Nanoscale Research Letters
a SpringerOpen Journal

NANO EXPRESS   **Open Access**

Mesoporous nitrogen-doped TiO$_2$ sphere applied for quasi-solid-state dye-sensitized solar cell

Peng Xiang, Xiong Li, Heng Wang, Guanghui Liu, Ting Shu, Ziming Zhou, Zhiliang Ku, Yaoguang Rong, Mi Xu, Linfeng Liu, Min Hu, Ying Yang, Wei Chen, Tongfa Liu, Meili Zhang and Hongwei Han[*]

Abstract

A mesoscopic nitrogen-doped TiO$_2$ sphere has been developed for a quasi-solid-state dye-sensitized solar cell [DSSC]. Compared with the undoped TiO$_2$ sphere, the quasi-solid-state DSSC based on the nitrogen-doped TiO$_2$ sphere shows more excellent photovoltaic performance. The photoelectrochemistry of electrodes based on nitrogen-doped and undoped TiO$_2$ spheres was characterized with Mott-Schottky analysis, intensity modulated photocurrent spectroscopy, and electrochemical impedance spectroscopy, which indicated that both the quasi-Fermi level and the charge transport of the photoelectrode were improved after being doped with nitrogen. As a result, a photoelectric conversion efficiency of 6.01% was obtained for the quasi-solid-state DSSC.

Introduction

Since a mesoscopic TiO$_2$-based dye-sensitized solar cell [DSSC] was reported by O' Regan and Grätzel in 1991 [1], DSSC has emerged as a promising candidate for the practical photovoltaic application due to its low manufacturing cost and high energy conversion efficiency. Even though DSSC is now commercially available, market expansion is still limited because of the use of a liquid electrolyte, which always signifies instability due to the leakage of the solvent and the erosion of the electrode. It seems a good way to replace the liquid electrolyte by a solid-state or quasi-solid-state medium [2,3]. Unfortunately, compared with liquid electrolyte, solid-state or quasi-solid-state DSSC still presents lower energy conversion efficiency. Therefore, how to improve the performance of DSSC composing of solid-state or quasi-solid-state medium is still a big issue.

As one of the key components, mesoscopic TiO$_2$ film plays an important role in determining the performance of DSSC, which assumes both the task of dye anchorage and charge carrier transport. Over the past decade, substantial efforts have been made to improve the performance of DSSC through the reformation of the TiO$_2$ film. The first strategy is to increase the light absorption efficiency of the photoanode by increasing the surface area of the TiO$_2$ film, which provides sufficient room for dye loading. Another strategy is to improve the electron injection efficiency by adjusting the conduction band edge to match the LUMO of the dye [4]. The last strategy is to increase the charge collection efficiency through the improvement of the electron transport or lifetime [5].

For an effective DSSC, the key parameters of the mesoscopic TiO$_2$ film such as porosity, pore size distribution, light scattering, electron percolation, and conduction band edge should be coordinated to the characterization of the dye and electrolyte medium, which could be controlled by precursor chemistry, hydrothermal growth temperature, binder addition, doping materials, and sintering conditions [6]. Recently, Chen et al. [7] reported a mesoporous anatase TiO$_2$ bead with high surface area and controllable pore size for DSSC, which indicated that the DSSC employing mesoporous TiO$_2$ sphere has demonstrated longer electron diffusion lengths and extended electron lifetimes over Degussa P25 titania electrodes due to the favorable interconnected, densely packed nanocrystalline TiO$_2$ particles inside the spheres, resulting in the improvement of the parameters. In 2005, Ma et al. [8] reported nitrogen-doped TiO$_2$ particles for DSSC that enhanced the incident photon-to-current conversion efficiency within the spectrum of 380 to 520 nm and 550 to 750 nm; as a result, the short-circuit photocurrent density was pronouncedly improved. After that, Tian et al. [9]

* Correspondence: hongwei.han@mail.hust.edu.cn
Michael Grätzel Center for Mesoscopic Solar Cells, Wuhan National Laboratory for Optoelectronics, Huazhong University of Science and Technology, Wuhan, 430074, Hubei, People's Republic of China

Springer

found that the position of the flatband potential edge was shifted to negative when doping nitrogen into the TiO_2 film, which is attributed to the formation of an O-Ti-N bond and results in the improvement of the open-circuit voltage in DSSC.

