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A novel quasi-solid-state dye-sensitized solar cell based on monolayer capped nanoparticles framework materials

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Abstract A new kind of 1-phenyl-3-methyl-4-octadecyl-5-pyrazolone (PMOP)-capped ZnO nanoparticle has been synthesized and characterized with UV–VIS, IR and fluorescent spectra. The material was used as a framework to form a quasi-solid-state electrolyte and employed in dye-sensitized solar cell (DSSC). Since the long alkyl-chain of PMOP interacts with liquid solvent, the quasi-solid-state DSSC with PMOP-capped nanoparticles shows higher stability in comparison with that of the liquid device and gives a comparable overall efficiency of 6.8% under AM 1.5 illumination.

Introduction

Dye-sensitized nanocrystalline solar cells (DSSCs) based on quasi-solid-state electrolytes have recently received considerable attention for their high-energy conversion efficiency and long-term stability [1–4]. A framework material is an important component in most of the quasi-solid-state electrolytes. Some polymers [4] and gelators [5] used as framework materials have been introduced to solidify the liquid electrolytes. Recently, Wang et al. [6] reported a gel DSSC with the efficiency of 6.2% using SiO_2 nanoparticles to solidify the liquid electrolytes.

It is well-known that the aggregation of the nanoparticle is one of the essential problems in its practical application. Surface modification of nanoparticles is used as a common method to avoid the aggregation, and functional groups such as thiol, pyridyl, amino, and carboxy, can be used to immobilize metal nanoparticles and metal oxide nanoparticles [7–10]. As an important functional group, β-diketonate can coordinate many metal cations such as lanthanide ions and transition metal ions to form functional complexes [11–13]. For example, 4-acyl-5-pyrazolone ligands can coordinate to the lanthanide ions (such as Tb^{3+}, La^{3+} and Lu^{3+}) and transition metal ions (such as Al^{3+} and Zn^{2+}) and form stable complexes [13–17]. Here, to improve the solubility of ZnO nanoparticle in organic solvents, we synthesized a new β-diketone surfactant, 1-phenyl-3-methyl-4-octadecyl-5-pyrazolone (PMOP) with a long alkyl chain, to modify ZnO nanoparticle, and then the PMOP modified ZnO nanoparticle was employed in the dye-sensitized solar cell to improve the operation stability of the device.

Experimental

The optically transparent conducting glass with fluorine-doped SnO_2 (CTO, 14 Ω/cm^2) was received as a gift from Genenal Electrical Company, USA. Titanium (IV) tetraisopropoxide, propylene carbonate (PC), *ter*-butylpyridine and 1-methyl-3-propylimidazolium iodine (MPII) were purchased from Acros. $Ru[L_2(NCS)_2]$ (donated as N3, L = 2,2′-bipyridine-4,4′-dicarboxylic acid) was synthesized according to the literature [18]. ZnO particles (6 nm in diameter) were obtained according to the method described by Spanhel and Anderson [19].

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1-phenyl-3-methyl-4-octadecyl-5-pyrazolone (PMOP) was synthesized as follows: 1-Phenyl-3-methyl-5-pyrazolone (PMP) (7.5 g, 0.05 mol) and 150 mL of dried 1,4-dioxane were placed in a 50-mL flask with a magnetic stirrer and heated at 70 °C for 10 min. To the resulting yellow solution, calcium hydroxide (9 g, 0.18 mol) and barium hydroxide (1 g, 0.03 mol) in small portions were added, and then the octadecyl chloride (8 mL, 0.058 mol) was added dropwise. The resulting mixture was heated to reflux for 24 h. The cloudy yellowish mixture was cooled to room temperature and poured into a stirred solution of ice-cold hydrochloric acid (350 mL of a 3 mol/L solution). The precipitated was filtered. Finally, the white solid was obtained by recrystalizing from acetone and water. Yield: 73%. ^{1}H-NMR (400 Hz, $CDCl_3$) (δ, ppm): 7.26–7.84 (5H, m, ArH), 2.73 (2H, t, CH_2), 2.48 (3H, s, CH_3), 1.74 (2H, m, CH_2), 1.24–1.43 (28H, m, $(CH_2)_{14}$), 0.88 (3H, t, CH_3).

