Porous CdS Nanowire Arrays Self-assembled in Anodic Aluminum Oxide Template

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Porous CdS nanowire (NW) arrays have been synthesized by self-assemble of CdS nanoparticles (NPs) inside Sn^{2+}/Pd^{2+}-activated nanochannels of anodic aluminum oxide (AAO) template. XRD analysis indicates that the as-synthesized CdS NWs are hexagonal crystalline. TEM and SEM observations reveal that the CdS NWs are porous and consists of self-assembled CdS NPs.

Porous nanowires (NWs) have attracted more attention in recent years, which have potential applications in catalysis, sensors, and optical devices.[1,2] Porous NWs have been synthesized by several techniques such as vacuum filtration with electrochemical deposition,[1] templateless wet-chemical approaches[3] and solution phase precursor route.[2]

Solid CdS NWs in the nanochannels of anodic aluminum oxide (AAO) templates have been synthesized by electrochemical process before.[4,5] In this letter, we report a simple way to synthesize porous CdS NW arrays by self-assemble of nanoparticles (NPs) in AAO templates. In the field of nanoscience, NPs have been widely used as fundamental building blocks and assembled into artificial architectures.[6–8] Our process is similar to oriented attachment growth, in which the aggregate of NPs is mainly driven by the interaction of the organic ligands rather than by the interaction of the particle core.[9] The activated AAO templates were immersed in a mixture solution of thioacetamide (CH_3CSNH_2) and $CdCl_2$, and heated at 80 °C to form porous CdS NWs.

The AAO templates were prepared using a two-step anodization described previously.[10] The diameter of the pores in the AAO template is about 55 nm. The through-hole AAO templates were immersed in an aqueous $SnCl_2$ solution ($10\,g\,L^{-1}$) to sensitize the pore walls for 5 min. After being taken out from the $SnCl_2$ solution, the AAO templates were washed in distilled water 2–3 times and dried in air for 24 h. Next, the sensitized AAO templates were placed in an aqueous $PdCl_2$ solution ($1\,g\,L^{-1}$) and ultrasonicated for 1 min to introduce $PdCl_2$ on the pore walls, and then rinsed in distilled water several times. Then the AAO templates were dried in air at 30 °C for 24 h. Subsequently, these AAO templates were immersed in a mixture solution containing 0.1 M CH_3CSNH_2 and 0.1 M $CdCl_2$, and then heated at 80 °C for 5, 15, and 25 min, respectively.

The as-synthesized products were characterized by a rotating anode X-ray powder diffractometer (XRD, D/MAX-Ra) with Cu Kα radiation ($\lambda = 1.542$ Å), transmission electron microscope (TEM, JEM 200CX), high-resolution transmission electron microscope (HRTEM, JEOL 2010), and scanning electron microscope (SEM, Sirion 200). For TEM observation, the obtained AAO templates with CdS NWs inside were put into a 5 wt % NaOH solution to dissolve the AAO templates. The remaining NWs in the solution were washed with distilled water, and then dispersed in ethanol by ultrasonication. Drops of the solution were dripped onto copper grids with holey carbon film. For SEM observations on the samples with short immersion time, broken pieces of the products were put on Cu stubs with cross-sectional surface on top, and then sputtered with conductive gold coating. Samples with 25-min reaction time were treated with a 5 wt % NaOH solution for 1 min to dissolve the AAO templates, then washed with distilled water, dried and put on Cu stubs with conductive gold coating. FI-IR absorption spectrum was determined by a Nicolet NEXUS Fourier transform infrared spectrometer. The CdS NWs deposited after 25 min in AAO template was mixed thoroughly with KBr powders. The IR spectra were obtained between 500 and 4000 cm^{-1}.

Figure 1 shows the XRD pattern of the as-synthesized CdS product (deposited for 25 min) embedded in the nanochannels of the AAO template. As shown in the pattern, hexagonal CdS-crystalline structure can be observed with relatively broad diffraction peaks attributed to the CdS NWs consisting of fine CdS NPs in the nanochannels of amorphous AAO template, which will be discussed below.

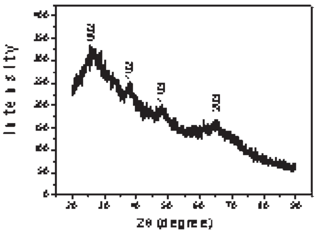

Figure 1. XRD pattern of the as-synthesized CdS in AAO template.