Therefore, it could be expected to promote the performance of DSSC from the improvement of both the short-circuit photocurrent density and the open-circuit voltage with the nitrogen-doped TiO_2 sphere. Herein, we attempted to synthesize a crystalline nitrogen-doped TiO_2 sphere under the hydrothermal condition and apply it in quasi-solid-state DSSC. The results indicated that with the nitrogen-doped TiO_2 sphere, the parameters of quasi-solid-state DSSC were improved in both the short-circuit photocurrent density and the open-circuit voltage. As a result, a power conversion efficiency up to 6.01% of quasi-solid-state DSSC was obtained under air mass [AM] 1.5 sunlight at 100 mW/cm^2.

Experimental details

Mesoporous TiO_2 spheres were synthesized with the hydrothermal method as follows: 8 g dodecylamine and 8 g titanium isopropoxide [TIP] were mixed with 360 mL ethanol. The urea solution was added into the dodecylamine-TIP mixture solution under vigorous stirring at ambient temperature. The molar ratio of the urea to TIP was adjusted to 0, 4, 8, and 16. Twelve hours later, the white TiO_2 suspension was transferred into a Teflon-lined autoclave and then heated at 210°C. After 12 h, the nitrogen-doped TiO_2 spheres were obtained and marked as T_{N0}, T_{N1}, T_{N2}, and T_{N3}, respectively.

Mesoscopic nitrogen-doped or undoped TiO_2 sphere pastes for screen print were prepared as reported [10]. Hydroxypropyl cellulose was dissolved in ethanol to form 10 wt.% ethanolic mixture. Two grams of mesoscopic nitrogen-doped TiO_2 sphere, 5 g 10 wt.% ethanolic mixture, 8.1 g terpineol, and 10 mL ethanol were mixed by ball milling for 12 h. Then, the slurry was sonicated for 30 min and concentrated to a paste with 20 wt.% TiO_2.

The mesoscopic nitrogen-doped or undoped TiO_2 sphere-based photoelectrode was coated on a fluorine-doped tin oxide [FTO] glass (TEC15; Pilkington TEC Glass™, IL, USA) by using a doctor blade and then sintered at 450°C for 30 min. The thickness of nitrogen-doped or undoped TiO_2 sphere film was controlled by the thickness of scotch tape. The photoelectrode with a 2-μm TiO_2 sphere layer was used for Mott-Schottky [MS] analysis. The electrode with a 12-μm TiO_2 sphere film was dyed with N719 ethanolic solution. A sandwich structure quasi-solid-state DSSC containing the mesoscopic TiO_2 sphere-based electrode, platinized counter electrode, and quasi-solid-state electrolyte was performed for photocurrent-voltage testing, which was sandwiched with a 100-μm

film of Surlyn (DuPont Surlyn, Wilmington, DE, USA) and then heated at 100°C for sealing.

The surface appearance of their films on FTO glass was performed using a Sirion 200 field emission scanning electron microscopy [FE-SEM] (FEI Company, Eindhoven, the Netherlands). Veeco Dektak 150 (Veeco Instruments Inc., NY, USA) was used to detect the thickness of the TiO_2 film. MS analysis was performed in a three-electrode cell under a dark condition, where the T_{N0}- and T_{N2}-based electrodes without dye (ca. 2 μm) were used as the work electrode, a saturated calomel electrode [SCE] served as the reference electrode, a platinum wire was used as the counter electrode, and the active area was 0.36 cm^2. The ethylene carbonate and propylene carbonate (1:1 volume ratio) solution containing 0.01 M iodine [I_2] and 0.1 M potassium iodide was used as an electrolyte for MS analysis. Intensity modulated photocurrent spectroscopy [IMPS] was characterized within T_{N0}- and T_{N2}-based DSSC and performed with a green light emitting diode (λ_{max} = 535 nm) driven by Zahner Zenium. The photocurrent density-voltage curves of the quasi-solid-state DSSC were perfomed with a Keithley 2400 SourceMeter (Keithley Instruments, Inc., Ohio, USA) under illumination with an Oriel solar simulator (Newport Corporation, CA, USA) composed of a 1, 000-W xenon arc lamp and AM 1.5 G filters. Light intensity was calibrated with a normative silicon cell. The electrochemical impedance spectroscopy [EIS] of the quasi-solid-state DSSC was characterized by a potentiostat (M2273; EG&G Inc., MD, USA) with a frequency range from 100 mHz to 1 MHz.

