

Short communication

Novel quasi-solid electrolyte for dye-sensitized solar cells

Fujun Li, Fangyi Cheng, Jifu Shi, Fengshi Cai, Mao Liang, Jun Chen*

Institute of New Energy Materials Chemistry, Nankai University, Tianjin 300071, PR China

Received 4 November 2006; received in revised form 1 January 2007; accepted 4 January 2007

Available online 16 January 2007

Abstract

A novel alkyloxy-imidazole polymer was prepared by in situ co-polymerization of alkyloxy-imidazole and diiodide to develop an ionic polymer gel electrolyte for quasi-solid dye-sensitized solar cells (DSCs). The DSCs with the polymer gel electrolyte of 1-methyl-3-propylimidazolium iodide (MPII) showed good photovoltaic performance including the short-circuit photocurrent density (J_{sc}) of 3.6 mA cm^{-2} , the open-circuit voltage (V_{oc}) of 714.8 mV, the fill factor (FF) of 0.60 and the light-to-electricity conversion efficiency (η) of 1.56% under AM 1.5 (100 mW cm^{-2}). As a comparison, the DSCs with the polymer gel electrolyte of 1,2-dimethyl-3-propylimidazolium iodide (DMPII) yielded a light-to-electricity conversion efficiency of 1.33%. The results indicated that the as-prepared polymers were suitable for the solidification of liquid electrolytes in DSCs.

© 2007 Elsevier B.V. All rights reserved.

Keywords: Dye-sensitized solar cell; Polymer gel electrolyte; Ionic liquid; Light-to-electricity conversion efficiency

1. Introduction

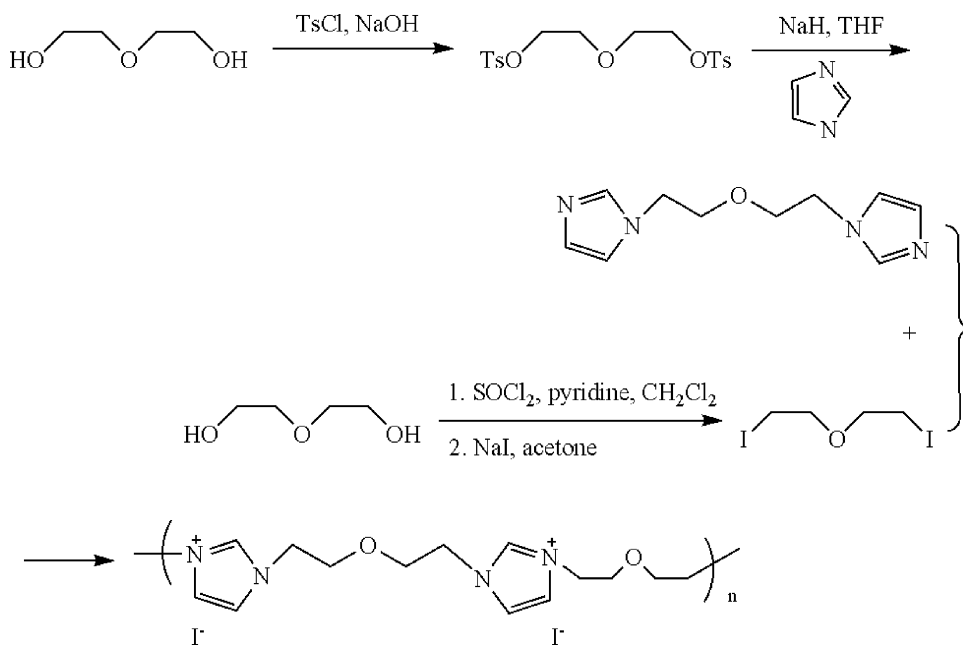
A high-energy conversion efficiency up to 11% [1] was achieved in dye-sensitized solar cells (DSCs) with an organic liquid electrolyte containing a I_3^-/I^- redox couple [2,3]. However, DSCs were confronted with poor durability, especially at high temperatures [4] because of the easy volatile and decomposing properties of the organic liquid electrolyte. Subsequently, the assembly of DSCs needs the sealing process, which results in a critical technical problem for the long-time practical applications. Upon pursuing a long-term stable and efficient electrolyte, considerable attempts have been made in replacing the liquid electrolytes with solid or quasi-solid state electrolytes, such as plastic crystal electrolytes [5,6], p-type semiconductors [7–9], organic hole-transfer conductors [10], solid polymer electrolytes [11] and polymer gel electrolytes [12–14].

