



Trade Science Inc.

Materials Science

An Indian Journal

Full Paper

MSAIJ, 2(6), 2006 [149-153]

Impregnation And Characterisation Of Semiconductor CdS Nanoparticles In Mesoporous SBA-15



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Received: 27th June, 2005Accepted: 12th July, 2006Web Publication Date : 27th December, 2006

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ABSTRACT

Semiconductor CdS nanoparticles have been grown inside the channels of mesoporous SBA-15 through a two-step impregnation technique at room temperature. SBA-15 is as host, while Cd(Ac)₂ and thiourea (including thiol group) as Cd and S source into the channels of SBA-15. XRD reveals that the size of the CdS particles are in nanometer-scale. High-resolution transmission electron microscopy reveals that the CdS nanoparticles are dispersed inside the channels of mesoporous SBA-15 and the nanoparticles have a size of about 3 nm. A blue shift is observed in UV-Vis absorption spectrum. Quantum confinement effect in the CdS nanoparticles is observed by UV-vis and photoluminescence measurement.

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KEYWORDS

Impregnation;
Mesoporous materials;
CdS nanoparticles.

INTRODUCTION

There has been a great deal of interests in the utilization of the pores in mesoporous materials as nanoreactor to synthesize monodispersive nanocrystals with uniform size due to the "particle-sieving effect" of mesoporous silica^[1-3]. Mesoporous silica MCM-41 with regular array of cylindrical channels has been

used for confined growth of semiconductor quantum dots and quantum wires. In the family of mesoporous materials, the SBA-15 material synthesized under acidic conditions exhibits larger pore size and thicker pore wall compared with M41S. The improved hydrothermal and thermal stability makes them the most promising catalytic materials. II-VI sulfide nanocrystals have unique electronic and op-

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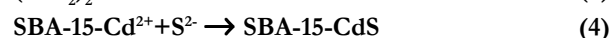
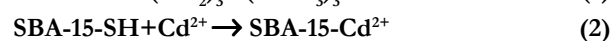
tical properties and are extremely useful in the fabrication of novel nanodevices^[4-6]. The semiconductor/ mesoporous composites exhibit interesting optical properties, such as blue-shift photoluminescence^[7,8]. Recent success in fabricating novel optoelectronic devices like light-emitting diodes (LED), single-electron transistors (SET), and field-effect thin-film transistors (TFT) using cadmium selenide (CdSe) semiconductor quantum dots (QDs) has stimulated considerable interest in developing a new class of electronic and optical devices based on QDs^[9-11]. CdS is a II-VI semiconductor with a band gap of 2.42 eV in the visible range^[12]. In this letter, we reported a method to load CdS nanoparticles into the holes of mesoporous SBA-15 through a simple and safe two-step impregnation at room temperature with cadmium acetate as the metal ion source and thiourea as the S source. Thiourea as S source is sufficient for the formation of CdS. CdS nanoparticles grown in nano-sized pores are resolved.

Sample preparation

The mesoporous silica of SBA-15 host was synthesized following the procedure previously reported in literatures using the tri-block copolymer poly (ethylene oxide) poly (propylene oxide) poly (ethylene oxide), $\text{EO}_{20}\text{PO}_{70}\text{EO}_{20}$, as a template in acidic conditions^[12,13]. The synthesis procedure of loading CdS into SBA-15 was initiated by drying 1.0 g SBA-15 in a vacuum oven at 150°C for 2.5 h. The internal surface of the channels in the mesoporous SBA-15 was then functionalized with thiol groups by suspending 1.0 g of SBA-15 and 10 ml (3-thiolpropyl)-trimethoxy silane in 100 ml dry toluene for two days. The sample was collected by filtering washing with sample amount of toluene, and finally dried in a vacuum. After washed and dried, 0.2 g functionalized SBA-15 (hereafter termed SBA-15-SH) was mixed with 20 ml $\text{Cd}(\text{Ac})_2 \cdot 2\text{H}_2\text{O}$ /ethanol solution (0.01 mol) by violent stirring for at least 24 hours. The resulting material is denoted as SBA-15-Cd²⁺. The Cd²⁺ outside the channels were washed away thoroughly, which could be tested by adding Na_2S into the washed ethanol solution till the solution color did not turn yellow, since the K_{sp} of CdS is very low. The remains were dried completely, $(\text{NH}_2)_2\text{CS}$ was added

into the SBA-15-Cd²⁺ water solution with stirring at 80°C for about 6 hours. The resulting material was CdS-loaded SBA-15 mesoporous silica, hereafter denoted as SBA-15-CdS. Note that it is important to make sure the loaded SBA-15 contains CdS nanoparticles only inside the pore channels. The product was then examined by Fourier transform infrared spectroscopy (FT-IR), X-ray diffraction (XRD), high resolution transmission electron microscopy (HR-TEM), energy dispersive spectroscopy (EDS), UV-vis absorption, and photoluminescence (PL) measurements.

