

Synthesis, Characterization and PL Properties of CdS Nanoparticles Confined within a Functionalized SBA-15 Mesoporous

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Abstract—A simple and dexterous in situ method was introduced to load CdS nanocrystals into organofunctionalized mesoporous, which used an ion-exchange method. The products were extensively characterized by combined spectroscopic methods. X-ray diffraction (XRD) and high-resolution transmission electron microscopy (HRTEM) demonstrated both the maintenance of pore symmetry (space group $p6mm$) of SBA-15 and the presence of CdS nanocrystals with uniform sizes of about 6 - 8 nm inside the functionalized SBA-15 channels. These mesoporous silica-supported CdS composites showed room temperature photoluminescence properties with a blue shift, indicating the quantum size effect of nanocrystalline CdS.

Keywords—semiconductors; luminescence; mesoporous material; CdS

I. INTRODUCTION

SINCE the development of M41S family of mesoporous materials [1] and subsequent discovery of SBA-n family (Santa Barbara) in 1998 [2], a remarkable amount of studies have started on understanding both the mechanistic formation [3] and characterization [4] of these nanostructures. Among the most studied families of mesoporous materials, MCM-41 and SBA-15 have found much more interests because of distinctive hexagonal array, uniformity and narrow pore distribution and high surface area (up to 1000 m²/g) of their mesoporous channels [2]. Recently, much attention has been paid to the incorporation of semiconductor nanoparticles inside these mesoporous materials [5]. Compound II-VI semiconductor sulfide nanocrystals are important among the semiconductor materials due to unique electronics and optical properties [6]. These materials can absorb some of the solar spectrum and have great potential applications in light emitting diodes, solar cells, photo-detectors, electro-photography and lasers [5, 6]. Four methodologies i.e. direct impregnation [7], covalent grafting [8], modification of the surface walls followed by loading of precursors via affinity interaction [9], and ion-exchange reaction [10] have been developed to insert precursor molecules or ions for assembly of nanoparticles inside the channels of mesoporous materials. Herein, we used a simple method to incorporate CdS nanocrystals into organofunctionalized SBA-15 via the ion exchange reaction. These materials showed room temperature photoluminescence properties.

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II. EXPERIMENTAL

0.2 g of amino/ or thiol-modified SBA-15 was mixed with 20 ml of 0.02 M Cd(NO₃)₂·4H₂O solution under stirring to adsorb Cd²⁺ into SBA-15 channels, then the solution of thioacetamide to glycerin (2:1 ratio) and buffer acetate was added to the above mixture and maintained under stirring for 30 minute (buffer acetate was used for justifying of PH about 3.5). Finally, the product were calcined at 300°C in N₂ atmosphere for 2 h.

XRD patterns of these products were recorded in ambient air with using a Holland Philips Xpert X-ray powder diffraction (XRD) (Cu K α , $\lambda = 1.5406 \text{ \AA}$), at scanning speed of 2°/min from 20° to 80° (2 θ). Investigations of high-resolution analytical transmission (HRTEM) electron microscopy were carried out in Philips-CM200 FEG and JEM-2010 with an electron kinetic energy of 200 kV. Cadmium and sulfur contents were analyzed on an atomic absorption spectrophotometer (AAS: Perkin-Elmer 2380) and an inductively coupled plasma-atomic emission spectrometer (ICP-AES: Jobin-Yvon Ultima-C), respectively. The photoluminescence (PL) spectrum was recorded on a RF-5301TC spectrophotometer at room temperature.

III. RESULTS

Figure 1 shows the XRD patterns of the as-synthesized SBA-15 samples. In the low angle region, all the samples display three reflection peaks (100), (110) and (200) due to the hexagonal structure, which corresponds to the characteristic of SBA-15 [11].

The hexagonal ordered structure is maintained after the CdS particles have been loaded into SBA-15. Obvious decrease of the low-angle peak intensity is observed after the loading, which may be due to the pore filling with CdS that reduces the scattering contrast between the pores and the walls of the mesoporous silica [12].

