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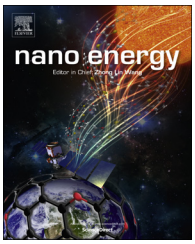

RAPID COMMUNICATION

A scalable electrodeposition route to the low-cost, versatile and controllable fabrication of perovskite solar cells

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Abstract
Hybrid organic/inorganic perovskite solar cells (PSCs) have emerged as a highly promising alternative renewable energy source because of their high efficiency and low-cost solution processable manufacturing technology. However, the commonly used spin coating process limits the large-scale manufacturing of perovskite layers for commercialization. Here we report on the development of an electrodeposition technique for fabricating perovskite layers and demonstrate its simplicity, versatility, scalability and roll-to-roll manufacturing compatibility. The key step is the electrodeposition of a PbO_2 layer on TiO_2 scaffold, which is then subjected to chemical bath conversion to sequentially generate PbI_2 and $CH_3NH_3PbI_3$ perovskite. Clearly demonstrated is the controllability of morphology and optical properties of the $CH_3NH_3PbI_3$ layer, leading to a higher power conversion efficiency (PCE) reproducibility and a higher average PCE when incorporated into carbon-based PSCs than with the spin coating technique. Remarkably, the cell area of electrodeposited PSCs could be easily scaled up to 4 cm^2 with an excellent perovskite film uniformity, rendering a PCE gain of 36.3% over the spin-coated counterpart. We further demonstrate the deposition of perovskite layers on complex shape substrates (e.g., stainless steel net), which would be rather difficult or impossible with other competing film deposition techniques. These results establish electrodeposition as a versatile and controllable route toward low-cost and large scalable manufacturing of high efficiency PSCs.

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Introduction

Hybrid organic/inorganic perovskite solar cells (PSCs) have emerged as promising alternative solar cells for large-scale deployment because of their high power conversion efficiency (PCE) but low-cost solution manufacturing process. Impressively, in the last five years, the PCE of PSCs has sky rocketed from a 3.8% to 20.1% [1-13], which makes it a very promising alternative to silicon-based solar cells. The perovskite layer (mainly $CH_3NH_3PbI_3$ [1,2,4,6,12,14,15], $CH_3NH_3PbI_{3-x}Cl_x$ [3,5,8], $CH_3NH_3PbI_{3-x}Br_x$ [1,7,16] and HC $(NH_2)_2PbI_3$ [10,17,18]) is at the core of PSCs and its quality greatly impact on the cell performance. So far, spin coating is almost the only method for fabricating the perovskite layer via one-step or two-step processes, and most of high efficiency PSCs are achieved by engineering the spin coating processes to fabricate high quality perovskite layers [4,6-8,19]. However, spin coating is only suitable for small area deposition on flat substrate, which would limit the commercialization of PSCs, and it is urgent to develop new alternative methods. Thermal evaporation, which has also been used for fabricating perovskite solar cells achieving PCEs of over 15% [5,20,21], is thought to be a scalable method and seems to have a better thickness control, but this method commonly requires high vacuum and high temperature, which restricts cost effectiveness and mass production. Therefore, one of the current challenges is to controllably fabricate large-scale and high quality perovskite layers for high efficiency PSCs via low-cost manufacturing processes.

Herein, we report a scalable perovskite fabrication route based on the electrodeposition technique. Electrodeposition is a low-cost and mature industrial technique for preparing large-scale and high-throughput mechanical or functional coatings via electrochemical reduction or oxidation. To date, it has added values to several solar cell technologies, especially for thin film solar cells, such as CdTe [22,23], $CuInSe_2$ [24,25], $CuInS_2$ [24], $CuInGaSe_2$ (CIGS) [26-28] and Cu_2ZnSnS_4 [29,30] since electrodeposition employing a continuous roll-to-roll process has greatly reduced manufacturing cost [26,27,31,32]. For example, roll-to-roll electrodeposited CIGS solar cells have been successfully scaled-up [27,31,33]. Therefore, successful application of electrodeposition for perovskite fabrication will surely facilitate the development of PSCs toward low-cost, large-scale, and roll-to-roll compatible manufacturing processes. Another obvious benefit of electrodeposition is its compatibility with a broad range of complex shape substrates, which would widen the application scope of PSCs, including flexible PSCs.