1-Phenyl-3-methyl-4-octadecyl-5-pyrazolone (PMOP)-capped ZnO nanoparticles were synthesized according to the modified method reported for TiO_2 [20]. A portion of 0.1 g freshly prepared ZnO particles in ethanol was added to 20 mL solution of 0.15 M PMOP in a round-bottom flask. The mixture was stirred slowly for several minutes. After evaporation of the solvent, 20 mL deionized water and 50 mL of toluene were added to extract the PMOP capped ZnO nanoparticles into the organic phase. The organic phase was dried with anhydrous $CaCl_2$. The dry PMOP-capped ZnO nanoparticles was finally obtained after rotary evaporation and recrystalization.

The TiO_2 colloidal was prepared according to the literature [18]. The colloidal solution was spread uniformly on the conducting glass followed by an annealing procedure at 450 °C in air-flow for 30 min. The TiO_2 films were obtained after repeating the above procedure several times and sensitized by N3. The liquid electrolyte is composed of 0.1 M I_2, 0.1 M LiI, 0.5 M *ter*-butylpyridine and 0.6 M 1-methyl-3-propylimidazolium iodine in a mixture of PC and acetonitrile (volume ratio 1:1). An amount of ZnO nanoparticles or PMOP-capped ZnO nanoparticles (in wt.% of liquid electrolyte) were added into the liquid electrolyte to form two types of quasi-solid-state electrolytes.

^{1}H NMR spectrum was recorded on Bruker ARX400 spectrometer. The elemental analysis was performed on a Carlo Erba 1106 elemental analyzer. UV–VIS spectra were measured with a Shimadzu mode 3100UV–VIS–NIR spectrophotometer. The fluorescence spectra were observed on a Hitachi F-4500 fluorescence spectrophotometer. Steady-state voltammograms were performed on CHI 660 electrochemical workstation at 25 °C. A two-electrode electrochemical cell was used, consisting of a Pt ultramicroelectrode with a radius of 5.0 μm as working electrode and a Pt foil as counter electrode. The current–voltage (*I*–*V*) characteristics 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 and AM 1.5 direct filters in the optical path to simulate AM 1.5 direct solar irradiance. All experiments were performed at AM 1.5 direct irradiation at 100 mW/cm^2 light intensity. Paraffin wax was used to temporarily seal the solar cells for a rapid comparing the advantage of different electrolytes. After each measurement, the solar cells were kept in dark at room temperature.

Results and discussion

Characteristics of PMOP-capped ZnO nanoparticles

The schematic structure of PMOP capped ZnO nanoparticle is shown in Fig. 1 inset. The optical absorption spectra of ZnO nanoparticles and PMOP-capped ZnO nanoparticle are shown in Fig. 1. It can be seen from Fig. 1 that the absorption band of PMOP-capped ZnO particle is red-shifted in comparison with that of non-capped ZnO nanoparticle, which indicates that a dipole layer induces an attractive potential to electrons inside the ultrafine particles and leads to a reduction of the band gap of the system [21]. Similar result was observed in dodenylbenzenesufonate (DBS)-capped TiO_2 ultrafine nanoparticles [20].

