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Brief Note

Organic dye-sensitized photovoltaic fibers

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ABSTRACT

This work reports photovoltaic fibers based on organic dyes and their waveguide photovoltaic modules. The organic photovoltaic fibers achieve energy conversion efficiency of > 3% via balancing dye adsorption and interface charge recombination. The waveguide modules achieve power output enhancement up to 2.7. Suitable partners of organic dyes and luminescent solar concentrators would break through conventional thinking of extending absorption region of organic dyes to improve photovoltaic performance and would contribute to high power output with narrow-absorption sensitizers. As far as we know, this is the first time that organic dyes are involved in fiber solar cells and their modules. Our study may open a door toward cost-effective, lightweight and efficient building integrated photovoltaic power sources.

1. Introduction

Nowadays, the fiber shaped solar cells, including inorganic, organic, dye-sensitized, perovskite photovoltaic devices constructed on wire or fiber substrates, are attracting increasing attention (Chen et al., 2013; Peng and Zou, 2015). The cylindrical symmetry shape endows the photovoltaic cells with three dimensional light harvesting property and the devices are promising candidates for flexible/wearable solar power sources (Fu et al., 2011; Yang et al., 2014; Zeng et al., 2014). Among various types, the dye-sensitized photovoltaic fibers have achieved rapid development due to its facile assembly, impressive performance, good environmental tolerance and reasonable high performance. Protype dye-sensitized solar cells (Hagfeldt et al., 2010) (Fig. 1a) consists of dye sensitizer (e.g. N719, organic dyes, et al.), semiconducting layer (e.g. TiO_2, ZnO, et al.), redox electrolyte (e.g. I_3^-/I^-, TEMPO, et al.) and counter electrode (e.g. Pt, carbon, et al.). Zou et al. developed the wire/fiber shaped dye-sensitized solar cells with two twisted functional electrodes for flexible and wearable electronics (Fan et al., 2008; Zou et al., 2010). Since then, the studies about dye-sensitized photovoltaic fibers (Fig. 1b) cover novel structure design of the device (Fang et al., 2014; Yang et al., 2014), morphology evolution of semiconductor oxides (Cai et al., 2014; Dai et al., 2012), interface engineering of photoanode (Fu et al., 2013a; Song et al., 2016), electrolyte selection for improved stability (Li et al., 2014; Wang et al., 2011), Pt-free functional materials as counter electrode (Chen et al., 2015; Sun et al., 2014), et al. Representative achievements include efficient devices with energy conversion efficiency of 8–9% (Liang et al., 2014; Liu et al., 2015), flexible devices with length of up to 30 cm (Peng et al., 2015), fiber solar modules with high power output (Fu et al., 2011; Peng et al., 2014a) and advanced hybrid energy system integrated with fiber energy storage devices (Fu et al., 2013b; Wang et al., 2015). But the absorption of electrolyte that shields the incident light for dye absorption is a limiting factor for dye-sensitized photovoltaic fibers. Breaking through electrolyte shielding via structure design is a way to improve solar energy harvesting for high power output.

As the functional layer for light harvesting, the sensitizer is of virtual importance to device performance. Ru-based sensitizer N719 has contributed to the most efficient fiber solar cells. Quantum dots, like CdS and CdSe, could also play a role in cost-effective fiber solar cells with moderate performance in both aqueous and gel electrolyte (Uddin et al., 2014; Yan et al., 2014). However, metal based sensitizers still suffer from limited source and potential

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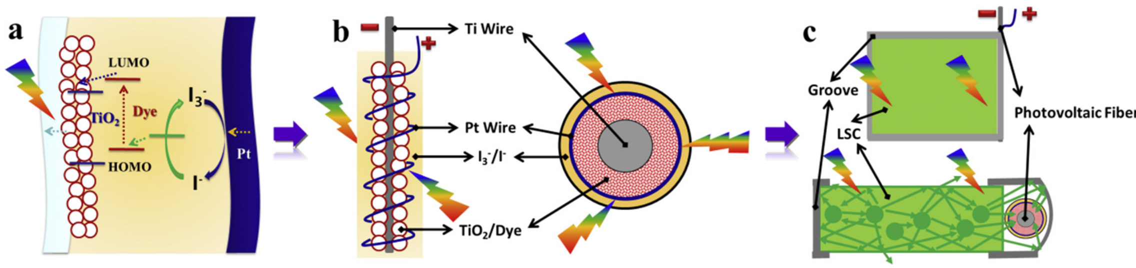

Fig. 1. (a) Schematic diagram of pro-type dye-sensitized solar cells. (b) Front and sectional view of dye-sensitized photovoltaic fibers, which is a structure revolution from pro-type dye-sensitized solar cells. The photovoltaic fiber is composed of a photoanode with dye-sensitized TiO_2 nanoparticle layer on the Ti wire substrate and a Pt wire electrode twisted on the photoanode. Due to the special symmetrical structure, the fiber solar cell could harvest light from the three dimensional environment. But the absorption of electrolyte would shield the incident light for dye absorption. (c) Front and sectional view of waveguide solar device integrating photovoltaic fiber with LSC. The green arrows present the waveguide path of the luminescent in the LSC. The aluminum grooves fix the photovoltaic fiber to the concentrating edge of LSC and provide additional reflex sites to complete the concentrating optical path.

environmental concerns. Metal-free dyes, which have advantages of abundant raw materials, easy to synthesis and low cost, are worth of exploring in solar fibers as a promising candidate. Still, few photovoltaic fiber based on organic dye is reported.

