

A Novel Route to Fabricate Au-Te Nanocables

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Abstract

Electrochemistry is a valuable strategy to create 1-dimensional nanostructures. Using electrochemical methods, nanocables and nanowires can be obtained by coating one face of a porous membrane with a metal film, which acts as a working electrode for further deposition inside the pores. Nanocables (Zhang et al., 2003) and composite nanowires (Xu et al., 2003) were thus obtained by axial growth of the deposited materials within the nanopores of the membrane (i.e. perpendicular to the metal film).

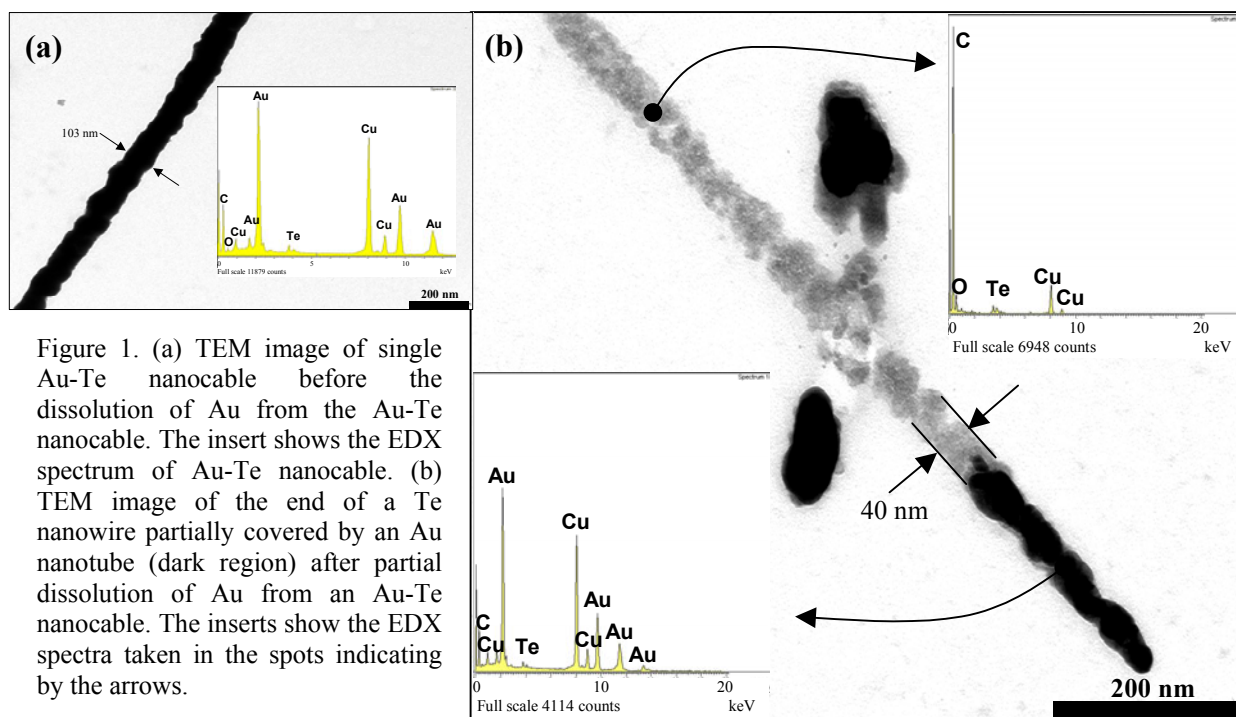
We report a novel route to fabricate nanocables that is based on a slow electrodeposition process in which the deposit grows radially inside the nanotubes. We can create nanocables by using a metal nanotube membrane (Hulteen and Martin, 1997) as the working electrode. Electroless plating has a slow deposition rate and can be used to plate non-conductive surface of membrane pores and make them conductive for further electrochemical depositions. After the metallic nanotubes were created, the following electrodeposited layer has a radial growth inside the membrane nanopores as long as the deposition rate is slow. Consequently, we can electrochemically deposit and grow radially additional materials on the inside walls of the metal nanotubes to form nanocables. If the electrochemical deposition is fast, blockage at the mouths of the pores will occur and the tubules cannot develop inside the surface of the pores in the membrane. (Hulteen and Martin, 1997)

