to orient themselves in an electric field.^[3, 12a, 180] First, electroactive polymers (EAPs) and their properties are briefly introduced. Then, the effect of symmetric TiO₂ nanoparticles with a high dielectric constant as fillers in these EAPs is tested. Next, Janus spheres are incorporated into the EAPs and their effect on the mechanical responses are discussed.

8.1 Introduction of electroactive polymers and their working principles

There are some “smart materials” that respond to external stimuli such as pH variations, ion concentration, temperature, electric field, etc. by changes in shape or size. Among them, electroactive polymers (EAP) are of great research interests due to their

promising applications in actuators, small-scale robots, mini-pumps or charge storage capacitors.^[181] There are two major categories of EAPs according to their activation mechanism: electronic and ionic. Generally the electronic EAPs (electrostrictive, electrostatic, piezoelectric, and ferroelectric) require activation fields higher than 150 V/ μm , which are close to the breakdown level of most polymers. One of the advantages of electronic EAPs is that they can hold the deformation induced under activation of a DC field. They also react to the electric stimulation fast and can be operated in air with no major constraints. On the other hand, ionic EAP materials (gels, polymer-metal composites, conductive polymers, etc.) need very low driving voltages. But there is a need to keep the materials hydrated and for most of them it is difficult to maintain DC-induced deformations. Both categories of EAPs can be designed to bend, stretch, or contract upon application of an electric field.

The electronic EAPs are very attractive as they can convert electric energy into mechanical deformation more rapidly and freely than other types of EAPs. They can be utilized as solid-state electromechanical actuators or motion sensors. According to the Maxwell stress effect, the transverse strain in the plane perpendicular to the field direction of an isotropic polymer can be expressed as: ^[181]

$$S_1 = S_{11} = 1/2 \epsilon s_{11} E_3^2 \quad (8.1)$$

And assuming that Poisson's ratio of the polymer (ratio of transverse contraction strain to longitudinal extension strain) is at its isotropic upper limit $1/2$, the longitudinal strain (along the field direction) is:

$$S_3 = S_{33} = -\epsilon s_{11} E_3^2 \quad (8.2)$$

where s_{ij} is the elastic compliance, ϵ is the dielectric permittivity, and E is the electric field applied. The dielectric tensor is reduced to one constant ϵ and the polymer contracts along the field direction due to the Maxwell stress. For a soft polymer with a large elastic compliance, the Maxwell stress induced strain can be quite significant, therefore for large strains, Eq. (8.2) should be modified to Eq. (8.3):

$$Y \ln(d_0/d) = \epsilon (V/d)^2 \quad (8.3)$$

where d_0 is the initial film thickness, d is the final thickness, Y is the Young's modulus ($Y = 1/s_{11}$), and V is the applied voltage. Theoretically, for small-strain cases we can expect the longitudinal strain response to an electric field according to modified Eq. (8.2):

$$S_3 = -K\epsilon_0 E_3^2 / Y \quad (8.4)$$

where K is the dielectric constant of the material and ϵ_0 is the vacuum dielectric permittivity (8.85×10^{-12} F/m). Extensive application of small K or large Y EAPs is presently limited by the high driving electric fields needed. Therefore, there is a great need for new types of polymer actuators of high dielectric constant (K) to enhance the electromechanical response for operation at low voltages.

Some high-performance EAPs include polymer electrets^[181, 182] and liquid-crystal (LC) polymers^[183, 184, 185]. A polymer electret is a polymeric dielectric that can retain a state of polarization after the applied electric field is removed. A new type of electrets based on a charged microporous structure shows a promisingly high piezoelectric coefficient.^[181] With the low elastic modulus of the specific structure and the large piezoelectric response, a small stress can induce a large dimensional change of the voids. In the case of very anisotropic liquid crystals, a reorientation of their molecules can

generate a large dimensional change.^[184, 185] LC polymer are more practical in applications because liquid crystal molecules cannot sustain or exert a mechanical stress due to their fluidic nature. LC polymers exhibit large electromechanical responses with the help of both large shape and dielectric anisotropy. In LC polymers rigid mesogenic units are either in the main chains alternating with flexible fragments or in the side chains connected to the main chains with flexible spacers.

Recent studies have demonstrated that the incorporation of dielectric filling materials, organic or inorganic, into polymers could yield composites with both the elastic modulus of the pure polymer and the high dielectric constant of the filler, leading to a decreased electric field needed to achieve the same electromechanical strain. One example of an organic filler of high dielectric constant is copper-phthalocyanine (Cu-Pc) (dielectric constant >10000) as reported by Zhang et al.^[186] The composite matrix of 40 wt% Cu-Pc loaded in the co-polymer poly(vinylidene fluoride-trifluoroethylene) (p(VDF-TrFE)) exhibits a much higher strain (~2% strain under a field of 13 V/ μ m) than the co-polymer only matrix under the same electric field. They also measured the dielectric constant and dielectric loss of the composite matrix and found that under a field of 10 to 15 V/ μ m, the dielectric constant of the composite could reach more than 400 (compared to ~60 for the co-polymer matrix), while the dielectric loss was nearly unchanged from that of the co-polymer matrix. Sometimes conductive polymers such as polyaniline are also used as the conductive filler with the double benefit of increasing the dielectric constant while still keeping the elastic modulus low.^[187] In the case of polyaniline, however, even a 23% (volume fraction) filling leads to a strain of only 3% at a relatively low electric field of ~20 V/ μ m. Recently, researchers tested new fillers such as titanium dioxide powder ($K =$

31, anatase; $K = \sim 114$, rutile phase)^[188] or strontium titanate ($K \approx 150$).^[189, 190]

However, these materials are not easy to process and an optimized dispersion of the fillers to get a uniform system with both high dielectric constant and small modulus is very difficult.^[191,192]

8.2 TiO₂ nanoparticles and Janus particles as fillers in poly(acrylate) polymer matrixes

In the following, we present (i) the preparation of two new fillers, (ii) their dispersion in acrylate polymer or co-polymer, and (iii) the electromechanical performance of these two polymer composites. One filler is a titanium dioxide (TiO₂) nanoparticle (NP) core with a high K value and coated with a polymer shell, which is loaded into copolymers of poly(ethylene glycol phenyl ether acrylate) p(EGPEA) and poly(butyl acrylate) (pBA). The other filler is a PVD-Au-capped surface-anisotropic polystyrene sphere loaded in a p(EGPEA) film and subsequently electrically aligned. Poly(acrylate)s are chosen because of their low glass transition temperature ($T_g = -36^\circ\text{C}$)^[193] resulting in the low modulus value Y (with an order of the magnitude MPa).^[194] Films with arrays of micron-sized pillars are prepared from the polymers, placed onto indium-tin oxide (ITO) glass using a replica molding method, and developed into delicate electric devices. EGPEA is a hydrophobic material and will have little interaction with the soft mold made of poly(dimethyl siloxane) (PDMS). A laser profile mapping setup is developed to measure the electromechanical performance and the strain in films of various compositions is measured and compared.

8.3 Materials and methods

Acrylate polymers are good candidates for electromechanical performance studies because of its low glass transition temperature as discussed above. A detailed description of the electroactive structure based on a specific acrylate polymer used, i.e., poly(ethylene glycol phenyl ether acrylate), and the procedures for device preparation, processing, and strain measurement are given below.

8.3.1 Materials processing

As monomer ethylene glycol phenyl ether acrylate (EGPEA, Sigma-Aldrich, inhibited with 100 ppm HQ) crosslinked by 1,6-hexanediol diacrylate (Sigma-Aldrich, 80%, inhibited with 100 ppm MEHQ) is used. 2-benzyl-2-(dimethylamino)-4'-morpholinobutyrophenone (Sigma-Aldrich, 97%) is added into the monomer-crosslinker mixture to act as photoinitiator to start the crosslinking when the liquid mixture is exposed to UV light. Butyl acrylate (BA, Sigma-Aldrich, 99+%, inhibited with 10-55 ppm MEHQ) is used to coat the TiO₂ nanoparticles and the BA monomer is mixed with EGPEA to help the dispersing of the TiO₂ NPs. The inhibitors in EGPEA and BA are removed by passage through a pre-packed inhibitor remover column (Al₂O₃ powder, Sigma-Aldrich) prior to use.

An array of micron-sized pillars made of poly(acrylate) is prepared employing lithography followed by soft template techniques (Scheme 8.1 A-E). Typically, a thin layer of a negative SU-8 photoresist spun onto a piece of clean silicon wafer (3M) is exposed to UV light (Sepectroline SB-100P, 365 nm) through a photomask and developed into the desired template. The template has a 3 cm × 3 cm area with a pattern of square pillars (cross-section: 100 μm × 100 μm) spaced 150 μm apart. The height of the pillars is determined by the thickness of the SU-8 layer, which can be controlled by

the spinning rate and the amount of SU-8 liquid. Different heights (z direction) of 30 and 25 μm are obtained with two SU-8 templates. Later the SU-8 pattern is used to prepare a so-called “soft mold” consisting of an array of holes from PDMS. The liquid mixture of PDMS base and agent is poured onto the SU-8 pattern, kept in vacuum for about 30 min to remove bubbles, and then cured at 80 $^{\circ}\text{C}$ in an oven for 2hr. The PDMS replica is highly preferred due to two of its properties. It is transparent to UV light and it is soft, which facilitates the curing of the polyacrylate and the spreading of liquid pre-polymer, respectively.

Oleic acid stabilized TiO_2 NPs are synthesized from titanium isopropoxide at Bell Labs.^[195] XRD confirms that the nanoparticles are in the anatase phase. The TiO_2 NPs are coated with poly(butyl acrylate) (pBA) through a ligand exchange reaction.^[196] The core TiO_2 particles analyzed by TEM (Philips CM-20 ultratwin high-resolution) are cylindrical with an average base of $13\text{ nm} \times 3.5\text{ nm}$ and a height of 20 nm after coating.

Gold-capped PS (Au-PS) spheres are prepared by physical vapor deposition onto a monolayer of sulfate-terminated PS spheres with the details for the procedure given in Chapter 4. $0.47\text{ }\mu\text{m}$ spheres are capped with a 20 nm gold thin film placed on a 5 nm titanium adhesion layer. The silicon wafers with the modified spheres are put into an appropriate amount of DI-water in clean containers and ultrasonicated for 2 min to free the spheres from the wafer. Then the sphere suspension is centrifuged at 11000 rpm for 5 min and the sediment is rinsed twice with DI-water. Ethanol (>99%, Fisher) is added to the sediment, the spheres are re-dispersed into ethanol by sonication, and centrifuged again. This procedure is repeated twice before the sphere precipitate is dried in a low-temperature oven. The mass of the spheres is determined by comparing the weight of the

container with the dried gold-capped spheres (m_f) to that before use (m_0). The ready-to-use pre-polymer solution is added to the dried sphere powder according to the desired concentration (mass/volume) and subsequently sonicated to re-disperse the spheres within the pre-polymer liquid.

