NEW APPROACHES TO SYNTHESIS AND ASSEMBLY OF NANOSTRUCTURED MATERIALS

by

Nathanael R. Sieb
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APPROVAL

Name: Nathanael Sieb
Degree: Master of Science
Title of Thesis: New Approaches to Synthesis and Assembly of Nanostructured Materials

Examining Committee:
   Chair: Paul C. H. Li
       Associate Professor

Byron D. Gates
   Senior Supervisor
   Assistant Professor

Gary W. Leach
   Supervisor
   Associate Professor

Michael H. Eikerling
   Supervisor
   Assistant Professor

Bonnie L. Gray
   Internal Examiner
   Assistant Professor

Date Defended/Approved: ________________________________
ABSTRACT

New techniques have been developed to synthesize and assemble nanostructured materials. Many solution-based approaches to synthesizing porous nanostructures exhibit limited control over the dimensions and properties of the final product. Instead of solution-based methods, electrochemical synthetic techniques are used to fabricate hollow nanorods with tunable diameters, lengths, porosities, and morphologies. In addition, it is a challenge to assemble insoluble materials, such as porous nanorods, into well-defined patterns on a surface using many well-established methods. A new technique is developed to circumvent many of the limitations of other patterning techniques and create patterns from materials with a wide range of physical and chemical characteristics. This patterning technique is demonstrated by selectively transferring polymeric and metallic nanoparticles from a liquid interface into a variety of continuous patterns covering large areas (>1 mm$^2$). This work has many potential applications, including the design of drug delivery vehicles and biosensors.

Keywords: Directed self-assembly; Liquid interface; Poly(dimethyl siloxane); Porous nanorods; Electrodeposition; Galvanic replacement

Subject Terms: Nanostructured Materials; Nanotechnology; Self-assembly; Electrochemistry
To my family for their unconditional support
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# GLOSSARY

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<th>Abbreviation</th>
<th>Description</th>
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<tr>
<td>EDS</td>
<td>Energy Dispersion X-ray Spectroscopy</td>
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<tr>
<td>FAS</td>
<td>Fluoroalkylsilane</td>
</tr>
<tr>
<td>OM</td>
<td>Optical Microscopy</td>
</tr>
<tr>
<td>PC</td>
<td>Polycarbonate</td>
</tr>
<tr>
<td>PDMS</td>
<td>Poly(dimethyl siloxane)</td>
</tr>
<tr>
<td>PFMD</td>
<td>Perfluoro(methyldecalin)</td>
</tr>
<tr>
<td>PS</td>
<td>Polystyrene</td>
</tr>
<tr>
<td>PVP</td>
<td>Polyvinylpyrrolidone</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning Electron Microscopy</td>
</tr>
<tr>
<td>SPR</td>
<td>Surface Plasmon Resonance</td>
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<tr>
<td>TASA</td>
<td>Template-Assisted Self-Assembly</td>
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<tr>
<td>TEAH</td>
<td>Tetraethylammonium hydroxide</td>
</tr>
<tr>
<td>TEM</td>
<td>Transmission Electron Microscopy</td>
</tr>
<tr>
<td>$T_g$</td>
<td>Glass Transition Temperature</td>
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<tr>
<td>$\mu$CP</td>
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CHAPTER 1: INTRODUCTION TO THE SYNTHESIS AND ASSEMBLY OF NANOSTRUCTURED MATERIALS

1.1 Goals of this Thesis

The goal of this thesis is to present new techniques to synthesize and manipulate well-defined nanostructured materials. With many current approaches to synthesizing these materials, it is difficult to control simultaneously various aspects of the final structures being produced. One of the goals of this work is to develop an engineered approach to fabricating anisotropic nanostructures with tunable characteristics, including length, diameter, pore size, and composition. These engineered nanostructures have a number of potential biomedical applications, such as delivering biologically active reagents to cells.\textsuperscript{[1,2]} In addition, some nanostructures produce heat when irradiated with light and this thermal response could be employed to destroy cancerous cells.\textsuperscript{[3]} There are many more potential applications for nanostructured materials, including sensors, electrodes, and photonic materials.

While engineered nanostructures have a number of unique applications, it is often difficult to incorporate nanostructures synthesized in the laboratory into functional devices. A major challenge is accurately controlling the position of nanostructured materials relative to each other on a substrate. In addition, many nanostructures often precipitate out of solution because the surface is incompatible with the solvent. Even when these nanostructures are soluble in
the solvent, they commonly settle out of solution due to the difference in density between the solvent and the nanostructure (e.g., \(d_{\text{H}_2\text{O}} = 1.0 \text{ g/cm}^3\), \(d_{\text{Au}} = 19.3 \text{ g/cm}^3\), \(d_{\text{Ag}} = 10.5 \text{ g/cm}^3\)). Nanostructures that precipitate or settle out of solution are difficult to assemble into patterns due to uncontrolled motion of the particles during these processes. Assemblies of colloidal particles can be created through evaporation of the solvent, but there are limitations to this approach.\(^4\) The evaporation rate is dependent on the solvent and increasing the temperature to evaporate a low boiling-point solvent (e.g., water) produces greater particle motion, resulting in a greater degree of disorder. If a universal patterning technique was developed to overcome many of these challenges, it could be used to create a wide range of patterns from a variety of micro- and nanoscale materials.

Another goal of this thesis is, therefore, to address the challenges of assembling insoluble nanostructured materials into well-defined patterns. A new technique is developed to assemble insoluble materials into patterns using a liquid–liquid interface. A universal technique to fabricate patterns of insoluble nanostructures on a surface has a number of applications. For example, this technique could be used to create photoresponsive switches and photonic waveguides. The technique could also be used to fabricate electrical connections on a flexible substrate. Many of these applications are beyond the scope of this thesis, but will be explored further in the future. The main purpose of this work is to introduce this original patterning procedure and discuss its strengths and limitations relative to previously developed techniques. The
techniques discussed in this thesis to engineer and assemble nanostructured materials have a number of advantages over other techniques. There are also a number of applications to be pursued in future projects that take advantage of these unique approaches.

1.2 Challenges to Synthesizing and Assembling Nanostructured Materials

In the continual search for smaller structures with advantageous properties, anisotropic nanostructures such as nanotubes and nanorods have been investigated due to their unique optical and physical properties. These structures can be used to transport heat and electricity, or as piezoelectric and optical switching devices.\textsuperscript{[5,6]} Many of the current techniques utilized to synthesize anisotropic nanostructures have limited control over the structural characteristics of the final structure. It is also difficult to assemble insoluble structures into regular patterns covering large areas. The number of applications for nanostructured materials synthesized in the laboratory could be significantly expanded by designing a way to assemble them into patterns.

Solution-phase synthetic methods are commonly used to synthesize anisotropic nanostructures and have a number of advantages and limitations (Table 1.1).\textsuperscript{[7-15]} A number of different materials can be synthesized in order to achieve specific physical, optical, or electronic properties. Solution-based methods often produce nanorods and nanowires (nanowires have larger aspect ratios than nanorods) with uniform dimensions, but with limited control over
Table 1.1: A few solution-phase synthetic approaches to synthesizing anisotropic nanostructures.

<table>
<thead>
<tr>
<th>Technique</th>
<th>Examples of Materials</th>
<th>Advantages</th>
<th>Disadvantages</th>
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<tr>
<td>Surfactant-mediated growth</td>
<td>Ag_{[7,8]} Au_{[9]}</td>
<td>Tunable length and diameter; control over aspect ratio</td>
<td>Surfactants required for tunability; high polydispersity</td>
</tr>
<tr>
<td>Self-seeded growth</td>
<td>Te_{[10]}</td>
<td>Monodisperse dimensions; simple procedure</td>
<td>Limited tunability of length and diameter</td>
</tr>
<tr>
<td>Sonochemical synthesis</td>
<td>Se_{[11]}</td>
<td>Room temperature synthesis; high yield</td>
<td>Limited control over aspect ratio</td>
</tr>
<tr>
<td>Solvothermal/hydrothermal</td>
<td>PbS, Cu_{2}S, MnO_{2}<em>{[13]} ZnO</em>{[14]} ZnS_{[15]}</td>
<td>Nanostructures with binary compositions</td>
<td>Limited control over diameter; high temperature</td>
</tr>
</tbody>
</table>

lengths and diameters. In the surfactant-mediated growth process, nanowires are grown from a colloidal solution of nanoparticle seeds.\(^{[7,9]}\) A solution containing a metal salt and a reducing agent is added to the seed solution and the metal is subsequently reduced onto the surface of the seeds. A surfactant is added to the solution that preferentially binds to one crystal facet of the seed, restricting growth in one direction, resulting in anisotropic growth. This procedure is used to synthesize silver nanowires with diameters from 30-450 nm and lengths up to 50 \(\mu\)m.\(^{[7,8]}\) It is, however, a challenge to simultaneously control both the length and diameter of the nanowires. Gold nanorods are also synthesized by the surfactant-mediated growth method.\(^{[9]}\) The aspect ratio of
these gold nanorods can be tuned from ~5-200 by varying the pH of the solution or the ratio of reactants in the solution. There is, however, a corresponding decrease in the yield and monodispersity of the nanorods as the aspect ratio is increased due to the pH sensitivity of the surfactant. Also, the surfactants used in this procedure may restrict the solubility of the nanorods in various solvents such as water. It is not a trivial matter to design a surfactant that preferentially binds to a certain crystal facet and is also soluble in an appropriate solvent. The surfactant-mediated growth process is used to synthesize metallic nanowires in solution, but requires the use of molecules that may adversely affect the desired properties of the synthesized nanowires.

Another method of growing anisotropic nanostructures is the self-seeded process. In this technique, the anisotropic growth is directed by the crystal structure of the material being reduced. For example, tellurium nanorods can be synthesized by reduction of a tellurium salt at an elevated temperature. Tellurium is reduced preferentially on one crystal face resulting in anisotropic growth. Unfortunately, in order to tune the average diameter from ~50-200 nm, the solvent has to be changed. Also, the diameter is non-uniform, varying by up to a factor of 5 from the tip to the middle of the nanowire. In addition, the growth rate is relatively low, requiring several hours to grow nanowires a few micrometers in length. The elevated temperature required (>100 °C) can be a further disadvantage with this technique. The temperature requirement is overcome through the development of a sonochemical approach to synthesize selenium nanowires. The sonication process provides the energy necessary
to begin the growth of selenium nanowires from selenium colloids without increasing the temperature of the bulk solution. There is, however, no straightforward technique to control the aspect ratio of these nanowires grown by a self-seeded technique.

A hydro- or solvothermal approach can also be used to synthesize nanowires in solution. In this technique, metal precursors are dissolved in an appropriate solvent (water for hydrothermal processes) and this solution is heated in an autoclave to a relatively high temperature in order to carry out the crystal growth process. The solvent and possibly other agents help to regulate the crystalline growth of the nanowires. These thermal approaches are often used to fabricate semiconductor or oxide nanowires such as MnO$_2$, Cu$_2$S, ZnO, and ZnS. In the solvo- and hydrothermal techniques, the diameter of the nanowires is tuned by changing the solvent conditions or growth-regulating agents. These changes require redesign of the system and are highly dependent on the composition and surface chemistry of the nanowire.

All of the previously discussed solution-based techniques are usually used to synthesize nanowires and nanorods with sub-100 nm diameters. It is often difficult to tune the diameter and length over a wide range of values (e.g., from nano- to micronscale diameters) using a solution-based synthetic method. In addition, since most of these techniques take advantage of a preferential growth direction rather than mechanical confinement, the monodispersity and dimensional control is limited. It is, therefore, desirable to develop a technique
that provides the ability to precisely engineer the dimensions of anisotropic nanostructures.

The surface chemistry of nanostructures often must be modified to uniformly disperse these structures in different solvents. For example, one reason why gold nanoparticles have so many applications is that the gold surface can be easily modified to change the properties of the nanoparticles.\textsuperscript{[16,17]} Either hydrophilic or hydrophobic ligands can be attached to the surface of gold nanostructures to change their solubility.\textsuperscript{[18,19]} These modifications are commonly performed by ligand exchange, ligand modification, or by the addition of a surfactant or phase transfer agent. The surface can be labelled with a fluorescent molecule\textsuperscript{[20]} or modified to increase the ionic conductivity of the nanoparticles\textsuperscript{[21]}. It is important to realize that these modifications may result in unintended changes to the solubility of the nanoparticles. Also, the surface may be non-uniformly modified by ligands that preferentially bind to specific crystal facets due to a low binding strength with other facets.\textsuperscript{[22]} In order to eliminate the potential complications of surface chemistry modifications and to work with a wider variety of materials, it is important to be able to incorporate nanostructures into devices regardless of their solubility.

One potential advantage of working with insoluble materials is that they will precipitate out of solution to a liquid interface (could be liquid–solid, liquid–air, or liquid–liquid). The nanostructures precipitate due to an incompatible solvent environment (e.g., hydrophobic particles suspended in water). Even soluble nanostructures may settle out of solution due to their high atomic density or
instability of the capping group in the solvent of choice, but these structures will also collect at a liquid interface. Currently it is difficult to assemble these non-colloidal materials into well-defined structures due to the degree of random motion during the precipitation process and a lack of control over the particle-particle interactions.

It is necessary to develop techniques to efficiently assemble nanostructures in order to increase the use of these nanostructured materials in devices. While some techniques have been developed to assemble arrays of nanostructures, they often require that the materials be suspended in solution.\textsuperscript{[23,24]} When the nanostructures are suspended in solution, they can be uniformly dispersed across a surface. As discussed previously it is, however, often impractical to suitably modify the nanostructures to adequately disperse them in solution. If the structures are insoluble then they will settle or precipitate out of solution, often aggregating into large, disordered structures. This aggregation results in a significant barrier to patterning arrays of individual nanostructures. In addition, the precipitated particles may collect on a solid surface and irreversibly bind to this substrate. It is, however, possible to collect many insoluble particles at a liquid–liquid interface.

The assembly of particles at liquid–liquid and liquid–air interfaces has previously been examined by a number of research groups.\textsuperscript{[25–28]} Often the focus of this research is to design new materials or to investigate the particle interactions at liquid interfaces. The observation of the behaviour of particles at these interfaces produces valuable information about colloidal self-assembly and
the forces acting on particles at liquid interfaces. This information can lead to a greater understanding of the formation of new materials such as photonic crystals.\textsuperscript{[25]} It has been observed that many nanostructured materials will self-assemble at a liquid–liquid interface into a thin film of close-packed particles.\textsuperscript{[26]} Liquid–liquid interfaces can also be manipulated to form shapes varying from spherical droplets to toroidal, donut-like structures.\textsuperscript{[27]} Currently, there are no techniques that use liquid–liquid interfaces to collect insoluble particles prior to fabricating patterns of them on a solid support. The challenges outlined in this section are just a few of the issues to consider when developing new approaches to synthesize and direct the assembly of nanostructured materials.

1.3 Overview of Thesis

A new procedure is established to engineer porous hollow nanorods with significant control over the dimensions and morphology of the final nanostructure. This procedure will address the challenge of creating tunable anisotropic nanostructures. Initially, solid nanorods are synthesized by electrodepositing silver into a well-defined porous mold. These metal nanorods are used as a sacrificial template to establish the dimensions of the final porous gold structure. The morphology of the porous nanorods is controlled through a galvanic replacement reaction and selective etching. This synthetic technique is used to engineer nanorods with selectable lengths, diameters, porosities, and compositions. In this thesis, the capabilities and limitations of this procedure are examined and potential applications are discussed.
Second, a new technique is introduced to direct the assembly of nanostructured materials that are insoluble, such as porous hollow nanorods. In this technique, insoluble polystyrene particles and gold nanoparticles are transferred from liquid interfaces onto a solid support. Polystyrene (PS) particles are initially used because they are easily obtained with a variety of diameters and they are often used in the field of colloidal chemistry. These particles also have a low glass transition temperature (T_g), which provides a simple route to physically adhere them to a surface through heating. Gold nanoparticles are utilized to determine that this technique can be used to create patterns of nanoparticles containing submicron feature sizes. The synthesis of these gold nanoparticles is simple and the surface chemistry can be easily modified. In addition, the conductivity and surface modification of gold nanoparticles provides a number of potential applications. Patterns composed of a variety of shapes are fabricated on both rigid and flexible substrates with this patterning technique. The efficiency of this technique is demonstrated by creating patterns of metallic or polymeric micro- and nanoparticles in less than 20 minutes. Finally, some current limitations and future applications of this technique are discussed.

