Thermally-stable hydroxyl radicals implanted on TiO_2 electron transport layer for efficient carrier extraction in PbS quantum dot photovoltaics

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ABSTRACT

The electron-transport layer (ETL) between the PbS colloidal quantum dots (CQDs) active layer and the FTO substrate plays a crucial role in the associated heterojunction photovoltaics. However, the presence of surface defects in the ETL limits the performance of the photovoltaics. Herein, we report the improved carrier extraction at the TiO_2/PbS interface of planar PbS CQDs photovoltaics, which can be easily accomplished through pre-implanting thermally stable hydroxyl radicals on the surface of TiO_2 nanoparticles (NPs) for constructing ETL. The pre-implantations on the surface of TiO_2 NPs realized using HNO_3 aqueous solution treatment under the hydrothermal condition surprisingly wouldn't be completely removed after the annealing procedure necessary for preparing the conventional ETL, and effectively eliminate the interband trap sites of the TiO_2 NPs by passivating intrinsic oxygen-deficient defects for achieving well-matched electron affinity and work function. As expected, the interfacial bimolecular recombination events are obviously suppressed thanks to the well-acceptable trap densities existing in TiO_2 ETL as well as favorable interfacial band alignment for carrier extraction. Consequently, the power conversion efficiency (PCE) is pushed up to 9.31%, much better than the control competitors. Undoubtedly, this work provides another opportunity for optimizing performance of the relevant PbS CQDs photovoltaics resorting to interface engineering guideline.

1. Introduction

As a promising candidate of the most light-harvesting materials for photovoltaics, PbS colloidal quantum dots (CQDs) have invoked tremendous amount of scientific interests for their size-tunable bandgap, solution process and multi-exciton generation effect over the past decade [1]. Benefited from optimization of preparing technology and device structure, a certified power conversion efficiencies (PCE) over 11% for PbS CQDs heterojunction photovoltaics (HJPs) has been achieved, which casts hopeful twilight on their future commercialization [2]. More importantly, compared to other kinds of solution-processed photovoltaics like organic and perovskite counterparts, recent progresses in PbS CQDs HJPs guarantee that the whole fabrication can be fully operated under open atmosphere without any protection of insert gas, which is ineluctable for the air-sensitive materials device like

the organic and perovskite to achieve high efficiency and performance stability [2–5]. However, for PbS CQDs HJPs, the performance still lags behind those of perovskite competitors at prototype-level, not to mention the fully-fledged silicon-based photovoltaics [6–10].

To date, the common developed metal sulfide CQDs HJPs is nearly defined by a formation of planar rectifying junction between metal oxide materials (served as ETL) and CQDs active layer [11–15]. Amongst these key components, ETL has been demonstrated to play a crucial role in carrier production, extraction and transport events [11,16,17]. Until now, TiO_2 is still widely regarded as one of the most popular ETL materials for the solution-processed heterojunction photovoltaics because of its matched conduction band (CB) with the active layer, such as perovskite and various CQDs materials, and thus the high efficiency of electron injection and collection can be realized [18–23]. Nevertheless, TiO_2 was also reported to exhibit some limitations in the

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photovoltaics owing to some disadvantage such as low conductivity and a large amount of defects, leading to the notorious carrier recombination [24]. This is also the reasons that the ZnO nanomaterials receive the most impressive records in PbS CQDs HJPs.

To improve the efficiency of PbS CQDs HJPs, tremendous efforts have been devoted to tackle the above ongoing concerns for TiO$_2$ ETL. Doping and interface engineering in term of ETL are the most explored strategies for improving the performance of TiO$_2$ based PbS CQDs HJPs. For example, the carefully selected metal ions (Zr, Al, Sb and Nb) doped TiO$_2$ have been proved to be competent for serving as efficient ETL compared to the pristine TiO$_2$, resulting from improved capability of carrier extraction based on the optimal band offset even in the absence of a strong electric field [11]. When it comes to interface engineering, the incorporation of a thin buffer layer between TiO$_2$ ETL and PbS CQDs active layer, such ZnO and PCBM, has also been justified for suppressing the recombination events at the interface [25,26]. Recently, it was reported that the high device-grade PbS CQDs active layer based on atomic iodine ligands suffered from inefficient carrier extraction due to the interfacial band level mismatch caused by its deep conduction band (CB) level, which would further lead to the severe accumulation of photogenerated electrons and recombination events [16]. Moreover, Kemp et al. have also confirmed that increasing the TiO$_2$ ETL electron affinity and also lowering the surface state density can each have a positive effect on suppressing recombination and subsequently improving V$_{oc}$ [25], which was also successfully put into practice in chloride passivated ZnO and SnO$_2$ ETL [16,27].

In this work, taking the excellent chemical stability and commercial availability of TiO$_2$ nanomaterials into account, we utilize the anatase TiO$_2$ NPs pre-implanted with thermally-stable hydroxyl radicals (denoted as TiO$_2$·OH) as ETL materials in PbS CQDs HJPs. The anatase TiO$_2$·OH NPs was obtained by hydrothermal treatment of the commercial P25 powder with HNO$_3$ aqueous solution, followed by centrifugation to separate anatase TiO$_2$·OH NPs. The relevant results indicate that the pre-plantations (·OH) with excellent thermal-stability couldn't be get complete removal from the surface of TiO$_2$ NPs, which serve as not only the effective agents to passivate intrinsic oxygen-deficient defects, but also optimize band alignment at the interface of PbS/TiO$_2$ to improve the interfacial charge extraction. Accordingly, the main photovoltaic merits like short current density (J$_{sc}$) and open circuit voltage (V$_{oc}$) for the devices based on TiO$_2$·OH ETL were both improved. Finally, the PCE of our champion device can reached 9.31% (J$_{sc}$ = 25.03 mA/cm^2; V$_{oc}$ = 0.62 V; F.F. = 60%), better than the commercial DHS-SCP04 ETL based device (8.10%) and the commercial P25 ETL based device (7.66%) of the control competitors.

