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Fabrication and Characterization of Hierarchical Porous TiO_2 Films

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Hierarchical porous TiO_2 films with macroporous and mesoporous structures are prepared by drop-coating a mixed solution of polystyrene spheres and TiO_2 colloid, followed by sintering to remove polystyrene spheres. XRD shows that crystal phase of TiO_2 particles is major anatase structure with minor brookite structure. AFM displays that particle size distribution of porous TiO_2 films ranges from 20-30 nm. SEM shows that TiO_2 films prepared by drop-coating TiO_2 colloid present mesoporous structure with a size of 8-50 nm. However, TiO_2 films prepared by drop-coating the mixture containing polystyrene spheres and TiO_2 colloid possess hierarchical porous structure with a mesoporous size of 8-50 nm and a macroporous size of about 600 nm. Besides, macropore ratios increase with increase of the ratio of polystyrene spheres to TiO_2 colloid. UV-visible absorption spectra indicate that porous TiO_2 films prepared at a polystyrene spheres/TiO_2 colloid ratio 1, have the highest absorption intensity.

Key Words: Porous TiO_2, Dye-sensitized solar cells, Fabrication, Characterization.

INTRODUCTION

There is currently a great deal of interest in synthesis of TiO_2 because of its important role in various applications, such as photo-catalysis[1], dye-sensitized solar cells[2,3], environmental purification[4], gas sensors[5] and electrochemical capacitors[6]. TiO_2 can be obtained by a wide range of synthetic methods, including but not limited to sol-gel method[7], hydrothermal method[8], precipitation[9] and electrodeposition[10,11]. Of these synthetic methods of TiO_2, sol-gel method is a most commonly applied method to make nanocrystalline TiO_2, however, nanoparticles made are amorphous in nature and require further heat treatment to obtain crystalline product[12]. Hydrothermal method is one of the most widely used methods for increasing the crystallinity of TiO_2 and can be used to change crystal structure, morphology and phase composition of materials under the different reaction conditions[13].

It is known that photo-catalytic activity of TiO_2 is strongly related to crystal structure, morphology, particle size, surface area and porosity[12]. Furthermore, the phase and the degree of crystallinity of TiO_2 particles have great influence on specific applications[14]. TiO_2 nanoparticles are widely used in environmental purification owe to the high chemical inter, stability and high photo-catalytic activity[15,16]. Porous nanocrystalline TiO_2 are used in dye-sensitized solar cells (DSSCs) because of their high-energy conversion efficiency, simple preparation technology and low production costs[2,17]. Morphology and microstructure of porous nanocrystalline TiO_2, including particle size, surface area and porosity, play an important role in energy conversion efficiency of dye-sensitized solar cells. There are many reports on porous TiO_2 widely used in dye-sensitized solar cells. However, these researches are only limited to mesoporous TiO_2 and hardly relate to hierarchical porous TiO_2 containing macroporous and mesoporous structures. Thus, it is necessary to study characterization of macroporous and mesoporous TiO_2.

In the present work, hierarchical porous films with macroporous and mesoporous structures were prepared by drop-coating the mixture containing polystyrene spheres and TiO_2 colloid with different ratios, followed by sintering to remove polystyrene spheres. Besides, UV-visible absorption spectra of dye adsorbed onto porous nanocrystalline TiO_2 films were studies. Thus far, there are several reports about syntheses of TiO_2 or TiO_2 composites by polystyrene spheres[18]. For example, Pei *et al.*[18] fabricated hollow TiO_2 capsules through aging dissolvation technique to remove the templates of core-shell composite spheres. However, hierarchical porous TiO_2 weren't prepared in their worker. The present paper aims to synthesize hierarchical porous TiO_2 with macroporous and mesoporous structures and study absorbance of UV-visible.

EXPERIMENTAL

All reagents were analytically pure and used without further purification. 600 nm polystyrene spheres were obtained from Interfacial Dynamics Inc. Phthalocyanine, isopropanol and tetrabutyl titanate were purchased from Sinopharm Chemical Reagent Ltd. Com., China. All of the solutions were prepared with deionized water purified by a Millipore Milli-Q Plus 185 purification system.

