

Novel Quasi-solid-state Dye-sensitized Solar Cell Based on Monolayer Capped TiO₂ Nanoparticles Framework Materials

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Dodecylbenzenesulfonate (DBS)-capped TiO₂ nanoparticles have been synthesized and employed in dye-sensitized solar cells to form a quasi-solid state electrolyte. Owing to the long alkyl-chain capping around the TiO₂ nanoparticles interacting with the liquid solvent, the dye sensitized solar cell based on such DBS-capped TiO₂ nanoparticle framework material gel electrolyte shows higher stability compared with the non-capped one in the long-term application and gives a comparable overall efficiency of 6.3% at AM 1.5 illumination.

Keywords dodecylbenzenesulfonate, capped TiO₂, dye-sensitized solar cells, quasi-solid state

Introduction

Nanoparticles exhibit a series of special physical and chemical properties that are promising for potential applications in the new generation solar energy conversion, nonlinear optics, and heterogeneous photocatalysis during the last decades.¹⁻⁴ However, the stabilization of the nanoparticles in preventing them from aggregation is one of the essential problems that have to be solved. Some examples for solving such problems by using surfactants^{5,6} or polymers^{7,8} have been recently reported. Generally speaking, the immobilization is often accomplished through the surface modification with functional groups such as thiol, pyridyl, amino, and carboxy, and they can be used to immobilize metal nanoparticles or metal oxide nanoparticles and so on.

Owing to their high-energy conversion efficiency and especially low production cost,⁹⁻¹³ as a cost-effective alternative to inorganic solar cells, dye-sensitized nanocrystalline solar cells (DSSC) have received considerable attention. However, some practical problems such as sealing and long-term stability may be the most obstacles in applying the liquid electrolyte. Though pure solid-state electrolytes such as p-type semiconductor,^{14,15} or solid hole transport organic material¹⁶ have been used in this domain, their efficiency or long term stability can not be comparable with those of the liquid electrolyte. Therefore, the quasi-solid state electrolyte attracts more interests and remains to be studied.

Polymers¹⁷⁻²⁴ or gelators²⁵⁻²⁷ have been introduced to gel the liquid electrolyte and have shown comparable efficiencies to those of solar cells using liquid electrolyte. Very recently, nanoparticles such as silica oxide²⁸

were introduced to solidify liquid phase and got very significant results ($V_{oc}=700$ mV, $I_{sc}=13.7$ mA, $FF=0.73$, $\eta=7.0\%$). However, these inorganic particles in solar cell might be unstable during a long term operation due to that the aggregation of nanoparticles occurs in solar cell. Here, in order to prevent nanoparticles from aggregating, we synthesized dodecylbenzenesulfonate (DBS) capped TiO₂ and used as framework materials to prepare quasi-solid-state electrolyte incorporating triiodide/iodide as a redox couple.

Experimental

Materials

Optically transparent conducting glass (TEC 15, 14 Ω/cm^2), with fluorine-doped SnO₂ (CTO) over layer, was received as a gift from Genenal Electrical Company, USA. Titanium(IV) tetraisopropoxide, propylene carbonate (PC) and *tert*-butylpyridine were purchased from Acros. All the other solvents and chemicals used in the experiments are of at least reagent grade (Beijing Chemical factory, Beijing, China) and used without further purification. *Cis*-Ru known as N3,⁹ and MP11²⁹ were synthesized according to the reported method.

Preparation of DBS-capped TiO₂ and the fabrication of dye sensitized quasi-solid solar cells

The sodium dodecylbenzenesulfonate (DBS)-capped nanoporous TiO₂ was synthesized according to the modified method reported for TiO₂.³⁰ Briefly, to 100 mL of freshly prepared TiO₂ colloids in water as synthesized according to the literature³¹ was added 20 mL of 0.2 mol/L DBS in a round-bottom flask. The resulting

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Received October 16, 2003; revised and accepted March 12, 2004.

Project supported by the State Key Program of Fundamental Research (No. G1998061308), the National High Technology Research Development Plan of China (Nos. 2002 AA 302403 and 0216nm040) and the National Natural Science Foundation of China (No. 20221101).

mixture was stirred slowly for several minutes. Then to the stirred solution, 50 mL of toluene was added to extract the TiO₂ nanoparticles into the organic phase. After accomplishment the phase separation, anhydrous CaCl₂ was added for overnight. Finally, the dry DBS-capped TiO₂ nanoparticles were obtained after rotary evaporation. The average diameters of TiO₂ and DBS-capped TiO₂ obtained estimatedly are 3 nm and 6 nm,³⁰ respectively.