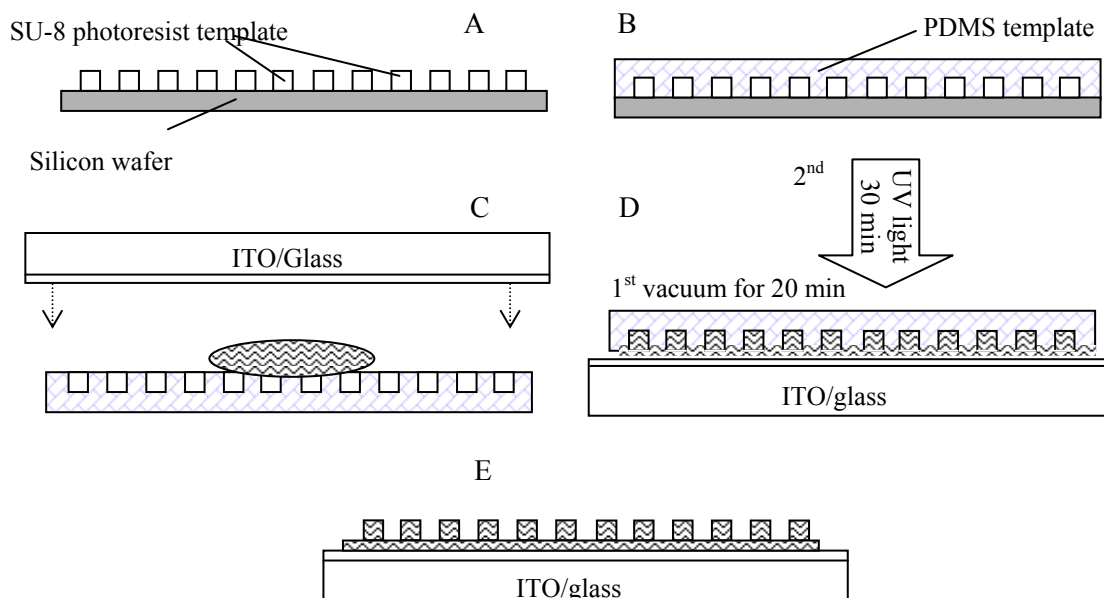
8.3.2 Pre-actuator (polymer film) preparation and characterization

TiO₂ NP loading into p(BA-EGPEA) copolymer films

The p(BA) coated TiO₂ NPs (TiO₂-pBA) are dispersed into BA monomer liquid with sonication, followed by addition of EGPEA according to the designed mass/volume ratio and the desired volume ratio of BA and EGPEA. Various weight concentrations of TiO₂-pBA NPs are loaded into the pre-copolymer liquid to study the effect of the NPs concentration on the electromechanical performance of the composite material (referred to as TiO₂-BE composite). The photo-initiator is added at a ratio of 0.86% (weight/volume, molar ratio 0.5%) to the pre-polymer mixture. Co-polymer films without TiO₂ NP (referred to as BE copolymer) loading are also prepared and are used for reference measurements.

Scheme 8.1 C-E summarizes the film preparation procedure: 30 – 40 μ L pre-polymer liquid is dropped onto a PDMS mold with the holes facing up and spreads upon placement of a piece of ITO/glass where the conducting ITO coated surface touches the liquid. The glass/liquid/mold sandwich structure is kept in -17 – -18 inHg vacuum (Precision Vacuum-oven Model 19) for 20 minutes with the glass slide facing up to make sure the liquid fills up most of the holes and forms a thin bottom film on the ITO/glass. After the vacuum treatment, the “sandwich” is put under 365 nm UV light and cured for 30 min. Following photopolymerization, the PDMS mold is detached carefully such that

the solidified film of patterned pillars stays on the ITO/glass. The surface character of the patterned films is checked with an optical microscope (Olympus BX51) and a Dektak³-30 surface profiler. With the vacuum method, the pillar height obtained polymer films is comparable to that of the SU-8 templates (30 or 25 μm), while the bottom film carrying the pillars can be made thinner than 5 μm . The pillar array with an inter-pillar spacing of 150 μm is designed to have the least interaction between contracted pillars when an electric field is applied along the z direction during the measurement.



Scheme 8.1 Schematic representation of the preparation of polymer films with an array of pillars

Gold-capped PS spheres loaded in p(EGPEA) films

The polystyrene spheres employed are coated uniformly with sulfate groups on the surface lending the spheres a uniformly negative charge. After vapor deposition, the hemisphere covered with the thin (20 nm) gold film breaks the balance of the original charge distribution and the spheres are believed to act more like bipolar particles.^[10] They

may move or assemble into well-defined orientations according to their charges, charge distribution, and the strength and direction of the electric field they are exposed to.^[22, 179] It has been published that an aligned LC polymer with a nematic director parallel to one direction is realized by applying a suitably oriented magnetic field. The prepared LC polymer pillars show recognizable contraction and expansion in response to small temperature changes.^[185] Similarly, the orientation of surface-anisotropic Au-PS spheres in EGPEA pre-polymer liquid may also be adjusted by an AC or DC field. Here, we introduce a practical approach to an electrically align Au-PS sphere/p(EGPEA) film. Subsequently, the effect of the loading of aligned Au-PS spheres on the electromechanical displacement of films is studied.

A well dispersed (3 wt%) Au-PS spheres/EGPEA pre-polymer liquid is employed to prepare pillar-patterned films on ITO-glass the same way as described above. The only difference is that a small DC electric field (also along the z direction) is applied during polymerization to align the surface-anisotropic Au-PS spheres. In order to create a DC field, the back of the PDMS mold is coated with a thick layer (~50 nm) of gold via PVD to serve as one of the electrode, while the ITO coating serves as the other electrode. Complete photo polymerization despite the gold coating is ensured by flipping the “sandwich” structure such that the UV light is directed towards the uncoated ITO glass slide side during the UV treatment. 6 V DC (3B U11760, AC/DC 13V/3A) are maintained for 5 min at the beginning of the UV polymerization then the polymer is kept under the UV light for an additional 25 minutes with the electrical supply turned off. The prepared films are referred to as DC-AuPS-EGPEA composite. Two additional types of films are also prepared as blanks for reference measurements: (i) electric-field exposed

plain p(EGPEA) films (referred to as exposed plain film) and (ii) non-aligned Au-PS sphere/p(EGPEA) composite films (referred to as AuPS-EGPEA composite).

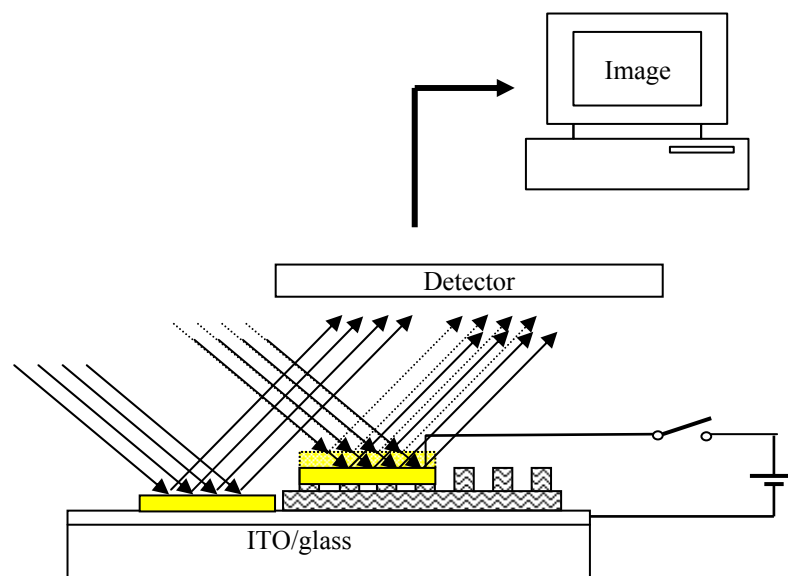
In all cases, the used PDMS molds are cleaned with kimwipe tissue, rub-washed under tap water, and then rinsed with DI-water. The reuse of the dried, clean PDMS soft mold results in a similar quality of films with no visible degradation in the quality of the pillar arrays.

8.3.3 Actuator electromechanical performance measurement

The optical method (laser profile mapping) widely used in microelectromechanical systems (MEMS) research to check device surface profiles is employed in this study to detect the deformation of pillars when exposed to an electric field. A typical optical surface profiler requires a light source, imaging optics, and a photo detector. The light source and focusing optics generate a collimated or focused beam of light that is projected onto a target surface. An imaging lens captures the scattered or reflected light and focuses it onto the photo detector, which gives a 2-D or 3-D image showing the surface geography. As the target changes position, the imaged spot shifts.

The electric device set-up is shown in Scheme 8.2. One plate of gold-coated silicon (5mm $\times$ 2mm) is attached to an area of the film that has a well-formed pillar pattern and is connected to a DC voltage supply (Keithley 247 high voltage supply) by a gold wire as one electrode (positive). Another plate sits directly on the ITO glass (cleaned with acetone) and acts as a reference. The two plates are placed next to each with a distance of about 0.3 mm to avoid unwanted electric contact. The ITO/glass at the bottom of the film is connected to the voltage supply through a copper wire as the other electrode (ground).

The deformation (contraction) of the polymer occurs mostly parallel to the z direction of the pillars.



Scheme 8.2 Schematic representation of the optical measurement set-up used for the determination of the electromechanical deformation of pillars on films

With good electrical contact, each pillar under the charged Au/Si plate is expected to contract when the voltage is on and an electric field is produced. Consequently, the contracted pillars lower the position of the charged plate. The scattered/reflected laser light beam changes positions, which is recorded in the surface geography. Comparing the relative position of the charged plate and the reference plate (not moving), we can determine the distance by which the field-exposed pillars have been contracted. The polymer strain is calculated as the contraction distance divided by the original pillar height. The electric field values are expressed as the applied voltage divided by the z-distance between the two electrodes, i.e., the sum of initial pillar height and local bottom film thickness. Several voltage levels (from low to high) are applied to produce different electric fields and each voltage is applied repeatedly in 3 or 4 on-off cycles. An average

value and error bars of one standard deviation are calculated. Shape memory effects and the deforming speed of the polymer actuators are also checked.

