Periodic Pulse Electrodeposition to Synthesize Ultra-high Density CdS Nanowire Arrays Templated by SBA-15 Mesoporous Films

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The high-density CdS nanowire arrays, which are the negative replica of the parent mesoporous thin films with a stoichiometric composition, have been synthesized through a newly developed periodic pulse electrodeposition route.

Rencently there has been a growing attention to mesoporous molecular sieves because of its possibilities as a template for the synthesis of nanostructured new materials.[1] The synthesized hybrid materials will find wide applications in different fields such as catalysis, sensors, and nonlinear optics.[2] To date, more studies have been focused on the growth of nanoparticles or wires inside mesoporous powder[3,4] rather than mesoporous thin films (MTFs), which, however, would find attractive applications in making nano-ordered devices.[5,6] As far as nanowires are concerned, only single element such as carbon,[7a] germanium,[7b] and metal[7c,d] have been successfully incorporated into the pore channels of MTFs. Binary compound arrays, such as metal sulfides semiconductors, have not been found to be reported. Herein, we develop, for the first time, a pulse electrodeposition route to prepare ordered CdS, a typical example of II–VI semiconductors, nanowire arrays templated by SBA-15 MTFs.

Pulse electrodeposition (PED) has advantages over the conventional direct current potentiostatic electrodeposition because of the possible beneficial effects on the morphology and compositional uniformity of the deposit.[8] Those effects are a consequence of the free choices of several variables independently, e.g., type of periodic waveform, potential, and duration of cathodic and anodic pulses for a particular deposition solution rather than simply the potential. In the current investigation, SBA-15 MTFs were prepared as previously reported[9] on ITO coated glass substrates. Deposition electrolytes were prepared by mixing 0.2 M cadmium chloride, 0.01 M sodium thiosulphate with concentrated hydrochloric acid added dropwise to adjust a PH range of ca. 2.5.[10] The PED was performed using a conventional three-electrode system in a glass cell with a Pt wire as a counter electrode and Ag/AgCl as a reference electrode under a variety of selected conditions, such as at 90 °C and with stirring. Square waveform pulses were applied with a duty cycle of 0.25, i.e., cathodic pulse time t_{on} of 300 ms and time between pulses t_{off} of 900 ms based on our trial and error experiments and electrochemical measurement results. In all cases, the electrolyte was freshly prepared and heated for 40 min at 90 °C prior to each deposition and N_2 gas was bubbled before and during the deposition to deoxygenate. After the deposition, the substrates were washed with running distilled water followed by heat treatment at 350 °C in H_2 atmosphere for 1 h.

The mechanism of electrodeposition CdS was reported to be the release of elemental sulfur from $S_2O_3{}^{2-}$ by the addition of HCl and consecutive reduction of S to H_2S.[11] When MTF-covered ITO was employed as a working electrode, the codeposition region of Cd and S was found to be from −0.55 to −0.95 V as shown in Figure 1. The $S_2O_3{}^{2-}$ ions react with Cd^{2+} ions, resulting in the electrodeposition of CdS nanowires into the channels of MTF-coated ITO at proper pulse potentials. The overall reaction of codeposition can be given as Eq 1.

Although G. Sasikala et al.[12] reported that the deposition of enriched cadmium dominated at the higher cathodic potential,

$$Cd^{2+} + S_2O_3^{2-} + 2e \rightarrow CdS + SO_3^{2-} \qquad (1)$$

which resulted in the color variations of the deposited CdS using a direct current electrodeposition route, the composition of our synthesized CdS nanowires entrapped in MTFs was found to be nearly independent of pulse potential in the range of −0.7 to −1 V. In fact, when a single pulse cycle was completed, the electrolytes had enough time, t_{off}, to diffuse into the channels of MTFs to initiate another cycle, which can explain the compositional uniformity of the deposited CdS at different voltage.

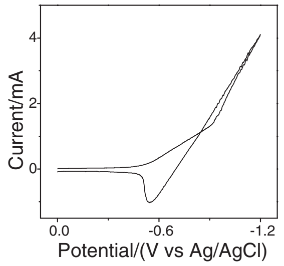

Figure 1. Cyclic voltammograms for the electrodeposition of CdS nanowires into the channels of MTFs recorded at a scan rate of 100 mVs^{-1}.