Laser particle size analyzer was used to monitor the size of TiO_2 colloid (Malvern, Mastersizer 2000). X-Ray diffraction (XRD) pattern was recorded on a Rigaku D/max 2500 with monochromatized CuK_α (λ = 1.54056 Å) incident radiation. Atomic force microscopy (PicoPlus, Agilent Technologies, CA, USA) was used to study the image of porous TiO_2. The size distribution and morphology of porous TiO_2 films were observed by scanning electron microscopy (FEI, Sirion200). An UV-3802 spectrophotometer was employed to record UV-Visible absorption spectroscopy of the samples.

General procedure

Preparation of TiO_2 colloid: 1 mL concentrated HNO_3 was added to a large conical flask with 150 mL water. Then, a mixture containing isopropanol and tetrabutyl titanate was dropwise added into the above solution under vigorous stirring at room temperature. The conical flask without being covered was put in a water bath. The reaction was carried out at 80 ºC for 8 h under vigorous stirring and colloid was prepared. The above colloid was poured into a Teflon-lined autoclave and placed in the oven at 200 ºC for 12 h. Finally, colloid treated by the autoclave was poured in beaker, redispersed by sonicating and concentrated to 10-11 %.

Preparation of porous TiO_2 films: TiO_2 colloid was mixed with polystyrene spheres with different ratios (polystyrene spheres/TiO_2 colloid = 0, 1:1, 2:1, 3:1). Two pieces of scotch tape were stuck on ITO as spacers to control the thickness of the film and the mixture containing polystyrene spheres and TiO_2 colloid was then coated in the space between the pieces of scotch tape. After rolled off the excessive mixture by a glass rod and dried, polystyrene spheres were then removed by sintering at 450 ºC for 0.5 h. As a result, porous TiO_2 films were prepared.

Dye absorption on porous TiO_2 films: Porous TiO_2 films were immersed for 5 h in an ethanol solution of phthalocyanine in dark conditions at room temperature. Then, property of UV-Visible absorption spectroscopy of the dye absorption on the porous TiO_2 films was detected.

RESULTS AND DISCUSSION

Particle size of TiO_2 colloid: Particle size distribution of TiO_2 colloid was observed by laser particle size analyzer. Fig. 1 shows that the average particle size of TiO_2 colloid is about 92 nm and colloid particle size distribution ranges from 50-200 nm. Fig. 2 is particle size distribution of TiO_2 colloid in Fig. 1 according to different segment. It can be seen from the data in Fig. 2 that particle size of TiO_2 colloid below 67, 92 and 130 nm account for 10, 50 and 90 %, respectively.

XRD analyses of porous TiO_2 powder: Fig. 3 displays the XRD pattern of porous TiO_2 powder obtained by sintering TiO_2 colloid at 450 ºC for 0.5 h. The XRD pattern can be indexed to (101), (004), (200), (105), (211), (204), (116), (220) and (225) planes of tetragonal phase anatase TiO_2. All the peaks in the pattern are assigned to the fact that the porous TiO_2 particles formed are a mixture of largely anatase phase and minor brookite phase. With respect to the anatase phase mixed with the brookite phase, this is because there are the (121, 221) diffraction peaks of brookite phase and the (120) diffraction peak of brookite phase overlaps the (101) diffraction peak of anatase phase at $2\theta = 25.3^9$. Crystallite size is estimated from Scherrer formula[19]. Crystallite size of porous TiO_2 calculated through above Scherrer formula is 26 nm.