Results and discussion

Figure 1 shows the SEM images of the TiO_2 films using T_{N0}, T_{N1}, T_{N2}, and T_{N3} powders. It could be found that films using T_{N0}, T_{N1}, and T_{N2} are composed of the interconnected mesoscopic spheres with the size around 550 nm, but the film using T_{N3} is composed of a three-dimensional network of interconnected nanoparticles. The TiO_2 film composing of large mesoscopic spheres with considerable quantities and small nanocrystalline particles presents the ability to scatter light and also provides sufficient surface area for the dye loading. However, urea and dodecylamine are used as the nitrogen source and dispersant, forming mesoporous TiO_2 spheres during the thermal treatment, respectively. Too much urea could destroy the accompaniment of the TiO_2 sphere. Therefore, the mesoporous spheres are dispersed into small particles with the increase of urea content in the precursor solution as shown in the film using T_{N3}.

Figure 2 presents the photocurrent density-voltage curves of the DSSC using T_{N0}, T_{N1}, T_{N2}, and T_{N3} as photoelectrodes. Here the electrolyte is 10 wt.% Poly (ethylene oxide) (M_w = 2 × 10^6 g·mol^{-1}), 0.1 M I_2, 0.1 M
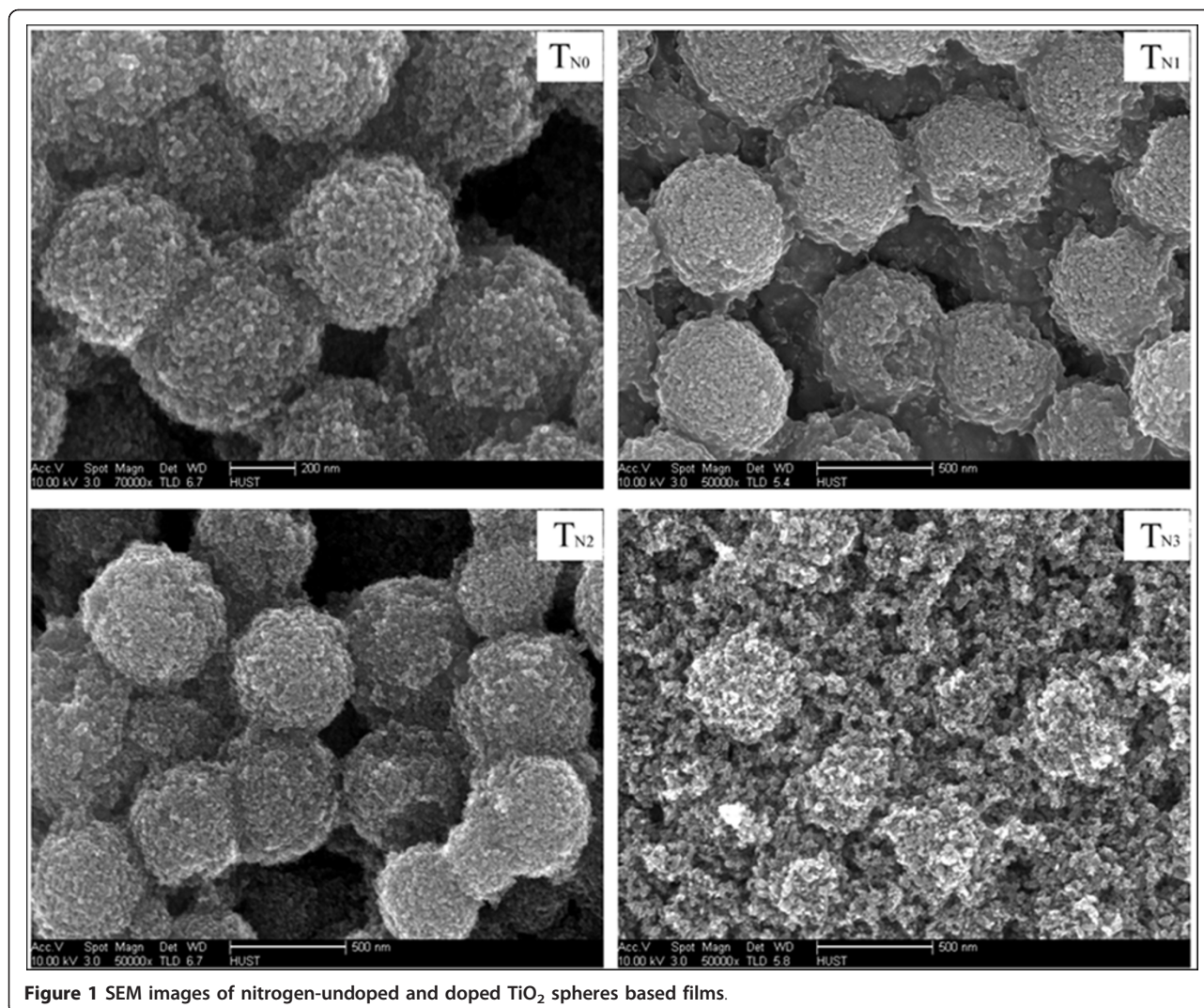
Figure 1 SEM images of nitrogen-undoped and doped TiO$_2$ spheres based films.