The techniques that are introduced in this thesis provide a high degree of control over the synthesis and assembly of nanostructured materials. Nanorods are engineered with highly tunable dimensions and morphologies. The patterning procedure provides a rapid method to assemble insoluble materials into nanostructured patterns. In addition, these bench-top techniques are economical and easy to use. The assembly and synthetic processes could also
be potentially scaled-up for use in an industrial setting. In summary, novel techniques have been developed that have the potential to significantly advance the ability to engineer and pattern nanostructured materials.
CHAPTER 2: SYNTHESIS OF DESIGNER POROUS HOLLOW NANORODS

Portions of this work are currently being prepared for publication.\textsuperscript{[29]}

2.1 Introduction to Engineered Nanostructures

Porous hollow nanostructures have a variety of applications in fields ranging from medical treatments to analytical chemistry. Nanoparticles have specific advantages over larger structures as drug delivery vehicles due to the efficient endocytosis of these small particles.\textsuperscript{[1]} Some research groups are employing the high surface area of porous structures to deliver a greater quantity of bioactive molecules to a desired target.\textsuperscript{[2,30]} Many nanostructures also have a characteristic range of absorption wavelengths corresponding to their surface plasmon resonance (SPR). The spectral position of their SPR wavelength is highly dependent on the dimensions and composition of the structures.\textsuperscript{[3,8]} For example, an increasing diameter will result in a red shift of the SPR adsorption peak. When the nanostructures are irradiated with light overlapping with the SPR spectral region, the electrons in the surface of the nanostructure are excited and their subsequent relaxation results in lattice vibrations. These lattice vibrations cause localized heating around the particles. This light-to-heat response is called the photothermal effect and has been used to destroy cancer cells.\textsuperscript{[3]} Porous structures can also be used as sensitive gas sensors.\textsuperscript{[31,32]} Nanostructures composed of SnO$_2$ or a Ag/Pd alloy have been used to detect
gases such as hydrogen, carbon monoxide, and ethanol vapours. The porous structures were found to exhibit a higher sensitivity compared to similar non-porous structures due to an increased surface area available for the adsorption of gases. The surface area available for reagent loading or gas sensing can be tuned by controlling the porosity of the nanostructures. Currently, many solution-based techniques for synthesizing nanostructures have limited control over lengths, diameters, and pore sizes. To address this limitation, a technique is developed to create porous nanostructures with selectable dimensions and morphologies.

Porous nanostructures are often fabricated by replacing a sacrificial template with a porous shell composed of another metal (Figure 2.1). The dimensions of the template used determine the dimensions of the final porous structure. It is, therefore, desirable to synthesize a template with tunable dimensions. It was determined that an electrodeposition technique would meet this requirement. The templates are fabricated by electrodepositing a metal into a mold containing uniform cylindrical pores. The metal inside the pores forms anisotropic structures, such as nanorods. These nanorods can be used as a sacrificial template to synthesize porous nanorods. Previously, nanorods composed of Au, Ag, and Ni, amongst others, have been synthesized by electrodepositing metal into a mold.[33-38] Electrodeposition was one of the first methods used to engineer one-dimensional nanostructures. The main requirement for this technique is a mold with uniform cylindrical pores that are permeable to a solution containing reducible metal salts. One side of the mold is
Figure 2.1: This schematic depicts the replacement of a sacrificial template with a porous shell. A porous shell is deposited on the exterior of the sacrificial template and is subsequently isolated by etching away the remaining template. The diameter of the synthesized shell is defined by the diameter of the original template.

capped with a metal film, which is also the working electrode in the electrodeposition procedure. The mold can be a nuclear track-etched polycarbonate (PC) membrane or a pseudo-hexagonally ordered porous alumina template.\[^{34,35}\] These molds are manufactured with a number of different pore sizes and a narrow pore size distribution. Track-etched PC membranes are made by exposing a thin PC film to collimated, charged particles.\[^{39}\] These charged particles leave tracks of depolymerised material that are subsequently etched away. Different pore sizes are achieved by varying the efficiency of the etching solution or the etching time (longer etch time = larger pore size). Porous alumina membranes are fabricated by oxidizing high purity aluminum in an acidic solution.\[^{35}\] The pore size is controlled by varying the oxidation parameters, such as the applied potential, time, and temperature. The pore size of the mold is important because it determines the diameter of the engineered nanorods. The length of the nanorods is determined by the deposition time. These tunable templates are subsequently used to define the length and diameter of the porous hollow nanorods.
There are two major approaches to creating porous nanostructures. One technique established is to use a selective etching process. In this method, a metal alloy is deposited into cylindrical pores and then one metal is selectively etched out of the nanorod. While the length and diameter are tunable, this technique has two significant limitations. One is that some selective etching processes require the use of a strong acid, such as nitric acid, as an etchant. Second, this technique can be used to create structures with pores throughout the entire nanorod, but not hollow structures with porous exteriors. A hollow structure has unique advantages such as the ability to encapsulate materials and has tunable optical properties.

Another approach to synthesize porous nanostructures is through a galvanic replacement reaction. This method can produce nanostructures that are hollow, as well as porous. Galvanic replacement has been previously used to synthesize porous cubes, particles, and rods. A metal with a high electrochemical reduction potential is used to galvanically replace a metal with a lower reduction potential. In most prior work, a silver template is replaced with a porous gold shell. Galvanic replacement reactions have, however, also been performed with other materials such as replacing silver nanowires with a silver/palladium alloyed shell. The silver templates used in the replacement reaction are often synthesized by the polyol process, which is a surfactant-mediated growth process introduced in section 1.2. With the polyol process, it is difficult to precisely control the dimensions of the silver templates. In the technique introduced in this chapter, rather than solution-synthesized nanowires,
electrodeposited nanorods are used as sacrificial templates to create porous nanostructures. These metal nanorods are synthesized by electrodeposition with a wider range of diameters and with finer control over the length and diameter than with the polyol process. After the galvanic replacement reaction, any remaining unreacted template is selectively etched out of the porous shell (Figure 2.1). The porosity and composition of the structure can be tuned by varying the conditions of the galvanic replacement reaction. This synthetic technique, therefore, exhibits a previously undemonstrated level of control over the dimensions, porosity, and composition of porous nanostructures.

2.2 Template-Based Synthesis of Silver Nanorods

Silver nanorods are used as sacrificial templates to create porous nanostructures. Since the dimensions of the template define the dimensions of the final structure, a technique was needed to synthesize templates with tunable dimensions. In addition, in order to produce nanostructures with well-defined optical properties, highly monodisperse templates are required. It was determined that an electrodeposition technique met these requirements and could be used to engineer nanostructures with well-defined lengths and diameters. These engineered nanostructures could subsequently be used to create porous nanostructures with well-defined structural parameters.

Silver nanorods with tunable dimensions are synthesized by electrochemically depositing silver into a mold. Silver was chosen because of its
electrochemical and crystallographic properties. The reduction potential of \( \text{Ag}^+/\text{Ag} \) vs. a saturated \( \text{Ag}/\text{AgCl} \) reference electrode is 0.60 V, which is less than the reduction potential of \( \text{AuCl}_4^-/\text{Au} \) (0.79 V). The higher reduction potential of gold results in a favourable galvanic replacement reaction, with gold being reduced and silver being oxidized. Also, the crystal structure of Ag and Au are very similar.\(^{[44,45]}\) Both metals have face-centered cubic crystal structures; gold has a unit-cell length of 4.08 Å while silver has a unit-cell length of 4.09 Å. The similar crystal structures permit the epitaxial deposition of gold onto the silver template. The galvanic replacement reaction is described in more detail in the next section.

Both porous alumina and track-etched PC membranes can be used to define the diameter of the nanorods during electrochemical deposition. Polycarbonate membranes are selected because they are commercially available with a variety of uniform pore diameters from 10 nm-30 \( \mu \text{m} \) (Figure 2.2a).\(^{[46]}\) The membranes also have well-characterized pore densities that aid in estimating the number of nanorods synthesized (Table 2.1). Additionally, the PC mold can be dissolved in common organic solvents such as chloroform. Aluminum is thermally evaporated (200-nm thick) on one side of the mold to cap one end of the pores and provide an electrical contact at the base of the pores. The open channels are filled with an electroplating solution containing AgCN. A negative potential is applied to the aluminum film to attract the positive silver cations and reduce them inside the pores. The mold constrains the diameters of the silver nanorods as they grow within the mold (Figure 2.2b). The nanorods are isolated
by removing the Al with KOH and dissolving the PC mold in chloroform (Figure 2.2c). These nanorods are determined to be polycrystalline by examining the transmission electron microscopy (TEM) image in the inset of Figure 2.2c. The different dark and bright regions of the image indicate the crystal grain

**SEM**

![SEM images](image1)

**Schematic**

![Schematic](image2)

**Figure 2.2:** (a) A polycarbonate (PC) track-etched mold containing vertical 100-nm diameter pores is used to define the diameter of the synthesized nanorods. (b) Silver is reduced into the pores of this mold and (c) the resulting nanorods are isolated by dissolving the PC mold in chloroform (the length ($L$) and diameter ($\Phi$) of these nanorods are 1 $\mu$m and 150 nm, respectively). The inset of (c) contains a magnified image of the nanorods that shows the polycrystalline grain boundaries. These images are acquired by scanning electron microscopy (SEM) and a schematic illustration is shown below each step.

**Table 2.1:** Reported data for Sterlitech polycarbonate track-etched membranes.

<table>
<thead>
<tr>
<th>Pore Size (nm)</th>
<th>Pore Density (pores/cm²)</th>
<th>Total Area of Membrane (cm²)</th>
<th>Estimated Number of Pores Per Membrane</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>$6 \times 10^8$</td>
<td>4.91</td>
<td>$2.95 \times 10^9$</td>
</tr>
<tr>
<td>50</td>
<td>$6 \times 10^8$</td>
<td>4.91</td>
<td>$2.95 \times 10^9$</td>
</tr>
<tr>
<td>100</td>
<td>$4 \times 10^8$</td>
<td>4.91</td>
<td>$1.96 \times 10^9$</td>
</tr>
</tbody>
</table>
boundaries of the silver nanorods. Using this electrodeposition technique, the length and the diameter of the synthesized nanorods can be controlled.

A number of modifications are made to the experimental procedure in order to increase the number of pores of the mold that are filled with silver and, therefore, the quantity of nanorods synthesized. The percentage of pores filled with silver is determined by examining the bottom surface of the PC molds after removing the aluminum film. With scanning electron microscopy (SEM), the filled pores appear as bright spots while the empty pores are dark spots (Figure 2.2b inset). Initially, the physical contact between the aluminum backing and the surface of the cathode (see Figure A.1) is increased by evaporating an alcohol solution between the two surfaces. The capillary action draws the two surfaces into close contact, completing the electrical connection. There is, however, a thin film of silver observed between the aluminum film and the PC mold (Figure 2.3a). Moreover, a low percentage of the pores are filled with silver. The thin film of silver forms due to the alcohol solution delaminating the aluminum layer from the surface of the mold. This silver film could cause significant aggregation of the nanorods if the film holds the rods together when they are extracted from the mold. These problems are addressed by using a saturated NaCl solution instead of an alcohol to increase the electrical contact between the aluminum film and the electrode. The aqueous solution does not cause the aluminum film to detach from the surface of the mold. While a film of silver is not observed under the PC mold, only ~30% of the pores are filled with silver (Figure 2.3b). This low percentage of filled pores is suspected to be due to an inability for the aqueous
electroplating solution to penetrate into the pores of the mold. If the mold is too hydrophobic, then an aqueous solution will not be able to fill many of the pores in the mold. Therefore, the mold is exposed to an air-based plasma to increase its hydrophilicity and enhance the ability of the electroplating solution to fill the pores (Figure 2.3c). After the plasma treatment, the percentage of pores filled with silver nanorods increases from ~30% to ~75%. After silver is reduced into the pores of a plasma-treated membrane with 100-nm diameter pores, the mold is dissolved in 5 mL of chloroform resulting in a solution with ~2.94x10$^8$ nanorods/mL (using the estimated pore density reported in Table 2.1). These experimental modifications of the electrodeposition procedure more than double the yield of nanorods produced.

**Figure 2.3:** (a) A large thin film of silver is observed by SEM on the bottom of an unmodified PC mold after deposition of silver using the original procedure. (b) When a salt solution is used to increase the electrical contact between the mold and the electrode a film of silver is not observed, but only ~30% of the pores are filled with silver. (c) After plasma treating the mold, the silver solution fills ~75% of the pores and results in a higher yield of nanorods.

A commercially available silver electroplating solution containing AgCN is used to electrodeposit silver inside the pores of the PC mold.$^{[48]}$ The optimal deposition conditions are determined by examining the effect of applying different potentials for different lengths of time. Both the current and the reduction
potential relative to a Ag/AgCl reference electrode are measured for 120 s at different applied potentials (Figure 2.4). The current flow is a measure of how quickly the silver ions are reduced and the voltage is measured to determine if the desired voltage is achieved. When a reduction potential of 1.00 V is applied there is no appreciable current flow, indicating that the potential was insufficient to reduce Ag$^+$ (Figure 2.4b). A potential difference of 1.50 V produced a current of ~20 mA while a potential difference of 1.75 V to 3.00 V produced a current of 30 to 35 mA. These results imply that a threshold reduction potential of approximately 1.50 V is required to achieve appreciable deposition. In the first 5 s, the increase in the current flow from ~5 to 30 mA is caused by an increase in the number of nucleation sites inside the pores.$^{[35]}$ After ~10 s, the nanorods are growing uniformly inside the pores and the current plateaus to a relatively constant value. The current plateaus because ions are being reduced at the surface faster than fresh Ag$^+$ ions reach the surface, implying that the electrodeposition of silver inside the pores is a diffusion limited process. It may be possible to increase diffusion of ions to the cathode by increasing the nitrogen flow rate in the silver solution above the PC mold or by increasing the temperature. Another interesting feature of these plots is that the recorded voltage is often smaller than the applied voltage and that this voltage decreases with time (Figure 2.4b). One possible reason for this decrease in voltage is that at high reduction potentials, the ions are quickly reduced. As the resistance decreases due to the deposition of highly conductive silver, and the current stays relatively constant, the voltage will decrease (V = IR). These electrical
characterizations indicate that this electrodeposition process is diffusion limited and that a minimum reduction potential of 1.50 V is required for metal deposition inside the pores.

Figure 2.4: (a) The electrodeposition current is measured for a series of different applied voltages. The current is negligible for 1.0 V and reached a stable value of ~32 mA for voltages greater than 1.75 V. (b) The recorded voltage is plotted for different applied voltage. The recorded voltage decreases with time as silver is deposited into the mold.
The influence of different applied potentials and lengths of deposition time on the nanorod growth is determined by examining the top surface of the PC molds after electrodeposition. Since these molds are only 6-µm deep, after the pores are completely filled, mounds of excess silver form on the top surface of the mold (Figure 2.5). It is observed that when potential differences >2.00 V are applied, the silver is reduced too quickly and results in overdeposition of silver (Figure 2.5a). This overdeposition is likely due to the initial high voltage rapidly filling the pores before the recorded voltage drops. The voltage decrease indicates that silver is being reduced on the top surface of the mold, rather than inside the pores. In addition, if the deposition continues for a longer time (e.g., 60 s at 1.75 V) then the pores are completely filled and excess silver is deposited on the top surface of the mold (Figure 2.5b). A voltage of 1.75 V for 30 s appears to give consistent results with no overgrowth of silver (Figure 2.5c). Through these studies, it is determined a potential difference of 1.75 V will electrodeposit silver into the pores of the mold with a slow enough deposition.

Figure 2.5: At high potential differences (a: 2.0 V, 30 s) or long electrodeposition times (b: 1.75 V, 60 s) significant overgrowth of silver is observed by SEM on the top surface of the PC molds. (c) When a voltage of 1.75 V is applied for 30 s, the top surface of the mold contains no overgrowth of silver.
rate to control the lengths of the nanorods fabricated while preventing overdeposition of silver.

