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Because fossil fuels are not renewable and have caused global environmental problems, we should develop a sustainable alternative to fossil fuels. Direct solar energy conversion to electricity with solar cells has the potential to fulfill the sustainable energy demand. Among the different designs of the solar cells, dye-sensitized solar cells are believed to be one of the most promising designs due to their projected low cost and comparably facile assembly. In this paper, we focus on an interesting concept of pn-type tandem dye-sensitized solar cells (pn-DSCs), in which two photoelectrodes with complementary absorption spectral are assembled in series. Our work describes a novel polymer based photocathode for the pn-DSCs. We develop a secondary porous structure to solve the problem of short exciton diffusion length in polymer and improve the performance of the photocathode. A narrow band gap polymer (PCPDTBT), which has a wide absorption range up to 850 nm is used as light absorber in the photocathode. By combining the photocathode with a typical N719 sensitized TiO₂ photoanode, complementary absorption between the two photoelectrodes is realized in the pn-DSCs for the first time. This result demonstrates a new approach towards the efficient, low cost pn-DSCs.

Cite this: DOI: 10.1039/c0xx00000x

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COMMUNICATION

Polymer based photocathodes for panchromatic tandem dye-sensitized solar cells

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DOI: 10.1039/b000000x

A novel polymer based photocathode with a secondary porous structure was developed for tandem dye-sensitized solar cells (pn-DSCs). We adopt a narrow band gap polymer PCPDTBT as the light absorber in the photocathode. Complementary absorption was realized in pn-DSCs by sandwiching the photocathode with a typical TiO₂ photoanode. The resulting tandem devices achieved a panchromatic absorption and a power conversion efficiency of 1.30%, which demonstrates the great potential of the polymer based photocathode for pn-DSCs.

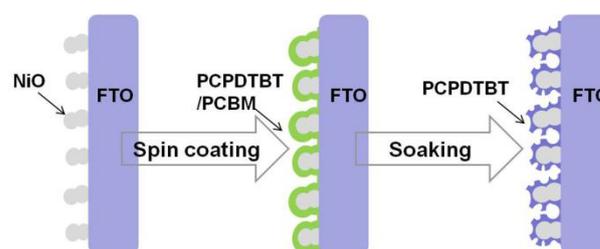
Dye-sensitized solar cells (DSCs) are believed to be one of the most promising alternatives to conventional solar cells due to their projected low cost and comparably facile assembly.¹ Traditional DSCs operate as single junction solar cells. Photons are only absorbed by the dye sensitized photoanode.² Dyes commonly used in photoanode can only absorb the visible part of the solar spectrum, resulting loss of the infrared (IR) part, which are about 49% of the solar spectrum.³ If those lost IR photons could be appropriately utilized, a great enhancement in power conversion efficiency (PCE) could be expected. Sandwiching a photocathode which has a near IR absorption with a typical photoanode into a tandem dye sensitized solar cells (pn-DSCs) is a simple and promising way to enhance the spectral coverage and improve the efficiency of DSCs (ESI Scheme S1). The theoretical upper limit for a DSC with only one photoactive electrode is around 30%. The corresponding limit for a pn-DSC with two photoactive electrodes is around 43%.^{3,4} Although co-adsorption or developing near IR dyes can also be used to enhance the light absorption, these methods can not enhance the theoretical upper limit because they still belong to the single junction solar cells.^{3,5}

The first pn-DSC was demonstrated in 2000 when the PCE was only 0.39%.⁴ Since then, many types of photocathodes have been developed for pn-DSCs.⁶⁻¹⁰ Among them, dye sensitized NiO photocathodes (p-DSC) are mostly studied.¹¹⁻¹⁵ In 2009, Gibson et al. improved the PCE of the pn-DSC to 0.55%.¹⁶ In 2010, A. Nattestad et al. reported a well optimized pn-DSC with a record PCE of 1.91%.¹⁷ Recently, a pn-DSC with a Se based photocathode was developed with a PCE of 0.98%.⁹ However, the performance of the pn-DSCs still lags behind that of DSCs at

present. Two main reasons are responsible for the low performance of pn-DSCs: NiO is not an optimal candidate for photocathodes;¹⁷⁻²⁰ none of those photocathodes for pn-DSCs previously reported could extend the absorption to near infrared, thus leading to significant spectral overlap between two photoelectrodes.^{13,17,19,21}

Polymer semiconductors could meet the demand of near IR absorption for photocathode. Lots of polymer semiconductors with absorption spectra extending to near IR region have been developed.²² And their bandgap and absorption spectra can be easily adjusted by changing the molecular structure.^{23,24} Generally, polymer semiconductors also have good hole transport capabilities.²⁵ These advantages make them promising alternatives to conventional light absorbers of photocathode for high performance pn-DSCs.

