



Controllable synthesis of organic-inorganic hybrid halide perovskite quantum dots for quasi-solid-state solar cells

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ABSTRACT

Photovoltaics are regarded as the promising solution to resolve energy and environmental problems owing to their high power conversion efficiency and zero emissions. However, the narrow-spectra absorption range and serious recombination reactions at electrode/electrolyte interfaces are two major drawbacks for high-performance solar cells. Herein, a new way of synthesizing organic-inorganic hybrid $\text{CH}_3\text{NH}_3\text{PbX}_3$ ($X = \text{Cl}, \text{Br}$ or I) perovskite quantum dots (PQDs) is demonstrated by dropping perovskite precursor solution into anhydrous toluene. After a systematic study, the results demonstrate that the energy levels of PQDs can be tuned through optimizing the stoichiometric ratio of halide ions, showing good optical properties for photovoltaic applications. A quasi-solid-state sensitized solar cell with configuration of FTO/*m*-TiO₂/PQDs/dye/long persistence phosphor/gel electrolyte/Pt/FTO is fabricated, yielding an impressive power conversion efficiency as high as 7.91%, which is higher than 7.26% for referenced device free of PQDs. The improved performances are mainly attributed to the increased light absorption as well as reduced recombination upon the incorporation of PQDs and long persistence phosphor into devices.

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1. Introduction

Photovoltaics are regarded as a promising solution to resolve energy and environmental issues due to their cost-effectiveness and zero environmental pollution [1–4]. Among various solar cells, mesoscopic-structured solar cells offer the solution-processable fabrication procedures, pushing the rapid improvement for future applications [5,6]. However, the state-of-the-art power conversion efficiency over 12% for dye-sensitized solar cell is still lower compared to traditional silicon solar cells and the high-profile perovskite solar cells, which is mainly attributed to the low light-harvesting ability and serious recombination reactions during charge-transfer processes [7]. To address these issues, many efforts have been made on co-sensitization or developing advanced light

absorbers covering the near and long-wave infrared part of the solar spectrum, aiming to improve the overall power conversion efficiency of photovoltaics [8–10]. Unfortunately, the extraction of photogenerated electrons from state-of-the-art N719 dye to mesoscopic TiO₂ is significantly limited because there is a large energy difference between the lowest unoccupied molecular orbital (LUMO) of N719 (−3.85 eV) and the conduction band (CB) of TiO₂ (−4.20 eV). This large energy difference at solar cell interface leads to serious charge recombination and therefore reduced photovoltaic performances. Therefore, the development of interfacial modification materials to optimize solar cell structure and to maximize photovoltaic performances are extremely important for high-performance photovoltaics.

Recently, organic-inorganic lead halide perovskite quantum dots (PQDs) have emerged as excellent materials for photoelectrical devices, stemming from their unique properties including high photoluminescence, easy fabrication and bandgap tunability [11]. Till now, the state-of-the-art PQDs are always used in light-emitting diodes with high external quantum efficiencies [12]. There are few reports on the application of PQDs as light-harvesters for solar cells, although the device based on $\text{CH}_3\text{NH}_3\text{PbI}_3$ PQDs can

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yield an efficiency of 6.5%. This efficiency is still lower than that of bulky perovskite film based devices owing to the serious recombination at interfaces as well as the degradation of perovskite [13]. On the contrary, previous reports have demonstrated that the interfacial engineering using PQDs as interfacial modification materials can significantly boost the charge extraction via optimizing energy alignment. These studies suggest that PQDs have promising application in solar cells [14].

In the current work, a modified anhydrous toluene assisted method is launched to synthesize $\text{CH}_3\text{NH}_3\text{PbX}_3$ ($X = \text{Cl}, \text{Br}$ or I) PQDs by tuning the stoichiometric ratio of halide ions in precursor. The PQDs are always synthesized by an antisolvent method through adding precursor into solvents with low polarity. In this fashion, the PQDs can be formed upon adding perovskite precursor in *N,N*-dimethylformamide (DMF) into anhydrous toluene. In comparison with traditional hot-inject method, this so-called anhydrous toluene assisted method can realize fast and large-scale synthesis of PQDs owing to the avoidance of any heat treatment processes. Through detailed spectroscopy study, the energy-level structures of PQDs can be easily tuned by changing constituent stoichiometries. The as-prepared PQDs are employed as charge-transfer bridge between TiO_2 and N719 dye to extract photo-induced charges from light-harvester. Furthermore, the absence of long alkyl molecules in synthesizing PQDs significantly improves the charge transfer ability of PQDs and therefore enhances the photovoltaic performances when incorporating them into solar cells [15].

2. Experimental

2.1. Synthesis of $\text{CH}_3\text{NH}_3\text{PbX}_3$ PQDs

$\text{CH}_3\text{NH}_3\text{X}$ ($X = \text{Cl}, \text{Br}$, or I) was synthesized by reacting methylamine with corresponding acids at 0°C . After vigorous agitation for 2 h, the solvent was evaporated with rotary evaporation equipment. The precipitates were rinsed three times with diethyl ether and dried under vacuum for use.

In a typical synthesis of $\text{CH}_3\text{NH}_3\text{PbX}_3$ PQDs, 250 μL of 0.2 M $\text{CH}_3\text{NH}_3\text{X}$ and PbX_2 ($X = \text{Cl}, \text{Br}, \text{I}$ or their mixture) DMF solution and 30 μL of *n*-octylamine was mixed and then added into 100 mL of anhydrous toluene at 25°C under vigorous stirring to produce a colloidal solution. The obtained colloidal solution was centrifuged at 7000 rpm for 15 min to remove the large yellow particles and the bright supernatant solution was kept for further use.

