Preparation and characterization of nanocrystalline ZnS/ZnO doped silica inverse opals

Ming Fu · Ji Zhou · Qunfang Xiao · Bo Li · Yang Bai · Longtu Li

Abstract ZnS/ZnO doped silica glass inverse opals were prepared by a sol–gel chemistry method via polystyrene colloidal crystals templating. After the infilling precursors were solidified in the void space among polystyrene spheres, the polymer templates were removed by calcinations and the doped silica glass films were generated with long-range order of the inverse replicas of the template arrays. The effective reflective index of the structure and reflective index of the doped silica glass is calculated by Bragg equation using wavelengths of optical stop band and periodicity diameters of the inverse opals. The result is well agreed with mixture rule approximation.

Keywords Semiconductor doped silica · Photonic crystals · Inverse opal

1 Introduction

Ordered structures with spatial periodic modulation of the dielectric constant, whose electromagnetic waves can be propagated controllably at certain frequencies, have been the subjects of great interest for possible application as photonic crystals (PCs) [1, 2]. Lots of methods have been developed among which the use of colloidal crystal as templates has been proven to be a simple and efficient approach for fabricating three-dimensional high-ordered macroporous materials, named as inverse opals. A wide variety of materials such as semiconductors [3], metals [4],

oxides [5] and polymers [6] can be infiltrated into inverse opals by various methods such as chemical vapor deposition, electrodeposition, polymerization and sol–gel method. In particular, silica inverse opals have attracted great interest for its preparation facilities and good optical properties [7, 8].

On the other hand, nanocrystalline semiconductor doped silica glass is one of the most promising materials with high third-ordered nonlinear optical susceptibility and picosecond nonlinear response [9, 10]. Photonic crystals with nonlinear properties are of great importance for complete optical switches and all optical microchips owning to their capabilities to manipulate light with light. Although the preparation of silica inverse opal structure has already been reported, to the best of our knowledge, this is the first time the preparation of nanocrystalline semiconductor doped silica inverse opals is reported. In this work, ZnS/ZnO doped silica inverse opal structures have been prepared by sol–gel chemistry method. Optical properties of the structure and reflective index of silica glass doped with nanocrystalline semiconductors have been studied while the semiconductor weight contents vary.

2 Experimental details

Preparation of colloidal crystals templates The colloidal crystals were made by a vertical deposition method via self-assembly process with monodispersed microspheres. Polystyrene microspheres, with mean diameters of 280, 330, 375 and 400 nm, respectively, were got from Bangs laboratories Inc. After washed in acetone and ethanol solvent, glass slides were placed vertically into a bottle which contains 0.8%vol of monodispersed microspheres solution. High-ordered colloidal crystals templates were

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formed on the glass slides as the solvent evaporating at 50 °C and 30% moisture.

Synthesis of inverse opal silica Before infiltrating to the interstices of the colloidal crystals, sols with precursor of silica and ZnO were prepared. Of the $Si(OC_2H_5)_4$, 0.1 mol was first partially hydrolyzed after dropped into a mixed solution of H_2O, C_2H_5OH and HCl. After stirring for 1 h, CH_3OH solution was added. It containing $Zn(CH_3COO)_2 \cdot 2H_2O$ whose weight was calculated by the mass content of ZnO in silica glass. Then the solution was stirred for another 1 h at room temperature. The resulting homogeneous solution was subsequently hydrolyzed in mixed solution of H_2O, C_2H_5OH and NH_4OH. After stirring for several hours, a few drops of sol were drawn out and dropped into the colloidal crystals which were coated on the glass slide. After the doped sol precursors were slowly infiltrated into the interstice of the colloidal crystal and the residual sols out of the templates surface were imbibed by filter paper, precursors gelated. Then the spheres and precursor composite were heated at 50 °C/h to 600 °C and kept for 2 h. In the thermal process, the polystyrene colloidal crystal templates were removed and inverse opal structure silica glass doped with ZnO was formed. At last the porous silica films were located in a H_2S atmosphere at room temperature for 1 day in airtight flask and ZnS doped silica glass inverse opal structure was obtained.

Characterization of the inverse opal structure films In this study, a Rigaku D/max-RB X-ray diffraction (XRD) which equipped with a Ni-filtered $Cu_{K\alpha}$ radiation ($\lambda = 0.15418$ nm) was employed for phase analysis of the doped silica. JEOL (JSM-6301F) scanning electron microscopy (SEM) was used to characterize three-dimensional colloidal crystals and doped silica inverse opals. The angular dependence transmission spectra of the inverse opal structure were get by ultraviolet-visible spectrophotometer (Unicam UV540) and the reflection spectra were characterized by microregion reflection spectrometer (Ocean Optic USB2000).

