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Hydrothermal Synthesis of TiO_2 Porous Hollow Nanospheres for Coating on the Photoelectrode of DSSCs

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1. Introduction

TiO_2 is an important multifunctional wide bandgap (Eg =3.2 eV) semiconductor with excellent physical properties, chemical stability, environmental compatibility and low production cost. TiO_2 offers a broad range of applications such as photocatalysis, water splitting, dye-sensitized solar cells and quantum-dots sensitized solar cells [1]. Recently, among these structures the hollow spheres have attracted an increasing interest compared with their solid counterparts because of their low density, high surface area, good surface permeability and large light-harvesting efficiency [2]. Multiple light diffraction and reflection can also occur because of the particular hollow structure of such spheres.
The various chemical and physicochemical methods have been used for the preparation of spheres in the literature such as reactive micro-emulsion precipitation, sol gel process, acid catalytic hydrolysis followed by hydrothermal treatment, facile and large scale synthesis by hydrothermal method, carbon spheres, CVD technique, template-free green wet-chemical route, 3-D architecture of TiO_2 hallow spheres by surface erosion route, PEG-400 polymer-induced anatase TiO_2 hollow structures and Mixed-phase titania nanospheres by laser ablation.

Typically, bilayered structures consisting of a main TiO_2 layer prepared from the tiny nanoparticles (10-30 nm) and a light-scattering layer (LSL) from the large particles (200-400 nm) have been designed for efficient utilization of the solar spectrum and enhancement of photovoltaic conversion efficiency [3-4]. The LSL on top of the main TiO_2 layer confines the incident light within an electrode or diffracts it backward. Thereby, the dye molecules anchored on the TiO_2 surface utilize solar spectrum more efficiently.
Conventionally, the large particles of rutile, ZrO_2, $SrTiO_3$ or other high-refractive-index metal oxides have been used as scattering layer for DSC. But TiO_2 based nanomaterial have large external structure, retaining well developed pores and a large surface area, will be suitable for this purpose, since these structures can generate photo-excited electrons due to the large amount of dye uptake and exhibit a considerable light-scattering property at the same time. Thus far, several TiO_2-based nanostructures such as hollow spheres [5], nanoporous spheres [6-7] and others have been successfully applied as LSL.

In this paper, hollow spheres were synthesized by two step process of controlled hydrolysis and subsequent hydrothermal method. The obtained TiO_2 nanospheres were mixed with colloidal solution and coated as a scattering layer on TiO_2 electrode.

2. Experimental

Hydrothermal Synthesis of TiO_2 Nanospheres

Nanoporous spherical TiO_2 structures with a diameter of 500 nm were synthesized by a two-step process of controlled hydrolysis and a subsequent hydrothermal reaction [8]. Typically, TTIP (15.0 mmol, Aldrich) stabilized in ethanol (10 ml, Aldrich) was dissolved in a premixed solution of ethanol (50 ml) and acetonitrile (40 ml, Aldrich) with methylamine (2.5 mmol) and water (60 mmol). The solution turned milky within a few seconds, and the prepared suspension was stirred for 1 h to form the amorphous TiO_2 nanospheres. The collected amorphous TiO_2 nanospheres were washed with ethanol, and transferred to an autoclave made of titanium containing ethanol (50 ml). The temperature of the autoclave was raised to 240°C at a rate of 5°C min^{-1}, and held at this temperature for 6 h. After hydrothermal reaction the product was washed and dried at 80°C.

Preparation of Working Electrode

Fluorine-doped SnO_2 conductive glass (FTO 10-15 /Asahi Glass, Japan) was used as the substrate for the deposition of TiO_2 film. Anatase TiO_2 colloidal solution was prepared by using the conventional method. Firstly, the film about 25 μm in thickness was prepared by using spray pyrolysis method. In this method 0.25 to 0.3 g of P25 (particle size ~25 nm TiO_2 powder) was mixed with 5-6 ml acetic acid and ground to avoid agglomeration. Then 20 ml colloidal solution (TKC-302, particle size ~3-6 nm) was mixed and allowed to ultrasonicate for homogeneous mixing. Secondly, 0.15 g of TiO_2 (500 nm) nanospheres were mixed with appropriate amount of acetic acid as well as 10 ml colloidal solution and finally 10 ml ethanol. The desired amount of spheres solution was sprayed on the surface of TiO_2 film. The pure TiO_2 and spheres coated film was sintered about 500°C for 3 h. The film was immersed into the N719 dye solution for adsorption overnight.

The preparation of liquid electrolyte

The compositions of 0.1 M LiI, 0.05 M I_2, 0.6 M 1, 2-dimethyl-3-*n*-propylimidazolium, 0.5 M 4-*tert* butylpyridine and finally 0.1 M GuSCN in acetonitrile was used as electrolyte. The sputtered Pt electrode was used as a counter electrode.

3. Results and discussion

X-ray Diffraction

The XRD measurement was carried out by using Rigaku RINT ultima-III in the angle range of 2θ from 10 to 70 degrees. The XRD profiles for the prepared spheres indicate pure anatase phase. The crystallite sizes of the anatase grains consisting of spherical structures were found to be in the range of 11-12 nm according to Sherrer's equation.

