Highly Ordered Pt-loaded CdS Nanowire Arrays for Photocatalytic Hydrogen Production under Visible Light

Ningzhong Bao, Liming Shen, Tsuyoshi Takata, Daling Lu, and Kazunari Domen*
Department of Chemical System Engineering, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656

(Received September 26, 2005; CL-051227; E-mail: domen@chemsys.t.u-tokyo.ac.jp)

Highly ordered crystalline Pt-loaded CdS nanowire arrays were prepared using a hard template of mesoporous silica and show good photocatalytic activity for hydrogen production under visible-light irradiation.

Photocatalytic H_2 production is an attractive method because it offers a way of capturing solar energy and converting it into valuable H_2.[1] CdS is a well-known photocatalyst with suitable bandgap of 2.4 eV for photocatalytic H_2 production under visible-light irradiation in the presence of S^{2-} and SO_3^{2-} that helps to prevent the decomposition of CdS.[2] If CdS can be prepared in form of nanocrystals, they could have much higher activity, because catalysts with large specific surface area have much more surface active positions.[3] However, it is still needed to study the influence of the shape and array of CdS nanocrystals on their photocatalytic activity, because the chemical and physical properties of nanocrystals are also governed by their shape, crystallinity, and particularly, the arrangement of nanocrystals.[4] Recently, several methodologies have been developed for preparing CdS nanocrystal arrays by using mesoporous silica as template,[5] by using surfactants as nano reactors,[6] or by using air-sensitive organocadmium complexes in organic solvents.[7] The photocatalytic activity of these CdS nanomaterials is low because of the low crystallinity, the residual surfactant, or the organic coating. Here, we report a simple synthesis method for preparing highly ordered crystalline CdS nanowire arrays, showing good photocatalytic H_2 production with a Pt cocatalyst, using sacrificial reagents under visible-light irradiation with (wavelength $\geq$ 420 nm).

For the typical synthesis of CdS nanowire arrays, 3 mmol of cadmium acetate and 6 mmol of thiourea were dissolved in 20 g of ethanol in a beaker, and 0.5 g of calcined mesoporous silica SBA-15, synthesized as described in the literature firstly,[8] was then added under stirring for 2 h. After evaporation of the ethanol in an oven at 40 °C for one day, the dried powders were calcined in air at 300 °C for 2 h. The silica template was dissolved by thrice dispersing the sample in 2 M NaOH for 1 d with stirring at room temperature. Photocatalytic reactions were conducted in a 200 mL aqueous solution containing 0.1 g of catalyst loaded with 10% (wt %) of Pt cocatalyst by photodeposition and sacrificial reagents of Na_2SO_3 and Na_2S under the visible light (wavelength $\geq$ 420 nm) irradiation of a 300 W Xe lamp. For comparison, hexagonal CdS nanoparticles with an average grain size of 18 nm calculated using the Scherrer equation were prepared in the absence of the SBA-15, keeping all other preparation conditions the same.

Figure 1A shows the low-angle X-ray diffraction (XRD) patterns of calcined SBA-15 for comparison and of ordered CdS nanowire arrays before and after dissolution of the silica template. Four well-resolved diffraction peaks, indexed as

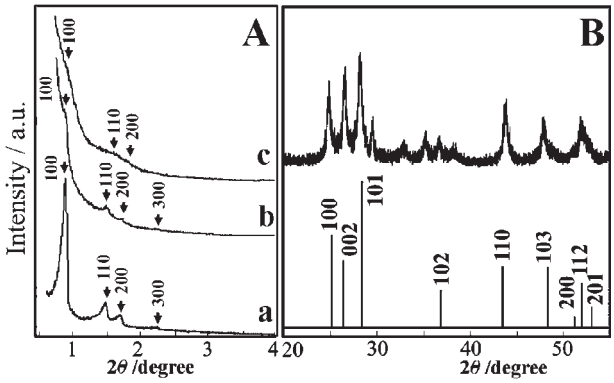

Figure 1. A: Low-angle XRD patterns of (a) SBA-15, (b) CdS/SBA-15, and (c) CdS nanowire arrays after removal of SBA-15. B: High-angle XRD pattern of the CdS nanowire arrays.