In contrast with the organic liquid counterparts, the solid-state electrolytes show the disadvantage of low light-to-electricity conversion efficiency, owing to the low ionic conductivity and poor electrolyte/electrode interfacial contact [4]. To solve these issues, scientists have prepared solid polymer electrolyte doped

with different inorganic materials (e.g., SiO_2 [4], TiO_2 [11], etc.) and developed polymer gel electrolytes (or quasi-solid electrolytes). In particular, DSCs with polymer gel electrolytes by in situ polymerization methods were expected to obtain comparable conversion efficiencies. Polymer gel electrolytes can be gelled in the cell directly after being heated up. This made it possible to improve the physical contact between the polymer gel electrolyte and the TiO_2 electrode [15], and subsequently the conversion efficiencies. Recently, Yanagida and coworkers [16] have prepared a new alkyl-imidazole polymer gel electrolyte for DSCs by in situ polymerization, and its energy conversion efficiency reached 1.3% under a light intensity of 100 mW cm^{-2} (AM 1.5). Hayase's group has also investigated a quasi-solid polymer electrolyte via the copolymerization of polyvinylpyridine and tetrabromomethylbenzene directly in the cells [15,17]. In addition, Wang et al. [14] have reported the quasi-solid-state DSCs by in situ polymerization of gel electrolyte.

Ethylene oxide chains in polymers can effectively improve the interaction between TiO_2 film and polymer electrolytes and the ion-dissociation provides excellent redox charge-transport properties [11,14]. On the other hand, an alkyl-imidazole polymer gel electrolyte with conversion efficiency of 1.3% has been reported [16]. Herein, we substituted the alkyl chains in alkyl-imidazole polymer with ethylene oxide chains. The conversion efficiencies of DSCs with alkyloxy-imidazole polymer gel elec-

* Corresponding author. Tel.: +86 22 23506808; fax: +86 22 23509118.
E-mail address: chenabc@nankai.edu.cn (J. Chen).



Scheme 1. Synthetic route to alkyloxy-imidazole co-polymer.

trolytes encapsulating 1-methyl-3-propylimidazolium iodide (MPII) and 1,2-dimethyl-3-propylimidazolium iodide (DMPII) reached 1.56 and 1.33% under AM 1.5 (100 mW cm⁻²), which were both over that reported by Yanagida and coworkers [16]. It is convinced that the design of alkyloxy-imidazole polymer is successful and there is still much room for the improvement of the conversion efficiency of the DSC based on the as-synthesized polymer.

2. Experimental

2.1. Synthesis of

1,1'-(2,2'-oxybis(ethane-2,1-diyl))bis(imidazole) (**1**) and diethylene glycol diiodide (**2**)

1 was prepared according to Ref. [18]. The brief synthetic route was shown in Scheme 1. In a typical synthesis, SOCl₂ was added dropwise into the mixed solution of diethylene glycol, pyridine, and CH₂Cl₂ at 40 °C. After refluxing for 12 h, the mixture was treated with concentrated HCl and washed several times to separate the oil layer that was first concentrated under reduced pressure and then subjected to column chromatography on silica gel (eluent: petroleum ether). The purity of the product was confirmed by ¹H NMR. ¹H NMR (300 MHz; CCl₃D): δ (ppm) 7.49 (s; 2 H); 7.04 (s; 2 H); 6.88 (s, 2 H); 4.07 (t, 4 H); 3.64 (t, 4 H). To yield **2**, pure product **1** and anhydrous NaI with the molar ratio of 1:1.5 were stirred in acetone at 60 °C for 48 h. ¹H NMR (300 MHz; CCl₃D): δ (ppm) 4.07 (t, 4 H); 3.64 (t, 4 H).