The 120 g/L TiO₂ colloid was prepared according to the literature.⁹ Three drops of the colloid was spread uniformly on the conducting glass (2 cm×8 cm) followed by annealing at 450 °C in air flow for 30 min. The 10-μm-thick TiO₂ films were obtained after repeating the above procedure several times. Dye-coated film used as working electrode, while the counter electrode was ITO glass on which 200-nm-thick layer of Pt was deposited by sputtering. The N3 was used to sensitize the electrodes, which was accomplished by immersing the electrodes in a 0.5 mmol/L solution of dye in absolute ethanol overnight. To avoid the absorption of water molecules, the films were heated to 150 °C and then cooled to 80 °C before immersion in the dye solution. The electrodes were kept in the dye solution until the measurement in the DSSC was performed. Liquid electrolyte was composed of 0.1 mol/L I₂, 0.1 mol/L LiI, 0.5 mol/L *tert*-butylpyridine and 0.6 mol/L 1-methyl-3-propylimidazolium iodine in a mixture of PC and ethanol (V : V, 1 : 1). An amount of non-capped TiO₂ or DBS-capped TiO₂ (wt% of liquid electrolyte) was added into the liquid to get two types of quasi-solid electrolytes respectively.

Methods

The current-voltage (I–V) characterizations of the solar cells were carried out using a Keithley 2400 Source Meter, which was controlled by a computer. An Oriel 1000 W xenon lamp served as the light source with the Oriel Air Mass (AM) 0 filter and AM 1.5 direct filter in the optical path to simulate AM 1.5 direct solar irradiation. All experiments were performed at AM 1.5 direct irradiation at 100 mW/cm² light intensity. In all experiments, the sample was illuminated through the conducting glass substrate with an illuminated area of 0.188 cm² and no corrections were made for the reflection and transmission losses in the CTO. Paraffin wax was used temporarily to seal the solar cells for a quick comparing the performance of different electrolytes. And after each measurement, they were kept in dark at room temperature.

Results and discussion

Characteristics of DBS-capped TiO₂ nanoparticles

Figure 1 shows that the optical absorption spectra of DBS-capped TiO₂ nanoparticles in DMF and anatase TiO₂ nanoparticles in water. The schematic structure of the dodecylbenzenesulfonate capped TiO₂ nanoparticles

is shown in Figure 1 (Inset). We can see that the absorption spectrum of DBS-capped TiO₂ particles is red shifted, which compared with that of non-capped nanoparticle TiO₂ itself. Similar results were observed in TiO₂ ultrafine nanoparticles³⁰ and such phenomena were attributed to a dipole layer that induced an attractive potential to electrons inside the ultrafine particles and led to reduction of the band gap of the system.³² The nanoparticles consist of a TiO₂ core of approximately 2–3 nm in diameter, surrounded by a shell of dodecylbenzenesulfonate tails connected to the surface via sulfonate group, involving bridging binding sites. Since the aggregation is dependent on surface chemistry resulting in either orientated or random attachment of particles, the strong binding of dodecylbenzenesulfonate shell prevents aggregation and consequently renders the nanoparticles soluble in common polar or apolar organic solvents.

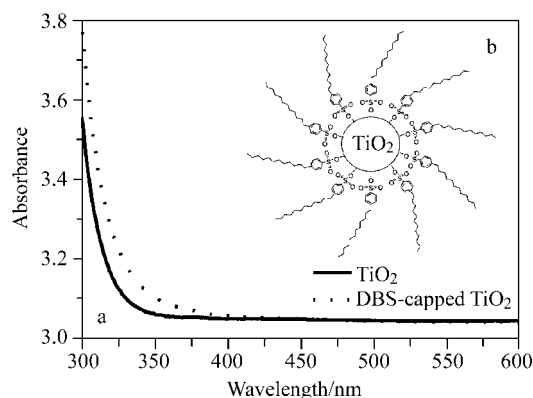


Figure 1 (a) Optical absorption spectra of anatase TiO₂ nanoparticles in water (solid line) and DBS-capped TiO₂ nanoparticles in DMF (dot line) [TiO₂]=1 mg/L; (b) schematic diagram of DBS-TiO₂ particles.