2. Materials and methods

2.1. Materials

The deionized water (DI water, 18.25 MΩ cm) from a Aike purification system (KL-UP-IV-5/10/20/40, Taiwan) was used. The commercial anatase-phase TiO$_2$ (DHS-SCP04), P25 (TPP2) spin-paste, and P25 (Degussa) powder were purchased from Dalian HeptaChroma SolarTech Co., Ltd. Lead(II) iodide (PbI$_2$, 99.999% trace metals basis, perovskite grade), lead(II) bromide (PbBr$_2$, 99.999% trace metals basis), lead(II) oxide (PbO, 99.999% trace metals basis), oleic acid (OA, technical grade, 90%), 1-octadecene (ODE, technical grade, 90%), acetone (ACS reagent, ≥ 99.5%), and hexamethyldisilathiane (TMS, synthesis grade) were purchased from Aldrich. Octane (anhydrous grade, ≥ 99%), N,N-dimethylformamide (DMF, for GC-HS, ≥ 99.9%), ammonium acetate (NH$_4$OAc, 99.996% metals basis), 1,2-ethanedithiol (EDT, 97%), 1-butylamine (Standard for GC, ≥ 99.7%), absolute ethanol (AR, water content ≤ 0.3%), and acetonitrile (HPLC Grade, ≥ 99.9%) were purchased from Aladdin Ltd. (shanghai, China). Toluene (Certified ACS) was purchased from Fisher Scientific. Nitric acid (HNO$_3$, GR, 65.0–68.0%) was purchased from Sinopharm Chemical

Reagent Co., Ltd. All reagents involving in this work were used as received without further purification.

2.2. Separation of anatase phase from P25 TiO$_2$ powder

In brief, 6.00 g of P25 TiO$_2$ powder was well-dispersed in 30 ml of acidic DI water (pH = 3.5 adjusted by HNO$_3$) via sonication, then the milky solution was loaded into a PPL liner sealed with stainless steel autoclave and heated to 150 °C under vigorous stirring condition for overnight. The resulting solution was then cooled down to room temperature and centrifugated with different centrifugal velocity. The supernatant containing anatase TiO$_2$·OH NPs was reserved for the subsequent characterizations and spin-casting solution for photovoltaic devices.

2.3. Synthesis of PbS CQDs

Oleic-acid-capped (OA-capped) PbS CQDs were synthesized via the classical hot-injection protocol under the N$_2$ insert gas as stated in previous report without any modification [13]. After the thrice centrifugal-washing, the OA-capped PbS CQDs were well-redispersed into octane with the concentration of 50 mg/ml for late use.

2.4. Synthesis of PbS CQDs photovoltaic ink

For producing the lead halide-passivated PbS CQDs photovoltaic ink via the phase-transfer ligand-exchange strategy, all the involving procedures were executed as depicted in previous report [2]. Briefly, the total volume of 5 ml homogeneous DMF solution containing (0.1 M PbI$_2$, 0.02 M PbBr$_2$ and 0.04 M NH$_4$OAc) with clearly yellowish color was prepared in advance. Then, 5 ml of the pre-diluted PbS CQDs octane solution (concentration: 10 mg/ml) was poured gently into the DMF solution, following by vigorous stirring for at least 5 min via the vortexer to realize the ligand-exchange reaction. After waiting for the formation of obvious phase-interface (sometimes, centrifugation process with low speed of 3500 rpm for a few seconds would be also advised to foster the separation of the two phases), the upper octane-phase with any possible flocculence or block sediment was removed by the single-use pipette. The reserved DMF solution containing lead halide-passivated PbS CQDs was washed thrice by the fresh octane to remove residual oleic acid ligands (i.e. OA). After that, the anti-solvent toluene was added into the dark DMF solution to precipitate the lead halide-passivated PbS CQDs via centrifugation. Finally, the as-obtained PbS CQDs were fully dried in the vacuum chamber for 20 min to remove any possible residual-toluene, which could guarantee the stable suspension of the PbS CQDs in the butylamine to form the targeted photovoltaic ink (concentration: ~200 mg/ml).

2.5. Photovoltaic device fabrication

TiO$_2$ ETL were deposited by spin-casting the solution (150 mg/ml) or the commercial TiO$_2$ paste (150 mg/ml diluted with absolute ethanol) onto the well-cleaned FTO substrates at 3000 rpm for 20 s, followed by thermal annealing at 450 °C for 30 min. The PbS CQDs active layers were spin-coated from the desired photovoltaic ink at 2500 rpm for 30 s in an air atmosphere. Next, two layers of EDT-treated PbS-CQD serving as P-type block layer were prepared using a layer-by-layer spin-coating process as the previous reported [16]. Finally, Au metal was deposited onto the EDT-treated PbS CQDs layer as the top electrode via the vacuum evaporation system with the final thickness of 80 nm.

2.6. Characterization

The X-ray diffraction (XRD) patterns of the TiO$_2$ nanoparticles were acquired on a X-ray diffractometer (Bruker, D8 Advance) with Cu Kα