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Chemical Strategies for Template Syntheses of Composite Micro- and Nanostructures

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The template method for preparing nanomaterials entails synthesis of monodisperse tubular and fibrillar nanostructures within the pores of a membrane or other nanoporous solid.[1] Nanostructured materials of this type constitute one of the most important frontiers in materials science,[1,2] and composite nanomaterials have been of particular recent interest.[3−13] While the template method has been used to prepare segmented nanowires, where different segments down the length of the wire are composed of different materials,[12,13] the chemically more challenging concept of synthesizing concentric tubular composites has never been reported. Synthetic strategies for preparing such concentric tubular composite structures are described here.

A conductor/insulator/conductor composite microstructure consisting of an outer gold tubule, surrounding an inner tubule of an electronically insulating polymer, surrounding an inner microwire of an electronically conductive polymer will serve to introduce the concept of sequential tubular-materials synthesis used throughout this work. These composite microstructures were synthesized in the rather large (3 μm diameter) pores of a polyester[1] template membrane (Figure 1A) so that the structures obtained after each synthetic step could be clearly imaged with the scanning electron microscope (Figure 1).

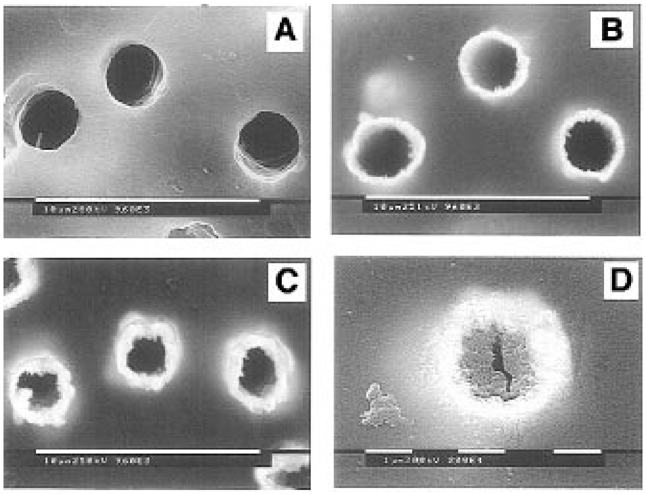

Figure 1. Scanning electron micrographs of the surface of the polyester template (A) and of the tubular structures obtained after each synthetic step in the preparation of the Au/PPO/polypyrrole composite microstructures (B−D). (B) Surface of the template after electroless deposition of the Au tubules within the pores. (C) Surface of the template after electropolymerization of the PPO tubules within the Au tubules. Note that the PPO causes the tubule wall to be thicker than in Figure 1B. (D) After electropolymerization of the polypyrrole microwires within the PPO tubules.

The outer gold tubes were prepared using an electroless deposition method[14,15] (Figure 1B). These Au tubules were then used to electro-polymerize tubules of the insulating polymer poly(2,6-dimethylphenol) (PPO)[16] onto the inner surfaces of these Au tubes (Figure 1C). This electropolymerization method yields PPO tubules with ultrathin (∼50 nm) walls.[16] Nevertheless, these insulating tubes are defect-free.[17] Cyclic voltammetry was used here to prove this point. Prior to deposition of the inner PPO tubules the Au tubule-containing membrane was immersed into an aqueous solution of the redox-active species Fe(CN)$_6^{3-}$.[17] The characteristic[17] Fe(CN)$_6^{3-/4-}$ voltammogram was observed at the Au tubes. After PPO deposition, no trace of this voltammetric signal could be seen, indicating that the outer Au tubules had been completely sealed by the inner PPO tubules.

An inner microwire of the electronically conductive polymer polypyrrole was then deposited down the center of each PPO tubule (Figure 1D). An electropolymerization method[18] was used. An Au film sputtered[19] onto one face of the template membrane served as the polymerization electrode. Electropolymerization using IO$_4^-$ dopant was continued until the polypyrrole microwire propagated through the entire 10 μm thickness of the template (Figure 1D). Energy-dispersive spectroscopy confirmed the presence of polypyrrole in the composite microstructures with two new peaks at 3.9 and 4.2 keV identified as the L$_{\beta1}$ and L$_{\alpha1}$ emissions peaks of iodine (Figure 2).

