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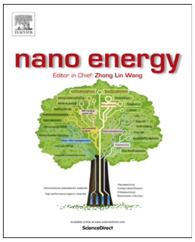

RAPID COMMUNICATION

Photovoltaic device based on TiO_2 rutile/anatase phase junctions fabricated in coaxial nanorod arrays

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Abstract

Phase-junctions formed in mixed crystalline phases of semiconductor based photocatalysts (TiO_2 and Ga_2O_3) shows enhanced photocatalytic activity owing to efficient separation of photogenerated charges. However, the phase junction effect on charge separation has not been directly verified yet. In this study, we fabricated a prototype photovoltaic device based on TiO_2 rutile/anatase coaxial nanorod arrays (NRAs) to demonstrate charge separation at the interface of polymorphic crystal phases. The device—FTO/rutile NRAs/anatase/ITO shows an ordinary photovoltaic response (open-circuit voltage V_{oc}: 154 mV, short-circuit current density J_{sc}: 1.76 mA/cm^2), contrasting with photo resistor behavior of two TiO_2 single phase devices of core-core (FTO/rutile NRAs/ITO) and shell-shell (FTO/anatase/ITO). Experimental evidences suggest that the built-in electric field at the interface of rutile/anatase phase junctions in the FTO/rutile NRAs/anatase/ITO device provides the direct driving force for efficient separation of photogenerated charges. The demonstrated strategy of fabricating phase-junction photovoltaic devices may inspire further investigations on new device converting solar into electrical energy and highlight the key role of the phase junction interface in the properties of the mix-phase photocatalysts.

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Introduction

Semiconductor heterojunction plays an important role in photogenerated charge separation of photocatalytic [1-3] and photovoltaic [4,5] systems for solar energy conversion. A heterojunction, usually formed between two different semiconductors [6-8] or semiconductors with different doping levels [9,10], provides the potential driving force for separating photoinduced charge carriers at the interface. In a similar fashion, many semiconductor materials exist in various crystalline phases—namely polymorphs [11-13]. The junctions formed between different phases of the same semiconductor material with identical chemical composition can be defined as *phase junctions* [13].

Photocatalysts with phase junctions has aroused substantial interest since it could deliver much higher activity than that of single phase catalyst [12-17]. TiO_2 nanoparticles with engineered surface anatase/rutile phase junctions give rise to enhanced photocatalytic properties, compared with single anatase or rutile phase [13,15-17]. Furthermore, Ga_2O_3 photocatalysts with tailored surface α-β phase junctions also show significantly enhanced activity for overall water splitting [12]. It was suggested that the enhanced photocatalytic activity is due to more efficient separation of photogenerated charges across the phase junction interface [12,14,15]. However, other studies indicate that the morphology of nanoclusters and the pore size distribution can be also contributed to the increased catalytic activity [16,17]. Clearly, the role of the phase junction in the photocatalytic systems has not been well understood yet.

Previous attempts suggest that the differences in lattice structures of rutile and anatase TiO_2 can cause different electronic densities and band structure, leading to slight difference in their band alignments [18]. EPR results indicate that anatase phase possess a higher conduction band level than rutile phase, in consistent with the mechanism that electrons migrate from the rutile phase to the shallow electron trapping sites in the anatase phase [19]. However, to date, there is no report on the charge transfer between the phase junctions detected from the external circuit.

The energy levels of rutile and anatase TiO_2 show slight difference (conduction band difference ΔE_c=0.3±0.1 eV and valence band difference ΔE_v 0.5±0.1 eV) [20-22], the potential barrier at the interface which provides the driving force for charge separation is thus limited. Nanorods facilitates directional motion of carriers due to reduced electron scattering or trapping at defects such as grain boundaries existed in nanoparticles, thus finding their way into frontiers of the photovoltaic (PV) field [23,24] and photoelectrochemical systems [25,26]. Core/shell architectures markedly increase the junction area and shortens the collection distance for carriers, which may be comparable to the diffusion length of minority carriers [10]. In order to collect enough charges, a structure of coaxial nanorods with large phase junction area and less grain boundaries would be highly desirable.

In this study, we fabricated photovoltaic devices based on coaxial rutile and anatase phase junctions and demonstrate the feasibility of phase junction PV device. We found that the device based on anatase/rutile junction can result an apparent photovoltaic effect with V_{oc} of 160 mV, I_{sc} of 1.1 mA/cm^2.

Experimental section

TiO_2 nanorod arrays were prepared by a hydrothermal method. TiO_2 anatase layer and ITO layer were fabricated by a physical vapor deposition (PVD) method. The fabrication process, general materials and instrumentation used in this work are described in more detail in Supplementary information.

Results and discussion

Firstly, TiO_2 nanorod arrays were prepared on fluorine doped tin oxide (FTO) coated glass substrates by a typical hydrothermal method [26] (see Supplementary information for details), followed by annealing in a muffle furnace at 500 °C for 2 h. The SEM image of pristine nanorod arrays (NRAs) shows that square-sectioned nanorods are formed (Figure 1a). The width of the nanorod is 75–150 nm, the width various with the qualities of the nanowires bundles (inset of Figure 1a). The cross-section SEM image (Figure 1c) of the NRAs displays a layer of roughly vertical nanorod arrays. The average length of nanorods is 3.8 μm and the cross sections of NRAs appear quite distinct and smooth (Figure 1c).

The TiO_2 shells were fabricated by a DC reactive physical vapor deposition (PVD) method and a subsequent annealing process (see Supporting information for details). Briefly, Ti atoms sputtered from the target reacted with oxygen, thereby TiO_2 particles deposited on the NRAs. Due to the highly anisotropic nanorods, TiO_2 particles aggregated along the axial and radial directions. In this way, coaxial core (TiO_2 nanorod)-shell (TiO_2 nanoparticles) structures were obtained. After deposition, both the outer diameter (ca. 500 nm) and length (ca. 4 μm) of the coated nanorods are larger than those of the pristine nanorods (Figure 1b and d).

The cross-section view of coaxial NRAs shows that the morphology of nanorod turns to be a baseball bar with a mushroom heads up. The top view of anatase layer shows a cauliflower-like morphology (Figure 1b), which is induced by the shadowing effect during deposition. Because the sputtering pressure (O_2+Ar mixture) was 1.0 Pa, collision between sputtered particles and the inert/reactive gas would affect the deposition process of particles. The present target-substrate distance (140 mm) is much larger than the mean free path of the sputtered particles, so that the TiO_2 particles are scattered by collision during traveling from the target to the substrate, thus resulting in restrained surface mobility. This causes a shadowing effect for TiO_2 deposition, which can account for the observed capping of anatase columns on the top of NRAs (Figure S1). Some TiO_2 particles enter the voids and crevices between nanorods and condense along the nanorods, giving rise to a gradient thickness of anatase coating. According to the SEM top and cross-sectional view images (Figure 1), the volume ratio between rutile NRAs and anatase in the mixed hybrids is about 4:1, roughly. The AFM 3D images of the coaxial NRAs indicates that the top surface show an inverted pyramid structure (Figure 1e), which is beneficial to facilitate light reflection and reabsorption inside the device.

The XRD pattern of the as-prepared TiO_2 nanorod arrays shows a single rutile phase (Figure 2a). The XRD pattern of