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Structural properties of ordered porous SnO_2 nanostructure

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Three-dimensional porous ordered SnO_2 nanostructures have been fabricated by templating a sol–gel pre- cursor solution against the polystyrene nanospheres for the first time. Field emission scanning electron micrography (FESEM) indicates that the surface of the nanostructures is highly regular and the porous structures are perfectly ordered. Besides a broad emission band at 600 nm, the porous SnO_2 nanostructures show an additional emission band at 430 nm, which is seldom seen in the bulk SnO_2 materials. Spectral examinations and analyses reveal that the 430 nm band is induced by the interfacial effects between the porous frameworks.

Keywords: SnO_2; Porous; Structural.

1. INTRODUCTION

It is well known that the performance of materials is greatly influenced by the morphological and structural features, including size, shape, surface–volume ratio, and porosity [1, 2]. In recent years, porous nanostructures have received considerable attention in the areas of catalysis, sensors, gas storage and luminescence due to their high surface areas. Tin dioxide (SnO_2) is a larruping *n*-type semiconductor with a wide band gap (E_g = 3.6 eV, at 300 K), which has been widely used in gas sensors, catalysts, and solar cells [3–5]. In particular, the porous SnO_2 nanostructures could have potential advantages in enhancing the sensor and catalytic activities for such structures not only have higher surface areas but also can supply more efficient transport for the reactant molecules to get to the active sites [6, 7]. In or- der to pursue the enhanced performance of catalysis and sensor, much more attention has been paid on the preparing of porous SnO_2 nanostructures in the past years. For example, Chen et

al. [8] prepared porous SnO_2 films using a pulse laser deposition method. Zhao et al. [9] synthesized the porous SnO_2 nanostructures through thermal decomposition the mixture solution of dibutyltin dilaurate and acetic acid. Feng et al. [10] prepared the porous SnO_2 nanostrips on the tin substrate by an anodization process. However, these methods need rigorous experimental conditions such as sophisticated instruments, high reaction temperature and complicated prior separation steps. More importantly, it is difficulty to realize the controlled growth or fabrication with the desired sizes. Recently, Scharrer et al. [11] fabricated the optically active ZnO photonic crystals by infiltrating polystyrene templates, and then removed the polystyrene by firing the samples at elevated temperatures. The resulting filling fractions show the high porosity and uniformly ordered structures. So, we could imagine that if we infiltrate the SnO_2 sol–gel solution into the fractions of the polystyrene templates, and then remove the polystyrene, one may hope to obtain the porous SnO_2 nanostructures. This method has obvious advantages: firstly, the size and the porosity of the SnO_2 nanostructures can be controlled through controlling the size and the thickness of the PS templates; secondly, for the template is an ordered colloidal crystal consisting of PS nanospheres, when moving the template, an ordered porous SnO_2 nanostructure also can be obtained. Based on the idea, polystyrene nanospheres as a template were firstly prepared on glass substrate and directly introduced into the SnO_2 sol–gel solution formed by the hydrolysis and condensation of tin chloride tetrahydrate, and then removal PS nanospheres by heating led to the formation of porous ordered SnO_2 nanostructures. The optical properties of the synthesized porous SnO_2 structures were also studied by Raman and PL spectra.

2. EXPERIMENTAL

The PS nanospheres templates are synthesized using a modification of the micromolding method reported by Kim et al. [12] The sol–gel resolution is prepared by commingling tin chloride tetrahydrate ($SnCl_4 \cdot 4H_2O$) and anhydrous ethanol in a water bath installation and kept at 80 °C for 10 hours. Then keep the solution at room temperature for 24 hours as staleness. Afterward, infiltrate the SnO_2 sol– gel solution onto the PS template for several times, and then keep the PS template at 120 ^{o}C for dehydration. Fi- nally, remove the PS templates by annealing at 500 ^{o}C for four hours. The morphologies and structures of the prod- ucts were characterized by scanning electron microscopy (SEM) (Hitachi S-4800), X-ray diffraction (XRD) (Shi- madzu 7000), and high-resolution transmission electron microscopy (HRTEM) (Philips Tecnai G2 F30 S-TWIN). The optical properties were conducted on Raman spectroscopy (Jobin-Yvon T640000), and PL spectroscopy (Edinburgh: FLS920).

