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Enhanced charge extraction by setting intermediate energy levels in all-inorganic $CsPbBr_3$ perovskite solar cells

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ABSTRACT

Perovskite-structured $CsPbBr_3$ halide is an emerging light-harvester for all-inorganic solar cells due to its superior stability against moisture and heat. However, the wide bandgap of $CsPbBr_3$ (2.3 eV) calls for serious charge recombination and low efficiency in its photovoltaics. We present here all-inorganic $CsPbBr_3$ perovskite solar cells (PSCs) by modifying $TiO_2/CsPbBr_3$ and $CsPbBr_3$/carbon interfaces with carbon quantum dots (CQDs) and phosphorus quantum dots (PQDs), respectively. The electron and hole extractions are markedly enhanced by setting intermediate energy levels, and the optimized PSC achieves a power conversion efficiency of 7.93% in comparison with 6.05% for the device free of CQDs and PQDs. Moreover, the unsealed PSCs are highlighted by long-term stability in high humidity over 1400 h. This work may provide new opportunities of promoting charge extraction at $CsPbBr_3$/charge-transporting material interfaces.

1. Introduction

Organic-inorganic hybrid perovskite solar cells (PSCs) have achieved an unprecedented development in power conversion efficiency (PCE) since the birth of first prototype [1–7]. Up to date, a certified PCE as high as 22.7% has been reported for state-of-the-art hybrid PSCs due to persistent innovations in material design, structure optimization and technology improvement [8]. Although the highest PCE of hybrid PSCs is comparable to that for monocrystalline silicon solar cells, the instability stemming from low tolerance to humidity and heat as well as halogen ion diffusion to back electrodes may be a challenging problem for practical applications [9–14]. Moreover, the high cost of precious metal electrodes and polymeric hole-transporting materials (HTMs) has been an economic burden for commercialization.

These intrinsic drawbacks of organic-inorganic hybrid PSCs may be supplemented by new devices with stable and cost-effective materials. Recently, perovskite-structured $CsPbBr_3$ halide with an energy bandgap of 2.3 eV is regarded as a promising light-harvesting material due to high humidity and thermal tolerances and stabilized crystal structure. Therefore, $CsPbBr_3$ halide has been successfully assembled for all-inorganic PSCs free of HTMs by replacing precious metals with carbon (including carbon black and graphene) electrode [15–22]. The all-inorganic $CsPbBr_3$ PSC with standard configuration of FTO/$TiO_2/CsPbBr_3$/carbon achieves the maximized PCE of 6.7% in prototype [15]. The lower efficiency in comparison to hybrid PSCs arises from two main reasons: (i) The wide bandgap of $CsPbBr_3$ halide (2.3 eV) results in light absorption at $\lambda < 550$ nm; (ii) The energy difference of 0.9 eV at $TiO_2/CsPbBr_3$ interface and 0.6 eV at $CsPbBr_3$/carbon interface lead to serious electron-hole recombination. Therefore, efficient charge extraction from $CsPbBr_3$ to TiO_2 or carbon layers by setting intermediate energy levels provides new opportunities for markedly enhancing solar cell performances.

Quantum dots (QDs) with tunable bandgaps and high absorption coefficients have great potentials as interfacial modification materials in PSCs to facilitate electron-hole separation [23–28]. Guided by this concept, we prepare phosphorus quantum dots

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(PQDs) with high hole mobility and electron-transporting carbon quantum dots (CQDs) by mild solution methods. By tuning the highest occupied molecular orbital (HOMO) of PQDs and lowest unoccupied molecular orbital (LUMO) of CQDs, intermediate energy levels are set at $CsPbBr_3$/carbon and TiO_2/$CsPbBr_3$ interfaces to extract holes and electrons, respectively. The preliminary results demonstrate an efficiency enhancement from 6.05% for pristine PSC to 6.71% for PQDs-only PSC and further to 7.93% for CQDs/PQDs modified solar cell. Detailed charge extraction behaviors of these interfacial modification materials and long-term stability of final PSCs are carefully studied to understand potential mechanisms behind performance enhancement.

2. Experimental

2.1. Materials and reagents

All starting materials including $PbBr_2$ (Aladdin; > 99.0%), CsBr (Aladdin; > 99.9%), red phosphorous (alfa; > 99.5%), graphite (CP; > 99.8%), carbon ink (MTW-OF-C-003; ~50%(wt)) were purchased from commercial suppliers and used without further purification. TiO_2 paste was synthesized according our previous work [29].

2.2. Preparation of PQDs and CQDs

10 mg of red phosphorous aqueous solution was hydrothermally treated in a Teflon-lined stainless-steel autoclave at 200 °C for 8 h and dispersed in 20 mL of isopropanol (IPA). Subsequently, the solution was ultrasonicated for 24 h in an ultrasonic-bath cleaning machine, and centrifuged at a speed of 7000 rpm for 25 min to obtain PQDs. 270 mg of graphite powders was mixed in 30 mL of *N*,*N*′-dimethylformamide (DMF) and hydrothermally processed in a Teflon-lined stainless-steel autoclave at 200 °C for 8 h. After cooling to room temperature, the brown transparent suspension could be obtained via discarding the black precipitates.