Herein, polymer based photocathodes were developed for pn-DSCs for the first time. A narrow band gap polymer, poly[2,6-(4,4-bis-(2-ethylhexyl)-4H-cyclopenta[2,1-b;3,4-b']dithiophene)-alt-4,7-(2,1,3-benzothiadiazole)] (PCPDTBT), which has a wide absorption range up to 850 nm, was used as light absorber. Near IR absorption of the photocathodes and complementary absorption between these two photoelectrodes were realized in the pn-DSCs by introducing the polymer based photocathode. The resulting tandem devices achieved an encouraging efficiency of 1.30% with a short-circuit current density (J_{sc}) of 2.13 mA cm⁻², an open-circuit voltage (V_{oc}) of 900 mV and a fill factor (FF) of 67.8%.



Scheme 1 Illustration of the process for preparing the photocathode.

A large polymer/electrolyte interface is needed for an efficient polymer based photocathode due to the short exciton diffusion length in polymer photoactive materials.²⁶ Therefore, we

introduce a secondary porous structure to enlarge the polymer/electrolyte interface. A simple process of preparing the secondary porous structure photocathode is shown in Scheme 1. Firstly, a mixed chlorobenzene solution containing PCPDTBT and [6,6]-phenyl-C61-butyric acid methyl ester (PCBM) is spin coated on mesoporous nickel oxide film. Then the PCBM was removed by simply soaking this hybrid film in 3-methoxypropionitrile (MePN). Fig 1a shows SEM image of the mesoporous NiO film (1 μm) covered by PCPDTBT/PCBM composites. Fig 1b shows that after the removal of PCBM, the PCPDTBT/PCBM composites turn into a porous PCPDTBT film. In order to display the formation of the porous PCPDTBT film clearly, SEM images of the PCPDTBT/PCBM film and the porous PCPDTBT film cast on FTO are also shown in Fig 1c and d. After the removal of PCBM, pores with 10 nm to 20 nm width were formed and uniformly distributed in the PCPDTBT film. The porous PCPDTBT film and the mesoporous NiO film substrate constitute a large polymer/liquid interface, thus enhancing the exciton separation.

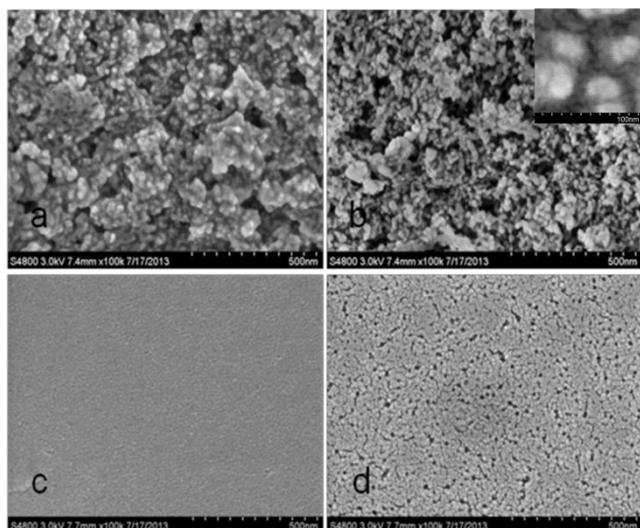


Fig. 1 SEM images of mesoporous NiO film covered by (a) PCPDTBT/PCBM composite, (b) porous PCPDTBT film after removal of the PCBM (inset, magnified image), and SEM images of FTO covered by (c) plane PCPDTBT/PCBM film and (d) porous PCPDTBT film after the removal of PCBM.

