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Short-length and high-density TiO_2 nanorod arrays for the efficient charge separation interface in perovskite solar cells

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ABSTRACT

The TiO_2 nanorod arrays with the length of 70 nm, the diameter of 20 nm, and the areal density of 1000 μm^{-2} were firstly prepared by the hydrothermal method using the aqueous grown solution of 38 mM titanium isopropoxide and 6 M hydrochloric acid at 170 °C for 60 min. Over-500 nm-thickness $CH_3NH_3PbI_{3-x}Br_x$ absorber layers were successfully obtained by sequential deposition routes using 1.7 M PbI_2·DMSO complex precursor solution and 0.465 M isopropanol solution of the methylammonium halide mixture with the molar ratio of $CH_3NH_3I/CH_3NH_3Br=85/15$. The perovskite solar cells based on the TiO_2 nanorod array and 560 nm-thickness $CH_3NH_3PbI_{3-x}Br_x$ absorber layer exhibited the best photoelectric conversion efficiency (PCE) of 15.93%, while the corresponding planar perovskite solar cells without the TiO_2 nanorod array and with 530 nm-thickness $CH_3NH_3PbI_{3-x}Br_x$ absorber layer gave the best PCE of 12.82% at the relative humidity of 50–54%.

1. Introduction

Over the last decades, TiO_2 nanorod arrays have been widely applied as one of the efficient charge separation and electron transporting materials in the fields of dye-sensitized solar cells [1–3], quantum-dot-sensitized solar cells [4], and organolead halide perovskite solar cells [5]. The length, diameter, areal density and surface hydroxyl group content of TiO_2 nanorod arrays strongly affected the interface charge separation and photovoltaic performance of the corresponding solar cells. To perovskite solar cells, Park [5] evaluated the influence of the rutile TiO_2 nanorod array length on the photovoltaic performance of perovskite solar cells using 1.25 M PbI_2 precursor solution and found that the TiO_2 nanorod array perovskite solar cells with the length of 1580 nm, 920 nm and 560 nm exhibited the photoelectric conversion efficiency (PCE) of 5.9%, 7.3% and 9.4%, respectively. Feng and Xu [6] prepared the rutile TiO_2 nanowire arrays with the length of 900 nm, 600 nm and 400 nm and the corresponding perovskite solar cells gave the PCE of 11.7%, 10.8%, and 9.7% using 1.2 M $CH_3NH_3PbI_3$ precursor solution. Hong [7] fabricated the perovskite solar cells using the 1800 nm-length TiO_2 nanorod array with 4.8 nm-thickness TiO_2 passivation layer and 1.0 M $CH_3NH_3PbI_3$ precursor solution and obtained the PCE of 13.45% without masking. Until recently, Li, Xie and Wang [8] assembled the perovskite solar cells with the 200 nm-length TiO_2 nanorod array using the 1.3 M $CH_3NH_3PbI_3$ precursor solution and obtained the highest PCE of 18.22%. Although the effect of the TiO_2 nanorod array length on the photovoltaic performance of the corresponding perovskite solar cells has been widely investigated, the influence of the TiO_2 nanorod array microstructure and surface feature on the interface charge separation has been rarely explored in perovskite solar cells, and the strategy with the combination of the short-length, high-density TiO_2 nanorod array and the high-thickness $CH_3NH_3PbI_{3-x}Br_x$ absorber layer has not been reported for assembling perovskite solar cells.

In this work, the TiO_2 nanorod arrays with the length of 70 nm, the diameter of 20 nm, and the areal density of 1000 μm^{-2} were prepared by the hydrothermal method using the aqueous grown solution of 38 mM titanium isopropoxide and 6 M hydrochloric acid at 170 °C for 60 min. The influence of different annealing temperatures on the surface hydroxyl group content of the TiO_2 nanorod arrays was analysed by X-ray photoelectron spectroscopy (XPS). Over-500 nm-thickness $CH_3NH_3PbI_{3-x}Br_x$ absorber layers were successfully obtained by sequential deposition routes using 1.7 M PbI_2·DMSO complex precursor solution and 0.465 M isopropanol solution of the methylammonium halide mixture with the molar ratio of $CH_3NH_3I/CH_3NH_3Br=85/15$. The interface charge separation and the photovoltaic performance of planar and the TiO_2 nanorod array perovskite solar cells with over-500 nm-thickness $CH_3NH_3PbI_{3-x}Br_x$ absorber layer were compared.