8.4 Results and discussion

The electromechanical performances of plain polymer films and films with different filling materials are described below. Further, the effect of the type of filling material used and the level of electromechanical strain are discussed.

8.4.1 Loading of TiO₂ nanoparticles or Au-PS spheres into polymer matrix

Experiments show BA helps the dispersion of NPs but the films with higher BA content tend to stick to the PDMS mold because of the low polarity of BA. Two volume ratios of 1:1 and 2:1 (BA:EGPEA) are tested to ensure the solubility of NPs in the pre-polymer liquid (BA) while also enhancing the strength of the polymer films. Dispersions of TiO₂-pBA NPs in BA-EGPEA are transparent with a light yellow color. The transparency of the liquid indicates that the NPs disperse well in the pre-polymer mixture and an even dispersion of NPs in films is anticipated. Slight sample cloudiness due to light scattering on larger particle agglomerates is observed at higher loadings of TiO₂-pBA.

Although typically a crosslinker is required for stabilizing these materials, actuation is enhanced in the absence of crosslinker since they tend to stiffen the elastomer. Therefore no crosslinker is added in this study and photoinitiator is added at 0.86% volume ratio based on the volume of the mixture. Preliminary studies ensured that the mechanical crosslinks (i.e. entanglements) present are sufficient in these materials to restore films to the original shape upon removal of the electric field.

The dispersion of Au-PS surface-anisotropic spheres in EGPEA pre-polymer liquid seems easier than the dispersion of TiO₂-pBA NPs. The liquid dispersion after ultrasonication shows a transparent whitish color with no visible floating or sedimentation of gold-capped PS spheres (density EGPEA: 1.104, PS: 1.055, gold 19.32, all g/cm³). A newly prepared liquid mixture with 3% (molar concentration) crosslinker and 0.86 wt% (molar ratio 0.5%) photo-initiator is used to prepare films with gold-capped spheres.

Usually polymerization for 30 min produces films strong enough to bear the tension they experience during peeling off from the PDMS templates. Plain p(EGPEA) or AuPS-EGPEA composite films are easily detached from the PDMS mold and stay on the ITO glass slide while p(BA-EGPEA) co-polymer films show more adhesion to PDMS due to their similar hydrophobicity. Neither metal coating nor UV-ozone treatment of the PDMS molds prior to film preparation affected the adhesion characteristics of the BA containing films. Therefore special care is necessary when removing the PDMS replica after polymerization. Large areas of films with ordered patterns of pillars can be achieved in about 30% of the samples for co-polymer and 80% of the samples for p(EGPEA) with or without Au-PS spheres. Exposure to an electric field during polymerization does not cause film decomposition when inspected with an optical microscope. However, more sticky and flexible films with a higher portion of pillars growing on the ITO/glass directly with no carrying bottom film (so-called “naked” pillars) are observed in some samples.

8.4.2 Polymerization and characterization of films

The pre-polymer liquid does not spread after application to the PDMS mold surface indicating the two have different surface hydrophobicities. After addition of the

ITO/glass, the liquid spreads quickly between the PDMS mold and the glass slide due to the pressure caused by gravity and capillary forces. The liquid fills the holes in the PDMS mold. Vacuum is applied to remove the air between the liquid and the mold and to force the liquid to fully fill the holes. Upon the application of vacuum, small bubbles are observed which join into several big bubbles. The “sandwich” structure is kept in vacuum for 20 min with the glass slide facing up to make the bottom film as thin as possible. After 20 min, the vacuum is removed by filling the dessicator slowly with nitrogen or air, e.g., 2 or 3 min from -17 inHg vacuum back to atmospheric pressure. Upon removing of the vacuum, the big bubbles begin to shrink slowly and the liquid spreads into the areas originally occupied by bubbles. Most of the area under the mold is clear and transparent indicating even spreading of the liquid. After removal of the remaining bubbles by flattening the soft PDMS mold gently with a pair of tweezers, the sample is kept under UV light for 30 min with the PDMS mold facing up.

After photopolymerization and cooling down, the PDMS mold is carefully removed, leaving an array of pillars extending from the bottom film that is attached tightly to the ITO/glass. The pattern can be seen with the bare eye, but an optical microscope is needed to check if the pillars have the correct pillar shape and to test the quality of the polymer film. A newly prepared PDMS mold gives the cleanest surface but the pre-polymer liquid spreads with more difficulty over a large area.

Most samples show large areas of continuous, patterned pillars. The top view of one sample film is shown in Figure 8.1. The smooth and flat small squares, each $100\text{ }\mu\text{m} \times 100\text{ }\mu\text{m}$ in size, are the top surfaces of evenly spaced pillars. The bottom film surrounding the pillars is also visible. The thickness of the bottom film and the pillar height are tested

with a Dektak³-30 surface profiler at 2 mg contacting force. Most pillars exhibit the heights of the pillars in the original SU-8 templates (either 30 or 25 μm). The roughness of the bottom film surface is within 0.1 μm and can be ignored compared to the thickness of the film: $\sim 5 \mu\text{m}$. In some area, the bottom film is as thin as 1 μm .

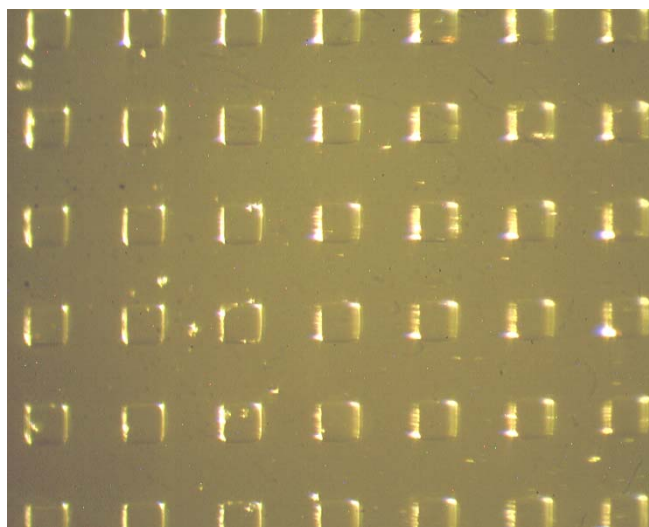


Figure 8.1 An optical image of a sample film (each small square: 100 $\mu\text{m} \times 100 \mu\text{m}$)

It is also observed that the films prepared from the pre-polymer liquid with no crosslinker or more BA are softer and more flexible, which suggests these films may have a larger modulus than the EGPEA films with crosslinker, thus higher deformation strains are expected from them when exposed to an electric field.

8.4.3 Electromechanical performance of actuators

The electromechanical performance of the actuators is measured through the motion of the top Au/Si electrode and expressed as the strain of the pillars, which is calculated as the average percentage of shrinkage of each pillar.

8.4.3.1 Actuation measurement employing optical profiling

The electric devices prepared from the films are measured with a WYKO optical profiler under high voltage starting from 150V or 200 V up to close to the breakdown voltage (~ 500 V) to produce the high electric fields necessary for polymer deformation. An initial map of the surface geometry with no applied voltage is recorded after laser fringe scanning. Upon voltage application, the fringes reflected by the top surface of the Au/Si electrode plate can be seen to move away from the original location, indicating the plate changed its position due to the deformation of the pillars underneath. The position change of fringes is very fast and occurs in about 2-4 seconds. Then scanning is done with the voltage kept on. This process takes about 1-2 minutes, depending on the scanning speed of the laser fringes. The fringes move back to (or close to) their original position after the voltage is turned off. The movement occurs at a lower speed within about 8-10 seconds. The slower motion suggests that the deformed pillars try to recover their original shapes, however, it takes more time to release the stored energy. The positions of the plates at voltage-off status are measured again and the geometry image is recorded and used as the initial position for the next cycle.

The deformations of the pillars are quantified from the 2-D profile crossing a certain line on the surface geography map. One sample 2-D cross-section profile is shown in Figure 8.2. The cross-section profile is composed of two regions. The left region displays the position of the charged electrode plate with voltage turned on and off. The right region represents the positions of the reference plate. In Figure 8.2, thin black line indicates the initial positions of the two plates. Thick red points are the plate positions during application of the voltage for the first time. In the experiment shown in Figure 8.2,

the electrode plate (left, charged) and the reference plate (right, uncharged) move in opposite directions. In such a case, the net motion (contraction) of the pillars under the electrode plate is calculated as the sum of the distance the electrode plate has moved down and the distance the reference plate has moved up. Both plates move back to their original positions after each cycle (data not shown). It is not clear why the reference plate is also moving (moving up and down, tilting, etc.) in some experiments. One possible reason is that there may be some electric repulsion between the two very close, although not connected, plates. In future work, a piece of plate made of an isolated material with only the top surface coated with gold may be used as the reference plate to avoid any interaction. In summary the optical profiling method provides a novel, efficient and practical method to quantify electromechanical strains of EAP actuators accurately.

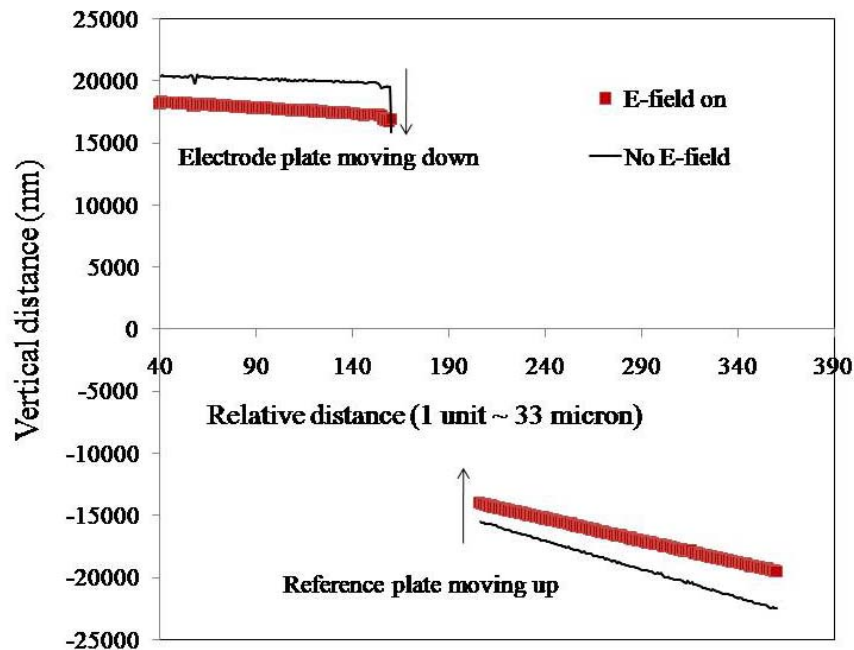


Figure 8.2 A sample of electromechanical deformation analysis based on 2-D profile from the optical geography map

8.4.3.2 Actuators made of p(BA- EGPEA) films with pBA coated TiO₂ NP as filler

p(BA-EGPEA) polymer matrices with two ratios, 1:1 and 2:1, of BA:EGPEA are studied with varying amounts of TiO₂ NPs to determine the effect of NP loading levels of NPs with high dielectric constant on the electromechanical performance of actuator films. A higher BA content enables better dispersion of the TiO₂ filler but leads to stickier and lower quality films.