Parameters of the solar cells based on DBS-capped TiO₂ nanoparticle quasi-solid electrolytes

The photocurrent-voltage curves for DSSC with different containing of DBS-capped TiO₂ quasi-solid electrolyte together with the DSSC fabricated with liquid electrolyte at irradiation of AM 1.5 sunlight are shown in Figure 2. All parameters of quasi-solid state solar cells with different concentration w =(1%, 2% and 5%) of DBS-capped TiO₂ were summarized in Table 1. Data show that the open circuit voltages (V_{oc}) of the cells based on DBS-capped TiO₂ gel electrolytes are little lower than that of the liquid electrolyte, while the photocurrent densities of these cells fabricated with DBS-capped TiO₂ framework gel electrolytes are alternating around that of the liquid electrolyte cell, thus the overall efficiencies of the cells based on DBS-capped TiO₂ framework gel electrolytes are comparable to that of the pure liquid electrolyte. After capping of TiO₂, the capped TiO₂ nanoparticles would make a netted matrix to cage the organic solvent, which would prevent the solvent to evaporate quickly and give a comparable efficiency to that of the liquid electrolyte.

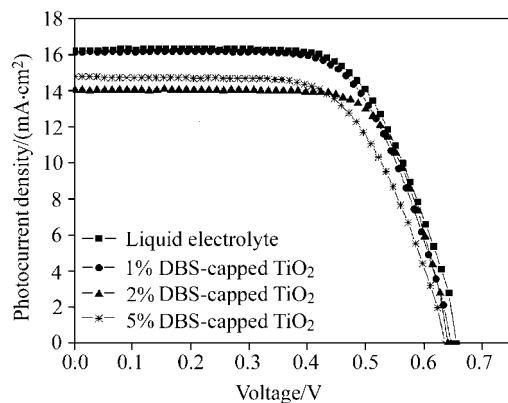


Figure 2 Photocurrent-voltage curves of the cells based on liquid electrolyte (square) and quasi-solid-state solar cells: 1% DBS-capped TiO₂ electrolyte (circle), 2% DBS-capped TiO₂ electrolyte (triangle) and 5% DBS-capped TiO₂ electrolyte (star).

Table 1 Comparison of the parameters for cells based on organic-capped nanoparticle framework gel electrolytes and liquid electrolyte (under AM 1.5 illumination 100 mW/cm², cell active area: 0.188 cm²)

Sample	V_{oc}/mV	I_{sc}/mA	FF	$\eta/\%$
Liquid electrolyte	656	16.2	0.65	6.9
1%DBS-capped TiO ₂	647	16.2	0.64	6.7
2%DBS-capped TiO ₂	641	14.0	0.70	6.3
5%DBS-capped TiO ₂	636	14.8	0.62	5.9

These results are consistent with those reported by Grätzel *et al.*²⁸ who investigated SiO₂ nanoparticle-filled quasi-solid electrolyte applied in dye sensitized solar cells (DSSC). The relationship among open circuit, photo voltage, short circuit photocurrent, overefficiency, fill factor of the DBS-capped TiO₂ framework quasi-solid-state cell and light intensity is illustrated in Figure 3, from which we can see that short-circuit photocurrents increase with increasing light intensity in the range of 0 to 100 mW/cm². This linearity shows that the photocurrent is not limited by diffusion of the iodide or triiodide ions within the nanocrystalline film up to light intensity of at least 100 mW/cm². From this point, we can get a conclusion that transportation of I^-/I_3^- is not influenced by the addition of DBS-capped TiO₂.

Comparison of the stability between the non-capped nanoparticle and DBS-capped nanoparticle-electrolyte

The obvious phase separation phenomena in the non-capped nanoparticle-filled quasi-solid electrolyte was observed (Figure 4 A) after one week keeping while the gel electrolytes containing DBS-capped nanoparticles showed much more homogeneous phase (Figure 4B). Furthermore, the latter DBS-capped nanoparticle framework gel electrolyte is very stable even after several months' preservation. With such evere problem faced in the non-capped nanoparticle-filled quasi-solid electrolyte, one can imagine that the added nanoparticles would be deposited on the

