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Photovoltaic performance of solid-state DSSCs sensitized with organic isophorone dyes: Effect of dye-loaded amount and dipole moment

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ABSTRACT

Two isophorone sensitizers (**S4** and **D-3**) were utilized in solid-state dye-sensitized solar cells (DSSCs) using *spiro*-OMeTAD as hole-transporting material. The dye-loaded amount of **D-3** was almost 1.5 times as that of **S4** which lead to higher light harvesting efficiency than **S4**. Moreover, the larger dipole moment along the direction for **D-3** could cause more negative charges located close to the TiO_2 surface than that of **S4**, resulting in a larger conduction band (CB) upshift of TiO_2 for **D-3** which was beneficial to an increase of V_{oc}. Promising results sensitized by **D-3** in solid-state DSSCs were achieved with a short-circuit photocurrent density (J_{sc}) of 3.4 mA cm^{-2}, an open-circuit photovoltage (V_{oc}) of 760 mV, a fill factor (*FF*) of 0.71, and an overall efficiency (η) of 1.92% while ruthenium dye **N3** produced a η of 2.55% under the same conditions (AM 1.5, 100 mW cm^{-2}).

1. Introduction

Dye-sensitized solar cells (DSSCs) have attracted intense interest due to their achievements of high performance in converting solar energy to electricity at low cost [1–4]. As the critical component of DSSCs, both ruthenium complexes [5,6] and metal-free organic dyes [7–13] have been investigated as sensitizers in the past decades. The ruthenium sensitizers exhibit a high solar-to-electrical energy conversion efficiency up to 11% under AM 1.5 irradiation by using I/I_3^- liquid electrolyte. However, the application of I/I_3^- liquid electrolyte brings several problems such as iodine sublimation, degradation of organic sensitizers, and solvent evaporation and leakage that result in critical challenge in hermetic sealing. Moreover, the use of rare metals with the heavy purification brings the major problem in cost and environmental issues. Therefore, it is highly expected to replace the liquid electrolyte DSSCs with a long-life stable solid-state device sensitized by organic dyes [14–18].

As well known, solid-state DSSCs usually produce higher open-circuit photovoltage than that of liquid-electrolyte-based DSSCs due to a smaller energy loss during the dye regeneration process [1]. However, the overall conversion efficiency of solid-state device remains significantly lower than that of liquid-electrolyte-based DSSCs due to the lower short-circuit photocurrent. Accordingly in solid-state DSSCs, it is preferable to explore thin TiO_2 electrode, around 1.5–3.0 μm, to ascertain quantitative collection of the photogenerated charge carriers and complete pore filling by the hole conductor [16]. A sensitizer with high molar extinction coefficient is helpful in pursuing high light capturing capability to compensate the limitation arisen from thin nanocrystalline TiO_2 electrode in solid-state devices.

With this in mind, two isophorone sensitizers (**S4** and **D-3**) were utilized in solid-state DSSCs using *spiro*-OMeTAD (Fig. 1) as hole-transporting material (HTM) which has been demonstrated as the most successful *p*-type organic HTM due to its twisted structure with good amorphism and solubility [19]. Detailed studies based on experimental results and theoretical calculations indicate that in addition with absorption spectra and energy levels, the dye-loaded amount and dipole moment are also very predominated with photovoltaic performance in solid-state DSSCs.

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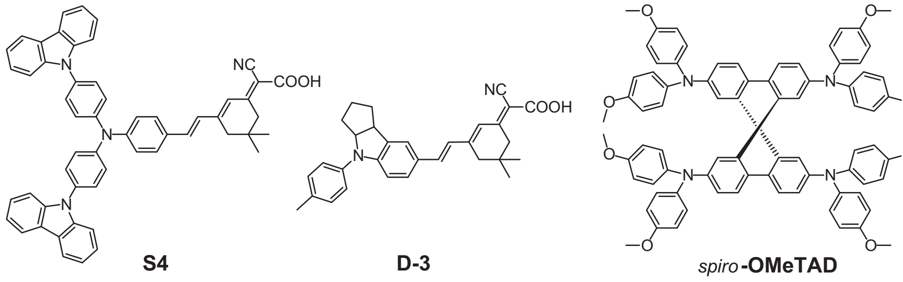

Fig. 1. Chemical structures of **S4**, **D-3**, and *spiro*-OMeTAD.

2. Experimental

The FTO conducting glass (fluorine doped SnO_2, sheet resistance <15 Ω/squire, transmission >90% in the visible) was obtained from Geao Science and Educational Co. Ltd., China. *Spiro*-OMeTAD, $Li(CF_3SO_2)_2N$ and *tert*-butylpyridine (TBP) were purchased from Aldrich. All the other solvents and chemicals with reagent grade were produced by Sinopharm Chemical Reagent Co., Ltd., China and used as received. UV–visible spectra were determined with a Varian Cary 500 spectrometer. Fluorescent spectra were recorded on Varian Cary Eclipse spectrometer. The cyclic voltammogram was determined with a Versastat II electrochemical workstation (Princeton Applied Research) using the dye-loaded TiO_2 electrode as working electrode, a Pt wire auxiliary electrode, and Ag/AgCl reference electrode in saturated KCl solution, 0.1 M tetrabutylammonium hexafluorophosphoric was used as supporting electrolyte. After the measurement, ferrocene was added as the internal reference for calibration. The dye-loaded amount was determined by desorbing the dye from surface of TiO_2 electrodes into NaOH solution and analyzed with UV–visible absorption spectrometer. The synthesis of **S4** and **D-3** were described previously [20,21].

