Fabrication of Three-Dimensionally Ordered Titania Hollow Sphere Thin Films and Their Optoelectronic Properties (Postprint)

Authors: Chen Ailian, Tang Zhaofang, Chen Yang, Chen Zhigang

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Abstract

To improve the photoelectric conversion efficiency of dye-sensitized solar cells (DSSC), three-dimensionally ordered TiO_2 hollow sphere (3DOHS-TiO_2) thin film materials were prepared using self-assembled colloidal crystals of polystyrene microspheres (290–300 nm) as a sacrificial template, and the photoelectric conversion characteristics of cells employing a P25-TiO_2/3DOHS-TiO_2 bilayer film as the photoanode were investigated. Scanning electron microscopy results revealed that the TiO_2 hollow spheres in the 3DOHS-TiO_2 sample exhibited a close-packed hexagonal arrangement with an inter-sphere center distance of 260–270 nm and a wall thickness of 40–50 nm, and adjacent TiO_2 hollow spheres were interconnected through pores; transmission electron microscopy results indicated that the TiO_2 hollow spheres were composed of anatase TiO_2 particles approximately 10 nm in size, with mesopores formed by interparticle packing present on their shell walls. Photoelectric performance test results demonstrated that the P25-TiO_2/3DOHS-TiO_2/DSSC achieved a photoelectric conversion efficiency of 6.98%, significantly superior to that of conventional P25-TiO_2/DSSC (4.32%), which was attributed to the enhanced light scattering and trapping capability of the 3DOHS-TiO_2 film in the bilayer photoanode.

Full Text

Synthesis and Photovoltaic Performance of Three-Dimensional Ordered TiO2 Hollow Sphere Films

Chen Ailian[1], Tang Zhaofang[2], Chen Yang[2,3], Chen Zhigang[3]

[1] School of Materials Science and Engineering, Changzhou University, Changzhou 213164, China
[2] Jiangsu Key Laboratory for Environment Functional Materials, Suzhou

University of Science and Technology, Suzhou 215009, China
[3] School of Materials Science and Engineering, Changzhou University, Changzhou 213164, China

Abstract

To improve the photoelectric conversion efficiency of dye-sensitized solar cells (DSSC), three-dimensional ordered TiO_2 hollow sphere (3DOHS-TiO_2) films were fabricated using colloidal crystals self-assembled from polystyrene microspheres (290–300 nm) as sacrificial templates. The photovoltaic characteristics of DSSCs based on P25-TiO_2/3DOHS-TiO_2 bilayer photoanodes were investigated. Scanning electron microscopy revealed that the TiO_2 hollow spheres in the 3DOHS-TiO_2 sample exhibited close-packed hexagonal arrangement with a center-to-center spacing of 260–270 nm and shell thickness of 40–50 nm; adjacent TiO_2 hollow spheres were interconnected through pores. Transmission electron microscopy showed that the hollow spheres consisted of anatase TiO_2 nanoparticles approximately 10 nm in size, with mesopores formed by interparticle stacking in the shell walls. Photovoltaic measurements demonstrated that the P25-TiO_2/3DOHS-TiO_2/DSSC achieved a photoelectric conversion efficiency of 6.98%, significantly outperforming conventional P25-TiO_2/DSSC (4.32%). This enhancement is attributed to the improved light scattering and harvesting capability of the 3DOHS-TiO_2 film in the bilayer photoanode.

Keywords: inorganic non-metallic materials, TiO_2, three-dimensional ordered structure, colloidal crystal template, dye-sensitized solar cell

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Introduction

Dye-sensitized solar cells (DSSC) are photoelectric conversion devices that mimic natural photosynthesis, converting solar energy into electrical energy. The fundamental working principle involves using a wide-bandgap oxide film as the photoanode, onto which a dye with strong visible-light absorption and energy levels matching the oxide is adsorbed. The dye molecules absorb sunlight and inject photogenerated electrons into the oxide conduction band, enabling effective charge separation and generating photocurrent in the external circuit to the counter electrode [1,2]. DSSCs consist primarily of three components: a photoanode, electrolyte, and counter electrode [3]. The photoanode is a semiconductor film sensitized by dye (such as polypyridyl ruthenium complexes), which utilizes its high surface area to adsorb the sensitizer layer as a carrier for charge separation and transport, making it the core of the entire cell system. Common oxide photoanode materials include TiO_2, ZnO, NiO_2, SnO_2, SnO_2/MgO, and CdO [4–8]. Based on photoelectric conversion efficiency, economic viability, and practicality, anatase TiO_2 nanocrystalline porous films remain the most promising and outstanding DSSC photoanode materials.