3. RESULTS AND DISCUSSION

Figure 1(a) shows the low magnification SEM image of the PS nanospheres template. It can be seen that the PS nanospheres show a highly ordered array on the substrate. There are some obvious cracks on the array which may originate from the shrinkage during the annealing process. High magnification SEM image in Fig. 1(b) further confirms that the nanospheres have a very smooth surface. And the diameter of the PS spheres is about 250 nm, which is closely

packed with a hexagonal cell. Figure 1(c) shows a magni- fied SEM figure of a crack, from which one can see that the spheres are four layers and the inner layers are also even- bedded. These PS nanospheres exhibit a hexagonal close- packed structure.

Figure 2 shows the SEM images of porous SnO_2 nano- structures that were formed by templating a sol–gel pre- cursor solution against a crystalline assembly 250 nm polystyrene nanospheres. Figure 2(a) shows an array of such porous structures after the polystyrene template has been decomposed by annealing at the 500 °C for 4 hours, and just left the porous nanostructures that needed. It can be seen that the nanoporous are existing at a three-dimensional form and the holes are orderly arrayed with a hexagonal cell in Figs. 2(a) and 2(b). It also can be seen that the diameters of the nanopores are on average about 250 nm and the wall thickness is about 50 nm, which is the same as the diameter of the PS spheres. So, the size and porosity of the as-prepared SnO_2 nanostructures can be easily controlled by controlling the sizes of the PS nanospheres through changing the concentrations of potassium persulfate and styrene as well as the speed of the magnetron in the preparation. Especially, the surface of the single pore unfolded at hexagonal forms instead of the rotundity of the beads can be described in terms of Voronoi tessellation in the plane of the PS surface [13, 14].

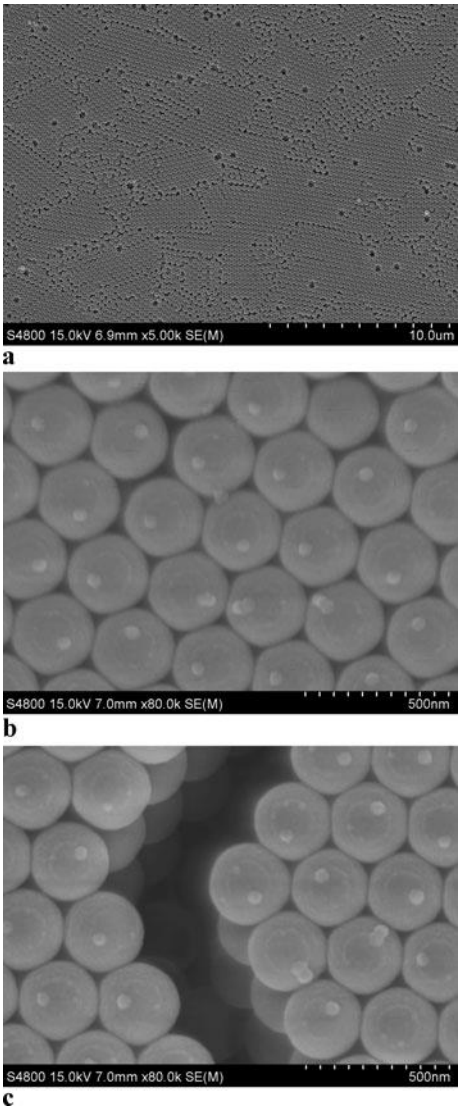

Fig. 1 (**a**) Low- and (**b**, **c**) high-magnification FESEM images of the as-prepared PS templates