2.2. Preparation of electrolytes

The liquid electrolyte was composed of 0.6 M MPII or DMPII, 0.05 M I₂, 0.1 M LiI, and 0.5 M 4-tert-butylpyridine

(TBP) in 3-methoxypropionitrile (MPN). A 30 wt% of **1** and **2** with the molar ratio of 1:1 was dissolved in the liquid electrolyte to give a homogeneous solution, which was heated up to 80 °C to accelerate the polymerization reaction of **1** and **2** (Scheme 1). After 1 h, a polymer gel electrolyte was obtained.

2.3. The assembly of DSCs

The nanocrystalline TiO₂ electrode [19] was fabricated by depositing TiO₂ colloidal paste (P25, Degussa) on a F-doped SnO₂ conducting glass substrate (FTO, 10 Ω sq⁻¹) using a screen-printing technique. Then, the coated substrate was treated with 50 mM of TiCl₄ solution and sintered at 450 °C in air for 0.5 h to obtain nanoporous TiO₂ film that has the thickness of about 10 μm. The TiO₂ thin film was immersed into an ethanol solution, which was composed of 0.3 mM dye cis-dithiocyanate-*N,N'*-bis(4,4'-dicarboxylate-2,2'-bipyridine)ruthenium(II) (N3), for about 12 h. The Pt counter electrode was prepared by spin-coating H₂PtCl₆ solution (50 mM in isopropanol) onto FTO glass and sintered at 390 °C for 0.5 h. Liquid electrolyte containing 30 wt% of **1** or **2** was dropped onto the sensitized TiO₂ electrode and then clamped a Pt counter electrode with two clips to form the DSC.

2.4. Instrument and measurement

¹H NMR spectra were obtained using a Varian Mercury 300 NMR. The precursors of polymer gel electrolyte containing liquid electrolytes were sandwiched by two identical platinized conducting glasses, and then heated to gel in situ to supply the samples for determining the ionic conductivity and the apparent diffusion coefficient of I₃⁻. Both cyclic voltammograms (CV) and electrochemical impedance spectroscopy (EIS) were carried out on a Princeton 2273 electrochemical work station at room

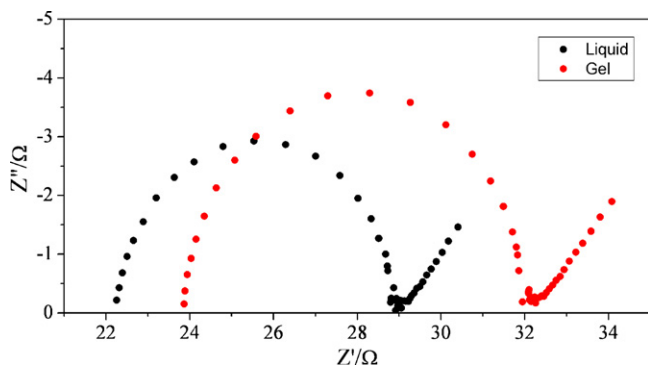


Fig. 1. Nyquist diagram of electrochemical impedance spectra of MPII liquid and polymer gel electrolytes.

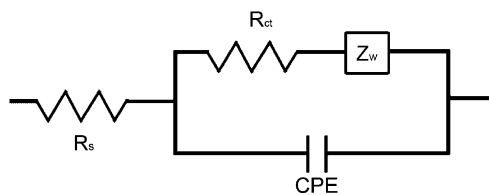


Fig. 2. Equivalent circuit for the impedance spectra in Fig. 1.

temperature with electrode area of 1 cm^2 and over frequency ranging from 0.1 Hz to 10 kHz. Photocurrent–voltage characteristics were measured by using a digital source meter (Keithley Instruments Inc., Model 2400) under 100 and 60 mW cm^{-2} illumination of a sunlight simulator (500 W xenon lamp, AM 1.5). The active area of the TiO_2 electrode is 0.16 cm^2 .