The dimensions of the isolated silver nanorods are tuned by varying both the deposition time and the diameter of the pores in the mold. The nanorods in Figure 2.6 are synthesized after applying a voltage of 1.75 V for periods from 10 to 60 s. After analyzing these results by SEM, the growth rate is calculated to

Figure 2.6: Silver nanorods of different lengths (L) are grown in a PC mold containing 100-nm diameter pores. The deposition time is changed from (a) 10 s, to (b) 30 s, to (c) 50 s. (d) As a potential difference of 1.75 V is applied, the growth rate exponentially decays from ~180 to ~20 nm/s over a period of 60 s. The diameter of these nanorods is ~160 nm.
decay exponentially with time from ~180 nm/s after 10 s to ~20 nm/s after 60 s. The apparent decrease in growth rate can be attributed to the presence of very short nanorods observed in Figures 2.6b and c. One possible reason for the presence of shorter nanorods is that the initial nanostructures have broken during the purification process due to repeated centrifugation and/or vortexing steps. Longer nanorods will be more susceptible to breaking since shorter rods have a greater rigidity. In addition, as the nanorods reach the maximum length of 6 µm, mounds of silver will grow on the top surface of the mold. When the nanorods are isolated, the top of the nanorods often remains attached to this mound while the remaining nanorod breaks off (Figure 2.6c inset). If the initial growth rate were constant, then the 6-µm deep pores would be filled in ~30 s. The decrease in apparent growth rate of the nanorods at times >20 s is an indication that longer nanorods are more fragile than shorter nanorods. Moreover, the greater polydispersity in the length of the longer nanorods is seen in the increasing error bars in Figure 2.6d. The length of the nanorods increases with time, but an increased number of broken nanorods will result in a lower overall calculated growth rate.

The diameter of the nanorods is tuned by depositing silver nanorods in pores with different diameters. The PC molds contain pore diameters of 10, 50, and 100 nm (Figures 2.7a-c). It is, however, significant that the diameters of the isolated nanorods are 50-60 nm larger than the reported pore diameter of the mold. The larger than expected diameters are likely due to cigar-shaped pores with larger diameters in the interior of the mold than at the surface of the mold.
Figure 2.7: Silver nanorods with diameters ($\Phi$) of (a) 57 nm, (b) 105 nm, and (c) 164 nm are grown in PC molds with reported pore diameters of 10 nm, 50 nm, and 100 nm, respectively. The diameter of the nanorod indicated in (d) increases from 110 nm at the bottom of the nanorod to 160 nm at the top. The arrow in (a) points to the fracture point of a nanorod that is almost broken.

This observation is consistent with previous literature on electrochemical deposition. In Figure 2.7d, the diameter of the indicated nanorod increases from 110 nm at the end nearest to the pore opening to 160 nm at the end closer to the interior of the mold. In addition, the nanorod fragility discussed earlier is seen in Figure 2.7a. The sharp kink of a nanorod that has almost broken is indicated by the arrow. Nanorods with smaller diameters, such as the 57 nm diameter nanorods in Figure 2.7a, are more likely to break than nanorods with
larger diameters. Using this electrodeposition technique, nanorods are reproducibly fabricated with diameters from 55 to 165 nm and lengths from 1.7 to 3.4 µm.

### 2.3 Porous Hollow Nanostructures

Porous nanostructures are synthesized by replacing the sacrificial templates of silver, synthesized in section 2.2, with porous gold shells. A galvanic replacement reaction is used to convert the silver templates into porous gold nanostructures.\(^{[3,42,43]}\) After adding a gold salt, chloroauric acid, the silver template is oxidized and a gold/silver alloyed shell is grown around the former template (Figure 2.8). As the gold salt is added, gold ions are reduced on the surface of the nanorod according to reaction 2.1. This reaction occurs spontaneously due to its positive standard redox potential of 0.19 V (Equation 2.1). The porosity and morphology of the final structure is dependent on the amount of gold ions that react with the silver template. After the galvanic replacement reaction, the remaining silver template is etched away with ammonium hydroxide, according to reactions 2.2 and 2.3.\(^{[43]}\) The products on the right side of reaction 2.3 are soluble in water, allowing for easy purification of

\[
\text{NH}_4^+ + \text{OH}^- \rightarrow \text{NH}_3 + \text{H}_2\text{O}
\]

\[
4\text{Ag} \text{ (s)} + 8\text{NH}_3 \text{ (aq)} + \text{O}_2 \text{ (g)} + 2\text{H}_2\text{O} \text{ (l)} \rightarrow 4[\text{Ag(NH}_3)_2]^+ \text{ (aq)} + 4\text{OH}^- \text{ (aq)}
\]
the porous nanostructures. The mechanism illustrated in Figure 2.8 is confirmed in the following paragraphs through a combination of SEM imaging and energy dispersion X-ray spectroscopy (EDS). The galvanic replacement of a tunable silver template with a porous gold shell is a straightforward approach to creating tunable porous hollow nanostructures.

**Figure 2.8:** A galvanic replacement reaction is used to create a porous nanostructure from a silver template. The porosity and morphology of the final structure is determined by how much $\text{Au}^{3+}$ reacts with the $\text{Ag}$ template. As subsequent amounts of $\text{Au}^{3+}$ are added, the resulting structure contains a higher fraction of gold. Ammonium hydroxide is used to remove any remaining silver template.

To create porous nanostructures, the silver template is replaced with a gold shell through the addition of gold ions. The shape and dimensions of the structure formed through the galvanic replacement reaction correspond to the shape and dimensions of the initial template. Silver nanorod templates are fabricated in and isolated from PC molds as described in section 2.2 (Figure 2.9a). Subsequently, these nanorods are dispersed in an aqueous solution
containing polyvinylpyrrolidone (PVP). This molecule is used to increase the stability of the nanostructures in water and reduce aggregation of the nanorods. It has previously been determined that PVP binds to the surface of silver through the carbonyl group.\textsuperscript{[22,50,51]} This binding mechanism was confirmed by X-ray photoelectron spectroscopy\textsuperscript{[52]} (observation of a peak corresponding to the O\textsubscript{1s} of silver nanostructures) at various stages of the galvanic replacement reaction:

\textbf{Figure 2.9:} SEM imaging is used to observe the progress of the galvanic replacement reaction. The silver nanorod templates in (a) are dispersed in water with PVP. As chloroauric acid is added to the solution of nanorods, gold is deposited on the outside of the nanorods and the silver core begins to be oxidized (b, [AuCl\textsubscript{4}^-] = 0.22 mM). As the reaction proceeds, pores form in the shell as silver in the shell is also oxidized (c, [AuCl\textsubscript{4}^-] = 0.44 mM). After an excess amount of gold ions react with the silver templates, the porous nanostructures begin to fall apart (d, [AuCl\textsubscript{4}^-] = 2.99 mM).
PVP bound to silver) and by Fourier transform infrared spectroscopy\textsuperscript{[53]} (observed widening and shift of C=O wavenumber when PVP is bound to silver). In addition, the PVP molecule binds preferentially to the \{100\} facets of these nanorods. Since these nanorods are polycrystalline (see Figure 2.2c, inset), there may be less dense regions of PVP coverage on these nanorods where other crystal facets are present.

When chloroauric acid is added to the nanorod solution, a porous shell begins to grow around the silver template (Figure 2.9b). During this process, the interior is slowly oxidized and solubilised in the aqueous solution while gold ions are reduced at the surface of the nanorod. The gold ions may initially only react where there is a low density of PVP coverage, forming a porous shell around the nanorod. As the galvanic replacement reaction proceeds the entire nanorod is covered by a metal layer. After a significant amount of the silver core is etched away, pores form in the shell and these pores subsequently increase in size, indicating that material in the shell is also being removed (Figure 2.9c). This removal of silver from the shell is one piece of evidence suggesting that it initially contains an alloy of both silver and gold. Eventually, after a large excess of the gold salt is added (e.g., 2.99 mM), the porous shell begins to fall apart and large cubic structures are formed (Figure 2.9d). These cubes are analyzed by EDS and determined to be composed of silver chloride (Figure 2.10). The silver chloride precipitates can be removed in a future etching step. By controlling the amount of gold ions added during a galvanic replacement reaction, the porosity of the resulting nanostructure can be tuned.
Figure 2.10: Energy dispersion X-ray spectroscopy (EDS) and SEM imaging are used to observe the etching of silver with ammonium hydroxide. (a) The sample contains silver nanorod templates and silver chloride cubes before etching the silver with ammonium hydroxide. (b) Both the silver core and silver chloride cubes are removed after etching the nanostructures with ammonium hydroxide for 48 hrs. The corresponding EDS spectra are displayed beside the SEM images.

In order to create nanostructures with a variety of porosities and a hollow interior, the remaining partially reacted silver template must be removed. This core is removed by etching excess silver away with a weak base, NH₄OH (Figure 2.10). Within 30 minutes of immersion of the porous nanostructures in this base, the majority of the remaining silver template is removed, resulting in a hollow porous nanostructure (Figure 2.11). Between 30 min and 72 hrs, no further
changes are observed in the structural characteristics of the porous hollow nanorods. The silver is converted into water-soluble $[\text{Ag(NH}_3\text{)}_2]^+$ ions according to reactions 2.2 and 2.3. The elemental composition of the nanorods before and after adding ammonium hydroxide is monitored by EDS. Before ammonium hydroxide is added, the rods contain a solid core and the sample is contaminated with cubic silver chloride precipitates (Figure 2.10a). Through EDS analysis, the porous nanorod sample is found to contain gold, silver, and chlorine. These elements exist in the silver core, the gold-silver alloyed shell, and the silver chloride precipitates. After adding ammonium hydroxide, the core is removed and all cubic structures are etched away (Figure 2.10b). After the etching process, the sample is found to contain only gold and a small amount of silver.

Figure 2.11: The porous nanostructures in this figure are created by etching 220-nm diameter porous nanorods with ammonium hydroxide for: (a) 0 hrs, (b) 0.5 hrs, (c) 1 hrs, (d) 4 hrs, (e) 31 hrs, and (f) 72 hrs.
In addition, the presence of hollow porous nanostructures after the centrifugation and mixing processes (see Appendix A for experimental procedure) indicate that these nanostructures are mechanically robust. Despite the fact that these structures do not have a solid core, they do not fall apart in solution. The galvanic replacement reaction followed by the etching reaction provides the ability to synthesize hollow porous nanostructures.

The diameter of the porous hollow nanostructures is defined by the diameter of the silver nanorod template. Porous nanorods are synthesized using templates with diameters of ~57, 105, and 164 nm. The resulting nanostructures have outer diameters of ~80, 140, and 220 nm (Figures 2.12a-c, respectively). These diameters are 20-60 nm larger than the original nanorod template, indicating that the reaction proceeds outwards from the surface of the template. The diameter increases because the gold is deposited initially on the surface of the nanorod before an appreciable amount of the interior has been oxidized.

![Figure 2.12: Porous nanorods are created from silver nanorods with diameters of (a) 57 nm, (b) 105 nm, and (c) 164 nm. The resulting porous nanorods have diameters of 80, 140, and 220 nm, respectively. The inset of (b) is a higher magnification image of the pore sizes observed. The inset of (c) is a TEM image indicating the particle-like nature of the shell. Any excess silver template remaining in these nanostructures has already been etched away with NH₄OH.](image)
Electrodeposited templates with tunable diameters are used to define the diameters of porous nanostructures synthesized through a galvanic replacement reaction.

The amount of gold ions that react with the silver template directly affects the porosity and morphology of the final structure. If a low concentration (e.g., 0.02 mM) of gold salt is added, a highly porous structure is formed because the shell around the template is not completed (Figure 2.13a). A moderate concentration (0.14 mM) of gold salt results in a mostly complete shell containing a gold-silver alloy (Figure 2.13b). As the shell is filled in, the pore decreases from ~50 nm with a low concentration of gold ions to ~30 nm with a moderate concentration of gold ions (Figures 2.13a, b insets). A high concentration (e.g., 0.53 mM) results in a porous shell composed of mainly gold due to the galvanic replacement reaction removing much of the silver in the shell (Figure 2.13c). The pore size increases from ~30 nm to ~70 nm as silver is removed from the gold-silver alloy in the shell (Figures 2.13b, c insets). It is also noteworthy that the nanostructures with an almost complete shell have the lowest quantity of pores. The sample shown in Figure 2.13b is likely composed primarily of hollow nanotubes with closed ends. The corresponding EDS spectra show the relative amounts of gold and silver in the final structure. As the galvanic replacement reaction proceeds, more of the silver is consumed leaving a higher fraction of gold in the porous shell. Both the composition and the pore size can be tuned by controlling the concentration of gold ions reacting with the nanorod templates.
Figure 2.13: As the galvanic replacement reaction proceeds, the silver in the alloyed shell is replaced with gold. (a) When the solution contains only 0.02 mM of chlorauric acid, a small amount of gold in the nanorods is detected by EDS. (b) As the concentration of gold salt is increased to 0.14 mM, more gold is observed by EDS. (c) Finally, when the concentration is increased to 0.53 mM, the majority of the structure contains gold with only a small amount of silver. The insets show high magnification views of the pore sizes. All samples are analyzed after the silver template is removed with NH$_4$OH.

2.4 Conclusions

Nanostructures with highly selectable lengths, diameters, porosities, and morphologies are synthesized by the method described in this chapter. In this technique, silver nanorods are employed as sacrificial templates and are galvanically replaced with porous gold shells. In order to control the dimensions of these templates, the silver nanorods are synthesized by electrodeposition. The diameter of the nanorods is tuned from 57 to 164 nm by simply using different molds to constrain the lateral growth of the nanorods. The length of
these templates is tuned over several micrometers by varying the deposition time from 10 to 60 s. The tunability of these templates provides control over the dimensions of the final structure.

A galvanic replacement reaction is used to convert the silver templates with tunable dimensions into porous gold shells. The dimensions of the final structure correspond closely to the dimensions of the original silver template. By limiting the amount of gold ions reacting with the silver templates, the porosity and the ratio of gold to silver in the resulting porous shells can be controlled. Ammonium hydroxide is used to etch away excess silver in the porous nanorods to create a hollow interior. It has been demonstrated that the new procedure introduced in this chapter provides significant control over the dimensions and morphology of porous hollow metallic nanostructures.

These engineered porous nanorods have a number of potential applications. For example, the gold surface of these nanostructures can be easily modified with various functional groups.\textsuperscript{[16,17]} This surface modification could be utilized to change the solubility of the nanostructures in various solvents or even to load bioactive molecules on the surface of the porous nanorods. The high surface area of these porous structures allows one to deliver a greater quantity of a specific molecule than would be possible with a solid structure, resulting in more efficient drug delivery.\textsuperscript{[2,30]} In addition, many porous hollow nanostructures will produce heat when exposed to light in the spectral region of the SPR wavelengths. The photothermal effect of porous structures has been used previously to destroy tumour growths.\textsuperscript{[3]} Tuning the dimensions and
porosity of these hollow nanostructures will allow one to tune the spectral position of the SPR wavelengths for these nanostructures to a desired wavelength (e.g., a wavelength that is efficiently transmitted through biological tissue). This work is an important step towards designing nanostructures with the specific dimensions and morphologies required for drug release and/or photothermal treatments.
CHAPTER 3: DIRECTED ASSEMBLY OF INSOLUBLE PARTICLES

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3.1 Introduction to Patterning Nanostructured Materials

The development of efficient techniques to pattern nanostructured materials has important applications in the design and fabrication of miniaturized devices. Currently, the most commonly used microfabrication technique is photolithography. In this technique, light and a photomask are used to create patterns covering several square centimetres with sub-100 nanometer resolution (see section 3.4 for an example of microfabrication by photolithography). As of 2008, Intel Corporation is creating microprocessors with 45-nm gate widths by photolithography. Photolithography does have a couple of major limitations. One limitation of photolithography is that the minimum feature size is restricted according to Rayleigh’s equation (Equation 3.1). In this equation, $F$ is the

$$F = k_1 \cdot \frac{\lambda}{N_A}$$

Equation 3.1

minimum feature size, $k_1$ is the Rayleigh constant, $N_A$ is the numerical aperture, and $\lambda$ is the wavelength of light. The parameter $k_1$ depends on the process used (type of mask, lenses, substrate, etc.) and generally is ~0.5. The main approach to decreasing the feature size is to decrease the wavelength of light or to increase the numerical aperture. Both of these approaches have been used to
create smaller features. The second disadvantage of photolithography is, however, that both of these approaches to decreasing feature size are extremely expensive and require extensive redesign of the fabrication process. The most recent fabrication plant that Intel built to create computer processors with 45-nm feature sizes cost over $3 billion dollars. In addition, many novel nanostructures, such as those presented in chapter 2 of this thesis, are created by techniques other than photolithography. In order to incorporate these structures into devices, a technique is required to assemble them efficiently into an appropriate pattern. For example, it would be possible to make a piezoelectric generator by aligning a series of BaTiO$_3$ nanowires on a flexible substrate between metal electrodes.$^{[57]}$ Also, an ultrasensitive gas sensor could be fabricated by aligning a series of porous SnO$_2$ nanowires between electrodes.$^{[31]}$ Another potential application is to create biosensors by depositing gold nanoparticles functionalized with antibodies onto electrodes.$^{[58]}$ Current assembly techniques are often slow and inefficient, or are limited to specific experimental conditions. There is a need to develop a universal, low cost, and efficient technique to manufacture nanostructured devices.

