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Size-Controllable Fabrication of Noble Metal Nanonets Using a TiO_2 Template

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We present herein a simple template method for preparing noble metal nanonets with defined sizes. The template utilized is a TiO_2 nanotube (NT) array prepared by anodic oxidation of a pure titanium sheet in an electrolyte solution containing sodium fluoride. Uniform NTs with defined sizes are obtained by controlling the anodic potential. Gold nanonets are prepared by electrodepositing gold onto the template and then dissolving the TiO_2 template in a 0.2 M HF solution. The pore size of the gold nanonet is determined by the TiO_2 NT hole size. The formation mechanism of the nanonet is elucidated from field-emission scanning electron microscopy and transmission electron microscopy. Although a lot of reports have been presented on the synthesis of nanostructure materials, no work has been reported on the template synthesis of gold nanonets. This paper gives a simple and universal way to prepare noble metal nanonets.

In recent years, nanostructure [nanoparticles, nanowires, nanorods, and nanotubes (NTs)] materials have attracted increasing research interest because of their unique electronic, magnetic, optical, and micromechanical properties[1−4] and potential applications such as chemo/biosensing, catalysis, microelectronics, photovoltaic cells, etc.[5−8] Various methods proposed for the preparation of nanostructure materials include sol−gel, hydrothermal synthesis, laser ablation, anodization, vapor deposition/transport techniques, template-assisted synthesis, etc. Among them, the template synthesis explored by Martin et al.[9−12] has proven to be a versatile approach for preparing nanomaterials with defined sizes. NTs and nanofibers composed of metals, semiconductors, polymers, and various composites of these materials[9−12] were prepared based on a polycarbonate (PC) membrane template. Besides the PC membrane template, anodized aluminum oxide is another widely used template with which NTs,[13] nanowires,[14,15] and nanorods[16] were synthesized. To our knowledge, however, no work has been reported on the template synthesis of metal nanonets with size-controllable and uniform structures up to now.

In this work, we exploited an electrochemical method to fabricate gold nanonets by using a TiO_2 NT array as a template. The TiO_2 NT template was prepared by anodic oxidation of a titanium sheet in a NaF-containing solution. A highly oriented and uniform NT array can be obtained by this method,[17,18] with the NT hole sizes controllable by tuning of the anodic potential.[19] The gold nanonets were prepared by electrodepositing gold on the template and then dissolving the template in a 0.2 M HF solution. The formation mechanism of the nanonet was elucidated from the field-emission scanning electron microscopy (FE-SEM) and transmission electron microscopy (TEM) results.

Titanium foil (99.8%, 0.127 mm thick) was purchased from Aldrich (Milwaukee, WI). Sodium fluoride, sodium hydrogen sulfate, and hydrogen tetrachloroaurate trihydrate of analytical reagent grade were purchased from commercial sources and used as supplied. Twice-distilled water was used throughout the experiments.

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Prior to anodization, a titanium ribbon was ultrasonically cleaned in acetone and then ethanol for 5 min each. The cleaned titanium ribbon was anodized in an electrolyte containing 0.1 M NaF and 0.5 M $NaHSO_4$ at room temperature for 3 h. The TiO_2 NT hole size was controlled by tuning of the anodic potential.[19] The unanodized top part of the titanium ribbon was used as the electrical contact position, and an electrically insulated copper wire was attached on the top by jointing. The efficient area of the titanium ribbon was 0.3 cm × 1 cm. Electroplating gold on the TiO_2 NT template was performed by employing the precise dc impulse mode of an electrochemical workstation (CHI 660B; CH Instruments, Inc., Austin, TX) with a platinum wire as the counter electrode and Ag/AgCl (saturated by a KCl solution) as the reference electrode. The electroplating conditions were as follows: 10 mM $HAuCl_4$; electroplating current, 5×10^{-5} A s^{-1}; efficient depositing time, 90 s; ratio of closed and open, 1. The gold-deposited template was then immersed in a 0.2 M HF solution for 30 s to dissolve the TiO_2 NT template, and the gold nets were peeled from the substrate without damaging the nanostructure. The formed gold nanonets were collected by centrifuging the solution at 12 000 rpm.

The details of the process are illustrated in Figure 1. The surface and lateral topography of the TiO_2 NT array were studied using FE-SEM operating at 5 kV (JSM 6700F; JEOL, Tokyo, Japan). The nanonet structure was confirmed using TEM operating at 300 kV (JEM 3010; JEOL, Tokyo, Japan). The energy-dispersive X-ray spectrometer fitted to a transmission electron microscope operating on a nanoprobe mode was used for elemental analysis.