3 Results and discussion

Figure 1(a) shows the typical SEM image of the polystyrene colloidal crystals made from microspheres with mean diameter of 280 nm. The colloidal crystals have long-ranged order in large-area. An FCC closepacking structure with (111) planes along the substrate is shown. Colloidal crystals made from microsphere with other diameters have the same good close-packed structures. The thickness of the opal films is controlled about 10 μm with 20–40 layers.
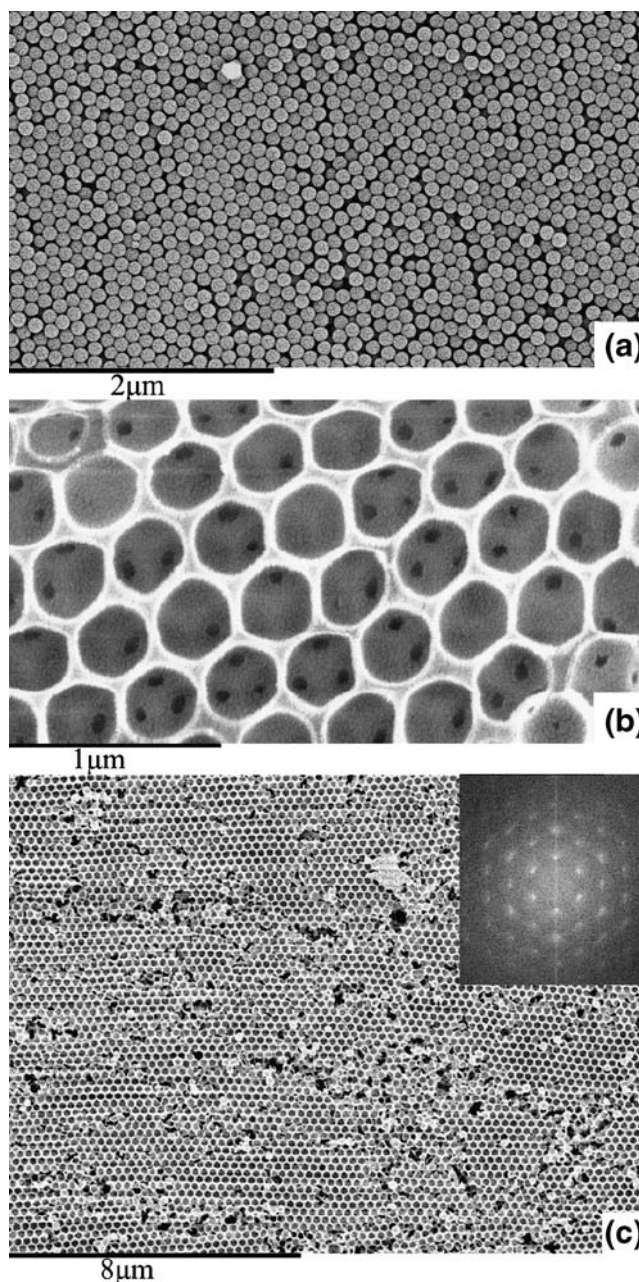

Fig. 1 Typical scanning electron microscopy images of (**a**) colloidal crystal made from microspheres with mean diameters of 280 nm. (**b**) Inverse opal structure of 1 wt.% ZnO doped silica glass. (**c**) Inverse opal structure of 1 wt.% ZnO doped silica glass

Figure 1(b) shows the typical high-magnification SEM image of the ZnO doped silica inverse opal structure. Three cavities can be seen in each hole which is induced by the removed colloidal microspheres in the next 111 face. Figure 1(c) shows a typical SEM image of ZnO doped silica inverse opal structure in large area. Templated by the colloidal crystals, long-range order of the macroporous silica film is confirmed by Fourier transform of low magnification image [Fig. 1(c), (inset)]. The ZnS doped silica inverse opals have the similar structures. The holes'
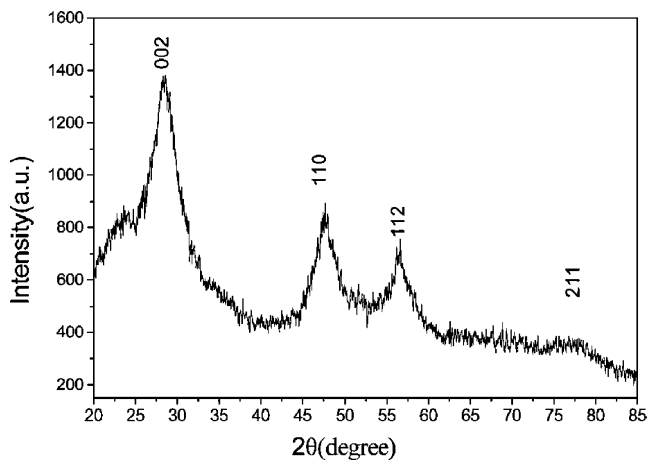
Fig. 2 XRD patters ZnS doped silica glass, and the weight content of ZnS in silica is 29%