Compared with the pure CH₃-SBA-15 sample, all peaks shift to slightly higher angles when the CdS nanoparticles are loaded. This shift can be caused by the thermal treatment (calcination of the samples at 300°C) that can induce the contraction of frameworks. Similar phenomena have been found during the calcinations of many mesoporous materials

The structure and crystalline state of the powders were characterized by X-ray diffraction. Fig. 2a and 2b showed a representative XRD pattern of the ZnO/SnO₂ and SnO₂ nanoparticles respectively. All the diffraction lines are assigned to tetragonal rutile crystalline phases of tin oxide which is consistent with the standard data file 21-1445. No

characteristic peaks of impurities, such as Zinc oxide or other tin oxides, were observed.

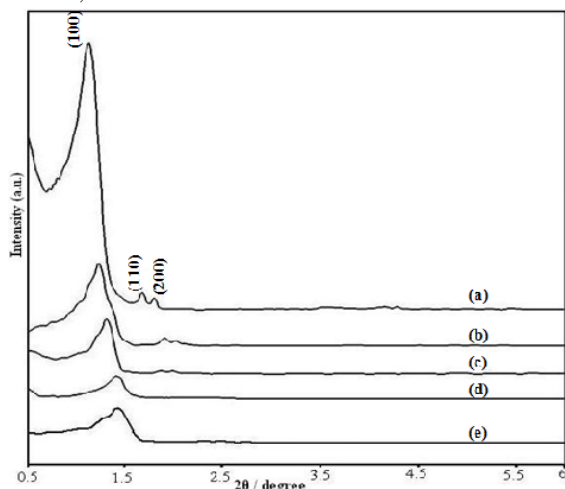


Fig. 1 Low-angle XRD patterns of (a) CH₃-SBA-15-extra, (b) CH₃-SBA-15-SH, (c) CH₃-SBA-15-NH₂, (d) sample II (e) sample I

Figure 2 shows the wide angle XRD patterns of the samples I and II. It shows the broad reflection of the amorphous wall structure of SBA-15 at about 23° and lattice planes of the hexagonal CdS, which are close to the values on JCPDS card (No. 41-1049) with the lattice constants of $a = 4.12 \text{ \AA}$ and $c = 6.68 \text{ \AA}$. The average crystal sizes of two samples, calculated by the Scherrer formula, are about 6 and 8 nm, which is consistent with the pore diameter of the modified SBA-15.

The results of AAS and inductively coupled ICP-AES show the elemental cadmium and sulfur contents of samples I and II that are 5.4 and 1.6 wt. % in sample I and 4.8 and 1.45 wt. % in sample II, respectively. The corresponding stoichiometric ratio of cadmium and sulfur contents for two samples is 1: 1, approximately. These results indicate that the cadmium ions completely converted to CdS in both samples I and II during the loading process.

TEM images show the hexagonal ordered pore structure as well as the columnar frameworks of the samples (Figure 3a). It reveals that the highly ordered pore structure of SBA-15 is maintained during the inclusion of CdS particles into the channels of SBA-15. In some areas of the TEM images, the framework of SBA-15 is indefinable (Figure 3b) due to the presence of the residual surfactant, which was not removed completely during the ion-exchange process [10].

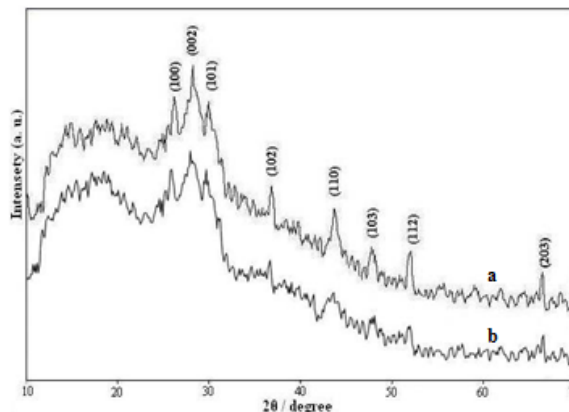


Fig. 2 High-angle XRD pattern of (a) sample II (b) sample I.