The properties of anatase TiO_2 photoanodes [3] depend on factors such as crystallite size, surface structure, pore ordering degree, specific surface area, pore size and distribution, and band structure. The microstructural characteristics of the film significantly influence light harvesting efficiency, light scattering performance, electron transport properties, interfacial charge transfer and recombination characteristics, and ultimately the photoelectric conversion efficiency. Research on TiO_2/DSSC photoanode materials has focused on ordered TiO_2 nanocrystal arrays [9–13] (such as nanotubes, nanorods, and nanowires), hierarchically three-dimensionally ordered macroporous TiO_2 films [14,15], ultra-high surface area TiO_2 mesoporous films [16,17], and doped TiO_2 nanocrystalline films [18,19].

In recent years, researchers have introduced TiO_2 hollow sphere (TiO_2-HS) materials into DSSC photoanode systems, substantially improving cell efficiency. Zhang et al. [20] first prepared anatase TiO_2-HS with an outer diameter of approximately 500 nm and shell thickness of about 25 nm using carbon spheres as templates, then embedded them into commercial Degussa P25 TiO_2 particles to form composite photoanode films, achieving nearly 14% improvement in photoelectric conversion efficiency, which was attributed to enhanced light scattering capability. Yu et al. [21] investigated the photovoltaic properties of DSSCs based on bilayer photoanodes composed of TiO_2-HS (outer diameter 800–1000 nm, shell thickness 300–700 nm) and P25 particles, demonstrating nearly 22% higher efficiency than conventional P25-TiO_2/DSSC. Yu et al. [22] further explored the photovoltaic performance of DSSCs based on TiO_2-HS/carbon nanotube composite films. However, it should be noted that the TiO_2-HS in these photoanode films were randomly arranged, while studies on ordered TiO_2-HS photoanode film systems are rarely reported. In this work, monodisperse polystyrene (PS) colloidal particles were first used as basic building blocks to construct high-quality PS colloidal crystal templates via vertical deposition, which were then combined with impregnation-calcination processes to prepare three-dimensional ordered TiO_2 hollow sphere (3DOHS-TiO_2) film materials. The performance of cells using P25-TiO_2 and 3DOHS-TiO_2 bilayer films as photoanodes (P25-TiO_2/3DOHS-TiO_2/DSSC) was investigated and compared with conventional P25-TiO_2/DSSC under identical testing conditions.

Experimental Methods

1.1 Materials Styrene (St) monomer was washed repeatedly with 5 wt% NaOH solution to remove inhibitors, dried with anhydrous $CaCl_2$, and stored at low temperature for later use. Other reagents included acrylic acid (AA), potassium persulfate (KPS), ammonia solution, concentrated sulfuric acid, hydrogen peroxide, isopropanol, Triton X-100, acetylacetone, anhydrous ethanol, titanium tetrachloride ($TiCl_4$), P25-TiO_2 paste, Pt paste, N719 dye, electrolyte (main components: 0.05 mol/L I_2, 0.5 mol/L LiI), and fluorine-doped tin oxide (FTO) conductive glass.

1.2 Sample Preparation and Characterization Three-dimensional ordered TiO_2 hollow sphere (3DOHS-TiO_2) films were prepared through a three-step process, as schematically illustrated in [Figure 1: see original paper].

Step 1: Preparation of PS latex particles. Monodisperse PS microspheres were synthesized via soap-free emulsion polymerization: Monomer (St, 5 g), stabilizer (AA, 0.75 g), and 50 mL deionized water were added sequentially to a four-neck flask equipped with a condenser and nitrogen inlet. The mixture was stirred magnetically while purging with nitrogen for 20 min to remove oxygen. The flask was then heated to 70°C in an oil bath, and initiator solution (0.125 g KPS dissolved in 50 mL deionized water, pH adjusted to 8 with ammonia) was slowly added to initiate polymerization. After 7 h of magnetic stirring under nitrogen protection, the condenser water was turned off and the mixture was cooled naturally to room temperature, yielding PS latex particle dispersion.