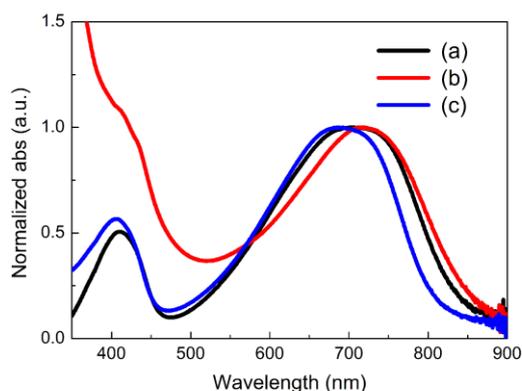


Fig. 2 UV-visible absorption spectra of (a) pristine PCPDTBT film (black); (b) PCPDTBT/PCBM film on FTO (red); (c) porous PCPDTBT film after the removal of PCBM (blue).

Fig 2 shows the UV-visible absorption spectra of the PCPDTBT/PCBM film and the porous PCPDTBT film. The absorption spectrum of the pristine PCPDTBT film is also shown for comparison. After soaking in MePN, the absorption features of PCBM can barely be detected from the absorption spectra of the porous PCPDTBT film. Bathochromic shifts in the absorption between solution and solid state films have been frequently observed for rigid conjugated polymers with a strong interchain interaction and are a sign of 2D stacking.²⁷ The blue shift in absorption spectra of the PCPDTBT porous film compared with pristine the PCPDTBT film could result from the weakening of the interchain interaction after the removal of PCBM.²⁸

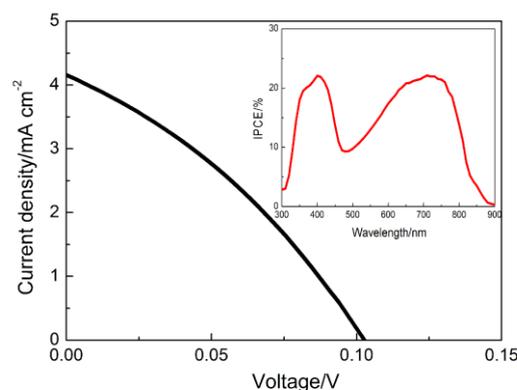


Fig. 3 Current density-voltage characteristics of PSC (the highest-performing device) under AM 1.5 solar simulator of 100 mW cm^{-2} . Active area= 0.25 cm^2 . Inset is the incident photon-to-current conversion efficiency spectra of the PSC.

A polymer based solar cell (PSC) was assembled with three parts, the secondary porous structure polymer based photocathode, a Pt counter electrode and I^-/I_3^- redox electrolyte (0.6 M N-methyl-N-butyl imidazolium iodide, 0.45 M N-methylbenzimidazole, 0.1 M LiI, 0.1 M I_2 in MePN). Fig 3 shows the photocurrent density-voltage (J - V) curve and the incident photon-to-electron conversion efficiency (IPCE) curve of the PSC (the highest-performing device). Under illumination PSCs achieve a PCE of 0.14%, with a J_{sc} of 4.15 mA cm^{-2} , a V_{oc} of 100 mV and a FF of 33.4%. Although an IPCE of 22% is moderate compared with the best p-DSCs with typical dye sensitized photocathodes, it is encouraging for a polymer/liquid device. Despite the moderate IPCE, the PSC achieves a J_{sc} of 4.15 mA cm^{-2} , which is comparable with the best p-DSCs, due to the superior spectral coverage of the PCPDTBT. PSCs with other photocathodes were also studied for comparison (ESI Fig S1): (a) photocathodes with porous PCPDTBT film (without mesoporous NiO film, Fig 1d), (b) photocathodes with mesoporous NiO film covered by pristine PCPDTBT. Cathodic photoresponses can still be recorded for PSCs with these two photocathodes, but giving relatively weak photocurrent of 0.55 mA cm^{-2} and 0.04 mA cm^{-2} for (a) and (b) respectively (ESI Fig S2), which could be limited by their smaller interfacial area. The V_{oc} and FF are similar with that of p-DSC with a NiO photocathode and a I^-/I_3^- electrolyte,

which are limited by the low hole transport properties of NiO, the serious recombination and the relatively high quasi-fermi level of NiO.^{9,18,29,30} If a more favorable p-type semiconductor becomes available to replace the NiO, a significant efficiency increase could be expected.