We introduce the fabrication Au-Te nanocables with a radial metal-semiconductor hetero-structure by a slow electrochemical deposition process by taking underpotential deposition (UPD). Commercial poly(carbonate) track-etched (PCTE) membranes (Poretics, Inc.), with a thickness of 6 μm , hydraulic pore diameter of about 105 nm and pore density of 6 pores/ μm^2 were used in all experiments. Using the PCTE membranes as the templates, Au was electroless deposited on the walls of the pores to form Au nanotubes, following the procedure reported by Martin and et al. (Wirtz and Martin, 2003; Wirtz et al., 2002; Menon and Martin, 1995; Jirage et al., 1997) After electroless Au deposition, the hydraulic pore size of the membrane was further reduced to about 38 nm. The Au nanotube membranes were then immersed in HNO_3 (25%) for 12 hours to remove impurities introduced by the electroless plating process. Subsequently, the Au nanotube membranes were used as a secondary template to electrochemically deposit Te on the surfaces of the Au nanotubes. The electrochemical cell consisted of the Au nanotube membrane as the working electrodes, Pt wire as the counter electrodes and $\text{Ag}/\text{AgCl}/(3\text{M NaCl})$ as the reference electrode. The electrolyte solutions used for electrochemical deposition contained TeO_2 (0.1 mM) and CdSO_4 (1 mM) in a H_2SO_4 (50 mM) solution. Cadmium was introduced into the electrolyte to lower the deposition rate of Te. Cyclic voltammetry studies have shown that the bulk deposition of Te was impeded by the presence of Cd ions in the solution. (Vidu, 2000) The electrochemical deposition was carried out at -62 mV vs. Ag/AgCl for 14 hours. After deposition, dichloromethane was used to dissolve the polycarbonate polymer and free the Au-Te nanocables from the PCTE membranes. Further, potassium iodide etchant was used to remove Au from the Au-Te composite nanowires to leave Te nanotubes or Te nanowires. Transmission electron microscopy (TEM) images were taken using Philips-CM12 at 100 kV equipped with energy-dispersive X-ray (EDX) spectroscopy for chemical analysis. Chemical

profiles were analyzed by electron energy loss spectrum detector (EELS, Gatan Inc.), which operated on a scanning transmission electron microscope (STEM, Tecnai G20).

In order to gain additional information on the electrochemical deposition mechanism at nanoscale, surface plasmon resonance (SPR)(Jin and Dong, 2003; Zayats et al., 2003; Artyukhin and Stroeve, 2003; Toyama et al., 2002; Knoll, 1998) and *in situ* electrochemical atomic force microscopy (EC-AFM) has been used. The experiments were performed using as a substrate either Au film on glass (for SPR experiments) or ultra flat Au (for the EC-AFM experiments). We used the EC-AFM to monitor the changes of the surface morphology in 50 mM H₂SO₄ + 0.1 mM TeO₂ + 1 mM CdSO₄ solution under potential control. The *in situ* EC-AFM imaging of the cathode surface was performed under potentiostatic conditions at room temperature using a Multimode AFM (NanoScope IIIA, Digital Instruments). Commercially available triangular gold-coated cantilevers with pyramidal tips of 0.05 N/m force constant were used.

Figure 1a shows a typical TEM image of a single Au-Te nanocable obtained after the PCTE membrane was dissolved with dichloromethane. The nanocable diameter corresponds closely to the pore diameter. The Au-Te nanocable has an average diameter of about 103 nm and the length of several micrometers. Energy Dispersive X-ray (EDX) analysis (Fig. 1a insert) of the single Au-Te nanocable confirms that the nanocable contains Au and Te. The copper peaks are from the TEM copper support grid. Figure 1b shows a TEM image of a single Te nanocable after it was treated with potassium iodide to remove the gold. The end of the nanocable is still partially covered by Au. The diameter of the Te nanowire (~ 40 nm, obtained from the TEM image) is close to the inner diameter of the Au nanotube (~ 38 nm, i.e. the hydraulic pore size of the membrane after electroless Au deposition). The EDX analyses (Fig. 1b insert) performed at the two locations marked by arrows confirm that the brighter area of the nanowire consists of Te, and the darker area consists of both Te and Au. The results in Figs. 1a and 1b show that Te nanowires can be grown inside Au nanotubes to form Au(shell)-Te(core) nanocables.



