

Organic Nanotube Induced by Photocorrosion of CdS Nanorod

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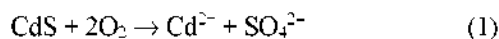
PMMA-coated CdS nanorod was prepared by encapsulation of CdS nanorod through the polymerization process of PMMA on the surface of CdS nanorod. PMMA organic nanotube was then obtained from the elimination of the CdS nanorod by the photocorrosion. For the photocorrosion reaction of the CdS nanorod, monochromatic light was irradiated to the oxygen-saturated aqueous methyl viologen solution with PMMA-coated CdS nanorod. Photocorrosion reactions of PMMA-coated CdS nanorod were investigated and characterized by utilizing UV-Vis absorption, X-ray diffraction (XRD) and scanning electron microscopic (SEM) and transmission electron microscopic (TEM) images.

Key Words : Organic nanotube, Photocorrosion, CdS nanorod, PMMA nanotube

Introduction

Nanotubes have been very attractive materials due to their unique physical, chemical, electrical and magnetic properties and their practical applications.¹ Two fundamental methods for the preparation of nanotubes have been proposed: Self-assembly of precursor compounds and template synthesis.² The former can't be applied for the preparation of such isolated simple organic nanotube which does not have self assembly function. The latter method involves elimination of template to obtain nanotubes. In general, chemical etching and combustion have been the methods for elimination of template. However, the inner structures of hollow nano-material are difficult to be controlled with these methods.³ Also, various impurities can be introduced during the both processes. Furthermore, the combustion process can not be applied for the preparation of organic hollow nano-materials due to the low melting point of organic composites.

Recently, photocorrosion has been utilized for the preparation of size-selective nanoparticles.⁴ Photocorrosion reaction of CdS consists of several photoanodic and photocathodic processes and the net reaction is the following:



Photocorrosion process requires an oxygen source as shown in equation 1 and strongly depends on the wavelength of irradiating light.

In this paper, we propose a new method to prepare the PMMA organic nanotube through the photocorrosion of CdS nanorod coated with PMMA. Their morphology and physical properties are characterized by XRD, FT-IR, absorption spectra, SEM, and TEM.

Experimental Section

In order to prepare the PMMA-coated CdS nanorod, 0.47 g (5 wt.%) of initiator, benzoyl peroxide (BP), was added to the 10 mL of methylmetacrylate (MMA) and was stirred for 30 min. On the other hand, CdS/ethanol suspension solution was prepared by dispersing 0.01 g (0.07 mmole) of the pre-made CdS nanorod in 20 mL of ethanol using ultrasonic homogenizer and was stirred at 60 °C. The BP/MMA solution (1.95 μL) was added to the CdS/ethanol suspension solution, and then this mixture was stirred for 12 hours. The PMMA-coated CdS nanorods were obtained from centrifuging and washing with EtOH.

Small amount of the resultant was suspended in an oxygen-saturated aqueous solution containing methyl viologen (MV^{2+}). Methyl viologen serves as a catalyst that relays electrons from the CdS nanorods to oxygen molecules. Photocorrosion were performed by irradiation of the monochromatic light of Nd-YAG laser (SERIE 5000, B.M.I.) at 355 nm with average power of 30 mW for 3 hours. The suspension solution was continuously stirred during photocorrosion reaction.

Absorption spectra of the PMMA-coated CdS nanorods were measured with a UV-Vis spectrophotometer (Shimadzu, UV3101PC). To investigate the photocorrosion of CdS, absorbance was monitored before irradiation and at every 1 hour.

The X-ray diffraction pattern of the PMMA-coated CdS nanorod was obtained by a X-ray diffractometer (MAC Science, M03XHF) with monochromatized Cu-K α radiation in the 2 θ range between 20 and 60° at scanning rate of 1°/min.

To prove the PMMA encapsulation of the CdS nanorod, vibrational spectra of the CdS nanorod and the PMMA-coated CdS nanorod were measured with a FT-IR spectrophotometer (Nicolet, Impact 400) with a resolution of 4 cm^{-1} .

Morphologies of the PMMA nanotubes were measured

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with a field-enhanced scanning electron microscope (FE-SEM, JEOL, JEM 2000EXII) under vacuum condition. The samples were gold-coated prior to SEM measurements.

Transmission electron microscopic images were obtained with a TEM (Gatan Co., USC 1000-model 894) using an accelerating voltage of 300 kV. The sample solution was applied onto Cu grid coated with amorphous carbon films.

