



High-efficiency hole-conductor-free rutile TiO₂-Nanorod/CH₃NH₃PbI₃ heterojunction solar cells with commercial carbon ink as counter-electrode

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ABSTRACT

This work demonstrates the fabrication of a high-efficiency, hole-conductor-free, solid-state perovskite solar cell with TiO₂-nanorod arrays (NRAs) as photoanodes and commercial carbon ink as counter-electrodes. TiO₂-NRA films of various thicknesses were deposited on FTO electrodes through hydrothermal method for different reaction durations. The effect of the thickness of TiO₂-NRA films on device performance was investigated in detail. The TiO₂ NRAs/CH₃NH₃PbI₃/C devices based on 688 nm-thick TiO₂-NRA films exhibited the optimal performance and power conversion efficiency (PCE) of as high as 8.56%. This value is comparable with the PCE of the recently reported TiO₂ NRA/Perovskite/HTM/Au solar cell.

1. Introduction

The problem of energy shortage is poised to become the major global problem within the next five decades. Approximately 94% of the energy consumed in China can be attributed to coal-based nonrenewable energy resources, such as petroleum and natural gas. In recent years, research in the photovoltaic field has focused on the development of solar energy as a safe and clean renewable resource. Many local and foreign researchers have proposed novel low-cost and highly efficient techniques for the fabrication of solar cells. Organic–inorganic hybrid perovskite-based heterojunction solar cells have recently attracted considerable attention in the field of photovoltaic research because of their inexpensive production process and excellent photoelectric conversion performance. Perovskite solar cells (PSCs) were first reported in 2009 (Kojima et al., 2009). PSCs initially demonstrated a photoelectric conversion efficiency (PCE) of 3.8% (Kojima et al., 2009), which has since been enhanced over 22% (Yang et al., 2017), making them superior to solar cells based on a-Si or organic polymers and to dye-sensitized solar cells (DSSCs) (Xing et al., 2013; Stranks and Eperon, 2013). Organic–inorganic hybrid perovskite (HOIP) crystals (CH₃NH₃PbX₃, X = Cl, Br, and I) are efficient light-absorbing materials with potential applications in next-generation solar cells. The major advantages of HOIP crystals include strong broadband absorption (Lee et al., 2012), low exciton binding energy (Stranks and Eperon, 2013),

long diffusion length (100–1000 nm) and lifespan (100 ns) of the electric charge carrier (Stranks and Eperon, 2013), high ambipolar charge migration rate (Giorgi et al., 2014) and low material cost (Jung et al., 2014). Moreover, HOIP crystals can be prepared into films under low processing temperatures through the solution method (Jung et al., 2014). These films, in turn, are suitable for applications in the construction of large-area devices. These characteristics contribute to the commercialization of HOIP-based solar cells. Novel, environmentally friendly solar cells based on large-area PSCs can be developed. These cells can exhibit high conversion efficiency and stability, large-scale industrialization, and low cost. Thus, they have extensive application prospects in various fields, including the construction of photovoltaic buildings and energy vehicles. Moreover, they may enable the fabrication of wearable flexible devices on flexible substrates, such as plastics and fabrics, in the future.

A typical PSC is a sandwich structure that mainly consists of a TiO₂ compact layer and a mesoporous layer that has been spin coated on a conductive glass substrate (Lotsch, 2014), a hybrid perovskite film, a hole-transporting layer, and a metal counter-electrode. When irradiated with light, the perovskite absorbs light and photogenerates electrons, which are subsequently transported to the TiO₂ conduction band and reach the counter-electrode through the external circuit. Studies on PSCs have mainly focused on optimizing the constituent parts of PSCs. The TiO₂ photoanode, an important component of PSCs, functions in

