TEMPLATE SYNTHESIS FOR ENERGY APPLICATIONS

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Abstract Template synthesis is one of the methods used today to produce nanostuctures such as nanowires, nanocables and nanorods. Our group extensively studied this method to produce nanowires and nanocables using electrochemical deposition from aqueous solutions. We use this technique to grow metalic, semiconductor and oxide nanostructures for energy applications. A few results on Ni/CdTe and CoSb3 systems will be discussed to demonstrate the capability of this method. Our approach to develop high-efficiency materials for energy applications is to combine the chemistry and the size effects. Our group has already obtained nanowires and nanowire arrays for various material systems, and demonstrated compositional and crystalline requirements for these compounds. Template-based technology for nanostructure synthesis is very versatile and the nanostructures can be made on virtually any substrate and template. Combining chemistry and size effects to create new thermoelectric materials has the potential to result in a significant improvement in the power to weight ratio of the device.

1. Introduction

Nanostructures are of great interest for numerous potential applications in various areas. Because of a broad range of enhanced optical and electronic properties compared to bulk (3D) materials of the same chemical composition, nanostructures are largely used as ultrasmall building blocks for energy applications.

In this paper various applications of nanostructures such as nanowires and nanocables obtained using template synthesis suitable for energy applications to create arrays of tailored nanomaterials will be presented. Template synthesis requires a nanoporous template, which is actually a membrane with transversal pores or channels in which the desired material is fabricated. Track-etch membranes (PCTE) and porous alumina (or annodized alumina membranes (AAO), are the most extensively used as templates [1, 2]. For energy applications, these templates have been used to fabricate various nanotube, nanowire, nanorod and nanocable structures of metals, semiconductors, carbons, conductive polymers, and composit materials (Figure 1 [3]).

Figure 1. Schematic illustration of template synthesis of nanotubes and nanowires.[3]

Among the techiques to grow nanostructures, electrochemical and electroless depositions, sol-gel deposition, and chemical vapour deposition are the major template synthesis strategies, which are pocesses that can be scaled up for comercialization. In particular, the template-based synthesis of carbon nanotubes [4] has been demonstrated as this is the most promising class of new carbon-based materials for electronic and optic nanodevices as well as reinforcement nanocomposites for energy applications [4-6].

2. Solar Energy

Electrodeposition in polymeric templates with transversal pores provides a large variety of nanostructures of controlled size, geometry, composition and surface morphology. The posibility to engineer the composition along the lenght of the nanostructure and to create, for instance p-n junctions on both axial and radial directions opens up unique possibilities in nano-device fabrication. Recent results obtained by our group [7-13] on the fabrication, surface modification and characterization of nanowires and nanocables synthesized by this technique are reviewed.

Nanocable structure was created in our group using a patented two-step process [9]. First, Au nanotube was fabricated using electroless deposition on a porous membrane. Electroless plating can be used to plate the nonconductive surfaces of membrane pores and make them conductive for further electrochemical applications. Second, Te nanowire was fabricated inside Au nanotube using electrochemical deposition. A particularity of this technique is that the Au−Te nanocables were produced with a radial metal−semiconductor heterostructure, using a slow electrodeposition process in which the Te semiconductor was grown radially inside the Au nanotubes. Thus, we created nanocables by using a metal nanotube membrane as the working electrode instead of using a metal-coating film on one side of the template (Figure 2). To grow nanocables, the radial electrodeposition rate inside the membrane pore have to be very slow in order to avoid the blockage at the mouth of the pore. Actually, at very low deposition rates inside the pores, multiple layers can be electrochemically deposited and grown radially on the inside walls of the metal nanotubes to form multi-layer nanocables.

In this example, Au nanotube membrane is used as a second template and Te was deposited on the inner surfaces of the Au nanotubes. Slow electrochemical deposition is achieved by taking advantage of the underpotential deposition (UPD) process. The deposition rate is slow compared to that of the axial mass transfer to grow nanocables coaxially within the Au nanotubes (Figure 3) [9]. 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). There are a few systems that show UPD and Te/Au is one of them [14].

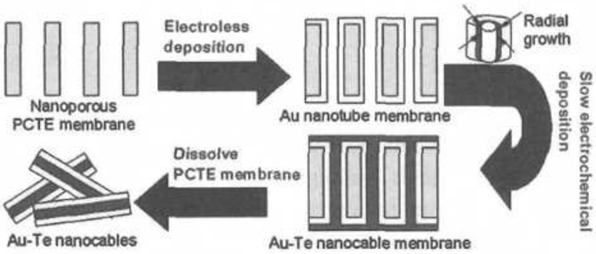

Figure 2. Fabrication steps of Au/Te nanocable structures using template synthesis [9].