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2. Experimental

2.1. Preparation of TiO_2 nanorod arrays

TiO_2 nanorod arrays were grown by hydrothermal method according to the similar procedure [1]. In brief, the hydrothermal method was carried out in a stainless steel autoclave with Teflon liner of 50 mL capacity. 20 mL of 37% hydrochloric acid was added in the 20 mL of deionized water and sonicated for 5 min, and then 450 μL of titanium isopropoxide was added and further sonicated for 5 min. The aqueous grown solution containing 38 mM titanium isopropoxide and 6 M hydrochloric acid was obtained. Subsequently, two pieces of fluorine-doped tin oxide transparent conductive glass (FTO, 2.0 cm×1.5 cm) with 60 nm-thickness TiO_2 compact layer [9] were positioned tilted inside the Teflon liner with the active layer facing the wall. The above aqueous grown solution was added into the Teflon liner containing two pieces of FTO. The properly sealed autoclave was placed inside the oven preheated to 170 °C and the reaction time was set to 60 min. After the autoclave was naturally cooled to room temperature in air, the two pieces of FTO were taken out from the autoclave, rinsed thoroughly, and annealed at 105 °C, 300 °C and 450 °C for 30 min in air prior to use.

2.2. Preparation of over-500 nm-thickness $CH_3NH_3PbI_{3-x}Br_x$ absorber layers

The 1.7 M PbI_2·DMSO complex precursor solution was obtained according to our modified procedure [10–12]. The 0.465 M isopropanol solution of the methylammonium halide mixture with the molar ratio of CH_3NH_3I/CH_3NH_3Br=85/15 was prepared according to our previous report [12,13].

To prepare $CH_3NH_3PbI_{3-x}Br_x$ absorber layers, 70 μL, 1.7 M PbI_2·DMSO complex precursor solution was spin-coated at 3000 rpm for 20 s and the PbI_2·DMSO complex thin films with and without the TiO_2 nanorod array were produced. Immediately, 100 μL, 0.465 M isopropanol solution of the methylammonium halide mixture was dropped on the top of PbI_2·DMSO thin films. After waiting for 30 s (with the TiO_2 nanorod array) or 60 s (without the TiO_2 nanorod array), the spin-coater was started and the thin films were spin-coated at 5000 rpm for 30 s to ensure the complete reaction of PbI_2·DMSO and CH_3NH_3I/CH_3NH_3Br and remove the residual isopropanol solution of the methylammonium halide mixture. Over-500 nm-thickness $CH_3NH_3PbI_{3-x}Br_x$ absorber layers were obtained.

2.3. Solar cell fabrication and characterization

The XPS analysis of the surface hydroxyl group content on the TiO_2 nanorod arrays was performed using X-ray photoelectron spectroscopy (ESCALAB250Xi, Thermo, USA). The electrochemical impedance spectroscopy (EIS) was obtained by applying sinusoidal perturbations of ± 10 mV over the bias of −0.90 V at frequencies from 1 to 10^6 Hz. The black and opaque film with the square aperture (3 mm×3 mm) adhered on FTO and the active area of 0.09 cm^2 was defined. The photoelectric conversion efficiency measurements were completed in atmosphere ambient with the relative humidity of 50–54%.

The preparation of the 60 nm-thickness TiO_2 compact layer, *spiro*-OMeTAD layer, 60 nm-thickness gold electrode, the characterization of FE-SEM, XRD, UV–Vis, UV–Vis–NIR, EDS, the fabrication and photovoltaic performance measurement of perovskite solar cells were the same as our previous reports [9,14–16].