lithium iodide, 0.6 M 1, 2-dimethyl-3-propyl imidazolium iodide, and 0.45 M *N*-methyl-benzimidazole 3-methoxypropionitrile solution [11]. An inverted vessel containing this electrolyte is shown in the inserted picture of Figure 2 and exhibits the characterization of the quasi-solid-state DSSC. The parameters of DSSCs are summarized in the inserted table, which demonstrates that compared with the undoped-nitrogen TiO$_2$ sphere-based quasi-solid-state DSSC, all the performance of doped-nitrogen TiO$_2$ sphere-based quasi-solid-state DSSC was improved. With the increase of nitrogen content within the TiO$_2$ spheres, the short-circuit photocurrent density [J_{sc}] is increased from 8.57 mA·cm^{-2} of the undoped TiO$_2$ sphere-based quasi-solid-state DSSC (T$_{N0}$) to 10.09 mA·cm^{-2} of the T$_{N1}$ and then reached to a maximum value of 12.82 mA·cm^{-2} of the T$_{N2}$. However, when the nitrogen content within the sphere is increased further, the J_{sc} is decreased to 11.43 mA·cm^{-2}

of the T$_{N3}$. Compared with J_{sc}, the open-circuit voltage [V_{oc}] is increased within a small amplitude with the increase of nitrogen content within the TiO$_2$ spheres, which exhibits 590.6 mV for T$_{N0}$, 596.3 mV for T$_{N1}$, 607.0 mV for T$_{N2}$, and 605.3 mV for T$_{N3}$, and the fill factor is almost at a constant value of around 0.78, which is presented as follows: 0.79 for T$_{N0}$, 0.78 for T$_{N1}$, 0.77 for T$_{N2}$, and 0.78 for T$_{N3}$. As a result, the highest energy conversion efficiency [η] of 6.01% was obtained for T$_{N2}$-based quasi-solid-state DSSC, which is 49% higher than that of T$_{N0}$ (η = 4.04%), 27% higher than that of T$_{N1}$ (η = 4.72%), and 11% higher than that of the T$_{N3}$-based device (η = 5.41%).