3. Results and discussion

3.1. Ionic conductivity

Fig. 1 shows the typical electrochemical impedance spectra of the MPII based liquid and the corresponding polymer gel electrolyte obtained at room temperature. Both of the impedance spectra consist of a semicircle at the high frequency region of the spectra and an inclined straight line rising with the slope angle of approximately 45° after the arc, related to the reaction at Pt/electrolyte interfaces and the diffusion process of species in the electrolytes, respectively. The equivalent circuit given in Fig. 2 was used for the curve fitting of the impedance of the electrolytes and the parameters obtained by fitting the experimental spectra with the equivalent circuit are shown in Table 1. R_s is the serial resistance that consists of the resistance of the electrolyte and the sheet resistance of the FTO films; R_{ct} is the charge-transfer resistance of the electrochemical reaction between the two Pt/electrolyte interfaces; CPE the constant phase element

Table 1
Parameters obtained by fitting the experimental spectra with the equivalent circuit in Fig. 2, at 25°C

	R_s (Ω)	R_{ct} (Ω)	Y_0 ($\mu\text{F s}^{n-1}$)	Z_w (Ω)	n
Liquid	22.3	6.6	17.2	0.5	0.86
Gel	23.9	8.2	13.5	0.4	0.88

whose admittance is expressed by the equation, $Y_Q = Y_0(j\omega)^n$, where n is a constant ranging from 0 to 1; Z_w is the finite-length Warburg diffusion impedance.

As shown in Table 1, the value of R_s for the MPII based polymer gel electrolyte is a little larger than that of MPII based liquid electrolyte, from which the conductivities are determined to be about 0.73 and 0.79 mS cm^{-1} , respectively. With respect to that of the MPII based liquid electrolyte, the R_{ct} of the polymer gel electrolyte, the indicator of the charge-transfer kinetic performance at the interface between the electrolyte and the platinum counter electrode, increases by 1.6Ω , about 24% of the liquid electrolyte. This indicates that more energy loss on the counter electrode for the reduction of I_3^- to I^- in the quasi-solid DSC would be necessitated. An error of about 10% was estimated for the values of Y_0 and Z_w fitting with the equivalent circuit (in Fig. 2). Under experimental error, Y_0 and Z_w can only be used for qualitative analysis. Y_0 values in both electrolytes are very closing, showing that the interfaces between the Pt/polymer gel electrolyte by a co-polymerization method are established in good condition because the 1-methyl-3-propylimidazolium cations on Pt counter electrodes almost gets saturated. The values of Z_w are correlated to the diffusion coefficients of I^- and I_3^- , the exact values of which are given in the following section.

3.2. Electrochemical measurement of the apparent diffusion coefficients of I_3^-

Fig. 3 presents the characteristic linear sweep voltammetry curves of the MPII based liquid electrolyte and the corresponding polymer gel electrolyte, in which the limiting current of the MPII based liquid electrolyte is nearly three times that of the polymer gel electrolyte. The resemblance between the anodic and cathodic limiting current plateaus indicates steady-state conditions. Herein, the triiodide ions (the molar ratio of I^- to I_3^- is 10:1) are the current-limiting species, and its diffusion coefficient can be determined by the current-limited measurement on the symmetrical FTO/Pt/electrolyte/Pt/FTO electrochemical cells.