Various loading levels of pBA-TiO₂ NPs in 1:1 (BA:EGPEA) films

Films with NP concentrations of 1 wt%, 5 wt%, 6.25 wt%, 10 wt% and 12.5 wt% (all g/100mL) in the co-polymer with a 1:1 (BA:EGPEA) (TiO₂-B1E1 composites) volume ratio are tested and compared to the p(BA-EGPEA) co-polymer with no NP loading (B1E1 copolymer). We observe that the performance of the films prepared from the same batch of pre-polymer liquid with the same NPs concentration varies much while the performance of the films without NPs is quite uniform. A possible rationale is the non-uniformness of film quality for composites with NPs. In the following, we only show data from the best performing samples of each concentration.

The deformation strains of films vs. electric field are plotted in Figure 8.3. The experimental data are averages of 2 to 4 voltage off-on cycles with the assumption that zero electric field gives zero strain. The pillar structure and the very thin bottom film help to reduce the voltage needed to obtain the required electric field value. With only 400 V, we can get an electric field of 14 V/ μ m for a film with 25 μ m high pillars and a 4 μ m thick bottom film.

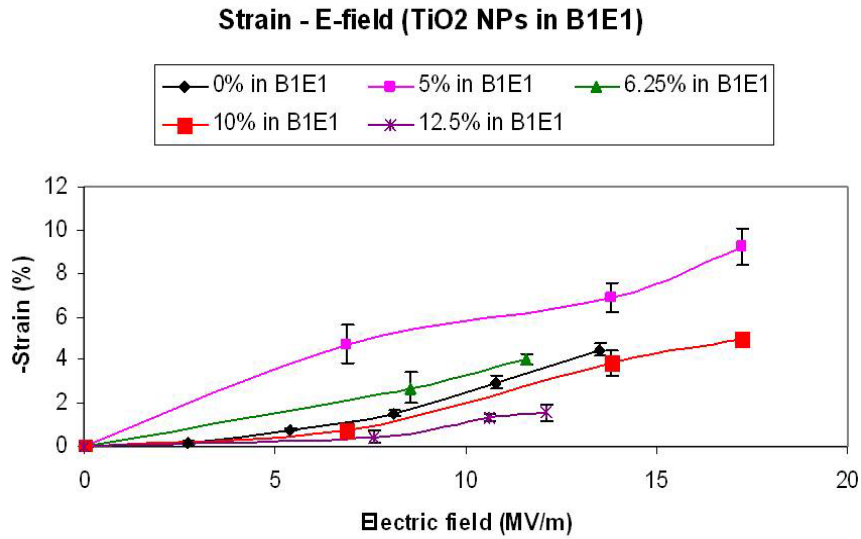


Figure 8.3 Strain vs. electric field of 1:1 (BA:EGPEA, volume ratio) films with various TiO_2 NPs loading levels (wt%)

First, Fig. 8.3 shows that with the increase of the electric field, the strain (absolute values) of all films increases. Most lines show a quadratic trend, which agrees well with the theoretical prediction summarized in Eq. (8.4):

$$\text{Strain} = -K\varepsilon_0 E^2 / Y \quad (8.4)$$

which can be written as AE^2 , where A is equal to $-K\varepsilon_0/Y$.

For a given uniform film, the dielectric constant K , the permittivity of free space ε_0 and the modulus Y are constant. Thus the strain is linearly proportional to the square of the electric field value, E^2 . Some of the lines in Fig. 8.3 do not exhibit quadratic behavior, for example, the 5% data. This can be attributed to the strong variation in measurements expressed by the large standard deviation ($\sim 20\%$ for the 7 MV/m data). Also Eq. (8.4) is not applicable at high strain values because we can no longer use the fixed d_0 to calculate the electric field. In several samples, a large variation is observed because the very different positional changes of the electrode plate recorded in 3 cycles (data not shown).

This is probably caused by the Au/Si plate electrode not being in tight contact with the pillars. Thus, the first application of a large voltage changes the plate position more than just by the pillar contraction. However, for all films displayed here the standard deviations at each tested electric field are relatively small ($< 20\%$) compared to the strain value. This suggests that our measuring method is within reasonable experimental error and the polymer films do not show aging after 3 or 4 cycles under high voltage exposure.

Comparison of films with different loading levels of NPs shows that films with a 5% NP concentration exhibit the highest electroactive strain among the tested concentrations, followed by the 6.25% sample. At around $7 \text{ V}/\mu\text{m}$, the strains of the 5% and 6.25% TiO_2 -B1E1 composites are 4.7% and 2%, respectively, higher than that of the blank film (0% NPs in B1E1 copolymer), which is slightly lower than 1%. However both 10% and 12.5% loading levels fall below the blank film for all electric fields tested (0 to $17 \text{ V}/\mu\text{m}$). The 12.5% NP loaded film responds with the lowest electroactive strain. Under the same electric field, the films containing 10% and 12.5% NPs contract less, giving strains of only $\sim 0.77\%$ and 0.5% , respectively.

The higher strains in 5% and 6.25% TiO_2 -B1E1 composite films indicate a larger A value in the strain equation, which might come from a higher K , a smaller Y , or both. Similarly, the negative effect on enhancing the electromechanical performance of the 10% and 12.5% TiO_2 -B1E1 composite films is because of a smaller K or an increased modulus. Our hypothesis is that higher loading levels increase the difficulty to obtain uniform dispersions of NPs in the pre-polymer mixture. As a result the effect of NPs on the dielectric constant of the NPs-polymer composites is not uniform. The high loading of

inorganic TiO₂ NPs may also affect the elastic modulus of the composites (loss of flexibility).^[186]

It is worth noting that the highest strain achieved here is 9.24% for the 5% NP loading at an electric field of 17.2 V/ μ m achieved with a voltage of 500V. This is among the highest longitudinal strain achieved for EAP films with inorganic fillers reported.^[181] In all cases, the films are able to contract within a second and bounce back to its original position within seconds. No sparking is observed at 500 V, indicating a breakdown point higher than this value. The accurate breakdown point is not determined in the studies presented here in order to enable the reusability of films for performance reproducibility studies.

Various loading level of pBA-TiO₂ NPs in 2:1 (BA:EGPEA) films

Poly(butyl acrylate) coated NPs were found to disperse better in the BA-EGPEA mixture at higher BA concentrations. Figure 8.4 shows the strain-electric field plots of five copolymer (BA:EGPEA 2:1, volume ratio) films: (i) blank film (0%), (ii) copolymer film with 3 wt%, (iii) 5 wt%, (iv) 6 wt% and (v) 10 wt% pBA coated NPs. The 2:1 films appear softer and somewhat sticky compared to the 1:1 films. For films with low concentration of NPs sparks are not observed even at 500 V, but for several 10% films, exposure to 400 V causes sparks, indicating a breakdown point close to this voltage. The wires or films are not melted when the voltage supply is removed immediately upon sparking. The highest voltage tested for 10% films is 350V, corresponding to a ~ 12 V/ μ m electric field for films with a 4 μ m thick bottom film and 30 μ m high pillars.

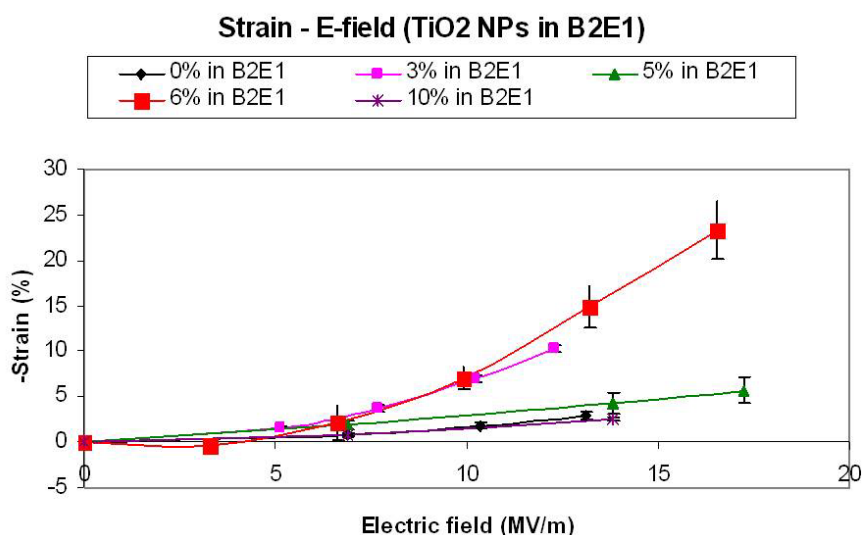


Figure 8.4 Strain vs. electric field of 2:1 (BA:EGPEA, volume ratio) films with various TiO₂ NPs loading levels (wt%)

Again all strain-electric field plots show the expected quadratic trend. The strains observed for 3% NP loading is highest at low electric field, followed by the strains of the 6% NP loaded films, which surpasses the 3% NP loading at electric fields higher than 10 V/ μ m. The blank film and the 10% NP loading experience the lowest strains. The performance of the 10% NP loading films in 2:1 (BA:EGPEA) co-polymer is comparable to that of the 10% NP-loaded 1:1 co-polymer films, i.e., it is just below the blank film. The 5% and 6% NP-loaded films show different behavior compared to the 5% and 6.25% NP-loaded 1:1 co-polymer films. The strain exhibited by the 6% NP-loaded sample increases much faster than the 5% NP-loaded sample. At 7 V/ μ m, both films reach a 2% strain, which is about twice as much as the strain of the blank film under the same electric field. At 13 V/ μ m, the 6% NP-loaded film strains to about 15%, 11% more than the 4% strain achieved by the 5% NP loaded film. The highest strain measured in this group is > 23% at an electric field of 16.5 V/ μ m (500 V) by a film with 6% NPs filling. This strain value is much higher than that of the 5% NP-loaded 1:1 co-polymer film. This

observation agrees well with the softer and more sticky appearance of the 2:1 (BA:EGPEA) copolymer films compared to both the 1:1 co-polymer and plain p(EGPEA) films.