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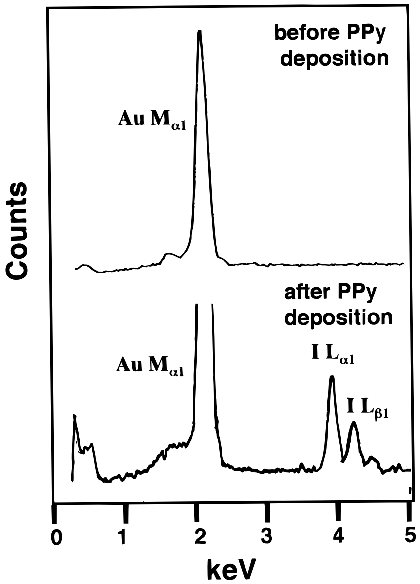

Figure 2. Energy-dispersive spectra before and after electropolymerization of polypyrrole into the Au/PPO composite microstructures. After polypyrrole deposition, two additional emmision peaks appear in the spectra which have been assigned to iodine in IO_4^- dopant for polypyrrole.

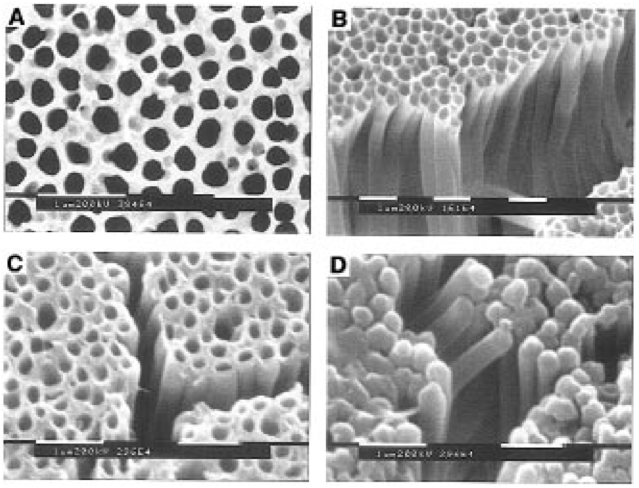

Figure 3. Scanning electron micrographs of the surface of the alumina template (A) and of the tubular structures obtained after each step of the synthetic procedure used to prepare the C/PAN/Au composite nanostructures (B–D). (B) The C tubules obtained after dissolution[20] of the template. (As noted in the text, the C/PAN/Au composites were prepared by doing the appropriate chemistries in sequence leaving the alumina template intact; however, it is easier to image these extremely small structures after dissolving the template.) (C) As per (B), but after polymerization of a PAN tube within each C tubule. Note that the PAN causes the tubule wall to be thicker than in Figure 3B. (D) After electrodeposition of a gold nanowire within each PAN tubule.

