## Journal of Materials Chemistry

Cite this: J. Mater. Chem., 2012, 22, 18380

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# Efficient light-scattering functionalized TiO<sub>2</sub> photoanodes modified with cyanobiphenyl-based benzimidazole for dye-sensitized solar cells with additive-free electrolytes<sup>†</sup>

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*Received 25th April 2012, Accepted 20th July 2012* DOI: 10.1039/c2jm32607h

Light-scattering functionalized cyanobiphenyl-based benzimidazole was synthesized and applied in the surface modification of dyed TiO<sub>2</sub> photoanodes for dye-sensitized solar cells (DSSCs). DSSCs based on the ionic liquid and all-solid-state electrolytes were fabricated and characterized, without the addition of additives in the electrolytes. Compared with electrolytes containing the additive *N*-butylbenzimidazole (NBB), surface modification of dyed TiO<sub>2</sub> photoanodes with cyanobiphenyl-based benzimidazole could enhance the values of the open-circuit photovoltage ( $V_{oc}$ ), short-circuit photocurrent density ( $J_{sc}$ ) and the overall PCE of the fabricated DSSCs, due to the suppressed charge recombination rate, the conductivity optimization of the electrolytes and enhanced light harvesting capability at the TiO<sub>2</sub> photoanode/electrolyte interface. Under the simulated air mass 1.5 solar spectrum illuminations at 100 mW cm<sup>-2</sup>, the fabricated devices achieved a cell efficiency of ~6.63% and ~5.82% for ionic liquid and all-solid-state electrolytes, respectively. These results provide an alternative strategy for high performance DSSCs with additive-free electrolytes.

#### Introduction

Much attention has been paid to dye-sensitized solar cells (DSSCs), owing to their advantages of simple assembly technology, high power conversion efficiency (PCE), and relatively low manufacturing cost.<sup>1-3</sup> Recently, a PCE over 12% (13.1% at 0.5 Sun) has been achieved by Yella and coworkers using a cobalt(II/III)-based tris(bipyridyl)tetracyanoborate complex as the redox mediator in combination with a custom synthesized donor-*m*-bridge-acceptor zinc porphyrin dye YD2-o-C8 and another organic cosensitizer Y123.3 In a DSSC device, photoexcitation of the monolayer sensitizer coated on the TiO<sub>2</sub> films enables the injection of electrons into the conduction band of the oxide. The electrons cross the films and are collected by a charge collector into the external current circuit, and then return to the device through the counter electrode. The complete separation of the functions of light absorption, electrons and holes transfer allows much more favorable materials selectivity and optimization.<sup>3</sup> However, the key point for efficiency enhancement is to

restrain the interfacial electron-hole recombination. The additives added in the electrolytes have been considered as one of the most important components, with which significant improvement in the photovoltaic parameter of the DSSCs could be achieved.4-6 The influence of electrolyte additives, including 4tert-butylpyridine (TBP),7 N-alkylbenzimidazole,8,9 benzimidazolyl functionalized ionic liquids,<sup>10</sup> and other alkylpyridines or N-heterocyclic compounds<sup>4</sup> has been extensively studied. In general, N-heterocycles could be effectively attached to the TiO<sub>2</sub> surface via the N-Ti4+ interaction, and shift the conduction band edge of TiO<sub>2</sub> toward higher energies and retard the interfacial electron recombination to increase the electron life time.4,7,11,12 Therefore, these additives could give significant improvement of the DSSCs with the high open-circuit photovoltage  $(V_{oc})$ , fill factor (FF), and the high PCE.7 Actually, addition of the additive generally decreases the conductivity of the electrolytes and the diffusion coefficients of the redox mediator species containing the redox couples (such as  $I^{-}/I_{3}^{-}$ ), resulting in a decrease of short-circuit photocurrent density  $(J_{sc})$ .<sup>13,14</sup> Therefore, optimization of the electrolytes with high conductivity and diffusion coefficients of redox mediator species, however, without any additives, is highly desirable for the DSSCs.