Organic dyes containing conjugated aromatic cycles usually have good light collection ability (large absorption coefficient) in the relative narrow wavelength range compared with typical metal based sensitizers (Ahmad et al., 2013). To compensate this drawback, concentrating light of a narrow wavelength range via integration design is a potential solution. Luminescent solar concentrators (LSCs) could collect light radiation over a large area, down-shift it by photoluminescence, and guide it to small edges for light concentration. They are thin, light, colorful, and semi-transparent plates, which could be potential building components in greenhouse panels and windows. Integrating fiber solar cells with LSC (Fig. 1c) could collect solar irradiation from the surroundings, red-shift the incident spectrum and concentrate the luminescent to photovoltaic fibers and achieve high power output (Peng et al., 2014b). For fiber solar cells, the luminescent with longer wavelength could escape the shielding effect of the electrolyte (Peng et al., 2014a). Due to different wavelength sensitivity, photovoltaic fibers based on different organic dyes would find its best LSC partner and achieve enhanced power output.

Hence, this work reports photovoltaic fibers based on organic dyes and their waveguide photovoltaic modules. The devices achieve energy conversion efficiency of > 3% via balancing dye adsorption and interface charge recombination; and the waveguide modules achieve power output enhancement of up to 2.7. As far as we know, this is the first time that organic dyes are involved in fiber solar cells and their modules. The partnership of organic dyes and LSCs would contribute to high power output with narrow-absorption sensitizers. And they have potential applications for building integrated photovoltaics.

2. Results and discussions

All the preparation and characterization details of organic photovoltaic fibers and waveguide solar devices are provided in supporting information. The metal-free dyes for dye-sensitized photovoltaic fibers marked as **Dye 1** is shown in Fig. 2a. Light harvesting and charge transfer are two main parameters as with fiber dye-sensitized photoanode affecting device performances. Optimizing the thickness of TiO_2 layer could ensure dye adsorption, balance optoelectronic transmission and interface combination. Organic dye-sensitized photovoltaic fibers with different TiO_2 thickness were fabricated and the corresponding photovoltaic and electrochemical parameters are summarized in Table 1. The *J-V* curves are shown in Fig. 2b. As the thickness of TiO_2 increases from 11 to 26 μm, *J*sc first increases from 6.15 to 7.54 mA/cm^2 and then decreases to 5.51 mA/cm^2. The trend of *J*sc does not follow that of the dye adsorption as the layer thickness (as shown in Fig. 2c), and the dye adsorption amount is not the limiting factor of *J*sc at thicker film thickness. *V*oc of the fiber solar cells decreases from 0.653 to 0.614 V as the film thickness increases. The trend is consistent with that of *R*ct fitted from the Nyquist plots (shown in Fig. 2d) according to the equivalent circuit (shown in Fig. 2e). Thicker TiO_2 layer increases the dye adsorption but leads to more charge recombination sites, a suitable layer thickness would balance these factors and contribute to optimized device performance. The energy conversion efficiency follows the "up-down" trend with highest η of 3.12% (*J*sc of 7.54 mA/cm^2, *V*oc of 0.644 V and *FF* of 0.643) at 13 μm thickness.

In some other trials, **Dye 2** (Fig. S1) based fiber solar cells achieved energy conversion efficiency of ~ 3% at similar thickness (Table S1). Meng et al. reported fibrous CdS/CdSe quantum dot on ordered TiO_2 nanotube for fiber solar cells with efficiencies of 1.49–3.18% (Huang et al., 2010). Li et al. prepared CdS on ZnO nanosheets and nano wires and obtained device efficiency of 0.01–0.6% (Chen et al., 2011). Cao et al. developed CdSe nanowires for fiber and fabric solar cells with efficiencies of 1–2.9% (Zhang et al., 2012). Metal-free dyes was applied in flexible dye-sensitized solar textiles with efficiency of 0.70–1.24% (Chae et al., 2015). Compared with the fiber devices with non-Ru sensitizers, the device performance in this work is quite acceptable. Still, the efficiency is lower than the planar devices (6.1–6.4%) (Thomas et al., 2008), indicating the room for further improvement. These results indicate the potential role of organic dyes in fiber solar cells.

To further exploit the potentialities for higher power output, the organic dye-sensitized photovoltaic fiber was integrated with several LSCs to fabricate the waveguide photovoltaic fibers. According to previous report, the IPCEs of **Dye 1**-sensitized solar cell are > 20% from 350 nm to 600 nm in the spectrum (Thomas et al., 2008). Four LSCs with peak emission wavelength at 429 (purple), 518 (green), 572 (orange) and 617 nm (red) were applied to find the matching relationship. Fig. 3a shows the *P-V* curves of solar modules based on **Dye 1**, and the photovoltaic parameters are summarized in Table 2. Among the parameters, the maximum power output (*P*max), and the power output enhancement factor (*N*) and the apparent energy conversion efficiency of the waveguide device (η_{LSC}) characters the photovoltaic performance of solar module as a whole; the energy conversion efficiency (η) reflects the effects of different LSCs on photoelectric energy conversion. The qualitative analysis concerning the luminescent spectrum, electrolyte absorption and IPCE region are shown in Fig. 3b.