Communication

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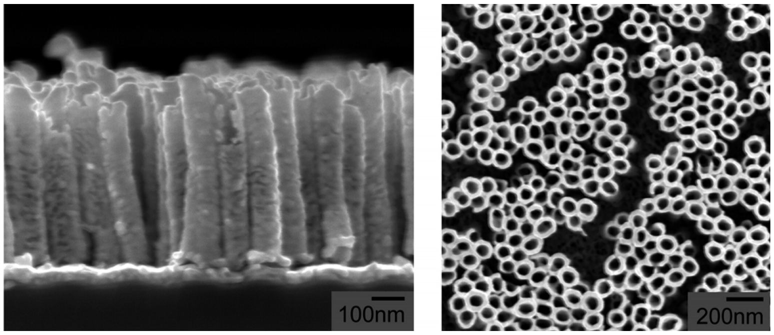

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Aligned Arrays of Nanotubes and Segmented Nanotubes on Substrates Fabricated by Electrodeposition onto Nanorods

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Nanotubes of metals, semiconductors, and polymers are of interest for a broad range of applications, and many approaches have been developed for their fabrication.[1] In particular, template-based methods of nanotube formation are useful because they enable good control over the nanotube dimensions and can be used to deposit a wide range of materials.[2−11] In addition to controlling the nanotube dimensions, for many applications it is also desirable to integrate nanotubes into organized arrays directly on substrates.

In this work, we describe a double-templating approach using simple electrochemical methods to create aligned arrays of nanotubes on substrates. Initially, nanorod arrays are fabricated by electrodeposition into anodic alumina templates. Then the alumina is removed, and the remaining nanorod array is employed as a template for conformal electrodeposition to create nanotube arrays. This approach allows us to both fabricate and organize nanostructures over large areas on substrates in the same process. Electrodeposition is a versatile method for fabricating nanostructures because the composition, morphology, and thickness of the deposit can be easily varied. Here we have fabricated gold nanotube arrays by electrodeposition onto nickel nanorods. In addition to uniform nanotubes, we have also created arrays of segmented nanotubes by using electrodeposited, layered nanorods as the templates for fabrication.

The method used to fabricate nanotube arrays is shown schematically in Figure 1. First, nanoporous templates are fabricated by anodizing aluminum films that have been evaporated onto silicon substrates.[12] By varying the anodization conditions, the pore diameter, spacing, and height can be tuned,[13−16] and the pore ordering can also be controlled.[17] Next, nickel nanorods are electrodeposited into the pores of the alumina. After deposition, the exposed ends of the nanorods are modified by anodization in a dilute KOH solution. Because the anodization is performed when the alumina is still in place, only the top ends of the nanorods are anodized. Then the alumina template is removed by a selective chemical etch, leaving an array of nickel nanorods with anodized tips. This nanorod array is then used for electrodeposition of gold nanotube arrays. The nanotube material deposits uniformly across the entire surface of the nanorod arrays, except at the anodized tips of the nanorods. Finally, the nickel nanorod array template is selectively removed, resulting in an array of open-ended nanotubes on the substrate.

We have used this approach to create gold nanotube arrays, as shown in Figure 2. The tubes in Figure 2A,B were deposited onto nickel nanorods with diameters of ∼70 nm and heights of ∼600 nm (Figure 2A) and 1.2 μm (Figure 2B). These tubes were deposited under two sets of electrodeposition conditions, resulting in different tube wall morphologies. The tubes in Figure 2A were deposited at −1 V (vs SCE) at room temperature, and the resulting nanotubes have a fairly porous wall structure. The rods in Figure 2B were deposited at −0.75 V (vs SCE) at 40 °C, leading to more uniform, dense tube walls, as seen in the TEM image (Figure 2C). The top view SEM image in Figure 2D corresponds to the tubes shown in

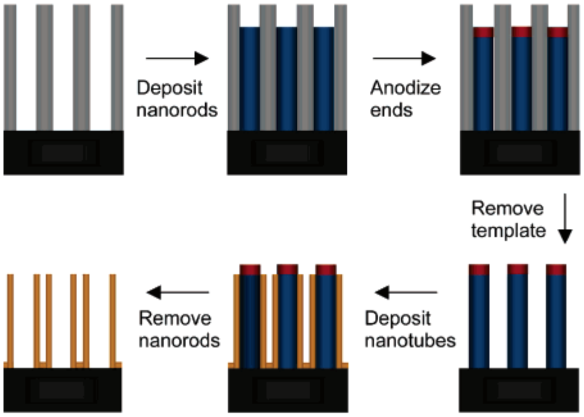

Figure 1. Schematic of method to fabricate nanotube arrays on substrates. Nanorods are electrodeposited into nanoporous anodic alumina template films, the alumina is removed, and then the nanorods are used as secondary templates for nanotube electrodeposition.