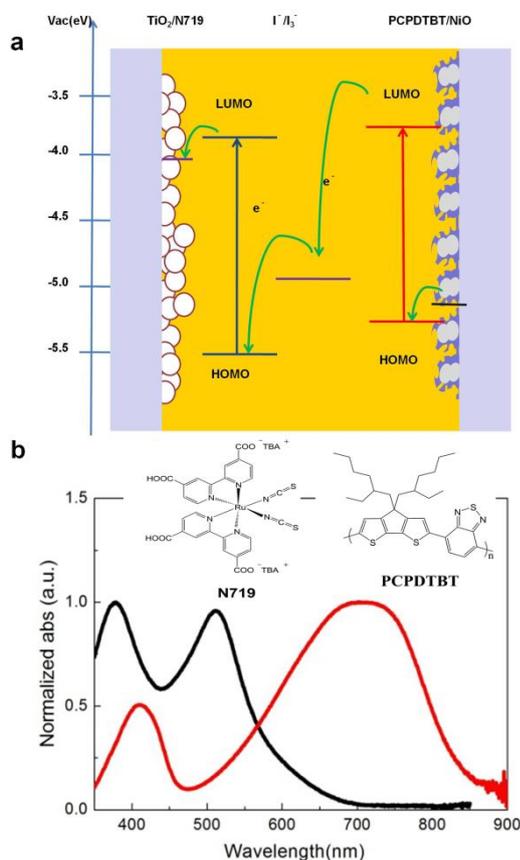


Fig. 4 (a) The device structure of the pn-DSCs. Also shown are the energy-level (versus vacuum level, Vac) diagram of the component materials and a simple electron transfer processes; (b) Normalized absorbance spectra of N719 dye (black, ethanol solution) and PCPDTBT film (red) with the molecular structure of the N719 dye and PCPDTBT.

The structure of the pn-DSC with the approximate energy levels of each component is shown in Fig 4a.^{17, 28} The pn-DSC is fabricated by sandwiching a typical RuL₂(SCN)₂ (where L is tetrabutylammonium 4'-carboxy-2,2'-bipyridine-4-carboxylate, N719) sensitized TiO₂ (1.7 μm) photoanode with the secondary porous structure polymer based photocathode (1 μm). The electrolyte used here is the same with which used in PSCs. PSCs and DSCs with the same photoelectrodes are also assembled for comparison. The absorption characteristics of N719 and PCPDTBT together with their molecular structures are shown in Fig 4b. Absorption spectra of the N719 and the PCPDTBT complement each other resulting in a panchromatic absorption. The absorption of the N719 covers the visible spectral range, while that of the PCPDTBT is weak in the visible spectral range. PCPDTBT shows a strong absorption bands in the near-IR spectral range between 650 nm and 850 nm arising from the interband π-π* transition of the PCPDTBT.²⁸

Under illumination, N719 dyes are excited by visible photons, and then inject electrons into the conduction band of TiO₂.

Oxidized dyes are reduced by gaining electrons from the redox couples. Near IR photons are transmitted to the photocathode. Under irradiation of these near IR photons, excitons are generated in the PCPDTBT and separated at the PCPDTBT/electrolyte interface by donating electrons to the redox couples. Detailed study on the mechanism of the charge generation and transportation in photocathodes is underway.

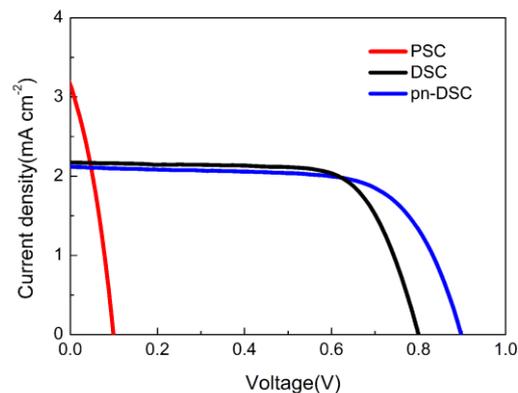


Fig. 5 Current density-voltage characteristics of a pn-DSCs (blue) as well as PSCs (red) and DSCs (black) under AM 1.5 solar simulator of 100 mW cm⁻². Active area=0.25 cm². The tandem pn-DSCs and DSCs were illuminated through the photoanode side; the PSCs were illuminated through the photocathode side.

Table 1 Photovoltaic parameters of pn-DSCs as well as PSCs and DSCs.

	V _{oc} (mV)	J _{sc} (mAcm ⁻²)	FF	PCE(%)
DSC	800	2.17	72.4	1.23
PSC	99	3.15	33.4	0.10
pn-DSC	900	2.13	67.8	1.30

⁴⁵ Taken under AM 1.5 solar simulator of 100 mWcm⁻². Active area=0.25 cm². The tandem pn-DSCs and DSCs were illuminated through the photoanode side; the PSCs through photocathode side.