diameters of the ZnO/ZnS doped silica inverse opals can be changed from 200 to 380 nm when different diameter of polystyrene microsphere is selected or the infilling process is modified.
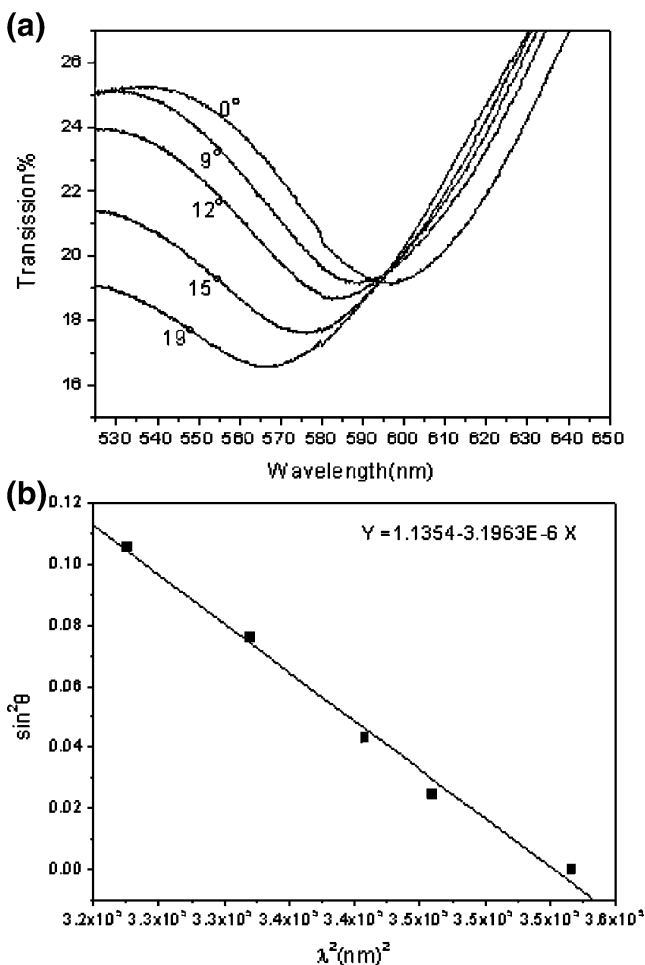

Fig. 3 (a) Angular dependence transmission spectra of the inverse opal structure, θ is the incident angle to the normal. (b) Relationship between the stop band and the incident angle. The *solid line* is the fitting curve of the Bragg formula

Figure 2 shows XRD patterns ZnS doped silica glasses. The structures show the typical amorphous halo pattern. In the XRD pattern of the ZnS doped silica glass, broad peaks indicate the formation of, hexagonal, wurtzite ZnS with fine crystals.

Though the silica film does not absorb in visible range, the silica films with inverse opal structure appear brightly colored from blue to red with variation of diameters of holes in inverse opals. The exhibiting colors are induced by the reflection of the inverse opal structure which have directional stop band gap in special wavelength, which is the basic property of photonic crystal. The angular dependence of the optical transmission spectra through one of our silica inverse opal structure are shown in Fig. 3(a). The angular dependence of the stop band is studied by changing the angle of incidence (θ) between the beam and normal axis of the inverse opal's surface from 0° to 19°. And the stop band is characterized by λ, the wavelength of minimal intensity in transmission spectra (i.e. the wavelength of maximum in reflection). It is seen that as the angle increased the stop band shifts to shorter wavelengths.

The spectral positions of the stop bands for an inverse opal photonic crystal can be calculated by a modified version of Bragg's law:

$$\lambda = 2d\sqrt{n_{\text{eff}}^2 - \sin^2 \theta} \tag{1}$$

where n_{eff} is the effective refractive index of the structure, d is the interplanar<111> spacing. In the FCC lattice, the relationship between d and diameters of the holes D (i.e. the periodicity of the inverse replicas) is: $d=(2/3)^{0.5}D$. The angular dependence of stop band shown in Fig. 3 is consistent with the Bragg equation. And Fig. 3(b) shows a linear plot of $\sin^2\theta$ versus λ^2, as predicted by the equation. From the intercept of the curve, the n_{eff} is estimated as 1.066.