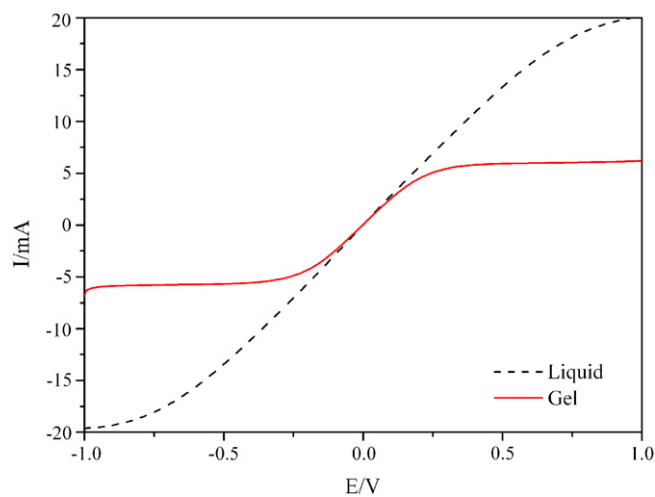


Fig. 3. Characteristic linear sweep voltammograms for the symmetrical electrochemical cells with the cell separation of $45 \mu\text{m}$ and surface area of 1.0 cm^2 filled with the MPII based liquid and polymer gel electrolytes. Scan rate: 10 mV s^{-1} .

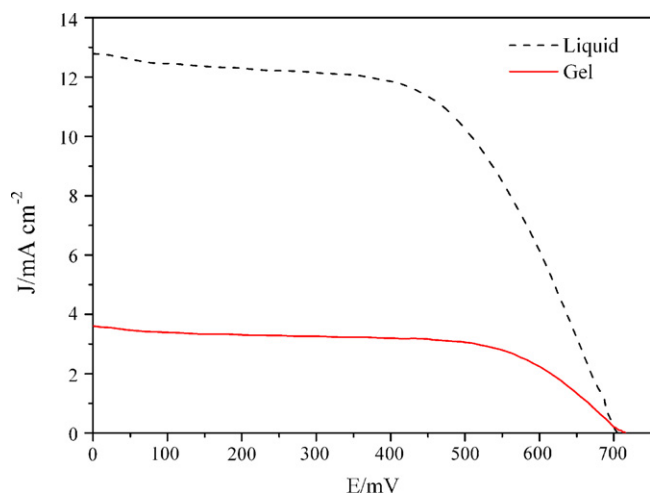


Fig. 4. Photocurrent density–voltage characteristics of DSCs incorporated with the MPII based liquid and polymer gel electrolytes under the illumination of 100 mW cm^{-2} (AM 1.5). Cell active area: 0.16 cm^2 .

Consequently, only the apparent diffusion coefficient (D_{app}) of triiodide ions can be calculated from the limiting current densities (J_{lim}) according to the following equation [20]:

$$J_{\text{lim}} = \frac{2nFC_0D_{\text{app}}}{d} \quad (1)$$

where $n=2$ is the electron-transfer number required for the reduction of triiodide to iodide, C_0 the bulk concentration of the triiodide ions, d the thickness of the cell and F the Faraday constant.

The apparent diffusion coefficient of triiodide in the MPII based polymer gel electrolyte at room temperature was calculated to be $1.4 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$, which was roughly one third that of the MPII based liquid electrolyte ($4.7 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$). The decrease in I_3^- diffusion coefficient of the polymer gel electrolyte was induced by the gelation of the MPII based liquid electrolyte, which restricted the free motion of I_3^- in the channel of polymer gel electrolytes. Therefore, the difference in I_3^- diffusion coefficient for the MPII liquid and polymer gel electrolytes will correspond to the changes between J values of solar cells, due to the current-limiting species of I_3^- in the system of electrolytes.

3.3. Photovoltaic performance

The typical photocurrent density–voltage curves for the cells with the liquid and polymer gel electrolytes at a light intensity of 100 mW cm^{-2} , AM 1.5, are presented in Fig. 4. The conversion efficiency (1.56%) and short-circuit photocurrent density (J_{sc} , 3.63 mA cm^{-2}) of the DSC assembled with MPII based polymer gel electrolyte is lower than that of the DSC with corresponding liquid electrolyte, but the open-circuit voltage (V_{oc} , 714.8 mV) is higher. The decrease in the J_{sc} (Fig. 4) of DSC with polymer gel electrolyte mainly originates from the lowered I_3^- diffusion coefficients, which reduce the supply of I_3^- to the counter electrode, retard the regeneration of N_3 [10], and