2.2. Preparation of $m\text{-TiO}_2/\text{PQDs}/\text{dye}/\text{LPP}$ photoanodes

TiO_2 colloid was synthesized by following the procedures in our previous report [16]. In details, 10 mL of titanium tetrabutanolatate was dropped into 100 mL of deionized water under vigorous agitation at 25°C . Then, 10 mL of acetic acid and 0.8 mL of nitric acid was added into the powders obtained from above reaction. After an agitation of 15 min at 80°C , 160 mL of deionized water was added into the colloid with persistent agitation until forming a semi-transparent solution. Later, the resultant solution was transferred into a Teflon-lined autoclave and heated at 200°C for 12 h. When cooling to room temperature, 0.4 g of commercial P25 were added under ultrasonic irradiation for 30 min and then heated at 200°C for 12 h again. Finally, the colloid was mixed with 0.8 g of poly(ethylene glycol) (PEG, $M_w = 20,000$) and 1 mL of OP emulsifier and subsequently concentrated at 80°C . Colloidal TiO_2 films with thickness of 10 μm and area of 5 mm \times 5 mm were fabricated by coating the TiO_2 colloid onto freshly cleaned FTO glass substrates ($12 \Omega \text{ sq}^{-1}$) by a doctor-blade method. The FTO glass was thoroughly rinsed in detergent, acetone, isopropanol, ethanol, and

deionized water for 30 min. Ultrafine green-emitting LPPs (purchased from Shenzhen HuiDuoSheng Luminous Material Co., Ltd.) dispersed in anhydrous toluene with the concentration of 0.25 g mL^{-1} was spin-coated onto TiO_2 film at 2000 rpm for 20 s. Subsequently, the FTO glass adhered colloidal TiO_2/LPP films were annealed in a muffle furnace at 450°C for 30 min in air to obtain $m\text{-TiO}_2/\text{LPP}$ photoanodes. Then the resultant $m\text{-TiO}_2/\text{LPP}$ electrodes were immersed into ethanol solution of 0.50 mM N719 for 24 h. The obtained sensitized $m\text{-TiO}_2/\text{LPP}$ electrodes were cleaned with ethanol again and dried with N_2 flow. The $m\text{-TiO}_2/\text{dye}/\text{LPP}$ was finally immersed into PQDs toluene solution for 48 h to obtain PQDs/dye co-sensitized photoanodes.

2.3. Solar cell assembly

0.65 M KI and 0.065 M I_2 were dissolved in 10 mL of propylene carbonate (PC), and then 8.5 g of polyethylene glycol ($M_w = 20,000$) were added to the mixture. The mixture was heated at 100°C under continuous stirring for 24 h in a three-necked flask under an atmosphere of nitrogen gas. Subsequently, the mixture was transferred to a Teflon autoclave and hydrothermally treated at 200°C for 12 h. Finally, a homogeneous viscous polymer gel electrolyte with a purplish black color was obtained [17].

The pyrolyzed platinum (Pt) electrode on FTO glass was used as a counter electrode [18]. In details, 0.4 mL of H_2PtCl_6 (1.0 wt%) isopropanol solution containing OP emulsification agent (1.0 wt%) was rapidly dropped onto heated FTO glass at 270°C . Each device was built by sandwiching a polymer gel electrolyte between a Pt counter electrode and a $m\text{-TiO}_2/\text{dye}/\text{PQDs}/\text{LPP}$ photoanode, sealed with a Surlyn film.

2.4. Characterizations

The characteristic photocurrent-voltage (*J-V*) curves of PQDs tailored solar cells were measured by a traditional electrochemical workstation (Chenhua, CHI660E) by reverse scan mode under standard AM1.5G (100 mW cm^{-2}) at a rate of 100 mV s^{-1} . The morphologies of PQDs were characterized by transmission electron microscopy (TEM) (FEI, Model Tecnai G2 F20). Ultraviolet–visible (UV–vis) absorption spectra of PQDs were conducted by UV spectrophotometer (Mapada, UV-3200s). The X-ray diffraction (XRD) patterns of the as-prepared films were recorded using an X-ray diffractometer (Bruker D8 ADVANCE) with $\text{Cu K}\alpha$ ($\lambda = 1.5406 \text{ \AA}$) radiation. The photoluminescence spectra of PQDs were collected on a fluorescence spectrophotometer (HORIBA Jobin Yvon, FluoroMax 4). The ultraviolet photoelectron spectroscopy (UPS) spectra of PQDs were examined by Ultraviolet Photoelectron Spectrometer. Time-resolved photoluminescence (PL) spectra of $m\text{-TiO}_2/\text{dye}$ and $m\text{-TiO}_2/\text{CH}_3\text{NH}_3\text{PbBr}_{1.5}\text{I}_{1.5}$ PQDs/dye films were characterized using a Transient Fluorescence Spectrometer (HORIBA Jobin Yvon, Deltapro).

3. Results and discussion

Organic-inorganic hybrid PQDs are prepared according to a modified synthesis method, in which *n*-octylamine and oleic acid are ligands [19]. To better highlight the inherent properties of PQDs, we have performed TEM characterization of the as-prepared PQDs. As shown in Fig. 1, the PQDs have spherical shape with an average particle size of 3–5 nm, showing a homogeneous distribution in toluene solution. Taking the CsPbBr_3 PQD as an example, the Bohr-radius is nearly 3 nm according to previous report [19], which is slightly smaller than the size of PQDs reported here. In this fashion, it can be deduced that the quantum confinement effects are negligible to determine the optical properties, and all the changes in

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