Fabrication and Characterization of Tin Oxide Inverse Opal by Template Method

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Abstract.

In this study, Tin Oxide (SnO_2) inverse opal was fabricated by infiltrating SnO_2 sol-gel precursor solution into Poly Styrene (PS) spheres crystal template which was generated via evaporative deposition self-assembling, then was heat treating at 500°C for two hours in controlled atmosphere box furnaces. PS spheres crystal template was characterized by Scanning electron microscope and Ultraviolet-visible-near infrared absorption spectrometer. The SnO_2 inverse opal was characterized by Scanning electron microscope, Energy Diffraction Spectrum, X Ray Diffraction. The large-area, highly ordered SnO_2 inverse opal was achieved in this paper.

Keywords: Opal, Tin Oxide, Inverse opal, Template method

1. Introduction

As an important gas sensitive material, SnO_2 has been found extensive applications in the past, and is still a hot topic of the research regarding gas sensitive materials. This is because SnO_2 has indispensable advantages such as high sensitivity, low cost and good availability, and high thermal ability. The larger superficial area of SnO_2 is achieved, the higher sensitivity shows. Several groups have fabricated and studied SnO_2 inverse opal ^{[1] [2] [3]}, but they could not achieve large-area, high ordered SnO_2 inverse opal. In this paper, the large-area, highly ordered SnO_2 inverse opal was achieved by template method ^{[4] [5]}.

2. Experimental Section

PS opal fabrication

Polystyrene (PS) spheres with diameter about 270nm and a standard deviation of less than 5% were prepared by using the emulsifier-free emulsion polymerization technique ^{[6] [7]}. The PS spheres produced were cleaned by consecutive centrifuging, decanting, and re-dispersing, first in water (three times) and then in ethanol (three times).

Glass microscope slides were cleaned in freshly prepared Piranha solution ($\text{H}_2\text{SO}_4/\text{H}_2\text{O}_2$, 3:1), and rinsed copiously first with deionized water and then with ethanol. 270nm PS sphere dispersions (10mL) with typical concentrations about 0.1wt % were placed in a cylindrical clear glass vial. The cleaned glass microscope slide was carefully centered in the cylindrical clear glass vial and vertically fixed with two small paper clips. Then the glass vial was taken into oven where the temperature was 55°C . After about 20 hours, the liquid volatilized over, the opal on the glass microscope was achieved.

SnO_2 inverse opal fabrication:

Mixed solution of 40ml SnCl_4 solution (0.13M) and 0.4g citric acid were stirred and heated to 50°C , ammonia water was added into the mixed solution until the pH of mixed solution was about 1.5-2, sediment came out at the same time ^[8]. The sediment was cleaned by consecutive centrifuging, decanting, and re-dispersing, until Cl^- in upper clear water could not be checked out with AgNO_3 solution. The sediment solution was heated to 50°C and dissolved with oxalic acid saturated solution as pH was about 1.5-2,

then was diluted with deionized water to 60ml.

The opal on the glass microscope was immersed in SnO_2 precursor solution, then taken into vacuuming box and vacuumed 15 minutes, then taken into oven where the temperature was 55°C to dry for 30 minutes. The operation above was repeated three times. After those operations, the infiltrated opal was heated from room temperature to 500°C for 140 minutes, maintained at 500°C for 2 hours, then cooled down to room temperature for 15 hours.

3. Result and discussion

A S-4800 II FESEM was used for direct characterization of the opal. Figure 1(a) shows typical SEM surface images of 270nm PS colloidal crystal which exhibits ordered close-packed arrangement of PS spheres. Figure 1(b) shows typical SEM cross-section images of 270nm PS colloidal crystals which exhibits inner lattice structure and some vacancies on the surface ^[9].

Figure 1. Scanning electron microscope image of 270 nm PS colloidal crystal: (a) top view; (b) cross-section view.

In order to further research the inner lattice structure, Cary 500 (UV-NIR) was used for characterization of the opal. Figure 2 shows that the 270nm PS colloidal crystal has good lattice structure. The photonic band gap position is in 620 nm that is corresponding to Bragg's law ^[10]:

$$\lambda_{\max} = 2d_{111}\sqrt{n_{\text{avg}}^2 - \sin^2 \theta}$$

Figure 2. Optical transmittance spectra of 270 nm PS colloidal crystal.

A S-4800 II FESEM was used for direct characterization of the inverse opal of SnO_2 . Figure 3 (a) shows that the hundreds of square millimeters of SnO_2 inverse opal could be achieved, but some defects can be checked from this picture, some of the defects were the photocopy of the PS spheres opal defects, some of the defects such as over-layer formation was in the process of excessive infiltration of SnO_2 precursor solution. The inlaying picture is the higher power of figure3 (a) which shows three holes under every surface hole. Figure 3 (b) exhibits the cross-section of SnO_2 inverse opal which has perfect ordered inner structure.

Fig 3. Scanning electron microscope image of SnO_2 inverse opal film based on 270 nm PS colloidal crystal: (a) top view; (b) cross-section view.

In order to further study the SnO_2 inverse opal, the EDS was used to detect the element of SnO_2 inverse opal. XRD was used to detect the crystal structure of SnO_2 inverse opal. Figure 4 exhibits the different elements of the glass microscope slides which clearly shows Tin element existing. Figure 5 is the crystal structure comparing between SnO_2 sol gel (heated at 500 °C for 2 hours) and inverse opal. It shows that the XRD peak position of SnO_2 sol gel and inverse opal are same, but the intensity of SnO_2 sol gel is stronger than SnO_2 inverse opal.

Fig 4. EDS analyses of SnO_2 inverse opal.

4. Conclusion

SnO_2 inverse opal was prepared by the self-assembly technique in combination with sol-gel infiltration method. The SnO_2 inverse opal has great specific surface area which can be a catalyst material and gas sensing material. But the fabricated SnO_2 inverse opal has some defects such as

multi-domains, cracking, over-layers that inhibit application. How to dissolve those defects is an important issue. Our research team is fabricating large-area, highly ordered, crack-free SnO_2 inverse opal film and dissolving those problems.

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