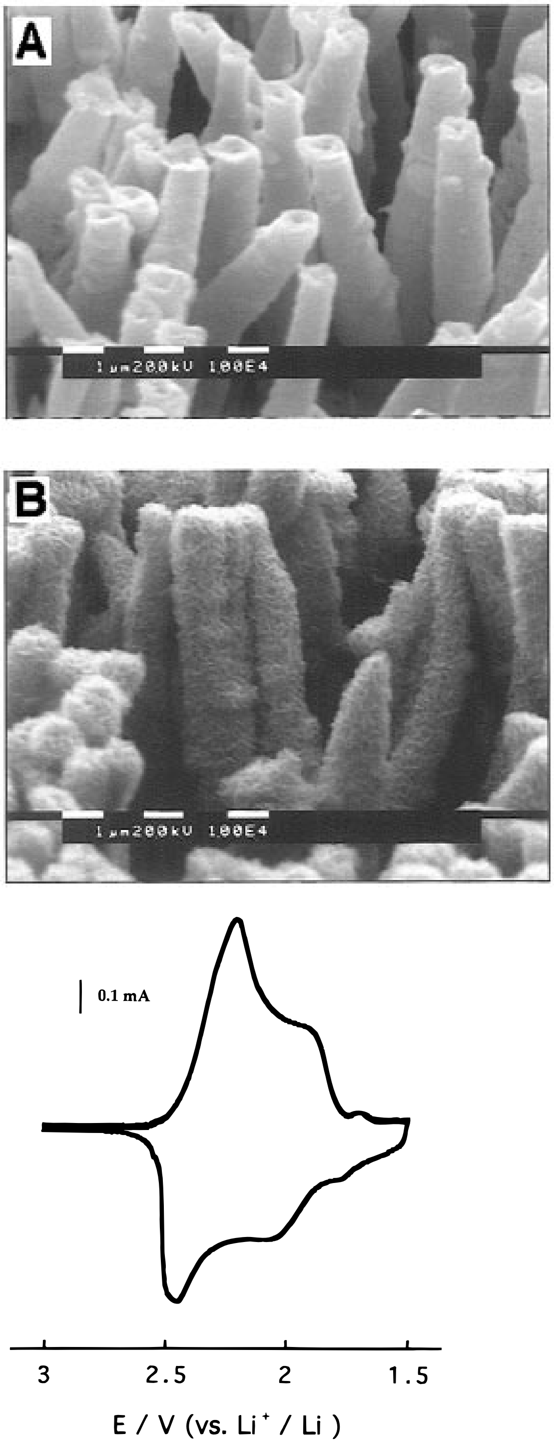

Figure 4. Scanning electron micrographs of an ensemble of Au tubules before (A) and after (B) CVD of the outer TiS_2 tubules. The tubules are protruding from the substrate Au surface layer. That the material deposited was, indeed, TiS_2 was confirmed using energy-dispersive spectroscopy and cyclic voltammetry (Figure 4C, scan rate = 0.3 mV s^{-1}).

An alternative set of chemistries was used to prepare a second insulator/conductor/insulator composite in the much smaller (200 nm diameter) pores of an alumina[1] template (Figure 3A). This composite consisted of an outer tubule of graphitic carbon, surrounding an inner tubule of the insulating polymer polyacrylonitrile (PAN), surrounding an inner gold nanowire. The chemistry used to prepare the carbon tubules[20] entails chemical polymerization of tubules of a precursor polymer (PAN), followed by thermal graphitization (Figure 3B). The PAN polymerization[20] was then repeated to yield PAN tubules within the carbon tubes (Figure 3C). An Au film was then sputtered[19] onto one face of the membrane. This film was used to electrodeposit Au nanowires down the centers of the inner PAN tubules.[19]

An ensemble of the completed C/PAN/Au composite nanostructures is shown in Figure 3D. In this case, the template membrane was dissolved away,[20] leaving the nanostructures protruding from a substrate surface like the bristles of a brush. The substrate may be either

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conductive[21] or insulating.[22] Alternatively, the composite structures can be left imbedded within the pores of the template membrane (e.g., Figure 1D). Both of these approaches allow for electrical contact to be made to all of the nanostructures in parallel;[14,21] this will be demonstrated below. Alternatively, the membrane can be dissolved away and the individual structures collected by filtration.[18]

Chemical vapor deposition (CVD)[23] can also be used as a synthetic step to prepare such tubular composites (Figure 4). The electroless method[14,15] was used to prepare Au tubules within the 1 μm- diameter pores of a polyester template membrane. One Au surface layer was removed,[15] and the membrane was dissolved by immersion into hexafluoro-2-propanol. The Au tubules (Figure 4A) were then placed in a home-built CVD reactor,[24] and TiS_2 tubules were deposited on the outer surfaces of the Au tubes (Figure 4B). CVD conditions: 200 mTorr of $TiCl_4$ and 600 mTorr of 1-methyl-1-propanethiol, substrate temperature = 250 °C, deposition time = 3 min.[24]

TiS_2 and other Li^+-intercalation materials are used as electrodes in Li-based batteries.[25] We have recently shown that electrodes composed of template-synthesized Li^+-intercalating nanostructures provide higher discharge capacities than conventional electrodes prepared from the same material.[26] These results suggest that nanomaterials may play a role in design of future Li-ion battery electrodes. However, one potential problem with this new approach for preparing such electrodes concerns the low electrical conductivities of many of the Li^+-intercalation materials.[26] The CVD-based composite approach described here should solve this problem. This is because each electrode particle is coated as a thin-walled tubule onto its own current-collecting electrode (the inner Au tubule, Figure 4).