(100), (110), (200), and (300), of Bragg reflections of the *P6mm* plane group, were observed in the XRD pattern (Figure 1A-a) of calcined SBA-15, indicating well-ordered hexagonal mesopores with a narrow diameter distribution. After the formation of CdS nanowires in the pores of the mesoporous silica, the same four diffraction peaks were observed in the low-angle XRD pattern (Figure 1A-b). However, the intensity of diffraction peaks decreased because of the weakened contrast of hexagonal mesostructures in the CdS/SBA-15 composite. After the silica template was removed, the CdS nanowire arrays obtained still exhibited three diffraction peaks, indexed as (100), (110), and (200) in the low-angle region (Figure 1A-c), which indicates that the resultant CdS nanowire arrays retained the highly ordered hexagonal mesoporous structure. The high-angle XRD pattern (Figure 1B) of the CdS nanowire arrays shows diffraction peaks belonging to the wurtzite structure with a hexagonal cell (JCPDS Card: No. 41-1049). The diffraction peaks were highly intense and broad, suggesting that the CdS was readily crystallized within the confined channels of the calcined SBA-15 and that the grain size was very fine. In addition, the high-angle XRD pattern (Figure 1B) revealed diffraction peaks ascribable to the small amount of CdO formed by the partial oxidation of CdS during crystallization at 300 °C due to the ambient oxygen. N_2 adsorption/desorption isotherms revealed that the calcined mesoporous silica had a BET surface area of 562 $m^2 g^{-1}$, a pore size of 7.2 nm, and a pore volume of 1.01 $cm^3 g^{-1}$. The prepared CdS nanowire arrays also have a relatively narrow pore size distribution of ca. 3.9 nm, a BET surface area of 73.6 $m^2 g^{-1}$ and a pore volume of 0.38 $cm^3 g^{-1}$.

A typical transmission electron microscopy (TEM) image (Figure 2a) shows that over 90% of the products are hexagonally packed CdS nanowire arrays that are seen to be in the same perfect hexagonal mesostructures as the pores of mesoporous silica.

Copyright © 2006 The Chemical Society of Japan

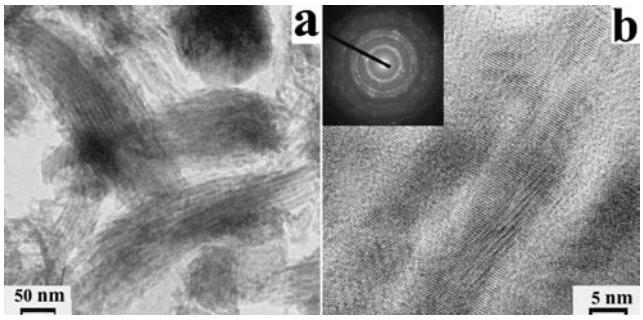

Figure 2. Typical TEM (a), HRTEM (b) and SAED (the inset to b) images of CdS nanowire showing the ordering in the CdS nanowire arrays and the high crystallinity of the CdS nanowires.

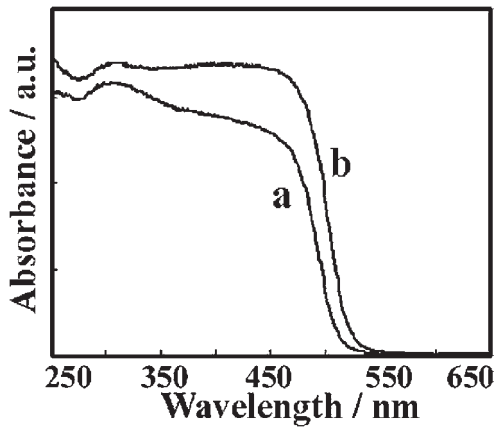

Figure 3. UV–vis diffuse reflectance absorption spectra of (a) the CdS/SBA-15 composite, and (b) as-made CdS nanowire arrays.

A typical high resolution (HR) TEM image (Figure 2b) of the local area of the CdS nanowire arrays shows parallel CdS nanowires with diameters in the 7–8 nm range, which is comparable to the size of the mesopores in the silica template. The distance between two adjacent CdS nanowires was around 3–4 nm, in agreement with the results of N_2 sorption analysis. The match in size between the mesoporous silica and the CdS nanowire arrays confirmed that the hexagonal mesopores in silica were well filled by CdS. The clear lattice fringes of CdS also confirm the high crystallinity of the CdS nanowires. The selected-area electron diffraction (SAED) pattern (the inset to Figure 2b) also corroborated the highly crystalline structure. The energy-dispersive X-ray spectroscopy (EDX) measurements indicate that no Si signal was detected. Thus, the silica template was totally removed.