Here the 5% and 10% samples are from the same batch of pre-polymer liquid while the 3% and 6% are from two other batches of pre-polymer liquid, so there might be variance attributed to batch solutions. However, the optimum loading level range of 6-10% is similar to that found in 1:1 copolymer samples.

In summary, with the 2:1 co-polymer mixture, the introduction of high dielectric constant NPs resulted in an actuation of more than 20% at fields below 15 V/ μm (DC field). This greatly reduces the external electric power needed for possible applications.

8.4.3.3 Actuators made of p(EGPEA) films with Au-capped PS sphere filler

It has been suggested that heterostructures including interface heterojunctions (e.g. core-shell CdSe/ZnS nanostructure) have large dipole moments.^[3] However, there has been no report discussing the incorporation of surface-anisotropic particles into EAP materials. Meanwhile, gold-capped polystyrene spheres have a large exposed homogeneous organic surface, which would enhance their dispersion in the pre-polymer liquid similar to the all-organic high dielectric constant composites.^[186] In order to test this hypothesis, we prepared Au-capped PS spheres and dispersed them in pre-polymer liquid. Subsequently, electromechanical performance of the new composites is studied. The displacement strain measured for films from a simple blend of Au-capped spheres and EGPEA liquid (3 wt%) (referred to as AuPS-E composite) is plotted in Figure 8.5a together with the performance observed for the plain p(EGPEA) film. The AuPS-E composite film (green squares) shows a slightly larger strain than the plain p(EGPEA)

film (red triangles) when exposed to the same electric field. For example, at a field of 7 V/ μm , the loading of Au-capped PS spheres doubles the strain from 0.7% to 1.4%, and at around 11 V/ μm , the AuPS-E composite film is only about 50% higher than the plain p(EGPEA) film. The AuPS-E film does not show the expected quadratic trend. Instead, it reaches a plateau within the range of electric fields tested. The reason for the plateau behavior is not clear. One possible explanation is that similar to the films loaded with the pBA-TiO₂ NPs, large variations due to the pronounced initial movement upon first exposure to an electric field also occur here. Another explanation is that the dielectric constant of the AuPS-E composite changes at higher electric fields.

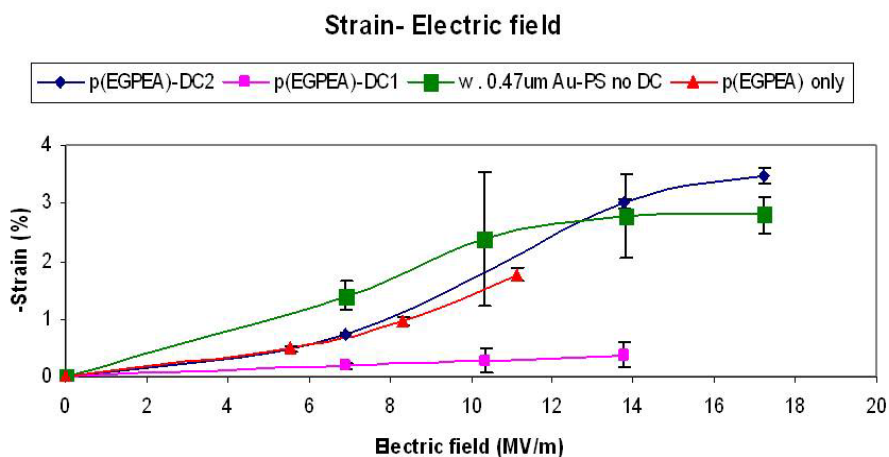


Figure 8.5a) Strain vs. electric field of EGPEA films with or without Au-sPS spheres

Next, we modified the simple mixing procedure by adding a DC-field exposure step during the polymerization of polymer. The resulting films are Au-PS spheres/EGPEA polymer nanocomposite with DC field-aligned Au-PS spheres (hereafter referred to as DC AuPS-E composite). The field exposure is realized by exposing the pre-polymer liquid and Au-PS sphere mixture to a small DC field (~ 0.2 V/ μm) during the initial 5 min of the photo-polymerization step. During the electric field induced-assembly, the charge-

anisotropic Au-PS spheres are supposed to undergo electrophoretic rotation and align along the direction of the DC field applied.^[22] Note, the movement of spheres towards the oppositely charged electrode end is slowed by the polymerization.

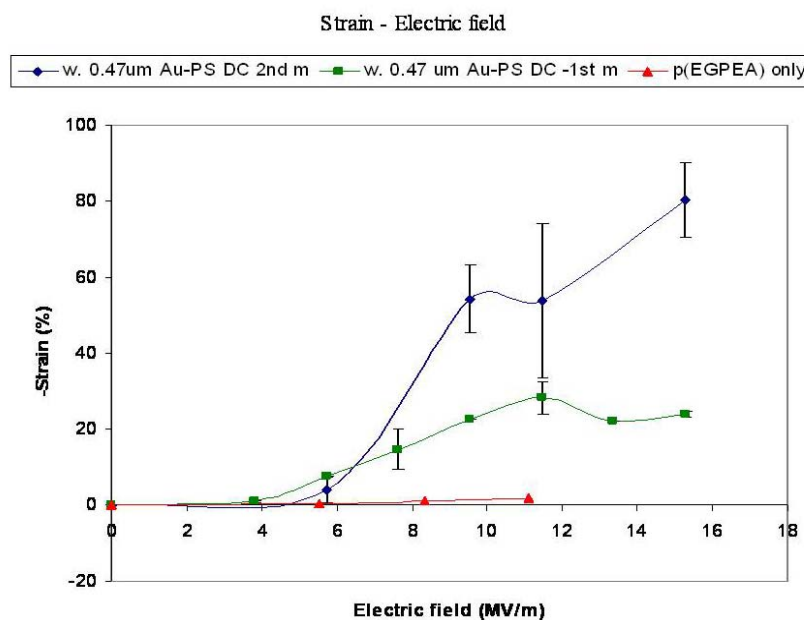


Figure 8.5 b) Strain vs. electric field of EGPEA films with electric field aligned Au-PS spheres

A couple of plain p(EGPEA) polymer films are also exposed to the DC field during polymerization (DC-E films) to serve as references. Strains experienced by the DC-E films (blue diamonds and purple squares) as a function of the applied electric field are also given in Figure 8.5a. As shown in the plot, the strains of the reference films are very low with strains of 3% or 4% at electric fields above 15 V/ μ m, close to the strains of p(EGPEA) films and AuPS-E composite films. While in Figure 8.5b, the DC-AuPS-E composite film exhibits a ~30% strain at 11.5 V/ μ m during initial measurement less than one week after the films are prepared (solid squares). This strain is 10 times higher than the strains of all reference samples in Fig. 8.5a. The strain decreases slightly with

increasing electric field, but is larger than 23% up to 13.5 V/ μm . After almost three months, we repeated the measurement (solid diamonds). The strains at lower electric field show a decrease compared to the initial measurement but at higher electric fields (> 7 V/ μm) the film shows an increased strain response. A 54% strain is measured at 9.5 V/ μm and 11.5 V/ μm , which increases to 80% strain at 15 V/ μm (400V). The trends are non-quadratic. But here the non-quadratic trend is most likely due to the inaccuracy of Eq. (8.4) at large strains (i.e., strain $> 20\%$). We calculate electric fields based on the initial pillar height and the film thickness in all plots above. But the initial distance (d_0) between the negative and the positive electrodes can no longer be used to estimate electric fields at large deformations. The actual electric field E ($E = V/d$, where d is the actual distance between the two electrodes) is larger than the electric fields ($E' = V/d_0$) shown in the plot ($d < d_0$). Eq. (8.3) should give the accurate plot of strain vs. electric field. Eq. (8.3) is simplified as follows. The left side of Eq. 8.3 can be rewritten as:

$$Y \ln(d_0/d) = - Y \ln(d/d_0) = - Y \ln(1-\delta/d_0) \quad (8.5)$$

where δ is the average contraction distance of pillars under the electrode from the measurement ($\delta = d_0 - d$) and $-\delta/d_0$ is the measured strain (S) used in the plot of Fig. 8.5b.

While the right side of Eq. 8.3 can be rearranged to:

$$\epsilon(V/d)^2 = \epsilon(V/d_0)^2(d_0/d)^2 = \epsilon E_0^2(d_0/d)^2 = \epsilon E_0^2(d/d_0)^{-2} = \epsilon E_0^2(1-\delta/d_0)^{-2} \quad (8.6)$$

where ϵ is the dielectric constant of the film material and E_0 is the “electric field” calculated using the initial pillar height and changes only with varying of the applied voltage. Combining of Eqs. 8.5 and 8.6 gives:

$$(1-\delta/d_0)^2 \ln(1-\delta/d_0) = - \epsilon E_0^2/Y \text{ or } (1-x)^2 \ln(1-x) = - (\epsilon/Y) E_0^2 \quad (8.7)$$

with δ/d_0 replaces by x . Hence if we have $y = (1-x)^2 \ln(1-x)$ (but here $x = S = |\text{measured strain}|$) and plot y (so-called modified “strain”) over E_0 , we should obtain a quadratic trend if both ε and Y are constants. Figure 8.6 is the plot from Eq. 8.7 using the data from the plot in Fig. 8.5b. As shown in Fig. 8.6, the reference film keeps its quadratic trend, while both the first and second measurements of the DC-AuPS-E composite initially show a quadratic increase which disappears at higher field strengths. This observation indicates that the ε/Y in Eq. 8.7 may not stay constant within the range of voltages tested. Therefore, it is very possible that the dielectric constant and modulus of the DC-AuPS-E composite change during the measurement due to the exposure to the high electric fields.