Several techniques have been developed to pattern nanostructured materials on a solid surface (Figure 3.1). Template-assisted self-assembly (TASA) is one method developed to create nanostructured patterns of colloidal particles.$^{[23,24,59]}$ In this technique, colloidal particles are collected inside the recesses of a fabricated template through capillary forces. TASA is an efficient method to assemble particles from a colloidal solution inside a number of
Figure 3.1: In template-assisted self-assembly (TASA) a colloidal solution flows across a patterned surface. As the meniscus encounters features in the surface, capillary forces trap the particles in these recesses. In micro-contact printing (µCP) a patterned stamp is 'inked' with a colloidal solution. The particles are then transferred from the ridges of the stamp onto a substrate by pressing the stamp onto the solid surface and subsequently removing the stamp.

patterned wells. The number of particles in each well is defined by the size of the well and patterning has been demonstrated on the scale of single particles. One limiting factor with this technique is non-specific settling of the particles. In addition, the particles can only be cleaned off the top surface of the template if the capillary force is greater than the adhesion forces between the particles and the substrate. Finally, with TASA it is necessary to fabricate a new template for each new pattern. In manufacturing techniques, it is not cost-effective to manufacture new templates for each new device.
A method called micro-contact printing (µCP) was developed to create patterned nanostructures on a solid surface without extensive template fabrication.[60-63] In µCP, a patterned stamp is coated with an ‘ink’ solution containing nanoparticles. This stamp is brought into contact with a solid substrate to transfer the particles onto the substrate. One advantage of µCP is that the patterned stamp can be reused. Micro-contact printing has been used to create micron-resolution, multilayer patterns composed of gold nanoparticles. This method is, however, limited by the adhesive properties of the materials used. The nanoparticles must adhere to the stamp (the inking step), but these nanostructures must have an even stronger adhesion to the substrate (the transfer step). This limitation prevents the use of nanostructures without the required adhesive properties. In addition, this technique works best with large quantities of nanostructures and relatively large, micron-sized features. Single nanostructure patterning is difficult because there is no defect correction process in µCP to ensure that the nanostructures are in the correct positions. Patterned films containing self-assembled nanostructures will also have a high concentration of defects if there is no step allowing for correction of these defects. A major goal of the work in this thesis is to develop a general technique to pattern many different kinds of insoluble materials onto various substrates. It is also desirable for this technique to be used to fabricate patterns with nanoscale features and to accurately position single nanostructures on a solid support.
Many materials are not easily suspended in solution due to various properties of the material such as its density relative to the solvent, the surface chemistry of the material, and its aspect ratio. A simple and efficient method is needed to assemble these insoluble structures into well-defined patterns. In order to manipulate insoluble materials, an interface is required that will collect the particles, but still allow them to be highly mobile relative to one another. Solid interfaces cannot be used because insoluble structures often adhere irreversibly to solid surfaces. A liquid-liquid interface was, however, determined to provide a number of advantages over a solid interface. A number of research groups have recently examined the assembly of particles at liquid–liquid and air–liquid interfaces. Due to the high mobility of particles at these liquid interfaces, the particles can assemble into close-packed arrays. The packing of the particles at this interface can be modified by changing the surface chemistry of the particles or selecting different solvents and surfactants. For example, alkyl chains can be used to screen charges on the surface of gold nanoparticles at a liquid–liquid interface and reduce their electrostatic repulsion, resulting in closer packing of the particles. The properties of the liquid–liquid interface, such as its interfacial tension, can also be adjusted by selecting different solvents or adding surfactants. Different solvent polarities, densities, and dielectric constants also provide an additional degree of control over particles at these interfaces. Aspects of the previously developed assembly techniques are combined with the advantages of a liquid–liquid interface to design a unique technique for patterning insoluble structures.
A general method was developed to create patterns of insoluble nanostructures on a solid support. One of the key advantages of this original technique is that different types of particles, including insoluble nanostructures, are collected at a liquid–liquid interface (Figure 3.2a). This interface allows the particles to rearrange relative to each other into a partially close-packed film of nanostructures. A patterned stamp is brought through this interface, trapping the particles under the stamp (Figure 3.2b). As the stamp continues to descend, the trapped particles assemble into a pattern defined by the stamp. To transfer the

Figure 3.2: In this patterning technique, (a) particles are collected at a liquid–liquid interface (see inset); (b) a patterned stamp is brought through this interface and the particles are displaced from the ridges of the stamp; and (c) this stamp is brought into contact with a planar substrate. Particles confined within the recesses of this stamp are transferred to the substrate and (d) after removing the stamp as well as the biphasic liquid system, form a well-defined pattern on the solid support (see inset).
patterned particles to a substrate, the stamp is brought into contact with the solid support (Figure 3.2c). After removing the stamp and solvents, a pattern of particles defined by the stamp is observed on the solid support (Figure 3.2d). A range of patterns can be created with this technique, with dimensions varying from 500 nm to 15 µm. In addition, polymeric and metallic particles can be patterned using a variety of liquid–liquid and air–liquid interfaces. After collecting particles at a liquid interface, well-defined patterns of these particles can be fabricated over an area greater than 1 mm² in less than 20 minutes.

3.2 Theory of Liquid–Liquid Interfaces

As discussed in the previous section, a liquid–liquid interface provides a number of advantages when assembling insoluble nanostructures. It is, however, noteworthy that particles at liquid–liquid interfaces can behave very differently depending on the materials and solvents involved. Since this patterning technique is very dependent on the behaviour of these particles at the interface, a relatively detailed understanding of the particle-particle and particle-solvent interactions is required. For example, if the particles form large aggregates at the interface, then they will not spread out uniformly under the stamp and large aggregates will be transferred to the substrate. In addition, if the aggregates are larger than the feature sizes on the stamp, then assembly of these particles into patterns will be highly unlikely. Conversely, if the particles randomly disperse across the interface then there will be non-uniform deposition across the substrate. An understanding of the forces acting on particles at a
liquid–liquid interface will assist in designing the interface to prevent these problems from occurring.

Air–liquid and liquid–liquid interfaces are defined by their surface or interfacial tension, which is a measure of how resistant the interface is to increases in its surface area. In nature, surface tension is the property that allows mesovelia (water-walking insects) to walk on the surface of water without falling through the air–liquid interface.\[69\] Surface tension is typically used to describe an air–liquid interface and interfacial tension to describe a liquid–liquid interface. The interfacial tension of some common solvents is listed in Table 3.1. Generally, the interfacial tension increases as the chain length of one solvent increases. Since paraffin oil contains hydrocarbons of various chain lengths, it is difficult to fit into this observed trend. It is also noteworthy that the interface between a fluorinated solvent and water exhibits a higher interfacial tension than any of the alkane-water interfaces listed in Table 3.1. Interfacial tension is an important variable in the Young-Laplace equation, which is often used to model interfaces. Equation 3.2 represents the most basic form of the Young-Laplace equation where \( \Delta P \) is the pressure difference between the two interfaces, \( \sigma \) is the interfacial tension, and \( R_1 \) and \( R_2 \) are the orthogonal radii of curvature of the interface. This equation represents the balance of forces at the interface and results in a minimization of the interfacial area. In other words, the interface opposes any deformations to it. The interfacial tension is an important property
of liquid–liquid interfaces and is an important consideration when determining how particles behave at these interfaces.\textsuperscript{[70,71]}

**Table 3.1:** Interfacial tension of some common solvents.

<table>
<thead>
<tr>
<th>Interface</th>
<th>Interfacial Tension (mN/m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Paraffin Oil–Water</td>
<td>31.5 \textsuperscript{[72]}</td>
</tr>
<tr>
<td>Hexane–Water</td>
<td>48.0 \textsuperscript{[68]}</td>
</tr>
<tr>
<td>Octane–Water</td>
<td>50.3 \textsuperscript{[68]}</td>
</tr>
<tr>
<td>Dodecane–Water</td>
<td>51.9 \textsuperscript{[68]}</td>
</tr>
<tr>
<td>Hexadecane–Water</td>
<td>53.3 \textsuperscript{[68]}</td>
</tr>
<tr>
<td>Perfluorodecalin–Water</td>
<td>55.6 \textsuperscript{[73]}</td>
</tr>
</tbody>
</table>

A number of other properties such as contact angle, gravity, capillary forces, electrostatic repulsion, van der Waals interactions, and thermal energy also influence particles at liquid interfaces. Particles often self-assemble at a liquid–liquid interface due to capillary attractions between the particles as they deform the interface (Figure 3.3).\textsuperscript{[19]} The particles move closer together in order to minimize the surface area of the interface, as required by the Young-Laplace equation. The deformation force (F_\text{d}) can be attributed to factors such as contact angle, gravity, and electrostatic interactions. For example, the deformation in Figure 3.3a could be caused by a heavy particle settling on the interface. However for particles with a diameter <10 µm the weight of the particles is usually not enough to deform the interface. Another potential cause of this
interfacial deformation is if the particle has a smaller contact angle with liquid 1 than with liquid 2 ($\theta_1 < \theta_2$). This difference in contact angle can occur if the particle is hydrophobic and liquid 2 is water. For example, when the surface of gold nanoparticles is modified with alkane chains, the nanoparticles become hydrophobic and have a smaller contact angle with water than with hexane.$^{[67]}$

Conversely, the deformation shown in Figure 3.3b could result from the particle

![Diagram](image-url)

**Figure 3.3:** A number of forces act on particles at liquid–liquid interfaces. Some, but not all, of these forces include electrostatic repulsion ($F_e$), deformation force ($F_d$), capillary action ($F_c$), and a normalizing force ($F_N$). Two potential scenarios for particles at liquid–liquid interfaces are shown in (a) and (b). The contact angles of liquid 1 and 2 are $\theta_1$ and $\theta_2$, respectively.
having a larger contact angle with liquid 1 than liquid 2 (e.g., a hydrophilic particle when liquid 2 is water). In addition, a difference in the dielectric constants of two fluids can result in an electrostatically induced deformation, as illustrated in Figure 3.3b.[74] As the dielectric constant of liquid 2 decreases, the surface charge density on the particles also decreases. The particles will adsorb to the interface to decrease the interfacial energy between the two liquids. In addition, as the charge density decreases, the electrostatic repulsion ($F_e$) between the particles will decrease. The particles will approach each other until the electrostatic repulsion is equivalent to the capillary attraction. In section 3.3, the electrostatic and solubility properties of colloidal particles are modified to transfer them to liquid–liquid interfaces.

If the energy of capillary attraction (caused by deformation of the interface) between the particles is greater than their thermal energy, defined by $kT$, then the particles will self-assemble into a uniform array. A number of the parameters discussed above can be modified, which provides control over the behaviour of particles at the interface. For example, the self-assembly of particles at a liquid interface can be controlled by varying the dielectric constant of a solvent or changing the hydrophobicity of a particle.[67,71,74] The packing of particles at an interface is also affected by ligands on the surface of the particle. Alkyl chains on the surface of a particle can induce close packing of the particles as attractive van der Waals interactions between the ligands become stronger than the electrostatic repulsion of charged particles.[67] These alkyl chains could also partially screen the surface charge of the particles. Conversely, highly charged
particles will repel each other due to strong electrostatic forces \( F_e \) in Figure 3.3. The ability to direct the particle-particle and particle-liquid interactions at an interface provides control over the transfer to and self-assembly of particles at a liquid–liquid interface. The mobility of particles at a liquid–liquid interface and the tunable properties of this interface provide significant advantages to the patterning technique presented in this chapter.

### 3.3 Particles at Liquid–Liquid Interfaces

Using the knowledge developed in section 3.2, two types of particles are chosen for assembly at a liquid–liquid interface. The first assembly of particles collected at a liquid-liquid interface is composed of polystyrene (PS) particles. These particles have been commonly used in experiments examining the self-assembly of particles at liquid–liquid interfaces.[27,64-65] Polystyrene particles have a number of characteristics that are beneficial to the patterning technique discussed in this chapter. These particles are monodisperse, well-characterized, and are commercially available with a wide range of diameters, from 25 nm to several mm.[75] The particles can also be purchased with a variety of functional groups on the surface, including carboxylic acid and primary amine groups. This surface chemistry can be modified to precipitate the PS particles to a liquid–liquid interface. Polystyrene also has a low \( T_g \) that allows one to easily physically adhere these particles to a solid surface with a low degree of heating (see section 3.5). In addition to the benefits that PS particles provide to the patterning technique, there are also a number of potential applications for assembled
patterns of PS particles in the field of photonics.\textsuperscript{[76-79]} For all these reasons, PS particles are a convenient choice to determine the effectiveness of this technique.

The second type of particles that are collected at a liquid interface is 16-nm diameter gold nanoparticles. These nanostructures are used to determine if the patterning technique can be employed to create well-defined patterns of insoluble nanoscale particles. Gold nanoparticles have been extensively studied at a liquid–liquid interface.\textsuperscript{[25,66,67,80]} One major advantage of using gold nanoparticles is that the surface chemistry of gold is easily modified. This property can be utilized to create particles with a desired solubility (or insolubility). In addition, the surface of gold nanoparticles can be modified with a number of different ligands, such as peptides or antibodies, for various applications such as biosensors.\textsuperscript{[58]} Gold nanoparticles are used to demonstrate that the patterning technique can be extended from micronscale polymeric particles to nanoscale metallic particles.

### 3.3.1 Polystyrene Particles at an Oil–Water Interface

Polystyrene particles are incorporated into the experimental setup by transferring these particles from an aqueous solution to a liquid–liquid interface (Figure 3.4). Initially, PS particles remain suspended in an aqueous colloidal solution through electrostatic stabilization.\textsuperscript{[81]} The as-purchased PS particles are functionalized with deprotonated carboxylic acid groups as stabilizing charges.
Figure 3.4: The polystyrene (PS) particles are destabilized by adding excess tetraethylammonium hydroxide (TEAH) to an aqueous solution of particles. The solutions above and below the paraffin oil–water interface are clear ~10 min after the addition of TEAH. The particles have a uniform size distribution as shown in the scanning electron microscopy (SEM) image. An image taken by optical microscopy (OM) from above the interface shows a dense layer of particles with a few vacancies and bubbles. The carboxylic acid groups are not shown on the second PS particle to conserve space.

In order to transfer these particles to a liquid–liquid interface, the solubility of the particles in water must be reduced. A phase transfer agent, tetraethylammonium hydroxide (TEAH) associates with the particle through electrostatic interactions, screens the stabilizing charges, and thereby reduces the charge density on the surface of the particles. In addition, the non-polar ethyl groups reduce the solubility of the particles in water, a polar solvent. The PS particles precipitate to the interface because of the hydrophobic ethyl groups and partial screening of the stabilizing charges. A solution of PS particles is observed to precipitate to a paraffin oil–water interface ~10 min after the addition of TEAH.
The behaviour of PS particles at an oil–water interface is examined by optical microscopy (OM) (Figure 3.5). Some self-assembly of the particles occurs at the interface, but there are also several defects such as solvent bubbles and voids in the assembly of particles. The particles self-assemble due to the capillary forces described in section 3.2 and form small islands of particles at low concentrations (Figure 3.5a). If no self-assembly of the particles occurred, then the particles would be randomly distributed across the interface. The capillary forces result from a deformation of the interface by the PS particles, likely caused by a difference in the contact angle of the two solvents with the TEAH-modified particles. Since the particles self-assemble into close-packed arrangements, the capillary attraction force between the particles is greater than their electrostatic repulsion. While the self-assembly of the particles at the interface can help to produce patterns of highly ordered particles, the defects at

Figure 3.5: Two different concentrations of PS particles are transferred to a paraffin oil–water interface. (a) At dilute concentrations, the particles self-assemble into ‘rafts’ with some close-packed regions. (b) At higher concentrations, the particles form an almost complete layer, but there are still particle vacancies and bubbles.
the interface could cause defects in the fabricated patterns. The solvent bubbles could be composed of excess TEAH or oil bubbles trapped in the water layer due to a decreased interfacial tension between the two solvents. These bubbles could potentially be reduced through careful control of the TEAH concentration. The voids in the particle assemblies are caused by an insufficient concentration of PS particles at the liquid–liquid interface. The concentration of particles at the interface could be increased by using a Langmuir-Blodgett trough to reduce the interfacial area. It is important to be aware of the behaviour of the particles at the liquid–liquid interface when the fabricated patterns are examined.