Figure 1 schematically shows the template synthesis process of the gold nanonets. Gold was mainly electrodeposited in the gaps between two neighboring NTs and on tube bottoms because of the relatively high electric field there. Gold deposited on the tube bottom formed separated nanoparticles with a size of around 10 nm (TEM images are not given). It was difficult to collect them because of the small size and trace amount. During immersion in a HF solution, the gold nanoparticles deposited on the tube bottom were removed with the template and the gold deposited in the gaps was left to form the nanonet. The SEM and TEM results (Figure 2) confirm the above-mentioned thought. Parts a and c of Figure 2 show that there exist gaps or at least grooves between two neighboring NTs. The semiconductivity of amorphous TiO_2 facilitated the electrodeposition. The pore size of the nanonet was identical with the NT size including the hole and the wall. By control of the TiO_2 NT hole sizes through tuning of the anodic potential,[19] gold nanonets with certain pore sizes can therefore be synthesized.

TiO_2 NTs fabricated by anodization are with open top and closed bottom.[17] Figure 2a shows that, after removal of the NTs, the imprints left in the substrate look like honey caves. The energy-dispersive X-ray spectrometry (EDS) spectrum indicates that the substrate is pure titanium. The strong dissolubility of the electrolyte (0.1 M NaF + 0.5 M $NaHSO_4$, pH 0.5) limits the NT length to a maximum of about 320 nm,[20] as shown in Figure 2a.

Figure 1. Schematic fabrication process of a gold nanonet. A small amount of gold was also deposited on the NT inner wall and wound up in an HF solution with the dissolution of TiO_2.

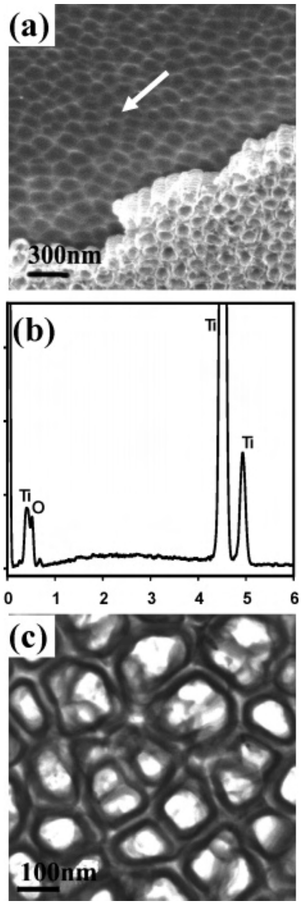

Figure 2. (a) SEM image of the TiO_2 NTs and the substrate (marked by a white arrow) after removal of the NTs. (b) EDS spectrum of the substrate. (c) TEM image of TiO_2 NT arrays, the top view.

Figure 3a shows the TEM image of a gold nanonet peeled off from a template that was anodized at 25 V for 3 h. The gold-deposited template was dissolved in HF for 10 s. As shown in the image, a lot of grids were jammed by TiO_2 and would have dissolved if the dissolving time had been prolonged. EDS analysis (Figure 3b) shows the existence of the undissolved titanium (marked by a black arrow). Once all of the TiO_2 had been dissolved, pure gold nets appeared. The copper peak in Figure 3b resulted from the copper grid that was used to support the sample.

The gold nanonets with grid sizes of 50, 100, and 140 nm were obtained by using TiO_2 NT array templates anodized at 10, 15, and 25 V, respectively. The widths of the gold nanonet bones varied from 12 to 15 nm and were independent of the template anodic potentials. The bone thickness was in the same range as that shown in Figure 4. Prolonging the gold electroplating duration increased the bone thickness, and a gold membrane was formed with a long enough electroplating duration. The gold nanonet hole size corresponded to the TiO_2 NT size, as shown in Figure 4. EDS

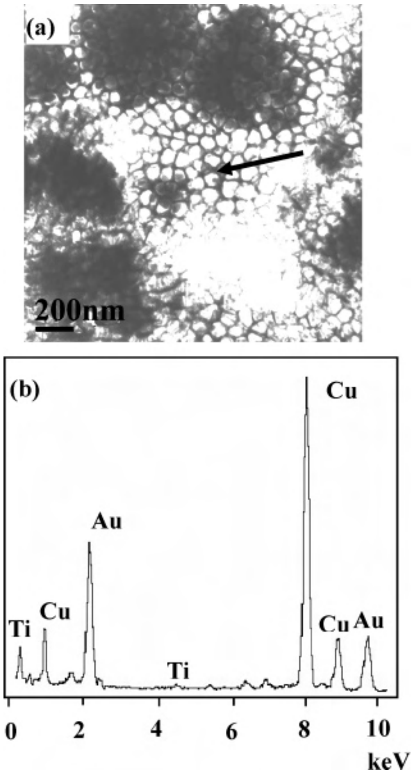

Figure 3. (a) TEM image of the nanonet peeled off from the TiO_2−Ti template anodized at 25 V for 3 h. (b) EDS analysis (marked by a black arrow) indicates the existence of the titanium. The copper peaks are rooted in the copper grid.

analysis (Figure 5) indicated that the composition of the net was pure gold.