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electron injection, collection, and recombination. Thus, it greatly influences the PCE of PSCs. Improving the photoelectric properties of cells relies on the comprehensive investigation of photoanode properties. The photoanode film of typical DSSCs consists of disordered TiO₂ nanoparticles and exhibits high PCE (Lotsch, 2014). However, numerous defects present in TiO₂-nanoparticle-based photoanode films cause the severe loss of photogenerated electrons during transmission. TiO₂ nanoparticles in a one-dimensional (1D) structure can provide a direct transmission channel for photogenerated electrons and ZrO₂ as a scaffold infiltrated with perovskite by Han's work (Mei et al., 2014; Xu et al., 2018; Yue et al., 2018), thus decreasing the number of photogenerated electrons captured by defects and therefore improving electron transmission efficiency (Liu and Aydil, 2009; Zhu et al., 2007; Law et al., 2011, 2006). Besides, the application of 1D-structured TiO₂, rather than nanoparticle films, can improve the charge transfer, low interfacial recombination and PCE of devices (Thakur et al., 2017; Enache-Pommer et al., 2007; Liu and Aydil, 2009; Mor et al., 2006).

Among the three crystal forms of TiO₂ (i.e., anatase, rutile, and brookite), anatase nano-TiO₂ exhibits the optimal PCE, and rutile-type TiO₂ is the most stable and demonstrates the best light-scattering performance (Bach et al., 1998). Under certain temperatures, anatase and brookite TiO₂ can be transformed into a rutile crystal form (Hodes and Cahen, 2012). Compared with photoanode films based on TiO₂ nanoparticles with a disordered structure, those based on rutile-type TiO₂ nanorods can be easily controlled in terms of diameter and length (Liao et al., 2012). Furthermore, the electronic mobility of TiO₂ nanorods is two orders of magnitude higher than that of TiO₂ nanoparticles (Feng et al., 2008). Rutile TiO₂ presents better chemical stability and a stronger light refractive index than anatase TiO₂ (Liu and Aydil, 2009; Kim et al., 2002; Park et al., 2000; Navab et al., 2018). Thus, in this study, a rutile TiO₂-nanorod array (NRA) was fabricated on a fluorine-doped tin oxide (FTO) substrate through a low-temperature hydrothermal method in accordance with previously reported procedures. The morphologies of the rutile TiO₂-NRA under different hydrothermal conditions were analyzed, and the photoelectric conversion performance of perovskite solar cells based on rutile TiO₂-NRA photoanodes under different hydrothermal conditions was also investigated.

Metallic materials, such as Au and Ag, are commonly used as counter electrode materials in PSCs. However, metal electrodes are expensive and are easily corroded by halide ions; corrosion consequently decreases the photovoltage of devices. Moreover, metal electrodes are unsuitable for large-scale industrial production, and the thermal evaporation technique used to produce metallic counter-electrodes is not ideal for PSC commercialization given its high energy consumption. In addition, Au is an expensive electrode, thus further increasing PSC cost. Although Ag is cheaper than Au, it is unstable in devices with non-hole-transporting layer structure. Cheap counter-electrode materials must be developed given the competitiveness of the photovoltaic market.

Carbon is one of the most abundant elements in the Earth's crust, and it is an environmentally friendly and good electrical conductor with the characteristics of light weight, easy availability, and excellent chemical and temperature stability. Numerous carbon allotropes have been successfully applied as electrode materials in photoelectronic devices, such as DSSCs, transistors, and supercapacitors (Wan et al., 2015). Moreover, the work function of carbon is -5.0 eV, which is approximately equal to that of gold electrodes (-5.1 eV). This characteristic suggests that the energy level of carbon can match the energy level of hybrid perovskite (the valence and conduction bands of CH₃NH₃PbI₃ are -5.43 and -3.93 eV, respectively). Therefore, carbon is an ideal material for PSC counter electrodes (CE). Yang prepared a counter-electrode from commercial carbon under low process temperatures. The optimized counter-electrode exhibited a PCE of 16.1%, which was the highest efficiency attained by a PSC based on a carbon counter-electrode. The novel low-cost and high-efficiency carbon-based PSC prepared by Yang demonstrated excellent stability and passed an

indoor 1000 h light-stability test (Zhang et al., 2016). In the present study, a carbon-electrode-based PSC without a hole-transporting material was assembled using commercial conductive carbon paste. In contrast to Han's work (Mei et al., 2014), PSCs were assembled in the present study in accordance with traditional working procedures for PSC assembly as follows: compact layer TiO₂ → mesoporous layer TiO₂ → hybrid perovskite → counter-electrode.