Occasionally, we have observed Te nanotubes along with Te nanowires after the Au was removed from the nanocables (Figure 2a). Figure 2b is a TEM image showing a single Te nanotube with a diameter of about 105 nm and a Te nanowire with a diameter of about 38 nm, which is closed to the pore size of the Au nanotube membrane. Analyzing the chemical profiles across nanocables before Au dissolution, additional information is revealed. Figure 3 shows the STEM image of Au-Te nanocables (Fig. 3a) obtained after the PCTE membrane was dissolved, along with the chemical profile (Fig. 3b) across the Au-Te nanocable analyzed by the EELS detector. In this case, the chemical profile suggests a concentric structure where Te is also present outside the Au nanotube. These results demonstrate the fact that Te can be deposited both on the inner and outer surfaces of the Au nanotube. This is possible if we consider the defective nature of the electroless Au film on PCTE membrane and the cleaning procedure that follows the electroless deposition process. After electroless deposition of Au, the Au-coated membrane was treated with nitric acid for 12 hours to remove all residual Sn or Ag left inside the Au nanotubes during the electroless Au deposition process (Menon and Martin, 1995). The nitric acid treatment to remove the residues may result in additional space for Te to be deposited between the Au and the PCTE membrane. These results show that it should be possible to obtain Te(shell)-Au(shell)-Te(core) nanocable structures under certain conditions.

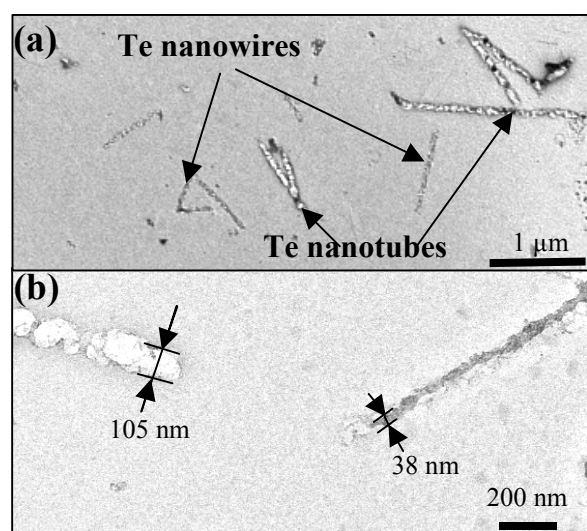


Figure 2. (a) TEM image of Te nanowires and Te nanotubes present after dissolution of Au; (b) enlarged TEM image of single Te nanowire and single Te nanotube.

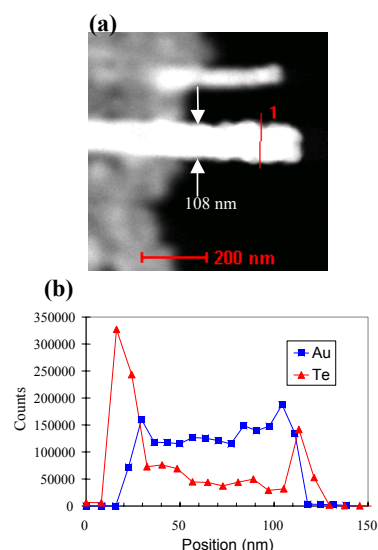


Figure 3. STEM image (a) of a single Te-Au-Te nanocable; (b) EELS chemical profile along the line 1 as marked in (a).