The modifying agent of the internal (channel) surfaces of SBA-15 used in our experiments is 3-thiolpropyltriethoxysilane, whose thiol groups have the ability to absorb Cd²⁺ into the channel in ethanol solutions. At 80°C, thiourea gradually releases S²⁻ and CdS nanoparticles grow inside the pore channels. The whole reaction can be described as follows:



RESULTS AND DISCUSSION

Figure 1 presents the Fourier transformation infrared (FT-IR) spectra measured on SBA-15 and SBA-15-SH, recorded using Nicolet Nexus 470 spectrometer. Prior to the modification, the absorption is dominated by the peak at 960 cm⁻¹ corresponding to

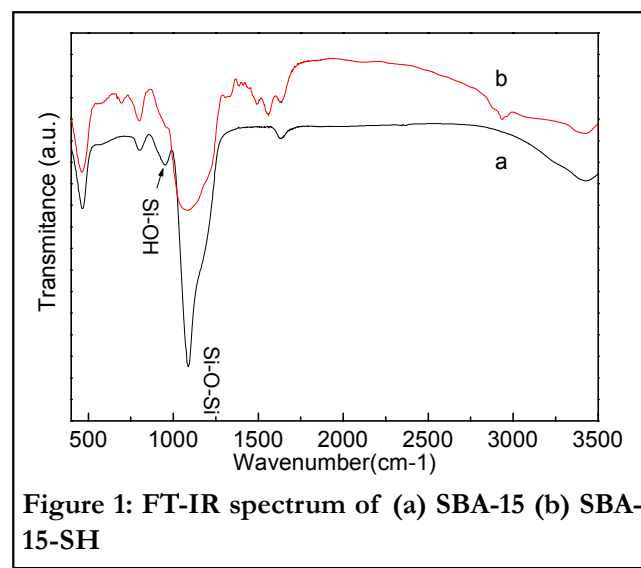


Figure 1: FT-IR spectrum of (a) SBA-15 (b) SBA-15-SH

the Si-O stretching/contracting vibration of the Si-OH bond. After modification, the peak due to Si-OH bond disappears, implying that reaction had occurred between 3-thiolpropyltriethoxysilane and SBA-15^[14]. The peak intensity of Si-O-Si bond (at 1080 cm⁻¹) increases. It also implies a reaction has occurred between 3-thiolpropyltriethoxysilane and SBA-15, resulting in Si-OH replacement by Si-O-Si.

Upon completion of the growth of the CdS nanoparticles inside the channels of SBA-15, X-ray diffraction patterns of the SBA-15-CdS powder were recorded with a Rigaku D/MAX 2550V using Cu K α line ($\lambda = 1.5406 \text{ \AA}$) in the 2θ region of 0.5 to 5°. Figure 2 shows that the intensity of the low-angle (100) peak decreases and the (110) and (200) peaks almost disappear after the CdS nanoparticles are loaded into SBA-15, which is a typical pore filling indication due to the reduction of the scattering contrast between the pores and the walls of the mesoporous material^[15]. At the same time, the (100) peak shifts toward larger angle, which is attributed to the contraction of the framework during the surface functionalization and the growth of CdS nanoparticles. Shown in figure 3 is the wide angle X-ray diffraction pattern of the SBA-15-CdS measured in the region of $10 \leq 2\theta \leq 80^\circ$. The very broad XRD peak at 23° stems from the diffraction of the amorphous wall in SBA-15. All other peaks can be in-

