γ-Fe₂O₃ as a novel Electron Transporting Material for Planar Heterojunction Perovskite Solar Cells by simple Room-Temperature Solution method

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Abstract. α-Fe₂O₃ has been demonstrated to be a promising electron transporting material (ETL) for fabricating efficient perovskite solar cells (PSCs) with good stability under ultraviolet light compared to the commonly used TiO₂. However, α-Fe₂O₃ films need to be processed over 500 °C, which is a serious impediment to fabricate devices on the flexible substrates. Herein, γ-Fe₂O₃ particles can be synthesized below 200 °C and the corresponding compact layers have been fabricated by a simple room-temperature solution process. The methylammonium lead iodide (MAPbI₃) PSCs based on γ-Fe₂O₃ show a power conversion efficiency of 12.86% with a short circuit current (Jsc) of 21.79 mA/cm², an open circuit photovoltage (Voc) of 0.93 V and a fill factor (FF) of 63.3%. These results indicate a possible direction for preparing flexible perovskite solar cells.

1. Introduction

Hybrid organic–inorganic perovskite solar cells (PSCs) have attracted much attention in the photovoltaic application due to its desirable characteristics such as high absorption coefficient, tunable energy band gap and longer charge carrier diffusion length [1-3]. Although efficient PSCs fabricated on electron transporting layer (ETL) such as TiO₂, ZnO, SnO₂, and ZnSnO₄[4-6] have been reported, recently our group has demonstrated that α-Fe₂O₃-based planar PSCs exhibit comparable efficiency with smaller hysteresis in contrast to that in TiO₂, which can be ascribed to the faster electron transfer between the perovskite and ETL. Herein, we first introduced a novel magnetic γ-Fe₂O₃ ETL which can be formed by simple room-temperature solution process. Our results show that the as-prepared γ-Fe₂O₃ ETL is compact and crack-free with densely packed γ-Fe₂O₃ nano-particles, which is beneficial to deposit a conventional smooth perovskite film. As a result, a noticeable PCE of 12.86% has been achieved in γ-Fe₂O₃-based planar PSCs. To the best of our knowledge, it is the first reported magnetic oxide material as ETL for fabricating PSCs. It is believed that γ-Fe₂O₃ opens a gate for innovate magnetic ETL in flexible PSCs.

2. Results and discussion

In order to elucidate the structural characteristic of all the samples sintered in air as a function of temperature, we performed X-ray diffraction (XRD) analysis. Figure 1a shows XRD patterns which revealed that favourable single γ-Fe₂O₃ phases with the cubic crystal system (JCPDS#39-1346) could
be achieved when sintered at 150 °C and 180 °C. Besides, the peaks of γ-Fe₂O₃ sintered at 180 °C is sharper and stronger compared to that sintered at 150 °C, which implies a better crystallization in case of 180 °C. However, when the sintering temperature increased up to 200 °C, other impure phases like α-Fe₂O₃ (JCPDS#80-2377) could be observed. Moreover, the characteristic peak of α-Fe₂O₃ gradually increased when further enhancing the sintering temperature as shown in case of 250 °C and 300 °C. The average crystalline size of γ-Fe₂O₃ particles calculated from Scherrer equation is about 49 nm for 150 °C and 43 nm for 180 °C, respectively. These XRD results reveal that the as-prepared nano-particles can be effectively converted to the pure γ-Fe₂O₃ phase in the experiment at 180 °C and α-Fe₂O₃ could be gradually observed over 200 °C. Figure 1b shows the scanning electron microscopy (SEM) image of the as-prepared powder synthesized at 180 °C. The SEM image exhibits nano-sized particles which is consistent with the XRD results.

Figure 1. (a) XRD patterns of γ-Fe₂O₃ nano-particles synthesized at different temperature. (b) SEM image of the as-prepared γ-Fe₂O₃ powder synthesized at 180 °C.