In addition, surface passivation of TiO<sub>2</sub> photoanodes by carefully optimizing and controlling the thickness of an ultrathin insulator layer, such as metal oxide,<sup>15,16</sup> carbonates,<sup>17</sup> organic silane<sup>18</sup> or poly(methylsiloxane)<sup>19</sup> has been applied to improve the performance in DSSCs.<sup>4,15–20</sup> Recently, dendrons<sup>21</sup> and metal–organic frameworks (MOFs)<sup>22</sup> coated on TiO<sub>2</sub>

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<sup>†</sup> Electronic supplementary information (ESI) available: Additional tables. See DOI: 10.1039/c2jm32607h

photoanodes also effectively enhance the device performance of DSSCs. Co-adsorbants, such as phosphonic acid and bis-(3,3-dimethy-butyl)-phosphinic acid<sup>23</sup> and donor-acceptor type molecules,<sup>24</sup> can also be applied for the surface modification of TiO<sub>2</sub> photoanodes to assist favourable packing of dye molecules by avoiding aggregation.<sup>4</sup> These surface passivation methods could suppress the electron recombination.

Due to their unique properties, cvanobiphenvl based liquid crystals (LCs) have been extensively studied and used as optical materials, such as in non-linear materials,25,26 display and photonic devices,<sup>27,28</sup> chemical and biological sensors.<sup>29,30</sup> The special and orientational direction of molecules at the molecular level and particular 3D network could provide effective pathways for the electroactive species to move freely.<sup>31,32</sup> In addition, they exhibit a wide transparency range with an optical absorption,23,24 and light-scattering properties.33-35 Recently, the cyanobiphenyl-functionalized liquid crystal-based electrolytes have been used as the electrolytes with light-scattering properties for DSSCs. Photoelectrodes with enhanced light-harvesting properties could improve the device efficiency.36 However, the extra additives in the electrolytes are still indispensable even in these cases. This triggered our interest in exploring the possibility to fabricate the DSSCs with additive-free in electrolytes.

Here, for the first time, cyanobiphenyl-based benzimidazole was synthesized and applied for the surface modification of TiO<sub>2</sub> photoanodes to increase the light-harvesting efficiency of photoanodes. DSSCs based on the surface modified TiO<sub>2</sub> photoanodes, using ionic liquid and all-solid-state electrolytes were fabricated, without the addition of any other additives in the electrolytes. Photovoltaic measurements show that cyanobiphenyl-based benzimidazole modified TiO2 photoanodes could enhance the  $V_{\rm oc}$ ,  $J_{\rm sc}$  and the overall PCE values of the fabricated DSSCs, due to the suppressive charge recombination rate, the conductivity optimization of the electrolytes and enhanced light harvest capability at the TiO<sub>2</sub> photoanode/electrolyte interface. Such an alternative strategy of surface modification of TiO<sub>2</sub> photoanodes for the DSSCs with additive-free electrolytes could be applied to the most DSSCs to achieve high device performances.

#### **Experimental procedure**

#### Materials

Benzimidazole, 1,6-dibromohexane, 4-cyano-4'-hydroxybiphenyl, tert-butyl alcohol and succinonitrile were purchased from Alfa Aesar and used as received. N-butylbenzimidazole (NBB) and iodine (I<sub>2</sub>) were purchased from Fluka. TiCl<sub>4</sub> and  $H_2PtCl_6$  were purchased from Aldrich. *cis*-RuLL'(SCN)<sub>2</sub> (L = 4,4'-dicarboxylic acid-2,2'-bipyridine, L' = 4,4'-dinonyl-2,2'bipyridine) (Z907) was purchased from Solaronix SA (Switzerland) and used without any further purification. Fluorine-doped tin oxide overlayer (FTO) glass electrodes (15  $\Omega$  per Sq), slurries containing 20 nm-sized mesoporous and 200 nm-diameter lightscattering TiO<sub>2</sub> colloidal were purchased from Dalian Hepat Chroma Solar Tech. Co., Ltd (China). 1,3-Dimethylimidazolium iodide (DMII), 1-ethyl-3-methylimidazolium iodide (EMII), 1ethyl-3-methylimidazolium tetracyanoborate (EMITCB) and guanidinium thiocyanate (GSCN) were purchased from Merck.

