Fabrication of 2D Ordered Porous ZnO Films Using 3D Opal Templates by Electrodeposition

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The fabrication of two-dimensionally ordered porous zinc oxide films using three-dimensional colloidal crystal templates by electrodeposition is reported. The hydrophilicity of the substrate and the hydrophobicity of the template are utilized to control the generated structures.

Two-dimensionally (2D) ordered porous structures have received many attentions for their potential applications in catalysis, photonic crystals, optoelectronic devices, and cell cultures.[1–4] Existing fabrication techniques typically involve colloidal crystal monolayer template-directed synthesis,[5] single-step evaporative self-assembly of macroporous nanocrystal films,[6] colloidal crystal-assisted capillary nanofabrication,[7] and surface-template approach of three-dimensionally (3D) ordered colloidal crystals.[8] Among these methods colloidal crystal monolayer template-directed synthesis is a common method which has been used for yielding porous structures of metals, oxides, and polymers.[9–12] Electrodeposition as an effective and economical technique has been demonstrated suitable for generating large-scale ordered porous films.[13] Cai et al. attained morphology-controllable 2D ZnO pore arrays by controlling the electrochemical deposition potential.[14] Although 2D ordered porous films can be conveniently synthesized based on monolayer templates, there usually exists a disadvantage that the top surface of porous structures may be coated by a solid layer of the infiltrated material. This will influence the surface quality and the thickness uniformity of synthesized porous films. Moreover, the fabrication of large 2D colloidal single crystals is problematic,[8] whereas the large-scale production of wafer-size 3D colloidal crystals is fairly mature.[15]

Here we present an alternative method that uses 3D opal templates deposited on conducting ITO-glass substrates for the generation of 2D ordered porous films by electrodeposition. The synthetic process is schematically illustrated in Figure 1. The prepared 3D opal templates are hydrophobic, whereas the substrates are hydrophilic. During the electrodeposition, the hydrophobic nature of the template blocks the electrolyte from infiltrating the interstices of the opal template excepting the monolayer contacting with the substrate. By this means, the electrodeposition process is confined. This confined electrodeposition provides a precise control on the thickness uniformity of the porous film.

Highly uniform polystyrene (PS) spheres were made using an emulsifier-free polymerization technique according to the literature.[16] The tin-doped indium oxide coated glass (ITO) substrates were treated with 1 M aqueous NaOH solution to improve their hydrophilicity. Using vertical deposition technique,[17] 3D ordered PS opal films were obtained and then treated at 105 °C for 5 min. A three-electrode electrodeposition system was exploited, with a saturated calomel electrode (SCE), a zinc plate and the PS-opal/ITO as reference electrode, anode electrode and working electrode, respectively. The samples were prepared by potentiostatic electrolysis at −0.96 V vs SCE in the aqueous $Zn(NO_3)_2$ solution (0.04 M) for a certain time, and the deposition temperature was kept at 62 °C. After electrodeposition the samples were dipped in toluene for 24 h to remove the templates, then washed by deionized water and dried for further characterizations.

Figure 2A displays a typical field-emission scanning electronic microscope (FE-SEM) image of a PS template. The image shows that the PS spheres possess highly uniform size and form closely packed structure. The average diameter of PS spheres is 328 nm as measured from the FE-SEM image. Figure 2B shows a normal incidence transmission spectrum of the 3D PS opal template, in which the sharp peak reflects highly ordered 3D arrangement of the PS spheres, and the peak position agrees well with the predicted data from the Bragg equation using sphere size as determined from FE-SEM.[17]

Figure 3 shows the FE-SEM images of the ZnO ordered porous films prepared with different deposition times of 40 min and 2 h. The two samples present uniform structure in which the pores are hemispherical in shape and orderly arranged.

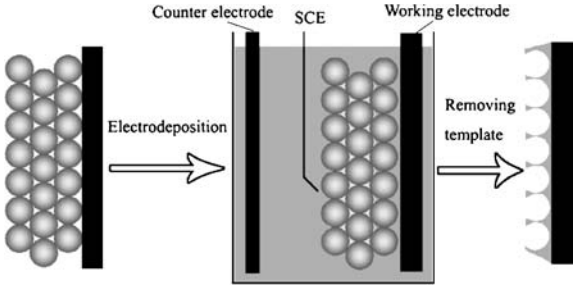

Figure 1. Schematic diagram of formation of 2D ZnO ordered porous films.