SEM Pictures

The surface morphologies of spheres coated TiO_2 electrode and powders were observed by field emission scanning electron microscope (JEOL JSM-6320F). In Fig. 1(a) spheres are very clear and their diameter is about 500 nm. Figure 1(b) shows SEM image of the spheres heated at 240°C for 1 h and indicates that the prepared spheres have hollow structures. It can be observed from Fig. 1 (c) that some of spheres exists on the top of TiO_2 but the coated spheres are mostly mixed with colloidal solution with particle size 3-5 nm, which suggests the improvement of interconnection of the spheres for good electrical connection. Figure 1 (d) shows a top view of the sample which indicates the presence of spheres on the top layer along with the smaller particles.

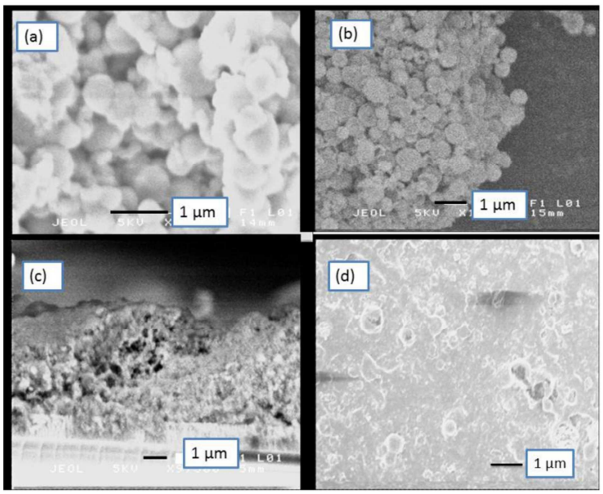

Fig. 1 SEM images of spheres (a,b), cross section (c) and top view (d) of the smaple.

IPCE Characterestic

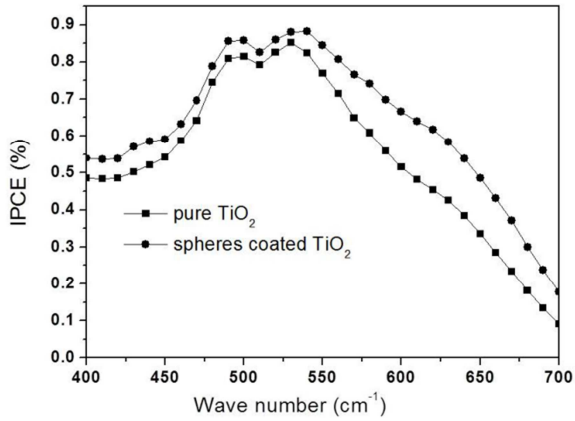

Fig. 2 IPCE curves of the samples with and without spheres coating.

The IPCE and current-voltage characteristics were measured by using a JASCO xenon lamp power supply XCS-150 in which a light intensity of 100 $mWcm^{-2}$. The active area of the cells was 0.25 cm^2. It is found from the IPCE curve as shown in Fig. 2 that the improved quantum efficiency by the spheres coating can be seen in the long wavelength range 550-700 nm. The effect is attributed to the scattering effect of the coated layer [9].

Photovoltaic Properties

The photovoltaic performances are summarized in Table for the prepared DSCs without and with the TiO_2 spheres coating derived from the I-V characteristics. By introducing the scattering later, short-circuit current density, J_{SC} is appreciably increased, while the fill factor and open-circuit voltage, V_{OC} are not changed. Generally, the coating of large particles increases surface area and a back scattering is possible for electrons, hence V_{OC} is slightly decreased. But in the present case we coated spheres by mixing with appropriate colloidal solution, which makes the surface smoother. The efficiency, η of DSC is improved from 8.4 to 9.56% by introducing the scattering layer with the particle size of 500 nm mixed with colloidal solution.

Table1 I-V characteristics of various DSSCs fabricated.

Sample name	V_{OC}	J_{SC}	FF	η (%)
Pure TiO_2	0.78	15.84	0.67	8.41
Pure TiO_2/10ml sphere coating	0.79	17.95	0.67	9.56
Pure TiO_2/20ml sphere coating	0.77	17.6	0.64	8.73
Pure TiO_2/ (0.3g /10ml mixing)	0.78	15.39	0.69	8.33
Pure TiO_2/ (0.15g/10ml mixing)	0.78	15.72	0.67	8.25

4. Conclusion

The hydrolysis and subsequent hydrothermal method is introduced to prepare the 500 nm-sized hollow spheres and the spheres are spray coated as a scattering layer on the top of pure TiO_2 electrode. The XRD reveals that the crystallite sizes are 11-12 nm for the particles with the spherical structure. The spherical particle size is found to be around 500 nm from the SEM observations and the spheres layer exists as a top layer of the TiO_2 electrode. Finally, DSCs are fabricated based on the electrode and its IPCE and I-V characteristics are measured. The maximum efficiency of 9.56% is achieved for the 10 ml sphere solution coated sample on the top of the TiO_2 electrode.

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