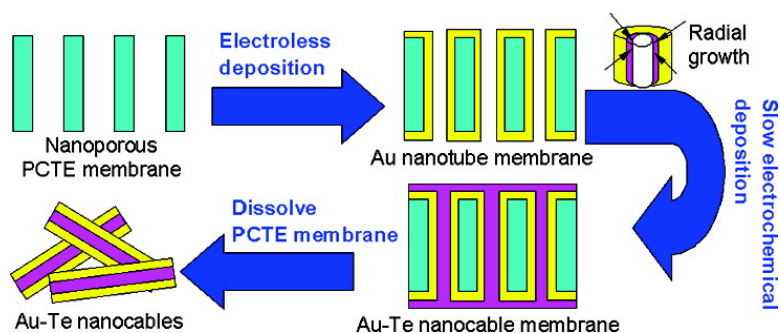


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Fabrication of Nanocables by Electrochemical Deposition Inside Metal Nanotubes

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Nanocables or composite one-dimensional nanostructures with radial heterostructures have been studied for coaxially gated field-effect transistors¹ and biosensors.² A valuable strategy to create one-dimensional nanostructures is electrochemical deposition. Using electrochemical methods, nanocables and nanowires can be obtained by coating one face of the membrane pore with a metal film, which acts as a working electrode for further deposition. The nanocables³ and composite nanowires⁴ are 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 for fabricating Au–Te nanocables, with a radial metal–semiconductor heterostructure, by a slow electrodeposition process in which the Te semiconductor⁵ grows radially inside the nanotubes. We can create nanocables by using a metal nanotube membrane as the working electrode instead of using a metal-coating film on one face of the template. Electroless plating can be used to plate nonconductive surfaces of membrane pores and make them conductive for further electrochemical applications. In the case of a slow deposition rate, electroless deposition has been used to fabricate 1-D nanostructures⁶ inside nanoporous membranes. The deposit has a radial growth inside the membrane nanopores when the deposition rate is slow. 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 membranes.⁶ Subsequently, we can electrochemically deposit and grow radially additional materials on the inside walls of the metal nanotubes to form nanocables. Figure 1 presents the fabrication steps used in our work to obtain Au–Te nanocables. Using nanoporous polycarbonate tract-etched (PCTE) membrane as the template, Au nanotubes were initially obtained by electroless deposition inside the nanopores of the PCTE membrane (Figure 1a,b). Then, using the Au nanotube membrane as a second template, Te was deposited on the surfaces of the Au nanotubes by slow electrochemical deposition, taking advantage of underpotential deposition (UPD). The deposition rate was slow compared to that of the axial mass transfer to grow nanocables coaxially within the Au nanotubes (Figure 1b,c).

The term UPD refers to the deposition of a metal on a foreign metal substrate at potentials more positive than that of the thermodynamic reversible potential (Nernst potential).⁷ The UPD mechanisms of Te and Cd electrochemical atomic layer epitaxy (ECALE) have been studied by Stickney et al.⁸ The ECALE approach to layer-by-layer deposition of CdS, InAs, CdTe, PbSe, and In₂Se₃ has been investigated.⁹ The fabrication method presented here for nanocables opens new opportunities to fabricate nanodevices, such as nanoscale transistors and biosensors.

We used commercial PCTE membranes (Poretics, Inc.), with an average hydraulic pore diameter of about 105 nm, a pore density of 6 pores/ μm^2 , and a thickness of 6 μm in all of the experiments. Using the PCTE membranes as the templates, electroless Au was

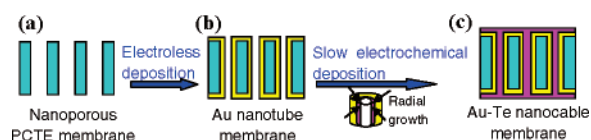


Figure 1. Fabrication steps: (a) bare nanoporous PCTE membrane; (b) Au nanotube membrane obtained after electroless Au deposition; (c) Au–Te nanocable membrane obtained after slow electrochemical deposition of Te.

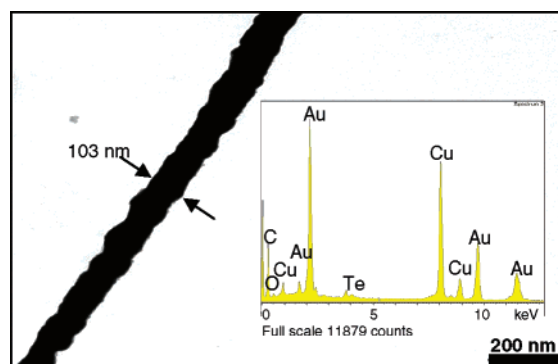


Figure 2. TEM image of single Au–Te nanocable with EDX spectrum (inset). The spectrum shows the presence of Au and Te. Copper peaks are a contribution from the TEM grid. The bar size is 200 nm.

