

Triton Facilitated Spherical TiO₂ Nanoparticles and Their Advantage in a Dye-Sensitized Solar Cell

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ABSTRACT

Spherical TiO₂ particles (60 nm) were obtained by using a Triton X-100. The surfactant was employed in two stages, *i.e.*, in the hydrolysis of TiCl₄ and then in the precipitation of the corresponding Ti (IV) polymers. The advantages of such spherical TiO₂ particles were examined in terms of photovoltaic characteristics of a dye-sensitized solar cell (DSSC) using Orange IV dye as sensitizer. Significantly higher overall solar energy conversion efficiency was obtained for a DSSC using the film of these spherical TiO₂ particles, compared with that of a cell using a TiO₂ film prepared without surfactant.

KEYWORDS

TiO₂ Nanoparticles; Triton; Orange IV; Dye-Sensitized Solar Cell

1. Introduction

The dye-sensitized nanocrystalline solar cell (DSC) invented by O'Reagan and Grätzel [1] is a cheap and versatile alternative to silicon based solar cells and has already achieved solar-to-electricity conversion efficiency as high as 11.5% [2,3]. The main stream of the research has been focusing on development of materials which would enhance the conversion efficiency, simplify the production of DSSC and assure their long-lifetime. Titanium dioxide is an n-type wide band gap semiconductor that absorbs in the UV region and is transparent for visible light. In a typical DSSC, the dye molecules are adsorbed on the surface of the TiO₂ to assure photoelectric conversion over a broad spectral range of the solar spectrum. When sunlight radiates onto the DSSC, the electrons in the dye molecules (HOMO level) absorb photons that become excited and jump to an unoccupied upper level (LUMO level). The electrons from the LUMO level are then injected into the TiO₂ semiconductor conduction band and pass through the TiO₂ layer to the transparent conductive oxide (TCO) coated glass and to a load. Fur-

ther, the vacant "HOMO" level is then filled with electrons supplied by the iodide (I⁻) ions in the electrolyte while iodide is oxidized to tri-iodide I₃⁻. Meanwhile the platinum counter electrode acts as a catalyst for the redox reaction of the ions in the electrolyte solution and reduces the tri-iodide back to iodide [4]. To realize high-efficiency DSSCs, a high surface area of the nanostructured TiO₂ layer is essential, because it allows adsorption of sufficiently large number of dye molecules needed for efficient light harvesting. Beside the high surface area of the TiO₂ layer, the morphology and structure of a TiO₂ film is one of the strategies adopted for improving the efficiency of a dye-sensitized solar cell (DSSC) [5-8], because the optical, electrical, conductive and other characteristics of a TiO₂ film vary greatly with the size and shape of the particles and the clusters comprising the film. A variety of TiO₂ films and materials have been produced using different types of surfactants as templates, *e.g.*, alkylphosphate [9], amphiphilic triblock copolymer [10], laurylamine hydrochloride/tetraisopropylorthotitanate [11], self-designed amphiphilic compounds containing cationic charge moieties [12], poly (alkylene

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oxide) block copolymer [13]. As can be seen above, primary surfactants were rarely used to improve the morphology, crystallinity or particle size of TiO_2 , thereby to improve the photovoltaics of a DSSC.

This paper essentially deals with the formation of spherical TiO_2 particles by means of the introduction of Triton X-100. This technique has been well known in order to provide simple and inexpensive alternative routes to synthesize nanoparticulate materials.

2. Experimental

Titanium tetrachloride was used as the starting material to prepare the TiO_2 films. All the chemicals were of analytical grade and used without further purification. The influence of Triton X-100 was examined in two steps: (1) the preparation of an aqueous solution of TiCl_4 (hydrolysis step), and (2) the precipitation of Ti (IV) polymers from the hydrolyzed TiCl_4 solution onto a conducting substrate (precipitation step) [14]. In the hydrolysis step, 22 mL of TiCl_4 was added dropwise to 78 mL of distilled water containing 1.3 mM Triton X-100 to produce a 2.0 M Ti (IV) solution. Before the precipitation process, fluorine-doped tin oxide (FTO) conducting glass plates (TCO glass, fluorine-doped SnO_2 overlayer, transmission >70% in visible and sheet resistance 20 Ω /square) were first cleaned with water and ethanol. In the precipitation step, 1.0 ml of the hydrolyzed 2.0 M Ti (IV) solution were pipetted into the conducting glass plates. The plates were dried at 353 K in order to allow the Ti (IV) polymers to deposit onto the conducting glass plates. Subsequently, the glass plates were annealed at 623 K for 1 h. The TiO_2 films thus obtained were coated with 0.3 mM of Orange IV in absolute ethanol for 24 h at room temperature. Carbon counter electrode was prepared by sputtering a thin layer of carbon on a transparent conducting glass support (TCO glass, fluorine-doped SnO_2 overlayer, transmission >70% in visible and sheet resistance 20 Ω /square) using a graphite rod. The carbon electrode was placed over the dye-coated electrode, and the edges of the cell were sealed. A redox electrolyte consists of a mixture of iodide/triiodide in acetonitrile was injected by a syringe into the space between the two electrodes. The resulting cell had an active area of $1 \times 2 \text{ cm}^2$. A schematic diagram showing the construction of the cell is represented in Figure 1.