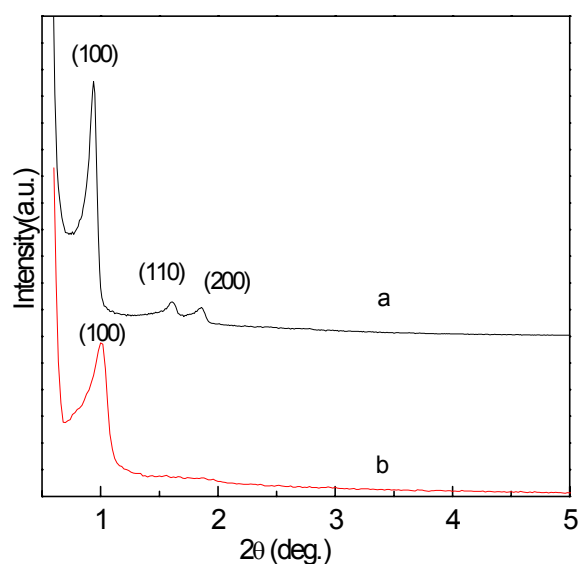


Figure 2: Low-angle XRD patterns of (a) Mesoporous SBA-15; (b) CdS-loaded SBA-15

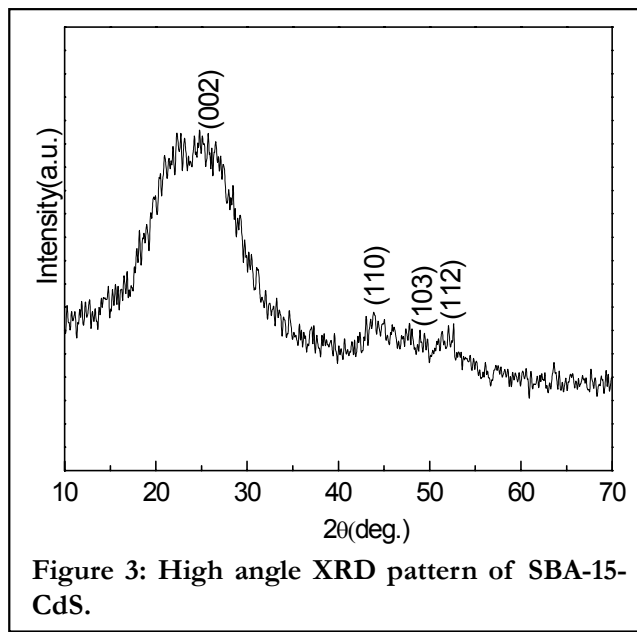


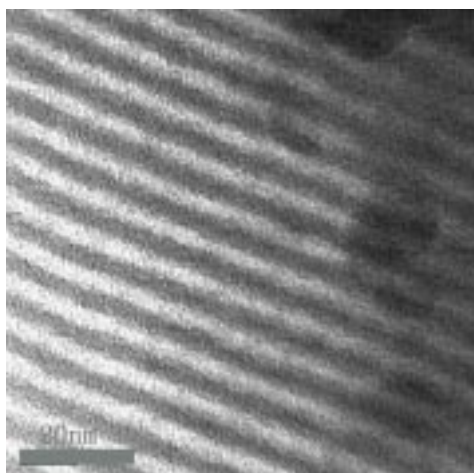
Figure 3: High angle XRD pattern of SBA-15-CdS.

dexed to the hexagonal cell of CdS (Wurtzite structure) that are very close to the values reported in the literature (JCPDS card, File No. 41-1049)^[7]. The broadening of the peaks in XRD pattern reveals that the size of the CdS particles are in nanometer-scale.

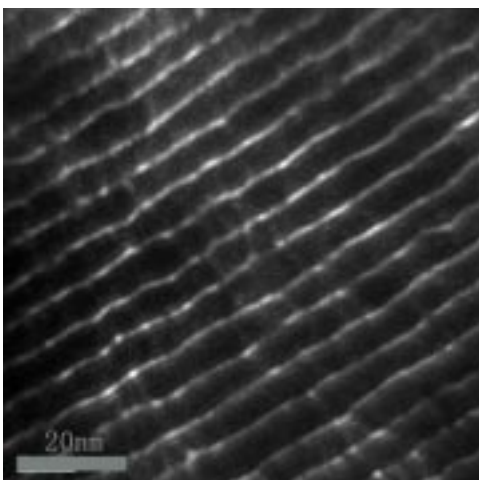
HR-TEM measurement was performed using a JSM-2010F system made by Jeol operating at 200 kV. Figures 4a and 3b show the HR-TEM images of SBA-15 and CdS-loaded SBA-15, respectively. It reveals that the highly ordered pore structure of SBA-15 has been preserved during the formation of CdS nanoparticles. Compared with pure SBA-15 (5~6nm), the channels have been made narrower due to functionalization with (3-thiolpropyl)-trimethoxysilane and apparent matter accumulation. In figure 4b, CdS nanoparticles show as dark regions inside the channels of SBA-15 and the distribution of the nanoparticles appears quite uniform. The particles' average size is about 3 nm.

Energy dispersive spectrum (EDS) measurements were performed using a Siron 200 scanning electron microscope made by FEI and an EDS spectrum measured on SBA-15-CdS is shown in figure 4c. The experimental sampling is in the mesoporous region and the EDS spectrum shows obvious S and Cd signals, together with strong signatures of elements Si and O. From the intensities of S and Cd lines, a ratio of 0.84:0.81 is calculated for S and Cd elements, very close to 1:1. This further evidences the

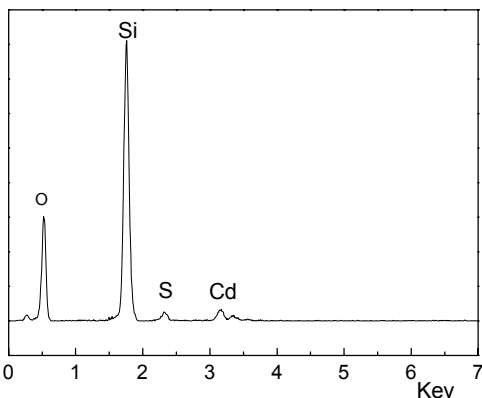
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(a)