Figure 2 shows the low angle XRD patterns of the as-synthesized SBA-15 parent MTFs and CdS nanowires loaded MTFs. Two intense diffraction peaks at $2\theta = 1.26$ and 2.48°, which can be indexed as (100) and (200) reflections, are characteristic of a 2-D hexagonal (*p6mm*) structure with d_{100} spacing of ca. 7.05 nm. The absence of the (110) reflection is typical in the XRD pattern for the hexagonal unit cells with the c and a axes

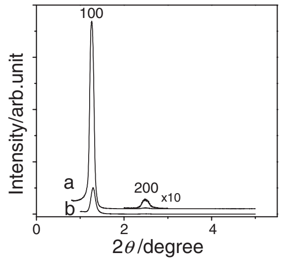

Figure 2. Low-angle XRD patterns of (a) primary MTFs without CdS and (b) CdS nanowires loaded after PED.

parallel to the film substrate.[9] An apparent decrease of the low-angle peak intensity is observed as shown in Figure 2b after PED, indicative of the pore filling of the SBA-15 during the loading process because the pore filling would reduce the scattering contrast between the pores and the walls of the MTFs.[7c,d] In addition, we found that the (100) peaks have slightly shifted to high-angle direction after CdS nanowires being deposited, which may be due to the further contraction of framework during the calcination process of composite films at 350 °C. Similar phenomena have been found by our group during the calcination of mesoporous materials.[3]

The typical TEM image of Figure 3 clearly shows that the uniform CdS nanowires are embedded in hexagonal channels after PED. The nanowires appear as dark rodlike objects between the walls of MTFs. It can be clearly seen that CdS have filled the channels completely and have a uniform size about ca. 6.5 nm corresponding to the pore diameter of the template, which is in agreement with the results of XRD. These measurements indicate the feasibility of controlling the diameter of the nanowires via the pore size of the templates. The inset is a selected area elctron-diffraction (SAED) pattern obtained from the region in Figure 3a, which indicates that CdS nanowires have well crystallized. Energy dispersive spectra (EDS) produce strong Cd and S signals (not shown). From the spectra, a stoichiometric ratio of 6.92:6.15 for Cd:S is calculated, which confirms the formation of CdS inside the channels of MTFs. The specta also provide a ratio of 6.92: 39.41 for Cd:Si and 6.15: 39.41 for S:Si, indicating a 16.58% molar percent or 39.79 wt % of CdS loading. In fact, almost no difference of the ratios of Cd:S and Cd:Si has been found with the direction of incident electron beams, which further indicates that CdS have been fully filled into the channels of MTFs.

Figure 3b shows the structure and morphology of unsupported nanowire arrays after the silica film matrix is removed by 2% HF solution. Large areas of nanowire bundles were observed when TEM was employed to directly visualize CdS nanowires. The length of CdS nanowires are identical to that of the pore channels and these large bundles of nanowires are of the uniform diameters consistent with the size of the ordered pores, separated by the repeating distance corresponding to the wall thickness of SBA-15 templates. This finger-like or swirling shape arrays are a complete reverse structure of SBA-15 MTFs,[7c] which further indicates that CdS nanowires have been fully filled the channels of MTFs. The diffraction rings in the inset support the fact that CdS nanowires have been crystallized.

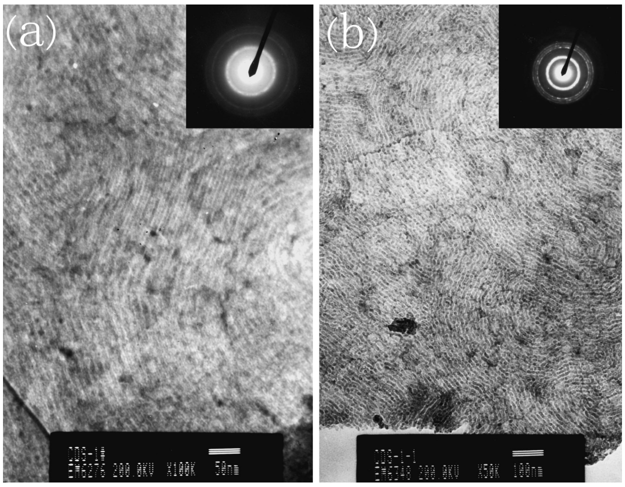

Figure 3. TEM images of CdS nanowires (a) confined in the framework of MTFs, (b) unsupported after the removal of silica matrix with 2% HF aqueous solution and the inset shows the corresponding SAED.

Further evidence for the composition and purity of the as-prepared nanowires is obtained by X-ray photoelectron spectra (not shown). The two strong peaks at 405.05 and 161.1 eV correspond to Cd_{3d} and S_{2p} binding energies, respectively.[13] The atomic ratio calculated from the intensity of Cd_{3d} and S_{2p} peaks was 52.3:47.7, which indicates the approximate stoichiometric formation of CdS in agreement with the results of EDS. In fact, when different pulse voltage in the range of -0.7 to -1 V was used to electrodeposit CdS nanowire arrays, almost the same XPS were obtained, indicating the composition of our synthesized nanowires are independent of pulse potential. These measurements further demonstrate that the compositional uniformity was maintained through PED, which can explain why our synthesized nanowire arrays have no color change at different deposition potential as mentioned above.

In summary, a general approach has been developed to incorporate CdS into the channels of MTFs to form nanowire arrays by PED. These nanowires are the negative replica of the pore structure of MTFs. Although this study has centered on the synthesis of CdS nanowire arrays, the method can be extended to a large number of sulfides, oxides and arsenides. It is believed that the periodic potential is a key factor to maintain the compositional uniformity of the binary compounds. Further work will be carried out on the synthesis of other compounds and to study the optical properties.

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