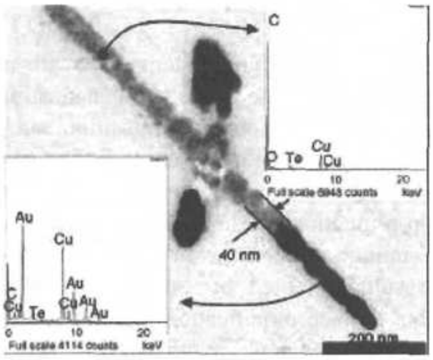

Figure 3 TEM image of single Au−Te nanocable with EDX spectrum (inset). The spectrum shows the presence of Au and Te. Copper peaks are a contribution from the TEM grid. The bar size is 200 nm.[9]

Using a similar technique, a more complex structures can be fabricated. For instance, a metallic nanowire array can be used as a substrate for solar cells. Figure 4 and 5 show an example of such structure for CdTe/CdS thin film solar cells [15]. This nanocable structure can be created by growing an array of nanowires followed by the deposition of multiple layers onto the array after template dissolution. This technique permits the integration of multiple jonctions on a single nanowire.

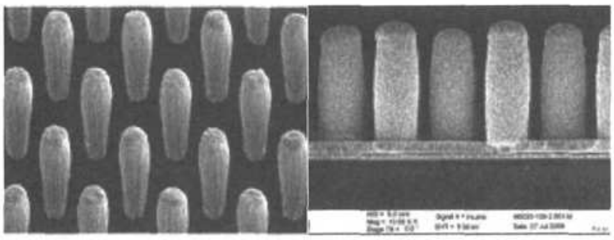

Figure 4. SEM images of metal nanowire array (left) and CdTe coated nanowire array (right) [15].

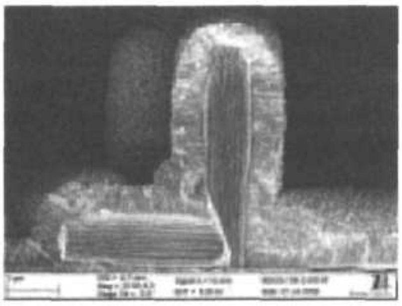

Figure 5. Cross-section image through a nanocable structure (i.e. semiconductor/metal) [15].

3. Thermoelectric (TE) device

Since theoretical calculations first predicted a drastic increase in thermoelectric properties of nanowires, significant progress has been made in synthesizing these structures by way of electrodeposition.

Among all the materals studied for their thermoelectric properties, cobalt triantimonide (CoSb$_3$) shows interesting properties at high temperature range for TE [7, 8]. Moreover, CoSb$_3$ belongs to a group that has the skutterudite (CoAs$_3$) structure indicated by MX3 where M represents a metal atom and X a pnictide atom. The compound crystallizes in a body-centered cubic structure with the space group Im3. The unit cells consists of eight corner-shared MX6 octahedra, which produce a large void at the body center position in the unit cell. This open site may be further filled with large, "rattling", rare earth ions (La or Ce) to decreases thermal conductivity.

CoSb$_3$ is a semiconductor with a band gap of 0.57 eV. Thermoelectric and electrical transport properties of CoSb$_3$ are sensitive to dopant concentrations. Important dopants include Fe and Ni (substituted for Co) and Sn and Te (substituted for Sb) [16-22].

Although most studies on skutterudites have been focused on the effects of rattler and dopant concentrations on thermoelectric properties, only recent work concentrated on low-dimension skutterudites such as thin films and nanowires. Therefore, CoSb$_3$ has a cage structure that offers a unique opportunity for nanowires to combine the rattling effect and quantum confinement in obtaining more efficient thermoelectric devices.

We obtained CoSb$_3$ nanowires using template synthesis. Figure 6 [7] shows the SEM image of nanowires after the template was partially dissolved in dichloromethane. Nanowires have a slightly larger diameter than the initial template size and a rough surface. This appearance is probably induced by the template itself. Although hydrogen evolution is unavoidable, the nanowires do not show signs of porosity. A better look at the tip of a nanowire (Figure 6b) shows a solid structure with what seems to be multiple terraces. For a 400 nm membrane, a constant potential deposition at −0.965 V results in $CoSb_3$ nanowires with a ratio of Co to Sb of 1:3 (Figure 6c). X-Ray Diffraction measurements confirmed the presence of $CoSb_3$ phase [7, 8].