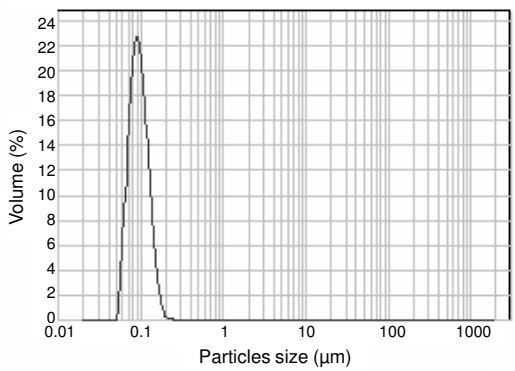

Fig. 1. Particle size distribution of TiO_2 colloid

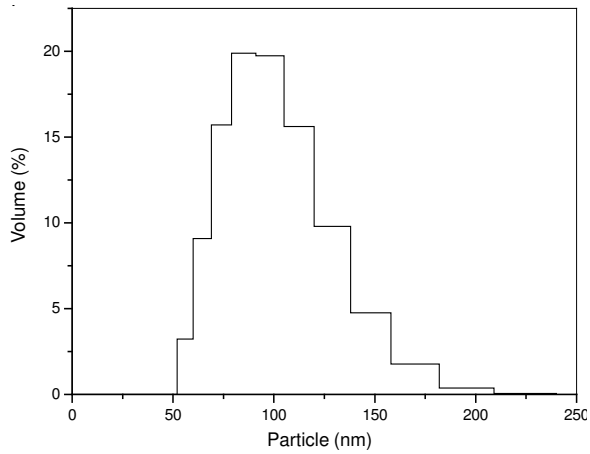

Fig. 2. Particle size distribution of TiO_2 colloid in the Fig. 1 according to different segment

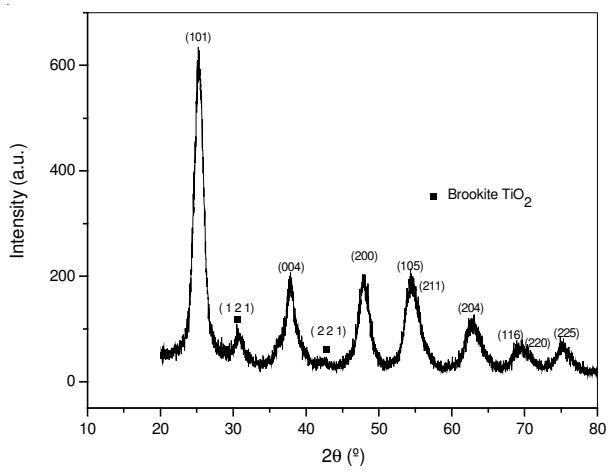

Fig. 3. XRD patterns of porous TiO_2 powder obtained by sintering TiO_2 colloid at 450 ºC for 0.5 h

AFM of porous TiO_2 films: AFM image of porous TiO_2 films obtained with a polystyrene spheres/TiO_2 colloid ratio of 0 are showed in Fig. 4. AFM image shows that the morphology of porous TiO_2 films consists of spherical-like particles with a size of 20-30 nm, which is agreement with those detected by XRD. Particle size of TiO_2 colloid detected by laser particle size analyzer is larger than those of porous TiO_2 detected by AFM and XRD. The above behaviour can be explained as follows: laser particle size analyzer estimates the size of aggregated particles in the suspension, whereas techniques such as AFM and XRD estimate the size of the primary particles that make up the aggregate.

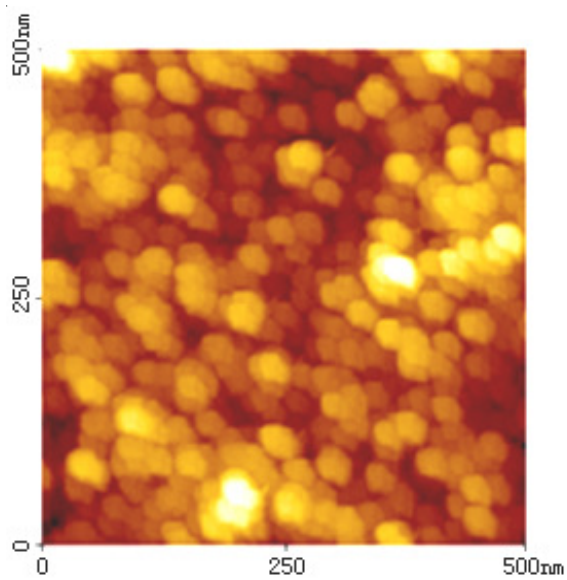

Fig. 4. AFM image of porous TiO_2 films obtained with a polystyrene spheres/TiO_2 colloid ratio of 0, followed by sintering TiO_2 colloid at 450 ºC for 0.5 h