Step 2: Self-assembly of colloidal crystal templates. Glass substrates were first hydrophilically treated with Piranha solution (H_2SO_4:H_2O_2 volume ratio 7:3), then ultrasonically cleaned sequentially in isopropanol, anhydrous ethanol, and deionized water. Following the method in reference [23], PS colloidal crystal templates were self-assembled on glass substrates via gravitational sedimentation at 35°C and 50% relative humidity. The templates were then pre-treated at 105°C for 30 min to enhance structural stability.

Step 3: Infiltration of TiO_2 precursor and template removal. In an ice-water bath, $TiCl_4$ solution was slowly added dropwise to deionized water using a syringe to prepare a 0.2 mol/L $TiCl_4$ solution. The pre-treated templates were immersed in the TiO_2 precursor solution for 12 h of full infiltration. The template/titania hydrate composite was then removed and completely dried in air in a fume hood. Subsequently, the template was placed in a programmable furnace, heated slowly to 500°C at 2°C/min, held for 2 h, and cooled to room temperature in the furnace to obtain 3DOHS-TiO_2 film materials.

The ordered structure of colloidal crystal templates was observed using a JSM-6360LA scanning electron microscope (SEM). Film samples were characterized using a 4800 field-emission scanning electron microscope (FESEM) and a JEM-2100 high-resolution transmission electron microscope (HRTEM). Phase structure was analyzed using a D/max 2500 PC X-ray diffractometer (XRD). Thermal analysis (TGA) was performed using an SDT Q600 thermogravimetric analyzer. Specific surface area and pore distribution were measured using an ASAP2010C surface area and porosity analyzer.

1.3 Cell Assembly and Testing The 3DOHS-TiO_2 film was carefully scraped from the substrate surface using an ultrathin surgical blade. The scraped film sample still consisted of regularly ordered TiO_2 hollow spheres ([Figure 1: see original paper]). Following the method in reference [14], small amounts of P25-TiO_2 and 3DOHS-TiO_2 were placed in agate mortars with appropriate amounts of deionized water, acetylacetone, and Triton emulsifier, and

stirred uniformly to obtain P25-TiO_2 and 3DOHS-TiO_2 pastes for photoanode construction.

To prepare P25-TiO_2/3DOHS-TiO_2 bilayer photoanodes, a layer of P25-TiO_2 paste was first uniformly coated on FTO conductive glass using the doctor-blade method, followed by a layer of 3DOHS-TiO_2 paste. After drying, the films were slowly heated to 500°C at 2°C/min, held for 2 h, and cooled in the furnace. When the temperature dropped to 80°C, the films were immediately immersed in 0.5 mmol/L N719 dye solution for 24 h, then rinsed with ethanol and dried. The total thickness of the bilayer film was measured to be approximately 14–15 m using a Bruker Dektak XT profilometer, with the 3DOHS-TiO_2 scattering layer thickness being about 5–6 m. A P25-TiO_2 photoanode of comparable total thickness was prepared following the same procedure, and Pt counter electrodes were fabricated according to the method shown in reference [24].

For testing, the dye-adsorbed photoanode and counter electrode were assembled into a sandwich structure, and electrolyte (composed of 0.5 mol/L LiI, 0.05 mol/L I_2, 0.5 mol/L 4-tert-butylpyridine, and 0.3 mol/L 1,2-dimethyl-3-propylimidazolium iodide in acetonitrile) was injected between the electrodes. Photovoltaic performance was measured under simulated sunlight (AM 1.5, 100 mW/cm^2) with an effective illumination area of 0.25 cm^2. The output photocurrent density-voltage (J-V) curves were measured using a Keithley 2400 source meter to obtain photovoltaic parameters including open-circuit voltage (Voc), short-circuit current density (Jsc), fill factor (FF), and photoelectric conversion efficiency ( ), where is defined as the ratio of the cell' s maximum output power to input power.

