Orthogonal Self-Assembly on Colloidal Gold-Platinum Nanorods**

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One of the reasons for the enormous recent effort in nanoparticle synthesis[1] is an interest in producing complex superstructures by self-assembly.[2] Most of this work has been carried out using spherical or isotropic particles, consequently leading to isotropic two- and three-dimensional materials.[3] One possible route to anisotropic structures, of interest for electrical[4] and optical[5] applications, is to use anisotropic nanoparticles as building blocks. We report here the fabrication of striped, bimetallic (Au-Pt-Au) rod-shaped colloidal particles (Scheme 1). We also show that the different chemical reactivity of Pt and Au towards thiols and isocyanides[6] can be used to effect spatially selective chemical modification within individual nanoparticles (Scheme 2). The preparation and chemical manipulation of anisotropic colloidal building blocks, described herein, represents a first step towards anisotropic mesoscale assembly and other materials chemistry applications.

The synthetic protocol used to prepare striped metal nanorods derives from the pioneering work of Martin and Moskovits on template-directed electrochemical synthesis.[7] In this approach (Scheme 1), metals are deposited electrochemically inside a porous membrane.[8] Our synthetic method differs from previous work in three respects. First, the electroplating is done in an ultrasonication bath. Second, the temperature is controlled using a recirculating temperature bath and third, different metals were plated sequentially to form striped rod structures (Fig. 1).[9] The first two modifications increase the reproducibility and monodispersity of rod samples by facilitating the mass transport of ions and gases through the pores of the membrane. The introduction of two different metals allows us to use the anisotropy of the rod structure to selectively functionalize portions of the nanoparticles.

Optical and electron microscopy was used to assess the quality and polydispersity of the rods. Figure 2 shows a histogram of lengths for 200 nm diameter gold rods for which the total charge passed was 1, 2, and 4 C. Rod length, measured by TEM, is proportional to the charge, the pore density, and the area of the membrane. We measured a polydispersity of ±8%, which is independent of the length of the rods.

**[**] This work was supported by DARPA and ONR under contract number N00014-98-1-0846. MJN thanks the Alfred P. Sloan Foundation for support in the form of a research fellowship. We also thank Prof. Charles Martin for providing a preprint of reference [21].

[9] The hexagonally ordered structure remains unchanged with addition of the initiator, as confirmed by optical polarized microscopy.
The diameter of a rod is equal to the diameter of the pore in which it was grown. In this case, rod diameters are nominally 200 nm, but can vary from batch to batch between 200 and 300 nm. We observed similar trends for pure Pt rods, except that more charge per unit length was needed than for Au.[11] Under the conditions used here, 1 C of Au = 4 C of Pt = 1.3 μm with a membrane active area of 3.14 cm². Since TEM cannot easily distinguish between Pt and Au, optical microscopy (Olympus BX60MF optical microscope) was used as a qualitative tool to image the relative lengths of metal sections in multimetal rods. An example of such an optical image is shown in Figure 1. Since the diameter of a rod is smaller than the wavelength of visible light, the apparent aspect ratios of the rods are decreased in the optical images.

In order to effectively manipulate and derivatize the rods in the bulk phase, two factors must be controlled: the tendency for the rods to aggregate due to van der Waals interactions, and the effect of gravity on the dense metal rods. Solvation of the rods can be enhanced by forming self-assembled monolayers (SAMs) with an appropriate tail group on the metal. For example, to enhance suspension of gold rods in water, a hydrophilic SAM such as 2-mercaptoethylsulfonic acid can be used. Likewise, to enhance suspension of platinum rods in hexane, a hydrophobic SAM such as 1-butaneisocyanide (BIC) can be used. Rod settling due to gravity can be minimized by slowly tumbling the sample. Tumbling at ca. 10 Hz can increase rod suspension lifetimes by one order of magnitude or more.