The device structure was FTO/γ-Fe₂O₃/perovskite/HTM/Au in this work which is illustrated in figure 2a. γ-Fe₂O₃ compact layer was coated on FTO substrate, which blocks direct contact between the perovskite and FTO. The upper layers were sequentially deposited as the process described in our published report [7]. Figure 2b shows a SEM image of a γ-Fe₂O₃ film deposited by a facile room-temperature spin-coating method. The film is compact, uniform and densely packed with γ-Fe₂O₃ NPs in a large scale. Thus, the upper perovskite layer consist of large grains is pin-hole-free covering the whole γ-Fe₂O₃ substrate, as shown in figure 2c. Photocurrent density-voltage (J-V) curves measured under simulated AM 1.5G illumination at an intensity of 100 mW/cm² and incident photon-to-electron conversion efficiency (IPCE) spectra of the devices fabricated using γ-Fe₂O₃ substrates are shown in figure 2d and figure 2e. The best performance based on this optimized γ-Fe₂O₃ ETL is presented in figure 2d in a reverse scan, yielding a power conversion efficiency (PCE) of 12.86 % with a short circuit current (JSC) of 21.79 mA/cm², an open circuit photovoltage (VOC) of 0.93 V, and a (fill factor) FF of 0.63. In figure 2e, the integration of the product of IPCE yields a current density of 18.98 mA/cm². Figure 2f shows a typical cross-sectional SEM image of complete device based on γ-Fe₂O₃. The thickness of γ-Fe₂O₃ electron-transport layer and perovskite active layers including a capping layer is ~40 nm and ~300 nm, respectively.
Figure 2. (a) Device structure of PSCs. (b) SEM topographical image of $\gamma$-$\text{Fe}_2\text{O}_3$ film deposited on FTO. (c) SEM image of MAPbI$_3$ perovskite layer fabricated on FTO/$\gamma$-$\text{Fe}_2\text{O}_3$. (d) J-V curves of the best-performing $\gamma$-$\text{Fe}_2\text{O}_3$-based PSC obtained by scanning from forward bias to short-circuit with a scan rate of 10 mV/s. (e) IPCE spectrum of the corresponding PSC. (f) Cross sectional SEM image of $\gamma$-$\text{Fe}_2\text{O}_3$-based PSC.

3. Experimental section

3.1. $\gamma$-$\text{Fe}_2\text{O}_3$ NCs Synthesis

Fe(NO$_3$)$_3$·9H$_2$O (0.5 mol/L) was dissolved in Dimethyl Formamide (DMF) and sintered in air with a heating rate of 1 °C/min at different temperatures for 2 hours. Subsequently, the as-prepared powder was thoroughly washed with deionized water for several times and get dried in the oven. The $\gamma$-$\text{Fe}_2\text{O}_3$ NCs inks were prepared by dispersing the obtained $\gamma$-$\text{Fe}_2\text{O}_3$ NCs in deionized water.

3.2. Device Fabrication

$\gamma$-$\text{Fe}_2\text{O}_3$ ETL was fabricated by spin-coating 10mg/ml $\gamma$-$\text{Fe}_2\text{O}_3$ NCs (synthesized at 180 °C) ink onto FTO/glass substrates at a speed of 5000 rpm for 40 s without annealing or other treatments. Subsequently, CH$_3$NH$_3$I and PbI$_2$ with a molar ratio of 1:1 were dissolved in anhydrous DMF, then stirring at room temperature to get a clear solution. CH$_3$NH$_3$PbI$_3$ perovskite films were fabricated on $\gamma$-$\text{Fe}_2\text{O}_3$ ETL by spin coating the prepared CH$_3$NH$_3$PbI$_3$ precursor solution at a speed of 5000 rpm for 40 seconds. 200 μL of anhydrous chlorobenzene was quickly dropped onto the spinning surface within the first 7 seconds of the one-step process. Then the as-prepared perovskite film was immediately transferred on a hot plate of 100 °C for 15 min. The hole transporting layer was synthesized according to our previous report [7]. Finally, ~40 nm-thick Au film was thermally evaporated on top of hole transporting layer under a high vacuum and the active area of all the cells was 0.16 cm$^2$.

3.3. Characterization

Photocurrent density-voltage (J-V) curves were measured by a digital source meter (2401, Keithley Instruments, USA) under AAA class solar simulator (91192, Oriel, USA) at AM 1.5G and 100 mW cm$^{-2}$ illumination, which was calibrated by a standard silicon reference cell. The incident photon to current efficiency (IPCE) were recorded on a solar cell quantum efficiency measurement system (QEX10, PV measurements, USA) as a function of wavelength from 300 nm to 800 nm. Field-emission scanning
electron microscopy images were obtained by using FESEM, JSM-7600F, JEOL, Japan to characterize the morphology of samples. The X-ray diffraction (XRD) patterns were recorded with X-ray diffraction system (Bruker D8 Advance diffractometer, Germany) with Cu Kα1 irradiation (λ = 1.5418 Å) at voltage of 40 kV and a current of 40 mA.

4. Conclusion
In summary, efficient PSCs based on γ-Fe2O3 compact layer were successfully fabricated through a controllable solution-processing under room temperature. We have demonstrated that the as-prepared nano-particles can be used to fabricate a kind of crack-free and densely packed γ-Fe2O3 film which is very efficient in extracting photo generated charge carries. As a result, γ-Fe2O3-based PSCs achieved a promising PCE of 12.86%. In conclusion, this study introduced a low-temperature process for fabricating efficient PSCs based on a innovate ETL. Future research should focus on optimizing the efficiency and elucidating the magnetic effect of γ-Fe2O3 on the performance of PSCs.

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