Quasi-type-II amorphous red phosphorus@TiO$_2$ hybrid films for photoanodic applications

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ABSTRACT

Owing to its optimal energy band position, red phosphorus (RP) has been considered as a promising elemental semiconductor for achieving simultaneous light-induced water oxidation and reduction. However, the photoelectrochemical performance of RP is limited by rapid charge recombination, low-charge carrier mobility, and poor water oxidation and film-forming capabilities. In this study, we explored the material strategies to address these limitations by developing a facile process to fabricate amorphous RP@TiO$_2$ core-shell hybrid films. We found that the amorphous RP@TiO$_2$ hybrid films annealed at low temperatures (e.g., 200–300 °C) in nitrogen exhibited significantly enhanced anodic photocurrent as compared to pure RP and pure TiO$_2$ films due to a combined effect of enhanced visible light absorption and efficient heterointerface charge separation. Through a systematic characterization combining electronic, optical and electrochemical measurements, we found that the high density of Ti^{3+}/oxygen vacancy complexes in amorphous TiO$_2$ created a defect band above the valence band of RP but below the water oxidation potential, thereby inducing a quasi-type-II band alignment in the amorphous RP@TiO$_2$ hybrid films; such electronic structure endowed amorphous TiO$_2$ with a "hole leaky" feature to separate and transport the photogenerated holes from RP nanoparticles to exhibit an enhanced photo-anodic performance.

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1. Introduction

Photoelectrochemical (PEC) water splitting has been widely pursued as a solution to reduce fossil fuel usage through hydrogen production from renewable solar light and abundant water on earth. Since Fujishima and Honda first demonstrated water splitting in 1972 by using TiO$_2$ photoanode and Pt cathode, considerable efforts have been devoted to developing photoanodic materials for efficient PEC water-splitting systems [1,2]. The focus of photoanode enhancement has mainly been on the practical performance of traditional metal oxides (TiO$_2$, WO$_3$, and Fe$_2$O$_3$) [3–7]. The large bandgap of these oxides leads to poor solar absorption and therefore limits the PEC efficiency of water splitting [8,9]. Recently, elemental red phosphorus (RP) has emerged as a promising photocatalyst for PEC applications not only because of its narrow bandgap (1.4–1.9 eV) but also because of its nontoxicity and abundance on earth [10–14]. Furthermore, RP possesses nearly ideal energy band edge positions that bridge the potentials of

hydrogen evolution reaction and oxygen evolution reaction; this feature is unique for achieving simultaneous visible light-induced water oxidation and reduction [15,16]. Nevertheless, RP suffers from intrinsic deficiencies with respect to PCE applications: first, similar to other elemental photocatalysts, the PEC efficiency of RP is limited by rapid charge recombination [11,16], low-charge carrier mobility [10], and few catalytic sites on the surface [15]; second, the poor chemical stability and inflammability of RP lead to poor film-forming capabilities for photoelectrode preparation [17,18], and more crucially, applying the widely employed high-temperature vapor deposition method to fabricate RP film photoelectrodes would be highly dangerous and expensive [19,20]. Third, the p-type feature of RP suggests its thermodynamic preference for hydrogen evolution rather than water oxidation because of downward band bending in aqueous solutions [13,19,20].

To improve the PEC performances of materials, the energy band engineering stratagems (e.g. element-doping [2,21] and hetero-junction synthesis [16,22]) are widely applied. In particular, heterostructured hybrid films have been proposed to effectively advance the PEC properties of RP-based materials, where the light-induced charge carriers in RP can be well separated in the hetero-active-

materials for transport and subsequent PEC reactions [14,23]. In addition, it has been suggested that the hybrid approach may allow for more flexible procedures for material and photoelectrode preparation [16]. Currently, most type-II RP-based heterostructured hybrids demonstrate efficient hydrogen evolution in aqueous solutions containing hole scavengers but lack activity for water oxidation [14,23]. This is because the staggered energy levels of the type-II alignment often result in a valence band edge that is more negative than the oxygen evolution potential, which increases the interface potential barrier for light-induced holes to trigger water oxidation. Recently, amorphous "hole leaky" TiO_2 has been shown to pair nicely with some narrow-bandgap materials, such as Si, CdTe, GaP, etc. to form a defect-modulated band alignment to conduct light-induced holes for promoting water oxidation with low interface potential barrier [24—28]. On the other hand, an amorphous TiO_2 film can be easily prepared through sol-gel coating methods, and its disordered structures may also favor the PEC water splitting process [29—31].

In this work, we explored a material strategy to combine the advantages of RP and amorphous TiO_2 and enable facile fabrication of nanostructured RP@TiO_2 hybrid films for PEC water oxidation. Nanostructured RP@TiO_2 core-shell particles were synthesized from ball-milled RP nanoparticles in a TiO_2 sol solution that was subsequently used to deposit amorphous RP@TiO_2 hybrid films, followed by an annealing treatment. We demonstrated that the annealing process at low-temperature (200—300 °C) produced an amorphous TiO_2 shell with a highly disordered structure, in which abundant Ti^{3+}/oxygen vacancy complexes created a defect band above the valence band of RP and below the oxygen evolution potential. When operated as a PEC photoanode in a 1 M aqueous Na_2SO_4 solution (pH 6.3), the RP@TiO_2 hybrid electrode exhibited a photocurrent of dozens-fold higher that of the previously reported RP-only electrodes [20], owing to the "hole leaky" characteristic of amorphous TiO_2 facilitating separation of photogenerated electron-hole pairs and hole conduction from RP nanoparticles. Besides, the hybrid electrode also showed a varied degree of photocurrent enhancement as compared to pristine amorphous TiO_2-based electrodes. The mechanism of the enhancement variation and its dependence on the annealing atmosphere and temperature were systematically investigated.