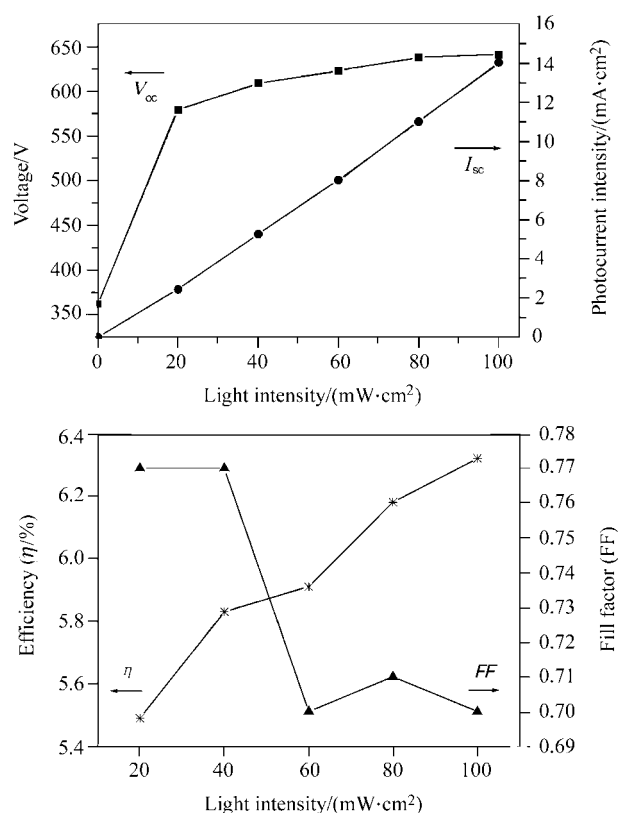


Figure 3 (A) Variation of short-circuit photocurrent (I_{sc}) (circle) and the open-circuit photovoltage (V_{oc}) (square) measured as a function of incident light intensity at AM 1.5 illumination, (B) Overall efficiency (η) (triangle) and fill factor (FF) (star) plotted as function of light intensity for the 2%DBS-capped TiO₂ gel electrolyte solar cell.

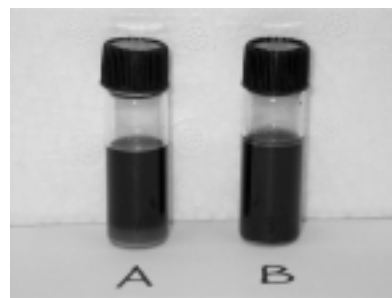


Figure 4 Photograph of the TiO₂ gel electrolyte (A) and DBS-capped TiO₂ gel electrolyte (B) one week after mixing.

adsorbed dye attached on the TiO₂ film and resulted in retarding of the diffusion of I^-/I_3^- during the long-term operation. On the other hand, in the DBS-capped nanoparticle gel electrolyte system, the TiO₂ nanoparticles act as the rigid center while the long alkyl-chains catch up with the organic solution or interact with each other to form a semi-solid electrolyte with channels for transporting I^-/I_3^- freely.

A comparison of the time-course changes in the photo-electro conversion efficiency for different solar cells is shown in Figure 5. The liquid electrolyte lost half photoconversion efficiency after 120 h while those of the quasi-solid electrolytes were only reduced about 10%—15%. What is more, the DBS-capped nanoparti-

cle framework gel electrolyte exhibits higher stability than the non-capped nanoparticle-electrolyte. Like polymer electrolyte, the long alkyl-chains may contribute to the maintenance of the efficiency of the solar cells through holding the organic solvent and suppression of vaporization of solvent. Since paraffin wax was used here to seal the cell devices for a quick comparing, the higher stability should be obtained after optimization of sealing.

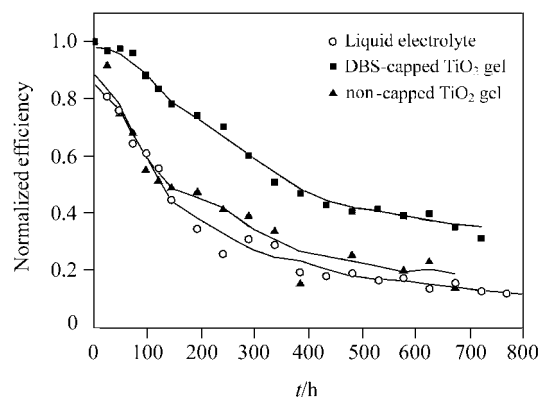


Figure 5 Time-course change of the normalized photoconversion efficiency of the liquid electrolyte (open circle) and quasi-solid-state solar cells: 2% DBS-capped TiO₂ gel electrolyte (square), TiO₂ gel electrolyte (triangle).

Conclusion

Organic material capped TiO₂ nanoparticles were introduced to form quasi-solid electrolytes, which show comparable efficiency to that of liquid electrolyte. The advantage of such quasi-solid electrolytes is their free phase separation during the long-term operation encountered by the other quasi-solid electrolytes in dye-sensitized solar cells. For the first time we introduced the organic material capped nanoparticles to solidify the liquid electrolyte in the research of quasi-solid-state dye-sensitized solar cells. And this paper gives a way to introduce such a superstructure that offers long alkyl-chain to form a quasi-solid electrolyte with channels for transporting I^-/I_3^- freely. It is predictable that, organic materials capped nanoparticles such as ZnO, Al₂O₃ and so on would be suitable to introduce and form quasi-solid electrolyte series, which would also show good performance as DBS-capped nanosized TiO₂ does in this article. Moreover, such quasi-solid electrolyte may have much more application in other fields.

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