Results and discussion

Figure 1 schematically illustrates the fabrication processes of $CH_3NH_3PbI_3$ on TiO_2 porous scaffold based on electrodeposition. Firstly, electrodeposition technique was applied to deposit PbO_2 on the TiO_2 scaffolds (Stage 1). The aqueous electrolyte contained lead acetate ($Pb(CH_3COO)_2$), sodium nitrate ($NaNO_3$) and nitric acid (HNO_3), which was very stable in ambient environment and could be reused for a long period. Electrochemical oxidation ($Pb^{2+}+2H_2O \rightarrow PbO_2+4H^++2e^-$) [34] was used to deposit PbO_2, which was conducted in a standard three-electrode system at room temperature. The electrodeposition mechanism was studied in detail and is given in Supporting Information (Figures S1-S3), which exhibits a bottom-up growth feature. During electrodeposition, the slightly gray TiO_2 scaffold was gradually changed to bright brown color, suggesting the deposition of PbO_2. Then the PbO_2 on TiO_2 scaffolds was converted to PbI_2 by immersing in HI ethanol solution at room temperature (Stage 2), accompanied by the change of

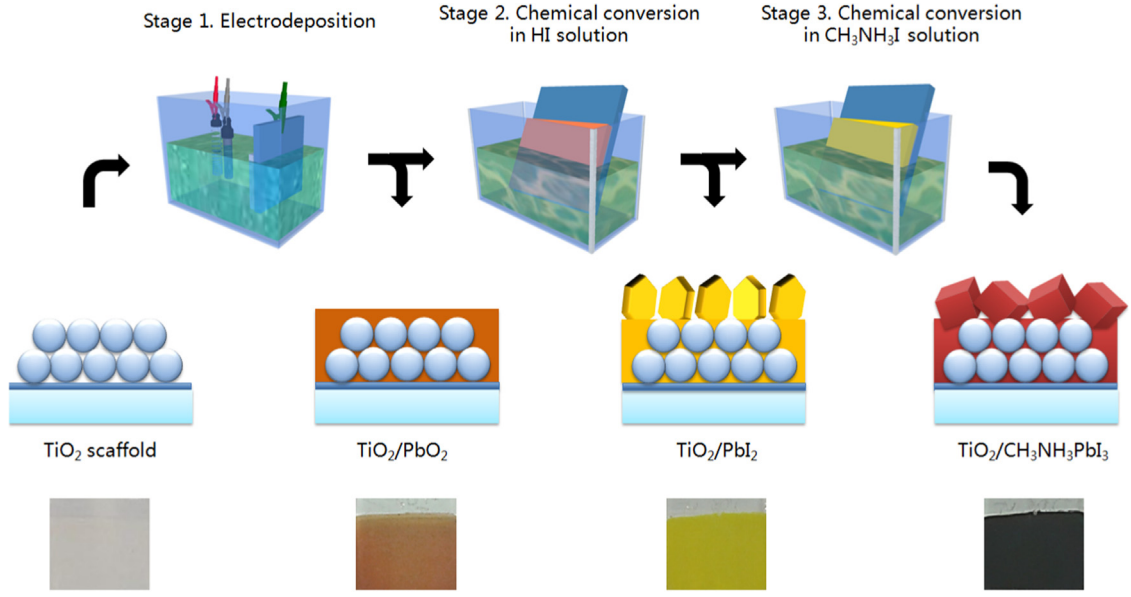

Figure 1 Schematic illustrating the fabrication processes of $CH_3NH_3PbI_3$ on TiO_2 porous scaffold based on electrodeposition. Stage 1: PbO_2 layer was electrodeposited in a standard three-electrode system at room temperature (RT) with the electrolyte containing 0.1 M $Pb(CH_3COO)_2$, 0.2 M $NaNO_3$ and 0.1 M HNO_3. Stage 2: PbO_2 layer was converted to PbI_2 layer in HI ethanol solution at RT. And stage 3: PbI_2 layer was converted to $CH_3NH_3PbI_3$ layer in CH_3NH_3I IPA solution at RT and then heated at 100 °C for 15 min.