2.3. Preparation of TiO_2 photoanode

FTO glass was etched by Zn powders and HCl for a slender strip pattern, and rinsed with ethanol and deionized water. A layer of *c*-TiO_2 was deposited on the FTO glass by spin-coating an ethanol solution of titanium isopropoxide (0.5 M) and diethanol amine (0.5 M) at 7000 rpm for 30 s and annealing in air at 500 °C for 2 h. The *m*-TiO_2 layer was then deposited by spin-coating a colloidal TiO_2 at 2000 rpm for 30 s and annealed in air at 450 °C for 30 min. Then the substrate was immersed in an aqueous solution of 0.04 M $TiCl_4$ at 70 °C for 30 min, rinsed with water and ethanol, and finally annealed at 450 °C for another 30 min. The defect and refractive index of *m*-TiO_2 film is modified by TiO_2 produced from reaction of $TiCl_4$ with H_2O.

2.4. Assembly of solar cells

90 μL of CQDs solution in DMF was spin-coated onto FTO/*c*-TiO_2/*m*-TiO_2 substrate at 2000 rpm for 30 s, which was then annealed at 90 °C for 30 min. A DMF solution of 1.0 M $PbBr_2$ was spin-coated onto the *m*-TiO_2 layer at 2000 rpm for 30 s, followed by drying at 80 °C for 30 min. Then, 90 μL of CsBr (0.07 M) methanol solution was coated onto FTO/*c*-TiO_2/*m*-TiO_2/$PbBr_2$ at 2000 rpm for 30 s, following heated to 250 °C for 5 min on a hotplate. This step was repeatedly performed for four times to form a high-purity $CsPbBr_3$ layer.

The PQDs solution in IPA was spin-coated at $CsPbBr_3$ film at 2000 rpm for 30 s, followed by drying at 80 °C for 2 min to form PQDs modified $CsPbBr_3$ film. Finally, a carbon back-electrode with an average area of $0.09\ cm^{-2}$ was used to cover PSC device by coating conductive carbon ink onto FTO/*c*-TiO_2/*m*-TiO_2/CQDs/$CsPbBr_3$/PQDs structure and heating at 70 °C for 60 min.

2.5. Photovoltaic measurements and characterizations

The photo current density-voltage (*J*-*V*) curves of solar cells were recorded on a CHI660E electrochemical workstation with scanning speed of $0.1\ V\ s^{-1}$ under irradiation of simulated solar light intensity controlled at AM 1.5 ($100\ mW\ cm^{-2}$). The photovoltaic performance of each device was repeatedly measured at least ten times to control experimental errors within ±5%. The surface morphologies of the prepared films were characterized by a field-emission scanning electron microscopy (FESEM, Japan Hitachi field emission SU8220). The crystal structures of the halides were assessed by an X-ray diffraction (PHILIPSPW1800 diffractometer with Cu-Kα radiation). The detailed microstructures of the samples were analyzed by using JEOL 200 kV field emission transmission electron microscope (JEM-2100F). The steady-state photoluminescence was obtained at room temperature by FLS920 all functional fluorescence spectrometer. The incident-photo-to-current conversion efficiency (IPCE) was characterized by a power source (Newport 300 W xenon lamp, 66920) with amonochromator (Newport Cornerstone 260) in the 300–850 nm wavelength range at room temperature. The absorption spectra were measured by an ultraviolet–visible spectrophotometer (UV-3600, Shimadzu) in the 300–800 nm wavelength range at room temperature. The Time-resolved PL measurement was carried out using time-resolved fluorescence (Horiba Jobin Yvon, FL).

3. Results and discussion

Fig. 1a presents the preparation processes of an all-inorganic PSC with configuration of FTO/TiO_2/CQDs/$CsPbBr_3$/PQDs/carbon (Fig. 1b). Both compact TiO_2 (*c*-TiO_2) and mesoscopic TiO_2 (*m*-TiO_2) layers are deposited by a spin-coating method. The $CsPbBr_3$ perovskite layer is prepared by a solution-processable multi-step method, i.e. spin-coating one layer of $PbBr_2$ and successive four times of CsBr. Finally, carbon slurry composing of carbon black and graphene is covered by a doctor-blade method as a back electrode. The detailed information is presented in experiment section. Upon sunlight illumination, the $CsPbBr_3$ halides absorb photons, and photon-induced electrons jump from valence band (VB) to conduction band (CB) and subsequently flow to CB of TiO_2, leaving holes transfer to work function of carbon electrode. Arising from large energy differences at TiO_2 (4.2 eV)/$CsPbBr_3$ (3.3 eV) and $CsPbBr_3$ (5.6 eV)/carbon (5.0 eV) interfaces [15], the charges (electrons and holes) suffer serious recombination. The energy levels for CQDs and PQDs are characterized by UV–vis absorption spectrum and VB spectrum from UPS characteristics. Based on the absorption measurements (Fig. S2a), the band gaps for CQDs and PQDs are determined to be ~1.78 and ~1.98 eV, respectively. The VB onsets of CQDs and PQDs coated on a silicon substrate are calculated to be ~5.63 and ~5.2 eV according to the UPS data, as shown in Figs. S2b and c. The VB of the PQDs matches well with that of both $CsPbBr_3$ perovskite film (−5.6 eV) and the work function of carbon (−5.0 eV). Meanwhile, the CB of CQDs calculated to be ~3.85 eV also matches well with that of $CsPbBr_3$ perovskite and TiO_2. Therefore, CQDs and PQDs are used as interfacial modification materials to set intermediate energy bands to promote electron and hole extraction (Fig. 1c), respectively.

Well-aligned, large grain-sized, high-purity $CsPbBr_3$ phase is beneficial to achieve high-performance PSC devices. We find in our experiment that either one-step or two-step method produces mixed phases of $CsPbBr_3$ and $CsPb_2Br_5$, which may be one of the