Figure 2 shows SEM micrographs of the as-synthesized CdS with different immersing time in the mixture solution (5, 15, and 25 min). With short immersing (reaction) time CdS NPs assembled uniformly on the surface of the pore walls (Figure 2a). This can be attributed to the uniformly distributed catalysts, Sn^{2+}/Pd^{2+} ions, which were introduced onto the surface of the pore walls from $SnCl_2$ and $PdCl_2$ solutions. Then CdS, from the reaction of CH_3CSNH_2 and $CdCl_2$, deposited on the active sites because of thermodynamical favorableness.[11] With the prolongation of reaction time (Figure 2b), more CdS NPs were formed and aggregated in the pore walls. When the reaction time reaches to 25 min (Figure 2c) porous CdS NWs consisting of NPs were formed.

A typical TEM image (Figure 3a) of the CdS NWs deposited for 25 min reveals that the CdS NWs are about 55 nm in diameter, in agreement with that of the nanochannels in the AAO template. But the NWs are not smooth, consisting of small NPs, in agreement with the SEM observation. Selected area electron diffraction (SAED) pattern taken from one NW indicates that

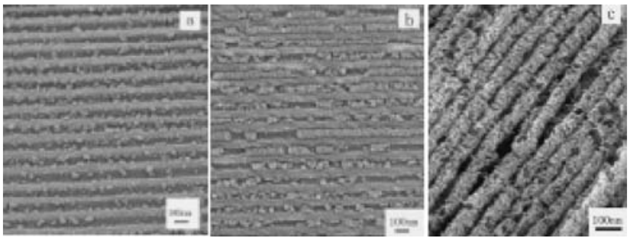

Figure 2. Side view SEM images of the self-assembled CdS NPs in the nanochannels of AAO templates with different periods of reaction time (a: 5 min; b: 15 min; c: 25 min).

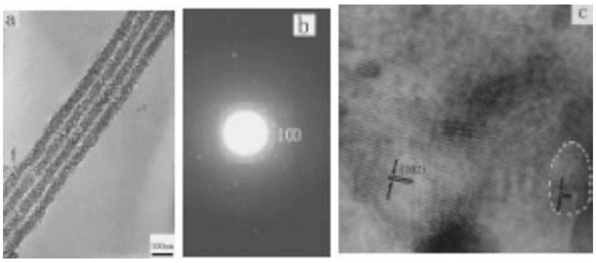

Figure 3. (a) TEM image of the CdS NWs with a deposition reaction time of 25 min; (b) SAED pattern of the NW shown in (a); (c) A High-resolution TEM image of a single CdS NW (one of the CdS nanoparticles was highlighted with white line contours for clarity).

the CdS NW is polycrystalline (Figure 3b). Lattice-resolved HRTEM image of one NW shows that the NW is indeed composed of NPs. The diameter of most particles is larger than that of the CdS Bohr radii, 2.3 nm.[12]

On the basis of the above experimental results, a possible mechanism for the formation of porous CdS NWs is proposed. (1) The pore walls of the AAO template have been activated by Sn^{2+} and Pd^{2+} ions. In this activation, Pd^{2+} ions are reduced to Pd by Sn^{2+} ions (Sn^{2+} ions are oxidized to Sn^{4+}) and deposited on the pore walls. (2) When heated, the reactant CH_3CSNH_2 is attacked by the strong nucleophilic O atoms of H_2O molecules, leading to the weakening of the C=S double bonds. The C=S bond will be broken and the S^{2-} anion will be slowly generated, which then reacts with Cd^{2+} to form CdS NPs. The preformed Pd on pore walls could serve as seeds for the heterogeneous nucleation and growth of CdS NPs. Then these CdS NPs will preferentially deposit on the active sites on the pore walls of the AAO template.[11] (3) At the beginning of the reaction, there are only a few CdS NPs, and the CH_3CSNH_2 can effectively cap most of the surface of the newly formed CdS NPs. If CdS NPs were capped by CH_3CSNH_2, there would be a spectroscopic consequence.[13] The new band at about 1760 cm^{-1}, different from C=S bond of free CH_3CSNH_2 at 1648 cm^{-1},[14] can be assigned to the C=S bond of adsorbed CH_3CSNH_2. (Figure 4). The increase of the observed wavelength number means that the vibrational transition of the C=S has been significantly affected by adsorption on the surface of CdS NPs. The result may indicate that CH_3CSNH_2 molecules are chemically adsorbed on the surface of CdS NPs. These CdS NPs protected by organic molecules are stabilized, without mutual aggregation.[15] (4) With the prolongation of reaction time, more and more S^{2-} will be supplied by CH_3CSNH_2, and the new crystalline seeds (CdS nucleate through homogeneous path) will form. Meanwhile the CdS NPs are capped with CH_3CSNH_2, then these NPs interact with each other via hydrogenbond to self-assemble into larger aggregates. (Evident broad peak at 3500 cm^{-1} may be attributed to the hydrogenbond action of the NH_2 group). Then diffusion controlled growth[16] occurs in the spherical aggregates as the particles are in closely contacted, leading to the formation of porous NWs. This mechanism is similar to that of oriented attachment where the small particles coated with small molecules are facilitate to attach, and because self-assemble occurs at multiple sites, leading to a coarser polycrystalline material.