2.1. Preparation of dye-sensitized nanocrystalline TiO_2 electrode

TiO_2 colloidal dispersion (100–150 g dm^{-3}) containing 40 wt% poly(ethylene glycol) (MW 20,000) was prepared by following the procedure reported in the literature [1] except that autoclaving was performed at 220 °C instead of 200 °C. Films of nanocrystalline TiO_2 colloidal on FTO were prepared by sliding a glass rod over the conductive side of the FTO. The thicknesses of TiO_2 film are controlled by adhesive tapes with different thickness and determined to be 1.5 μm. Sintering was carried out at 450 °C for 30 min. These films were soaked in the 0.2 M aqueous $TiCl_4$ solution overnight in a closed chamber. After washed with deionized water and fully rinsed with ethanol, the electrode was heated again at 450 °C followed by cooling to 80 °C and dipping into 0.3 mM solutions of **D-3**, **S4** and ruthenium dye **N3**, respectively, in ethanol for 12 h at room temperature. The dye-loaded nanocrystalline TiO_2 electrode was afforded after washed with ethanol and dried.

Spiro-OMeTAD was used as HTM. A solution of *spiro*-OMeTAD (0.2 M) containing *tert*-butylpyridine (TBP, 0.1 M) and $Li(CF_3SO_2)_2N$ (0.2 M) as additives is then applied on the porous dye-loaded electrode. After allowing the solution to permeate partially for 1 min, it was then spin-coated at 1500 rpm for 30 s to form the hybrid heterojunction. The counter electrode was formed by vacuum evaporation of a gold film.

2.2. Photovoltaic performance measurements and characterization of DSSCs

The photovoltaic performances of the solar cells were measured under AM 1.5 irradiation (Newport Co., Ltd., 100 mW cm^{-2}). The photocurrent action spectra were measured with a Model SR830 DSP Lock-In Amplifier and a Model SR540 Optical Chopper (Stanford Research Corporation, USA) and other optical system. The active area of solar cells were 6.0 mm^2 controlled by a metal mask. Each value was an average of three samples.

3. Results and discussion

3.1. Photophysical and electrochemical properties

The sensitizers in DSSCs always play a great important role in realizing high power conversion efficiency. Generally, the efficiency of metal-free organic DSSCs can be improved by two channels: (i) improving short-circuit photocurrent density (J_{sc}) via increasing spectral response and molar extinction coefficients; (ii) increasing open-circuit photovoltage (V_{oc}) via tuning orbital levels. Accordingly, it is very flexible in molecular designs for metal-free organic sensitizers to improve the photovoltaic properties of DSSCs. Absorption peaks (λ_{max}) in $CHCl_3$ are observed at 480 and 532 nm in visible region for **S4** and **D-3**, respectively, corresponding to the typical intramolecular charge transfer (ICT) band (Fig. 1). Their molar extinction coefficients are determined to be 2.50×10^4 M^{-1} cm^{-1} at 480 nm (S4) and 3.52×10^4 M^{-1} cm^{-1} at 532 nm (**D-3**). Obviously, the donor indoline unit can exhibit better absorption performance with respect to triphenylamine unit. As known, the nano-TiO_2 electrode used in solid-state DSSCs is very thin (1.5–3.0 μm). Thus, a higher molar extinction coefficient is preferred. When adsorbed on TiO_2, the absorption of both dyes was broadened (Fig. 2 inset) and hypsochromically shifted to different extents. In contrast, the absorption thresholds are bathochromically shifted to about 700 nm. Notably, after anchoring on 1.5 μm

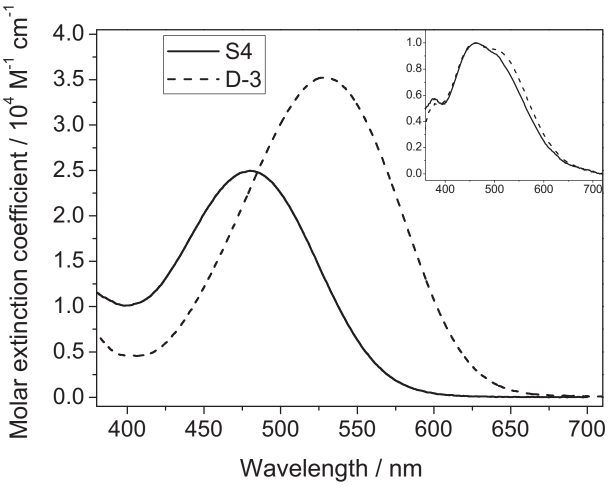

Fig. 2. Absorption spectra of **S4** and **D-3** in $CHCl_3$ and on 1.5 μm TiO_2 film (inset).