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Efficiency enhancement of hybridized solar cells through co-sensitization and fast charge extraction by up-converted polyethylene glycol modified carbon quantum dots

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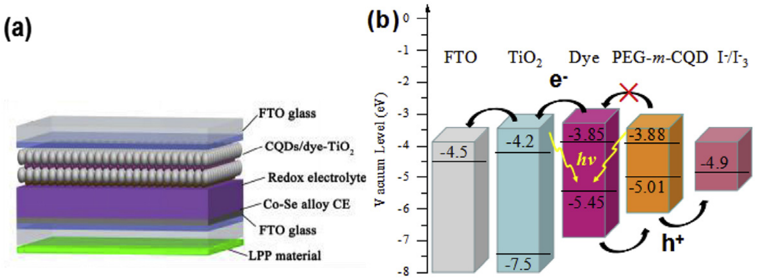
HIGHLIGHTS

- Hybridized solar cells are realized by N719, PEG-*m*-CQDs and LPP.
- PEG-*m*-CQDs can convert NIR into visible light.
- PEG-*m*-CQDs can extract holes from N719 dye to redox electrolyte quickly.
- LPP are used to store solar energy and release at dark.

GRAPHICAL ABSTRACT



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ABSTRACT

Photovoltaics are promising solutions to energy crisis and environmental pollution problems. The dye-sensitized solar cells with mesoscopic structures have attracted growing interests because of zero emissions, easy fabrication, scalable materials and techniques, *etc*. However, the state-of-the-art dye-sensitized solar cells have narrow spectral absorption for photoelectric conversion and high electron-hole recombination rate under sunlight illumination. Therefore, it is a persistent object to make wide-spectral absorption and fast charge extraction solar cells for energy harvest in both solar and dark-light conditions. To address this issue, we present here experimental realization of a category of solar cells converting visible and near-infrared light into electricity by co-sensitizing photoanode with N719 dye and polyethylene glycol (PEG) modified carbon quantum dots (PEG-*m*-CQDs), arising from up-conversion and hole-transporting behaviors of PEG-*m*-CQDs as well as photofluorescence of green-emitting long persistence phosphors. The optimized solar cell yields maximized photoelectric conversion efficiencies of 9.89% and 25.81% under simulated sunlight (air mass 1.5, 100 mW cm^{-2}) illumination and dark conditions, respectively. This work is far from optimization, but the physical proof-of-concept hybridized solar cell may markedly increase electricity generation time and total power output of photovoltaic platforms.

1. Introduction

Solar cells are photoelectric devices for converting solar energy into electricity with zero emissions [1–3]. Among several potential solar cells, dye-sensitized solar cells (DSSCs) have attracted

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tremendous scientific interests because of simplicity in their fabrication procedures and advances in technical aspects [4]. Until now, the narrow light absorption spectral of commercial N719 dye molecules, sluggish hole transportation from N719 to redox electrolyte, and sunlight-dependent conversion are regarded as the main barriers for the development of these photovoltaic devices. Various solar cell architectures have been applied to harvest extraordinary solar-energy from nature, and therefore increasing the power output. Li et al. have designed an integrated photovoltaic device assisted with a fluorescent concentrator for enhancing the response to sunlight [5]. Peng et al. have realized omnidirectional absorption via assembling a DSSC in a light weight waveguide fiber [6]. In addition to these light-harvesting designs, some inorganic quantum dots (QDs) that can absorb near-infrared light are always used as light absorbers, such as PbS [7,8] and GaSb [9]. However, the toxicity of these QDs has limited their applications in photovoltaics. Arising from lower toxicity [10], size- and synthesis-dependent optical absorption [11], and multiple exciton generation effects [12], carbon quantum dots (CQDs) are ideal alternative light absorbers in solar cells [13–19]. In fact, quantum dot-sensitized solar cells with CQD-only sensitizers yield lower power conversion efficiencies because of the weak affinity between CQDs and mesoscopic TiO_2 [20,21]. Moreover, the highest occupied molecular orbitals (HOMO) of N719 dye is −5.45 eV in comparison to potential (−4.9 eV) of redox I^-/I_3^- electrolyte, giving a large energy difference of 0.55 eV and therefore limited charges (electrons, holes) extraction. One of the solutions to this impasse is to improve interfacial charge extractions in competing with carrier trapping and even thermalization/cooling.

Another bottleneck problem for current solar cells is that they can only output electricity under sunlight illumination, while the power generation is low or zero in foggy, rainy and night *etc* dark-light conditions. Therefore, a challenging but promising topic is to realize persistent electricity-generation in all weathers [22]. Recently, we have taken the first step to create bifunctional all-weather DSSCs tailored by graphene [23], graphene based coating films [24] or platinum alloys [25] to harvest solar and rain energies. The final solar cells yield maximized photoelectric conversion efficiency of 10.38% [25] under solar irradiation as well as current of 5.97 μA and voltage of 227.8 μV under simulated rain droplets [24]. A remaining problem is that the above-mentioned solar cells are still unavailable at rain-free nights and other dark-light environments.