Figure 4C demonstrates this concept. An ensemble of Au/TiS_2 microstructures (Figure 4B) was immersed into a 30:70 (v/v%) mixture of ethylene carbonate and diethyl carbonate that was 1 M in $LiClO_4$. The Au/TiS_2 microstructure ensemble served as the working electrode, and Li metal films were used as the reference and counter electrodes.[26] Cyclic voltammetry was used to drive the following reversible Li^+ intercalation reaction:

$$TiS_2 + xe^- + xLi^+ \rightarrow Li_xTiS_2 \qquad (1)$$

The cyclic voltammogram obtained (Figure 4C) shows that Li^+ is reversibly inserted and removed from the outer TiS_2 tubules.

Finally, we have recently shown that sol−gel syntheses can be accomplished within the pores of the alumina templates to make semiconductor tubules.[27] Figure 5 shows that TiO_2 tubules prepared in this way[27] can be filled with polypyrrole nanowires to make semiconductor/conductor composites. The polypyrrole nanowires were grown using a simple chemical polymerization method.[22] TiO_2 is a promising material for photoelectrochemical energy production, and it has been shown that high surface area forms have higher photo efficiencies.[28] TiO_2/conductor nanocomposites may prove to be useful photocatalysts because the template synthesized TiO_2 nanostructures have very high surface areas.[27] Furthermore, as discussed previously, each outer tubular TiO_2 catalyst particle has its own current collecting electrode inside.

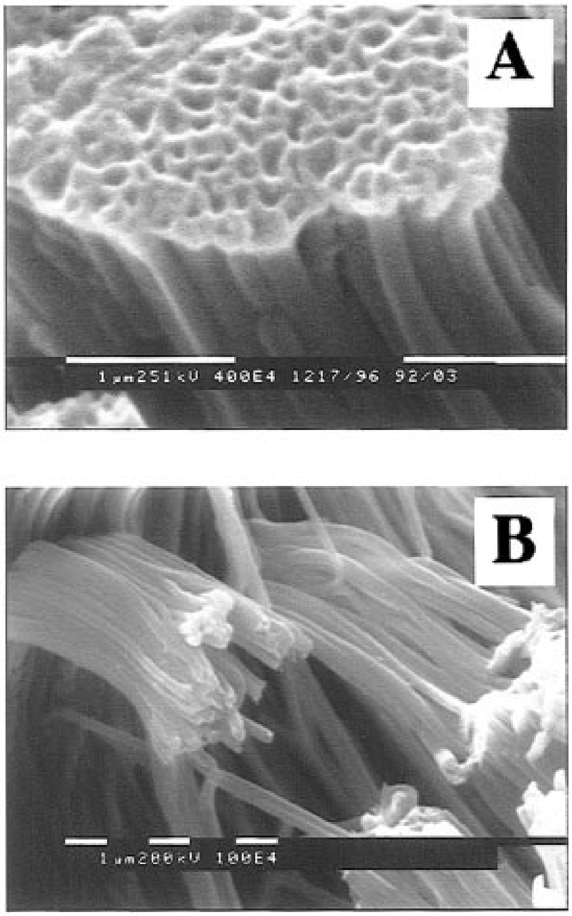

Figure 5. Scanning electron micrographs of TiO_2 nanotubules prepared by sol−gel template synthesis before (A) and after (B) filling with polypyrrole nanowires.

A broad arsenal of chemical synthetic methodologies has been used, in sequence, to make composite tubular micro- and nanostructures within the pores of various template membranes. Composites composed of a variety of different conducting, insulating, semiconducting, photoconducting, and electroactive materials have been prepared.

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