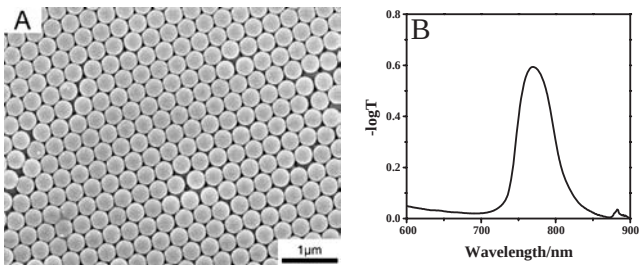

Figure 2. A typical FE-SEM image (A) and a normal incidence transmission spectrum of the PS template (B).

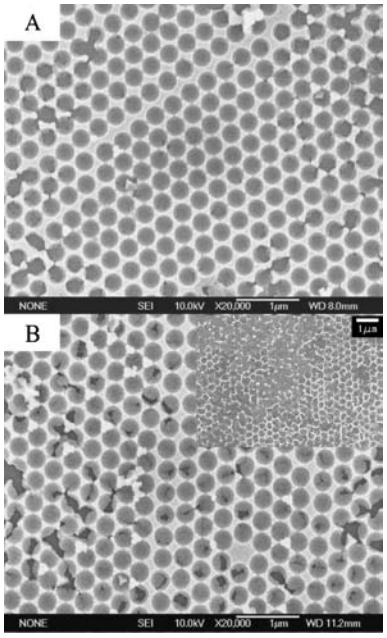

Figure 3. FE-SEM images of the 2D ZnO ordered porous films at different deposition times: (A) 40 min, (B) 2 h, Inset: the corresponding edge of the ZnO porous film.

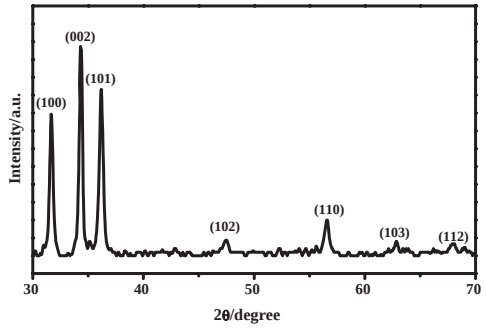

Figure 4. XRD pattern of the ZnO porous film deposited for 40 min.

It is clearly seen that the ZnO ordered porous films have only one layer by comparing the cracked region with the perfect one. The cracked regions should originate from repeated washing and drying treatments. The solid hexagonal region, which should be a pore, results from the point defect of the original PS colloidal crystal template.

The XRD pattern of the porous film deposited for 40 min is presented in Figure 4. It can be identified as hexagonal wurtzite ZnO (JCPDS 80-0075). The ZnO crystal growth exhibits preferential orientation along the [001] direction compared with the standard data.

In our experiments the ITO-glass substrates were dipped in 1 M aqueous NaOH solution for a certain time before preparing PS colloidal crystal templates. This is a crucial step in which an extremely hydrophilic substrate can be acquired. It should be mentioned that the prepared PS spheres were hydrophobic by our synthetic method. Consequently the working electrode was composed of hydrophilic ITO-glass substrate and hydrophobic PS colloidal crystal template. During the electrodeposition, the aqueous $Zn(NO_3)_2$ solution spread from the edge of the substrate to the middle region. Owing to the hydrophobicity of the PS spheres the electrolyte can hardly penetrate from the surface of the PS template to the substrate. It can be inferred that except the layer contacting with the substrate, the interstices of the other layers cannot be infilled by electrolyte as illustrated in Figure 1. This is supported by the fact that the increase of deposition time led to the almost same structure with 2D ordered pore arrays. It is further validated from the disorder of the edge region of the ZnO porous film in the inset of Figure 3B. By keeping the other conditions, while changing the solvent to make the $Zn(NO_3)_2$ solution wet the PS template, we obtained not 2D, but 3D inverse opal films. In addition, most pores are not through by comparing the cracked region with the intact one. It indicates that the PS template did not closely contact the ITO-glass substrate during the electrodeposition. Because the adhesion between the PS template and the substrate is not very strong, the template will be lightly lifted up under the surface tension of aqueous solution. Similar process has been confirmed in the case of PS monolayer colloidal crystals.[10] Consequently the electrolyte spread into the former contact region between the PS template and the substrate, in which ZnO crystallites deposited from the solution and resulted in no through pores.

In conclusion, we have described a simple method to fabricate 2D ordered porous ZnO films by electrodeposition using 3D PS opal templates. The uniform film thickness can be achieved by making use of the hydrophilicity of ITO-glass substrates and the hydrophobicity of PS opal templates. By this mechanism, more complex structures may be generated. And this approach should be suitable for preparing 2D ordered porous films of other materials in aqueous solution system.

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