In order to ascertain the role of doping nitrogen, two typical mesoscopic TiO$_2$ sphere photoeletrodes with (T$_{N2}$) and without doping nitrogen (T$_{N0}$) were investigated by MS analysis, EIS, and IMPS. Normally, the V_{oc} of DSSC could be improved by retarding interfacial
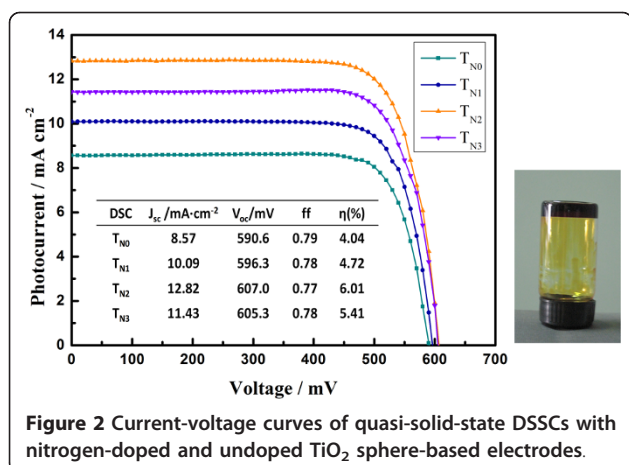
Figure 2 Current-voltage curves of quasi-solid-state DSSCs with nitrogen-doped and undoped TiO$_2$ sphere-based electrodes.

Figure 4 IMPS plots of T$_{N0}$- and T$_{N2}$-based quasi-solid-state DSSCs.

recombination, shifting the conduction band of TiO$_2$ to more negative potentials, and engineering a more favorable equilibrium Fermi-level position [12]. The flat band potential [E_{fb}] is a very useful quantity in photoelectrochemistry as it facilitates location of the energetic position of the valence and conduction band edge of a given semiconductor material [13], which could be detected by MS analysis [9-12]. Figure 3 presents the MS plots of T$_{N0}$- and T$_{N2}$-based electrodes. E_{fb} could be calculated by the following equation [14]

$$(C_{sc})^{-2} = 2\left(E - E_{fb} - kT/e\right)/N_D \varepsilon \varepsilon_0 eA^2$$

where C_{sc} is the space charge capacity, N_D is the electron density, ε is the dielectric constant, ε_0 is the permittivity of vacuum, and A is the active surface area. E_{fb} is the intercept extrapolating a straight line from the plot of the square of the space charge capacity against the applied voltage, which found that the E_{fb} of the electrode using T$_{N0}$ and T$_{N2}$ are about -0.55 V and -0.68 V
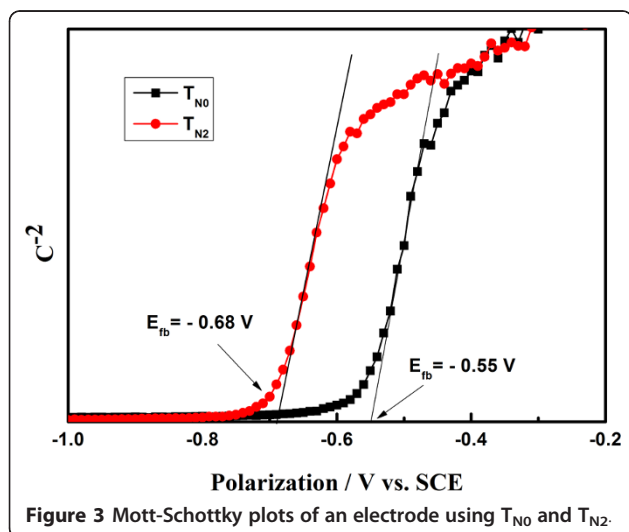
(vs. SCE), respectively. Compared with the undoped TiO$_2$ sphere-based electrode, the E_{fb} of the nitrogen-doped TiO$_2$ sphere-based electrode is shifted to about 0.13 V negatively, which suggests that a higher quasi-Fermi level could be obtained by doping nitrogen, resulting in the enhancement of V_{oc} of the mesoscopic nitrogen-doped TiO$_2$ sphere-based DSSC.

