

Fabrication of nanostructure via self-assembly of nanowires within the AAO template

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Abstract The novel nanostructures are fabricated by the spatial chemical modification of nanowires within the anodic aluminum oxide (AAO) template. To make the nanowires better dispersion in the aqueous solution, the copper is first deposited to fill the dendrite structure at the bottom of template. During the process of self-assembly, the dithiol compound was used as the connector between the nanowires and nanoparticles by a self-assembly method. The nanostructures of the nano cigars and structure which is containing particles junction are characterized by transmission electron microscopy (TEM). These kinds of novel nanostructure will be the building blocks for nanoelectronic and nanophotonic devices.

Keywords Self-assembly · AAO template · Nanostructure · TEM

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Introduction

Nanoscale electronics promise to deliver ultra high-density memory and logic circuits that can be realized with dimensions well below the scaling limits of

conventional microfabrication techniques. To realize this aim, considerable attention has been devoted to developing molecular-level devices that function as nonlinear circuit elements and nanowires that interconnect these circuit elements. Nanowires have attracted extensive interest because of their interesting electronic and optic properties and because of their potential applications as building blocks for nanoelectronic and nanophotonic devices [1]. These metal nanowires are synthesized in the different ways. In one method, they are grown in the solution phase by using a surfactant mixture, which provides selective control over growth rates of different crystal faces [2, 3]. In another method, they are also prepared within the nanoporous template electrochemically.

Compared to solution and vapor-phase techniques, the template method fulfills the requirements of future electronic applications particularly well because it provides the simple technique, inexpensive synthesis of uniform nanowires with controllable aspect ratio as well as the possibility of the spatial selectivity in the functionalization of nanowires.

In 1995 Masuda and Fukuda reported the two-step anodization process, in which they obtained self-ordered alumina structures [4]. Based on this process, new areas of applications have emerged in the fields of magnetic storage [5], solar cells [6], carbon nanotubes [7], catalysts [8] and metal nanowires [9, 10]. This increasing attraction of porous alumina as template is mainly due to both its ease and its low-cost of processing. Under appropriate anodic oxidation conditions, very regular self-ordered, honeycomb-like hexagonal arrays with a circular pore at the centre of each hexagon can be obtained. Using the ac electro-deposition, the desired metals are deposited within the

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pores of membrane. Therefore, the chemical modification spatially is realizable on the exposed top of nanowires by self-assembly method.

Mallouk et al. have prepared the metal nanowires containing in-wire monolayer junctions of 16-mercaptohexanoic acid by replicating of the pores of 70 nm polycarbonate track etch membrane [11]. However, fabricating the novel nanostructures by combining the nanoparticles with template-synthesized nanowires by the self-assembly method are seldom reported. In our paper, we used a very simple technique of spatially modifying the nanowires within the template to fabricate the novel nanostructures. The nanostructure like “cigarette” were synthesized by self-assembly of the multiple layers of nanoparticles on the top of the nanowires. The incorporation of self-assembled nanoparticles between the nanowire segments was obtained by the electrodeposition the gold layer over the nanoparticles within the anodic aluminum oxide (AAO) membranes.

Experimental section

Chemicals

$\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ and 1,9-nonanedithiol were obtained from Aldrich Chemical Co. All the other chemicals were used without further purification.

Fabrication of AAO template and gold nanowires within the template

The highly purity aluminum sheets (99.99%, 40 mm × 10 mm × 0.25 mm) were degreased and annealed at 400 °C for 2 h to remove the mechanical stresses and to recrystallize structure [12, 13]. To smooth the surface morphology, the aluminum sheet was electropolished in a 5:1 v/v mixture solution of $\text{C}_2\text{H}_5\text{OH}$ (95%)/ HClO_4 (70%) at 10 V for 2 min. In the anodization step, the treated aluminium sheet was anodised at constant voltage of 40 V in the 0.3 M oxalic acid solutions at 5 °C for 3 h in order to form the porous structure. Subsequently, the oxide layer is removed by wet chemical etching in a mixture of phosphoric acid (6 wt%) and chromic acid (1.8 wt%) at 60 °C. To get more uniform and ordered porous template, the second anodization step with the same parameters was repeated. During the anodization process, the electrolyte was vigorously stirred during anodization in order to maintain temperature and electrolyte concentration uniformity.