SEM of porous TiO_2 films: Fig. 5 illustrates SEM images of porous TiO_2 films prepared with a polystyrene spheres/TiO_2 colloid ratio of 0 (Fig. 5 a), 1:1 (Fig. 5b), 2:1 (Fig. 5 c) and 3:1 (Fig. 5d). As shown in Fig. 5a, the morphology of TiO_2 particles consists of spherical-like particles with a size of 8-30 nm and displays highly porous structure with a mesoporous size of 8-50 nm. However, except for porous structure with a mesoporous size of 8-50 nm, porous structure with a macroporous size of about 600 nm is observed in Fig. 5b-d due to removal of polystyrene spheres during sintering a mixture containing polystyrene spheres and TiO_2. In other words, hierarchical porous TiO_2 with macroporous and mesoporous structures is displayed in Fig. 5b-d. In addition, Fig. 5b-d also indicate that the ratio of macropore to mesopore increases with increase of the ratio of polystyrene spheres to TiO_2 colloid.

UV-Visible absorption spectra: Fig. 6 indicates UV-visible absorption spectra of phthalocyanine adsorbed onto porous TiO_2 films prepared with a polystyrene spheres/TiO_2 colloid ratio of = 0 (curve 1), 1:1 (curve 2), 2:1 (curve 3) and 3:1 (curve 4). There are two absorption peaks in all curves. In curves 1 and 4, the absorption peaks are exhibited at 411 and 586 nm. Absorption peaks exhibited 406 and 586 nm are shown in curve 2. Absorption peaks exhibited 408 and 586 nm are shown in curve 3. Bedsides, it can be observed that curve 2 (porous