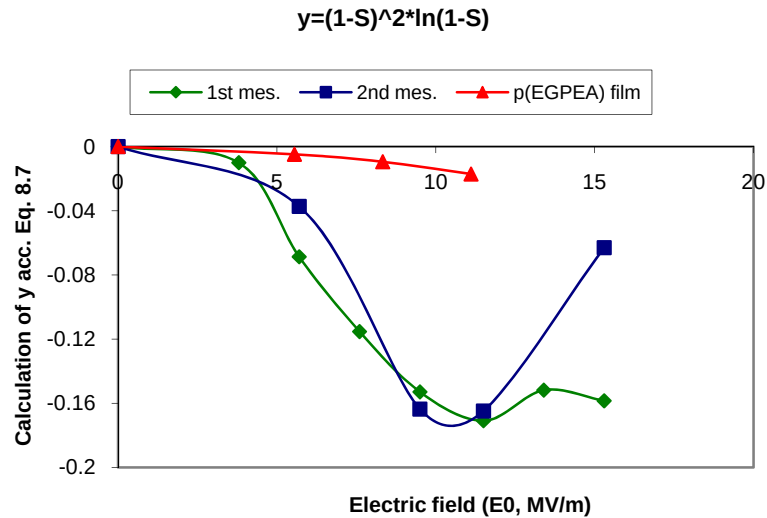


Figure 8.6 Plot of modified “strain” of EGPEA films with E-field aligned Au-sPS spheres vs. apparent E-field (E_0) according to Eq. 8.7

No sparking is observed up to 400 V in the DC AuPS-E composite measurements and the highest voltage applied is 400 V or 380V to avoid film breakdown. With more films prepared in the future, the breakdown point should be determined. Note, the initial measurement is carried out in a different way from the standard procedure. The voltages

are applied from low (100 V) to high (400 V) with only one off-on cycle at each voltage, which is then repeated twice. This change in measuring procedure may have some effect on the strain difference observed, but undoubtedly the DC-AuPS-E composite film keeps its high performance within a relatively long period of time.

The net concentration of Au-PS spheres is about 3 wt% in the DC AuPS-E composite films, therefore the significant improvement of strains is very promising when compared to both the plain p(EGPEA) film and the AuPS-E composite film. The observed increase in strain can be rationalized by a high dielectric constant, a small elastic loss, and more importantly, the possible aligned orientation of the uniformly distributed dipole-carrying surface anisotropic spheres. A theoretical model on the composites consisting of a high-dielectric constant and a low-dielectric constant media shows that the exchange coupling at the interface can result in a significant change in the local polarization level at the interface region.^[197] This can result in a large enhancement in both the dielectric constant and the strain response of the composite.^[181] More importantly, the electric-field induced orientation of Au-PS spheres mimics a group of well-dispersed dipoles, which are all parallel to each other. This alignment causes all electric dipole moments to point towards (or close to) one direction and results in a large dipole when exposed to an electric field during the strain measurements.^[198]

Due to the limitation of equipment, we are unable to measure the dielectric constant, the dielectric loss or the elastic modulus of our films. These properties would be helpful in understanding our systems better and are suggested for future work.

8.5 Conclusion

This chapter discusses the study of the electromechanical performance of micrometer-sized actuators with a pillar array structure prepared from an acrylate polymer elastomer modified with organically coated titanium dioxide nanoparticles as well as surface-anisotropic submicron spheres. A simple, efficient, and direct optical setup that can be used to measure the electromechanical deformation accurately has been developed and is employed to measure strain vs. electric field curves. The study has shown that the dispersion of TiO_2 nanoparticles in the elastomer results in an improved electromechanical performance compared to the plain elastomer actuators of the same geometry. The results also show that the array structure quality and the loading of the nanosized fillers play important roles in enhancing the electromechanical performance. The electric field necessary to obtain significant axial strain is greatly reduced by an order of magnitude from $100 \text{ V}/\mu\text{m}$ ^[189] to $10 \text{ V}/\mu\text{m}$. Furthermore, aligned incorporation of surface-anisotropic sub-micron particles into the p(acrylate) polymer increased the axial strain significantly from $< 10\%$ to 80% without the need of pre-straining at an electric field below $20 \text{ V}/\mu\text{m}$. This 80% strain is the highest recorded result for this type of polymer actuators to date.

Future work should include determination of the dielectric constant and the modulus of the films. Further, other technical facts for these new films such as the breakdown voltages and the electromechanical behavior in an AC field are of great interest and should be studied in the future.

Chapter 9 Conclusion and Outlook

In this thesis, a novel and economic templating process is developed for the manufacture of Janus spheres via the electroless deposition (ELD) method. An easy-to-process, flexible template based on a polydimethyl siloxane (PDMS) film and a sphere monolayer is designed for partial coverage of the spheres. The PDMS film is pre-heated (70 °C, 9-11 min) to decrease its viscosity and ensure only partial embedment of micrometer sized spheres. Templated polystyrene (PS) spheres (2.4 μm in diameter) are modified with a silver cap composed of 50-200 nm nanoparticles (NPs) through the ELD process. The deposits are found to be stable over time and under physical treatment.^[140]

Successful, partial embedment of sub-micron spheres (1.0 and 0.5 μm in diameter) is also realized by adjusting the PDMS template pre-heating time. Asymmetric deposition on the templated sub-micron Janus spheres is subsequently carried out successfully and it is found that the substrate sphere curvature influences the ELD modification by way of the functional group coverage and distribution as well as the size ratio of the substrate sphere to the NPs deposit.

The templating process is further employed for surface anisotropic electroless/wet chemical deposition of two new metals (gold and palladium) and one metal oxide (TiO_2). Using ELD, gold and palladium NPs are successfully deposited onto sPS spheres, while TiO_2 deposition is observed, but is not uniform. The adsorption of thiols on the gold cap of the modified Janus sphere suggests that the deposit can be further chemically modified for assembly studies allowing the tuning of sphere-sphere interactions.

The Janus particles prepared via ELD carry a rough surface compared to the modifications prepared via physical vapor deposition (PVD). In addition, a detailed study

of the ELD mechanism finds that the surface roughness of the modification can be controlled by varying the ELD reaction conditions to adjust the amount of deposit and the size distribution of the silver NPs deposited.^[199] For example, stirring rate, silver precursor, and formaldehyde concentration increases lead to more deposition, while an increase of the ammonia concentration enables the control of the deposition. The varying surface morphology can be used to study the assembly of Janus spheres with smooth and rough caps. We find that the surface morphology has a significant effect on the sphere-sphere interaction. The PVD-Au or PVD-Ag smooth-capped spheres tend to assemble into planar 2-D structure while the ELD-Ag rough-capped spheres mainly form 3-D cluster structures. The observation of the difference in assembly orientation inspired us to prepare dual-cap spheres with both a smooth cap from the PVD procedure and a rough cap from the ELD procedure. Interestingly, a new type of Janus spheres with caps of PVD-Au and ELD-Ag and an ELD-Ag belt is discovered. More importantly, the assembly of the dual-cap/mono-belt Janus particles confirms that the surface roughness plays an important role in determining the orientation of Janus spheres during assembly.

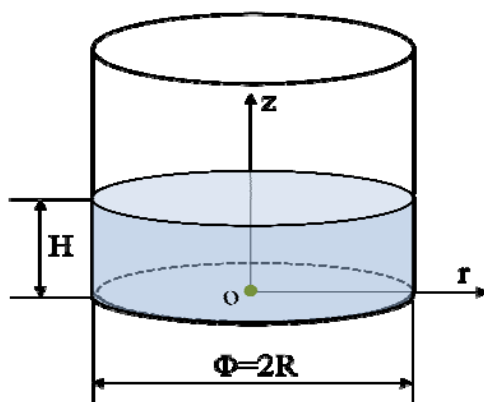
In chapter 8, we report for the first time the introduction of Janus spheres into electroactive polymers (EAP) as fillers to enhance the electromechanical performance of EAP materials. The EAP used in this thesis is an acrylate polymer. A traditional high dielectric constant filler (polymer-coated TiO₂ nanoparticles) is also studied and the electric field necessary to obtain significant axial strain is reduced by an order of magnitude from 100 V/ μm ^[189] to 10 V/ μm .^[200] While the incorporation of the electric-field aligned Au-caped sPS spheres causes the axial strain to increase significantly from

below 10% to 80% at an electric field below 20 V/ μm . A strain of this magnitude at a relatively low electric field has not been seen in any previous studies.^[201]

In conclusion, our templating procedure works efficiently for the preparation of Janus spheres employing the electroless deposition method. In addition, ELD presents an alternative way to tune the surface morphology of the asymmetric modification, which provides access to studying the effect of surface morphology on their properties such as surface plasmon resonance and directional properties such as interparticular forces. In this thesis, the assembly of spheres with very smooth (roughness ~ 0) and very rough (roughness ~ 1) surface modifications is discussed. In the future, Janus spheres with different roughness degrees can be prepared by varying the ELD conditions, such as reactant concentrations, reactant ratios, stirring rates, substrate sphere size, or material deposited. The detailed study of the self-assembly and field (electric or magnetic) induced assembly of these spheres will be needed to help us understand the interactions between Janus spheres and designer particle structures. The results reported on the application of Janus spheres in the enhancing of the electromechanical performance of EAPs present an exciting new development and require further studies to determine of the dielectric constant and the modulus of the polymer matrixes with incorporated Janus sphere fillers. In addition the behavior of these matrixes in AC fields will be interesting, lead to a better understanding of the field-induced orientation of Janus spheres, and result in many new and exciting applications.

Appendix A Approximation of Formaldehyde Diffusion in an Aqueous Solution

Our system is an aqueous liquid body kept in a glass vial and can be stated as a cylinder with the diameter of $2R$ and height of H as shown in Scheme A.1. At the beginning (time $t = 0$), a certain amount of formaldehyde, n_A (mol) was released at the vial bottom, where $r = 0$ and $z = 0$, and started diffusing in the static liquid body (volume V) due to the concentration gradient. The diffusivity of this system (formaldehyde A in water B) is D_{AB} and the concentration of formaldehyde is much lower than that of water. During the diffusion, formaldehyde molecules meet and react with the silver-ammonia complex at given a reaction rate R_A . We are interested in finding the time required for formaldehyde to diffuse to the top interface of the liquid cylinder at $z = H$.



Scheme A.1 Formaldehyde diffusion from center (green point) into the aqueous liquid body for a cylindrical system

According to the law of conservation of mass, the mass balances for a specific chemical species over a thin shell of fluid can be written as:

$$\begin{aligned}
 & \{\text{rate of mass A in}\} - \{\text{rate of mass of A out}\} \\
 & + \{\text{rate of production of mass of A by homogeneous chemical reaction}\} \\
 & = \{\text{rate of change of mass of A in volume element}\}
 \end{aligned}$$

With this, the equation of continuity of A in our static cylindrical system (zero velocity of fluid in all three directions r, θ, z) is developed as shown in Eq. A.1, assuming the reaction rate R_A is much slower than the diffusion rate of formaldehyde^[202]:

$$\partial C_A / \partial t = D_{AB} [(1/r) \times \partial(r \partial C_A / \partial r) / \partial r + \partial^2 C_A / \partial z^2] \quad (\text{A.1})$$

where $C_A(r, z, t)$ is the mole concentration of formaldehyde and is a function of three variables r (the distance to the point of origin along the radius direction), z (distance to the point of origin along the vertical axis direction), and t (time). Here, the partial differentiation of concentration over the third coordinate, variable θ , is neglected since the diffusion is symmetric in θ direction.

