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Efficient development of *Type-II* TiO_2 heterojunction using electrochemical approach for an enhanced photoelectrochemical water splitting performance

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ABSTRACT

Type-II-heterojunction TiO_2 nanorod arrays (NAs) are achieved by a combination of reduced and pristine TiO_2 NAs through a simple electrochemical reduction. The heterojunction-structured TiO_2 NAs exhibit an enhanced photo-efficiency, with respect to those of pristine TiO_2 NAs and completely reduced black TiO_2. The improved efficiency can be attributed to a synergistic effect of two contributions of the partially reduced TiO_2 NAs. The light absorption is significantly increased, from the UV to the visible spectrum. Moreover, the *type II* structure leads to enhanced separation and transport of the electrons and charges. The proposed electrochemical approach could be applied to various semiconductors for a control of the band structure and improved photoelectrochemical performance.

1. Introduction

Water splitting using photoelectrochemical (PEC) cells with metal oxides attracts a significant research interest, owing to the potentials to overcome energy and environmental issues [1]. Over the past four decades, various oxides have been investigated, including TiO_2 [2], ZnO [3,4], Fe_2O_3 [5,6], $BiVO_4$ [7,8], WO_3 [9,10], etc. [11–13], whose band structures are suitable with respect to the water redox potentials. However, the photoefficiency is still very low for photoanodes based on a bare material, mainly owing to the narrow absorption range in the visible spectrum and high probability of electron-charge recombination [14]. Therefore, the development of efficient methods to overcome the above challenges is required for the improvement of the photoefficiency for water splitting.

Several strategies were proposed to enhance the overall photoefficiency [13], including an introduction of foreign elements and formation of heterojunction structure [15]. As a typical example, a sub-stoichiometric TiO_2 was extensively studied for an enhanced performance in photocatalysis. This structure can be formed by annealing pristine TiO_2 under an oxygen-deficient/-reducing environment; it exhibits black-color characteristics [16]. In addition, it exhibits significantly improved optical properties, with a narrower band gap for an enhanced visible-light absorption. Furthermore, oxygen vacancies can form, which increase the charge carrier density. The abundant charge carriers could increase the efficiency of charge separation by enhancing the band bending at the interface between TiO_2 and electrolyte [5]. However, this method is time-consuming and complex [17]. Recently, a rapid electrochemical method was developed to facilitate the formation of a sub-stoichiometric metal oxide

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photoelectrode [18]. This method was widely employed, as it is simple and cost-effective [19–22]. It was also employed in other metal oxides; for example, reduced WO_3, ZnO, and $BiVO_4$ were successfully obtained in different environments to enhance the PEC water splitting efficiency [20]. In the electrochemical approach, the deposition of elements is driven by the formed electrostatic field between the anode and cathode. Therefore, for a determined electrostatic field strength, the deposition of elements can be easily controlled by the duration of the applied potential. In the transient state, before the completion of the formation of black TiO_2, Ti(III) oxide is induced at the bottom, near the substrate, while the Ti(IV) oxide is preserved at the top, far away from the substrate, which exhibit distinct electronic and optical properties, and form a heterostructure.

In general, three types of heterojunction structure are employed in the design of a photoanode, as illustrated in Fig. 1. For an efficient use of the electrons and charges in the redox reaction, the *type II* band alignment is the most suitable alignment, as it provides an efficient extraction of the photo-generated electrons and charges for the interfacial reactions of hydrogen and oxygen evolutions. It reduces the possibility for recombinations, and improves the overall water splitting efficiency. $TiO_2/BiVO_4$ [23], $ZnO/BiVO_4$ [24], and TiO_2/Fe_2O_3 [25], exhibited significantly improved PEC water splitting efficiencies. However, in these systems, at least two materials are needed for the formation of the heterojunction; therefore, the synthesis normally required sophisticated procedures with limited candidates of suitable materials, and the performances were not easily reproducible.

