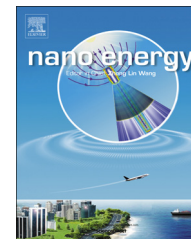




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RAPID COMMUNICATION

Synthesis of oriented TiO₂ nanocones with fast charge transfer for perovskite solar cells



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Abstract

One-dimensional (1D) rutile TiO₂ nanostructures on fluorine-doped tin oxide (FTO) substrates are interesting building blocks of solar cells, and they have been traditionally prepared under highly acidic conditions. In this article, a green, facile hydrothermal approach was exploited to grow oriented rutile TiO₂ nanocones on FTO under nearly neutral conditions in a high-control way. XRD, SEM, TEM, HRTEM, and Raman spectroscopy were used to characterize the nanocones, showing rutile phase with single-crystalline structure, and the length of nanocones can be tailored in the range of 700~1400 nm by varying the reaction durations. As building blocks of CH₃NH₃PbI₃-based perovskite solar cells, 11.9% power conversion efficiency was achieved for the TiO₂ nanocone devices, which is significantly superior to the state-of-the-art efficiency for other 1D nanostructure counterparts (~10% for TiO₂ nanorods and 11% for ZnO nanorods, respectively). It was further revealed by time-resolved photoluminescence spectroscopy (TRPL) that electron transfer from CH₃NH₃PbI₃ to TiO₂ nanocones is significantly faster than to TiO₂ nanorods, an important factor to suppress charge recombination and improve device performance. These characteristics make nanocones to be a promising candidate as electron transport materials for photovoltaic devices.
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Introduction

Solar energy utilization is among the best choices of developing clean energy, and nanostructured titanium dioxide (TiO₂) play a key role in this issue, especially as

photoanode materials in sensitized solar cells. It has been recognized that 1D nanostructures on transparent conductive oxide (TCO) substrate can provide a direct pathway for electron transport, and also offer open channels for filling with light absorbers and HTM for solar cells. Moreover, oriented nanorod-like materials on TCO are characteristic of efficient charge separation and transport properties, thus favorable for achieving good device performance [1-5]. Therefore, growth of oriented TiO₂ nanorods (NRs) on TCO substrate has drawn extensive research interests in solar energy utilization in the past years.

Hydrothermal/solvothermal synthesis is a facile approach to grow rutile TiO₂ nanorods (NRs) on TCO, and is traditionally carried out under highly acidic conditions (typically in ~6 M HCl solution) [3,6-11]. This is because of the fact that the extremely low pH can dramatically suppress the hydrolysis rate of titanium precursors, which is essential to the growth of the 1D oriented rutile TiO₂ NRs on TCO. However, such strong acidity of the growth medium could lead to inferior consequences, for example, the resulting TiO₂ NRs could peel off from substrates upon prolonging the growth period due to the corrosive nature of the growth medium [4,6,10], and more importantly, it is not benign to environment and manipulation during synthesis. It is hence of great interest in exploiting an efficient approach to grow 1D TiO₂ nanostructures on TCO in a green way for device applications, for example, in solar cells. Theoretically, nanocone-based heterojunction exhibits an electrostatic potential profile that facilitates carrier transport and suppresses charge recombination much more effectively in comparison with the widely studied nanorod-based heterojunctions [12], thereby favoring enhancement in device performance. However, this superiority in photovoltaic cells remained experimentally unexploited [12,13]. On one hand, the most important reason is the lack of an efficient way to fabricate nanocones (e.g., TiO₂) on TCO; on the other hand, it is not a trivial to find an appropriate system to fabricate nanocone-based and nanorod-based junctions in a well-controlled way.

In the past two years, organolead halide perovskite sensitized solar cells have experienced a fantastic progress by simple solution processing [14-19]. Excellent photovoltaic performance was obtained by varying either photoanode materials [20-22], or light absorbers [23-27], or hole transport materials (HTMs) [23,24,28-33], and interfacial modification [34,35], and over 15% power conversion efficiencies and >1 V open circuit voltage (V_{oc}) can be achievable for these devices. Remarkably, organolead halide perovskite is also suitable as the building blocks in non-sensitized configurations, exhibiting efficiency comparable to the sensitized ones [36-42]. Interestingly, HTM-free perovskite solar cells relying on the junctions between mesoscopic TiO₂ and CH₃NH₃PbI₃ can also work well [43-45]. Therefore, organolead halide perovskites exhibit great potentials in developing high-efficiency solar cells in various configurations, making them competent as model systems to study effect of novel nanostructures on device performance, for example, in nanocone-based solar cells.

In this work, for the first time, we have exploited a green hydrothermal growth of oriented single-crystalline rutile TiO₂ nanocones on FTO substrate under nearly neutral conditions (pH=5~7), which is in a stark contrast with

the extensively studied nanorods that can only be prepared under highly acidic solution. Experimental results showed that the length of nanocones can be controlled in the range of 700~1400 nm by varying the reaction time. TiO₂ NCs were further employed as building blocks of organolead iodide perovskite CH₃NH₃PbI₃-based solar cells, showing a power conversion efficiency (PCE) as high as 11.9%, which outperforms the state-of-the-art efficiency for any 1D nanostructured perovskite solar cells (e.g., 11% for ZnO nanorod-based and 10% for TiO₂ nanorod-based devices). Moreover, time-resolved photoluminescence (TRPL) spectroscopy revealed that electron injection from CH₃NH₃PbI₃ to TiO₂ NCs is significantly faster than to TiO₂ NRs, which can suppress effectively charge recombination, thereby enhancing the photovoltaic performance for the resulting perovskite solar cells.

Experimental section

Preparation of TiO₂ dense layer film

A compact TiO₂ layer was fabricated according our previous report [23]. Typically, 1.8 mL DI water in 50 mL of ethanol was added dropwise into a mixture solution containing 34 mL of tetrabutyl titanate and 8.3 mL of diethanolamine in 105 mL absolute ethanol. After stirring for 24 h at room temperature, a compact TiO₂ layer was dip-coated on a cleaned FTO glass substrate with the TiO₂ organic solution, followed by annealing at 500 °C for 30 min.

Growth of TiO₂ nanocones on the compact TiO₂ layer of FTO substrate

The rutile nanocones were synthesized by a disodium ethylenediamine tetraacetate (Na₂EDTA, Sinopharm) assisted hydrothermal approach. In a typical synthesis of TiO₂ nanococones, 0.3 mL of TTIP was first dissolved in 2 mL of acetylacetone (ACAC, Alfaesar 97+%, resulting in ACAC chelated Ti precursor for nanocone growth (Solution A). Separately, 0.56 g of Na₂EDTA was dissolved in 18 mL water to form 0.075 M Na₂EDTA solution (B). Solution A was then added into solution B, and stirred for ~30 min. The mixed solution turned into transparency slowly, and was then transferred to a Teflon-lined stainless steel autoclave. The hydrothermal growth was conducted at 200 °C for 7~24 h. Then the autoclave was cooled down to room temperature, and the sample was taken out, rinsed extensively with ethanol and DI water.

Growth of TiO₂ nanorods on the compact TiO₂ layer of FTO substrate

TiO₂ nanorods were also grown on the compact TiO₂ layer by a hydrothermal method [6]. In brief, 100 mL of 37% hydrochloric acid and 100 mL of DI water were mixed, to which 2.86 mL of titanium (IV) n-butoxide was added. After stirring for 30 min, 60 mL of the mixed solution and a compact TiO₂ coated FTO glass was sealed in an autoclave, and kept in a preheated oven at 150 °C for several hours. After cooling down to room temperature, the TiO₂ nanorod

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