Template Synthesis of Arrays of One-dimensional Gold Nanowires Standing on a Carbon Film

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(Received September 5, 2006; CL-061020; E-mail: tera@anal.chem.tohoku.ac.jp)

Arrays of 1D gold nanowires with a diameter of 3–5 nm standing on a carbon film were fabricated on the basis of template-assisted electrodeposition by using an alumina membrane with surfactant-templated silica-nanochannels as the template.

One-dimensional (1D) nanostructures, such as nanowires or nanotubes, have attracted much interest in recent years because of their inherent physical properties based on their size effects.[1] Various synthetic methods have been developed to achieve the 1D nanostructure growth, and template-assisted electrodeposition has often been used for preparing a variety of inorganic and/or organic nanosized wires.[2–5] In the template-assisted electrodeposition, porous anodized alumina (PAA) and track-etched filtration membranes composed of columnar-pore arrays have been commonly employed as the templates. However, the pore size in these porous membranes generally ranges from tens to hundreds of nanometers.[3,4]

In order to explore the synthetic methods for the mesosized 1D nanostructures with a diameter of less than 10 nm, mesoporous silica materials have attracted much attention because of their highly ordered pore structures with a narrower uniform pore size (2–10 nm) than that of the PAA and track-etched membranes.[6,7] To date, various surfactants have been used to prepare mesoporous silica membranes on a solid substrate.[8–12] Among them, alkylammonium derivatives, particularly cetyltrimethylammonium bromide (CTAB), are well known for their ability to produce silica nanochannels with a diameter of about 3 nm.[8,9] However, when mesoporous silica membranes composed of assemblies of 1D silica nanochannels are formed on the solid substrate using CTAB, the orientation of as-prepared 1D nanochannels is parallel to the substrate surface,[8] making it impossible for the reactants to transport across the membrane and to react on the conductive substrate by template-assisted electrodeposition.

In our recent work, we developed a hybrid membrane in which assemblies of 1D silica–surfactant (CTAB) nanochannels with a diameter of 3.4 nm were filled within the columnar pores of a PAA membrane, and the hybrid membrane is referred to hereafter as a nanochannel-incorporated alumina membrane (NAM). In this membrane, the nanochannels are oriented perpendicularly to the surface of the PAA membrane.[13] This membrane was applied to size-selective filtration and charge-selective extraction of molecules.[13,14] The perpendicular orientation of nanochannels allows transport of molecules and/or ions across the NAM, and the NAM can act as a template providing a suitable robust framework for template-assisted electrodeposition. We herein demonstrate the formation of arrays of mesosized 1D gold nanowires by DC-electrodeposition utilizing the NAM as a template.

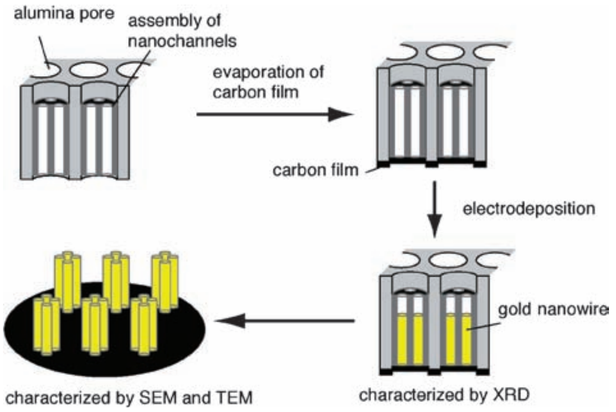

Figure 1. NAM template-electrodeposition of 1D gold nanowires on a carbon film.

The procedure for the electrodeposition of gold nanowire arrays is shown in Figure 1. The NAM was prepared by using an acidic precursor solution containing CTAB and tetraethylorthosilicate according to the method reported previously.[13] A carbon film (thickness ca. 300 nm) was deposited on one side of the NAM by carbon evaporation, and scanning electron microscopy (SEM) confirmed that the carbon film entirely covered the NAM surface. After removing the alumina membrane, it was also confirmed that the arrays of silica–surfactant nanochannels were standing on the carbon film (see Figure S1).[15] The carbon film on the NAM is used as a cathode in an electrochemical cell containing an aqueous $AuCl_4^-$ solution in order to electroplate gold nanowires inside the silica–surfactant nanochannels by conventional DC plating at room temperature (see Figure S2).[15] Since anionic compounds undergo facilitated extraction into the silica–surfactant nanochannels by replacing bromide ions of the CTAB surfactants with anionic compounds,[14] the NAM was used without removing the CTAB surfactants to attain the facilitated distribution of $AuCl_4^-$ which is the precursor to form gold nanowires into the silica–surfactant nanochannels.