Results and Discussion

The XRD pattern of CdS in PMMA-coated CdS nanorod (1 : 4, wt./wt.) is shown in Figure 1. PMMA is known to be an amorphous polymer and shows the broad peaks at 12° and 30° while CdS can possess either cubic or hexagonal structure depending on the particle shape in nano-phase.⁶ From the XRD spectrum, the sharp peaks for CdS with crystalline phase are clearly observed. Among the several diffraction peaks, the diffraction peak of (002) phase is stronger than the others. It indicates that CdS particle is preferentially oriented along the c-axis and has a rod like shape.⁷ In the PMMA-coated CdS nanorods, CdS nanorods also has a hexagonal wurzite structure with the cell constants shown in the literature (JCPDS card, File No. 41-1049). It implies that the crystal structure is not affected by the encapsulation with PMMA.

Encapsulation of the CdS nanorod with PMMA was confirmed by the characteristic vibrational modes of PMMA. FT-IR spectra of the CdS nanorod and the PMMA-coated CdS nanorod are shown in Figure 2(a) and (b), respectively. In the PMMA-coated CdS, the vibrational spectrum contains new peaks that are not observed from the CdS nanorod. The peak at 1712 cm^{-1} (marked with arrow) corresponds to the C=O stretching mode in PMMA. In general, stretching mode of carbonyl group is centered at 1730 cm^{-1} in PMMA raw material. However, this peak is shifted to the lower frequency (1712 cm^{-1}) due to the interaction between carbonyl group and cadmium ion in PMMA-coated CdS nanorod, implying that PMMA is well coated on the surface of CdS nanorods.⁸

On the other hand, the peaks at 1010 cm^{-1} and 1120 cm^{-1}

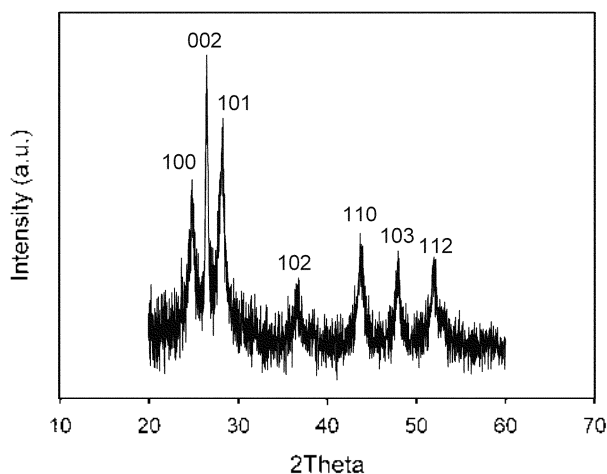


Figure 1. XRD pattern of the PMMA-coated CdS nanorod.

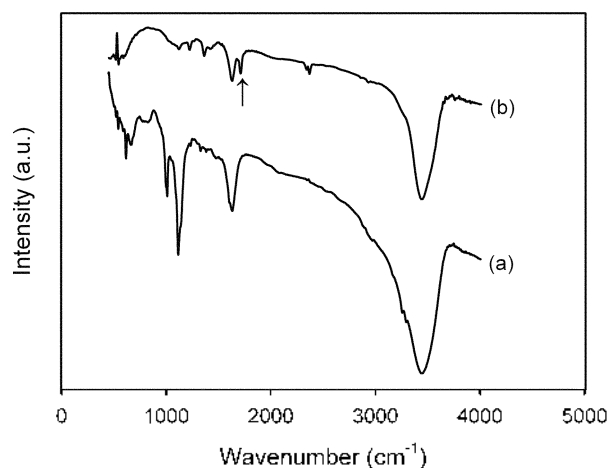


Figure 2. FT-IR spectra of (a) the CdS nanorod and (b) the PMMA-coated CdS nanorod at room temperature.

in Figure 2(a) are disappeared for the PMMA-coated CdS nanorod as shown in Figure 2(b). These peaks correspond the vibrational modes induced by the coordination of ethylene diamine to Cd^{2+} ion in the CdS nanorod. Therefore, the absence of these peaks suggests that during the encapsulation process, Cd^{2+} ions are preferentially coordinated with carbonyl groups of PMMA and the ethylene diamine molecules are decoupled from Cd^{2+} ions. From the IR result, it is considered that the CdS nanorod is effectively encapsulated by the PMMA without having the ethylene diamine at their interface.