The home-made ac electrochemical deposition system has been set up, which provides up to 20 W (rms,

30 V, 10 Hz to 10 kHz) output [14]. During the experiments, we found that it is difficult to obtain the well-dispersed individual gold nanowires due to the dendrite structure at the bottom. To solve this problem, the copper was deposited to fill in the dendrite structure prior to the gold deposition. The copper was deposited in the pH: 4.5 electrolytes consisting of 0.2 M CuSO_4 and 0.1 M H_3BO_3 at 20 °C and 10 V ac (200 Hz). Gold was deposited onto the copper layers in the electrolyte containing $\text{HAuCl}_4 \cdot 4\text{H}_2\text{O}$ (0.93 g/L) and boric acid (30 g/L) at 20 °C using graphite counter-electrodes. The aluminum base was removed by immersing the plate in the saturated HgCl_2 solution to remove the aluminium substrate and obtain the Au/Cu/AAO membrane.

Fabrication of nano “Cigarette” by self-assembly

The site-specific anchoring of nanoparticles on nanowires to form the novel structures-nano “cigars” within the porous AAO template was obtained as following the steps of Fig. 1. The spatial modification of the gold nanowires within the AAO membrane was treated by first immersion in the ethanol solution of 1,9-nonanedithiol (1 mM) for 2 h to form the monolayers on the top of the nanowires within the template. The membranes were then rinsed by ethanol to remove the excess of dithiol physically absorbed on the surface of the membrane. Subsequently, the treated sample was immersed in the gold sol solution to incubate overnight. (The stable and dispersed 5–8 nm gold nanoparticles in toluene were prepared by a two-phase method which was originally created by our lab [15]. The two-phase redox reaction was carried out by AuCl^- transferred from aqueous solution to toluene using tetraoctylammonium bromide as the phase-transfer reagent and reduced with aqueous sodium borohydride.) The modification procedures steps are repeated for several times to form the multiple layers on the exposed top of the gold nanowires within the template [16, 17].

In order to enhance the dispersion of gold nanorods in aqueous solution, the aminodextran polymer-surfactant is introduced into dissolving the alumina membrane. Aminodextran containing free amines and sugars can react with gold surfaces as ligand. The membrane was placed in 500 μL of 1 M NaOH, 50 μg aminodextran (FW: 70,000 MW) and was left to stand for 2 h. The solution is centrifuged once to remove the excess NaOH and then treated by 1 M HNO_3 to dissolve part of the copper nanowires. The centrifugation was employed again to remove the excess acid solution.

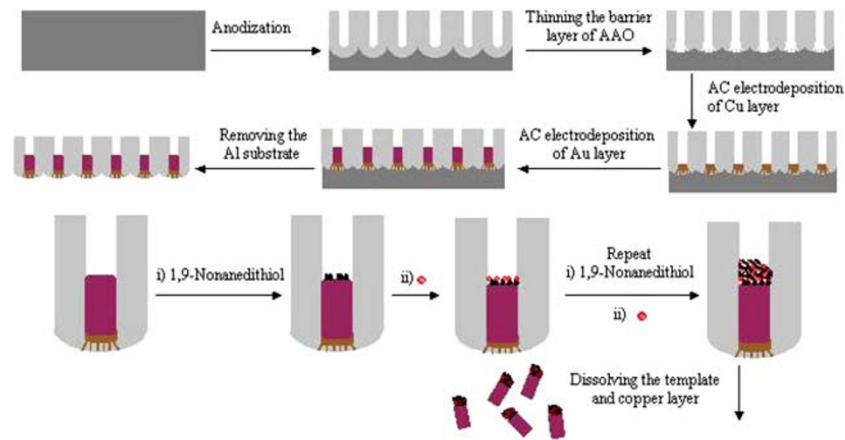


Fig. 1 Schematic diagram describing the fabrication steps of nano “cigars” based on the porous AAO template. Prior to the electrodeposition step, the thinning of the barrier layer is necessary to form the dendrite structure at the bottom. The copper as the first layer was electrodeposited and gold is then