The initial condition is $C_A \rightarrow +\infty$ at $r = 0, z = 0$ while $C_A = 0$ elsewhere;

The boundary conditions are:

$\partial C_A / \partial r = 0$ at $r = 0, R$ and $\partial C_A / \partial z = 0$ at $z = 0, H$ assuming no mass flux across the vial walls or the air/liquid interface;

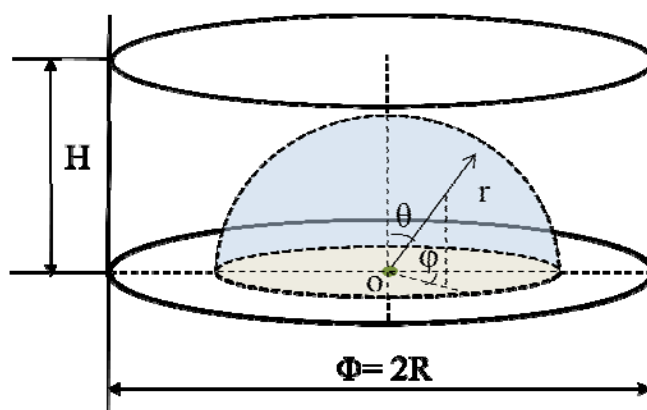
Also $C_A = 0$ at $r = \infty$ and $z = \infty$ for all $t > 0$;

In addition, at all $t > 0$, the integration of C_A over the whole liquid volume (V_{total}) equals to a constant: the amount of formaldehyde added at the very beginning, n_A , or $\int_V C_A dV = n_A$.

And the question to answer becomes at what time t , formaldehyde concentration C_A (any $r, z=H, t$) reaches a detectable amount.

This 2-dimensionl, unsteady-state PDE is quite difficult to solve accurately using an analytic approach and thus numerical solutions are suggested. A detailed discussion and assessment of a similar problem can be found in literature.^[203]

However, here an alternative approximation is suggested, which employs the spherical coordinate system taking advantage of the very *small* amount of formaldehyde released instantaneously at a *point* (infinite small area). Further we assume that the diffusion is identical in all directions above the bottom surface (Scheme A.2). More accurately, the liquid body can be approximated as a half-infinite-space compared to the point source (the point of origin).



Scheme A.2 Formaldehyde diffusion from center (green point) into the aqueous liquid body for a spherical system

The equation of continuity for formaldehyde, Eq. A.1, then can be changed to ^[202]:

$$\partial C_A / \partial t = D_{AB} [(1/r^2) \times \partial(r^2 \partial C_A / \partial r) / \partial r] \quad (\text{A.2})$$

The partial differentiations over variables θ and ϕ are both neglected due to the symmetric distribution along these two directions (a half-spherical shell).

The initial condition is now $C_A(t = 0) \rightarrow +\infty$ at $r = 0$ while $C_A = 0$ elsewhere;

The boundary conditions are:

$\partial C_A / \partial r$ at $r = 0$ assuming no mass flux across the vial bottom;

Also $C_A = 0$ at $r = \infty$ for all $t > 0$;

It holds true that at all $t > 0$, the integration of C_A over the whole liquid volume (V_{total}) equals to a constant: the amount of formaldehyde added at the very beginning, n_A , or $\int_V C_A dV = n_A$. Note, here V is the volume of the Half Sphere ($r = 0-\infty$, $\varphi = 0-2\pi$ while θ is only from 0 to $\pi/2$ instead of 0 to π for a Whole Sphere).

In our system, the liquid height H is smaller than the vial radius R . As the first formaldehyde molecule is approaching the distance H , it is reasonable to claim that it cannot feel that there is an “edge”. Therefore the solution to Eq. (A.2) can still be used to calculate the concentration distribution within the half-sphere of $r \leq H$.

The solution to Eq. (A.2) is easier and can be done with the *method of separation of variables* according to the similar velocity distribution problem. ^[204]

The final answer is given as ^[205]:

Instantaneous point source emitting into Infinite Space:

$$C_A = [n_A/8(\pi D_{AB}t)^{3/2}] \exp(-r^2/4D_{AB}t) \quad (\text{A.3})$$

Instantaneous point source on an infinite plane emitting into Half Space:

$$C_A = [n_A/4(\pi D_{AB}t)^{3/2}] \exp(-r^2/4D_{AB}t) \quad (\text{A.4})$$

In both Eqs. (A.3) and (A.4), n_A is the initial material amount (mol or gram) released at the center point, and C_A is the concentration (mole or mass) at a certain position r and time t . The radius of the liquid body is $R = 1.2$ cm, while the liquid height is $H = 0.34$ cm. The total formaldehyde added to the reaction liquid is $n_A = 0.00016$ mole, which will give a final ($t = \infty$) uniform formaldehyde mole concentration of 1.04×10^{-4} mol/cm³. The diffusivity D_{AB} is estimated as 1×10^{-5} cm²/s. ^[206]

The calculation according to Eq. A.4 shows that a first trace of formaldehyde should be observed at the top surface ($r = H$, $\theta = 0$) by between 4.13 second (0.00 mol/cm³) and

4.14 second (1.84×10^{-302} mol/cm³) after addition of the formaldehyde. However, it is impossible to calculate the exact time when the first molecule arrives at the top surface of the liquid. Here, we set a more practicable measuring scale. We set the formaldehyde concentration to be reached at the top surface of the liquid as 0.1% of the final equilibrium concentration (1.04×10^{-4} mol/cm³). It is found at $t = 214.8$ s, the concentration at $r = H = 0.34$ cm calculated is 1.04×10^{-7} mol/cm³. At $t = 300$ s, the formaldehyde concentration at the shell of $r = H = 0.34$ cm according to Eq. A.4 is calculated as 2.86×10^{-6} mol/cm³, still only $\sim 3\%$ of the equilibrium concentration, while at the vial wall where $r = R = 1.2$ cm, the formaldehyde concentration is only 3.35×10^{-54} mol/cm³. The numerical integration over the half sphere of radius $r = 0.34$ cm at $t = 300$ s gives a total amount of formaldehyde of 0.000159 mole, more than 99.5% of the total amount.

A mass distribution as described in the previous paragraph indicates that Eq. A.4 gives a negligible error for the approximation of formaldehyde diffusion within a short time of 300 s. The distribution also explains the observation of very few silver nanoparticles formed on the polystyrene spheres embedded in the PDMS mask after a 5 min exposure to the static reaction solution assuming there actually **is** homogeneous reaction consuming formaldehyde during the diffusion as discussed in Chap. 6.

The concentration distribution vs. position at certain time calculated from Eq. A.4 is given in Figure A.1 for short times (1, 5, and 10 sec) and Figure A.2 for longer times (50, 300, and 350 sec). At 350 s, the formaldehyde concentration at shell $r = H = 0.34$ cm reaches almost 10% of the equilibrium concentration and the application of Eq. A.4 is no longer reliable.

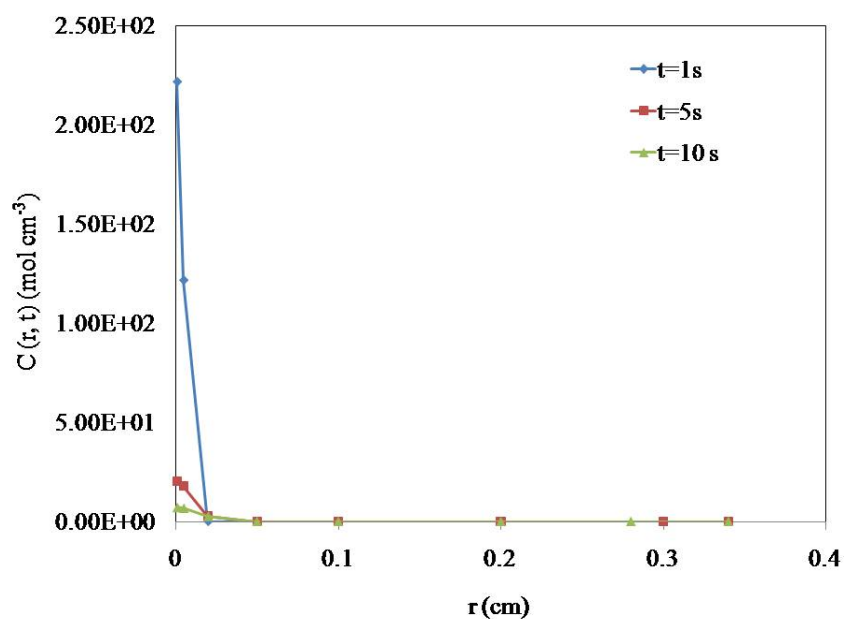


Figure A.1 Formaldehyde distribution in liquid body after short time of diffusion

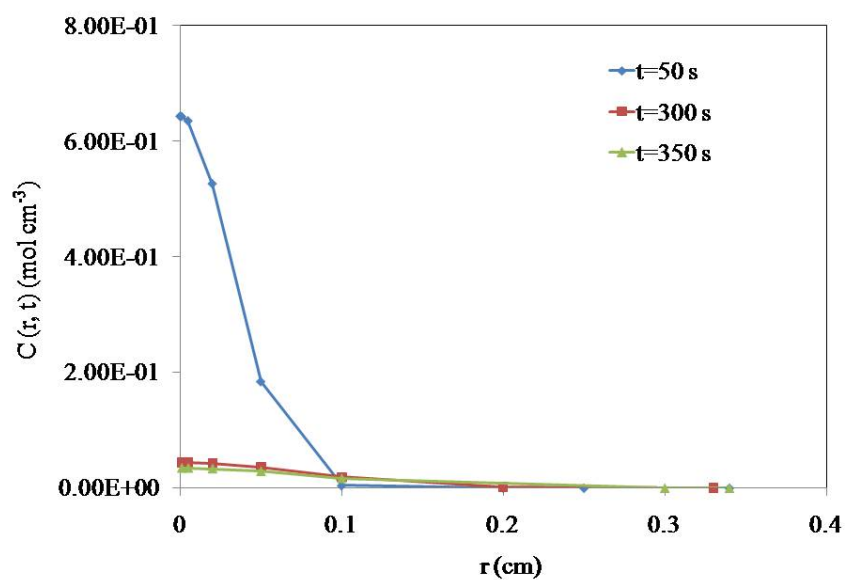


Figure A.2 Formaldehyde distribution in liquid body after 50 s, 300 s or 350 s of diffusion

Appendix B Data

B.1 Chapter 6 data

Table B.1: Data for Graph 6.1. Effect of stirring rate on total # and deposit volume of silver nanoparticles per sphere and size distribution of NPs.