Figure 3 show the UV–vis diffuse reflectance spectra of the CdS/SBA-15 composite (Figure 3a) and the as-made CdS nanowire arrays (Figure 3b), corresponding to a bandgap of ca. 2.43 and 2.38 eV, respectively, both of which are comparable to the measured value for the standard bulk CdS sample (ca. 2.4 eV). With each 10-h reaction run, the photocatalytic activity of the Pt-loaded CdS nanowires decreased slightly, as shown in Figure 4. After four reaction runs, the sample retained 95% of the initial photocatalytic activity under visible-light irradiation and reached a stable H_2 yield of 0.26 mmol h^{-1}. However, the CdS nanoparticles prepared without using the mesoporous silica as template had a very low photocatalytic H_2 yield of 0.02 mmol h^{-1}.

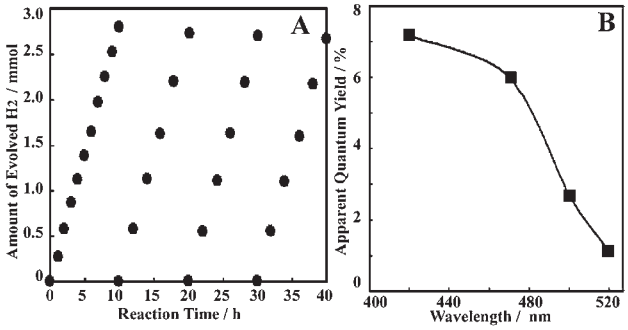

Figure 4. A: Time evolution of photocatalytic H_2 production on Pt-loaded mesoporous CdS nanowires. The system was evacuated every 10 h, and the reaction was continued in order to observe the change in activity. B: Wavelength dependence of the apparent quantum yield for H_2 production in a 200 mL aqueous solution containing 0.1 g of catalyst, 0.25 M Na_2SO_3, and 0.35 M Na_2S under the visible-light irradiation.

The apparent quantum yield for H_2 production as a function of wavelength has been determined for the Pt-loaded CdS nanowire arrays. The highest apparent quantum yield of 7.2% appears at 420 nm and the lowest apparent quantum yield of ca. 1% appears at wavelength of >520 nm. H_2 evolution did not appear by absorption in the region of >550 nm because only photons of a wavelength shorter than 525 nm can induce photochemical reactions in Pt-loaded CdS nanowire arrays.

In summary, we have synthesized highly ordered CdS nanowire arrays with very good crystallinity, high specific surface area, and ordered mesostructure by using mesoporous silica as a hard template. Efficient photocatalytic H_2 production under visible light (wavelength $\geq$ 420 nm) irradiation has been achieved over the prepared CdS nanowire arrays.

We gratefully acknowledge the Japan Society for the Promotion of Science (JSPS) Fellowship, Research Grant-in-Aid of the Ministry of Education, Culture, Sports, Science and Technology of Japan (MEXT), the New Energy and Industrial Development Organization (NEDO) and the Solution Oriented Research for Science and Technology (SORST) program of the Japan Science and Technology (JST) Corporation.

References

1 A. Kudo, H. Kato, I. Tsuji, *Chem. Lett.* **2004**, *33*, 1534.
2 M. Matsumura, S. Furukawa, Y. Saho, H. Tsubomura, *J. Phys. Chem.* **1985**, *89*, 1327.
3 a) A. Kudo, I. Tsuji, H. Kato, *Chem. Commun.* **2002**, 1958. b) I. Tsuji, H. Kato, H. Kobayashi, A. Kudo, *J. Am. Chem. Soc.* **2004**, *126*, 13406. c) I. Tsuji, H. Kato, H. Kobayashi, A. Kudo, *J. Phys. Chem. B* **2005**, *109*, 7323.
4 C. Burda, X. Chen, R. Narayanan, M. A. El-Sayed, *Chem. Rev.* **2005**, *105*, 1025.
5 F. Gao, Q. Lu, D. Zhao, *Adv. Mater.* **2003**, *15*, 739.
6 P. V. Braun, P. Osenar, S. I. Stupp, *Nature* **1996**, *380*, 325.
7 J. Joo, H. B. Na, T. Yu, J. H. Yu, Y. W. Kim, F. Wu, J. Z. Zhang, T. Hyeon, *J. Am. Chem. Soc.* **2003**, *125*, 11100.
8 D. Zhao, J. Feng, Q. Huo, N. Melosh, G. Fredrickson, B. Chmelka, G. D. Stucky, *Science* **1998**, *279*, 548.

Published on the web (Advance View) February 18, 2006; DOI 10.1246/cl.2006.318