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Preparation and physical properties of Nano-ZnSe/SiO_2 mesoporous composite for assembly system

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Abstract A novel synthesis route of ZnSe/gel-glass mesoporous composite was described. SeO_4^{2-} and Zn^{2+} were loaded into the porous framework of silica gel-glasses by immersion. Followed by drying and the reductive thermal treatment, the transparent, homogeneous ZnSe/SiO_2 samples with the color of light yellow were prepared. The specific surface area, grain size, structure and phase properties of nano-sized ZnSe/SiO_2 mesoporous composites were studied by powder X-ray diffraction, nitrogen sorption, SEM. The effects of pore structure properties and loading solution concentration on the optical absorption of ZnSe/SiO_2 were investigated by UV-vis absorption. It is found that the optical absorption edges of ZnSe nanoparticles in mesoporous silica shift to the red as ZnSe loading concentration increases, which is attributed to the quantum size effect. The nonlinear optical property of these samples was presented by the open aperture z-scan technique. This method has some potential advantages in comparison to the conventional methods.

Keywords ZnSe · Mesoporous composite · Nanocrystals · Sol-gel · Optical property

1 Introduction

Putting the nanoparticles into pores of mesoporous solids forms a new material, which we call mesoporous composite [1–3].This material exhibits unusual physical properties of technological and has received a growing interest in the recent years both for fundamental studies and application [4, 5]. ZnSe, which is an important wide band-gap II-VI semiconductor, attracted a significant amount of renewed interest in recent years [6]. Since the band-gap of ZnSe is 2.58 eV at room temperature and is within the blue region of the optical spectrum, ZnSe nanocrystals have promising applications in non-linear optics and optical switches [7]. However, the reports of ZnSe-doped glass synthesized by mesoporous composite method and sol-gel technique are much fewer [8–10]. Here we report a novel preparation route of ZnSe/gel-glass and first attempt to locate nano-ZnSe particles into the pores of monolithic mesoporous silica. The mesoporous composite we got is transparent and bright yellow, which is consistent with the color of ZnSe solid powder. Its absorption edge could shift with a change in the loading amount of ZnSe. Because of the quantum size effect, the nonlinear optical property of samples is also affected by the loading amount of ZnSe. Compared to conventional one-step doping and synthesis method [8], this novel route could control the nanocrystal size effectively and make the synthesis process more controllable.

2 Experiment

The silica gel glasses as mesoporous solids were obtained in the following process [11]. Tetraethylorthosilicate (TEOS) was first dissolved in ethyl alcohol (EtOH). Then, with constant stirring of the mixture of TEOS and EtOH, a dilute aqueous solution of HCL was slowly added. In this mixture, the molar ratio of TEOS/EtOH was 1:4.The whole solution was stirred using a magnetic stirrer for about 30 min, resulting in formation of a uniform sol. The sols were transferred to vessels and gelled within 2–3 days at

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45 °C. Then transparent gels were prepared. These wet gels were hermetically kept at room temperature for some days, until they were entirely dry. Finally the dry gels were annealed at 600 °C for 1 h. In this way, SiO_2 gel-glasses were obtained as mesoporous solids.

$ZnSeO_4$ solutions as soaking solution were prepared by mixing H_2SeO_4 and $Zn(CH_3COOH)_2$. The preformed SiO_2 was immerged in the $ZnSeO_4$ solutions with different concentrations(0.05, 0.10, 0.20 mol/L) at room temperature for 7 days. Then the samples were taken out, cleaned, dried and reduced in CO gas at about 500 °C for 1 h. The assemblies of nano-ZnSe particles/SiO_2 gels were gotten. In order to make comparison, the SiO_2 host without doped was also subjected to the same procedure.

The nitrogen sorption isotherms were obtained using a gas adsorption apparatus (model: ASAP2010). XRD pattern was recorded with a Rigaku D/max-2400 diffractometer with CuKα radiation(λ=0.15432 nm). UV-vis absorption spectra were measured by a JASCO V-570 UV-vis-NIR spectrophotometer at room temperature. SEM pictures were taken by a JSM-6700F scanning electron microscope.