Stirring rate (rpm)	# of Ag NPs	Deposit V ($\times 10^{-3} \mu\text{m}^{-3}$)	# of Ag nanoparticles of certain size (/sphere)			
			< 100 nm	100-150 nm	150-200 nm	>200 nm
0	29 $\pm$ 3	28.4	8.6 $\pm$ 4.6	17.3 $\pm$ 5.3	3.1 $\pm$ 3	0
90	62.7 $\pm$ 6.7	45.7	26.1 $\pm$ 8.9	35.1 $\pm$ 10	1.4 $\pm$ 0.8	0
180	54.7 $\pm$ 8.2	29.3	36 $\pm$ 7.5	17.6 $\pm$ 4.7	1 $\pm$ 1.2	0.14
270	72.9 $\pm$ 3.1	50.2	36 $\pm$ 7	34.4 $\pm$ 6.3	2.3 $\pm$ 1.7	0.14

Table B.2: Data for Graph 6.1. Effect of exposure time on total # and deposit volume of silver nanoparticles per sphere and size distribution of NPs.

Exposure time (min)	# of Ag NPs	Deposit V ($\times 10^{-3} \mu\text{m}^{-3}$)	# of Ag nanoparticles of certain size (/sphere)			
			< 100 nm	100-150 nm	150-200 nm	>200 nm
5	1.2	0.49	0.78	0.33	0	0.11
10	37.8 $\pm$ 7	16.9	9.3 $\pm$ 8	27.3 $\pm$ 5.9	1.2 $\pm$ 1	0.17 $\pm$ 0.39
20	49.3 $\pm$ 9.9	24.5	6.9 $\pm$ 2.2	38.6 $\pm$ 7.8	3.2 $\pm$ 1.8	0.58 $\pm$ 0.9
30	45.5 $\pm$ 8.6	24.0	7.3 $\pm$ 2.6	31.8 $\pm$ 6.9	5.3 $\pm$ 2.1	1.1 $\pm$ 0.9

Table B.3: Data for Graph 6.3. Effect of silver precursor concentration on total # and deposit volume of silver nanoparticles per sphere and size distribution of NPs.

Ag(ac) concn. ($\times$)	# of Ag NPs	Deposit V ($\times 10^{-3} \mu\text{m}^{-3}$)	# of Ag nanoparticles of certain size (/sphere)			
			< 100 nm	100-150 nm	150-200 nm	>200 nm
0.5	23.7 $\pm$ 6.1	6.27	22.4 $\pm$ 6.8	1.3 $\pm$ 1.5	0	0
1	53.3 $\pm$ 6.4	14.5	50.7 $\pm$ 6	2.3 $\pm$ 1.1	0.33 $\pm$ 0.7	0
1.5	61.1 $\pm$ 3.6	22.5	51.6 $\pm$ 6.6	8.9 $\pm$ 3.9	0.71 $\pm$ 1	0
2	61.9 $\pm$ 3.4	23.7	51 $\pm$ 4.8	10.1 $\pm$ 2.5	0.75 $\pm$ 0.5	0

Table B.4: Data for Graph 6.4. Effect of ammonia concentration on total # and deposit volume of silver nanoparticles per sphere and size distribution of NPs.

Ammonia concn. ($\times$)	# of Ag NPs	Deposit V ($\times 10^{-3} \mu\text{m}^{-3}$)	# of Ag nanoparticles of certain size (/sphere)			
			< 100 nm	100-150 nm	150-200 nm	>200 nm
0.5	152.7 ± 8.5	34.6	17 ± 11	130.3 ± 15.6	5.3 ± 3.2	0.14 ± 0.4
1	120.8 ± 14.6	26.7	7 ± 1.8	112 ± 15.4	1.8 ± 1	0
2	88.4 ± 32.6	20.2	5.4 ± 2.4	80.7 ± 32.1	2.3 ± 1.1	0
4	90.1 ± 15.4	19.7	5.9 ± 2.8	83 ± 15.2	1.29 ± 1	0

Table B.5: Data for Graph 6.5. Effect of formaldehyde concentration on total # and deposit volume of silver nanoparticles per sphere and size distribution of NPs.

HCHO concn. ($\times$)	# of Ag NPs	Deposit V ($\times 10^{-3} \mu\text{m}^{-3}$)	# of Ag nanoparticles of certain size (/sphere)			
			< 100 nm	100-150 nm	150-200 nm	>200 nm
0.5	18.9 ± 5	6.4	12.4 ± 4.4	4.4 ± 2.7	2 ± 1.7	0
1	17.3 ± 4.6	3.1	14.1 ± 3.9	3.1 ± 1.6	0	0
2	74 ± 6.3	15.2	57 ± 8.1	16.7 ± 6.8	0.3 ± 0.5	0
4	66.7 ± 5.5	11.8	58.6 ± 5.4	7 ± 2	0.9 ± 1.1	0.3 ± 0.5

Table B.6: Data for Graph 6.6. Effect of agent bound concentration on total # and deposit volume of silver nanoparticles per sphere and size distribution of NPs.

FD + Am concn. ($\times$)	# of Ag NPs	Deposit V ($\times 10^{-3} \mu\text{m}^{-3}$)	# of Ag nanoparticles of certain size (/sphere)			
			< 100 nm	100-150 nm	150-200 nm	>200 nm
0.5	39.9 ± 7.2	17.4	16.1 ± 3	19.9 ± 4.3	3.7 ± 2.1	0.1 ± 0.4
1	48.1 ± 5.2	14.5	29.9 ± 6.1	16.4 ± 3.8	1.6 ± 0.5	0.3 ± 0.5
2	66.9 ± 7.2	22.9	38.7 ± 8.6	24.1 ± 4.8	3 ± 1.2	1 ± 1.2
4	54.3 ± 4.7	22	27.9 ± 4.2	21.6 ± 3.9	3.3 ± 1.4	1.6 ± 0.5

B.2 Chapter 8 data

Table B.7: Data for Figure 8.3. Strain vs. electric field of 1:1 (BA:EGPEA, volume ratio) films with various TiO₂ NPs loading levels (wt%).

0% filling in 1:1 (BA:EGPEA)			5% filling in 1:1 (BA:EGPEA)		
E field (MV/m)	-Strain (%)	std.dev	E-field (MV/m)	- Strain (%)	std. dev
0	0	0	0	0	0
2.70	0.14	0.08	6.88	4.74	0.87
5.41	0.77	0.04	13.8	6.88	0.68
8.11	1.54	0.13	17.24	9.24	0.82
10.81	2.97	0.28			
13.51	4.47	0.29			

6.25% filling in 1:1 (BA:EGPEA)			10% filling in 1:1 (BA:EGPEA)		
E-Field (MV/m)	- Strain (%)	std. dev	E-field (MV/m)	-Strain (%)	std.dev
0	0	0	0	0	0
8.54	2.71	0.70	6.9	0.77	0.34
11.59	4.03	0.28	13.8	3.84	0.56
			17.24	4.92	0.27

12.5% filling in 1:1 (BA:EGPEA)		
E-field (MV/m)	-Strain (%)	std.dev
0	0	0
7.57	0.45	0.29
10.6	1.35	0.15
12.12	1.56	0.4

Table B.8: Data for Figure 8.4. Strain vs. electric field of 2:1 (BA:EGPEA, volume ratio) films with various TiO₂ NPs loading levels (wt%).

0% filling in 2:1 (BA:EGPEA)			3% filling in 2:1 (BA:EGPEA)		
E-field (MV/m)	-Strain (%)	std. dev	E-Field (MV/m)	-Strain (%)	std.dev
0	0	0	0	0	0
6.9	0.8	0.09	5.12	1.66	0.13
10.34	1.85	0.24	7.67	3.68	0.35
13.1	2.94	0.33	10.23	6.94	0.35
			12.27	10.27	0.31

5% filling in 2:1 (BA:EGPEA)			10% filling in 2:1 (BA:EGPEA)		
E-field (MV/m)	-Strain (%)	std. dev	E-Field (MV/m)	-Strain (%)	std.dev
0	0	0	0	0	0
6.88	1.91	0.48	6.88	0.79	0.18
13.8	4.28	1.07	13.8	2.53	0.12
17.24	5.70	1.42			

6% filling in 2:1 (BA:EGPEA)		
E-Field (MV/m)	-Strain (%)	std.dev
0	0	0
3.31	-0.3	0
6.61	2.2	1.95
9.92	7.08	1.17
13.22	14.9	2.26
16.53	23.3	3.18

Table B.9: Data for Figure 8.5a Strain vs. electric field of EGPEA films with or without Au-sPS spheres.

None filling but E-field treated 2			None filling but E-field treated 1		
E-field (MV/m)	-Strain (%)	std.dev	E-field (MV/m)	-Strain (%)	std.dev
0	0	0	0	0	0
6.90	0.73	0.03	6.90	0.19	0.06
13.79	3.00	0.08	10.34	0.28	0.23
17.24	3.47	0.12	13.79	0.37	0.22

3 wt% 0.47 μm Janus spheres, blend			None filling, no E-field treatment		
E-field (MV/m)	-Strain (%)	std.dev	E-field (MV/m)	-Strain (%)	std.dev
0	0	0	0	0	0
6.9	1.40	0.25	5.55	0.49	0.04
10.34	2.37	1.15	8.33	0.96	0.08
13.8	2.78	0.73	11.11	1.76	0.12
17.24	2.80	0.31			

Table B.10 Figure 8.5b Strain vs. electric field of EGPEA films with electric field aligned Au-sPS spheres.

2 nd meas., 3 wt% aligned 0.47 μm Janus spheres			1 st meas., 3 wt% aligned 0.47 μm Janus spheres		
E-field (MV/m)	-Strain (%)	std.dev	E-field (MV/m)	-Strain (%)	Std.dev
0	0	0	0	0	0
5.73	3.96	3.35	3.82	1.02	0.19
9.54	54.25	8.96	5.73	7.76	0
11.45	53.78	20.31	7.63	14.64	5.34
15.27	80.31	9.77	9.54	22.47	0
None filling plain polymer			11.45	28.27	4.25
E-field (MV/m)	-Strain (%)	std.dev	13.36	22.18	0
0	0	0	15.27	24.00	0.89
5.55	0.49	0.045			
8.33	0.96	0.08			
11.11	1.76	0.12			

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