Paulose and Grimes[21] reported a self-assembled fabrication of Al−Si nanowire networks by dealloying an Al−Si alloy thin film through selective chemical etching. Pore dimensions of the alloy nanowire network ranged from 30 to 200 nm, which depended on the composition and structure of the Al−Si alloy. In this work, the pore size of the gold nanonet is uniform and can be easily controlled by the TiO_2 template. This technique is effective for the synthesis of other noble metal nanonets. Such noble metal nanonets can be potentially applied in biosensing, catalysis, and molecule sieves because of their high surface areas and uniform nanostructures. For example, a biosensor with gold nanonets as the interface would have high sensitivities and rapid response times because of the perfect biocompatibility characteristics and fast electron transfer on the nanonets. The nanonets of platinum would exhibit a high activity in catalytic oxidation, and the palladium nanonets would exhibit improved efficiency in hydrogenation.

A simple and universal method was proposed for the template synthesis of noble metal nanonets with defined sizes. Gold was used as the model. The template was an anodized TiO_2 NT array, the size of which can be easily controlled by tuning the anodic potential. Metal can be electrodeposited on the semiconductive TiO_2 template. Such nanonets are expected to have wide applications in chemo/biosensing, catalysis, molecule sieves, etc. because of their uniform nanonet structures, unique physical/chemical properties, and perfect biocompatibility characteristics.

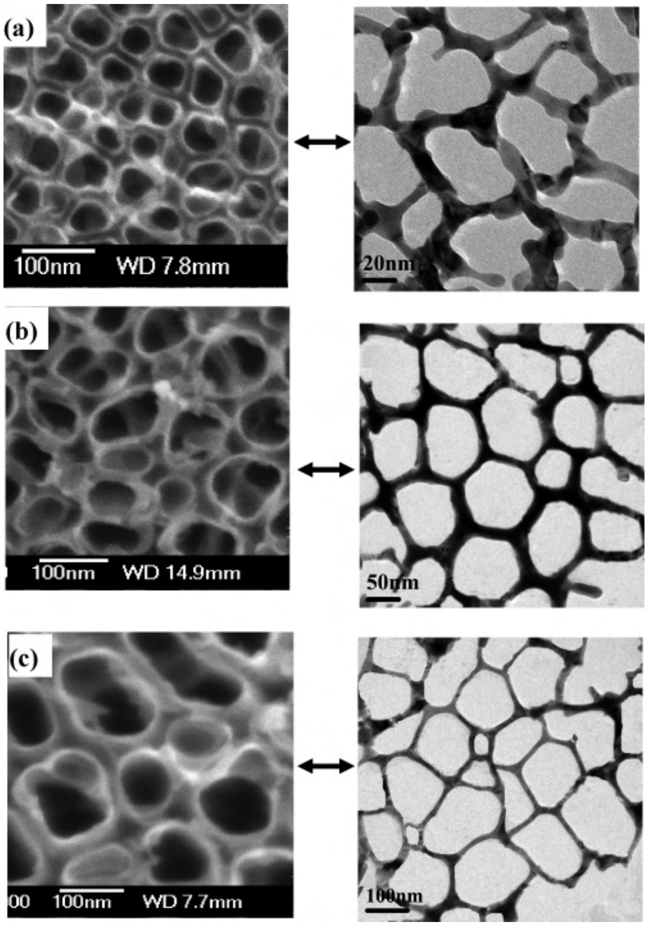

Figure 4. SEM images of the TiO_2−Ti templates prepared at 10, 15, and 25 V and the corresponding TEM images of the gold nanonets. The pore sizes are (a) 50, (b) 100, and (c) 140 nm.

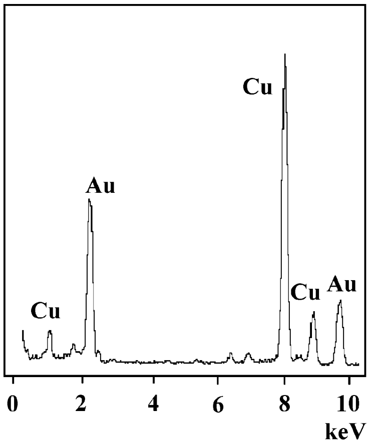

Figure 5. EDS analysis showing a pure gold nanonet. The copper peaks are rooted in the copper grid.

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