# ZnO Inverse Opals Using Colloidal-Crystal Template Assisted Hydrothermal Method

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**Abstract.** Both two-dimensional (2D) ZnO nanobowl arrays and three-dimensional (3D) ZnO inverse opals were fabricated using hydrothermal method with assistance of the three-dimensional colloidal crystal templates. Scanning electron microscope measurements showed the morphological evolutions of ZnO from rods to 2D monolayer nanobowl arrays and 3D porous films by controlling the concentration of hydrothermal solutions and reaction time. The photonic stop b and was characterized using reflections spectra presenting the 3D periodic geometry. The photoluminescence spectra indicate good crystalline quality via the hydrothermal route.

# Introduction

Crystalline arrays of colloidal spheres represent one of the most promising templates for inverse opal fabrication. Porous materials are attracting considerable attention with technological applications that include separations, sensors, catalysis, bioscience and photonics [1-6].Various types of ordered porous materials, such as simple and ternary oxides, chalcogenides, non-metallic and metallic elements, and polymers[7-13],have been synthesized by three-dimensional colloidal crystal template.

Zinc oxide is a direct wide band gap semiconductor with a large excitation binding energy, which is one of the most important functional oxide nanostructures, exhibiting near-UV emission, transparent conductivity, and piezoelectricity. It has novel applications in optoelectronics, sensors, transducers and biomedical sciences [14, 15]. Ordered ZnO inverse opal are useful for the applications in sensors and improved mass transportation originated from size-controlled macropores[16].

Generally, two- and three-dimensional ordered porous films are prepared with assistant of monolayer and multilayer colloidal crystal templates, respectively. Scharrer et al. [17] synthesized inverse opal ZnO photonic crystals by atomic layer deposition. Hydrothermal method, as a more convenient and cost effective method, has been used to produce ZnO layer by JinHyeok Kimet al.[18].In this work, we prepared both 2D and 3D ordered porous ZnO films with uniform color using 3D opal templates by hydrothermal method with different reaction time. Just by changing the reaction time, 2D or 3D ordered porous ZnO films were obtained, which exhibited clear photonic stopbands in the visible spectrum and efficient photoluminescence.

# Experimental

The multilayer PS opal films were obtained on the Si coated with ZnO substrates using vertical deposition technique [19]. The Si coated with ZnO substrates were treated by oxygen plasma before they were used for the preparation of the PS templates. For the preparation of ZnO porous films,  $Zn(NO_3)_2$  and HMTA were used as reacting agents in aqueous solution. Typically, equimolar aqueous solution of  $Zn(NO_3)_2(0.1M)$  and HMTA (0.1 M) were quickly mixed at room temperature,

and then a piece of Si foil coated with ZnO was put into the mixture with the colloidal crystal template side up. The reaction vessel was sealed and kept at 95 °C for a certain time (typically 3 h). Then the sample was taken out and rinsed in tetrahydrofuran remove the PS templates.

#### **Results and Discussion**



Fig.1 A typical SEM image of the PS opal templates.(a) The top views of colloidal crystal template arrays. (b)The cross section of colloidal crystal template arrays.

Fig. 1a displays the SEM image of the PS opal template showing ordered close-packed arrangement on the Si substrate. The colloidal crystal template was made from highly uniform polystyrene microspheres whose diameterswere155 nm. The polystyrene microspheres consist of about 30 layers and the thickness of the microsphere arrays is estimated to be  $2-3\mu$ m (Fig. 1b).



Fig.2. SEM images of ZnO rods films without PS (a) and the 2D ordered ZnO porous films with assistant of PS (b).ZnO inverse opal films synthesized in the solutions with different reaction times:(a) 3h and 6h (d).

Fig. 2ashows the SEM images of the ZnO rods which were synthetized in the aqueous solutions containing  $Zn(NO_3)_2$  (0.1M) and HMTA (0.1 M) without PS. Using PS template, ordered the ZnO porous films can be synthesized in the same condition. Because the reaction time is so short (2h),

the obtained ZnO inverse opal was 2Dordered porous films (Fig. 2b).

When the reaction time was increased, 3D ZnO inverse opal was obtained. As shown in Fig. 2c,d, the ZnO inverse opal films were prepared in the solutions with different reaction time, 3h and 6h, respectively. The reaction time influenced the surface morphology of ZnO inverse opal. When the growth time was short, most regions were uniform and the ordered pore periodicity was perfect. While the reaction time was increased, the surface pores shape became disordered.



Fig.3. Reflectance spectra of ZnO inverted opals with different reaction time (a) and reflectance spectra compari son of ZnO inverted opals and ZnO rods (b).

The highly ordered arrangement of the ZnO inverse opal can be reflected by reflectance spectrum. Fig. 3a shows the normal incidence reflectance spectra of the ZnO inverse opal films prepared by hydrothermal method with different reaction times. The reflectance spectra show band gap position in the same visible light spectrum (about 450nm). When the reaction time was increased, the peak gradually became flat and the intensity of peak become weak. It means that the ZnO inverse opal became more disordered as the reaction time increase. According to Fig. 3b, ZnO rods do not have photonic band gap.



Fig.4. (a) PL spectrum of ZnO inverted opal obtained from different time. (b) PL spectrum of ZnO inverted opal of ZnO rods.

Photoluminescence measurements of the ZnO inverted opals show efficient emission in the UV as well as a defecte mission band at longer wavelength (Fig. 4a). This proves that ZnO inverted opals fabricated by hydrothermal method have high crystallization quality. And as the reaction time

increases, ultraviolet and visible light intensity ratio (I uv / I visible) gradually increases. It indicates that ZnO inverse opals have higher crystallization quality as the reaction time increased. But ZnO inverse opals obtained with assistant of PS template has more defect compared with ZnO rods (Fig. 4b).

# Summary

In summary, we have fabricated 2D and 3D ZnO inverse opals by hydrothermal method using 3DPS templates. The ZnO inverse opals exhibited clear photonic stop bands in the visible spectrum and good crystalline quality. The morphology of ZnO inverse opal can be controlled by reaction time. The2D ZnO porous films were obtained with a reaction time of 2hand the 3D ZnO inverse opal films were obtained with a relative longer time. The obtained ZnO structures exhibit clear photonic band gaps and strong photoluminescence.

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