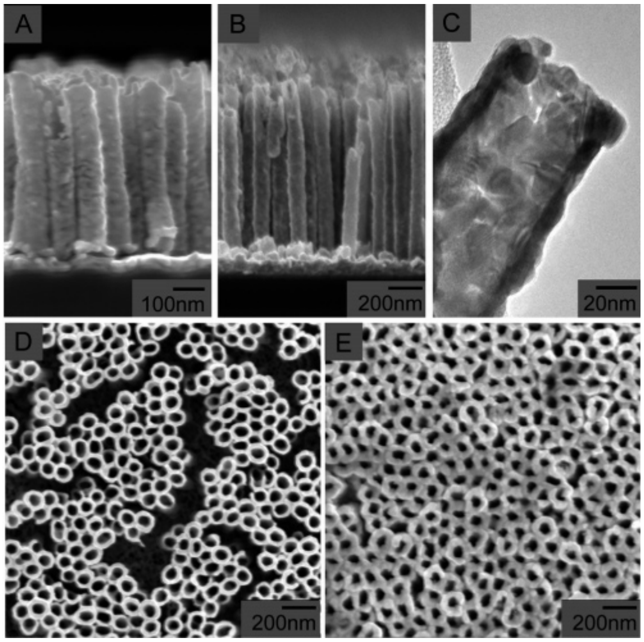

Figure 2. Images of electrodeposited gold nanotubes. Side view scanning electron microscopy (SEM) images of gold nanotubes on silicon substrates with heights of (a) ∼600 nm and (b) ∼1.2 μm; a few nanotubes were broken when the samples were cleaved for analysis. (c) Transmission electron microscopy (TEM) image of the end of a gold nanotube removed from the substrate. Top view SEM images of (d) the gold nanotube array shown in (a), and (e) a gold nanotube array with thicker tube walls created by a longer electrodeposition time.

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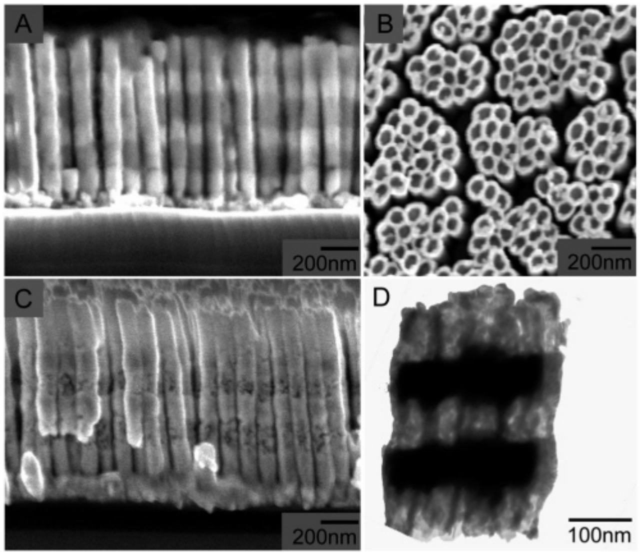

Figure 3. Images of segmented nanostructures. (a) Side view SEM image of layered gold−nickel nanorods on silicon substrate; the brighter segments are due to the heavier gold portions. (b) SEM image of the top of a segmented gold nanotube array after nickel removal. (c) Side view SEM image of the segmented gold nanotube array in (b). (d) TEM image of several segmented gold nanotubes after removal from the substrate; the lighter regions are nanotube segments and the darker regions are gold-filled nanorod segments.

Figure 2A, while the tubes in Figure 2E were deposited at the same conditions for a longer time, resulting in thicker tube walls. In both of these top view images, the open ends of the nanotubes are apparent. Open-ended tubes are formed when the tops of the nickel nanorods are anodized before gold nanotube deposition, which prevents electrodeposition on the top of the rods. When the nickel nanorod ends are not anodized, gold deposits over the entire surface of the nanorod, resulting in nanotubes with closed ends (see Supporting Information, Figure S1).

In addition to creating uniform nanotubes, it is also possible to modify the morphology along the length of the nanostructure using this approach. For example, we have created segmented gold nanotubes, as shown in Figure 3. These nanostructures were fabricated using the same method as outlined in Figure 1, except that the starting nanorods consisted of layers of gold and nickel. An SEM image of a gold−nickel layered nanorod array is shown in Figure 3A. After gold nanotube deposition and nickel removal, the top ends of the segmented tubes are open (Figure 3B). Along the length of the nanostructures, there are three segments of open gold nanotube alternating with three segments of gold-filled nanotube corresponding to the gold segments in the initial nanorods, as seen in Figure 3C. The segments are more clearly apparent in the TEM image of a few nanostructures shown in Figure 3D. When the tubes were prepared for TEM imaging, the tubes broke off the substrate at the top of the gold-filled segment next to the substrate. The image shows the three hollow gold tube segments (lighter regions) and two gold-filled segments (darker regions) of the nanostructures. The slight porosity of the tube walls ensures complete dissolution of the nickel segments during immersion in dilute phosphoric acid.

In summary, we have demonstrated a method to prepare arrays of electrodeposited, open-ended nanotubes aligned vertically on substrates. The nanotubes are deposited onto nanorod templates, which are themselves fabricated by electrodeposition into nanoporous alumina films. The nanotube inner diameter, spacing, and height are determined by the nanorod dimensions, which in turn correspond to the alumina film characteristics. The nanotube morphology and wall thickness depend on the electrodeposition parameters. We have fabricated gold nanotube arrays with tube walls <10 nm thick, inner tube diameters of 70 nm, and aspect ratios >15. Because these dimensions can be tuned by varying the dimensions of the pores in the starting alumina templates, it may be possible to create ordered arrays of nanostructures with thinner tube walls,[18] smaller diameters (<10 nm),[19,20] and higher aspect ratios using this approach. We have demonstrated that we can vary the tube wall morphology by changing the tube electrodeposition potential and temperature. Further refinement of the deposition conditions may lead to even better control of the of the nanostructure morphology, as has been shown recently by the fabrication of single-crystalline electrodeposited nanowires.[21] In addition to open nanotubes, we have demonstrated that the morphology can be varied by using segmented nanorods as templates to create alternating sections of nanotubes and rods along the length of the nanostructure. The general nanotube array fabrication approach described here may be used to create various metal, semiconductor, or polymer nanotubes by electrodeposition using either nickel or another nanorod material as a selectively removable template. This method is also potentially amenable to fabricating multiwalled nanotubes[22] by sequential electrodeposition of different materials.

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Supporting Information Available: Details of the experimental methods and additional images of the nanotubes. This material is available free of charge via the Internet at http://pubs.acs.org.

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