The photocurrent-voltage (I - V) curves were obtained using a digital source-meter (Keithley 2400). Direct sunlight was used to illuminate the working electrode. The surface morphology was examined using SEM (Jeol JXA-840 electron probe microanalyzer). The XRD measurements were carried out with Diano Corporation USA diffractometer using Co radiation radiation. The surface areas were measured using a conventional or classical

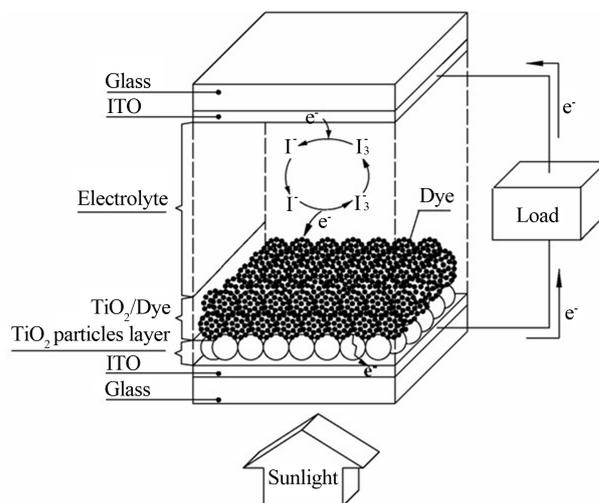


Figure 1. Schematic of the dye-sensitized solar cell with a sandwich TiO_2 thin-film.

volumetric apparatus. FTIR spectra were taken using Thermo Avtar 370 spectrometer.

3. Results and Discussion

Figure 2 shows the influence of Triton X-100 on the XRD patterns of the TiO_2 films, deposited on FTO. It can be seen that the TiO_2 film formed with Triton X-100 completely crystallize as anatase (DB card, No. 01-070-7348).

The average crystallite size of the anatase TiO_2 was calculated using the Scherrer equation [15]. The determined average size of the prepared TiO_2 was found to be 60 nm.

FT-IR studies of the TiO_2 film show the characteristics of the formation of high-purity material. The FT-IR spectrum of Figure 3 clearly shows the peaks corresponding to TiO_2 . Peaks located in the area of 400 - 650 cm^{-1} correspond to the vibration of Ti-O and Ti-O-O bonds [16]. It is also clear from data of Figure 3 the presence of peak at 2900 cm^{-1} corresponds to $-\text{CH}_2$ and at 1500 cm^{-1} corresponds to C-O-C due to organic moiety of Triton X-100.

Figure 4 shows the top view SEM image of clusters of the film. The Triton X-100 influenced clusters have a uniform size and consist of well defined spherical TiO_2 particles. The clusters composed of these particles tended to fuse together to form large aggregates.

The BET surface areas were 31.1 and 44.6 $\text{m}^2 \cdot \text{g}^{-1}$ for the TiO_2 powders (without and with Triton) and TiO_2 formed with Triton, respectively. This increase in surface area was further evidenced by the observation that the amount of dye desorbed from the Triton influenced TiO_2 film surface higher than that from the film without the Triton. This observation is consistent with the observation derived from XRD pattern that Triton facilitates

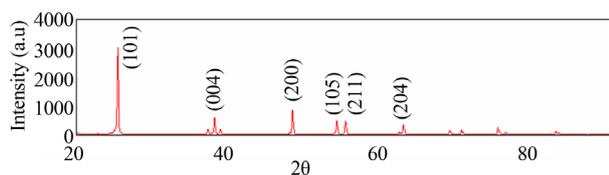


Figure 2. X-ray diffraction patterns of TiO₂ electrode.

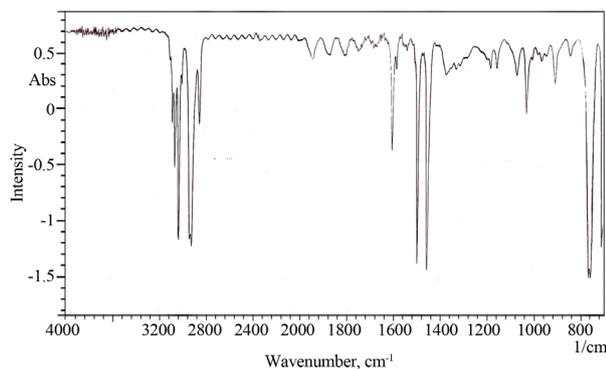


Figure 3. FTIR spectra of TiO₂.