*N*-Methyl-*N*-butylpyrrolidinium iodide  $(P_{1,4}I)$  was synthesized and purified as described in the literature.<sup>37</sup>

#### Synthesis of 1-bromo-6-(4-cyanobiphenyl-4'-oxy)hexane (BrCH)

BrCH was synthesized by the reaction of 4-cyano-4'-hydroxybiphenyl (3.90 g, 20 mmol) with a large excess of 1,6-dibromohexane (12.20 g, 50 mmol) in dry acetone (100 mL) with potassium carbonate (13.80 g, 100 mmol) as a base.<sup>38</sup> <sup>1</sup>H NMR (400 MHz, CDCCl<sub>3</sub>): 7.60–7.72 (m, 4H), 7.53 (d, 2H), 6.98 (d, 2H), 4.0 (t, 2H), 3.43 (t, 2H), 1.91 (m, 2H), 1.83 (m, 2H) 1.53 (m, 4H). Formula mass: 358.27. Microanalysis Calcd: C, 63.69%; H, 5.64%; N, 3.91%. Found: C, 63.61%; H, 5.72%; N, 3.80%.

### Synthesis of *N*-6-(4-cyanobiphen-yl-4'-oxy)hexyl benzimidazole (NCHB)

To a stirred solution containing benzimidazole (1.42 g, 12 mmol) and BrCH (3.58 g, 10 mmol) in 20 mL of dry acetonitrile, ground powered KOH (1.40 g, 25 mmol) was added.<sup>7</sup> After stirring for 8 h at 0 °C, the mixture was washed with acetonitrile and then poured into water (100 mL), and finally extracted by dichloro-ethane (50  $\times$  3 mL). White powder, 2.94 g (yield: 74.3%). <sup>1</sup>H NMR (400 MHz, CDCCl<sub>3</sub>): 7.90 (s, 1H), 7.82 (d, 1H), 7.60–7.70 (dd, 4H), 7.52 (d, 2H), 7.41 (d, 1H), 7.24–7.34 (m, 2H), 6.96 (d, 2H), 4.20 (t, 2H), 3.97 (dd, 2H), 1.72–2.02 (m, 4H), 1.35–1.62 (m, 4H). Formula mass: 395.5. Microanalysis Calcd: C, 78.95%; H, 6.38%; N, 10.63%. Found: C, 78.83%; H, 6.47%; N, 10.58%.

#### **Device fabrication**

The fabrication of DSSCs was as reported previously.<sup>39,40</sup> In brief, the cleaned FTO glass was covered at two parallel edges with an adhesive tape to control the thickness of mesoporous TiO<sub>2</sub> film. Two layers of TiO<sub>2</sub> particles were deposited onto cleaned FTO glass and used as photoelectrodes. A 10 µm thick film of 20 nm sized TiO<sub>2</sub> particles was deposited onto the FTO glass electrode using the doctor-blade technique. The film was dried at 125 °C for 5 min. Then, a second 5 µm thick layer of 200 nm light-scattering anatase particles were coated on the top of the first TiO<sub>2</sub> layer. The resulting TiO<sub>2</sub> films were annealed at 500 °C for 15 min. After cooling to 80 °C, the obtained TiO<sub>2</sub> electrode was immersed in 0.3 mM solution of Z907 in acetonitrile and tert-butyl alcohol at room temperature for 24 h. Afterward, the dye-sensitized TiO<sub>2</sub> electrode was washed with anhydrous ethanol and dried with nitrogen stream. To prepare the Pt counter electrode, two drops of 5 mM H<sub>2</sub>PtCl<sub>6</sub> in ethanol was placed onto the cleaned FTO glass substrate, followed by drying and annealing at 400 °C for 15 min.

Before the device fabrication of Devices C, D and G, 50  $\mu$ L of 0.3 M NCHB (or NBB) solution in acetonitrile/dichloroethane (10 : 1, v : v) was filled into the porous dye-coated TiO<sub>2</sub> photo-anode. Then the solvent was evaporated under vacuum at 80 °C.

DSSCs were fabricated by sandwiching the completely melted electrolyte (80–100 °C) between a dye-sensitized TiO<sub>2</sub> electrode and a pre-drilled Pt counter electrode by a 25  $\mu$ m hot melt ring (Surlyn, DuPont). The resulting cells were placed at 80 °C in a vacuum to remove air and guarantee optimum filling and fine electrical contact. The produced devices were sealed with a Surlyn sheet and a thin glass cover by heating. The employed electrolyte for Devices

A, C and D contains DMII/EMII/EMITCB/I<sub>2</sub>/GSCN (12:12:16:1.67:0.67), without NBB. While the reference electrolyte used for Devices B contains DMII/EMII/EMITCB/I<sub>2</sub>/NBB/ GSCN (12:12:16:1.67:3.33:0.67), with NBB.<sup>9</sup> The reference all-solid-state electrolytes for Devices E and G are composed of  $P_{1,4}I : I_2$ : succinonitrile (5:1:100),<sup>39</sup> and with an additional 0.5 M NBB in the electrolyte for Device F.

