

Controlled assembling of CdSe nanoparticles into the mesopores of SBA-15 via hot soap method

J. Bao^a, Y. Shen^a, Y. Sun^a, J. Wu^a, X. Chen^a, N. Dai^{a,*}, J.C. Zhang^b

^aNational Laboratory for Infrared Physics, Shanghai Institute of Technical Physics, Chinese Academy of Sciences, Shanghai 200083, China

^bDepartment of Electronic Information Materials, School of Material Science and Engineering, Shanghai University, Shanghai 200072, China

Received 22 May 2007; received in revised form 5 November 2007; accepted 5 November 2007

Abstract

We describe a hot soap method for assembling CdSe nanoparticles inside the channels of mesoporous SBA-15 materials. X-ray diffraction (XRD), transmission electron microscopy (TEM), energy dispersive spectrometry (EDS), UV–vis absorption spectra, and fluorescence spectra have been successfully used to characterize the structure and the optical properties of the mesoporous materials. EDS analysis carried out on the pores of composite mesoporous silica shows strong Cd and Se signals, confirming the formation of CdSe nanoparticles inside the SBA-15 pores. TEM image shows that the CdSe nanoparticles are about 4–5 nm in sizes and uniformly dispersed inside the pores of mesoporous silica. In the UV–vis absorption spectra of the CdSe nanoparticles inside the SBA-15 hosts, a significant blue shift is detected and attributed to the confinement of channels of SBA-15.

© 2007 Elsevier B.V. All rights reserved.

PACS: 73.61.Tm; 81.05.Dz; 81.05.Rm

Keywords: Assembly; CdSe nanoparticles; Semiconductor; Mesoporous SBA-15

1. Introduction

Semiconductor nanocrystals are extremely attractive physical systems due to their strong confinement applied on electrons and holes that lead to dramatically different optical and electronic properties compared to bulk semiconductor [1]. Recently, quantum dots (QDs) prepared by solution chemistry have been excellent candidates for tunable light absorbers and emitters in LEDs [2], optical probes in biological diagnostics [3], as well as photo-detectors and electro-photography in visible range [4]. CdSe QDs, a typical II–VI semiconductor with direct band gap energy at 1.75 eV [5], have been extended in bio-label and biological imaging due to their bright fluorescence, narrow emission, broad UV excitation and high photostability [6–8]. Moreover, QDs have been expected to extend their applications and fundamental investigations in

the fields of photonics and electronics. In these applications and studies, it is desirable to define the position and array of given QDs and to improve the stability and controllability of the QD systems. Therefore, the stability and immobilization of QDs have attracted considerable attentions and become an utmost important subject. Existing effective methods for stabilizing and immobilizing QDs focus on the assembly and composite of QDs in some dielectric oxides and functional polymers. Mesoporous materials such as SBA-15 and porous anodic aluminum oxides have been used to immobilize and stabilize monodisperse QDs. For example, CdS [9], PbS [10], $Zn_{1-x}Mn_xS$ [11] and CdSe [12] have been synthesized inside the pores of SBA-15. Compared with sulfides, there are fewer reports on assembling selenide nanoparticles inside mesoporous materials so far. Shan et al. [13] proposed a method for loading CdSe inside the pores of SBA-15, with Se element provided by Na_2SeSO_3 in water solution. However, the releasing process of Se^{2-} from the aqueous Na_2SeSO_3 solution was very slow, and the requirement to control the pH value within 8–9 limited

*Corresponding author. Tel.: +86 21 65420850x24407; fax: +86 21 65830734.

E-mail address: ndai@mail.sitp.ac.cn (N. Dai).

the growth efficiency and the formation stability of CdSe QDs inside the pores of silica.

In this letter, we propose an alternative method to grow CdSe nanoparticles inside the pores of SBA-15 using selenium powder in tributylphosphine (TBP), rather than Na_2SeSO_3 to provide Se^{2-} . Our approach offers with the easiness for Se atoms to enter into the channels of SBA-15 with the assistance of TBP and then react with cadmium source, increasing the nucleation efficiency of the stable CdSe QDs. Moreover, the formation and assembly of CdSe nanoparticles in mesoporous SBA-15 are achieved within 1 h, and do not depend on the pH value. The optical properties of CdSe QDs inside the pores of silica can be varied by manipulating the experimental parameters (e.g. reaction time) for the size control.