In addition to the oil–water interface used in this chapter, PS particles have previously been transferred to a water–perfluoro(methyldecalin) (PFMD) interface (Figure 3.6). There were, however, larger bubbles and more aggregates observed at the water–PFMD interface than at the paraffin oil–water interface. One possible reason for the poor uniformity at the water-PFMD interface is that the contact angle of the PS particles with both water and PFMD will be high. The particles will, therefore, prefer to aggregate together in order to

![Figure 3.6: Polystyrene particles with a diameter of 1.0 µm are transferred to a water–PFMD interface in ~10 min. The same procedure is used to precipitate PS particles to a water–PFMD interface as was used to transfer PS particles to a paraffin oil–water interface (screening the stabilizing charges on the particles with TEAH).](image)
reduce the surface area in contact with either solvent. This aggregation will result in a non-uniform array of particles at the water–PFMD interface, which is not practical to use in the patterning procedure.

A charge-screening process is employed to transfer PS particles with diameters from 25 nm to 1.0 µm to a paraffin–oil water interface. The assembly of particles with a diameter of 1.0 µm is observable by OM and patterns of these micronscale particles will also be visible by OM. Well-ordered patterns of these particles could have applications in creating photonic wave guides and band-gap materials.\textsuperscript{[76-79]} Polystyrene particles are transferred to a paraffin oil–water interface and provide the ability to rapidly examine the advantages and limitations of the patterning technique by optical microscopy.

3.3.2 Gold Nanoparticles at a Hexane–Water Interface

Gold nanoparticles are also incorporated into the experiment by transferring them to a liquid–liquid or air–liquid interface. The most common method of transferring gold nanoparticles to an air–liquid or liquid–liquid interface is to functionalize them with hydrophobic alkyl chains. The gold nanoparticles are synthesized with diameters of 16 nm by a modified Turkevich method.\textsuperscript{[83]} In this method, chloroauric acid is reduced with trisodium citrate in a ratio of 3:1 to synthesize monodisperse gold nanoparticles. The citrate groups on the surface of the gold nanoparticles provide high nanoparticle stability in water, producing a solution of gold nanoparticles with a uniform red colour (Figure 3.7). The surface
chemistry of these nanoparticles is subsequently modified to precipitate them to a hexane–water interface. The aqueous solution of gold nanoparticles is mixed with a solution of 1-dodecanethiol in hexane. The alkanethiol ligands bind to the surface of the gold nanoparticles through the gold-sulphur bond. This modification produces nanoparticles with an insolubility with both water and hexane. In addition, ethanol is added to the water layer to decrease its dielectric constant. The change in the dielectric constant results in a decrease of surface...
charge on the nanoparticles as described in section 3.2. This surface charge reduction and change in solubility causes the gold nanoparticles to adsorb to a hexane–water interface to minimize the interfacial energy. When the nanoparticles precipitate to this interface, the red colour of the aqueous layer disappears and a metallic sheen appears at the liquid–liquid interface. The surface modification of gold resulted in a visually uniform layer of gold nanoparticles at a hexane–water interface. These nanoparticles can be used to determine if the patterning technique will work with nanoscale particles.

3.4 Reusable Patterned Stamps

One major requirement for this patterning technique to be effective is the ability to create patterned stamps with nanoscale features. Moreover, in order for the technique to be cost efficient, it is desirable to have reusable stamps. It is also necessary to be able to modify the surface of the stamp to achieve the desired surface properties such as surface energy and contact angle. Poly(dimethyl siloxane), or PDMS, is examined to determine if it meets these requirements.

Poly(dimethyl siloxane) is a flexible, reusable, and relatively inexpensive elastomeric material. It is easy to fabricate PDMS stamps through replica molding.\textsuperscript{[84,85]} With replica molding, the patterns in the PDMS stamps are lithographically defined and can be fabricated with feature sizes from several nanometers to micrometers. The procedure to make these stamps is briefly
outlined in Figure 3.8. First, a master is made by standard photolithographic techniques (exposure of photoresist to collimated UV light through a photomask and rinsing away regions of exposed photoresist). Next, PDMS is poured onto this master, thermally cured, and the lithographically defined PDMS stamp is removed. Both the master and the stamp can be reused a number of times.

Each stamp with a patterned area of $1 \text{ cm}^2$ weighs $\sim 1 \text{ g}$ and only costs $0.11$ (the

**Figure 3.8:** In order to prepare a PDMS stamp, a master is first prepared by photolithography. An optical mask is placed over a positive tone photoresist and the photoresist is exposed to collimated UV light. The exposed regions are removed in a solution of base and surfactant. The master is then protected with a silane to allow the PDMS to easily release from the surface. PDMS is poured onto the master and cured in an oven. Finally, the stamp is removed from the master. Both the master and the stamp can be reused a number of times.
bulk cost of PDMS is \(~\$110/kg\).\[^{86}\] Using these reusable stamps in the patterning technique is an economical approach to fabricate patterns of nanoparticles. In addition to the low cost of PDMS, the stamp is stable in most solvents. While some solvents penetrate into the stamp and swell it, many others do not.\[^{87}\] A number of different stamps are fabricated, containing both isolated and continuous features (Figure 3.9). These features varied from 15-µm long teardrop-shaped structures to 500-nm wide continuous lines.

Figure 3.9: The following PDMS stamps are imaged by bright-field optical microscopy: (a) 15-µm long teardrop-shaped posts; (b) 10-µm wide triangular posts; (c) 5-µm wide lines; and (d) 500-nm wide parallel ridges and recesses (darker areas are recessed).

In order to prevent unwanted adhesion between the insoluble particles and the PDMS stamp, the surface of the stamp must be modified to lower its
surface energy. The surface energy is a property that is indicative of how many bonds at the surface are uncoordinated relative to the number of covalent bonds within the bulk material. A higher energy surface results in a more hydrophilic surface that is more likely to adsorb contaminants, such as nanoparticles, to reduce the surface energy. The PDMS surface can be easily modified with silane-based ligands to decrease its surface energy.\textsuperscript{[88]} It was determined that a fluoroalkylsilane (FAS) will lower the surface energy of PDMS from $\sim20 \text{ mJ/m}^2$ to $\sim15 \text{ mJ/m}^2$.\textsuperscript{[89]} The vapour deposition procedure illustrated in Figure 3.10 is utilized to deposit 1H,1H,2H,2H-perfluorodecyltrichlorosilane onto the surface of the PDMS stamp.\textsuperscript{[88]} First, the surface of the PDMS stamp is oxidized by exposing it to an air-based plasma. The FAS molecule is then vapourized in a chamber containing the oxidized stamp and binds to the hydroxyl groups on the PDMS surface through a condensation reaction. This reaction is driven to completion by heating the stamp to 80 °C for 3 hrs. After modifying the surface of the PDMS stamp with FAS molecules, the surface properties are characterized to verify any potential changes.

The changes in the PDMS surface due to the presence of FAS molecules are monitored by measuring the contact angles of both paraffin oil and water on the surface (Table 3.2). A slight increase ($\sim7^\circ$) in the contact angle of water is observed on a FAS-modified flat PDMS surface, indicating an increased hydrophobicity of the surface. This increase is caused by the non-polar fluorinated chains on the surface of the PDMS. In addition, a significant increase ($\sim32^\circ$) in the contact angle of paraffin oil on PDMS is observed. The decreased
The surface of the PDMS stamp is modified to decrease its surface energy in order to prevent particles from adhering to the stamp. The PDMS stamp is plasma treated to produce hydroxyl groups on the surface. A fluoroalkylsilane (FAS) molecule is vapour-deposited on the surface by lowering the pressure in a chamber containing the stamp and the FAS to 0.5 Torr. The molecule condenses on the surface and bonding to the PDMS stamp is ensured by heating the stamp to 80°C for 3 hrs.

Table 3.2: Contact angle measurements of water and paraffin oil on a flat PDMS surface before and after the deposition of a fluoroalkylsilane (FAS) molecule.

<table>
<thead>
<tr>
<th></th>
<th>Water Contact Angle</th>
<th>Paraffin Oil Contact Angle</th>
</tr>
</thead>
<tbody>
<tr>
<td>Before deposition of a FAS</td>
<td>104.4 ± 1.6°</td>
<td>52.9 ± 3.1°</td>
</tr>
<tr>
<td>After deposition of a FAS</td>
<td>111.1 ± 1.2°</td>
<td>84.4 ± 1.5°</td>
</tr>
</tbody>
</table>

The evidence that this surface treatment prevented unwanted adhesion between the particles and the stamp is presented in section 3.5. Through this surface modification, it is confirmed that the FAS molecule has lowered the surface energy of the stamp.
PDMS stamps meet the chemical requirements for the stamps, in addition to the physical requirements described earlier in this section.

### 3.5 Patterning of Polystyrene Particles

Patterns of polystyrene particles are fabricated to determine the effectiveness and any potential limitations of the patterning technique. By using stamps with different feature sizes and shapes, it can be established how these particles are transferred from a liquid–liquid interface to a solid support. In addition, patterns composed of both micron- and nanoscale PS particles are created in order to determine if this technique can be employed to pattern materials with a variety of diameters. Various patterns containing PS particles are assembled to determine the resolution and other characteristics of this technique.

The schematic in Figure 3.2 depicts the general procedure for fabricating patterns of insoluble particles. Polystyrene particles are collected at a paraffin oil–water interface, as described in section 3.3.1. A patterned PDMS stamp is used to transfer the PS particles from the liquid–liquid interface to a silicon substrate. After transferring the particles to the silicon substrate and removing all solvents, the adhesion between the particles and the substrate is increased by heating the substrate above the glass transition temperature of PS ($T_g = 93^\circ C$ [90,91]). The heat will slightly deform the PS particles, resulting in better adhesion to the planar substrate due to a larger surface area of the particle.
contacting the substrate. When substrate is heated, it also evaporates any remaining water on the surface of the silicon. The removal of excess solvents prevents the liquids from washing the PS particles off the silicon surface or affecting the lateral positioning of the particles.

In order to determine any sources of defects in this patterning technique, a film of polystyrene particles is transferred to a solid substrate after they have assembled at a liquid–liquid interface. After transferring PS particles from an oil–water interface using a flat, non-patterned PDMS stamp, the film of particles is examined by OM and SEM (Figure 3.11). This film contains islands of assembled PS particles including both single- and multilayers. The brighter regions in the images are due to multiple layers of particles on the surface. The voids and multilayers in the film of transferred particles could potentially cause significant defects in the final patterns. Similar features were previously observed at the liquid–liquid interface (Figure 3.5), suggesting that the assembly

![Image](image_url)

**Figure 3.11**: These films of PS particles are transferred from an oil–water interface onto a silicon substrate using a flat PDMS stamp. These images are acquired by (a) OM and (b) SEM.
and coverage area of the transferred particles results from the assembly and
coverage area of the particles at the interface. In future studies, it may be
necessary to reduce or eliminate these defects in the assemblies of particles.
These results indicate that the quality (packing and defects) of an assembly of
particles transferred to a solid surface is similar to the quality of the assembled
particles at the liquid interface.

The effectiveness of the PDMS surface modification described in section
3.4 is evaluated by examining the surface of a flat PDMS stamp after transferring
the PS particles to a silicon substrate. The same heating process described
previously is employed to promote adhesion between the particles and the solid
substrate. After attempting to transfer PS particles from an unmodified PDMS
surface to a solid support through heating, a significant amount of the PS
particles stick to the stamp surface (Figure 3.12a). The particles adhere to the
stamp due to its surface energy of \( \sim 20 \text{ mJ/m}^2 \) and because paraffin oil wets the

![Figure 3.12:](image)

**Figure 3.12:** In these images, the surface of a flat PDMS stamp is shown after attempting to transfer PS particles from a paraffin oil–water to a silicon substrate through heating. The PDMS surface displayed in (a) is not modified with a FAS while the stamp surface in (b) is modified with a FAS.
surface of the PDMS (contact angle of 53°). The film of oil will trap the particles against the stamp surface, preventing their transfer to the solid substrate. After the surface of the PDMS stamp is modified with FAS molecules (see section 3.4), significantly fewer PS particles adhere to the surface of the stamp during the transfer procedure (Figure 3.12b). The modified surface has a lower surface energy of ~15 mJ/m² and is not easily wet by paraffin oil (contact angle of 84°), which limits two main sources of particle adhesion to the surface of the PDMS stamp. Some of the PS particles still adhere to the stamp, likely due to the surface energy of the stamp or defects in the surface modification. An additional reduction in the surface energy of the PDMS surface through a further surface modification may further reduce the adhesion of particles to the surface of the stamp. The FAS modification does successfully prevent the majority of the PS particles from adhering to the PDMS stamp, resulting in maximum transfer of the particles to the solid substrate.

In order to ascertain the mechanism of the patterning process, two PDMS stamps are employed that contain complimentary relief structures. One stamp contains 15-µm long teardrop-shaped posts and the other contains teardrop-shaped wells with the same dimensions. The SEM images of the patterns fabricated using these stamps are shown in Figures 3.13a and b, respectively. In Figure 3.13a, the layer of PS particles is seen to contain an array of teardrop-shaped voids. This pattern is formed due to the displacement of the particles from the ridges of the teardrop-shaped posts and their collection in the recessed area around them. The displaced particles collect in a multilayer around the
Figure 3.13: It is determined that the polystyrene particles collect in the recesses of the stamp by analyzing the patterns formed when using stamps with complementary topographies. (a) In the first pattern, the stamp used contains teardrop-shaped posts. The particles are displaced from the posts on the stamp and collect in the recessed area surrounding them. (b) In the second pattern, the stamp contains teardrop-shaped wells. The particles collect in these wells until they are full and then remain trapped under the ridges of the stamp.

posts, as observed around the edges of the teardrop-shaped voids in the pattern (Figure 3.13a, inset). These localized multilayers are an indication that the displaced particles do not move far from their original position. If the particles moved freely under the stamp then one would expect to observe a uniform pattern deposited onto the silicon substrate, rather than a higher concentration of particles surrounding the teardrop-shaped voids. The regions between the features in the pattern contain a monolayer of particles with some close-packed arrangements. The close-packing observed is likely a reproduction of the self-assembly occurring at the liquid–liquid interface.

When a stamp containing teardrop-shaped wells is used to transfer the particles to a solid support, the pattern is composed of an array of teardrop-shaped regions of particles (Figure 3.13b). This pattern forms due to the
particles collecting in the teardrop-shaped recesses of the stamp after being displaced from the ridges on the stamp. Since the wells in the stamp are only ~1.5-µm deep, they only contain enough volume to hold a bilayer of particles (Figure 3.13b inset). After the wells are full, the excess particles remain trapped under the ridges of the stamp. These trapped particles are another indication of the limited mobility of the particles under the stamp. If the particles moved freely under the stamp, then one would expect excess particles to be completely displaced from the bottom of the stamp. While the patterning mechanism has been determined, a couple of sources of defects have also been identified in the fabricated patterns. Developing a further understanding of these sources of defects will help to improve this technique in the future.

The defects arising from overfilled recesses and limited particle mobility is illustrated in Figure 3.14. When the recesses are completely filled the excess particles remain trapped under the stamp and are non-selectively transferred to the substrate (Figure 3.14a). Particles far from the recesses in the stamp remain trapped under the ridges due to the significant distance between the particles and the recesses (Figure 3.14b). Since the 1.0-µm diameter PS microspheres are ~10% of the width of the stamp features, the particles appear to travel a maximum distance of 5x their diameter. A possible method to increase the particle mobility beneath the stamp would be to increase the fluid flow or shear flow under the stamp. This fluid flow could result from increasing the descent rate of the stamp, changing the angle of the stamp relative to the interface, or introducing an external fluid flow across the surface of the stamp. To date,
experiments to introduce a shear flow across the bottom of the stamp have been unsuccessful in significantly improving the quality of the assembled patterns. These experiments will be examined further in the future. In summary, creating patterns of PS particles using two complimentary stamps confirms that the particles collect in the recesses of the stamp, but have limited mobility under the stamp before the pattern is transferred to the substrate.

![Diagram](image)

**Figure 3.14:** There are two major sources of defects in this patterning technique. (a) If the recesses are completely filled, then excess particles remain under the ridges of the stamp near the recesses. (b) If the lateral features of the stamp are too large relative to the diameter of the particles, then the particles are not displaced far enough to collect in the recesses of the stamp.