IR spectrum of the free ligand PMOP exhibits the carbonyl vibration peaks at 1,626 cm^{-1} for C=O in 5-position of pyrazolone ring and 1,559 cm^{-1} for C=O in 4-acyl group, respectively. The difference of the two C=O vibration peaks is 67 cm^{-1}, that is, $\Delta v = 67$ cm^{-1}. In the case of PMOP capped ZnO nanoparticle, the former of carbonyl vibration peak shifts to higher wavenumber of 1,620 cm^{-1}, while the latter shifts to lower wavenumber of

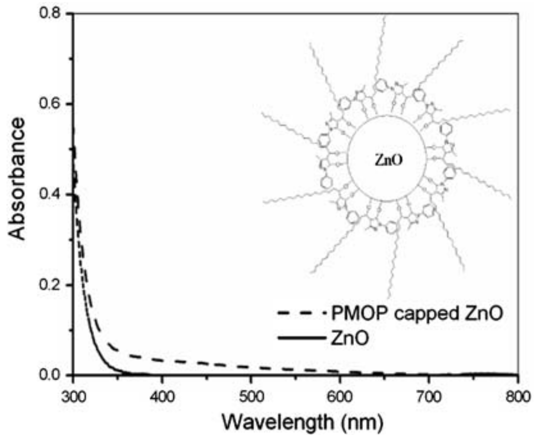

Fig. 1 Optical absorption spectra of ZnO nanoparticles in water (solid line) and PMOP-capped ZnO nanoparticles in DMF (dot line) [ZnO] = 1 mg/L; Inset: schematic diagram of PMOP–ZnO particles

1,594 cm^{-1}, that is, $\Delta\nu = 24$ cm^{-1}. The fact suggests that PMOP capped successfully onto the surface of ZnO nanoparticle and the two carbonyl groups become more uniform due to the forming of six membered ring [22].

The fluorescence spectra of free ligand PMOP, PMOP-capped ZnO nanoparticles, and Zn(PMOP)$_2$ complex were shown in Fig. 2. It can be seen from Fig. 2 that the fluorescence intensity of the ligand is very weak with a peak at 308 nm (excited with 256 nm). However, the PMOP capped ZnO nanoparticle exhibits a strong blue fluorescence peaked at 425 nm which is the same as that of Zn(PMOP)$_2$. This fact strongly supports that the ligand PMOP capped successfully onto the surface of ZnO nanoparticle.

A comparison of electrochemical properties between the different electrolytes

Steady-state voltammograms of the liquid electrolyte and the quasi-solid-state electrolyte with PMOP-capped ZnO nanoparticle (2 wt.%) are shown in Fig. 3. The curves of these two samples are nearly the same in the anodic and cathodic steady-state currents (I_{ss}). The apparent diffusion coefficients (D_{app}) of iodide and triiodide can be calculated according to the equation as follows [23]

$$I_{ss} = 4\,n\,c\,a\,F\,D_{app}, \qquad (1)$$

where *n, a, F* and *c* stand for the electron number per molecule, the microelectrode radius, the Faraday constant and the bulk concentration of electroactive species, respectively. The calculated diffusion coefficients of triiodide and iodide are 1.08×10^{-6} and 4.13×10^{-7} cm^2 s^{-1} for the liquid electrolyte, while 1.10×10^{-6} and 4.02×10^{-7} cm^2 s^{-1} for the quasi-solid-state electrolyte containing PMOP-capped ZnO nanoparticle, respectively. This fact indicates that the addition of the capped ZnO does not affect the diffusion rates of I^- and I_3^- in the experimental concentration range.

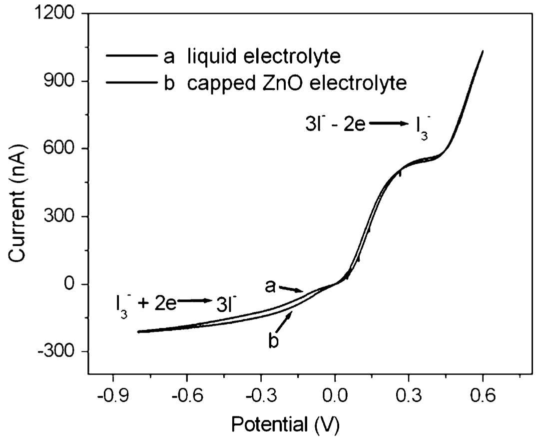

Fig. 3 Steady-state voltammograms of the liquid electrolyte and PMOP-capped ZnO quasi-solid-state electrolyte (2 wt.%) with a Pt ultra-microelectrode. Scan rate: 10 mV s^{-1}