2. Experimental

2.1. Preparation of TiO₂ compact layer

TiO₂ compact layers were formed by spin coating clean FTO glasses with 0.15 M titanium diisopropoxide(bis-2,4-pentanedionate) in n-butanol solution at 3000 rpm for 30 s. The coated glasses were then heated at 125 °C for 5 min. After the coated film was cooled down to room temperature, the same steps were repeated five times using 0.3 M titanium diisopropoxide(bis-2,4-pentanedionate) in n-butanol. The obtained FTO glasses with TiO₂ precursor solutions were then heated at 500 °C for 15 min.

2.2. Growth of TiO₂-NRA

Transparent TiO₂ mesoporous precursor solution was prepared by adding 30 mL of HCl to 30 mL of deionized water. Then, 1.2 mL of Ti(OC₄H₉)₄ was added dropwise to the solution, and the solution was then stirred for 5 min. A FTO (2 cm × 2 cm) glass covered with compact TiO₂ layer was placed into a hydrothermal reactor. The precursor solution was transferred to the hydrothermal reactor. A series of TiO₂-NRAs were grown by allowing the hydrothermal reaction to proceed at 180 °C for 50, 60, 70, 80, and 90 min. Finally, the TiO₂-NRA coated FTO was annealed at 550 °C for 2 h after cleaning and drying.

2.3. Fabrication of solar cells

Prepared TiO₂-NRA films were coated with perovskite precursor solution (40 wt.% DMF solution with PbI₂ and CH₃NH₃I of equal molar ratios) at 4000 rpm for 45 s, then heated at 90 °C for 1 h under argon. Commercial carbon paste was coated onto (CH₃NH₃)PbI₃-sensitized TiO₂-NRA films and heated at 100 °C under vacuum to yield carbon-based CE. A series of devices were thus obtained (Fig. 1). Commercial Ag-conductive paste was also applied as a counter-electrode (Fig. 2). However, it caused the CH₃NH₃PbI₃ layer to turn yellow after a period of time given that the polar solvent in the Ag-conductive paste can decompose CH₃NH₃PbI₃ into PbI₂ and CH₃NH₃I, which are yellow in color. Thus, devices based on Ag-conductive paste exhibited nearly no efficiency. By contrast, the carbon-conductive paste did not cause the color of the perovskite layer to change, indicating that the carbon paste did not damage the perovskite structure.

3. Results and discussion

The morphologies of TiO₂ NRAs fabricated through the hydrothermal method with different reaction times were characterized through scanning electron microscopy (SEM). Top-view SEM images (Fig. 3a–d) show that various dense and highly oriented one-dimensional TiO₂ NRAs were uniformly distributed on compact TiO₂/FTO. Scale bars on the images Fig. S1(a)–1(c) (Supporting Information) are 500, 100 nm, respectively. Cross-sectional SEM images (Fig. 3(a)–1–(d)–1)) reveal that the length and diameter of the TiO₂ NRAs changed with reaction time under high pressure. The length and diameter of nanorods prepared with the reaction time of 50 min were 200 and 20 nm, respectively. The length and diameter of TiO₂ NRAs increased gradually with increasing reaction time. The cross-sectional images also reveal that over time, the nanorods grew and intertwined to form a thin compact layer (Mor et al., 2006). The top-view images indicate that

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