and $G$ is the gravitational constant. From the meniscus seen in the cross-sectional SEM image, the contact angle is estimated to be about $85^\circ$. When we insert into Equation 1 the surface tension ($\sim 30$ dyne/cm) and density (0.95 g/cm$^3$) of SBS and $L$ of 300 nm, a maximum height of 1.87 m is obtained, which indicates that the height of the patterned polymer can be made quite large. In fact, we were able to fabricate polymer structures with a step height as high as 5 $\mu$m for an 80 $\mu$m line-and-space pattern. If we take into account the interaction at the polymer/substrate interface and the solid-like properties of the polymer melt, the theoretical maximum height would be reduced. For a more accurate model, further study would be required.

The time it takes for the polymer melt to fill up the void space between the mold and the polymer film can be estimated. If we neglect the effect of gravity, then the surface tension and viscosity of the polymer melt and the size of the capillary determine the rate of flow such that the time is given by

$$ t = \frac{2 \eta z^2}{\pi R_y \text{polymer/air} \cos \theta} $$

where $z$ is the length of capillary to be filled, $t$ is the time, $\eta$ is the viscosity of the polymer melt, and $R$ is the hydraulic radius (the ratio of the volume of the liquid in the capillary section to the area of the solid and liquid interface), which is approximately one half the width $L$. We observed that it took about 30 min for the SBS polymer to completely fill the void in the mold with a step height of 600 nm and a width of 400 nm at 100 $^\circ$C. The viscosity of the SBS is about $10^6$ [Pa s] from the rheometrics spectroscopy (RMS) measurement at zero shear stress. When we use these values in Equation 2, the time needed to fill the void in the mold is calculated to be 1377 s ($\sim 23$ min), which is a little shorter than the observed value.

Capillary force lithography presented here is a simple and yet robust method for large-area patterning. With further development the technique could become a strong candidate for an alternative to photolithography in fabricating large-scale integrated circuits.

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Seed-Mediated Growth Approach for Shape-Controlled Synthesis of Spheroidal and Rod-like Gold Nanoparticles Using a Surfactant Template**

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The size- and shape-controlled synthesis of metal nanoparticles is important in present day advanced materials, as almost every property within the nanometer regime are size and shape dependent.[1] Common methods for size control employ capping agents,[2] such as surfactants, ligands, polymers, or dendrimers, to confine the growth in the nanometer regime. These methods commonly produce spherical particles due to the low surface energy associated with such particles. However, the procedures for shape-controlled preparation of monodispersed nanoparticles are limited. Occasionally capping agents allow shapes other than spheres.[3] The mechanism of such shape control has recently been studied by El-Sayed et al. and Reetz et al.[4] Structures other than spheres form as a result of specific interaction of the capping agents with different growing faces of the particles.[4]

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Controlling shape of nanoparticles has been most successfully achieved using a template. Templates provide a constrained environment during the nanoparticle growth and thus shapes are tuned according to the template. Commonly used templates are porous alumina,[5] polycarbonate membranes,[6] carbon nanotubes,[7] and micelles.[8] In practice, the presence of templates does not produce 100% shape monodispersity; rather, a significant fraction of thermodynamically favorable spheres are also formed. In addition, soft templates such as micelles may not be stable under the experimental conditions (e.g., boiling), and thus the template may not function.[9] A common reason for the failure of the template mechanism is the change in template microstructures by reactants. We propose that the mechanism of conventional nanoparticle synthesis, which proceeds through successive nucleation and growth steps (the two steps tend to overlap with each other), also has direct consequence on the template mechanism. During nanoparticle synthesis, nucleation and successive growth are extremely sensitive to physical and chemical parameters.[2] In some of the solution-phase metal nanoparticle synthesis procedures, the control of nucleation and growth steps are done by changing the reducing agent or stabilizer concentration. In doing so, the size and shape of nanoparticles can be controlled.[2a,k,4] Similarly the control of nucleation and growth can produce different sizes and shapes of semiconductors (CdSe).[10] For solution-phase Au nanoparticle synthesis, we have observed an initial slow nucleation followed by a nucleation burst associated with autocatalytic surface growth.[11] We have controlled the nucleation and growth steps to prepare different sized spherical particles through a seed-mediated growth approach. Others have successfully employed a similar method for nanoparticle size control.[12] Herein we used this same growth strategy in the presence of a rod-shaped micelle[13] for template-mediated shape control. The same template was used earlier to prepare gold nanorods by an electrochemical approach.[14] Earlier attempts using photochemical reduction of a gold salt in the presence of the micellar template produced a mixture of nanorods and nanowires in addition to a significant fraction of small spheres.[15] A possible reason for the polydispersity in shape is the difficulty in controlling nucleation and growth and due to continuous nucleation occurring throughout the entire growth process. Pileni et al. reported successful shape control of copper nanorods by using a reverse micellar template.[8b] A similar template was also used for the preparation of barium sulfate,[6c] barium carbonate,[6c] and calcium sulfate nanowires.[9d]

