Low-Temperature synthesis of FeOOH Quantum Dots as Promising Electron-Transporting Layers for High-Performance Planar Perovskite Solar Cells

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Abstract. The development of a low-temperature processed electron-transporting layers (ETL) is highly desirable for high-performance planar perovskite solar cells (PSCs) toward large-scale and flexible devices, yet remains a great challenge. Herein, a low-temperature route was applied to synthesize FeOOH quantum dots (QDs) as promising ETL for PSCs. A systematic survey of the structure, morphology and band structure was carried out, and the device performance further illustrates that the device based on FeOOH QDs ETL achieves a high efficiency of 17.3% with negligible hysteresis. Moreover, a stable current output at 0.8 V in 400 s was observed in the champion device. As a result, the low-temperature preparation of FeOOH QDs ETL and the corresponding excellent performance of PSCs present great commercial potential for future applications.

1. Introduction
Organic-inorganic lead halide perovskite solar cells (PSCs) have drawn tremendous interest recently owing to their superior photovoltaic and optoelectronic characteristics, such as high optical absorption coefficient, low exciton binding energy, long charge carrier lifetime [1-5]. In just several years, their power conversion efficiency (PCE) has increased dramatically from initial 3.8% in 2009 to the latest certified value of 25.2 % [6-10], close to the PCE value of industrial silicon solar cells. One of the main reasons for the rapid development of PSCs is their high PCE, low-cost, as well as simple solution processing capability [11-14]. Although PSCs exhibit remarkable performance, the current record efficiency of PSCs are mainly used TiO2 as an electron-transport Layers (ETL), which requires a high annealing temperature (>450 °C) and shows poor ultraviolet light stability due to its strong photocatalytic effect [15-17], resulting in large energy consumption and further impeding its implementation in flexible devices. Thence, it is imperative to exploit a new ETL with low-temperature process for realizing highly performance and durability PSCs.

Herein, FeOOH quantum dots (QDs) firstly were used as a promising ETL in PSCs via a low-temperature spray process. As-obtained FeOOH QDs ETL reveal uniform particle size and compact structure. The ultraviolet photoelectron spectroscopy spectra (UPS) and UV-Vis absorption spectrum illustrate that FeOOH QDs possess suitable energy band structure with promoted kinetics for charge transfer from perovskite layer to the ETL layer. As a result, PSCs based on FeOOH QDs ETL exhibit enhanced performance with efficiency of 17.3% with negligible hysteresis.
2. Experimental

Chemical. All chemicals were used as received without further purification. Iron chloride hexahydrate (FeCl₃·6H₂O, 99.9%), ammonium bicarbonate (NH₄HCO₃, 99.9%), N, N-dimethylformamide (DMF, anhydrous, 99.8%), chlorobenzene (CBZ, anhydrous, 99.8%) and dimethyl sulfoxide (DMSO, anhydrous, 99.8%) were purchased from Sigma-Aldrich. Lead iodide (PbI₂, 99.9985%) was purchased from Sigma-Aldrich. The other perovskite as well as HTL materials were obtained from Xi’an Polymer Light Technology Corp.

Preparation of FeOOH QDs. FeOOH QDs were prepared according to previous report [6]. Briefly, 2 mmol of FeCl₃·6H₂O as well as 6 mmol NH₄HCO₃ were dissolved in 100 mL of DMSO and then stirring at room temperature for 10 h. Then, the products were collected by centrifugation and washed several times with distilled water.

Devices fabrication. The Fluorine-doped tin oxide (FTO)-coated glass substrate is cleaned sequentially by detergent (2% Hellmanex in water), distilled water, acetone and isopropanol, respectively, and then treated by UV-ozone for 15 min to remove possible residues. A uniform and compact FeOOH QDs ETL film are prepared by spray of ethanol solution with dispersed FeOOH QDs on FTO coated glass substrates. After FeOOH QDs ETL deposition, the Cs₀.₀₅FA₀.₈₁MA₀.₄₄PbI₂.₅₅Br₀.₄₅ precursor solution (1.1 M) composed of PbI₂/PbBr₂ (molar ratios of 0.85: 0.15), FAI/FAI+MABr (0.05: 0.95), and (FAI+MABr+CsI)/(PbI₂+PbBr₂) with 1:1 was deposited by two-step spin-coating with 2000 rpm for 10 s and 6000 rpm for 20 s. During spin-coating, 180 μL chlorobenzene was dropped on the center of the substrate in the last 10s. The substrate was then heated at 100 °C for 60 min to form perovskite layer. Next, the hole-transport layer was deposited on perovskite film by spin-coating with 4000 rpm for 30 s. Finally, Au electrodes were deposited on top of the cell by thermal evaporation.

Characterization. Field Emission Scanning Electron Microscopy (FESEM, JEOL, JSM-6701F) and Transmission Electron Microscope (TEM, JEOL, JEM-2010) were employed to characterize the morphology of samples. The J-V characteristics are recorded using Keithley 2400 sour-cemeter under the solar simulator (Newport Oriel Sol3A) with simulated AM 1.5G illumination (100 mW cm⁻²).