3 Results and discussion

Figure 1 shows the SEM micrographs of ZnSe/SiO_2 mesoporous systems before and after doping. From the Fig. 1, we can see clearly that some kind of nano-size particles had existed in not only the sample's surface but also its interior after immersion and reductive thermal treatment. Because ZnSe/SiO_2 mesoporous system is not conductive, we first sprayed aurum over the samples before SEM test. Since the diameter of Au particle is similar to the aperture of the silica host, the holes of SiO_2 host cannot be distinguished clearly in part a, c (Fig. 1).

The existence of particles within pores can also be confirmed by the isothermal nitrogen sorption experiment. Figure 2 indicates the N_2 sorption isotherms and distributions of pore diameters for ZnSe nanocrystals/silica mesoporous systems (ZnSe/SiO_2) before and after doping. Since nano-particles had put into the pores of SiO_2 after doping, the sorption isotherm had fall. We can clearly see that ZnSe particles are mainly located within the pores less than 4 nm diameter. The size is similar to the diameter of Au particle sprayed over, so only the bigger size particles doped can be seen on part b, d (Fig. 1). In order to confirm

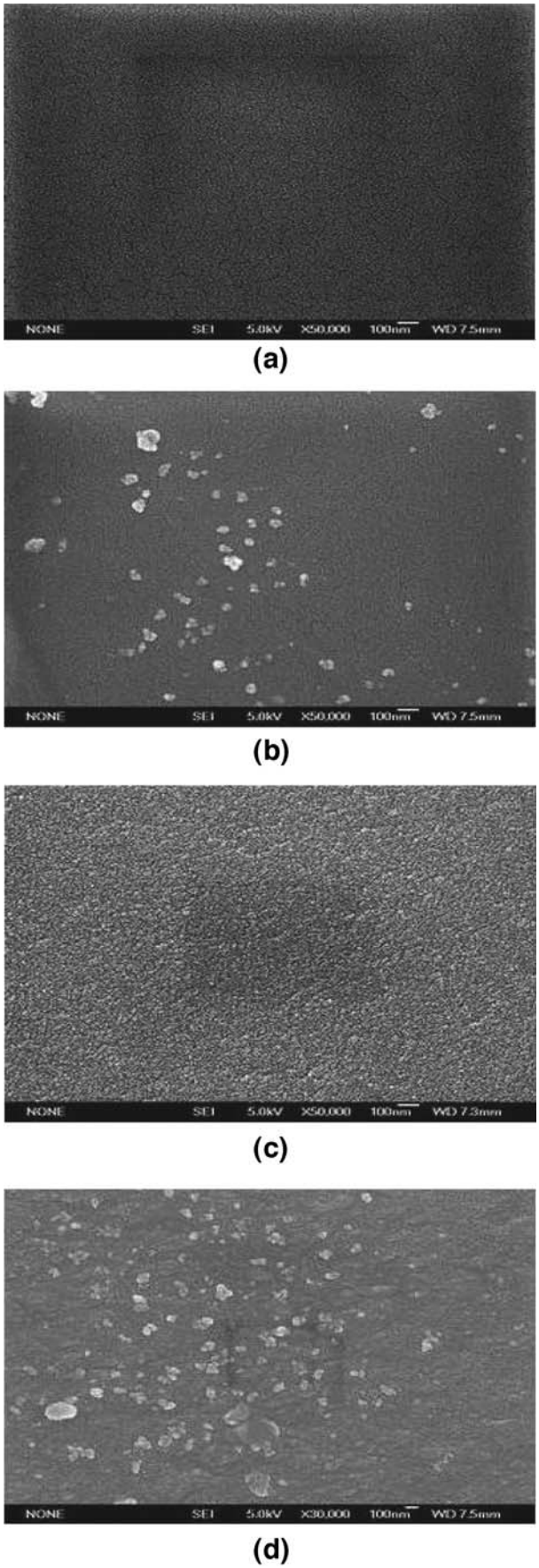

Fig. 1 SEM micrographs of the ZnSe/SiO_2 mesoporous composite and the pure SiO_2 Sample 1: Pure SiO_2 Sample 4: ZnSe/SiO_2 composite soaked in 0.20 mol/l $ZnSeO_4$ (**a**) SEM micrograph of pure SiO_2's surface (before doped) (**b**) SEM micrograph of ZnSe/SiO_2's surface (after doped) (**c**) SEM micrograph of pure SiO_2's cross section (before doped) (**d**) SEM micrograph of ZnSe/SiO_2's cross section (after doped)