The basic principle for our method of shape-controlled synthesis involves two steps: First, the preparation of small size spherical gold nanoparticles, and second, growth of the prepared spherical particle in rod-like micellar environment. Initial addition of preformed seeds has two advantages: first, it increases the overall reaction rate, and hence the growth rate; second, the particle size is controlled by varying the ratio of metal salt to seed, thus restricting the particle size to the nanometer regime. We employed ascorbic acid as the reducing agent of $Au^{III}$ salts in the growth stage. Ascorbic acid is a mild reducing agent and cannot reduce the gold salt in the presence of the micelle without the presence of seed. Consequently, minimal additional nucleation occurs during particle growth.

We prepared roughly spherical borohydride-reduced gold nanoparticle seeds with a mean diameter between 3 and 4 nm and mixed them with a growth solution containing gold salt, a rod-shaped micellar template, ascorbic acid (as the reducing agent), and small amount of silver ions (for shape induction). The importance of silver ions in the preparation of gold rods was observed earlier in the electrochemical synthesis of gold rods, where increasing silver ion concentration increased the aspect ratio of the gold rods.[14] Our results show successful production of spheroidal or rod-like gold particles exhibiting aspect ratios (varied from 1 to 10) that are dependent on the gold seed to gold salt ratio.

Figure 1a–h shows the ultraviolet-visible (UV-vis) spectra of rod-shaped gold particles with varied seed concentrations. A single peak around 530 nm appears for solutions containing relatively high seed concentrations (a and b). For sets c–h, two peaks appear for the gold surface plasmon band. One appears around 530 nm and is a conventional plasmon band for spherical particles. A separate plasmon band appears in the longer wavelength region, and its position depends on the aspect ratio of the rod. This band appearing, around 600–1600 nm, corresponds to the longitudinal plasmon resonance characteristic of rod-shaped particles.[1a,5,8,14] As the amount of seed was decreased, the aspect ratio increased, and this longer wavelength plasmon band gradually red-shifted and broadened. The seed performs a crucial role in the growth process. With increasing amount of seed, the rate of particle formation also increases. In the absence of seed, particle formation rate is very slow, no solution color change is observed, and a gray precipitate forms after approximately 24 h.
Figure 2 shows the transmission electron microscopy (TEM) graphs of gold nanoparticles (sets a–h) that correspond to the absorption spectra shown in Figure 1. The particles are either spherical (a and b), spheroidal (c and d), or rod-like (f–h). The average aspect ratio of the particles increased with decreasing amount of seed as the spheroidal particles gradually grew into rod-like structures. Spherical side products were also observed with the spheroidal and rod-like particles. However, the relative percentage of side products decreased considerably compared to previously reported solution synthetic methods where no seed was used. [15] This was corroborated from the appearance of additional intense plasmon bands at longer wavelength region that correspond to spheroids/rods. The average number of spherical side products ranged between 40–50 % of the total particles, as determined from counting ~1000 particles in the TEM images.

The lower aspect ratio spheroids are unstable under our experimental conditions and gradually convert to spheres. This was confirmed by their change in plasmon absorbance with time. For example, the long wavelength plasmon band of spheroidal particles in set c (aspect ratio ~1.5) gradually disappears within 24 h, leaving only one plasmon band at ~530 nm. However, all other spheroids and rods are stable for at least one month.