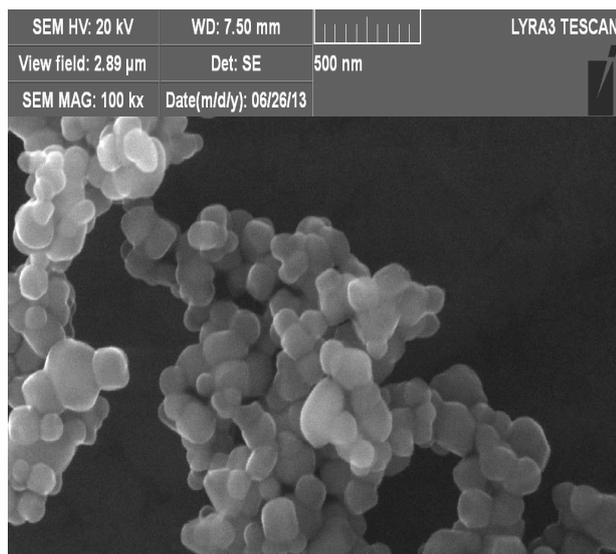


Figure 4. SEM images of the prepared TiO₂.

smaller TiO₂ particles.

From the above results; we expected an enhanced performance of a DSSC fabricated with a Triton-influenced TiO₂ film. The rationale behind this expectation lies in the regular structure of the film, composed of spherical particles and clusters. Figure 5 and Table 1 present the photocurrent-voltage (*I* - *V*) curves and photovoltaic performance data of DSCs fabricated with the TiO₂ film electrodes in the presence and absence of Triton. The DSSC fabricated using the Triton-influenced TiO₂ film shows a higher short-circuit photocurrent (*I*_{sc}), open-circuit voltage (*V*_{oc}) and solar conversion efficiency than that prepared without Triton. The increase in *I*_{sc} may be

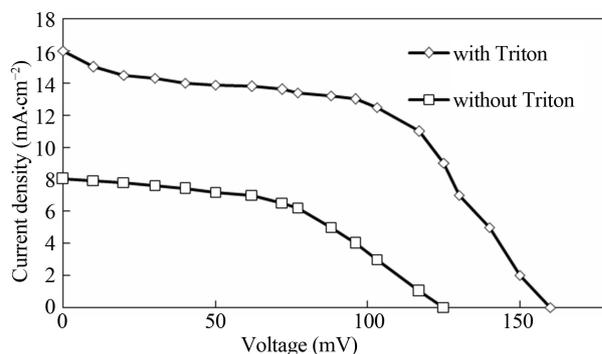


Figure 5. *I* - *V* curves of the DSSCs fabricated with TiO₂ films and orange IV dye.

Table 1. Photovoltaic parameters of Orange IV dye-sensitized nanocrystalline TiO₂ solar cells.

Samples	<i>I</i> _{sc} (mA·cm ⁻²)	<i>V</i> _{oc} (mV)	<i>I</i> _m (mA·cm ⁻²)	<i>V</i> _m (mV)	FF	η × 10 ⁻² %
With Triton	16	160	12.5	103	0.5	0.12
Without Triton	8	125	6.2	77	0.4	0.04

*I*_{sc}: Short circuit current; FF: Fill factor; *V*_{oc}: Open circuit voltage; η: overall energy conversion yield; *I*_m: Maximum current; *V*_m: Maximum voltage.

primarily related to the increased surface area. Furthermore, this increase in *I*_{sc} can be related to an increase in the number of pathways due to the increased packing of round particles [14]. A more densely packed film improves inter-particle electrical contact. The observed increase in *V*_{oc} might be due to an increase packing density of the TiO₂ particles in the film. Increasing packing of small and round TiO₂ particles produce small pores. The effective concentration of *I*₃⁻ ions in the TiO₂ film with smaller pores would be lesser than that in the film with larger pores, because the rate of *I*₃⁻ ion replenishment in the TiO₂ film with smaller pores becomes slower. This slow replenishment of *I*₃⁻ ions leads to the accumulation of photo-injected electrons in the TiO₂ conduction band in the open-circuit condition, which in turn leads to an increase in the *V*_{oc}.

4. Conclusion

Spherical TiO₂ nanoparticles were obtained using Triton X-100 in a hydrolyzing of TiCl₄ solution. XRD results reveal that Triton generally suppresses the formation of anatase phase of TiO₂. The DSSC prepared with TiO₂ film using Orange IV as sensitizer showed improved *I*_{sc}, and *V*_{oc} as well as substantially improved solar energy conversion efficiency, compared with those of a cell fabricated with TiO₂ film obtained without Triton.

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