Results and Discussion

2.1 Sample Characterization Monodisperse colloidal particles serve as the fundamental building blocks for colloidal crystals and are essential for preparing high-quality colloidal crystal templates, which are key to synthesizing three-dimensionally ordered materials. [Figure 2: see original paper] shows SEM images of PS colloidal crystal templates. As shown in [Figure 2a: see original paper], the PS colloidal particles on the template surface exhibit large-area regular ordering with only a few vacancy defects. High-magnification SEM images ([Figure 2b: see original paper]) reveal that the prepared PS microspheres are highly monodisperse with diameters of 290–300 nm. The PS microspheres in the template self-assemble into hexagonally ordered arrangements, representing the thermodynamically stable structure with lowest free energy and minimum void fraction, corresponding to the (111) plane of face-centered packing. Cross-sectional SEM images ([FIGURE:2c,d]) show that the colloidal microspheres are arranged in closest packing from top to bottom throughout the template, with an estimated thickness of 25–30 layers.

[Figure 3: see original paper] presents TGA curves of the colloidal crystal template and template/titania hydrate precursor. The weight loss occurs at 300–

480°C, primarily attributed to polystyrene molecular chain decomposition and template removal. The TGA curve essentially plateaus above 500°C, indicating complete template removal. While titania can exist in multiple crystalline forms (anatase, brookite, rutile) after calcination at different temperatures, anatase TiO_2 nanocrystalline porous films are typically selected as photoanode materials for DSSCs. Therefore, to ensure complete PS template removal and obtain high-purity anatase TiO_2, the calcination temperature was set at 500°C.

The XRD pattern of calcined 3DOHS-TiO_2 samples ([Figure 4: see original paper]) shows sharp diffraction peaks at 25.3°, 37.9°, 48.1°, 53.9°, 55.1°, 62.7°, 68.8°, 70.1°, and 75.1°, corresponding to the (101), (004), (200), (105), (211), (204), (116), (220), and (215) crystal planes of anatase TiO_2 (JCPDS 21-1272). This indicates that the sample consists of pure anatase TiO_2 with high crystallinity and no impurity phases.

[Figure 5: see original paper] shows FESEM images of the surface and cross-section of 3DOHS-TiO_2 samples. [Figure 5a: see original paper] demonstrates that the 3DOHS-TiO_2 sample faithfully replicates the ordered structure of the original colloidal crystal template, with TiO_2 hollow spheres also in close-packed hexagonal arrangement. High-magnification images ([Figure 5b: see original paper]) reveal pores on the sample surface and occasional broken hollow spheres (indicated by arrows), further confirming the hollow sphere structure. The cross-sectional morphology ([Figure 5c: see original paper]) shows that the sample interior also consists of TiO_2 hollow spheres. High-magnification FESEM images ([Figure 5d: see original paper]) of horizontally fractured hollow spheres (indicated by arrows) allow estimation of the TiO_2 hollow sphere shell thickness at approximately 40–50 nm and show interconnection between adjacent hollow spheres through pores in their contact regions. Further observation reveals that the center-to-center spacing of surface hollow spheres is 260–270 nm, slightly smaller than that of PS microspheres in the original template (290–300 nm), indicating slight shrinkage of the three-dimensional ordered hollow sphere framework during template removal. Similar phenomena were observed by our group in preparing three-dimensionally ordered macroporous CeO_2 materials [25]. Based on these analyses, the prepared titania film material consists of TiO_2 hollow spheres with a highly ordered three-dimensional structure.

Additionally, during SEM observation of colloidal crystal templates, localized regions were found where PS microspheres adopted square arrangements ([Figure 6a: see original paper]), and corresponding square-ordered TiO_2 hollow spheres were also observed locally on the 3DOHS-TiO_2 sample surface ([Figure 6b: see original paper]). Existing research [26] indicates that driving forces or interaction forces for latex particle self-assembly, including gravity, surface tension, capillary forces, electrostatic forces, or magnetic forces, significantly influence the structure of two- or three-dimensional ordered colloidal crystals.