In the CV curve of a 24 mM $AuCl_4^-$ aqueous solution, a reduction peak appeared at a potential of −0.18 V vs. Ag/AgCl. This potential is close to the reduction potential of $AuCl_4^-$ on a bare glassy carbon electrode (GC) (−0.16 V vs. Ag/AgCl; reduction of Au^{III} to Au^0), indicating that a carbon film on the NAM can indeed work as a conventional carbon electrode like GC. Cathodic electrodeposition of gold into the nanochannels was done at a potential of −1.0 V vs. Ag/AgCl for 30 min by monitoring the *i*–*t* curve (see Figure S3).[15] The *i*–*t* curve was similar to that obtained for the growth of nanowires in polycarbonate or alumina nanopores.[3]

The NAM processed by electrodeposition (ED-NAM)

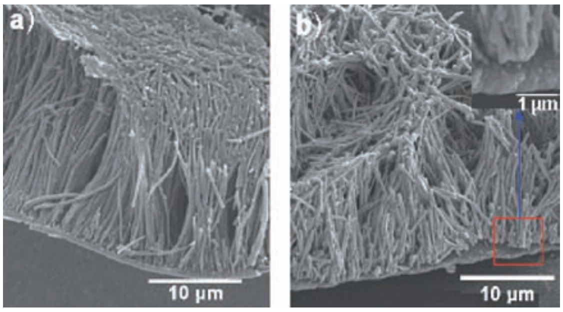

Figure 2. SEM images of (a) silica-nanochannel arrays containing gold after removing the alumina matrix and (b) gold nanorods standing on the carbon film after etching of the alumina and the silica matrices. The inset in Figure 3b is a magnified image at the surface of the carbon film.

was thoroughly rinsed with water, dried, and then characterized by X-ray diffraction (XRD) with Cu Kα radiation. In the wide-angle XRD patterns (see Figure S4),[15] three peaks appeared at 38.15, 44.37, and 64.56°, which could be indexed as [111], [200], and [220] reflections of face-centered cubic (fcc) crystalline Au ($a = 4.080 \pm 2$ Å), respectively (see Figure S4).[15]

Figure 2 shows SEM images of the ED-NAM after etching the alumina matrix (Figure 2a) using 10 wt % phosphoric acid solution and after etching both alumina and silica matrices (Figure 2b) using 2 M NaOH solution. Energy dispersive X-ray (EDX) spectroscopy was also used for the elemental analysis (see Figure S5).[15] As shown in Figure 2a, rod structures were standing on the carbon film, and the EDX data indicated that the rod structures were composed of silica and gold. Even after the silica matrix was etched, we could still observe that the rod structures composed only of gold were standing on the carbon film (Figure 2b). The results obtained by SEM, EDX, and XRD measurements indicated that the crystalline gold was formed within the rod structures.

The local structure of the rods shown in Figure 2b was further examined by transmission electron microscopy (TEM). In the TEM image shown in Figure 3a, had at least three rods standing on the carbon film. Figures 3b to 3e reproduce high-magnification TEM images of the selected regions of the rod structures shown in Figure 3a. In all of the selected regions, 1D gold nanowires were recognized as oriented perpendicularly to the surface of the carbon film, and their diameter was around 3 to 5 nm, corresponding to the average diameter of the silica framework (3.4 nm) formed in the columnar alumina pores. A selected area electron diffraction (SAED) pattern (the inset of Figure 3b) indicated that as-prepared gold-nanowire arrays are single-crystal-like, and it gave similar crystallite size with that evaluated by the XRD data. All the above results confirmed that the rod structures shown in Figure 3a were composed of assemblies of mesosized 1D gold nanowires.

In summary, arrays of mesosized 1D gold nanowires with a diameter of 3–5 nm were fabricated on the basis of template-assisted electrodeposition by using the NAM with a carbon film. This method employing NAM as a template can be readily extended to the preparation of various mesosized 1D nanowires including catalytic metals, polymers, semiconductors, and oxides.

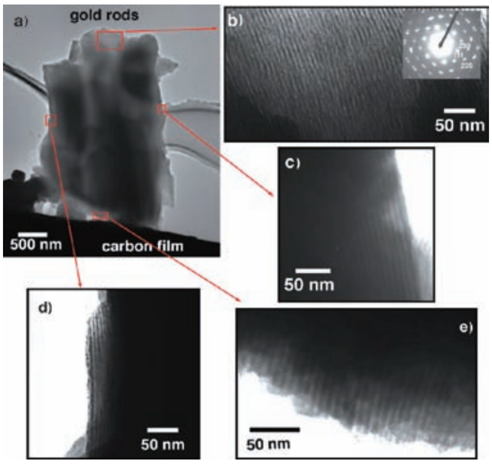

Figure 3. TEM images of (a) gold rods standing on the carbon film and (b–e) selected areas. The inset in b is the corresponding SAED.

This work was partly supported by Grants-in-Aid for Scientific Research (No. 17205009) from the Ministry of Education, Culture, Sports, Science and Technology, Japan. Dr. Y.C. acknowledges the financial support of JSPS-PD fellowship.

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15 Supporting Information is available electronically on the CSJ-Journal web site; http://www.csj.jp/journals/chem-lett/index.html.

Published on the web (Advance View) October 28, 2006; doi:10.1246/cl.2006.1352