In order to determine the limitations of this technique, patterns of PS particles containing both isolated and continuous features are deposited onto silicon substrates. One pattern contains an array of parallel, 5-µm wide continuous lines composed of 1.0-µm diameter microspheres (Figure 3.15a). This well-defined pattern covers an area of ~0.25 mm² and was created in <20 minutes. The lines are mostly parallel, but some curvature of the lines is observed in the bottom right corner of Figure 3.15a. The curvature of these lines indicates that after heating, the particles have a greater adhesion to each other than to the silicon substrate. As the stamp is removed from the silicon substrate, the lines shift slightly, but retain their overall structural integrity. In Figure 3.15b, the observed lines are very well-defined with an edge roughness proportional to
the size of the particles assembled. The patterns containing 1-µm diameter particles have an edge roughness of ~1 µm (Figure 3.15b inset). A pattern containing isolated 10-µm wide triangular features is used to determine the ability to pattern isolated features (Figure 3.15c). In this pattern, a number of particles appear to be missing near the corners of the triangular voids in the pattern. These defects are likely caused by unintended stamp motion, pushing the

![Figure 3.15: These patterns are composed of insoluble PS particles transferred from a paraffin oil–water interface to a polished silicon substrate. The particles in (a–c) have a diameter of 1.0 µm, and the particles in (d) have a diameter of 110 nm. Patterns of PS particles are assembled using PDMS stamps containing an array of: (a, b) 5-µm wide parallel lines; (c) 10-µm wide triangular posts; and (d) 500-nm wide parallel recessed lines. The images in (a and c) are acquired by dark-field optical microscopy while those in (b and d) are acquired by SEM.](image-url)
particles off the silicon surface, or solvent flow under the stamp. The stamp motion could be due to either the stamp shifting while in contact with the substrate or the stamp swelling in the solvent. The solvent flow could result from thermal convection and evaporation of any fluids remaining under the stamp during the adhesion process. Some bubbles are observed to be escaping from under the stamp indicating that solvent flow may be a more likely source of these defects. In Figures 3.15a-c, the microspheres are less well-defined than in Figure 3.13. The apparent flattening of the particles is due to the slightly higher temperatures and pressures applied during the adhesion of these microspheres than was used in the studies reported above (see Figure 3.13). The particles in Figures 3.15a-c are heated to 100 °C while the particles in Figure 3.13 are only heated to 97 °C. This temperature difference results in a thin film of partially melted particles, as observed in the inset of Figure 3.15c, while the PS particles in Figure 3.13 retain their individual spherical shapes. Despite the melting of the particles in these images, the features in the pattern are still well-defined. Many different patterns containing feature sizes >5 µm are fabricated with 1.0-µm diameter PS microspheres.

Finally, this patterning technique is evaluated for its ability to fabricate patterns of nanosized particles. For these experiments, patterns of 110-nm diameter PS nanoparticles are transferred to a silicon substrate (Figure 3.15d). Due to the smaller size of these nanoparticles, they adhere at a slightly lower temperature of 94 °C. The pattern in Figure 3.15d contains 500-nm wide parallel lines. These lines are observed to have an edge roughness of ~100 nm and to
contain defects resulting from some slight overfilling of the recesses (Figure 3.15d inset). The overfilling is attributed to a higher concentration of particles at the interface than will fit in the recesses of the stamp. This possible source of defects is illustrated in Figure 3.14a. Also, despite the lower temperature used to adhere the nanoparticles to the solid support, the particles are largely indistinguishable after the substrate has been heated. The 110-nm diameter nanoparticles are more sensitive to heat and pressure than the 1.0-µm diameter microspheres. While both sizes of PS particles may contain crosslinkers, it is suspected that the different sensitivities are due to size of the particles and not the amount of crosslinker. One possible reason for this sensitivity difference is that small deformations (e.g., a 10-nm compression) of 110-nm diameter particles will be much more obvious than small deformations of 1.0-µm diameter particles. The creation of these patterns indicates that this patterning technique can be employed to fabricate patterns with smaller feature and particle sizes.

Using the patterning technique introduced in this chapter, different diameters of PS particles have been assembled into a variety of patterns containing various feature sizes. Through these experiments, it is determined that the edge roughness of this technique is proportional to the size of the particles being patterned. Polymeric particles with diameters as small as 110-nm can be assembled into patterns containing continuous and isolated features.

One potential application of these patterns is to use the parallel lines of nanospheres as an optical waveguide. These photonic materials are based on the crystalline packing of microspheres into regular arrays. The properties of
the material is tuned by varying the diameter of the particle used. The simple technique described in this chapter can be used to efficiently fabricate patterns of well-ordered microspheres that can control the direction and wavelength of light propagation. This application and other related applications will be pursued in the future.

3.6 Patterning of Gold Nanoparticles

With the patterning technique introduced in this chapter, it is also possible to rapidly fabricate patterns containing insoluble gold nanoparticles. Gold nanostructures are chosen for a number of reasons. Due to the high conductivity of gold, patterns of these nanoparticles have potential electronic and thermal applications. For example, patterns of gold nanoparticles on polymer surfaces could be employed to create flexible electronic devices or arrays of biochemical sensors.\cite{58,92,93} In addition, by taking advantage of the gold-sulphur bond, patterns of these nanoparticles can be deposited on thiolated surfaces.\cite{16,94} The smaller diameter of these particles (16 nm) demonstrates the ability to create patterns of small nanostructures in an efficient manner. In addition, since the gold nanoparticles are transferred to a hexane–water or air–water interface, rather than an oil–water interface, the dependence of the technique on the composition of the liquid interface is examined. Creating patterns of gold nanoparticles is essential to further characterize this technique and demonstrate some potential applications.
In the initial experiments with gold nanoparticles, insoluble particles are transferred from a hexane–water interface onto a bare silicon substrate with a flat, non-patterned PDMS stamp (Figure 3.16). The silicon substrate is cleaned with piranha (7:2, H₂SO₄:H₂O₂) to remove any organic residue prior to transferring the gold nanoparticles from the liquid interface. No heat is required to adhere the nanoparticles to the silicon wafer surface due to the higher surface energy of silicon dioxide (72 mJ m⁻²\(^{[95]}\)). In addition, the use of a hexane-water interface avoids some adhesion problems caused by paraffin oil. Heat is required to adhere the PS particles, in part, because the oil forms a protective film on the silicon substrate and prevents adhesion between the particles and the substrate. This problem is no longer an issue since hexane and water are easily displaced from the silicon surface, resulting in the gold nanoparticles adhering to the substrate. Since the sample does not need to be heated, patterns of gold nanoparticles can be fabricated in less than 10 minutes.

The film of transferred gold nanoparticles contains a number of interesting features. It appears that the nanoparticles form close-packed arrays, likely reflecting the self-assembly of the nanoparticles at the hexane–water interface. While this film covers a large area (>100 µm²), it does contain a number of defects. For example, the brighter regions in Figure 3.16b indicate that multilayers of particles are present. These multilayers form at the interface and could be reduced by adjusting the concentration of thiols on the surface of the gold nanoparticles and/or varying the amount of ethanol used to precipitate the particles out of solution\(^{[67]}\). Changing these experimental conditions allows one
Figure 3.16: Gold nanoparticles are transferred onto a silicon substrate using a flat PDMS stamp. (a) The first SEM image shows a large portion of the area the film covers and (b) the higher magnification images show the assembly and defects in the film of gold nanoparticles.

to vary the forces acting on the particles at the interface (e.g., ethanol changes the dielectric constant of water). There are also a number of voids in the film that could be reduced by increasing the concentration of gold nanoparticles at the liquid–liquid interface. This interfacial concentration could be increased by adding a greater quantity of gold nanoparticles or by using a Langmuir-Blodgett trough to reduce the interfacial area. As was seen previously with PS particles, the film of transferred gold nanoparticles contains a number of defects, but these defects may be reduced in future studies by modifying the conditions affecting the self-assembly of the particles at the liquid–liquid interface.

Through the use of stamps containing micron-sized features, it is confirmed that insoluble gold nanoparticles are transferred from the ridges of the stamp. A PDMS stamp containing teardrop-shaped posts is utilized to clearly determine whether the particles transfer from the ridges or recesses of the
stamp. The teardrop-shaped region of gold nanoparticles on the substrate after pattern transfer indicates that the particles remain trapped under the ridges of the stamp (Figure 3.17a). The 5-µm wide lines in Figure 3.17b are also created from nanoparticles transferred from the ridges of the stamp. The particles are trapped under the ridges of the stamp because they are much smaller than the feature size of the stamp (a diameter of 16 nm is <1% of the feature width). In order for these nanoparticles to be displaced from the ridges and collect in the recesses of

Figure 3.17: These patterns are created by selectively transferring 16-nm diameter gold nanoparticles from a hexane–water interface onto a silicon substrate. In (a), the stamp used contains 15-µm long teardrop-shaped posts. In (b, c) a stamp containing 5-µm wide lines is used. (c) The wide area panorama is composed of a number of SEM images merged together to demonstrate the area of coverage of these patterns. The red line in (a) indicates the approximate area of the feature on the stamp.
the stamp, they would need to travel more than 100x their diameter. The gold nanoparticles exhibit the same limited mobility under the stamp as the PS particles. In addition, unlike with PS particles and despite the surface modification of the PDMS stamp, a larger portion of the gold nanoparticles adhere to the surface of the stamp. One possible reason for the nanoparticle adhesion is that hexane is absorbed by the PDMS stamp, resulting in swelling of the stamp and intimate contact between the nanoparticles and the stamp.\[^{87}\] This adhesion will further reduce the mobility of gold nanoparticles under the PDMS stamp and will prevent most nanoparticles from transferring from the recesses of the stamp. Despite a number of gold nanoparticles adhering to the surface of the PDMS stamp, a pattern composed of insoluble gold nanoparticles is fabricated that covers a very large area of \(~1.75\ mm^2\) in \(<10\ min\) (Figure 3.17c). The rapid patterning of a large area with gold nanoparticles demonstrates the efficiency of this patterning technique.

The microstructured patterns of gold nanoparticles are observed to contain regions of close-packed particles and/or defects. In the high magnification inset of Figure 3.17b, some close-packing of the nanoparticles is seen on the substrate, reflecting the self-assembly of the particles at the liquid–liquid interface. The patterns of insoluble gold nanoparticles also contain a number of defects. A major defect in Figure 3.17a is non-selective deposition of nanoparticles around the teardrop-shaped feature. This defect could result from some particles trapped in the recesses of the stamp, in addition to the nanoparticles under the ridges of the stamp, transferring to the substrate. Even
though the particles are not completely displaced into the recesses of the stamp, some particles will still be trapped in these regions and may settle onto the surface of the substrate during the transfer step. These non-selectively deposited particles adhere to the silicon surface through the same process as those transferred from the ridges of the stamp. In Figures 3.17b and c, the 5-µm wide lines have a number of gaps and discontinuities. These defects were also seen when a non-patterned film of nanoparticles was transferred to a solid support (Figure 3.16). This problem may result from an insufficient concentration of gold nanoparticles at the hexane–water interface. It is also possible that the discontinuities result from the nanoparticles adhering to the stamp rather than the substrate. The fabrication of patterns of insoluble nanoparticles using stamps with micronscale features demonstrates that the patterning technique discussed in this chapter can be employed to selectively transfer nanoscale particles from the ridges of the stamp into patterns covering large areas.

Nanoscale patterning of insoluble nanoparticles, in addition to micronscale patterning, is demonstrated in order to increase the range of potential applications for the patterning technique. In an attempt to improve the quality of the patterns, gold nanoparticles are transferred from an air–water interface. The nanoparticles are initially collected at a hexane–water interface and the hexane layer is subsequently allowed to evaporate. The use of an air–liquid interface reduces the defects in the patterns by preventing the PDMS stamp from swelling in hexanes, as observed in previous studies. A stamp containing 500-nm wide recesses and ridges is used to create the patterns shown in Figure 3.18. The
smaller feature size reduces the travel distance of the nanoparticles and confirms the ability to create high-resolution patterns.

**Figure 3.18:** The patterns shown in these SEM images are created by transferring 16-nm diameter gold nanoparticles from an air–water interface onto a silicon substrate. The patterned stamp used for the transfer process contains 500-nm wide parallel recesses and ridges. The images in (b) and (d) are magnified views of the images in (a) and (c), respectively. In (c) and (d) the gold nanoparticles are transferred onto a thiol-modified silicon surface.

The parallel lines observed in Figure 3.18 are composed of nanoparticles transferred from the recesses of the stamp. The particles are displaced from the ridges of the stamp into its recesses because the particles only have to travel a
distance of ~10x the diameter of the nanoparticles. This distance is an order of magnitude less than the travel distance required for the patterns with micronscale features. In addition, the adhesion between the nanoparticles and the stamp appears to be reduced by eliminating the use of hexane. The lines have only a few discontinuities and there is some close-packing of the nanoparticles (Figure 3.18a). The patterns containing 16-nm diameter insoluble gold nanoparticles have an edge roughness of ~50 nm, confirming that the resolution of the patterning technique is limited by the size of the particles in the pattern (Figure 3.18b). The edge roughness will also be influenced by any roughness in the stamp features.

The area covered by the patterns containing nanosized features is ~40 µm² (Figure 3.18a). This area is less than was achieved using micronscale features but the patterns created with nanoscale features have fewer defects. The brighter regions in Figure 3.18a indicate that a multilayer of nanoparticles is transferred from the recesses of the stamp. These defects form as excess particles collect in the recesses of the stamp. There are, however, fewer multilayers present in the patterns shown in Figure 3.18 compared to those shown in Figure 3.17. This reduction in multilayers could be an indication of less particle aggregation at the air–liquid interface compared to the liquid–liquid interface. The gold nanoparticles may form multilayers in the hexane phase because hexane is a favourable solvent for the dodecane chains (C₁₂) on the surface of the nanoparticles. Air is an unfavourable environment and the gold
nanoparticles will spread out across the air–water interface to reduce the surface area of the nanoparticles exposed to air.

Patterns of gold nanoparticles can also be deposited onto a thiol-modified silicon surface. Mercaptosilane molecules are vapour-deposited onto a clean silicon wafer using a procedure similar to the one used to modify the surface of the PDMS stamp. The wafer is plasma treated for 30 s and then placed in a desiccator with a mercaptosilane at a low pressure (~0.5 Torr). The silane group on the molecule binds to the silicon surface and the thiol group is available to form bonds with the gold nanoparticles. The patterns observed after transferring particles from an air–liquid interface onto a thiol-modified substrate (Figures 3.18c and d) are very similar to those formed when particles are transferred onto a bare silicon substrate (Figures 3.18a and b). One difference is that patterns transferred to the thiol-modified substrate appear to have fewer multilayers than the patterns on the unmodified substrate. This difference is most likely due to a greater adhesion between the substrate and the first layer of nanoparticles compared to subsequent layers of particles. The increased adhesion for the first layer is due to the binding strength of the gold-thiol bond. To sum up, the patterns of insoluble nanoparticles containing nanoscale features appear to have fewer defects, but cover a smaller area than the patterns fabricated with micronscale features. Some applications of patterning metal nanoparticles on a silicon substrate include depositing nanoparticles as catalysts, electrical contacts, and sensors.
Patterning particles on polymer surfaces demonstrates the ability to fabricate patterns on a variety of substrates. To demonstrate this capability, patterns of insoluble gold nanoparticles are created on both a hard and a flexible polymer surface. Due to the high affinity of gold to bind to thiols\textsuperscript{96} a UV-curable, mercapto-ester polymer from Norland Optical Adhesives called NOA61 is used. The polymeric surface is prepared by washing a silicon wafer with piranha and spin-coating the polymer onto the surface. The polymer is exposed to UV light ($\lambda = 365$ nm) to cure the polymer into a hardened surface. A pattern of gold nanoparticles is also fabricated on a flexible, flat PDMS substrate. The PDMS substrate is modified with thiol ligands to increase the adhesion of the gold nanoparticles to the surface of the PDMS. A layer of mercaptosilane molecules are vapour-deposited onto the surface of the PDMS using the same process as discussed in section 3.4. The gold nanoparticles are assembled and transferred from a hexane–water interface onto polymer surfaces using the same method as was previously used with silicon substrates. The two patterned stamps that are used contain an array of parallel ridges and recesses; one stamp has a line width of 5 $\mu$m (Figures 3.19a and b) and the other has a line width of 500 nm (Figures 3.19c and d). No heat is required to increase the adhesion between the nanoparticles and the polymer because the gold nanoparticles form a gold-sulphur bond with the exposed thiols on the surface of the polymer.