Other groups have reported anisotropic particles and assemblies. Using the template method, Moskovits and Martin have made magnetic ferrite rods,[12] conducting polymers,[13] hollow tubules,[14] and rod-like semiconductor particles.[15] In addition, some work has been carried out on multi-metal striped rods of Co/Cu,[16] and Ni/Cu,[17] which have applications in giant magnetoresistance. The multi-metal structures reported in those studies resemble alternating thin metal disks stacked together, rather than long segments of a single metal. Some examples of non-template based anisotropic colloid production include surfactant-induced electrochemical synthesis of rod-shaped gold colloids, which vary in length but have very monodisperse diameters.[18] Also, the shape of platinum colloids (cubic, tetrahedral, octahedral, or icosahedral) can be controlled by adjusting the ratio of capping material to Pt²⁺.[19] BaCO₃ fibers with giant aspect ratios (10 000) have been made by allowing ions stabilized in reverse micelles to react together in solution.[20] Recently, Martin and coworkers have also shown that biotin–streptavidin interactions can be used to link template-bound metal rods to latex spheres.[21] Whitesides’ group has experimented with millimeter scale self-assembly of anisotropic particles. Polymer cubes have been assembled into large 3-D cubic lattices using hydrophobic/hydrophilic interactions.[22] Similar chemical interactions...
were also used to organize hexagonal structures into pre-defined assemblies based on the geometry of the functionalized surfaces, a process akin to molecular recognition.[23]

Like Whitesides’ millimeter scale self-assembled structures, the functionalized rods presented here have the potential to be programmed for self-assembly. In this work we selectively derivatized Au/Pt/Au rods using an orthogonal self-assembly scheme originally described by Whitesides and Wrighton (Scheme 2).[6] Isonitriles form SAMs on both gold and platinum, but thiols displace isonitriles from gold when the thiol solution is sufficiently concentrated (40:1 thiol to isonitrile ratio). In order to demonstrate that multi-metal rods had been produced, and that orthogonal self-assembly was effective with this colloidal system, the gold portion of a multi-metal rod was tagged with Rhodamine B isothiocyanate and then imaged using fluorescence microscopy.

Studies on fluorescently-tagged monolayers have addressed the issue of fluorescence quenching near a metal surface. Although fluorescence in a SAM is attenuated by nonradiative energy transfer to the metal, it is still strong enough for detection.[24] For example, Karpovich and Blanchard studied the signal from a 1-pyrenebutanethiol fluorophore in a 1-octadecanethiol SAM.[25] They used a mixed monolayer, with the fluorophore inserted in a monolayer of SAM-forming molecules with unreactive tail groups. We have used a similar strategy, by covalently attaching an isothiocyanate-functionalized probe molecule with the terminal amine groups of thiol molecules inserted into a BIC monolayer. Scheme 2 illustrates the procedure used to derivatize multi-metal rods. The “naked” Au-Pt-Au rods shown in Figure 1 were first derivatized with BIC, then 2-mercaptoethylamine (MEA), and finally Rhodamine B isothiocyanate.[26]

Following the surface derivatization steps outlined above, the rods were analyzed using fluorescence microscopy. Figure 3 shows fluorescence micrographs of three separate samples of derivatized Au, Pt, and Au-Pt-Au rods. Fluorescence images were obtained using a Nikon Optiphot microscope fitted with a green fluorescence cube, and were compared to dark-field images obtained from the same regions. The first image (Fig. 3a) clearly shows that 8 C platinum rods do not fluoresce at all when subjected to the treatment outlined above. In contrast, 2 C gold rods (Fig. 3b) fluoresce along the entire length of the rod. Figure 3c shows a fluorescence micrograph of the same multi-metal 1 C Au/8 C Pt/2 C Au rods shown in Figure 2. Only the gold tips of the multi-metal rods are fluorescent as a result of the thiourea link between Rhodamine B and mercaptoethylamine bound to the gold surface. The control experiments show that the fluorescent tips of the multi-metal rods are not an artifact. A final control experiment was carried out by derivatizing a striped rod sample with BIC, 1-decanethiol, and then Rhodamine B isothiocyanate, under conditions similar to those described above. This sample contains no amine tail groups to form isothiocyanate link-
proped up by flanking BIC molecules. The change in orientation and proximity of the fluorophore could increase the efficiency of nonradiative energy transfer from Rhodamine B to gold. Alternatively, BIC could separate and space the MEA groups in a way that reduces self quenching of the Rhodamine B molecules. Fluorescence was always observed when the rods were exposed to BIC followed by MEA. We are currently carrying out more detailed structural characterization experiments to determine the differences between MEA monolayers prepared by the two methods.