Photocorrosion reaction was performed with a monochromatic laser light at 355 nm and was investigated from the absorption spectra. Figure 3 shows the absorption spectra of the PMMA-coated CdS nanorod before and after irradiation of the monochromatic light in the presence of methyl viologen (MV^{2+}) and O_2 . Absorbance of the CdS nanorod largely depends on the irradiation time. After 1 hour, the absorbance is about 26% comparing with that

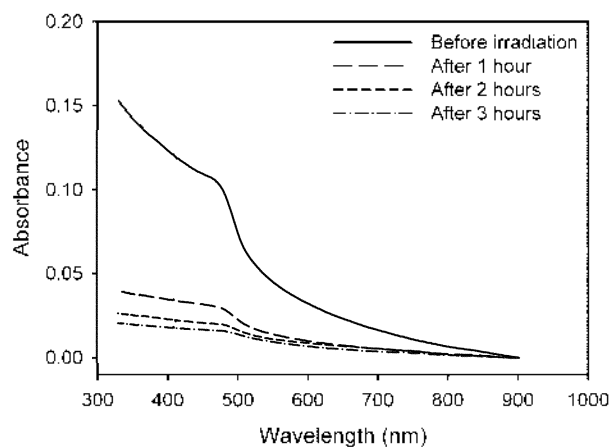


Figure 3. Absorption spectra of the PMMA-coated CdS nanorods measured at different irradiated times: before irradiation (solid line), after irradiation for 1 hour (long dash line), 2 hours (short dash line) and 3 hours (dash dotted line).

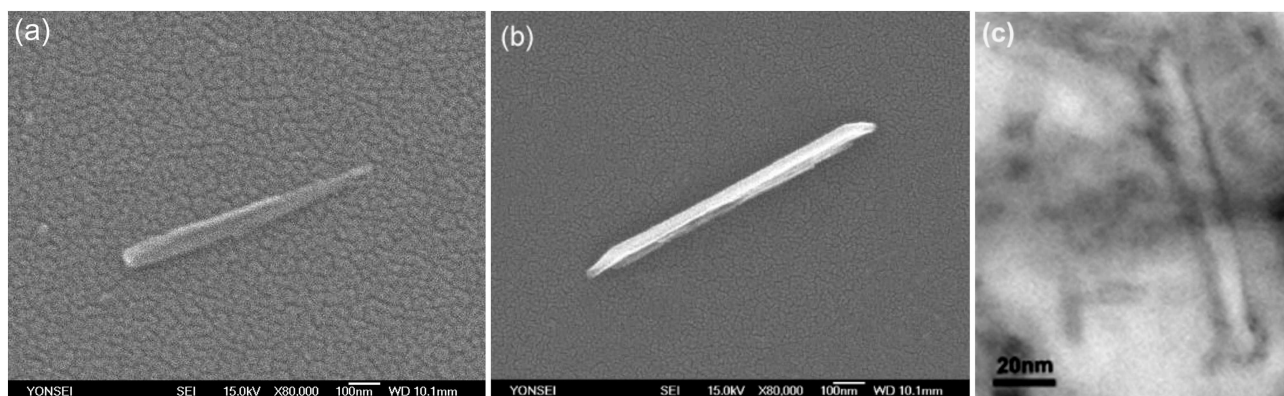


Figure 4. SEM images of (a) the PMMA-coated CdS nanorod and (b) the PMMA nanotubes and TEM image of (c) the PMMA nanotubes obtained from photocorrosion of PMMA-coated CdS nanorods.

before the photocorrosion. The photocorrosion speed is gradually decreased with increase of the irradiation time. It indicates that the amount of oxygen is largely reduced because oxygen is continuously consumed and is slowly supplied from the suspension solution. After 3 hours, the absorbance of the CdS nanorods is largely reduced and most of the CdS nanorods are eliminated from the PMMA-coated CdS nanorod.

Figure 4 shows the SEM and TEM images of the PMMA-coated CdS nanorod and the PMMA nanotubes after photocorrosion for 3 hours. The PMMA-coated CdS nanorods have the average diameter about 30 nm as shown in Figure 4(b). It is observed that PMMA is well coated on the surface of the CdS nanorod and its thickness is approximately estimated to be 5-10 nm, based on the size range (10-20 nm in diameter) of the CdS nanorods utilized in this study. After irradiation of 3 hours, most of them show the nanotubes without any deformation as shown in Figure 4(b). However, there are some deformed structures of cleaved form observed although their amount is very little. TEM image also supports the photocorrosion of the CdS nanorod. Figure 4(c) represents the TEM image of the PMMA nanotubes after photocorrosion of 3 hours. From this image, the empty PMMA nanotubes are clearly observed. However, there is still a little trace of the CdS nanocrystal remained partially in a few PMMA nanotubes and the amount of the remaining trace depends on the irradiation time (data not shown).