In Figure 3.19a, the pattern of nanoparticles containing 5-\textmu m wide lines covers an area of $\sim0.2$ mm$^2$. As described earlier, these particles transfer from the ridges of the stamp due to the large width of the features relative to the
Figure 3.19: A stamp containing 5-µm wide lines is used to transfer gold nanoparticles onto a thiol-containing polymer surface. (a) A wide-area view is acquired by dark-field OM and (b) a magnified image is acquired through SEM with a low field strength of 1 kV to prevent charging. In addition, a stamp containing 500-nm wide lines is used to transfer a pattern of gold nanoparticles onto a thiol-containing polymer (c, SEM) and mercaptosilane-modified PDMS (d, brightfield OM).

Similar defects are observed in the patterns on polymer surfaces, such as discontinuities in the lines (Figure 3.19b), as were observed in patterns on silicon substrates. This similarity indicates that most defects form as the stamp descends through the interface and are independent of the composition of the substrate. The main source of these defects is likely the formation of a non-uniform layer of particles at the liquid–liquid interface. By improving the quality of the layer of particles at the interface (e.g., increased concentration of gold nanoparticles, use of a Langmuir-Blodgett trough, and
refined surface modifications of gold nanoparticles), it should be possible to reduce the defects observed in the patterns. In Figures 3.19c and d, the arrays of 500-nm wide lines are created by transferring the particles from the recesses of a stamp. The transfer of particles from the ridges of 5-µm wide lines and the recesses of 500-nm wide lines is the same as was observed for patterning on the silicon substrate. This result implies that the assembly mechanism for the patterning technique is independent of the composition and rigidity of the solid support. While there are a number of defects, a pattern composed of insoluble nanoparticles is successfully deposited onto a flexible PDMS surface and covers an area of ~100 µm² (Figure 3.19d). These patterns of nanoparticles on polymer surfaces demonstrate that this patterning technique can be employed to fabricate patterns on a variety of substrates. The technique does, however, require further optimization to reduce defects and achieve a better understanding of the patterning mechanism.

In this section, the ability to create patterns of insoluble gold nanoparticles on a wide range of substrates with a sub-100 nm edge roughness has been demonstrated. In particular, the ability to create patterns of gold nanoparticles on a polymer surface has a number of potential applications. Some of these applications include patterning wires and electrodes on flexible substrates and creating arrays of biosensors. These applications will be described in more detail at the end of this thesis.
3.7 Conclusions

A quick, simple, and efficient technique has been developed to fabricate patterns containing insoluble materials. It has been determined that this technique can be utilized to create patterns composed of several different types and sizes of materials, including gold nanoparticles and polystyrene microspheres. Prior to patterning, the surface chemistry of the gold and PS particles is modified in order to promote their self-assembly at a liquid–liquid interface. A patterned PDMS stamp is used to assemble these particles into patterns containing both isolated and continuous features. Particles with diameters <5% of the stamp feature size are observed to transfer from the ridges of the stamp while particles >5% of the stamp feature size transfer from the recesses of the stamp. Further studies are needed to accurately determine the minimum size of particle that will collect in the recesses of a stamp. The proposed assembly mechanism is attributed to the limited mobility of particles under the stamp surface. When gold nanoparticles are transferred from a hexane-water interface, the adhesion between the particles and the surface of the stamp increases, further reducing the mobility of these particles under the stamp. The edge roughness of the fabricated patterns is determined to be proportional to the size of the particles patterned. Patterns with an edge roughness of ~50 nm are created using gold nanoparticles and ~1 µm using polystyrene microspheres. The patterning technique presented in this chapter is a highly efficient method to create nanostructured patterns of insoluble particles in less than 20 minutes.
The universality of this technique has been demonstrated by depositing patterns of gold nanoparticles onto both semiconductor and polymeric surfaces. In various tests of the patterning procedure, different nanostructured materials, interfaces, and substrates have been utilized. It should also be possible to fabricate patterns of several different types of insoluble nanostructures using this technique. For example, the patterning method could be used to create patterns of the porous nanostructures that were synthesized in chapter 2. These patterns could have potential applications as gas sensors. In addition, the only limitation to selecting a substrate is that there must be a process to adhere the nanostructures to the substrate. Some of the preliminary patterns composed of nanoparticles on a polymeric surface demonstrate that further optimization of the technique is necessary to reduce defects. This technique does show incredible promise as a method to fabricate patterns of insoluble nanostructured materials.
CHAPTER 4: CONCLUDING REMARKS

4.1 Future Work and Applications for These Techniques

Much of the future work with porous nanorods involves addressing a few challenges with the synthesis and developing applications for the porous nanostructures. One problem that must be addressed is to reduce the aggregation of these nanorods in solution. If these nanorods are not dispersed uniformly in solution then many of their optical properties will be incoherent. For example, an SPR peak is not detected for a suspension of the porous hollow nanorods due to their high degree of aggregation. Currently, PVP is used to reduce aggregation of the nanorods, but this surfactant is insufficient for complete dispersion of these nanostructures in water. A better choice may be a molecule with a thiol on one end to bind to the silver and/or gold and a carboxylic acid group on the other end to assist in dispersing the nanorods in solution. After the aggregation of the porous nanostructures is reduced, it should be possible to tune the SPR wavelength through the visible region and into the infrared region by tuning the structure and composition of the nanorods.\[^{41}\]

The porous hollow nanorods have numerous applications in the field of medicine. One key advantage of these structures is that the gold surface can be modified with specific ligands, such as bioactive molecules. This property could be utilized to target the porous nanoshells to a specific area in the body by modifying the surface with antibodies.\[^{1}\] Since the porous nanorods have a much
higher surface area than solid structures with similar dimensions, a large quantity of drugs can be delivered to the biological system inside the body that was targeted by the antibody. The tunability of these porous nanorods will allow one to tune their optical properties, such as their SPR wavelength. The dimensions of the nanostructure can be used to tune the wavelength and the porosity can be used to tune how efficiently the nanostructure absorbs light. One benefit of this tunability is that the dimensions could be tuned to select an SPR wavelength in the infrared region, which passes more efficiently through the body than visible light.[3] The photothermal effect could be activated at this wavelength to produce localized heating of the nanostructure.

Another future study is to develop a method to trap air inside these porous nanorods. These ‘protected air bubbles’ could be used as ultrasound contrast agents due to the large density difference between air and a liquid. Provided the nanorod-encapsulated bubbles are large enough, acoustic waves will strongly reflect off these structures. Finally, patterns of these porous hollow nanorods could also be fabricated by employing the patterning procedure described in chapter 3. Patterns of well-defined porous nanostructures could be used as highly sensitive gas sensors. After tuning the solubility of these nanostructures, there are a number of potential medical and optical applications for porous hollow nanorods.

The potential applications for the patterning method are as diverse as the materials that can be patterned with the technique. Before further applications are pursued, the defects in the fabricated patterns need to be reduced. One of
the major sources of defects appears to be non-uniform packing at the liquid–liquid interface. This packing could be improved by increasing the concentration of particles at the liquid–liquid interface. A higher concentration of particles should increase the area covered by an array of close-packed particles. The concentration can be increased by adding more particles and/or using a Langmuir-Blodgett trough to compress the particles at a liquid–liquid interface (Figure 4.1). A uniform monolayer of particles covering a large area of the liquid–liquid interface will allow one to create a larger pattern with fewer defects.

![Diagram of Langmuir-Blodgett trough](image)

**Figure 4.1:** A Langmuir-Blodgett trough can be used to decrease the area of a liquid–liquid interface containing particles, resulting in a monolayer of particles with greater uniformity.

In addition to reducing the defects in the patterns, there also needs to be further characterization of the current patterns. Specifically, the conductivity of the linear lines of gold nanoparticles should be measured. The conductivity can be measured by attaching an electrode to one end of the patterned line and using a conductive atomic force microscope tip to scan along the line of nanoparticles in order to identify breaks in the conductivity. With this information, the continuity of the lines of nanoparticles can be determined, as well as the conductivity between metal nanoparticles as a function of their surface modifications. The conductivity can also be measured to determine any changes in the value after annealing the nanoparticles at a high temperature. The
annealing process may change the conductivity of the line of nanoparticles by melting the particles together and/or removing ligands from the surface of the particle. These conductivity measurements will help to determine the applicability of this technique to fabricate gold nanoparticle-based wires.

The patterning technique has a number of potential applications. One interesting experiment is to use this technique to create multilayered patterns of nanostructures. For example, a stamp with parallel lines can be used to fabricate an array of crossed lines by transferring particles from the interface, rotating the stamp 90°, and transferring particles from the interface again. It would also be of interest to fabricate multiple patterns composed of different materials on the same substrate by changing the particles at the interface between transfer processes. Patterned thin films of batteries and capacitors could be created by assembling layers of the appropriate materials. These patterns could be deposited onto a flexible substrate to pursue flexible electronic applications. Flexible substrates are of interest due to their portability and mechanical robustness. With this patterning technique, well-defined patterns composed of multiple materials can be fabricated on a variety of substrates.

While a number of different materials could be used with this technique, there are a few materials with particularly interesting applications. One is to deposit gold nanoparticles as biosensors. Gold nanoparticles could be modified with an appropriate bioactive ligand and collected at a liquid-liquid interface. These nanoparticles would then be selectively transferred onto electrodes, which could be used to measure any changes in the electronic
properties of the nanoparticles. By exchanging the nanoparticles at the interface with a new solution of particles with different bioactive ligands, distinct regions of nanoparticles with different sensing abilities could be patterned on the same substrate. The electrical responses of this biosensor chip could be measured to analyze a biological solution for specific properties such as its pH and composition. This patterning technique could provide the ability to rapidly and efficiently fabricate multiple sensing devices on a single chip.

Patterns of anisotropic nanostructures would have applications that take advantage of some of the unique properties of nanowires. For example, patterned selenium nanowires could be used to create photoresponsive nanowire switches, a potential component in a nanowire-based circuit (Figure 4.2). In addition, piezoelectric nanowires could be patterned on a flexible substrate to create a small power supply. A technique to efficiently pattern nanowires could open up new avenues of research into nanowire-based circuits. The patterning

![Figure 4.2: This figure illustrates a possible selenium nanowire-based photoresponsive switch. The conductivity and, therefore, the current flow dramatically increase upon exposure to light.](image)

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technique developed in this thesis could be used for a number of these unique applications, varying from flexible electronics to photoresponsive switches.

4.2 Results and Implications of This Work

In this thesis, new techniques have been introduced to synthesize and pattern nanostructured materials. These techniques have a number of applications in many fields of scientific research. To begin with, a new procedure was developed to engineer porous hollow metallic nanorods. A major advantage of this technique is that there is excellent control over the diameter, length, porosity, and composition of these nanostructures. These parameters are modified through simple changes to the experimental conditions and do not require extensive redesign of the experiment. Hollow nanorods are synthesized with diameters from 80 to 220 nm and with pore sizes from 30 to 70 nm. The porosity of these nanostructures is tuned from a solid shell to a porous shell through a galvanic replacement reaction. This process was also utilized to tune the composition of the final structure from a gold-silver alloy to a predominately gold structure. Porous nanorods have many applications ranging from gas sensors to drug delivery vehicles.30-32 These applications can be enhanced by controlling the structural properties of these nanostructures to tune their optical and physical properties. For example, the gas sensitivity and drug delivery efficiency (amount of drug delivered per nanorod) could be adjusted by varying the porosity and dimensions of the tunable nanostructures. The development of a method to precisely control the structural properties of an anisotropic
nanostructure is an important step towards synthesizing designer nanostructures with tunable properties.

One significant difficulty with many nanostructured materials, such as the porous nanorods, is that they are insoluble in many solvents and are, therefore, difficult to assemble into patterns. In order to address this challenge, a new patterning method was devised that can be used to create patterns of insoluble nanoparticles. One key aspect of this technique is that insoluble particles are collected at a liquid–liquid interface. The particles subsequently self-assemble into close-packed arrangements at the liquid–liquid interface prior to patterning them on a substrate. A patterned PDMS stamp is used to selectively transfer these particles from the liquid–liquid interface to a solid support. The particles are displaced from the ridges of the stamp (for particles with diameters >5% of the lateral feature sizes of the stamp) and collect in the recesses of the stamp. Patterns containing both isolated and continuous features are fabricated from insoluble polystyrene particles of various diameters and 16-nm diameter gold nanoparticles. These patterns are fabricated in <20 min and have an edge roughness that is determined by the size of the materials being patterned. In addition, patterns of gold nanoparticles can be deposited onto both semiconductor and polymeric surfaces. This technique has been demonstrated with a variety of insoluble particles, different liquid interfaces, and various substrates. One key strength, therefore, of this patterning technique is that it can be utilized with a greater diversity of materials than is possible with many current patterning techniques. A large number of applications for this technique are
anticipated due to the variety of nanostructured materials that can be patterned. Some of these potential applications include biosensor arrays and flexible electronics.[58,92,93,98]

The new methods presented in this thesis open doors to wide range of applications. These techniques can be used to create highly tunable nanostructures and assemble a variety of nanostructured materials into patterns. The synthetic technique developed allows one to engineer nanostructures with specific dimensions and properties. Chemists who previously faced challenges to synthesizing anisotropic metallic materials with specific properties can use this technique to fabricate nanostructures tailored to meet a specific requirement for a particular application. In addition, the patterning method can be employed to create well-defined patterns from a diverse set of materials. This universal technique can be used to incorporate nanostructures synthesized in the lab, which were previously difficult to pattern, into devices utilizing the unique properties of many nanostructures. The techniques introduced in this thesis to synthesize and assemble designer nanostructures and patterns have a diverse range of applications and are relevant to many fields of science.
APPENDIX A: SYNTHESIS OF POROUS HOLLOW NANORODS

A.1 Electrodeposition of Silver into Polycarbonate Molds

Polycarbonate membranes (25-mm diameter, Sterlitech Inc. in Kent, WA) were used as molds for the electrodeposition of silver nanorods. The pore diameters of these membranes varied from 10-100 nm. In order to increase the hydrophilicity of the PC mold, it was exposed to an air-based plasma at ~0.5 Torr for 30 s using a plasma cleaner from Harrick Scientific (Pleasantville, NY). On the bottom side of the mold, ~200 nm of aluminum (99.99%, Strem Chemicals in Newburyport, MA) was deposited at ~1 nm/s by thermal evaporation (thermal evaporator from CHA Industries, Fremont, CA). The electrodeposition apparatus included working, counter, and reference electrodes connected to a BioPotentiostat (Model AFCBP) from Pine Instruments (Grove City, PA), which was controlled using PineChem 2.5 software (Figure A.1). The working electrode consisted of an aluminum plate in contact with the Al-coated mold. A glass tube containing a silver wire and a saturated aqueous AgCl solution was used as the reference electrode. The counter electrode was a Pt wire (~99.95%, Strem Chemicals) inserted in a glass tube containing the electroplating solution with a glass frit at the bottom of the tube.

A saturated NaCl solution, prepared from sodium chloride pellets (Caledon Inc., Georgetown, ON), served as a conductive solution between the Al film on
the PC mold and the working electrode. Approximately 3-4 drops of this solution was deposited on the working electrode, onto which the aluminum side of the polycarbonate mold was placed. The apparatus was then assembled as shown in Figure A.1. Silver nanorods were synthesized by electrodepositing silver from

![Figure A.1: The electrodeposition setup contains a reference Ag/AgCl electrode, a platinum anode, and an aluminum cathode. The aluminum-coated PC mold was placed on top of the cathode. The glass container was filled with the electroplating solution and a stream of nitrogen gas was used to increase the deposition uniformity by mixing the silver salt solution.](image)
A standard silver electroplating solution (contains 2.6-4.6% (wt/v) AgCN, purchased from Transene Co. in Danvers, MA) into the pores of the PC mold. The silver electroplating solution was continually agitated with nitrogen gas injected into the solution through a glass pipette at a rate of ~0.5 mL/s. A potential of -1.75 V was applied to the counter electrode for 30 s and the PineChem software was used to plot the current and potential vs. time. After 30 s, the mold was quickly transferred to a beaker containing ~10 mL of 18.2 MΩ water. The aluminum film was removed from the mold by immersing it in an aqueous solution of 30% (wt/v) potassium hydroxide (made from KOH pellets purchased from EMD Inc., Gibbstown, NJ) for 30 s. This mold was washed in 18.2 MΩ water and completely dried under a stream of nitrogen gas. Finally, the silver nanorods were isolated from the PC mold by dissolving it in 5 mL chloroform (99.8%, Caledon Inc.) for 5 minutes.