Photoelectric conversion properties of the dye-sensitized solar cells

Figure 4 shows the photocurrent-voltage curves of DSSCs with different concentrations of PMOP-capped ZnO quasi-solid-state electrolyte at an irradiation of AM 1.5 sunlight. The device efficiencies with different electrolytes are listed in Table 1. As a comparison, the photocurrent–voltage curve of DSSC with the liquid electrolyte is also shown in Fig. 4. Data show that the open circuit voltages (V_{oc}), short photocurrent (I_{sc}) and fill factor of the cells based on PMOP-capped ZnO (1–5 wt.%) quasi-solid-state

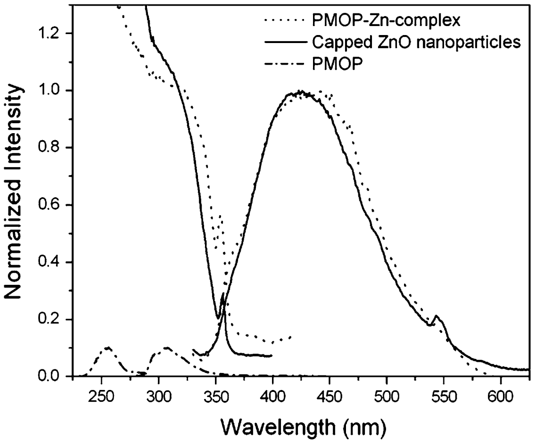

Fig. 2 Excitation and emission spectra of PMOP-capped ZnO nanoparticle, Zn(PMOP)$_2$ and PMOP ligand in CHCl$_3$. [ZnO] = 1 mg/L]

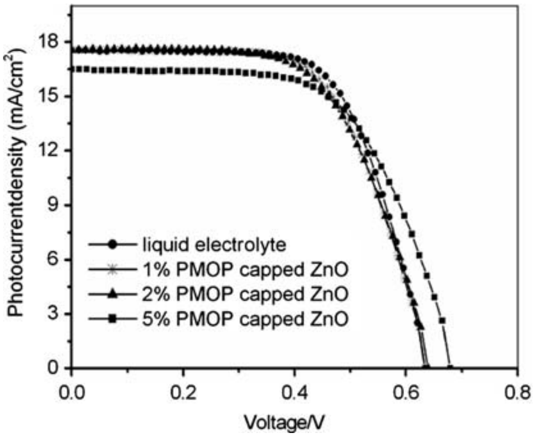

Fig. 4 Photocurrent–voltage curves of the liquid solar cells (circle) and quasi-solid-state solar cells with 1 wt.% PMOP-capped ZnO electrolyte (star), 2 wt.% PMOP-capped ZnO electrolyte (triangle) and 5 wt.% PMOP-capped ZnO electrolyte (square)

Table 1 Photoelectric conversion parameters of the solar cells with different electrolytes (under AM 1.5 illumination 100 mW/cm^2, cell active area: 0.188 cm^2)

Sample	V_{oc} (mV)	I_{sc} (mA)	FF	η (%)
Liquid electrolyte	634	17.6	0.64	7.2
1 wt.% PMOP-capped ZnO	636	17.6	0.62	6.9
2 wt.% PMOP-capped ZnO	640	17.4	0.60	6.8
5 wt.% PMOP-capped ZnO	679	16.4	0.60	6.8

electrolytes are almost the same as those of the liquid electrolyte (see Table 1). Therefore, the overall efficiencies (η) of the cells based on PMOP-capped ZnO framework (1–5 wt.%) quasi-solid-state electrolytes are comparable to that of the pure liquid electrolyte. For example, when the concentration of PMOP-capped ZnO reaches 5 wt.%, the corresponding device parameters are $V_{oc} = 679$ mV, $I_{sc} = 16.4$ mA cm^{-2}, FF = 0.60 and $\eta = 6.8\%$ (see Table 1), respectively. Compared with the liquid electrolyte, no obvious influence on the diffusion of I^-/I_3^- was observed in the electrolyte with PMOP-capped ZnO nanoparticle. Therefore, the quasi-solid-state cell exhibits a comparable efficiency to that of the liquid cell.

