Template synthesis of polymer-insulated colloidal gold nanowires with reactive ends†

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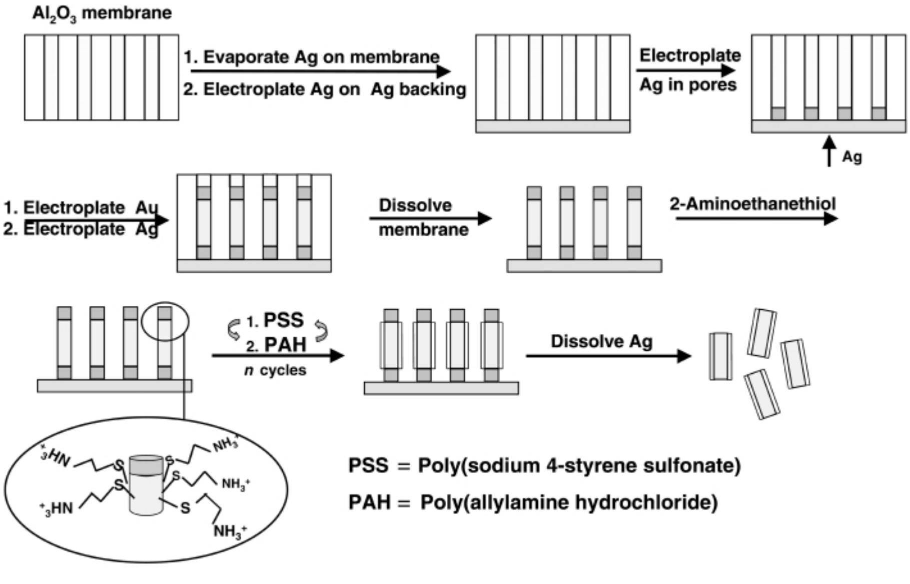
Alternate adsorption of anionic and cationic polyelectrolytes creates smooth organic films on the walls of template-grown Au nanowires, which can be made chemically reactive on their ends by removal of a sacrificial Ag layer.

Much of the current research on nanophase materials focuses on the synthesis of colloidal particles of controlled size, shape, and surface chemistry. These particles are interesting as building blocks of larger superstructures, which have possible applications in electronics, photonics, catalysis, chemical sensing, and other areas. Monodisperse collections of spherical and polyhedral nanoparticles are known to crystallize into well ordered two- and three-dimensional arrays.[1] On the other hand, it is now becoming clear that less symmetric particles and linkers can give rise to more complex and interesting superstructures, both on the nanoscale[2] and on larger length scales.[3] Recently, we have studied the synthesis and assembly of rod-shaped colloidal particles.[4] This synthesis, which involves the electrochemical replication of porous alumina and polycarbonate membranes, allows one to make cylindrical wires with a controlled sequence of ‘stripes’ along their length. Different metal stripes selectively adsorb self-assembled monolayers (SAMs) or DNA oligomers, which can be used to direct the assembly of these particles on surfaces. Here, we report the stepwise formation of multilayered organic films on the cylindrical walls of Au nanowires by alternate adsorption of monolayers of poly(styrene sulfonate) (PSS) and poly(allylamine hydrochroride) (PAH). By removing a sacrificial Ag layer from the tips, it is possible to prepare nanowires that are chemically insulated along their length, but reactive at their ends. This reactivity is demonstrated by covalently linking fluorescent dye molecules exclusively to the exposed ends of the nanowires.

The porous templates used for the electrosynthesis of Au nanowires were commercially available Anodisc alumina membranes (200 nm pore size, 8.9 × 10^8 pores cm^{-2}, 60 μm thickness). Au replicas were made by a modification of the methods of Possin,[5] Martin[6a] and Moskovits.[6b] Ag was thermally evaporated onto the branched side of the alumina membrane to make the membrane electrically conductive (*ca.* 200 nm thick Ag). Ag was then electroplated (using Technic Silver 1025 plating solution) onto the evaporated Ag film to increase its thickness around to *ca.* 2 μm. The narrow branched pores were filled with Ag at a current density of 0.55 mA cm^{-2} of the membrane. Au was then grown electrochemically inside the pores by changing the electroplating solution (to Technic Orotemp 24). After the Au wires were grown to the desired length (2–6 μm), another 500–800 nm of Ag was grown. The metal-filled membrane was then glued to a glass slide and the alumina template was dissolved using NaOH solution. This left the Au nanowire array attached to a silver base, and left each nanowire capped with Ag. Suspensions of free Au nanowires were prepared by first dissolving the alumina membrane in NaOH and then the Ag backing and capping layers in nitric acid.

The surface derivatization of Au nanowires by polyelectrolyte multilayers[7] was performed as shown in Scheme 1. The nanowire array was first reacted with 2-aminoethanethiol hydrochloride to render the Au surface positive. The derivatized surface was then dipped in a solution of poly(sodium 4-styrene sulfonate) (PSS) (average molecular weight ≅ 70,000), which



Scheme 1 Strategy for formation of a multilayer polyelectrolyte film on a gold nanowire array.