A.2 Purification of Silver Nanorods

The solution of silver nanorods was washed 3 times by centrifugation (at 2000 rpm for 2 min) with 0.4% (wt/v) polyvinylpyrrolidone (PVP) in ethanol (99.5%), both acquired from Sigma-Aldrich (Oakville, ON). The nanorod/PVP/ethanol solution was then mixed for 3 h, which was followed by 3 solvent washes in 0.4% (wt/v) PVP in 18.2 MΩ water. The final solution contained silver nanorods in 5 mL of 0.4% PVP/water. Multiple samples of nanorods could be combined to achieve a greater sample volume. The
concentration of the nanorod solution was estimated to be $2.94 \times 10^8$ nanorods/mL (see section 2.2).

**A.3 Galvanic Replacement of Silver Templates with Gold Shells**

To obtain porous gold nanostructures, the silver templates were replaced with porous gold shells. A 10 mL aqueous solution of the silver nanorods was refluxed at 90 °C for 10 min in a round-bottom flask. A solution of 1 mM chloroauric acid, made from hydrogen tetrachloroaurate trihydrate (99.99%, Sigma-Aldrich), was prepared at least 24 hrs in advance to allow complete dissolution of the gold salt. Next, 0.10 mL of 1 mM chloroauric acid was added to the refluxing solution of silver nanorods. After 1 min, a 1.0 mL aliquot of the reaction solution was removed and an additional 0.10 mL of chloroauric acid was added to the reaction vessel. This step was repeated up to 12 times. The solutions of porous nanostructures were washed 2 times by centrifugation (1000 rpm, 2 min) using 18 MΩ water.

**A.4 Removing Excess Silver Templates with Ammonium Hydroxide**

After the porous gold shells were synthesized through the galvanic replacement reaction, some of the silver templates still remained within the porous shells. This excess silver was etched out of the porous structures with ammonium hydroxide (~30% in water, EMD Inc.). Ammonium hydroxide was
added to an aqueous solution of the reacted templates at a ratio of 50% (v/v). This solution was vigorously mixed for 60 min and then allowed to stand for >48 hrs to complete the reaction. After 48 hrs, the basic solution of porous hollow nanorods was washed twice by centrifugation (1000 rpm, 2 min) with isopropanol (99.5%, Anachemia in Lachine, QC).

A.5 Imaging of Porous Hollow Nanorods

The purified porous hollow nanorods were prepared for SEM imaging by depositing a few droplets of the nanorod solution on a polished silicon (100) wafer received from Silicon Sense, Inc. (Nashua, NH). The isopropanol evaporated and left the porous nanorods on the silicon substrate. This substrate was positioned onto an aluminum stub with carbon tape and inserted into a FEI 235 Strata Dualbeam scanning electron microscope. Unless stated otherwise, all SEM images were collected below a pressure of 3x10^-5 mbar with an accelerating voltage of 10 kV. EDS spectra are collected on the same SEM using an EDAX detector cooled with liquid nitrogen. The EDS spectra was acquired over an area of ~1 µm^2 and integrated for ~30 s.

Porous nanorods were prepared for TEM imaging by depositing one droplet of the nanorod solution on the Formvar/carbon side of a 300 mesh copper TEM grid from Electron Microscopy Sciences (Hatfield, PA). The isopropanol was evaporated with the assistance of a 50 W halogen lamp for 30 min and the dried grid was stored in a desiccator. The grid was loaded into a Tecnai G^2
STEM for TEM imaging. The TEM images were collected in brightfield mode at a pressure below $1 \times 10^{-7}$ mbar with a field emission strength of 200 kV and a beam current of ~32 µA. Digital images were acquired with a Gatan 794 1k×1k multiscan CCD camera.
APPENDIX B: DIRECTED ASSEMBLY OF INSOLUBLE PARTICLES

B.1 Polystyrene Particles at a Paraffin Oil–Water Interface

Polystyrene colloids were prepared for patterning by destabilizing these particles and transferring them to a liquid–liquid interface. This approach demonstrates the applicability of the patterning technique to manipulate insoluble particles. A liquid–liquid interface was formed by mixing 20 mL of 18 MΩ water and 20 mL of light paraffin oil (Saybolt viscosity of ~130 SUS at 100 °F), purchased from EMD Chemicals, in a glass bottle. To this mixture, 100 µL of a solution of tetraethylammonium hydroxide (20% in water from Sigma-Aldrich) was added, which increased the pH of the water layer to ~11. In order to completely dissolve the TEAH, the pH of the water layer was adjusted to ~3 through the addition of ~25 µL concentrated hydrochloric acid (36.5-38.0% in water) from Anachemia. Carboxylic acid functionalized PS microspheres (10.1% solids in water with 0.05% NaN₃) with a diameter of 1.04 µm were obtained from Bangs Laboratories (Fishers, IN). PS nanospheres with a 110-nm diameter and functionalized with carboxylic acid (2% solids in water with 2 mM NaN₃) were purchased from Molecular Probes (Eugene, OR). After the TEAH completely dissolved, 15 µL of the PS microsphere solution or 25 µL of the PS nanosphere solution was added to the mixture. The final solution was vigorously mixed for at least 3 min to destabilize the particles by screening the stabilizing electrostatic
charges on the surface of the particles. These particles precipitated out of solution to the liquid–liquid interface.

**B.2 Gold Nanoparticles at a Hexane–Water Interface**

Gold nanoparticles were synthesized by a modified Turkevich method.\[83\]

Before synthesizing the gold nanoparticles, all glassware was rinsed with 18 MΩ water and freshly prepared aqua regia (1:3, HNO$_3$:HCl) to remove all traces of metal oxides. The glassware was then rinsed with 18 MΩ water and freshly prepared piranha (2:7, H$_2$O$_2$:H$_2$SO$_4$) to remove any organic residue. A 5 mM solution of trisodium citrate was prepared by dissolving 6.58 mg of trisodium citrate (99%) from BDH Inc. (Toronto, ON) in 5 mL of 18 MΩ water. A 0.15 mM solution of chloroauric acid was prepared by diluting 1.45 mL of a previously aged 5.11 mM HAuCl$_4$·3H$_2$O (99.99%, Sigma-Aldrich) solution to 50 mL with 18 MΩ water.

The synthesis of the gold nanoparticles began with heating the gold solution to boiling using a heating mantle. When the solution started boiling, preheated trisodium citrate solution was added to it. After addition of trisodium citrate, the colour changed from clear to pinkish red. The solution was boiled for 10-15 min to complete the reaction. Based on TEM analysis (Figure 3.7) the size of these particles was determined to be 16 ± 2 nm.

To precipitate the nanoparticles to a liquid–liquid interface, 25 mL of hexanes (98.5%, EMD Chemicals) was added to 50 mL of the gold nanoparticle
solution prepared by the modified Turkevich method. The surface of the gold nanoparticles was modified by adding 5 µL of 1-dodecanethiol (98%, Sigma-Aldrich). The nanoparticles were destabilized and precipitated to the hexane–water interface after adding 15 mL of ethanol (99.5%, Sigma-Aldrich) to the biphasic solution. Both liquid layers were colourless and the nanoparticles formed a reflective metallic sheen with a golden colour at the liquid–liquid interface. The hexane layer could be subsequently evaporated to collect the gold nanoparticles at an air–liquid interface.

### B.3 Fabrication of Patterned PDMS Stamps

Poly(dimethyl siloxane), or PDMS, stamps were fabricated from polymer precursors purchased from Dow Corning (Midland, MI; Sylgard 184). To prepare the PDMS stamps, previously established lithographic procedures were followed.\[85\] The bulk prepolymer and crosslinker were mixed in a ratio of 10:1 for 5 min. Next, the mixture was degassed by placing it under vacuum (~0.5 Torr) until most visible bubbles had dissipated. The mixture was then poured onto a master template, which had been previously fabricated by standard photolithographic techniques. Any remaining bubbles were removed under a stream of nitrogen gas. Finally, the PDMS was cured in an oven at 70 °C for 90 min.

The relief structures on the surface of the PDMS stamp could have a range of patterns and dimensions. Relief patterns used in this thesis included continuous lines and discrete structures (e.g., teardrops and triangles). The
teardrop-shaped posts were ~15-µm long, ~10-µm wide at their widest point and narrowed to ~1-µm wide at their tip. A stamp containing structures complimentary to the teardrop posts (i.e., teardrop-shaped wells) was fabricated by casting PDMS against the stamp containing the posts. The triangular posts had 10-µm long edges and the lines were 5-µm and 500-nm wide. The depth of the relief structures was determined to be ~1.4 µm with a Tencor P-10 profilometer.

When the feature size of the master template is <1 µm, a different formulation of PDMS was used. A thin layer of hard-PDMS[99] was deposited on the top of the master template. Hard-PDMS is more brittle than standard PDMS, but is better for replicating small features. This formulation was made by mixing 3.765 g (7-8% vinylmethylsiloxane)-(dimethylsiloxane) copolymer with 18 µL platinum-divvinyltetramethyl-disiloxane complex in xylene (both compounds from Gelest, Inc. in Morrisville, PA). To this mixture, 1 droplet of 2,4,6,8-tetramethyl-2,4,6,8-tetravinylcyclotetrasiloxane (Sigma-Aldrich) was added and the solution was mixed for 60 s. The polymerization began after the addition of 1.00 g (25-30% methylhydrosiloxane)-(dimethylsiloxane) copolymer (from Gelest, Inc.). This viscous mixture was stirred for 30 s and spin-coated on top of the lithographically-defined master template (1000 rpm for 30 s). The film of hard-PDMS was cured in an oven at 70 °C for 10 min. Finally, standard PDMS (10:1 ratio) was added on top of the hard-PDMS and was cured at 70 °C for 90 min.

After the PDMS was cured, the PDMS stamp was removed from the master template. In order to adhere the PDMS stamp to a glass slide, the flat
side (i.e. non-patterned) of the PDMS stamp and a glass microscope slide were exposed to a 10.2 W air-based plasma at ~0.5 Torr for 30 s. The plasma-treated side of the PDMS stamp was then positioned onto the glass slide and placed into an oven at 70 °C for 30 min, in order to bond the PDMS to the glass surface.

To reduce the surface energy of PDMS, the surface was modified with a fluoroalkylsilane (FAS). The silane 1H,1H,2H,2H-perfluorodecyltrichlorosilane, which was purchased from Alfa Aesar (Ward Hill, MA), can be covalently bonded to the surface of oxidized PDMS. The PDMS surface was oxidized by exposing the surface to an air-based plasma (10.2 W) at ~0.5 Torr for 30 s. The stamp was then rinsed with 18 MΩ water and dried under a stream of nitrogen gas. The dry PDMS stamp was placed in a desiccator with 25 µL 1H,1H,2H,2H-perfluorodecyltrichlorosilane and evacuated down to a pressure of ~0.5 Torr. After 24 hrs at this low pressure, the stamp was placed in an oven at 80 °C for 3 hrs to complete the condensation reaction.

B.4 Preparation of Substrates

The PS particles were deposited onto polished silicon (100) wafers as-received from Silicon Sense, Inc (with a root mean square roughness of ~75 pm [100]). The gold nanoparticles were also deposited onto silicon substrates, but these substrates were pre-cleaned first. The silicon wafer was pre-cleaned in piranha to remove any contaminants from the surface. The adhesion between the gold nanoparticles and a silicon wafer was increased by modifying the surface of silicon with 3-mercaptopropyl-trimethoxysilane from Gelest, Inc. The
pre-cleaned silicon wafer was exposed to an air-based plasma for 30 s, rinsed with 18 MΩ water, and dried under a stream of N₂ gas. The wafer and 25 µL of the mercaptosilane molecule were stored under vacuum (~0.5 Torr) for 24 hrs. Finally, the wafer was placed in an oven at 100 °C for 3 hrs to complete the surface modification. All silicon substrates were broken into smaller pieces by scoring with a diamond-tip pen prior to patterning the particles. The majority of the silicon dust generated when the wafer was broken was removed from the surface of the wafer under a stream of N₂ gas.

Gold nanoparticles were also transferred onto polymer surfaces. A UV curable polymer, called NOA61, was purchased from Norland Products (Cranbury, NJ). The gold nanoparticles adhere to the mercapto-ester groups in this polymer. The polymer surface was prepared by spin-coating NOA61 onto a pre-cleaned silicon wafer at 2500 rpm for 30 s. This polymer was hardened by curing it with a B-100AP UV lamp (365 nm, 100 W) from UVP, Inc (Upland, CA). The sample was placed 15 cm away from the lamp and exposed to ultraviolet radiation for 1 hour. In addition to the UV curable polymer, a pattern of gold nanoparticles was also fabricated on a mercaptosilane-modified PDMS substrate. This substrate was prepared in the same manner as the FAS-modified PDMS stamps (see previous section).
B.5 Selective Transfer of Insoluble Particles from a Liquid Interface

After the particles were collected at a liquid–liquid interface, they were selectively transferred onto a substrate in a pattern defined by a PDMS stamp. The topography of this PDMS stamp captures the particles as it passes through the interface. In preparation for this transfer, the substrate onto which these particles adhere (e.g., silicon) is placed inside a glass container. To this container, the water layer from a solution of destabilized particles was slowly added to ensure there is no contact between the particles at the liquid–liquid interface and the substrate. Next, the remainder of this particle solution was carefully added to the container, again ensuring there is no contact between the particles and the substrate. After a short time, the liquids separate into two distinct layers with the particles at the liquid–liquid interface. If necessary, the top solvent (e.g., hexane) was evaporated to form an air–liquid interface. A PDMS stamp was then brought through the liquid interface to transfer these particles to the substrate. The lateral and vertical positioning of this stamp were controlled with a computer-controlled motorized stage constructed with mechanical parts from Thorlabs, Inc. (Newton, NJ) (Figure B.1a). The PDMS stamp was brought through the interface at a downward rate of 20-200 µm/s until the stamp contacted the substrate (Figures B.1b and c). There was no apparent affect on the assembly of the particles with different rates of descent. While the stamp was still in contact with the substrate, the solvents and non-transferred particles were removed from the container. The adhesion between the 1.0 µm PS microspheres and the Si substrate was increased by heating the base of the
container to $97 \pm 1 \, ^\circ\text{C}$ for 10 min with a thermoelectric module from Ferrotec Corporation (Nashua, NH). Bubbles of water were released from under the stamp for $\sim 5\text{ min}$. When the solution of PS nanospheres was used, the substrate was heated to $94 \pm 1 \, ^\circ\text{C}$ for 5 min. to reduce melting of the nanospheres. (No heat was required to adhere gold nanoparticles to the silicon or polymer surfaces.) After 10 min, the substrate was cooled to $25 \, ^\circ\text{C}$ and the PDMS stamp was removed.

**Figure B.1:** (a) The overall setup of the assembly apparatus involves mechanical parts for stability, a computer controlled motor for position/velocity control of the stamp, and a thermoelectric heater and associated cooling lines for thermal control. (b) A magnified view of the assembly container before the PDMS stamp was brought through the liquid–liquid interface. (c) A magnified view of the assembly container after the PDMS stamp was brought through the interface into contact with the silicon wafer. This figure is reproduced with permission from ref. 54.
B.6 Imaging of Assembled Patterns

The assembled patterns of particles were examined by optical microscopy with a Zeiss Axio Imager.M1m microscope. Both dark-field and bright-field optical microscopy techniques were used to observe the samples. Scanning electron microscopy images were acquired with an FEI 235 Strata Dualbeam SEM at an accelerating voltage of 10 kV following the same procedure as was used to image the porous nanorods (see section A.5). The patterns containing polystyrene particles were sputter-coated with ~5 nm gold to assist with charge dissipation prior to imaging by SEM. TEM images of the gold nanoparticles were collected following the same procedure described in section A.5.
REFERENCES


39. Information from Sterlitech Corporation (Kent, WA).


46. Companies supplying these membranes include Sterlitech Corporation, SPI Supplies (West Chester, PA), and Whatman (Piscataway, NJ).
47. Pore density information from Sterlitech Corporation.
48. The silver electroplating solution was purchased from Transene Company, Inc. (Danvers, MA).


75. Polystyrene particles with diameters from 25 nm to 1 mm are available from Bangs Laboratories, Inc. (Fishers, IN).


86. Pricing information courtesy of Dow Corning (Midland, MI).