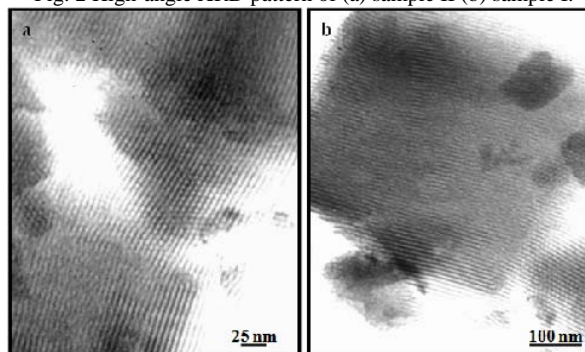


Fig. 3 HRTEM images of CdS-loaded SBA-15 samples

Figure 4 shows the PL spectra with an excitation wavelength of 350 nm. As noted, the onset of emission for the samples I and II is obviously blue shifted relative to the bulk CdS particles. The significant blue shift in these samples can be attributed to the quantum size effect of nanocrystalline CdS. The PL spectrum of the sample II shows broad emission band at 452 nm while, sample I shows two broad emission bands at 457 nm and 550 nm. The emission at 452 and 457 nm to band-edge emission is attributed to excitonic recombination. Also, the largely Stokes-shifted emission at 550 nm for the sample I is attributed to the recombination of an electron trapped in a sulfur vacancy with a hole in the valence band of CdS [13]. These results reveal that there is a relatively strong host-guest effect between the CdS and thiol groups in comparison with amino groups that show a good compatibility with Hard-Soft acid Base (HSAB) theory [14].

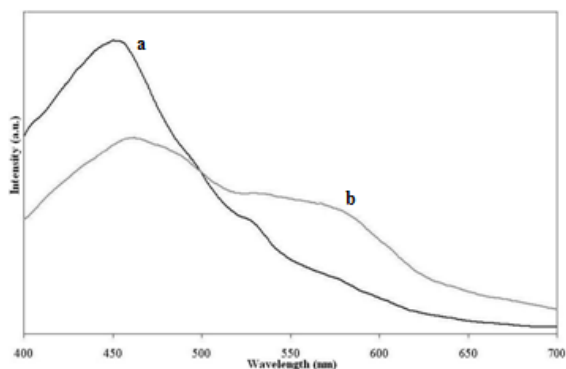


Fig. 4 PL spectrum of (a) sample II (b) sample I

IV. CONCLUSION

In summary, we reported a simple method to load CdS nanocrystals into the functionalized SBA-15. The products have been extensively characterized by combined spectroscopic methods, indicating that the CdS nanocrystals are mostly incorporated in the channels of the functionalized SBA-15. The large blue shifts in the emission spectra of these materials have been attributed to the size quantization effects. Also, the increase of the PL intensity for CH₃-SBA-15 (II) sample is due to the strong interaction between the CdS clusters and thiol groups. We believe that the ordered mesoporous materials modified by functional groups will play a significant role in host-guest chemistry development.

REFERENCES

- [1] Beck J S, Vartuli J C, Roth W J, Leonowicz M E, Kresge C T, Schmitt K D, J. Am. Chem. Soc. 1992; 114: 10834- 10843.
- [2] Zhao D, Feng J, Huo Q, Melosh N, Fredrickson G H, Chmelka B F, et al., Science 1998; 279: 548- 552.
- [3] Vartuli J C, Kresge C T, Leonowicz M E, Chu A S, McCullen S B, Johnson I D, et al., Chem. Mater. 1994; 6: 2070- -2077.
- [4] Morishige K, Ito M, J. Chem. Phys. 2002; 117: 8036- 8041.
- [5] Pickett N L, Brien P O', Chem. Rec. 2001; 1 : 467- 479.
- [6] Parala H, Winkler H, Kolbe M, Wohlfart A, Fischer R A, Schmechel R, et al. , Adv. Mater. 2000; 12:1050-1055.
- [7] Zhou H J, Cai W P, Zhang L D, Mater. Res. Bull. 1999; 34 :845-849..
- [8] Chomski E, Dag O, Kuperman A, Coombs N, Ozin G A, Chem. Vap. Deposition 1996; 2 :8- 13.
- [9] Zhang W H, Shi J L, Chen H R, Hua Z L, Yan D S, Chem. Mater. 2001; 13 :648- 654.
- [10] Wang S Z, Choi D, Yang S M, Adv. Mater. 2002;14: 1311- 1314.
- [11] Shan Y , Gao L, Mat. Chem. Phys. 2005; 89 :412-416.
- [12] Marler B, Oberhagemann U, Vortmann S, Gies H, Microporous Mater. 1996; 6 :375-383.
- [13] Chae W-S, Ko J-H, Hwang I-W, Kim Y-R, Chem. Phys.Lett. 2002; 365:49- 56.
- [14] Pearson R G, Inorg.Chem. 1988; 27:734-740.