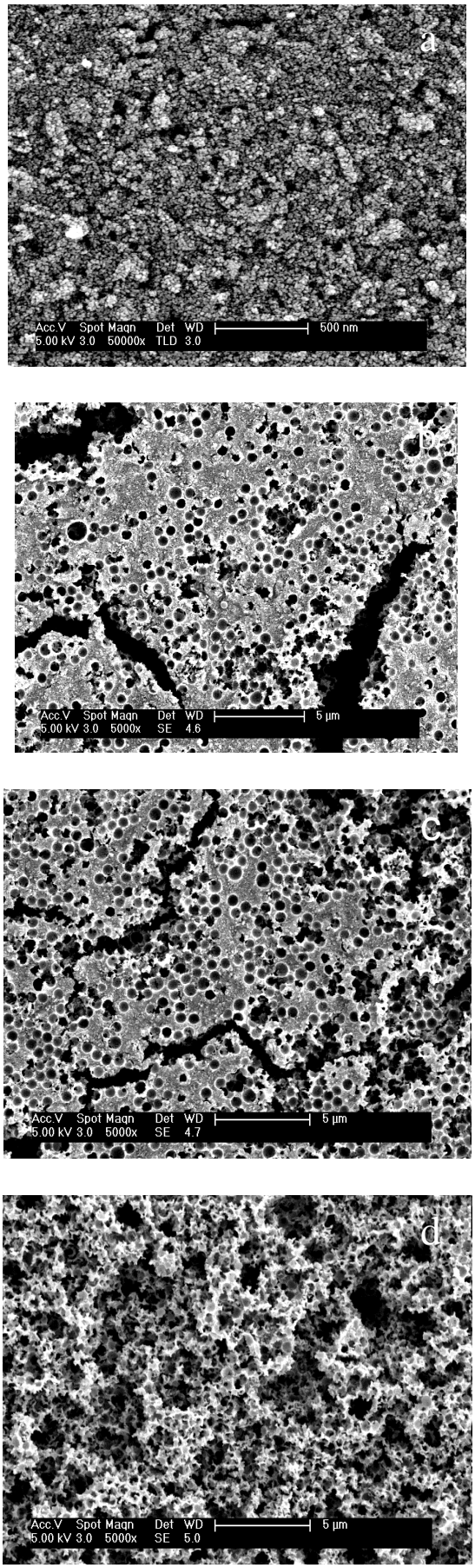

Fig. 5. SEM images of porous TiO_2 films prepared with a polystyrene spheres/TiO_2 ratio of 0 (a), 1:1 (b), 2:1 (c) and 3:1 (d), followed by sintering TiO_2 colloid at 450 ºC for 0.5 h

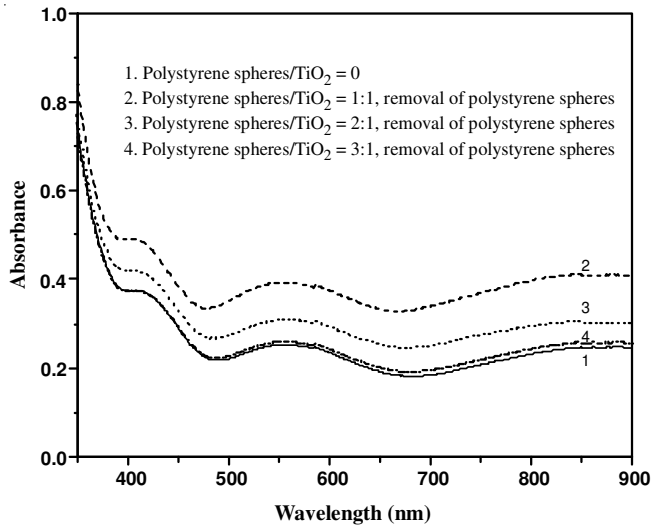

Fig. 6. UV-Visible absorption spectra of phthalocyanine adsorbed onto porous TiO_2 films

TiO_2 films prepared with a polystyrene spheres/TiO_2 colloid = 1:1) has the largest absorbance in all curves. Absorbance of curve 3 is inferior to that of curve 2, but superior to curves 1 and 4. It illustrates that porous TiO_2 films with the different ratio of macropore to mesopore have different UV-visible absorption intensity. The largest absorbance observed in curve 2 is possible attributed to the following interpretation: (1) porous TiO_2 have the optimum ratio of mesopore to macropore when they are prepared at a polystyrene spheres/TiO_2 colloid ratio of 1, since the size of the macropores (*ca.* 600 nm) is similar to the wavelength of the incident radiation (350-900 nm); (2) adsorption process itself in the porous TiO_2 films prepared at a polystyrene spheres/TiO_2 colloid ratio of 1 has the highest concentrations of dye and thus affects the intensities of the measured spectra. Shape and size have a significant impact on the optical and electronic properties of nano-particles[20]. It implies that porous TiO_2 prepared at a polystyrene spheres/TiO_2 colloid ratio 1 will possible have the highest energy conversion efficiency when they are used in dye-sensitized solar cells.

Conclusion

Hierarchical porous TiO_2 films with macroporous and mesoporous structures are successfully prepared. The result shows that crystal phase of TiO_2 are major anatase with minor brookite. Particle size distribution of porous TiO_2 films ranges from 20-30 nm. Porous TiO_2 films prepared by TiO_2 colloid present highly porous structure with a mesoporous size of 8-50 nm, whereas porous TiO_2 films prepared by using the mixture containing polystyrene spheres and TiO_2 colloid possess highly porous structure with a meso-macroporous size of 8-50 and 600 nm, macropore ratios increase with increase of the ratio of polystyrene spheres to TiO_2 colloid. UV-Visible absorption spectra indicate that porous TiO_2 films prepared at a polystyrene spheres/TiO_2 colloid ratio of 1 have the highest absorption intensity. It implies that porous TiO_2 films prepared at a polystyrene spheres/TiO_2 colloid ratio 1 will possible have the highest energy conversion efficiency when they are used in dye-sensitized solar cells.

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