



Investigation of the stability for self-powered CsPbBr₃ perovskite photodetector with an all-inorganic structure

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ABSTRACT

All-inorganic cesium lead halide perovskites have attracted intensive interest as light absorbing materials due to their large absorption coefficient, long charge carrier lifetime and diffusion length, especially they show better stability than their organic and inorganic hybrid counterparts. Herein, we demonstrate a high-performance self-powered CsPbBr₃ perovskite photodetector based on an all-inorganic structure. Our self-powered devices show high performance with the responsivity of 0.3 A/W, detectivity of 1.15×10^{13} cm Hz^{1/2}/W and on/off ratio of 4.5×10^2 . Notably, ZnO nanorods as a scaffold, which functions as a protection layer, are used to effectively enhance the stability and durability of perovskite photodetectors. Our all-inorganic device exhibits improvement of the stability in the air, has a certain high temperature endurance and shows the anti-corrosion ability to water and alcohol. These good performances and high stability present a potential application in harsh environments without external power sources.

1. Introduction

Hybrid organic-inorganic halide perovskites with an ABX₃ structure have attracted wide attention in the past few years, including solar cells, photodetectors (PDs), light-emitting diodes (LED) and lasers [1–5]. Hybrid organic-inorganic halide perovskite materials used as light absorbers in photovoltaics possess excellent merits such as a direct band gap with large absorption coefficient, long charge carrier lifetime and diffusion length [6–8]. However, the stability of hybrid organic-inorganic halide perovskite materials in oxygen and moist conditions inhibits their further application [9]. Comparatively, all-inorganic CsPbX₃ (X = Cl, Br, I) perovskite materials have been demonstrated to have higher chemical stability, electronic properties and with low trap-state density [10–13]. However, it is challenging to prepare high quality inorganic perovskite polycrystalline thin film with large grain, so the high performance of the inorganic perovskite PDs is limited [14,15].

The inorganic perovskite PDs with self-powered performance have attracted intensive attention for their self-sufficient potential for operation, wireless performance, independence and sustainability [14,15]. Self-powered PDs have been reported with various structures, such as the Schottky, p-i-n junction type and photoelectrochemical cell type [16–20]. Of the various self-powered PDs, the inorganic p-i-n junction type is more promising because of its simple manufacturing process and stability. In the p-i-n junction, to gain more stable device, inorganic electron and hole

transport materials are very important. In these materials, ZnO and MoO₃ have been widely used as electron and hole transport layers (ETL and HTL) in perovskite solar cells and PDs, respectively, due to their low price, wide band gap and high stability [21–23].

Here, a high-performance self-powered CsPbBr₃ perovskite photodetector based on an all-inorganic structure is introduced, in which ZnO nanorods (NRs) are used as an ETL due to their large exciton binding energy (60 meV) and high carrier mobility with efficient electron transport capability in the radial direction. The configuration of the PD consists of glass/FTO/ZnO NRs/CsPbBr₃/MoO₃/Au. Our self-powered devices show high performance with the responsivity, detectivity and on/off ratio of 0.3 A/W, 1.15×10^{13} cmHz^{1/2}/W and 4.5×10^2 , respectively. More importantly, ZnO nanorod scaffold layer can function as a protection layer to effectively enhance the stability and durability of perovskite photodetectors. Furthermore, our all-inorganic device displays improvement of the stability in the air, a certain high temperature endurance and the anti-corrosion ability to water and alcohol.

2. Experiment section

2.1. Device fabrication

A fluorine-doped tin oxide (FTO) coated glass substrate with a sheet resistance of 18 Ω/sq (from Wuhan Jing-solar Energy Technology Co.,

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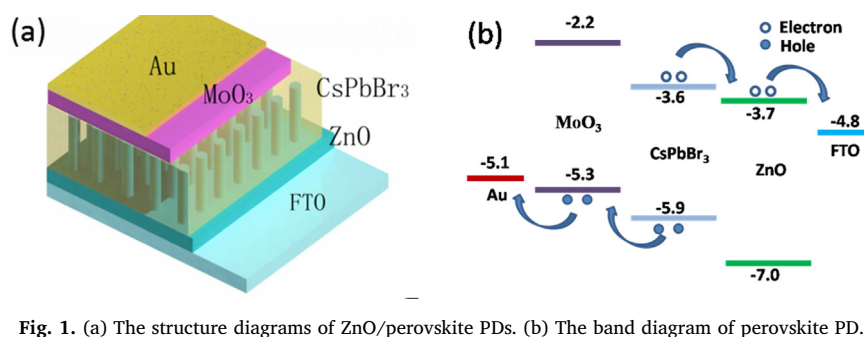


Fig. 1. (a) The structure diagrams of ZnO/perovskite PDs. (b) The band diagram of perovskite PD.