It is worth mentioning the absence of Cd in the composition of the nanostructures created by this method. When the electrolyte solution contained only Te ions and all the other deposition conditions were kept constant (Te ion concentration, potential and time), Au-Te nanocables were very short (~250 nm, not shown here). In order to understand the effect of the UPD process on the kinetics of nanostructures created by electrodeposition, SPR measurements have been carried out at various deposition potentials. Figure 4 shows the deposition kinetics as measured by surface plasmon resonance (SPR) spectroscopy in two different solutions (i.e. with and without Cd^{+2} in Te-containing solution) at constant potential. SPR results show that the deposition rate (the slope of the deposition kinetics in Fig. 4) of Te is much faster in the absence of Cd^{+2} than in the presence of Cd^{+2} when electrodeposition occurs

at -62 mV vs. Ag/AgCl. Further SPR investigations are presently carried out to probe the deposition rate variation over the whole underpotential window. Additionally, EC-AFM observation was performed to gain a more complete understanding of the deposition process. Morphological data provided by the in situ EC-AFM observation at nanoscale offer important information about interfacial phenomena. Figure 5 shows the AFM images of the surface obtained after deposition at -62 mV for 30 min. in Te-containing solution with and without Cd. The morphology of the surface in the electrolyte that contains only Te ions (Fig. 5b) is evidently more granulated than that obtained in Te and Cd ions-containing solution (Fig. 5a). It becomes evident that the presence of Cd ions into the solution enhances the surface diffusion of the adatoms during deposition. In the absence of Cd ions, the surface diffusion of Te adatoms is slow (Vidu, 2000) and the resulting surface has island-type morphology. The reason of a slower Te deposition rate and a smoother morphology of the deposit surface in the presence of Cd ions into electrolyte are not yet clear. Two possible explanations can be proposed. First, due to the competition between the two ions (Te and Cd), bulk deposition of Te is slowed down to low rates in the underpotential region of Cd. (Vidu, 2000) Second, Cd may modify the natural growth mode of Te (i.e. Stranski-Krastanov growth mechanism, which is an island growth on a pre-deposited monolayer) without significant level of Cd incorporation. (Vidu, 2000) This process is similar to that observed in vacuum during the growth of an epitaxy layer, where surface-modifying species are added into the system to smooth the film. (Hornvohoege et al., 1994; Copel et al., 1990) For instance, in molecular beam epitaxy (MBE), the growth of Ge on Si(001) and Si on GeSi(001) can be altered by a monolayer of As and Sb to modify the surface properties of the system without significant alteration of the bulk properties. As a consequence, the morphology of the deposited film is completely changed due to the alterations in surface energetics. (Hornvohoege et al., 1994; Copel et al., 1990)

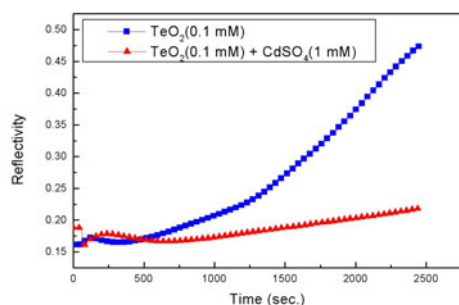


Figure 4. Comparison of the adsorption kinetics as measured by SPR in two different solutions: with and without Cd ions.

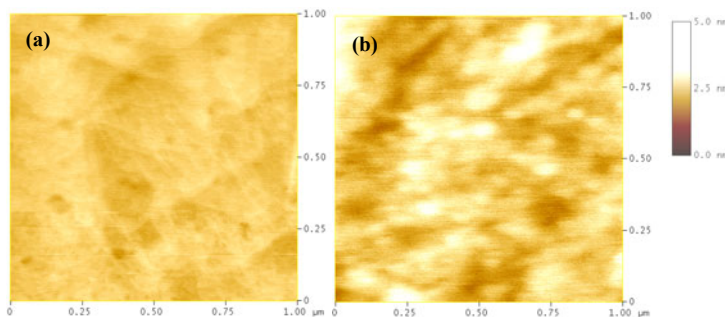


Figure 5. EC-AFM images of the surface observed after electrochemical deposition at -62 mV vs. Ag/AgCl for 30 min in 50 mM H_2SO_4 + 0.1 mM TeO_2 solution with (a) and without (b) 1 mM CdSO_4 .

In summary, we have demonstrated a novel method of fabrication of Au-Te nanocables by slow electrochemical deposition within the UPD region of Cd. Because the rate of the electrochemical reaction is controlling, the mass transfer of Te ions into the Au nanotubes is very fast leading to a radial growth of Te on the inside of the nanotubes. The Au-Te nanocables are Au(shell)-Te(core) nanocables and have radial dimensions consistent with the starting templates.

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