The stability of the dye-sensitized solar cells based on the different electrolytes

The time-course changes in the photoelectric conversion efficiency for the solar cells based on different electrolytes are shown in Fig. 5. As expected, the quasi-solid-state cells showed excellent durability comparing with the liquid solar cell. The liquid DSSC loses one thirds of photoelectric conversion efficiency after 350 h, while those of the quasi-solid-state DSSCs only reduce about 10–15%. Moreover, it can also be seen from Fig. 5 that the quasi-solid-state DSSCs based on the PMOP-capped ZnO nanoparticle framework exhibits higher stability than ZnO nanoparticle based quasi-solid-state DSSC does. For example, after 1,000 h, the former device still holds about 70% of photoelectric conversion efficiency, whereas the latter loses about half of the efficiency. Generally, ZnO nanoparticle is easily aggregated and might cause phase separation. Hence, the added ZnO nanoparticle would be deposited on the adsorbed dye attached on the TiO$_2$ film and retard the diffusion of I^-/I_3^- during the long-term operation. For the presence of octadecyl groups, PMOP capped nanoparticle may be the non-ion surfactant like PEO polymer, and can interact with itself and organic solvents. The interaction maybe result into the self-polymerization of PMOP capped ZnO nanoparticle and the formation of some channels. These channels favorite the free transportation of I^-/I_3^- and the blocking evaporation of the organic solvents. Therefore, the operation lifetime is prolonged. Earlier works have shown better stability in quasi-solid-state electrolyte by introduction of polymer into the liquid electrolytes [2, 24]. We believe that the PMOP-capped ZnO nanoparticle should behave the similar effects as polymer does.

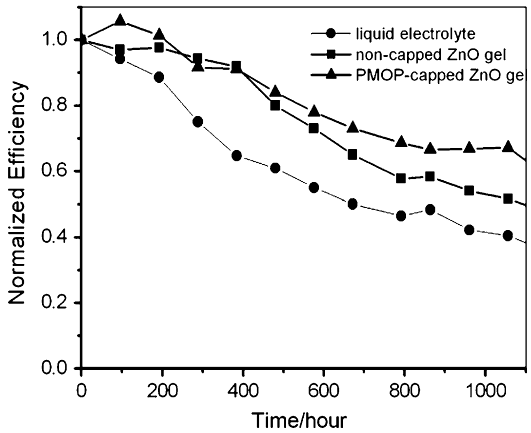

Fig. 5 Time-course change of the normalized photoelectric conversion efficiency of the liquid electrolyte (square) and quasi-solid-state solar cells with 2% PMOP-capped ZnO quasi-solid-state electrolyte (circle), ZnO quasi-solid-state electrolyte (triangle)

Conclusion

ZnO nanoparticle modified by amphiphilic β-diketone PMOP was introduced to solidify the liquid electrolyte and to form quasi-solid-state electrolytes. Such quasi-solid-state electrolytes are favorable to prolong the long-term operation lifetime because such a long alkyl-chain superstructure of PMOP capped ZnO nanoparticle offers channels for the free transportation of I^-/I_3^-. The DSSCs based on these quasi-solid-state electrolytes show comparable efficiency to that of the liquid device. We believe that such a class of amphiphilic material can cap the metal oxide nanoparticles (such as Al$_2$O$_3$, ZrO$_2$ and rare earth oxides) to form quasi-solid-state electrolytes series.

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