In conclusion, we have shown that it is possible to make segmented multi-metal rods of controllable length by electroplating in a porous template membrane. In addition, it is possible to control the surface chemistry of different metals within a single colloidal particle, after it has been released from the membrane, by means of orthogonal self-assembly. Ultimately it may be possible to use specific attractive and repulsive interactions between selectively functionalized segments of these rods to direct the assembly of rod dimers and oligomers, to prepare 2-D assemblies based on rod-substrate epitaxy, and to prepare 3-D colloidal crystals from rod-shaped objects. Experiments along these lines are currently in progress.

Received: March 26, 1999

[8] Rods were deposited using commercially available gold (Technic Ortem temp 24) and platinum (Technic TP) plating solutions while sonating at a constant current density of 0.55 mA/cm² until the desired rod length was achieved. A 200 nm pore diameter Whatman Anopore disk was pretreated by evaporating 150 nm of silver on the branched side of the membrane. Since this evaporated silver does not completely fill the pores on this side, 1 C of silver was electroplated at a current density of 0.55 mA/cm² onto the evaporated silver. A final silver plating step at the same current density into the pores of the membrane ensures that no leaks will occur through the back electrode. After the electroplating of gold and platinum was complete, the silver electrode was removed by brief immersion of the membrane in 6 M nitric acid, and the alumina membrane was dissolved in 0.5 M KOH for 2 h. The resulting Au, Pt, or Au-Pt-Au rods were repeatedly centrifuged and washed with water to remove residual base and salts. In order to grow “striped” Au-Pt or Au-Pt-Au rods, the gold plating solution was rinsed out of the membrane with Nanopure water under conditions of low cathodic current density (0.1 mA/cm²), before a platinum plating solution was added. The ionic strength of the solution was increased to 0.55 mA/cm² until the desired rod length was achieved. A 200 nm pore diameter Whatman Anopore disk was pretreated by evaporating 150 nm of silver on the branched side of the membrane. Since this evaporated silver does not completely fill the pores on this side, 1 C of silver was electroplated at a current density of 0.55 mA/cm² onto the evaporated silver. A final silver plating step at the same current density into the pores of the membrane ensures that no leaks will occur through the back electrode. After the electroplating of gold and platinum was complete, the silver electrode was removed by brief immersion of the membrane in 6 M nitric acid, and the alumina membrane was dissolved in 0.5 M KOH for 2 h. The resulting Au, Pt, or Au-Pt-Au rods were repeatedly centrifuged and washed with water to remove residual base and salts.

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Rods, suspended in ca. 2 mL hexane, were added to 2 mL of 1 mM 1-

This is a consequence of the fact that the reduction of Pt II requires
twice as much charge as that of Au I. In addition, the current efficiency is lower for Pt, in part because the surface acts as a catalyst for hydrogen evolution.

Liquid-crystalline (LC) polymers containing photochromic side groups have attracted great interest because of their potential application as unique materials for data recording and optical data storage. Many publications have been devoted to comb-shaped LC polymers containing side-chain azobenzene groups. [1,2] The appearance of induced birefringence in the films of such polymers under the action of polarized light and possible applications of such materials for data recording have been studied in detail.

Another wide class of photochromic compounds involves derivatives of spiropyran and spirooxazine [1–5] These compounds are characterized by a marked photochromism. In this case, UV irradiation leads to the appearance of an intensive absorption peak in the visible spectral region (550–620 nm), which is explained by the transition of the spiro forms of such compounds to merocyanine forms, as shown in Scheme 1. [1,3,5] This process is thermally and photochemically reversible, which allows one to use such compounds for repeated data recording and optical data storage.

Numerous works have been devoted to photosensitive polymers containing spiropyran and spirooxazine side groups. [1,4–6,8] However, one should note that, despite intensive study, no information concerning cholesteric polymers containing such photochromic groups is available. A combination of photochromic properties and helical supramolecular structure in the united polymer system offers wide opportunities for varying optical properties of such materials under the action of external fields (electric and magnetic fields) and light illumination. Furthermore, the presence of photosensitive units allow one to use such copolymers for reversible data recording on colored backgrounds (with selective light reflection).

**Photosensitive Cholesteric Copolymers with Spiropyran-Containing Side Groups: Novel Materials for Optical Data Recording**

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![Scheme 1](image-url)