In this study, a *type-II*-heterojunction TiO_2 nanorod arrays (NAs) are obtained by a combination of reduced and pristine TiO_2, through a conventional electrochemical reduction. The obtained TiO_2 heterojunction structure is characterized by electrochemical and spectroscopic measurements. It exhibited an increased photoefficiency by more than three times and by approximately 20%, with respect to those of the pristine TiO_2 NAs and completely reduced black TiO_2, respectively. Two factors contribute to the enhanced water splitting efficiency. For the partially reduced TiO_2, the light absorption is significantly increased, from the ultraviolet (UV) to the visible spectrum. Moreover, the *type II* heterostructure provides efficient charge separation and transport, which leads to an improved PEC water splitting efficiency [26]. This highly controllable approach can be easily employed for various semiconductors for the control of the band structure [27], with applications in energy harvesting, conversion, and storage [28–30], as well as sensor and biology applications [31,32].

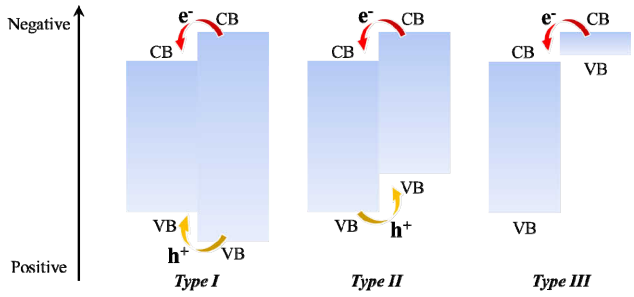

Fig. 1. Illustration of the three types of heterojunction structure of a photoanode

2. Experimental

2.1. Preparation

TiO_2 NAs were synthesized through hydrothermal methods. First, 0.1 mol/L $TiCl_3$ was dissolved in a solution that consists of a mixture of 13 ml hydrochloric acid and 15 ml water. The as-prepared solution was transferred into a 50-ml teflon-line stainless-steel autoclave, and several clean fluorine-doped tin oxide (FTO) glasses were submerged into the solution. The sealed autoclave was heated in an oven at 150 °C for 5 h, and cooled down to room temperature. TiO_2 NAs were homogeneously deposited on the FTO glass, and the samples were thoroughly washed with deionized (DI) water. The as-prepared TiO_2 NAs were further annealed at 550 °C for 1 h to obtain a ratio between anatase and rutile of approximately 3:1. The electrochemical reduction was performed using a VSP-300 electrochemical station (Bio-Logic), with a typical three-electrode system. TiO_2 NAs, Pt foil, and Ag/AgCl were used as the anode, cathode, and reference electrode, respectively. The TiO_2 NAs underwent an electrochemical reduction under a negative potential (–0.5 V vs reversible hydrogen electrode (RHE)) in 0.05 M H_2SO_4 solution for different time periods. The reduced electrode was dried at ambient conditions for 1 h.

2.2. Characterization

The morphology and elemental composition of the photoanode were studied using field-emission scanning electron microscopy (FE-SEM, Jsm-6700F). Ultraviolet-visible diffuse reflectance spectroscopy (UV-VIS DRS, Varian Cary 500 Scan UV-VIS system) was employed to study the optical properties of the photoanode. The crystallinity of the samples was investigated using X-ray powder diffraction (XRD, Bruker D8 Advance with Cu $K_{\alpha1}$ radiation, λ = 1.5406 Å). In addition, electrochemical impedance spectroscopy (EIS) was employed, and Mott-Schottky and Nyquist plots were obtained.

2.3. Measurement

The as-prepared TiO_2 NAs photoanode was used in the same electrochemical station with a typical three-electrode system. The edge of the modified TiO_2 electrode was sealed using insulating epoxy resin, except for an active surface area of 1×1 cm^2; it was functionalized as a photoanode, while a Pt foil and Ag/AgCl were used as the cathode and reference electrode, respectively. Liner sweeps and electrochemical impedance spectra were obtained in 1 mol/L NaOH (pH = 13.6) using an AM 1.5 solar simulator (Newport 94023A). The incident-photon conversion efficiency (IPCE) was measured using the same electrochemical setup with an IPCE station (Newport,