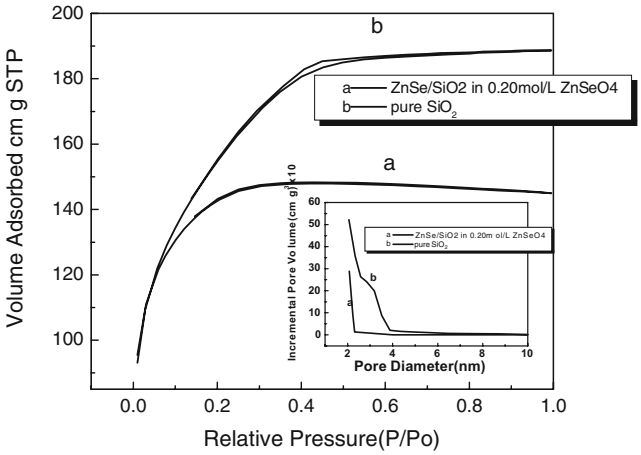

Fig. 2 N_2 isothermal sorption. Curve *a*:ZnSe/SiO_2 composite soaked in 0.20 mol/l $ZnSeO_4$. Curve *b*: pure silica. Inset: distribution of pore diameter

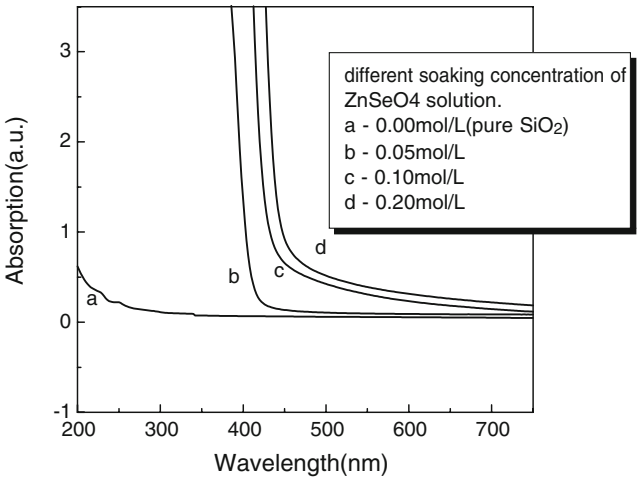

Fig. 4 Absorption for the ZnSe/SiO_2 mesoporous composites with different soaking concentration of $ZnSeO_4$ solution. The *lines* from left to right, respectively represent the samples soaked in the concentration of $ZnSeO_4$: 0.00, 0.05, 0.10, 0.20 mol/l

what these nanoparticles doped in silica host are, we had made the following analysis.

The phase structure for the particles within pores can be determined by X-ray diffraction. Figure 3 exhibits the XRD pattern of ZnSe/SiO_2 mesoporous systems before and after doping within the 2θ range of 20°~80° .The scanning speed is 200unit/min. The pattern shows the existence of cubic zinc blende structure of ZnSe and three broadened peaks can be attributed to the (111), (220) and (311) lattice planes. There is another broad peak at around 22°, which is corresponding to the diffuse peak of noncrystalline silica matrix. No other obvious peaks were seen in the XRD pattern, besides the diffractive peaks of ZnSe and SiO_2 matrix. As a result, we can confirm the nanoparticle put into the pore of SiO_2 host is ZnSe, not $ZnSeO_4$ or anything else.

We studied optical character of the mesoporous composite, too. The optical absorption edge can be modulated by heat treatment and the loading amount of nanoparticles within pore. The loading amount can be controlled by the pore properties of mesoporous solid and the concentration of the soaking solution. In this paper, we only investigated the influence of the concentration of the soaking solution. Figure 4 shows the room temperature optical absorption spectra of ZnSe/SiO_2 mesoporous composite soaked in various molar concentrations of $ZnSeO_4$ solution at the same thermal treatment process. The absorption edge is shifted to shorter wavelength than bulk ZnSe (480 nm) due to the quantum confinement effects. In addition, as the soaking concentration decreases, the absorption edge shifts continual to shorter wavelengths, as shown in Fig. 4. The phenomenon can be explained that the quantity of the nanoparticles reduced in unit volume's silica host with the decreasing of soaking concentration, therefore the size of ZnSe quantum dots, which formed in the course of heat treatment, reduced correspondingly.