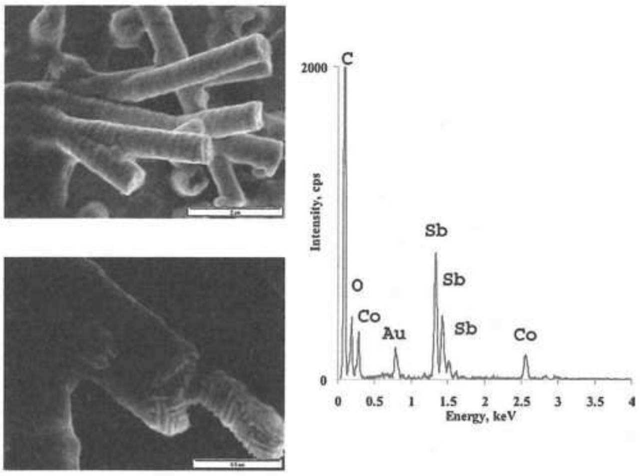

Figure 8. (a) SEM micrograph of nanorods grown inside a 400 nm PCTE template at −0.965 V; (b) SEM image of a nanowire tip showing multiple terraces of various orientations suggesting the impingement of growing nuclei; (c) EDS on nanowires. [7]

Interestingly, there is a quite large difference in composition of the deposit obtained as a thin film, nanowires or overgrown nanowire films (i.e. mushroom caps) [7]. This observation opens up the possibility to engineer naostructures with integrated jonctions and unique nano-architectures including structural and compositional gradients.

4. Storage: Li-ion Batteries

Another application that benefits from low-dimensionality is the energy storage [23-25]. In Li-ion batteries, nanostructured electrodes provide a larger interface compared to clasic materials, increase the available power and decrease the time required to recharge the battery. Also, from a design point of view, fully accessible nanostructured metallic current collectors should be in intimate contact with high capacity stable electrode materials to increase loading per unit area without significant loss in rate capability. Stability and cyclability

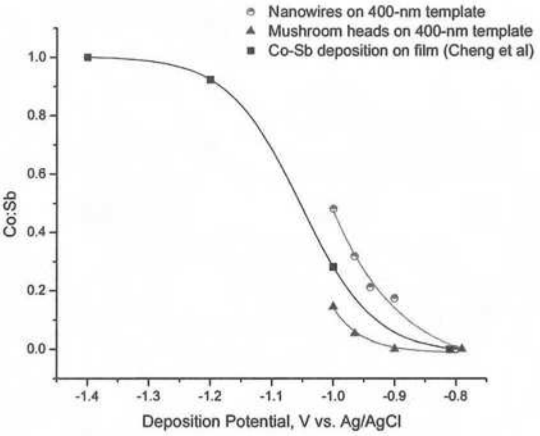

Figure 9. Atomic ratio of Co to Sb as a function of deposition potential for 400 nm nanorods and their resultant mushrooms/"films" [7].

Another benefit of using nanostructured materials for Li-ion batteries is that less electrode material can be used, reducing the possibility of catching fire.

However, nanostructured electrodes could be fragile and unstable to repeated charge-discarge cycles. One way to overcome this disadvantage is to coat and protect the electrode surface (Figure 9) with a material that is designed to permit the transfer of Li-ions and to accomodate the plastic deformation associated with the charge-discharge process.

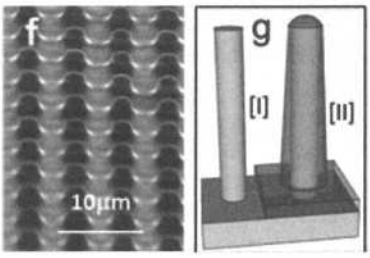

Figure 9. Conformal polymer coating over nanostructured electrode (left). Schemtics of the polymer integrated onto a micro- or nano-structured electrode (right).

5. Conclusions

Nanostructured materials have unique properties that can be exploited in energy applications. An important aspect brought by nanotechnology is the high ratio of surface area to volume, which is a key factor in interface processes associated with light and heat harvesting, conversion and storage. Electrochemical template synthesis is one of the inexpensive route to fabricate nanomaterials for a variety of applications.Taking advantage of the special properties stemming from nanoscale dimensions and combining them with novel architectures have the potential to increase the efficiency of energy conversion.

6. References

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