(b)



(c)

Figure 4: (a) HR-TEM image of SBA-15 (parallel to the channels) (b) HR-TEM image of SBA-15-CdS (parallel to the channels) (c) EDS spectrum of the CdS loaded in SBA-15

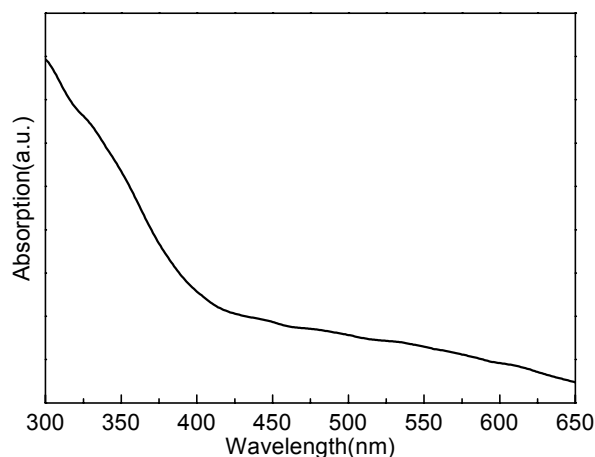


Figure 5: UV-Vis absorption spectrum of SBA-15-CdS

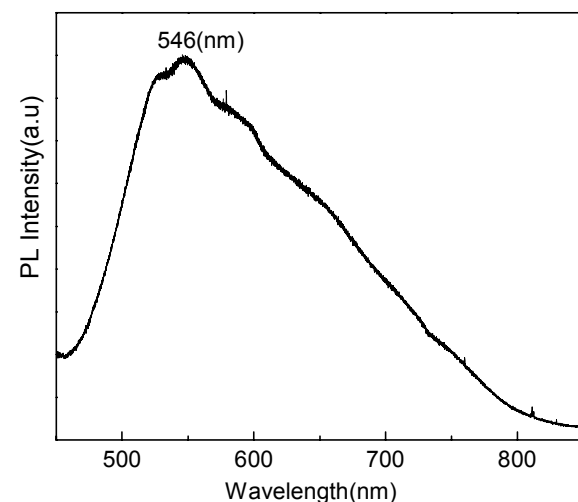


Figure 6: PL spectrum of SBA-15-CdS

formation of CdS inside SBA-15. EDS measurement also gives 6.29% weight percent of CdS loaded inside the pore channels.

The UV-vis absorption spectrum was recorded with a Perkin-Elmer Lambda 2S spectrophotometer on CdS-loaded SBA-15 dispersed in toluene. The absorption onset of SBA-15-CdS (Figure 5) was at 400nm, a blue-shift for 115 nm with respect to that of the bulk at 515 nm due to the strong quantum confinement imposed on electrons in the CdS nanoparticles with their sizes limited by SBA-15 channels. From the absorption onset, the size of the CdS nanoparticles was calculated to be 3 nm^[6] consistent with our HR-TEM observation. Room temperature PL spectrum was recorded with a high resolu-

tion micro-photoluminescence spectrometer at room temperature with an excitation wavelength at 405 nm. The PL spectrum presented in figure 6 is dominated by a broad peak centered at 546 nm, attributable to the recombination of an electron trapped in a sulfur vacancy with a hole in the valence band of CdS^[17]. It is such a broad peak is expected since the small CdS nanoparticles were prepared in the air so that there exists high density of surface states.

SUMMARY

In summary, CdS nanoparticles were synthesized by using mesoporous SBA-15 silica as template. The CdS-loaded SBA-15 was characterized using FT-IR, XRD, HR-TEM, UV-vis absorption and PL measurements. The XRD measurement indicates that the CdS are in nanometer scale and the HR-TEM image shows that the CdS nanoparticles have a size of about 3nm and are loaded inside the channels of the mesoporous SBA-15. The UV-vis absorption of the loaded CdS nanoparticles are blue-shifted relative to bulk materials due to the effect of quantum confinement.

ACKNOWLEDGEMENTS

This work was supported by Shanghai City Committee of Science and Technology (Grants No. 0452nm085 and 03DJ14002) and one of the authors (N. Dai) would like to thank the support of the "Outstanding Young Scholar" program by National Science Foundation in China (Grant No. 60225004). Y. Shen acknowledges the support by K. C. Wong Education Foundation of Hong Kong; Post-doctors Foundation of Shanghai, and National Laboratory Foundation for Infrared Physics.

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