#### Characterization and measurements

<sup>1</sup>H NMR spectra were recorded on a Varian 400 MHz spectrometer. The conductivity of electrolytes was characterized in an ordinary cell composed of a Teflon tube and two identical stainless steel electrodes (diameter of 1 cm) on a CHI660c electrochemical workstation at room temperature. Fourier transform infrared (FTIR) spectra of the synthesized compounds were recorded on a Varian CP-3800 spectrometer in the range of 4000-400 cm<sup>-1</sup>. Absorption spectra of NCHB and the transmittance of the dyed TiO<sub>2</sub> films without and with NCHB (illuminated from the FTO side) were observed with a UV Lambda 750 UV-vis/ NIR spectrometer in the range of 350-800 nm. While, the reflectance of the dyed TiO<sub>2</sub> films without and with NCHB (illuminated from the NCHB side) were recorded on the same spectrometer equipped with barium sulfate-coated integrating sphere. Thermal analysis was carried out on Universal Analysis 2000 thermogravimetric analyzer (TGA). Samples were heated from 50 to 500 °C at a heating rate of 10 °C min<sup>-1</sup> under a nitrogen flow. Differential scanning calorimetry (DSC) measurements were performed under a nitrogen atmosphere with a heating rate of 10 °C min<sup>-1</sup> in a temperature range of -50-250 °C on a DSC-Q200. EIS measurements on a Tafel plots were recorded on a CHI660c electrolchemical workstation at room temperature in two-electrode mode of DSSCs. The EIS of devices were tested using a CHI660c electrochemical workstation. Under dark conditions, the bias voltage for the impedance measurement was -0.70 V and the frequency ranged from  $0.01-10^5$  Hz. The photocurrent density-voltage (J-V) curves of the assembled DSSCs shielded by an aluminum foil mask with an aperture area of  $\sim 0.1$  cm<sup>2</sup> were measured with a digital source meter (Keithley, model 2612) under simulated air mass (AM) 1.5 solar spectrum illumination at 100 mW cm<sup>-2</sup>. Incident photo-to-current conversion efficiency (IPCE) plotted as a function of excitation wavelength was recorded on a Keithley 2612 source meter under the irradiation of a Xenon lamp with a monochromater (Oriel CornerstoneTM 260 1/4). The photoelectrochemical parameters, such as the fill factor (FF) and power conversion efficiency (PCE) were calculated according to the previous reports.

#### **Results and discussion**

Scheme 1 shows the synthetic route, chemical structure and the thermal properties of *N*-6-(4-cyanobiphenyl-4'-oxy)hexyl benzimidazole (NCHB). The purity and chemical structure are confirmed by <sup>1</sup>H nuclear magnetic resonance (NMR) (Fig. S1 and S2, ESI<sup>†</sup>) and Fourier transform infrared spectroscopy (FTIR). As shown in Fig. 1, a broad absorption peak at 2900 cm<sup>-1</sup> is assigned to the stretching vibrations of N–H of benzimidazole rings.<sup>41</sup> The stretching vibration belonging to the O–H group of 4-cyano-4'-hydroxybiphenyl is observed at about



**Scheme 1** Synthetic route, chemical structure of *N*-6-(4-cyanobipheny-l-4'-oxy)hexyl benzimidazole (NCHB), and its thermal properties (melting point (mp), and decomposition temperature( $T_d$ )).



Fig. 1 FTIR spectrum of (a) benzimidazole, (b) 4-cyano-4'-hydroxybiphenyl, (c) BrCH, and (d) NCHB.