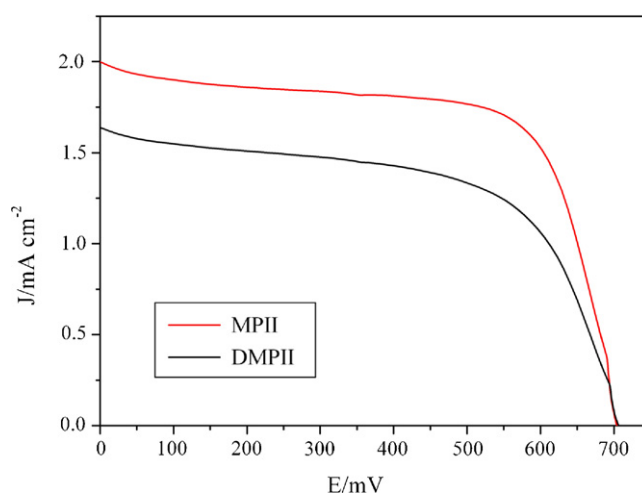


Fig. 5. Photocurrent density–voltage characteristics of DSC incorporated with the MPII and DMPII based polymer gel electrolyte under the illumination of 60 mW cm^{-2} (AM 1.5).

subsequently induce the recombination of the injected electrons with the oxidized dye; on the other hand, the ionic conductivity of the polymer gel electrolyte is comparable to the corresponding liquid electrolyte. The slight increase of V_{oc} for the DSC with polymer gel electrolyte may result from the composition of the polymer (Scheme 1). When the co-polymerization of precursors occurs in the cells, the polymer chains containing hydrophilic oxygen atoms may be physically adsorbed onto the surface of dye-anchored TiO_2 . Thus, the polymer contacting the surface of TiO_2 suppresses the back electron-transfer reaction from the conduction band of TiO_2 electrode to the I_3^- in the polymer gel electrolyte, resulting in a higher V_{oc} value [21].

The power irradiation is also an important factor to the conversion efficiencies of DSCs. To explore the best conversion efficiency, the DSC with the MPII based polymer gel electrolyte was subjected to the illumination of 60 mW cm^{-2} , AM 1.5 and the typical photocurrent–voltage curve was presented in Fig. 5. A conversion efficiency of 1.59% was obtained, a little larger than that measured at 100 mW cm^{-2} (1.56%). This may be caused by the limitation in mass transport such as I_3^- in the polymer gel electrolyte for DSCs at a high light intensity, that is, when the light intensity is increased, a large current density passing through the DSCs is necessitated.

To further investigate the ability of the synthesized alkyloxyimidazole polymer of the solidification of liquid electrolytes, DMPII based polymer gel electrolyte was also employed as the electrolyte of the DSC. Under the same determination condition, V_{oc} , J_{sc} , FF and η of the DSC with the DMPII based gel electrolyte in Fig. 5 reached 715.93 mV , 1.85 mA cm^{-2} , 0.66 , 1.47% , respectively, which are close to the corresponding values of MPII based gel electrolyte. For comparison, the conversion efficiencies of DSCs with MPII and DMPII liquid electrolytes were measured to be 5.22% and 5.78% , respectively, which are lower than that reported in Refs. [22,23]. These features indicate that TiO_2 porous films in our experiment are not well optimized, in other words, increased photovoltaic performance is expected

by optimizing the porosity, thickness and roughness of TiO₂ films. Further work on optimizing the TiO₂ porous properties and the DSCs' stability is under way.

4. Conclusions

A novel alkyloxy-imidazole polymer was prepared and successfully utilized to encapsulate MPII and DMPII based liquid electrolytes for DSCs by in situ co-polymerization. The energy conversion efficiencies of DSCs with MPII and DMPII liquid electrolyte based polymer gel electrolytes are 1.56% and 1.33%, respectively. Although the energy conversion efficiencies are still low in comparison with their liquid counterparts, they are free of strict sealing problem and their photovoltaic performance might be further improved by optimizing the TiO₂ films and the composition of the polymer gel electrolytes, indicating their potential application in the solidification of liquid electrolytes for DSCs.

Acknowledgements

This work was supported by the National NSFC (20325102) and 973 Program (2005CB623607).