electrodeposited on it. The spatially chemical modification of the gold cap was performed by immersing the membrane in the dithiol ethanol solution and gold sol solution, respectively. The nano cigars’s structure was obtained after dissolving the alumina porous template and the copper layer in the etching solution

Fabrication of nanoparticles junctions between the nanowires

Figure 2 shows the fabrication steps of in-wire junction of nanoparticles by layer-by-layer assembly within the porous template.

Based on the above procedure, the Au/Cu/AAO substrate is directly immersed in 1,9-nonanedithiol (1 mM) in ethanol for a few hours. After that, membranes were rinsed by ethanol to remove the excess of dithiol physically absorbed on the surface, and then immersed in the gold sol solution for overnight. Subsequent layers were deposited by repeated alternated immersion in gold sol and dithiol solution, respectively. Afterwards, the sheet was immersed in the saturated HgCl_2 solution to remove the aluminium substrate and obtain the An/NPs/Au/Cu/AAO membrane. The membrane was placed in

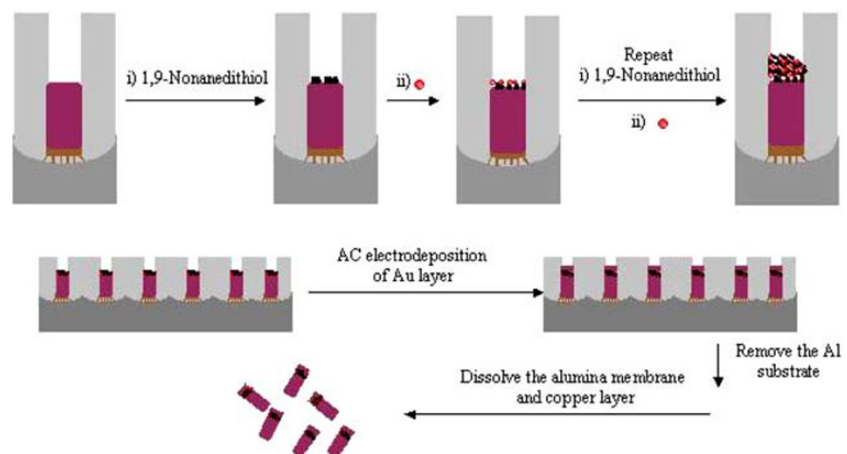
500 μL of 1 M NaOH, 50 μg aminodextran (FW: 70,000 MW) and is left to stand for 2 h. The solution is centrifuged once to remove the excess NaOH and then treated by 1 M HNO_3 to dissolve the part of copper nanorods. The centrifugation was employed again to remove the excess acid solution and the gold nanorods were then dispersed in the distilled water.

Apparatus

The explorer scanning probe microscope (SPM) (Veeco Instruments Ltd. UK) was employed to characterize the surface morphology of the AAO template membrane. (noncontact silicon cantilevers, full tip cone angle less than 20°).

Specimens for inspection by TEM were prepared by the evaporation of one drop of an aqueous solution containing the nanowires with particles onto a

Fig. 2 Schematic diagram describing the fabrication steps of in-wire junction of nanoparticles by layer-by-layer assembly within the porous template



carbon-coated copper mesh grid. All samples were examined in a JEOL 2000 EX TEM operating at 200 kV. The samples were all washed and centrifuged to remove the excess salt and surfactant prior to the characterization.