By addressing above-mentioned issues, it is desirable to study interfacial engineering of DSSCs by setting environment-friendly QDs at anode/electrolyte interface, acting as light converter and superfast bridge to facilitate hole injection from anode to redox electrolyte. In the current work, polyethylene glycol (PEG) molecules are used for CQDs passivation, realizing down- and up-conversion under excitation of ultraviolet (UV) and near infrared (NIR) light, respectively. The experimental results have shown that the power conversion efficiency of photovoltaic device is markedly enhanced using co-sensitizers from PEG-*m*-CQDs and N719 dye in comparison with N719-only based DSSC. The mechanism behind this enhancement is that the PEG-*m*-CQDs widens light absorption ranging from visible to NIR regions as well as fast hole extraction for efficient electron-hole separation. Moreover, transparent metal selenide counter electrode (CE) is modified by green-emitting long persistence phosphors (LPPs) to harvest scattering light from surrounding atmosphere and emit green photofluorescence for several hours at dark-light conditions. In this fashion, this fluorescent counter electrode may be considered as a “light absorber” in bright conditions and a “photosource” in dark-light environments.

2. Experimental

2.1. Preparation of CQDs

CQDs were prepared by a hydrothermal method using glucose as a raw material. In details, 2 g of glucose was heated at 195 ± 5 °C using a heating mantle for 6 min until the liquid was changed from colorless to orange. Subsequently, the resultant solution was dissolved in 50 mL of deionized water to obtain CQD aqueous solution.

2.2. Preparation of PEG-m-CQDs

0.2 g of PEG ($M_w = 4000$) was added into 30 mL of CQD aqueous solution, and vigorously agitated until complete dissolution.Then the solution was transferred into a Teflon lined autoclave and heated at 170 °C for 2, 4, 6, 8 or 10 h. After cooling to room temperature, the solution was subjected to filtration, centrifugation (8000 rpm) and dialysis in a dialysis bag (3500 D) for 3 days and the final PEG-*m*-CQDs aqueous solution was thus obtained. Subsequently, the PEG-*m*-CQDs aqueous solution was freeze-dried under vacuum to obtain solid powers which were dispersed in ethyl alcohol to form 1 mg mL^{-1} solution for use.

2.3. Preparation of CoSe CE and co-sensitized photoanodes

The CoSe alloy CE and TiO_2 colloid were prepared according to our previous reports [26]. The rear side of CoSe alloy CE was coated by ultrafine green-emitting LPP phosphors, which were mixed in the glue and then solidified in air for 12 h to obtain the LPP|CoSe CE. Colloidal TiO_2 films was fabricated by coating colloid onto freshly cleaned FTO glass substrates with 0.25 cm^2 by a doctor-blade method and then calcined at 450 °C for 30 min in air. The resultant mesoscopic TiO_2 anodes were sensitized by a 0.50 mM N719 ethanol solution for 24 h to obtain dye-sensitized N719 photoanodes. Then the N719-sensitized photoanode was spin-coated by PEG-*m*-CQDs ethyl alcohol solution for 30 s at a speed of 2000 rpm to obtain N719/PEG-*m*-CQDs co-sensitized photoanodes.

2.4. Solar cell assembly and measurement

Each solar cell device was built by sandwiching a I^-/I_3^- redox electrolyte between a CE and a photoanode. A liquid electrolyte consists of 0.1 M tetraethylammonium iodide, 0.1 M tetramethylammonium iodide, 0.1 M tetrabutylammonium iodide, 0.1 M NaI, 0.1 M KI, 0.1 M LiI, 0.05 M I_2 and 0.05 M 4-*tert*-butyl-pyridine in acetonitrile. The photocurrent density-voltage (*J-V*) curves of various solar cells with an active area of 0.25 cm^2 were recorded on a CHI660E electrochemical work station under irradiation of simulated solar light from an intensity controlled to 100 mW cm^{-2} xenon arc lamp. Before measurement for dark *J-V* curves, the solar cells were illuminated by a simulated solar light for 1 min. Immediately, the devices were covered in a completely dark condition and the *J-V* curves were recorded on a CHI660E electrochemical workstation in air. To calculate the dark efficiency, the fluorescent light intensity of LPP|CoSe CE was recorded by a standard silicon solar cell. Therefore, the dark cell efficiency was obtained according to $\eta = P_{max}/P_{in}$, P_{in} was the fluorescent light intensity of LPP|CoSe CE.

3. Results and discussion

Fig. 1a shows the synthesis process of PEG passivated CQDs using glucose as a raw material through bottom-up routes. Upon dehydration process through pyrolyzing reaction, glucose molecules are converted into CQDs through nucleation and epitaxial