The presence of AgNO₃ is essential for producing and controlling the aspect ratio of spheroids/rods. In absence of Ag⁺, fewer rods (~10–20 % of the total particles) form and their aspect ratios are higher and have a wide distribution, ranging from ~5–15. The aspect ratio could not be controlled by varying the seed-to-metal salt ratio when silver ions were not present in solution. We performed separate experiments to understand the fate of the silver ions added for shape control. After adding silver salt to a solution mixture of gold seed, cetyl-trimethyl ammonium bromide (CTAB), and ascorbic acid, we did not observe the characteristic silver plasmon band at 400 nm. We propose that the Ag⁺ forms AgBr (Br⁻ from the CTAB), and because ascorbate is a weak reducing agent, it cannot reduce the silver ion. However, when the pH of the solution was increased by adding NaOH, the reducing power of ascorbate also increased.[16] As a result, silver ions reduced to form silver nanoparticles as judged by a plasmon band occurring around 400 nm. This result confirms that silver ions are not reduced under our experimental (lower pH) reaction conditions. The mechanism by which Ag⁺ assists in controlling metal particle shape is not completely understood; however, we observed a decrease in particle formation rate in the presence of silver salt. We hypothesize that Ag⁺ adsorbs at the Au particle surface in the form of AgBr and restricts growth. The adsorption of AgBr at the Au particle surface appears to stabilize the spheroids and rods. In absence of Ag⁺ the spheroids formed, but due to their instability, converted to spheres. The higher aspect ratio rods were more stable and formed even in the absence of Ag⁺. By using larger amounts of silver ions we were able to prepare φ shaped particles, which appear as hybrids between spheres and rods (Fig. 3).

In the previous electrochemical synthesis, cyclohexane was used in the preparation of gold rods.[14] The role of the cyclohexane was to elongate the micellar structure to form a more rod-like template.[13] We have seen that rods are formed in the absence of cyclohexane, but addition of cyclohexane increases the aspect ratio. If we consider that additional nucleation does not appear, and only autocatalytic surface growth...
occurs at the preformed seed surface, then the final particle size can be calculated for spherical particles from the following equation:

\[ r = r_c \left( \frac{[M_0]}{[M_0] + [M_1]} \right)^{1/3} \tag{1} \]

where \( r_c \) and \( r \) indicate particle radius for seed and larger particle, and \([M_0]\) and \([M_1]\) indicate metal concentrations in seed and added ion.\(^{11,12}\) Our observations show that final particle sizes closely match the calculated value for spherical side products and lower aspect ratio spheroids but were larger (1.5–3.0 times) for rods. Faster growth rates along the nanorod long axis possibly contributes to the larger size of the rods. The role of micellar template is to direct the particle growth along one dimension, and finally stabilize the rods. Thus a simple seed-mediated growth approach is used to prepare gold spheroids and nanorods with different aspect ratios which can be controlled by varying the ratio of seed to metal salt.

**Experimental**

**Instrumentation:** Absorption spectra of the prepared solutions were measured using a CARY 500 Scan UV-vis-near-infrared (UV-vis-NIR) spectrophotometer. TEM images were acquired with a JEOL JEM-100CXII electron microscope.

**Preparation of Growth Solution:** First, 100 mL of 250 \( \mu \)M HAuCl\(_4\) aqueous solution was prepared in a conical flask. Next 3.0 g of solid CTAB, 1.5 mL of cyclohexane, and 2.0 mL of acetone were added to the gold salt solution. The role of acetone is to loosen the micellar framework, and cyclohexane is necessary to enhance the rod-like micellar structure. The solution was heated to 60°C while stirring to dissolve the CTAB. After allowing to cool to room temperature, the solution was used as the growth solution.

**Preparation of 3–4 nm Au seeds:** First, a 20 mL aqueous solution containing 0.25 mM HAuCl\(_4\) and 0.25 mM trisodium citrate was prepared (trisodium citrate acts as a capping agent and thus restricts particle growth). Next, 0.6 mL of a 0.01 M NaBH\(_4\) solution was added at once into the gold solution under constant stirring. Stirring was continued for another 30 s. The solution turned a wine red color indicating particle formation. The solution was used as a stock gold seed solution 4 h after its preparation, allowing all the excess borohydride to degrade. The solution should be used within 24 h of its preparation. Beyond this time a thin gold film forms at the water surface, indicating particle aggregation.