Results and discussion

The AAO template was obtained by two-step anodization of aluminum in the oxalic acid. After the first anodization step, the porous film was stripped by immersing the sample in a solution comprised of a mixture of phosphoric and chromic acids, leaving behind an aluminum surface textured with a hexagonal scalloped pattern. This was followed by a second anodization step to produce the almost perfect hexagonally arranged pore domains on the surface. The top-view AFM micrograph of the nanopore array of AAO template by two-step process was shown in Fig. 3. The hexagonally ordered pores are surrounded by six hexagonally ordered columnar oxides in the domains, which are interconnected to form a network structure. The pore diameter was dependent on the anodization voltage. The anodization time favored not only increasing the pore depths but also extending the uniformity of the AAO membrane.

Before the metal electrodeposition within the pores of template, the voltage for anodization was decreased stepwise 1 V/min to thin the barrier layer. The pores branch out at the formation because the equilibrium number of the pores per square centimetre is inversely

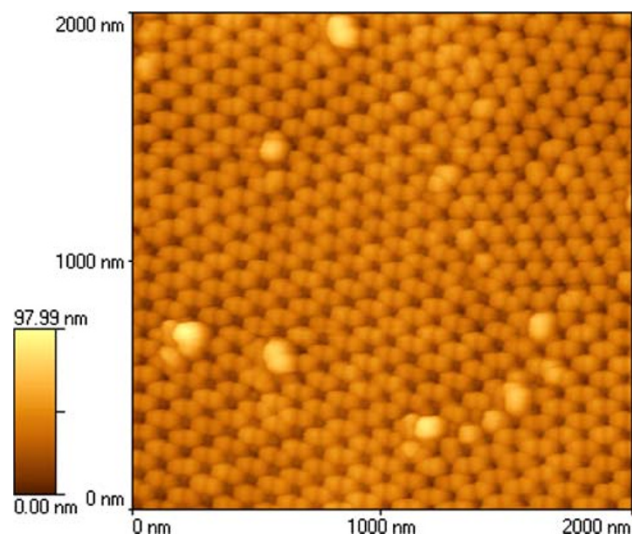


Fig. 3 AFM top-view micrograph of the as-prepared AAO template by two-step anodization with the pore diameter of 40 nm

proportional to the square of the anodization potential [18, 19]. The split up of the pores in the layers between the ordered alumina structure and the aluminium substrate favours the formation of nucleation sites in each pore at the beginning of the ac electrodeposition [20]. The gold nanowires with dendrite structures are obtained by dissolving the AAO membrane containing the gold in the basic solution. Figure 4 showed typical gold nanowires with the dendrite nanostructures. Under the high magnification, it is clearly demonstrated that some dendrite structures (which are caused by a slow decrease in voltage at the end of the anodization step) existed at the bottom of the nanowires. The gold nanowires with this kind of structure are connected at the bottom to form bundles when the Au/AAO membranes are dissolved in the NaOH solution. It brings the difficulties in dispersion of nanowires in aqueous solution. To solve this problem, the copper metal was chosen as a first layer to fill the dendrite structure at the beginning of the deposition, subsequently removed by the acid solution at the end of the process. Once the copper is deposited within the template, the gold plating solution was then used to deposit the gold on the top of copper.

Within the AAO template, the self-assembly method spatially functionalized the nanowires. The self-assembled monolayers of dithiols could be grown at the exposed tip of nanowire because of gold–sulfur bonds. The nanoparticles synthesized by two-phase reduction was deposited on the molecular layers and then as the anchor to attach the dithiol group in the following steps. This modification was repeated three times to form the multiple nanoparticle layers on the gold nanowires within the membrane. After removing the AAO template and copper part at the bottom, the morphologies of well-dispersed nanowires by site-specific modification were characterized by transmission electron microscopy (TEM) and the related images are shown in Fig. 5. Figure 5(A) shows a large scale image of the dispersed nanowires capped with nanoparticles. Figure 5(B) and (C) shows images of nanowires, which look much like a “lighted cigarette”. The bottom of the nanowire in Fig. 4(C) is very smooth and has no dendrite structures because the copper was first deposited in the dendrite and removed in acid solution. The diameter of gold nanowire is 40 nm, which is consistent with the diameter of the porous template we used in the experiment.