Conclusion

In this study, it is shown that PMMA organic nanotubes are successfully synthesized by utilizing the photocorrosion reaction of CdS nanorods. In particular, such photocorrosion reaction opens the possibility for the precise morphology control of organic nanotubes, depending on the shape and size of the CdS template. Therefore, photocorrosion reaction is suggested to be one of the most effective methods for the preparation of the porous nano-materials through selective elimination of photochemically active inside nano-material from nanocomposites.

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References

- (a) Mitchell, D. T.; Lee, S. B.; Trofin, I.; Li, N.; Nevanen, T. K.; Söderlund, H.; Martin, C. R. *J. Am. Chem. Soc.* **2002**, *124*, 11864. (b) Wirtz, M.; Parker, M.; Kobayashi, Y.; Martin, C. R. *Chem. Eur. J.* **2002**, *8*, 3573. (c) Chang, H. J.; Chen, Y. F.; Lin, H. P.; Mou, C. Y. *Appl. Phys. Lett.* **2001**, *78*, 3791. (d) Che, G.; Lakshmi, B. B.; Fisher, E. R.; Martin, C. R. *Nature* **1998**, *393*, 346. (e) Jirange, K. B.; Hulteen, J. C.; Martin, C. R. *Science* **1997**, *278*, 655.
- (a) Ai, S.; Lu, G.; He, Q.; Li, J. *J. Am. Chem. Soc.* **2003**, *125*, 11140. (b) Steinhart, M.; Wendorff, J. H.; Greiner, A.; Wehrspohn, R. B.; Nielsch, K.; Schilling, J.; Choi, J.; Gösele, U. *Science* **2002**, *296*, 1997. (c) Bong, D. T.; Clark, T. D.; Granja, J. R.; Ghadiri, M. R. *Angew. Chem. Int. Ed.* **2001**, *40*, 988. (d) Jung, J. H.; Lee, S. S.; Shinkai, S.; Iwaura, R.; Shimizu, T. *Bull. Korean Chem. Soc.* **2004**, *25*, 63.
- (a) Liang, Z.; Susha, A. S.; Yu, A.; Caruso, F. *Adv. Mat.* **2003**, *15*, 1849. (b) Zygmunt, J.; Krumeich, E.; Nesper, R. *Adv. Mat.* **2003**, *15*, 1538.
- (a) Torimoto, T.; Reyes, J. P.; Iwasaki, K.; Pal, B.; Shibayama, T.; Sugawara, K.; Takahashi, H.; Ohtani, B. *J. Am. Chem. Soc. Comm.* **2003**, *125*, 316. (b) Torimoto, T.; Reyes, J. P.; Murakami, S.-Y.; Pal, B.; Ohtani, B. *J. Photochem. Photobio. A* **2003**, *160*, 69. (c) Torimoto, T.; Kontani, H.; Shibutani, Y.; Kuwabata, S.; Sakata, T.; Mori, H.; Yoneyama, H. *J. Phys. Chem. B* **2001**, *105*, 6838. (d) Dijken, A. V.; Janssen, A. H.; Smitsmans, M. H. P.; Vanmaekelbergh, D.; Meijerink, A. *Chem. Mater.* **1998**, *10*, 3513.
- (a) Matsumoto, H.; Sakata, T.; Mori, H.; Yoneyama, H. *J. Phys. Chem.* **1996**, *100*, 13781. (b) Spanhel, L.; Haase, K.; Weller, H.; Henglein, A. *J. Am. Chem. Soc.* **1987**, *109*, 5649.
- (a) Li, B.; Hu, Y.; Liu, J.; Chen, Z.; Fan, W. *Colloid Polym. Sci.* **2003**, *281*, 998. (b) Ge, X.; Ni, Y.; Zhang, Z. *Rad. Phys. Chem.* **2002**, *64*, 223.
- Yang, J.; Zeng, J.-H.; Yu, S.-H.; Yang, L.; Zhou, G.-E.; Qian, Y.-T. *Chem. Mater.* **2002**, *12*, 3259.
- Tretinnikov, O. N.; Ohta, K. *Macromolecules* **2002**, *35*, 7343.