**Growth of Spheres and Rods:** Eight different sets of solutions were prepared each containing 10 mL of growth solution and varying amounts (1.00, 0.50, 0.25, 0.125, 0.09, 0.06, 0.03, and 0.015 mL) of Au seed solution. 5 mL of 10 mM AgNO\(_3\) was added to each set and mixed thoroughly. Finally, 0.50 mL of freshly prepared ascorbic acid (10 mM) was mixed with each set. The color of the solutions turned pink to violet within 10 min, depending upon the amount of seed present.

**Preparation of TEM Grid:** The TEM graphs were taken after separating the surfactant from the metal particles by centrifugation. Typically 1 mL of the sample was centrifuged for 12 min at a speed of 14,000 r/min. The upper part of the colorless solution was removed and the solid residue was dispersed in 1 mL of water. 2 \( \mu \)L of this redispersed particle suspension was placed on a carbon coated copper grid and dried at room temperature.

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**Sol–Gel Template Synthesis of an Array of Single Crystal CdS Nanowires on a Porous Alumina Template**

By Huaqiang Cao, Yan Xu, Jianming Hong, Huibiao Liu, Gui Yin, Baolong Li, Chenyang Tie, and Zheng Xu*

The research field of one-dimensional nanostructured materials constitutes one of the most important frontiers in materials science. These materials are of fundamental importance, e.g., nanowires and nanotubes have great potential for testing and understanding fundamental concepts about the roles of dimensionality and size on physical properties, and they hold promise for a wide range of potential applications, including chemistry, physics, electronics, optics, materials science, and biomedical sciences. Many attempts have been made to fabricate one-dimensional nanostructured materials. However, it is still a challenge to produce an ordered, monodisperse, single crystal nanowires array. The template method is one of the most efficient methods for the synthesis of well-distributed tubular and fibrillar nanostructures within the pores of an alumina membrane or other nanoporous solid. Alumina membranes have been used as an ideal template to prepare cylindrical nanowires with a narrow diameter distribution, because they possess uniform and nearly parallel porous structures. But the template method generally produces polycrystalline materials. With the sol–gel template method we have fabricated arrays of single crystal C_{30} and C_{70} nanowires.

Cadmium sulfide is an important semiconductor material, and has received much interest. Electrochemical deposition of CdS nanowires in the pores of an alumina membrane has been reported. However, this method results in a lot of stacking faults and twinned segments in these nanowires; moreover, the alumina membrane is not stable in conventional aqueous acid electrolytes containing Cd^{2+} and sources of colloidal sulfur. Recently, an aligned CdS single-crystal nanowire array was synthesized by electrochemical deposition. Here we report a new way to fabricate an ordered array of single-crystal CdS nanowires in an alumina membrane by the sol–gel method.

The array of CdS nanowires was obtained in the pores of an alumina membrane with 100 nm diameter. The alumina template was immersed in a Na_{2}S solution containing mercapto ethanol (HSCH₂CH₂OH). It well known that alumina is a Lewis acid with the acidity center on Al³⁺; the S²⁻ ions will preferably attach to the alumina wall, at the reaction with Cd^{2+}, and induce the deposition of colloidal CdS particles on the alumina membrane. It is important to note that deposition does not work when the alumina template is immersed in the CdCl₂ solution first, and the CdS mainly precipitates on the surfaces of the alumina membrane. HSCH₂CH₂OH is used as a protecting agent absorbed on the surface of the CdS colloidal particles to make the CdS particles very fine. Figure 1 shows scanning electron microscopy (SEM) images of the CdS nanowires arrays. The lengths of the nanowires are ca. 60 μm, corresponding to the thickness of the alumina template.

Figure 2a shows a transmission electron microscopy (TEM) image of the CdS nanowire obtained after removal of the alumina membrane by dissolution in 6 N NaOH. The electron diffraction data are shown in Figure 2b. Analysis of the electron diffraction pattern proves that only crystals with a wurtzite structure are present. Furthermore, the CdS nanowires synthesized here are single crystals, and the pattern can be indexed as (102), (104), (203), and (105) with d = 2.421, 1.502, 1.439, and 1.244 Å, respectively. This matches well with the hexagonal crystalline CdS (ASPDF 6-0314) structure with an error <3%.

The length of isolated nanowires is shorter than the thickness of the alumina template, which may be disrupted when pol-