The multiple layers of nanoparticles were assembled at the tip of an electrochemically grown nanowire, and the gold layer was then electrodeposited on top of the monolayer. Figure 6 shows the different magnifications of the nanoparticles junction between the gold

Fig. 4 (A) TEM image of gold nanorods with the branch parts at the bottom in low magnification, which is consistent with the dendrite structure drawn in Fig. 1. (B) the high magnification image of the brunch parts at one end of gold nanowires

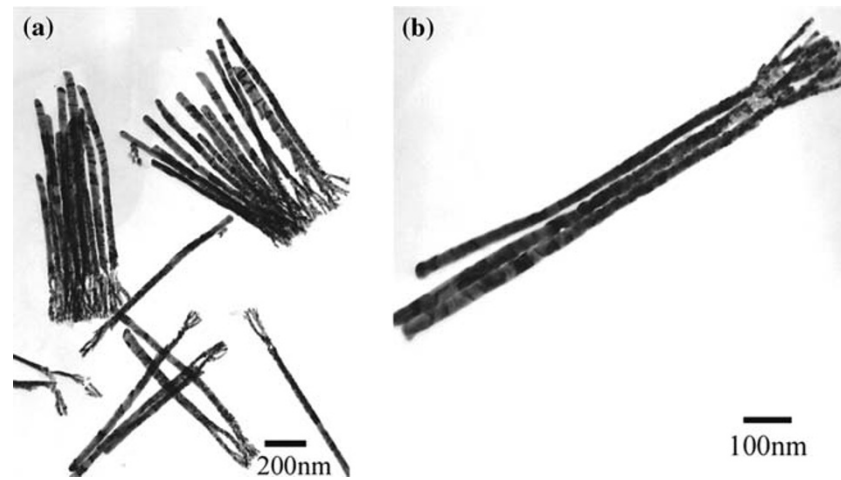


Fig. 5 TEM images of gold nanorods functionalised by gold nanoparticles (A) the large scale of gold nanorods dispersed by aminodextran (B) two gold nanorods with the smooth bottom after removing the branch part of copper metal (C) the nanorod was selectively modified by gold nanoparticles, which look like the “lighting cigarette”