Figure 2(c) is a magnified crack image of the as- prepared nanostructures, which is used to interpret the inner porous structures. It can be seen that there are four porous layers and the inner layers are also with a porous nanostructure like the surface. The EDS patterns from the porous samples are revealed in Fig. 2(d). It is indicated that the as synthesized samples are just composed of tin and oxygen and there are no organic elements or any other impurity left. Figure 3 shows the XRD pattern of the as-prepared nanoporous samples. Compared with the tetragonal rutile SnO_2 structure (JCPDS: 41-1445) showed in the bottom, all the diffraction peaks are matching the standard data file well and can be ascribed to the standard rutile structure with no exception. The peaks are relatively broadened than those of the bulk counterpart, indicating that the samples have more intrinsic defects. It is known that the optical properties of SnO_2 nanostructures are very sensitive to the morphologies, synthetic conditions, etc.

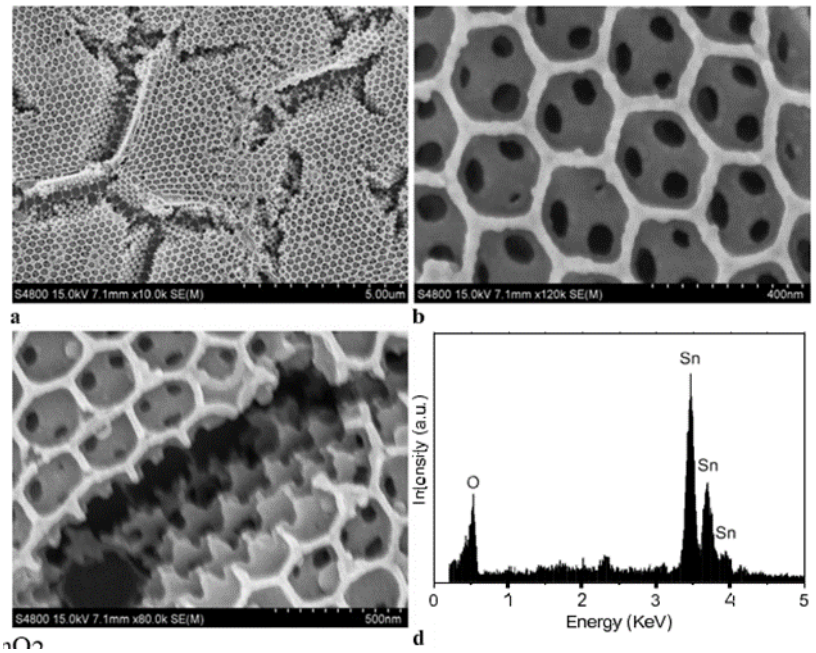

Fig. 2 (**a**) Low- and (**b**) high-magnification FESEM images of the as-prepared porous SnO2 nanostructures. (**c**) Magnified crack image of the as-prepared nanostructures. (**d**) EDS spectrum of the as-prepared porous SnO2

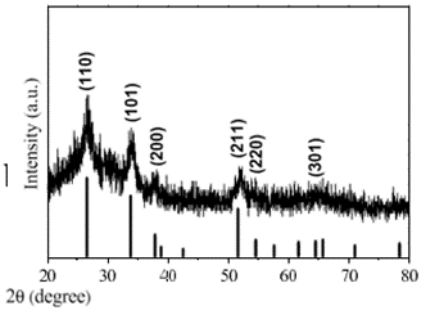

Fig. 3 Typical XRD patterns of the as prepared nanoporous SnO2 and the standard XRD pattern of the bulk SnO2 (bottom).

4. CONCLUSIONS

In conclusion, we have fabricated the porous ordered SnO2 nanostructures by templating a sol–gel precursor solution against the polystyrene nanospheres for the first time. It is revealed that the porous SnO2 nanostructures have the tetragonal rutile form with the perfectly ordered porous structures. PL results show that the emission peak at 600 nm originates from the

electronic state determined by the oxy- gen vacancies, while the ubiquitous emission peak at 430 nm arises from the interfacial effects between the porous frame- works. The work provides a new way to synthesize the ordered porous SnO2 nanostructures.

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