3380 cm<sup>-1</sup> (Fig. 1b).<sup>42</sup> Compared with Fig. 1a, the sharp band at 2230 cm<sup>-1</sup> (Fig. 1b–d) is indicative of the presence of the C $\equiv$ N group.<sup>42</sup> The relatively high melting point and decomposition temperature (>330 °C, Fig. S3, ESI†) of the compound indicate that NCHB could offer a high thermal stability, far beyond the operating temperature (50–80 °C) of the DSSCs.<sup>43</sup>

Fig. 2 shows the photocurrent density–voltage (J–V) curves for all the devices under simulated AM 1.5 solar irradiance at 100 mW cm<sup>-2</sup>. As shown in Table 1, the photovoltaic parameters of the DSSCs without (Devices A, C and D) and with (Devices B) the additive, *N*-butylbenzimidazole (NBB) in the electrolytes, respectively. Compared with Devices A and C, Device B with NBB as the additive in the electrolyte as previously reported by Grätzel shows a relatively higher cell efficiency (PCE = 5.98%),<sup>9</sup> indicate that NBB could effectively improve the photovoltaic parameter of the DSSCs. However, Device C which was treated



**Fig. 2** J-V characteristics of Devices A–D measured under simulated AM 1.5 solar spectrum irradiation at 100 mW cm<sup>-2</sup> (solid curves) and in the dark (dash curves). Cell area is 0.1 cm<sup>2</sup>.

Table 1J-V characteristics of Devices A–D measured under simulatedAM 1.5 solar spectrum irradiation at 100 mW cm<sup>-2</sup>. Cell area: 0.1 cm<sup>2</sup>

Device <sup>a</sup>	TiO <sub>2</sub> surface coating/additive	$V_{\rm oc}  [{ m V}]$	$J_{\rm sc} [{\rm mA~cm^{-2}}]$	FF	PCE [%]
А	/	0.567	14.21	0.663	5.34
В	—/NBB	0.611	14.79	0.662	5.98
С	NBB/—	0.598	14.31	0.666	5.70
D	NCHB/—	0.643	15.36	0.671	6.63

<sup>*a*</sup> The reference ionic liquid electrolyte for Device B containing: DMII/ EMII/EMITCB/I<sub>2</sub>/NBB/GSCN (12:12:16:1.67:3.33:0.67),<sup>9</sup> and without the additive NBB for Devices A, C and D. No surface modification has been done for the reference Devices A and B, while NBB and NCHB are used for surface modification for Devices C and D, respectively.

with NBB at the dyed TiO<sub>2</sub> photoelectrode/electrolyte interface does not achieve a comparative efficiency in comparison to Device B, which might be due to the fast dissolution of NBB from the photoelectrode/electrolyte interface into the electrolyte to increase the electron recombination. On the other hand, NCHB is insoluble in the ionic liquid electrolyte applied in this work due to the anisometric molecules including van der Waals interactions and  $\pi$ - $\pi$  stacking.<sup>44</sup> Moreover, the employed electrolyte without NBB shows a higher conductivity of  $9.06 \times 10^{-4}$ S cm<sup>-1</sup> than that of NBB-based electrolyte ( $8.52 \times 10^{-4}$  S cm<sup>-1</sup>), which also leads to a higher performance for Device D. Therefore, addition of NCHB does not decrease the conductivity of the electrolyte, and Device D with the modification of NCHB at the dved TiO<sub>2</sub> electrode/electrolyte interface represents the best solar cell performance (PCE = 6.63%), which is much higher than that of the reference Device B (PCE = 5.98%), resulting in about 11%efficiency improvement. Furthermore, NCHB treatment can increase the light-harvesting efficiency of photoanodes as discussed below (Fig. 4). These results demonstrate the possibility of fabricating high performance DSSCs based on additive-free electrolytes.

Fig. 3 represents the incident photo-to-current conversion efficiency (IPCE) values of typical Devices A, B and D. The broad feature appears covering the visible spectrum range from 450 to 650 nm. The maximum IPCE values at 530 nm are 69%, 75% and 81% for Devices A, B and D, respectively. As previously reported,<sup>45</sup> using a solar photon flux of standard AM 1.5 spectrum, a simple multiplication with the IPCE spectrum and the