2. Experimental

2.1. Material preparation

A sol-gel coating method was used to fabricate the hybrid RP@TiO_2 core-shell photoelectrodes. First, RP core particles were prepared through a ball-milling method. Ten grams of commercial RP powder (99.99% trace metal basis, Sigma-Aldrich) was ground using a ball mill at a revolving speed of 300 r/min for 12 h in water. Subsequently, the RP slurry obtained was dispersed into 200 mL of water through ultrasonic treatment for 2 h. After aged for 2 days, the supernatant suspension was centrifuged at 6000 r/min for RP nanoparticle collection. The RP nanoparticles obtained were washed with methanol ($\geq$99.9%, Sigma-Aldrich), and then centrifuged three times at 6000 r/min, and finally dried at 80 °C in nitrogen. To synthesize the RP@TiO_2 core-shell hybrid films, the dried RP nanoparticles were dispersed into 5 mL of absolute ethanol (isotope ratio, Sigma-Aldrich) and mixed with 0.025 mL of ethanolamine ($\geq$99.5%, Sigma-Aldrich) and 0.01 mL of deionized water through ultrasonic treatment for 2 h. Subsequently, 0.04 mL of titanium isopropoxide ($\geq$97%, Gelest) was added dropwise into the RP ethanol solution and the synthesis was performed at 40 °C under continuous magnetic stirring for 24 h. The products were collected by centrifugation at 3000 r/min followed by washing with

ethanol three times until the milky white hydrolyzed titanium had been removed from the products. For the comparative study, pristine TiO_2 products were synthesized using the same recipe but without adding the RP nanoparticles.

To fabricate the photoanodes, the washed products were dried with nitrogen and dispersed into 5 mL of absolute ethanol. A dip-coating method was used to deposit a uniform film onto a fluorine-doped SnO_2 (FTO) electrode with a pulling speed of 10 mm/s. After each dip-coating iteration, the coated electrode was annealed at 100 °C in nitrogen for 10 min. Once the coated electrode had cooled to room temperature, one more film was coated onto the electrode through the same procedure. In total, six layers of film were coated onto the electrode, which was subsequently pre-annealed at 200 °C in nitrogen for 1 h. Finally, the samples were further stabilized through annealing at 200 °C in nitrogen for 1 h, 300 °C in nitrogen for 1 h, 400 °C in nitrogen for 1 h, 400 °C in nitrogen for 2 h, 200 °C in air for 1 h, and 300 °C in air for 1 h, respectively. The prepared electrodes were labeled based on the various annealing conditions; for example, RP@TiO_2-N_2/200 °C/1 h refers to the RP@TiO_2 film annealed at 200 °C in nitrogen for 1 h. To investigate the optical properties of the materials, the films were deposited on quartz substrates through the aforementioned procedures. It should be mentioned that the morphology of the hybrid film has important effects on the PEC properties of the photoelectrodes [32—36]. For RP, we have tried to reduce the size of the particles but due to the limitation of the ball milling method, we cannot obtain a sufficiently wide range of particle size that may allow us to find the "optimal diameter of RP". For TiO_2, we have varied its precursor concentration to optimize the thickness of the TiO_2 shell and the film preparation. The concentration used here has been optimization.

2.2. Characterization

The optical morphological features of the prepared films were examined using optical microscopy (Olympus BH2-UMA), field-emission scanning electron microscopy (FE-SEM, Hitachi S-4300 FEG equipped with energy dispersive spectroscopy at 10 kV accelerating voltage), and transmission electron microscopy (TEM, FEI Tecnai F20 microscope at 200 kV accelerating voltage). The crystalline features were characterized using grazing incidence X-ray diffraction (GIXRD, Rigaku SmartLab X-ray diffractometer with $CuK_{\alpha 1}$ radiation at a wavelength of 1.5406 Å) at a grazing angle of 0.2° with a scan step size of 0.02° over a 2θ range of 20—80°. To remove signal from the substrate, we deposited the films on glass substrates by the same procedures for the XRD measurement. The optical absorption spectra were recorded by using an ultraviolet—visible—near infrared spectrophotometer (Shimadzu UV-3600) in a wavelength range of 300—1400 nm. The chemical states were determined by X-ray photoelectron spectroscopy (XPS) using an ESCALAB 250XI photoelectron spectrometer (Thermo Fisher Scientific) with a monochromatic Al K_{α} X-ray source. The XPS spectra obtained were calibrated with a reference with C1s at 284.8 eV. The photoluminescence (PL) spectra were recorded by using a confocal laser Raman microscope (LabRAM HR800) with a 30-mW He-Cd laser (325 nm). All aforementioned tests were measured at room temperature.

All electrochemical and photoelectrochemical experiments were performed at room temperature in a three-electrode configuration with an Ag/AgCl (3 M KCl) reference electrode, a platinum foil counter electrode (0.5 cm^2), and the pristine TiO_2 films and the RP@TiO_2 core-shell hybrid films with an active area of 0.2 cm^2 as the working electrodes. The measurements were conducted in a 1 M aqueous Na_2SO_4 solution (pH 6.3) by using a potentiostat (Bio-Logic SP-200) equipped with a low-current probe. The