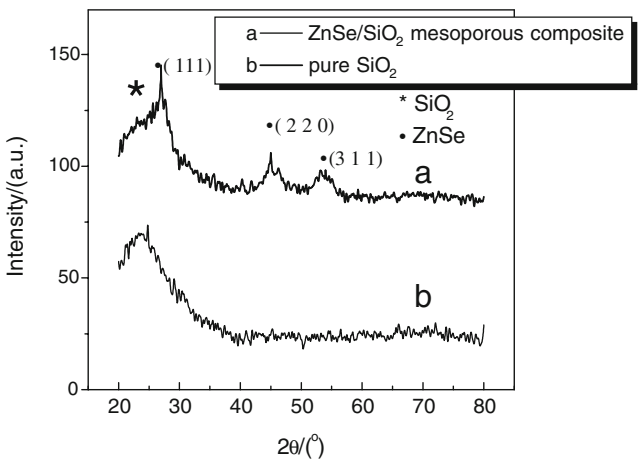

Fig. 3 XRD pattern of the pure SiO_2 and the ZnSe/SiO_2 composite soaked in 0.20 mol/l $ZnSeO_4$

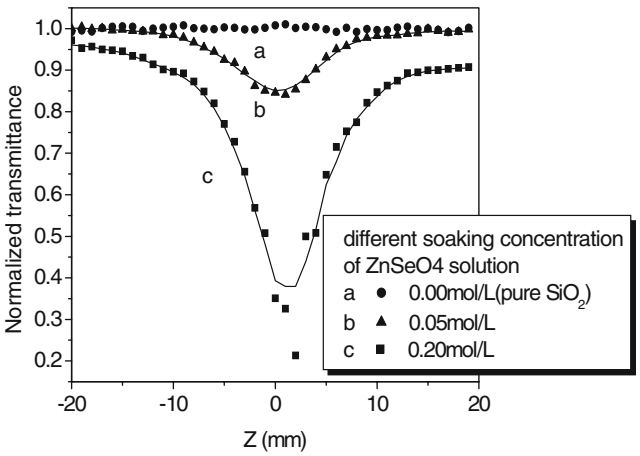

Fig. 5 Open aperture z-scan traces for the different samples *a* pure SiO_2 *b* ZnSe/SiO_2 soaked in 0.05 mol/l $ZnSeO_4$ *c*: ZnSe/SiO_2 soaked in 0.20 mol/l $ZnSeO_4$

Figure 5 shows the normalized transmittance versus the sample position (Z) measured with open-aperture z-scan at different samples with various soaking molar concentrations [12]. All scans besides pure SiO_2 performed a decrease of transmittance at positions close to the focus. These transmittance valleys indicate the presence of nonlinear absorption in the samples. But for the pure SiO_2, no transmittance change was observed in Fig. 5. So the nonlinear absorption should owe to the existence of ZnSe nanocrystals. And the higher the soaking concentration of the samples is, the faster the transmittance value descended at positions close to the focus [13].

4 Conclusion

A novel synthesis and characterization methods of the $ZnSe/SiO_2$ mesoporous composites was reported. SEM micrographs and XRD results approved that ZnSe nanocrystals had been embedded in the SiO_2 host. The phase of ZnSe is zinc blende structure and the average size of the nanocrystals is smaller than 4 nm in diameter according to the nitrogen sorption isotherms. The optical property of $ZnSe/SiO_2$ mesoporous composites is influenced by the size of ZnSe nanocrystals. We investigated the influence of the concentration of the soaking solution to the size of nanocrystals. Raising the soaking concentration will cause the size of nanocrystals to increase. These properties may offer promising applications in future optical information devices. The method has many potential advantages: it is simple, it saves time, and the solution can be recycled. This process may be easily applied to the synthesis of a range of nanoparticle/mesoporous composites.

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