**Fig. 3** The IPCE *vs.* wavelength profiles for typical Devices A, B and D, respectively.

**Table 2** The  $J_{sc}$  calculated from the IPCE spectrum and measured from the J-V curves for Devices A, B and D

	Device				
	А	В	D		
Calculated $J_{\rm sc}$ (mA cm <sup>-2</sup> ) Measured $J_{\rm sc}$ (mA cm <sup>-2</sup> )	11.15 14.21	12.36 14.79	13.42 15.36		

elementary charge will lead to a calculated  $J_{sc}$  value, which are consistent with the measured data, as shown in Table 2. It should be noted that liquid-based DSSCs showed slower response times than that of solid-state photovoltaics.<sup>4</sup> The deviation of the measured  $J_{sc}$  values was acceptable since the filling of trap states should be responsible for the current response results because of the large internal surface of the photoelectrodes.<sup>46</sup> In addition, low stead-state value of photo-induced current at large bias light intensity (1 Sun) will slight decrease the IPCE values, due to the ion transport limitation of the electrolyte.<sup>47</sup>

As shown in Fig. 4, the light-transmitting and light-scattering properties of the dyed TiO<sub>2</sub> films were investigated. Compared with the film control, it is observed that coating a scattering of 200 nm TiO<sub>2</sub> particles on the control film can reduce the transmittance and enhance the reflectance of TiO<sub>2</sub> photoanodes. However, a small amount of light leakage through the scattering layer could be observed. Further addition of light scattering layers can reflect more visible light, however, cracks of TiO<sub>2</sub> photoanodes during sintering processes could not be avoided.48-50 Here, the treatment of TiO2 photoanodes with NCHB could further decrease the transmittance and increase the reflectance of the TiO<sub>2</sub> photoanodes (Fig. 4). Moreover, the low UV absorption of NCHB film (Fig. S4, ESI<sup>†</sup>) represents a wide transparency range with an optical absorption. Therefore, NCHB could effectively reflect the light of the dyed TiO<sub>2</sub> film. The high reflectance in the visible light region indicates the multi-reflection of light in TiO<sub>2</sub> film leading to an increase of

ransmittance (%) (%) Reflectance 500 600 700 Wavelength (nm) 400 500 600 700 Wavelength (nm) out NCHB Transmittance (%) 10 500 600 700 Wavelength (nm)

**Fig. 4** (a) The transmittance of dyed  $TiO_2$  films: control, control + scattering layer, and control + scattering layer + NCHB; (b) the reflectance of dyed  $TiO_2$  films: control, control + scattering layer, and control + scattering layer + NCHB; (c) the transmittance of a DSSC without and with NCHB, respectively; (d) schematic representation for the sunlight scattering principle of a DSSC.

Table 3 EIS results and calculated electron life time before recombination for Devices A, B and D at -0.70 V in the dark

Device	$R_1/\Omega$	$R_{\rm ct}/\Omega$	$R_3/\Omega$	$f_{\rm max}$	τ <sub>e</sub> /ms
A	0.97	36.82	9.14	25.82	6.17
B	1.39	39.51	9.58	24.13	6.60
D	1.21	50.96	8.95	21.66	7.35

light-harvesting efficiency of the photoelectrode. Therefore, the transmittance of the DSSC treated with NCHB at the photoelectrode/electrolyte interface is obviously lower than that without NCHB modification (Fig. 4c), demonstrating the sunlight harvest is enhanced by NCHB treatment, which results in the remarkable enhancement in device performance, including  $J_{\rm sc}$  and IPCE as mentioned above (Table 1 and Fig. 3). A hypothesized operational scheme of such a device is shown in Fig. 4d.

Photovoltaic electrochemical impedance spectra (EIS) were further used to investigate the interfacial charge transfer processes of the DSSCs measured at -0.70 V in the dark, <sup>51–54</sup> and the resistance values of devices were summarized in Table 3. Fig. 5a shows the typical Nyquist plots of EIS spectra of Devices A, B and D. From low to high frequency, three semicircles are observed in the Nyquist plots.  $R_1$ ,  $R_{ct}$ , and  $R_3$  represent chargetransfer resistance at the counter electrode, the resistance of TiO<sub>2</sub>/FTO, TiO<sub>2</sub>/electrolyte interface, and the Nernst diffusion in the electrolyte, respectively.<sup>54</sup> The semicircle in the intermediatefrequency region is larger, the electron recombination at the TiO<sub>2</sub>/electrolyte interface is weaker.<sup>54,55</sup> Thus, higher  $R_{ct}$  renders the suppressive electron recombination, which is favourable of the performance enhancement. The low values of  $R_1$  represent a favourable charge-transfer process for the reduction of  $I_3^-$  to  $I^$ at the Pt counter electrode/electrolyte interface. It can be seen that Device B shows higher  $R_1$  and  $R_3$  values than those of Devices A and D, indicating that the addition of NBB in electrolyte reduces the conductivity of the electrolyte, which is undesirable for performance improvement.