[Figure 7: see original paper] shows TEM images and selected-area electron diffraction (SAED) patterns of 3DOHS-TiO_2 samples to further analyze microstructural characteristics. Regular stripe-like structures observed in low-

magnification TEM images ([Figure 7a: see original paper]) indicate overall sample ordering. The TEM image from the sample edge ([Figure 7b: see original paper]) clearly shows that 3DOHS-TiO_2 samples consist of TiO_2 hollow spheres. High-magnification TEM images ([Figure 7c: see original paper]) reveal that TiO_2 hollow spheres are composed of ~10 nm nanoparticles with irregular stacking pores between particles (indicated by arrows, pores ~5 nm). Furthermore, clear lattice fringes with interplanar spacing of approximately 0.35 nm are observed in HRTEM images ([Figure 7d: see original paper]), consistent with the (101) plane spacing of anatase TiO_2 from JCPDS card (21-1272) [27]. The inserted SAED pattern shows distinct polycrystalline diffraction rings, with the five rings from inner to outer corresponding to the (101), (004), (200), (105), and (204) crystal planes of anatase TiO_2.

The nitrogen adsorption-desorption isotherm and pore size distribution curve for 3DOHS-TiO_2 samples ([Figure 8: see original paper]) show a Type IV isotherm. In the low relative pressure region, the relatively flat isotherm may result from macropores (TiO_2 hollow sphere cavities) in the sample [25]. In the high relative pressure region, an H2-type hysteresis loop appears due to capillary condensation, possibly caused by delayed evaporation of nitrogen molecules from hollow sphere pores during desorption due to obstruction by mesopores in the shell [28]. This indicates the presence of mesopores, consistent with HRTEM observations ([Figure 7c: see original paper]). The BET specific surface area is 59.8 m^2/g. The pore size distribution curve (inset) calculated from the desorption branch shows a broad distribution concentrated at approximately 4 nm and 17 nm.

[Figure 9: see original paper] shows the photocurrent density-voltage characteristics of DSSCs using P25-TiO_2 and P25-TiO_2/3DOHS-TiO_2 bilayer films as photoanodes under identical test conditions. Combined with the photovoltaic parameters listed in , both P25-TiO_2/DSSC and P25-TiO_2/3DOHS-TiO_2/DSSC exhibit comparable open-circuit voltages (Voc) of 0.77 V and 0.78 V, respectively. However, the short-circuit current density (Jsc) increases to 14.31 mA/cm^2 upon introducing the 3DOHS-TiO_2 scattering layer in the bilayer photoanode, significantly higher than that of conventional P25-TiO_2/DSSC (9.48 mA/cm^2). This results in a photoelectric conversion efficiency ( ) of 6.98% for P25-TiO_2/3DOHS-TiO_2/DSSC, representing nearly 62% improvement over P25-TiO_2/DSSC (4.32%). This demonstrates that the 3DOHS-TiO_2 scattering layer in the bilayer photoanode significantly improves DSSC performance. The probable reasons are: in the P25-TiO_2/3DOHS-TiO_2 bilayer composite photoanode, the upper 3DOHS-TiO_2 film enhances light scattering and harvesting capability of the photoanode film [21], while its high specific surface area and interconnected pore structure increase dye adsorption and facilitate electrolyte penetration and diffusion. The underlying P25-TiO_2 nanocrystalline layer ensures good electrical conductivity between the photoanode and FTO substrate [29], enabling excellent photovoltaic performance in P25-TiO_2/3DOHS-TiO_2/DSSC.

Conclusion

Using colloidal crystals self-assembled from monodisperse polystyrene microspheres as sacrificial templates combined with impregnation-calcination processes, three-dimensionally ordered TiO_2 hollow sphere (3DOHS-TiO_2) film materials were successfully prepared. The obtained 3DOHS-TiO_2 samples consist of closely packed TiO_2 hollow spheres interconnected through pores. The TiO_2 hollow spheres have a center-to-center spacing of 260–270 nm and shell thickness of 40–50 nm, with the spheres composed of ~10 nm anatase TiO_2 nanoparticles. Under identical test conditions, the P25-TiO_2/3DOHS-TiO_2 bilayer photoanode DSSC achieved a photoelectric conversion efficiency of 6.98%, representing nearly 62% improvement over conventional P25-TiO_2 nanocrystalline photoanode cells (4.32%).

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Note: Figure translations are in progress. See original paper for figures.