3. Result and discussion

3.1. Influence of annealing temperatures on the surface hydroxyl group content of TiO_2 nanorod arrays

Fig. 1 shows the surface and cross-sectional SEM images of TiO_2 nanorod arrays on FTO and 60 nm-thickness TiO_2 compact layer. The TiO_2 nanorod array possesses the length of 70 nm, the diameter of 20 nm, and the areal density of 1000 μm^{-2}. The high areal density should be related to the small diameter of the TiO_2 nanorod array and beneficial to the charge separation in the interface of the TiO_2 nanorod array and perovskite. Moreover, its appearance using titanium isopropoxide as a Ti precursor in our experiment is cylindrical in shape, which is obviously different from the tetragon in shape with square top facets using titanium butoxide as a Ti precursor [1].

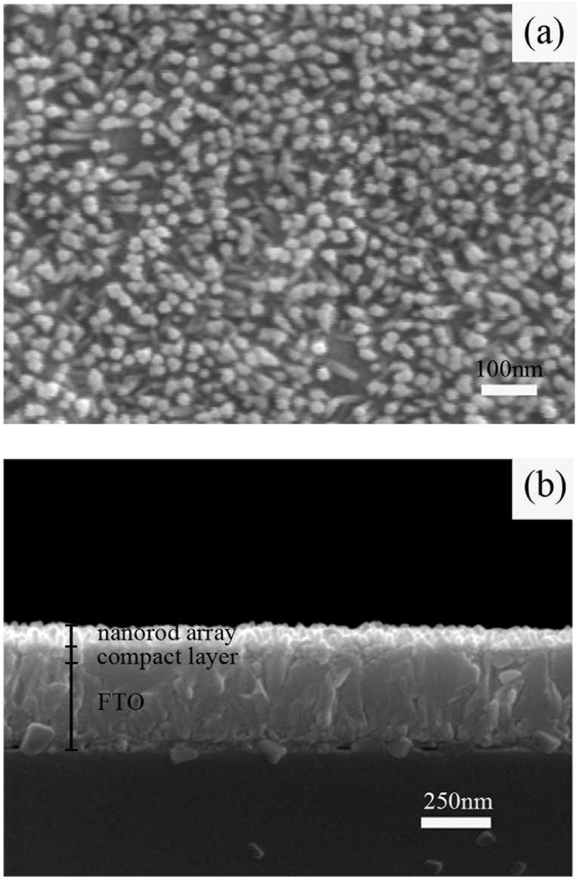

Fig. 1. Surface and cross-sectional SEM images of the TiO_2 nanorod array.

Fig. 2 presents XPS spectra of O_{1s} in the TiO_2 nanorod arrays at the annealing temperatures of 105 °C, 300 °C and 450 °C. The characteristic peaks at 531.4 eV and 530.0 eV can be seen in the high-resolution O_{1s} spectra. The former peak is closely related to the hydroxyl groups (-OH) resulting mainly from the chemisorbed water, and the later peak is described to the O atom bound to Ti (-OTi) [17]. Therefore, the atomic ratio of O in the TiO_2 nanorod arrays can be estimated by Gauss fitting and the corresponding result is –OH: –OTi=0.57:1 of 105 °C, 0.39:1 of 300 °C and 0.38:1 of 450 °C. The–OH content of 105 °C is higher than that of 300 °C and the -OH content of 300 °C is similar to that of 450 °C. The result implies that TiO_2 nanorod arrays can dehydrate the chemisorbed water at the annealing temperature of 300 °C and the chemisorbed water has almost completely been dehydrated at the annealing temperature of 300 °C for 30 min.

3.2. Morphology, absorption spectra and crystal phase of $CH_3NH_3PbI_{3-x}Br_x$ absorber layers

Fig. 3 displays the cross-sectional and surface SEM images of $CH_3NH_3PbI_{3-x}Br_x$ absorber layers using 1.7 M PbI_2·DMSO complex precursor solution. From the cross-sectional SEM image, the $CH_3NH_3PbI_{3-x}Br_x$ absorber layer thickness with the TiO_2 nanorod array was 560 nm and the $CH_3NH_3PbI_{3-x}Br_x$ absorber layer thickness

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