Photovoltaic parameters of the DSCs, PSCs and pn-DSCs are shown in Table 1. Because of the series connection of the two photoelectrodes, the photocurrents of the pn-DSCs will be determined by the smaller one of two photoelectrodes, whereas photovoltages are additive.¹⁷ Through adjusting the performance of photoanode, good current matching of the two photoelectrodes is obtained. Fig 5 shows the *J*-*V* curve of pn-DSCs, DSCs and PSCs. The *J*_{sc} of pn-DSCs are similar to that of the DSCs, whereas the *V*_{oc} of 900 mV matches the sum of DSCs (800 mV) and PSCs (99 mV). A high FF of 67.8% for the pn-DSC further indicated a good current matching of the two photoelectrodes. This results in an efficiency of pn-DSCs (1.30%) higher than that of the corresponding DSCs (1.23%) and PSCs (0.1%), and this value is comparable with the record value (1.91%) of the well optimized pn-DSCs with typical dye sensitized photocathodes.^{5,17} These results demonstrate the great potential of the polymer based photocathode for pn-DSCs.

⁶⁵ The IPCE curves of PSCs and DSCs are shown in Fig 6. Each single cell shows the spectral response, which is in excellent agreement with its absorption spectrum. The spectral complementary features of the two photoelectrodes also can be

clearly identified from IPCE curves. The DSCs exhibits an IPCE curve covering the visible spectral range, while the PSCs have two dominant peaks in near IR spectral range and ultraviolet (UV) spectral range.

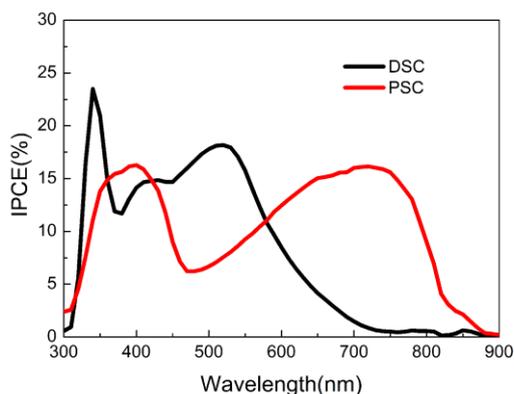


Fig. 6 Incident photon-to-current conversion efficiency spectra of the DSCs (black) and PSCs (red).

Conclusions

In conclusion, we developed a novel polymer based photocathode for pn-DSCs. A secondary porous structure was introduced to enhance the polymer/electrolyte interface area. By introducing a narrow band gap polymer PCPDTBT as the light absorber of the photocathode, complementary absorption between the two photoelectrodes was realized in pn-DSCs for the first time. The resulting PSCs and pn-DSCs achieved PCEs of 0.14% and 1.30%, respectively. The preliminary results are encouraging, and further improvement could be expected through optimization of the polymer based photocathode. These results offer a practical solution for the spectral overlap problem in pn-DSCs and open a new path of research on pn-DSCs.

Acknowledgements

We are very grateful for the help of Pro. Mohammad K. Nazeeruddin and Pro. Jian Chen in preparation of this article.

This work was financially supported by the National Basic Research Program of China (Grant No. 2011CBA00700), the National High Technology Research and Development Program of China under Grant No. 2011AA050510, National Natural Science Foundation of China (Grant No. 21103197) and National Natural Science Foundation of China (Grant No. 21273242). The Program of Hefei Center for Physical Science and Technology (2012FXZY006).

Notes and references

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- [†] Electronic Supplementary Information (ESI) available: [Experimental details, photovoltaic parameters of PSCs with photocathode (a) and (b) and the stability test of PSCs] See DOI: 10.1039/b000000x/
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Polymer based photocathodes for panchromatic tandem dye-sensitized solar cells

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A novel polymer based photocathode with a secondary porous structure was developed for tandem dye-sensitized solar cells (pn-DSCs). We adopt a narrow band gap polymer PCPDTBT as the light absorber in the photocathode. Complementary absorption was realized in pn-DSCs by sandwiching the photocathode with a typical TiO₂ photoanode. The resulting tandem devices achieved a panchromatic absorption and a power conversion efficiency of 1.30%, which demonstrates the great potential of the polymer based photocathode for pn-DSCs.