deposited on the walls of the pores to form Au nanotubes, following the procedure reported by Martin et al.¹⁰ After electroless Au deposition, the hydraulic pore size of the membrane was further reduced to about 38 nm. 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, a Pt wire as the counter electrodes, and Ag/AgCl/(3 M NaCl) as the reference electrode. The electrolyte solutions used for electrochemical deposition contained TeO₂ (0.1 mM) and CdSO₄ (1 mM) in an H₂SO₄ (50 mM) solution. The reason cadmium was introduced into the electrolyte was to lower the deposition rate of Te. Cyclic voltammetry studies have shown that the bulk deposition of Te is affected by the presence of Cd ions in the solution.¹¹ The potential of the slow electrochemical deposition was –62 mV versus Ag/AgCl, and the electrochemical reaction took place for 14 h. After the synthesis of nanocables, dichloromethane was used to dissolve the polycarbonate polymer and free the Au–Te nanocables from the PCTE membranes. Potassium iodide etchant was used to remove Au from the Au–Te nanocables to leave Te nanowires. Transmission electron microscopy (TEM) images of the nanocables were taken using a Philips-CM12 at 100 kV equipped with energy-dispersive X-ray (EDX) spectroscopy for chemical analysis.

Figure 2 shows a typical TEM image of a Au–Te nanocable obtained after the PCTE membrane is dissolved with dichloromethane (see the Supporting Information). The nanocable cor-

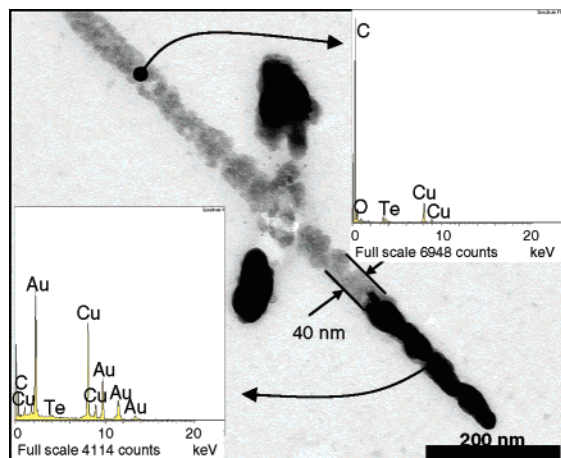


Figure 3. TEM image of the end of a Te nanowire partially covered by a Au nanotube (dark region) after dissolution of most of the Au from a Au–Te nanocable. The insets show the EDX spectra taken at the spots (indicated by the arrows). Copper peaks are a contribution from the TEM grid. The bar size is 200 nm.

responds closely to the pore diameter. Figure 2 shows a single Au–Te nanocable with an average diameter of about 103 nm and a length of several micrometers. Energy-dispersive X-ray analysis (Figure 2 inset) 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 3 shows a TEM image of a single Te nanocable after treatment with potassium iodide etchant to remove most of 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 (Figure 3 inset) performed at the two locations marked on Figure 3 confirm that the brighter area of the nanowire consists of Te, and the darker area consists of both Te and Au. The results in Figures 2 and 3 demonstrate that Te nanowires can be grown inside Au nanotubes to form Au(shell)–Te(core) nanocables.

It is important to mention the absence of Cd in the composition of the nanostructures created by this method. When the electrolyte solution contained only Te ions and all of the other deposition conditions were kept the same (Te ion concentration, potential, and time), the Au–Te nanocables were short (~ 250 nm, not shown here). These results and our experiments with surface plasmon resonance (SPR) spectroscopy (not shown here) show that the deposition rate of Te on gold in the absence of Cd^{2+} is faster than it is in the presence of Cd^{2+} . The reason for a slower Te deposition rate on gold in the presence of Cd ions into electrolyte is 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 to low rates in the underpotential region of Cd.¹¹ Second, Cd may modify the natural growth mode of Te without a significant level of Cd incorporation.¹¹ This process is similar to that observed in a vacuum during the growth of an epitaxy layer, where surface-modifying species are added into the system to smooth the film.¹²

In summary, we have demonstrated a novel method of fabrication of Au–Te nanocables by slow electrochemical deposition within the UPD region of Cd. This technique provides a novel approach to deposit and grow radially additional materials on the inside walls of the metal nanotubes to form nanocables. Using nanoporous PCTE membrane as the template, Au nanotubes were initially obtained by electroless deposition. Then, using the Au nanotube membrane as a second template, Te was electrochemically deposited on the surfaces of the Au nanotubes. 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 those of the starting templates.

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Supporting Information Available: Background, additional results, and applications. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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