Fig. 5b shows the Bode phase plots for the DSSC measured at -0.70 V in the dark. The frequency ( $f_{max}$ , the maximum frequency of the frequency peak) and the electron life time before recombination ( $\tau_e$ ) (Table 3) were calculated according to the following equation:<sup>56</sup>

$$\tau_{\rm e} = \frac{1}{\omega_{\rm max}} = \frac{1}{2\pi f_{\rm max}}$$

Compared with Devices A and B, the highest values of  $R_{ct}$  (50.96  $\Omega$ ) and  $\tau_e$  (7.35 ms) were obtained for Device D, indicating



Fig. 5 (a) Nyquist plots of EIS spectra and (b) Bode phase plots measured for Devices A, B and D at -0.70 V in the dark.



Fig. 6 Time-course variation of the efficiencies for Devices A–D, during accelerated aging tests under the successive one sun visible-light soaking with UV cutoff filter at 50  $^\circ$ C.

that the adsorption of the dyed  $\text{TiO}_2$  electrode with NCHB could effectively reduce the electron recombination, leading to enhanced electron transfer and further improved cell performance. These results show good consistency with the previous J-V values, demonstrating that the treatment of dyed  $\text{TiO}_2$ electrode with NCHB is an efficient method for the high performance DSSCs without any additives in the electrolytes.

The long-term stability of the fabricated DSSCs was investigated *via* an accelerating aging test at 50 °C with successive one sun visible-light soaking shown in Fig. 6. After an accelerating aging test of 50 days, Devices A–D remained at 91%, 89%, 88% and 91% of their initial efficiency, respectively. All the devices retained almost over 90% of their initial efficiency in this period. However, Device C shows a sharp reduction of the PCE during the initial few days because of the dissolution of NBB from the dyed TiO<sub>2</sub> electrode into the electrolyte to leading to increased electron recombination and resultant decreased cell performance. It should be noted that the Device D treated with NCHB at the photoanode/electrolyte interface still maintains almost 91% of its initial performance over 50 days, and also represents a good stability.

Application of NCHB is further extended to all-solid-state DSSCs based on *N*-methyl-*N*-butylpyrrolidinium iodide ( $P_{1,4}$ I)-doped succinonitrile plastic crystal electrolytes, as reported by Grätzel.<sup>39</sup> The *J*-*V* curves for Devices E–G are shown in Fig. 7, and the photovoltaic parameters are summarized in Table 4. Under the same experimental conditions, Device G, in which the



**Fig.** 7 J-V characteristics of solid-state Devices E, F and G measured under simulated AM 1.5 solar spectrum irradiation at 100 mW cm<sup>-2</sup> (solid curves) and in the dark (dash curves). Cell area is 0.1 cm<sup>2</sup>.

**Table 4** J-V characteristics of Devices E–G measured under simulatedAM 1.5 solar spectrum irradiation at 100 mW cm<sup>-2</sup>. Cell area: 0.1 cm<sup>2</sup>

Device <sup>a</sup> co	iO <sub>2</sub> surface pating/additive	$V_{\rm oc}  [{ m V}]$	$J_{\rm sc} [{\rm mA~cm^{-2}}]$	FF	PCE [%]
E –	-/	0.577	12.39	0.682	4.87
F –	-/NBB	0.614	13.16		5.33

a	Solid-state	electrolyte	for	Devices	E	and	G	containi	ng
F	$P_{1,4}I : I_2 : succ$	cinonitrile (5 :	1:	100), <sup>39</sup> and v	with 0	.5 M N	<b>IBB</b>	for Device	F.



Fig. 8 (a) Nyquist plots of EIS spectra and (b) Bode phase plots measured for Devices E–G at -0.70 V in the dark.