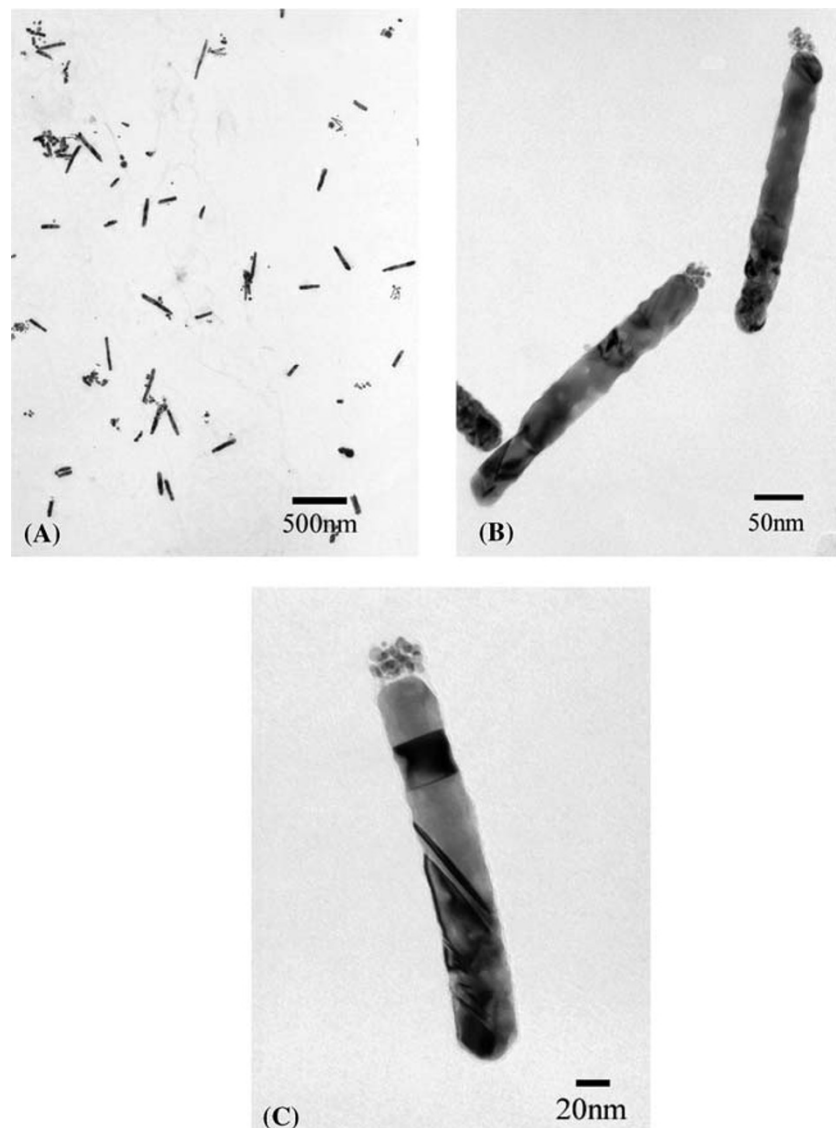
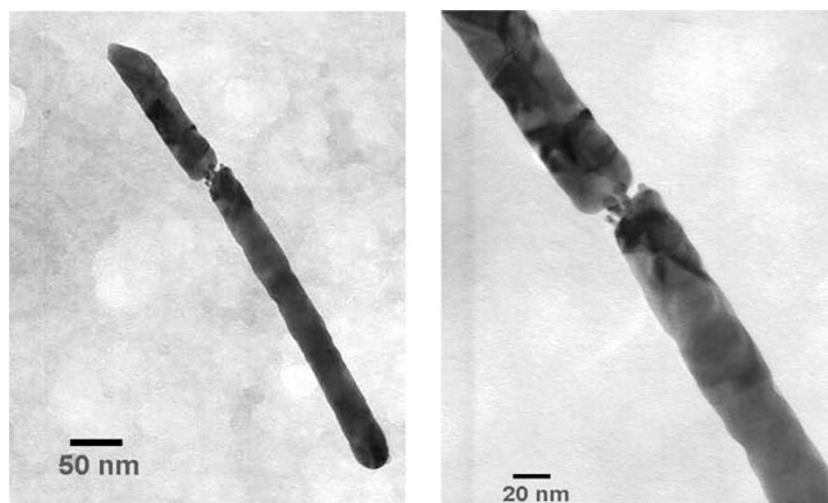


Fig. 6 TEM images of nanostructure with nanoparticles/dithiols junction between gold segments nanowire



nanowires, imaged by TEM. The second electroplating step was performed after the self-assembly step of dithiol layer in the final step. The dithiol layer could act as the anchor to attach the electrodeposited gold. From the TEM images, the junction of nanoparticles is quite clear. The length of the junction was adjusted by modifying different time variables in the experimental section. The well-dispersed nanowires without the dendrite structures was observed and the diameter of nanowires is the same as that of the porous membrane as template.

In conclusion, we have successfully created gold nanowires by alternate adsorption of the dithiol and gold nanoparticles. The images of the nanowires with different morphology in every procedure were characterized by the TEM. This process leads to nanoparticles modified at the specific area of the nanowires electrodeposited within the template, not at the all surfaces of nanowires. It will supply the possibilities in applications of nanoscale electronics and other areas.

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