2. Experiment

2.1. Synthesis of CdSe nanoparticles inside the mesopores of SBA-15

The preparation of TBP precursor can be found in some literatures [14]. The mesoporous silica, the SBA-15 host, was synthesized following the procedure reported in Ref. [15]. SBA-15 (1.0 g) was immersed in a hot solution of sulfate acid at 120 °C, producing more –OH groups inside the channels of SBA-15. The –OH groups were helpful for the absorption of Cd^{2+} . The synthesis procedure of assembling CdSe inside the pores of SBA-15 was as following: 0.20 g SBA-15 was mixed with 0.01 mol $\text{Cd}(\text{Ac})_2 \cdot 2\text{H}_2\text{O}$ in 50 ml of water by violent stirring and ultrasonication for at least 24 h. Subsequently, the left-over Cd^{2+} outside the channels were washed away and the remains were dried in vacuum. This leads to Cd^{2+} functionalized SBA-15 on the internal surfaces of the channels, denoted by SBA-15– Cd^{2+} . The growth of CdSe nanoparticles inside the host material was initiated by following the synthetic strategy adopted for the growth of colloidal CdSe nanoparticles. SBA-15– Cd^{2+} (0.20 g) in 1.00 g tri-*n*-octylphosphine oxide (TOPO), were added into the vigorously stirred TOPO solution in the reaction flask at 150 °C. Selenium powder (0.15 g) in 2.0 ml TBP was then added into the flask quickly. All the reactions were carried out under argon atmosphere. Rapid nucleation and growth of nanoparticles were achieved by maintaining the reaction temperature at 150 °C. The reaction mixture was cooled to room temperature under argon and was then repeatedly washed with toluene to remove TOPO and the CdSe outside the pores of mesoporous silica. Finally, the CdSe-assembled SBA-15 was dried at room temperature and denoted as SBA-15–CdSe. Using this growth technique, it was easy to assemble the QDs in porous SBA-15 with high efficiency and to control the growth parameters.

Removing the CdSe QDs outside the SBA-15 channels was realized by centrifuging the as-prepared SBA-15–CdSe in solution. Centrifuging process gave rise to the separation of the SBA-15–CdSe from CdSe QDs outside the SBA-15

channels in the solution, with the CdSe QDs outside the channels staying on top of the solution and the SBA-15–CdSe powders staying at the bottom.

2.2. Instruments

X-ray diffraction (XRD) patterns of the SBA-15–CdSe powder were recorded with a D/MAX 2550 V (Rigaku, Japan) using Cu $\text{K}\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$). Transmission electron microscopy (TEM) operated at 200 kV and energy dispersive spectrometry (EDS) studies were performed using a Japan JEM-2010F. The UV–vis absorption spectra were recorded with a Perkin-Elmer Lambda 2S spectrophotometer and the fluorescence spectra with a SCINCO fluorescence spectrophotometer (Fluoromate Fs-1).

3. Results and discussion

3.1. XRD analysis

Fig. 1 shows the XRD patterns of the mesoporous SBA-15 and the SBA-15–CdSe composites in the 2θ range from 0.5° to 5°. Three reflection peaks are detected on SBA-15, corresponding to the characteristic hexagonal structure of SBA-15. After the CdSe nanoparticles are assembled into the pores (see curve b), the intensity of the small-angle (100) peak decreases and the (110) and the (200) peaks become much weaker. This is a typical pore filling indication caused by the reduction of the scattering contrast between the pores and the walls of the mesoporous material with nanoparticles inside of the pores [16]. Note that in Fig. 1 the (100) peak shifts very little after assembling the CdSe QDs, attributed to the fact that growth of CdSe nanoparticles does not change the channel structures of SBA-15.

3.2. TEM analysis

Figs. 2a and b present TEM images of SBA-15 and SBA-15–CdSe (the reaction time was 10 min) paralleled to the

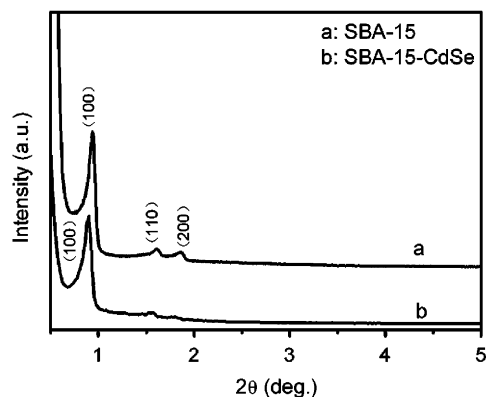


Fig. 1. Low-angle XRD curves of (a) mesoporous SBA-15, (b) CdSe assembled in SBA-15. The curves are vertically shifted for clarity.

Download English Version:

<https://daneshyari.com/en/article/1546134>

Download Persian Version:

<https://daneshyari.com/article/1546134>

[Daneshyari.com](https://daneshyari.com)