References

- [1] M. Grätzel, J. Photochem. Photobiol. A 164 (2004) 3–14.
- [2] B. O'Regan, M. Grätzel, Nature 353 (1991) 737–740.
- [3] K. Hara, T. Nishikawa, K. Sayama, K. Aika, H. Arakawa, Chem. Lett. 32 (2003) 1014–1015.
- [4] H.X. Wang, H. Li, B.F. Xue, Z.X. Wang, Q.B. Meng, L.Q. Chen, J. Am. Chem. Soc. 127 (2005) 6394–6401.
- [5] P. Wang, Q. Dai, S.M. Zakeeruddin, M. Forsyth, D.R. MacFarlane, M. Grätzel, J. Am. Chem. Soc. 126 (2004) 13590–13591.
- [6] Q. Dai, D.R. MacFarlane, P.C. Howlett, M. Forsyth, Angew. Chem. Int. Ed. 44 (2005) 313–316.
- [7] Q.B. Meng, K. Takahashi, S.T. Zhang, I. Sultano, T.N. Rao, O. Sato, A. Fujishima, Langmuir 19 (2003) 3572–3574.
- [8] G.R.A. Kumara, A. Konno, K. Shiratsuchi, J. Tsukahara, K. Tennakone, Chem. Mater. 14 (2002) 954–955.
- [9] V.P.S. Perera, P.K.D.D.P. Pitigala, P.V.V. Jayaweera, K.M.P. Bandaranayake, K. Tennakone, J. Phys. Chem. B 107 (2003) 13758–13761.
- [10] U. Bach, D. Lupo, P. Comte, J.E. Moser, F. Weissortel, J. Salbeck, H. Spenitser, M. Grätzel, Nature 395 (1998) 583–585.
- [11] T. Stergiopoulos, M.A. Loannis, G. Katsaros, P. Falaras, Nano Lett. 2 (2002) 1259–1261.
- [12] D.W. Kima, Y.B. Jeong, S.H. Kima, D.Y. Lee, J.S. Song, J. Power Sources 149 (2005) 112–116.
- [13] X. Zhang, H. Yang, H.M. Xiong, F.Y. Li, Y.Y. Xia, J. Power Sources 160 (2006) 1451–1455.
- [14] L. Wang, S.B. Fang, Y. Lin, X.W. Zhou, M.Y. Li, Chem. Commun. (2005) 5687–5689.
- [15] Y. Shibata, T. Kato, T. Kado, R. Shiratuchi, W. Takashima, K. Kaneto, S. Hayase, Chem. Commun. (2003) 2730–2731.
- [16] K. Suzuki, M. Yamaguchi, S. Hotta, N. Tanabe, S. Yanagida, J. Photochem. Photobiol. A 164 (2004) 81–85.
- [17] S. Sakaguchi, H. Ueki, T. Kato, T. Kado, R. Shiratuchi, W. Takashima, K. Kaneto, S. Hayase, J. Photochem. Photobiol. A 164 (2004) 117–122.
- [18] X.R. Gu, R.G. Xie, M.S. Cai, Synthetic Commun. 29 (1999) 1217–1222.
- [19] F.S. Cai, J. Chen, R.S. Xu, Chem. Lett. (2006) 1266–1267.
- [20] A.G. Kontos, M. Fardis, M.I. Prodromidis, T. Stergiopoulos, E. Chatzivasiloglou, G. Papavassiliou, P. Falaras, Phys. Chem. Chem. Phys. 8 (2006) 767–776.
- [21] R. Komiya, L. Han, R. Yamanaka, A. Islam, T. Mitate, J. Photochem. Photobiol. A 164 (2004) 123–127.
- [22] P. Wang, S.M. Zakeeruddin, P. Comte, I. Exnar, M. Grätzel, J. Am. Chem. Soc. 125 (2003) 1166–1167.
- [23] P. Wang, S.M. Zakeeruddin, J.E. Moser, M.K. Nazeeruddin, T. Sekiguchi, M. Grätzel, Nat. Mater. 2 (2003) 402–407.