The charge transport within the nanocrystalline semiconductor of the photoelectrode could be detected by IMPS, and Figure 4 presents the IMPS of the photoelectrode using T$_{N0}$ and T$_{N2}$. The transport time [τ_d] of the injected electrons through the TiO$_2$ film can be calculated from the equation $\tau_d = 1/(2\pi f_{d, min})$ [15], where $f_{d, min}$ is the characteristic frequency at the minimum of the IMPS imaginary component. The simulation results show that τ_d values are estimated to be 1.72 and 1.18 ms in the films using T$_{N0}$ and T$_{N2}$, respectively. In addition, the electron diffusion coefficient [D_n] could be calculated from the equation $D_n = d^2/(2.35\tau_d)$ [15], where d is the thickness of the photoeletrode. Therefore, the D_n in the films using T$_{N0}$ and T$_{N2}$ are calculated to be 9.9×10^{-6} and 1.44×10^{-5} cm$^2 \cdot$s^{-1}, respectively. It is clear that the charge transport within the T$_{N2}$ film is faster than that of the T$_{N0}$ film, which suggests that the charge collection efficiency and J_{sc} of DSSC could be improved by nitrogen doping.

EIS was carred out in the dark condition to investigate the discrepancy of the interfacial recombination between the electrodes using T$_{N0}$ and T$_{N2}$. Figure 5 presents the typical Nyquist plots of the T$_{N0}$- and T$_{N2}$-based cells. The interfacial impedance related to the electron transfer from the conduction band of TiO$_2$ to the electrolyte can be described by the semicircle of the middle frequency region in the Nyquist plot. Their charge transfer resistance [R_{ct}] values are evaluated by fitting the spectra

Figure 3 Mott-Schottky plots of an electrode using T$_{N0}$ and T$_{N2}$.

Figure 5 Nyquist plots of T_{N0}- and T_{N2}-based quasi-solid-state DSSCs.
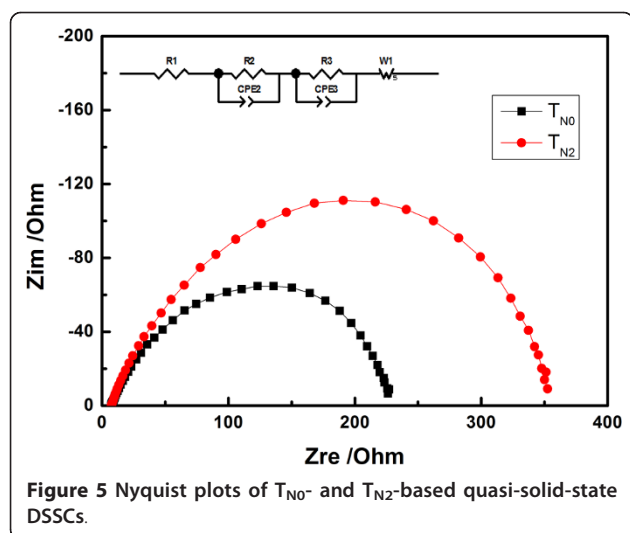
with the equivalent circuit shown in the inset, which shows 281 Ω of T_{N0}- and 362 Ω of T_{N2}-based cells. Compared with the pure TiO_2 sphere-based cell, the R_{ct} of the mesoscopic nitrogen-doped TiO_2 sphere-based cell is increased to 29%, suggesting that the interface resistance between the TiO_2 sphere electrode and electrolyte is increased by introducing nitrogen. Therefore, the interface recombination between photoelectrode and electrolyte within DSSC would be retarded with this nitrogen-doped TiO_2 sphere, resulting in the decrease of dark current and the improvement of J_{sc} and V_{oc}.

Conclusions

A series of mesoscopic nitrogen-doped and undoped TiO_2 spheres for quasi-solid-state DSSC have been prepared by the hydrothermal method. The effects of nitrogen within TiO_2 spheres on the photovoltaic performance have been investigated, which show that the introduction of nitrogen increases J_{sc}, V_{oc}, and efficiency. The photoelectrochemistry of nitrogen-doped and undoped TiO_2 sphere-based electrodes was performed with MS, IMPS, and EIS. The results indicated that the quasi-Fermi level and the charge transport of the photoelectrode were improved, and the interfacial recombination was retarded after being doped with nitrogen within a mesoscopic sphere-based electrode. As a result, a DSSC with a power conversion efficiency of 6.01% under AM 1.5 sunlight at 100 mW/cm^2 has been obtained with N719 dye in combination with a quasi-solid state electrolyte. Higher parameter DSSC could be expected with this mesoscopic nitrogen-doped TiO_2 sphere.