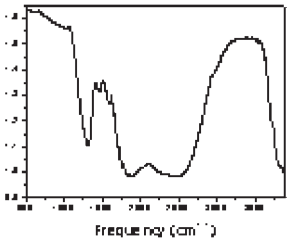

Figure 4. IR spectrum of the porous-CdS NWs in AAO template.

In conclusion, porous CdS NWs have been synthesized by self-assemble of CdS NPs in Sn^{2+}/Pd^{2+}-activated nanochannels of AAO templates. In the reaction, CH_3CSNH_2 was used as both the sulfur source and capping ligands. SEM and TEM observations revealed the growth stages of the porous NWs, on the basis of which a possible procedure has been proposed for the formation of the porous CdS NWs. This facile approach might be exploited to synthesize other porous NWs composed of important inorganic materials.

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References

1 F. Li, J. B. He, W. L. Zhou, and J. B. Wiley, *J. Am. Chem. Soc.*, **125**, 16166 (2003).
2 Y. L. Wang, X. C. Jiang, and Y. N. Xia, *J. Am. Chem. Soc.*, **125**, 16176 (2003).
3 G. Ramanath, J. Darcy-Gall, T. Maddanimath, A. V. Ellis, P. G. Ganesan, R. Goswami, A. Kumar, and K. Vijayamohanan, *Langmuir*, **20**, 5583 (2004).
4 J. S. Suh and J. S. Lee, *Chem. Phys. Lett.*, **281**, 384 (1997).
5 D. Routkevitch, T. Bigioni, M. Moskovits, and J. M. Xu, *J. Phys. Chem.*, **100**, 14037 (1996).
6 H. T. Liu and A. P. Alivisatos, *Nano Lett.*, **4**, 2397 (2004).
7 Z. Kónya, V. F. Puntes, I. Kiricsi, J. Zhu, A. Paul Alivisatos, and G. A. Somorjai, *Nano Lett.*, **2**, 907 (2002).
8 M. T. Crisp and N. A. Kotov, *Nano Lett.*, **3**, 173 (2003).
9 C. Pacholski, A. Kornowski, and H. Weller, *Angew. Chem., Int. Ed.*, **41**, 1188 (2002).
10 H. Masuda and K. Fukuda, *Science*, **268**, 1466 (1995).
11 X. Y. Yuan, G. S. Wu, T. Xie, Y. Lin, G. W. Meng, and L. D. Zhang, *Solid State Commun.*, **130**, 429 (2004).
12 Y. Kanemitsu, T. J. Inagaki, M. Ando, K. Matsuda, T. Saiki, and C. W. White, *Appl. Phys. Lett.*, **81**, 141 (2002).
13 S. L. Horswell, C. J. Kiely, I. A. O'Neil, and D. J. Schiffrin, *J. Am. Chem. Soc.*, **121**, 5573 (1999).
14 X. J. Zhang, Q. R. Zhao, Y. P. Tian, and Y. Xie, *Cryst. Growth Des.*, **4**, 355 (2004).
15 T. Tsuruoka, K. Akamatsu, and H. Nawafune, *Langmuir*, **20**, 11169 (2004).
16 L. Manna, E. C. Scher, and A. P. Alivisatos, *J. Am. Chem. Soc.*, **122**, 12700 (2000).