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† Electronic supplementary information (ESI) available: colour versions of Scheme 1 and Figs. 1 and 2. See http://www.rsc.org/suppdata/cc/b0/b007999p/

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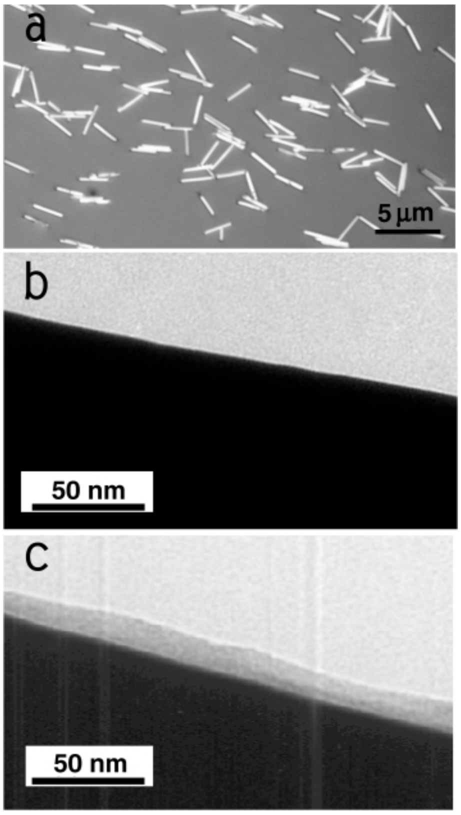

Fig. 1 (a) Optical micrograph at 1000× magnification of 2.4 µm Au nanowires, and TEM images of (b) an untreated Au nanowire and (c) an Au nanowire derivatized with a multilayer film of alternating polyanions and polycations as shown in Scheme 1.

contains negatively charged sulfonate groups in the polymer chain. In this step, anionic PSS adsorbs onto the positively charged surface and inverts the surface charge. The samples were then washed several times with water and reacted with poly(allylamine hydrochroride) (PAH) (average molecular weight ≅ 15,000), which contains positively charged $-NH_3^+$ groups. The polyanion, wash, polycation, wash cycles were repeated 10 times in order to produce multilayer films. Finally, the derivatized Au nanowires were freed from the surface by dissolving their Ag backing and caps in aqueous HNO_3.

Optical and electron microscopy was used to assess the quality of the nanowires and surface films. Fig. 1(a) and (b) show optical and transmission electron micrographs (TEM) of the nanowires. Many identical particles are produced by replication of a single membrane, and the underivatized nanowires have smooth, clean surfaces after the alumina template is dissolved away. Fig. 1(c) shows a TEM image of the surface of a gold nanowire modified by ten alternate adsorptions of PSS and PAH according to Scheme 1. Note the formation of a smooth polymer film with a thickness of *ca.* 13 nm, which is consistent with the 1 nm per bilayer typically found for adsorption of PSS/PAH on planar substrates.[7]

Because the top and bottom of the nanowires are capped with Ag during the polyelectrolyte adsorption steps, removal of Ag creates a clean surface that is chemically distinct from the 'insulated' cylindrical walls. This property was tested by reacting the free nanowires with 2-aminoethanethiol to form a self-assembled monolayer on the exposed surface. The thiol-treated nanowires were then reacted with fluorescein isothiocyanate and imaged using fluorescence microscopy. Studies on fluorescently-tagged monolayers have addressed the issue of fluorescence quenching near a metal surface. Although fluorescence is attenuated by non-radiative energy transfer to the metal, it is still strong enough for detection.[4,8,9] Fig. 2 compares a fluorescence optical micrograph of the derivatized nanowires with brightfield reflectance images from the same regions. Only the tips are fluorescent as a result of the thiourea link between isothiocyanate-functionalized probe molecule and 2-aminoethanethiol bound to the Au surface, confirming that both ends are accessible to the probe molecules. In contrast, the length of the nanowires are non-fluorescent, confirming that they are covered by a multilayer films that is not affected by the thiol–isothiocyanate derivatization steps.

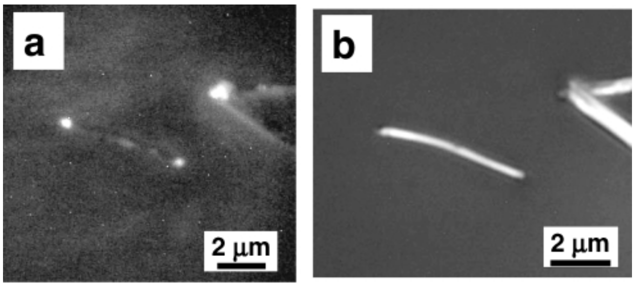

Fig. 2 Optical micrographs of Au rods derivatized with polymer multilayers according to Scheme 1, then etched to remove Ag from the tips and reacted with 2-aminoethanethiol and fluorescein isothiocyanate. (a) Fluorescence micrograph image and (b) a bright-field micrograph image of the derivatized rods on a quartz substrate.

In conclusion, we have successfully derivatized gold nanowires by alternate adsorption of the anionic and cationic polyelectrolytes poly(styrene sulfonate) and poly(allylamine hydrochroride). This process leads to smooth multilayer films around the Au surface, but not on surfaces that are first capped with Ag. It is now possible to selectively derivatize these nanowires, thus opening a door to possible applications in nanoscale electronics and other areas.

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