3. Results and discussions

FeOOH QDs were prepared via a simple hydrolysis and dehydration process of FeCl₃·6H₂O in DMSO with the existence of NH₄HCO₃ at room temperature, as schematically depicted in Figure 1a. TEM images (Figure 1b) reveal that as-synthesized FeOOH QDs possess uniform size distribution of about 3-5 nm. Corresponding elemental distribution mapping in Figure 1b indicates that Fe and O elements are uniformly distributed on as-prepared FeOOH QDs samples. Crystal characteristics of as-synthesized FeOOH QDs are characterized via the powdered X-ray diffraction (PXRD). As indicated in Figure 1c, two weak diffraction peaks were observed and can be assigned to the (021) and (002) of goethite (JCPDS 29-0713), and no other impurity are observed. A uniform and compact FeOOH QDs ETL film are prepared by spray of as-synthesized FeOOH QDs ethanol dispersion onto FTO substrates (Figure 1d).
Figure 1. (a) Schematic illustration of room temperature prepare of FeOOH QDs, (b) TEM images of FeOOH QDs and corresponding elemental distribution mapping and (c) XRD pattern of as-prepared FeOOH QDs powders, and (d) Spray of FeOOH QDs solution for ETL.

Figure 2a and b present the top-view SEM images of bare FTO and FTO/FeOOH QDs ETL. As a result, ultra-small FeOOH QDs are homogeneous deposited onto FTO substrate after spray of FeOOH QDs ethanol dispersion compared to the rough bare FTO caused by large FTO grains. Figure 2c exhibits a compact perovskite film with uniform grain size deposited on FeOOH QDs ETL/FTO substrate, which is similar to that on other ETL substrates. As shown in Figure 2d, the cross-sectional SEM image depicts a typical planar heterojunction PSC based on FeOOH QDs ETL. The film thickness of FeOOH QDs layer, perovskite, Spiro-OMeTAD and Au electrode was determined to be ca. 20, 370, 120 and 70 nm, respectively. It can be observed that a very smooth interface between FeOOH QDs layer and perovskite, which is beneficial for device fabrication [18].
To investigate the effect of FeOOH QDs ETL on the carrier transfer property of PSC, ultraviolet photoelectron spectroscopy spectrum (UPS) and UV-Vis absorption spectrum are conducted to further investigate the energy band structure of FeOOH QDs. As demonstrated in Figure 3a-c, the Fermi level ($E_F$), Fermi edge level ($E_{F, edge}$) and bandgap ($E_g$) of FeOOH QDs are -3.13, 3.67 and 2.82 eV, respectively, according to the UPS and UV-Vis results, and the valance band maximum ($E_{VB}$) can be calculated to be -6.80 eV by $E_{VB} = E_F - E_{F, edge}$. The conduction band ($E_{CB}$) of FeOOH QDs is reflected from $E_g$ and $E_{VB}$, which is calculated as -3.98 eV. According to the results, the $E_{CB}$ of FeOOH QDs is close to that of perovskite layer, which could enhance charge transfer from perovskite layer to the ETL layer. The direct current conductivity ($\sigma$) of the FeOOH QDs and TiO$_2$ thin films were obtained by direct current-voltage ($I$-$V$) measurement, as depicted in Figure 3d. The $\sigma$ of FeOOH QDs and TiO$_2$ is calculated to be $2.39 \times 10^{-4}$ S/cm by $\sigma = D/(SR)$, respectively, where S and D are the active area and thickness of ETL, and R is resistance value estimated by $V = IR$ [19]. The result indicates that FeOOH QDs ETL possess better electron transporting ability than TiO$_2$ ETL.
Figure 3. (a) Ultraviolet photoelectron spectroscopy spectra (UPS) Fermi edge and cut-off energy of the FeOOH QDs film, (b) Tauc plot of FeOOH QDs film, (c) Energy band structure of PSC, and (d) Current-voltage curves of FTO/TiO₂ or FeOOH QDs ETL/Au.

Figure 4 illustrate the cell performance of as-prepared device employing FeOOH QDs film as ETL. Figure 4a presents the current density vs. voltage (J-V) characteristics of the champion cell from FeOOH QDs ETL are measured under AM 1.5G illumination, and the corresponding photovoltaic parameters are summarized in the inset. As indicated, the highest efficiency of 17.3% with a short-circuit current density (Jsc) of 23.20 mA cm⁻² was achieved, together with an open-circuit voltage (Voc) of 1.01 V and a fill-factor (FF) of 74% under reverse. The forward scan PCE is determined to be 16.1% with Jsc of 23.01, Voc of 0.97 V, and FF of 72%. To investigate the reliability of obtained PSC, the stabilized photocurrent density of the cell is measured under an applied bias at the maximum power point, as illustrated in Figure 4b. A stabilized PCE of 16.1% with a steady-state Jsc of 22.07 mA cm⁻² was achieved under continuous light soaking over 400 s, which matched well the PCE value obtained from the J-V measurements (Figure 4a).

Figure 4. (a) J-V curves of the best PSC performance under reverse scan and forward scan, and (b) Maximal steady-state photocurrent output of the best-performing device and their corresponding power output.
4. Conclusions
In summary, we report a low-temperature processed FeOOH quantum dots (QDs) as a novel ETL for PSCs. SEM results reveal that a uniform and compact FeOOH QDs film are prepared by spray. The investigation on energy band structure indicates that of as synthesized FeOOH QDs possess suitable energy band position, and enhance the carrier transfer property of PSC. Those features of FeOOH QDs enable PSCs to achieve a high efficiency of 17.3% with negligible hysteresis. Moreover, a stable current output at 0.8 V in 400 s was observed in the champion PSC.

Acknowledgements
This work was supported by the National Natural Science Foundations of China (No. 51702036, 61761016, 61965010 and 51775152).

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