Authors' contributions
PX carried out the DSSC studies, participated in the sequence alignment and drafted the manuscript. XL, HW, GL, TS, ZZ, and WC participated in the design of the study and performed the statistical analysis. ZK, YR, MX, LL, MH, YY, TL, and MZ carried out material synthesis. HH conceived of the study and participated in its design and coordination. All authors read and approved the final manuscript.

Competing interests
The authors declare that they have no competing interests.

References
1. O'Regan B, Gratzel M: **A low-cost, high-efficiency solar cell based on dye-sensitized collidal TiO2 films.** *Nature* 1991, **353**:737-740.
2. Bach U, Lupo D, Comte P, Moser JE, Weissortel F, Salbeck J, Spreitzer H, Gratzel M: **Solid-state dye-sensitized mesoporous TiO2 solar cells with high photon-to-electron conversion efficiencies.** *Nature* 1998, **395**:583-585.
3. Wang H, Liu GH, Li X, Xiang P, Ku ZL, Rong YG, Xu M, Liu LF, Hu M, Yang Y, Han HW: **Highly efficient poly(3-hexylthiophene) based monolithic dye-sensitized solar cells with carbon counter electrode.** *Energ Environ Sci* 2011, **4**:2025-2029.
4. Jose R, Thavasi V, Ramakrishna S: **Metal oxides for dye-sensitized solar cells.** *J Am Ceram Soc* 2009, **92**:289-301.
5. DiCarmine PM, Semenikhin OA: **Intensity modulated photocurrent spectroscopy (IMPS) of solid-state polybithiophene-based solar cells.** *Electrochim Acta* 2008, **53**:3744-3754.
6. Kalyanasundaram K, Gratzel M: **Applications of functionalized transition metal complexes in photonic and optoelectronic devices.** *Coord Chem Rev* 1998, **177**:347-414.
7. Chen DH, Huang FZ, Cheng YB, Caruso RA: **Mesoporous anatase TiO2 beads with high surface areas and controllable pore sizes A superior candidate for high-performance dye-sensitized solar cells.** *Adv Mater* 2009, **21**:2206-2210.
8. Ma TL, Akiyama M, Abe E, Imai I: **High-efficiency dye-sensitized solar cell based on a nitrogen-doped nanostructured titania electrode.** *Nano Lett* 2005, **5**:2543-2547.
9. Tian HJ, Hu LH, Zhang CN, Liu WQ, Huang Y, Mo L, Guo L, Sheng J, Dai SY: **Retarded charge recombination in dye-sensitized nitrogen-doped TiO2 solar cells.** *J Phys Chem C* 2010, **114**:1627-1632.
10. Ito S, Murakami TN, Comte P, Liska P, Gratzel C, Nazeeruddin MK, Gratzel M: **Fabrication of thin film dye sensitized solar cells with solar to electric power conversion efficiency over 10%.** *Thin Solid Films* 2008, **516**:4613-4619.
11. Shi YT, Zhan C, Wang LD, Ma BB, Gao R, Zhu YF, Qiu Y: **The electrically conductive function of high-molecular weight poly(ethylene oxide) in polymer gel electrolytes used for dye-sensitized solar cells.** *Phys Chem Chem Phys* 2009, **11**:4230-4235.
12. Feng X, Shankar K, Paulose M, Grimes CA: **High open-circuit voltage-tantalum-doped TiO2nanowire arrays.** *Angew Chem* 2009, **48**:8095-8098.
13. Gratzel M: **Photoelectrochemical cells.** *Nature* 2001, **414**:338-344.
14. Van de Krol R, Goossens A, Schoonman J: **Mott-Schottky analysis of nanometer-scale thin-film anatase TiO2.** *J Electrochem Soc* 1997, **144**:1723-1727.
15. Zhang W, Zhu R, Ke L, Liu X, Liu B, Ramakrishna S: **Anatase mesoporous TiO2 nanofibers with high surface area for solid-state dye-sensitized solar cells.** *Small* 2010, **6**:2176-2182.