Table 5 EIS results and calculated electron life time before recombination for Devices E–G at -0.70 V in the dark

Device	$R_1/\Omega$	$R_{\rm ct}/\Omega$	$R_3/\Omega$	$f_{\rm max}$	τ <sub>e</sub> /ms
E F	0.94 1.66	36.85 43.28	8.88 12.23	27.17 23.91	5.86 6.66
G	1.12	56.39	8.21	21.39	7.44

dyed TiO<sub>2</sub> photoanode is treated with NCHB, shows the highest PCE of 5.82%, much higher than that of the reference Device E (PCE = 4.87%), leading to an efficiency enhancement of 19.5%. In the Nyquist plots and Bode phase plots of all-solid-state Devices E–G shown in Fig. 8 and Table 5, low  $R_1$  values also represent an effective charge-transfer process relying on the I<sub>3</sub><sup>-/</sup> I<sup>-</sup> redox couple for oxidized dye regeneration. Compared with Devices E and F, larger  $R_{\rm ct}$  (56.39  $\Omega$ ) at the photoelectrode/ interface and longer  $\tau_e$  (7.44 ms) for Device G is also indicative of a more effective suppression of charge recombination by NCHB treatment. Furthermore, higher  $R_3$  value of Device F (12.23  $\Omega$ ) than those of Devices E and G indicates that the addition of NBB in all-solid-state electrolyte reduces the conductivity of the electrolyte, which is unfavourable for performance enhancement. The solid-state electrolyte without NBB shows a higher ionic conductivity of  $3.87 \times 10^{-4}$  S cm<sup>-1</sup> than that of NBB-based electrolyte  $(3.52 \times 10^{-4} \text{ S cm}^{-1})$ , resulting in a higher performance for Device G. These results further confirm the conclusion that NCHB with light-scattering properties could successfully enhance the device performance of the DSSCs by a simple treatment at the photoelectrode/electrolyte interface.

As shown in Fig. 9a, a broad feature appears covering the visible spectrum range from 450 to 700 nm, and the maximum IPCE values at 530 nm are 64%, 70% and 76% for Devices E–G, respectively, which are consistent with the calculated data (Table 6). The long-term stability of Devices E–G was also investigated and the characterization data were presented in Fig. 9b. During



Fig. 9 (a) The IPCE vs. wavelength profiles for Devices E–G and (b) Time-course variation of the efficiencies for Devices E–G, during accelerated aging tests under the successive one sun visible-light soaking with UV cutoff filter at 50  $^{\circ}$ C.

**Table 6** The  $J_{sc}$  calculated from the IPCE spectrum and measured from the J-V curves for Devices E–G

	Device		
	Е	F	G
Calculated $J_{sc}$ (mA cm <sup>-2</sup> ) Measured $J_{sc}$ (mA cm <sup>-2</sup> )	10.28 12.39	11.91 13.16	13.74 13.65

the first ten days, the efficiency is moderately enhanced due to an increase of the regeneration of dye Z907 and thus an increase of  $J_{\rm sc}$ .<sup>9</sup> By the accelerating aging test, Devices E–G remained 93%, 90% and 95% of their initial efficiency, respectively, showing an excellent long-time stability. These results further confirm the conclusion that NCHB with light-scattering properties could successfully enhance the device performance of the DSSCs by a simple treatment at the photoelectrode/electrolyte interface.

#### Conclusions

In conclusion, we demonstrate herein a simple strategy for the fabrication of high performance DSSCs *via* covering modification of TiO<sub>2</sub> photoanode surface with light-scattering functionalized cyanobiphenyl-based benzimidazole. Compared with the electrolytes containing NBB, surface modification of dyed TiO<sub>2</sub> photoanode with NCHB could enhance the  $V_{oc}$  and  $J_{sc}$  values and the overall PCE of the fabricated DSSCs because of the suppression of charge recombination, the conductivity optimization of the electrolytes and the enhancement of light-harvesting efficiency of the TiO<sub>2</sub> photoanodes. This alternative strategy of surface modification could be applied to most DSSCs including quasi- or solid-state ones to achieve high device performances.

#### Acknowledgements

This work was supported by Natural Science Foundation of China (no. 21174102), The Natural Science Foundation of Jiangsu Province (BK2011274), Research Fund for the Doctoral Program of Higher Education (20103201110003), and the Project Funded by the PAPD of Jiangsu Higher Education Institutions.

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