Table 1 Theoretical and experimental results for silica doped with ZnO.

Wt. %	Vol. %	λ (nm)	D (nm)	neff	F (%)	n[a] Bragg	n[b] Mixture
1	0.47	552.8	320.5	1.056	10	1.467	1.459
5	2.41	557	322.7	1.057	10	1.474	1.477
9	4.43	536.3	310.4	1.058	10	1.482	1.496
17	8.76	550	316.1	1.065	10	1.533	1.535
29	16.1	545.6	310.7	1.075	10	1.602	1.598
5[c]	2.41	581.9	327.9	1.087	15	1.485	1.480

[a] Reflective index of ZnO doped silica glass calculated by Bragg Equation
[b] Reflective index of ZnO doped silica glass calculated by mixture rules of Eq. 4. And the common literature values of 1.45 and 2.2 are used for the refractive index of silica and ZnO.
[c] Inverse opal structures prepared via a multi-infiltration process

Furthermore, n_{eff} can be independently estimated using the following relation:

$$n_{eff}^2 = n^2 f + n_{air}^2 (1-f) \qquad (2)$$

where f is the filling factor of the doped silica, n and n_{air} are the refractive index of doped silica glass and air. A solid volume fraction of 26% would be predicted for an exact inverse replica of close-packed spheres. However, the actual solid volume fraction is often much lower than 26% as a result of condensation of the precursors.

The wavelength (λ) of the stop band in micro-region can be measured by reflection spectra from the normal direction, and the average diameters (D) of holes can be measured by SEM. Therefore, n_{eff} and n of silica films doped with different weight contents(wt.%) of ZnO can be estimated by Bragg equation:

$$n_{eff} = (3/8)^{0.5} \lambda / D. \qquad (3)$$

As the inverse opal silica doped with different weight contents have the same mass lost during gel generation and template removal, the volume fraction can be consider as the same. Volume fraction of 10% is estimated for the silica inverse opal structure and the refractive index of the doped silica material is consequently calculated. The relevant data of experimental and calculational results are summarized in Table 1. And as the mixture rule approximation results of reflective index are typically in closer agreement with calculation by Bragg diffraction, equation

$$n^2 = \text{Vol.\%}_{ZnO} n_{ZnO}^2 + \text{Vol.\%}_{silica} n_{silica}^2 \qquad (4)$$

is also valid in refractive index estimation of the nano-crytalline semiconductor doped glass.

The inverse structures in the last line of Table 1, whose volume fraction has notable increment, were prepared by infilling precursor sols for three times. This result provides an effective way to increase the filling ratios via colloidal crystals templating by sol–gel method.

4 Summary

In conclusion, a sol–gel method was applied for preparing ZnO/ZnS doped silica glass inverse opal structure by templating with polystyrene colloidal crystals. The effective reflective index of the structure and reflective index of the doped silica glass calculated by Bragg equation are well agreed with calculation of mixture rules. Furthermore, the filling ratios of the structure could be increased by multi-infiltration process. The photonic crystals with semiconductor doped silica would have further application in all-optical fields.

References

1. E. Yablonovitch, Phys. Rev. Lett. **58**, 2059 (1987)
2. S. John, Phys. Rev. Lett. **58**, 2486 (1987)
3. P.V. Braun, P. Wiltzius, Nature. **402**, 603 (1999)
4. O.D. Velev, P.M. Tessier, A.M. Lenhoff, E.W. Kaler, Nature. **401**, 548 (1999)
5. B.T. Holland, C.F. Blanford, A. Stein, Science. **281**, 538 (1998)
6. S.A. Johson, P.J. Ollivier, T.E. Mallouk, Science. **283**, 963 (1999)
7. O.D. Velev, T.A. Jede, R.F. lobo, A.M. Lenhoff, Nature. **389**, 447 (1997)
8. R.C. Schroden, M. Al-Daous, C.F. Blanford, A. Stein, Chem. Mater. **14**, 3305 (2002)
9. M. Nogami, K. Nagaska, E. Kato, J. Am. Ceram. Soc. **73**, 2097 (1990)
10. S. Lu, Y. Han, L. Zhang, X. Yao, J. Chinese Ceram. Soc. **22**, 71 (1994)