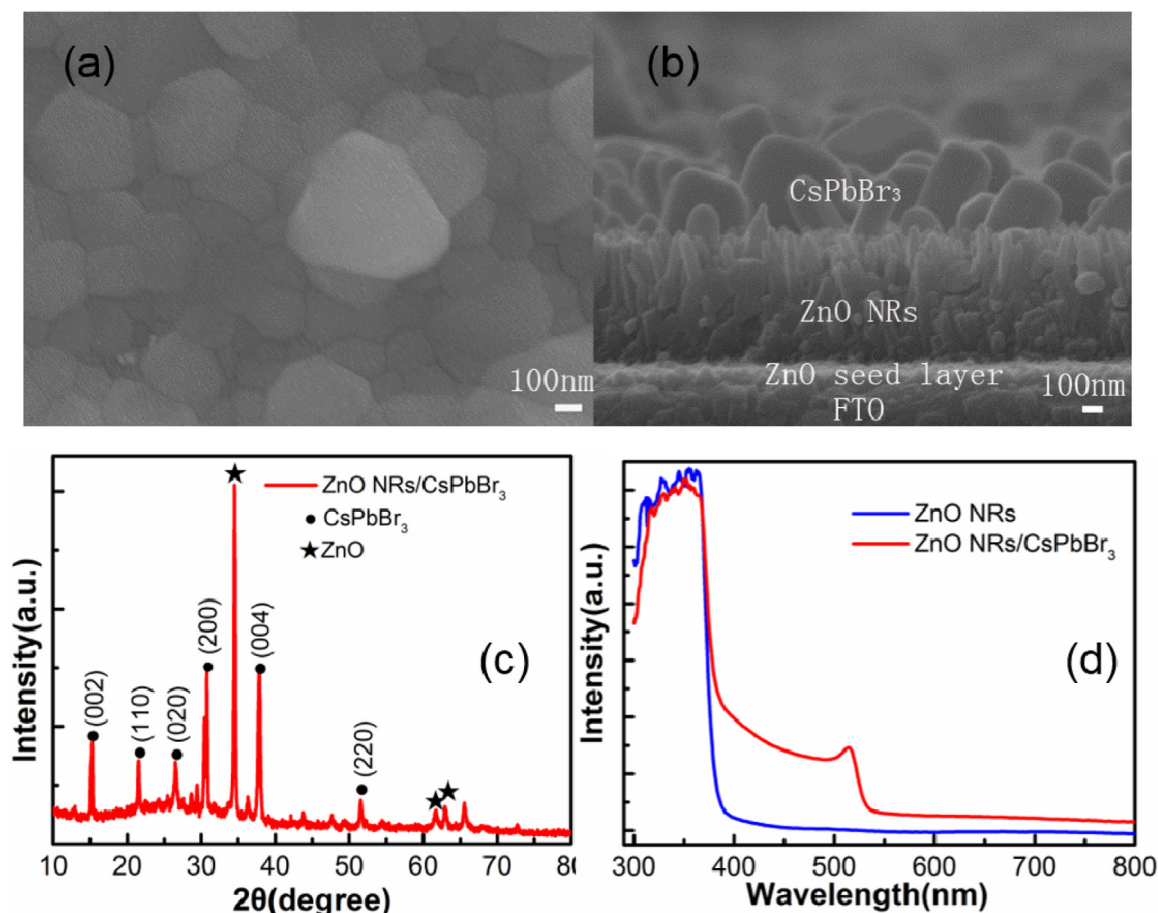


Fig. 2. (a) surface morphology of ZnO NRs/perovskite heterojunction. (b) cross section view of ZnO NRs/perovskite heterojunction. (c) XRD patterns of ZnO NRs/perovskite heterojunction. (d) UV-vis absorption spectra of ZnO, ZnO/perovskite, respectively.

Ltd) was cleaned using deionized water, acetone, alcohol in sequence for 15 min each in an ultrasonic cleaner and then cleaned in ultraviolet ozone atmosphere for another 30 min treatment.

ZnO seed layer was deposited onto the FTO substrate through spin coating method. A 0.15 M solution of zinc acetate dihydrate ($\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$) was completely dissolved in methanol and then spin coated on the FTO glass at 4000 rpm for 20 s. Then the samples were transferred into the muffle furnace to anneal for 2 h. After annealing in the muffle furnace, 0.6 g PEI (polyethylenimine), 50 mmol/L zinc nitrate hexahydrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), 30 mmol/L hexamethylenetetramine ($\text{C}_6\text{H}_{12}\text{N}_4$) were then dissolved after stirring for 30 min. The ZnO NRs were growing through hydrothermal method for 2 h. After taking out of the samples from the high pressure and temperature reaction kettle, the samples were heated at 350 °C in muffle furnace and kept warm for 2 h.

The inorganic perovskite CsPbBr_3 was synthesized according to Michael Kulbak et al. [24] The CsPbBr_3 films were prepared by two-step sequential deposition. 1 M of PbBr_2 was dissolved in *N,N*-dimethylformamide (DMF) solution and then kept at 70 °C for 15 h until the PbBr_2 precursor was completely dissolved. It was then filtered using a 0.2 μm pore size syringe filter. The solution was spin-coated on hot substrates for 30 s at 2500 rpm and were dried on a hot plate at 70 °C for 30 min. Then the PbBr_2 film was dipped in CsBr solution for 10 min and annealed for 10 min at 250 °C.

The HTLs, MoO_3 was deposited on the top of ZnO/perovskite using thermal evaporation method at a deposition rate of 0.2 \AA s^{-1} . The thickness of MoO_3 has been optimized and the optimal thickness is 12 nm. Then a 60 nm thick Au cathode was deposited on the top of MoO_3 at a deposition rate of 0.7 \AA s^{-1} .

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