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Enhanced photoelectrochemical performance of WO₃ film with HfO₂ passivation layer

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ABSTRACT

In this article, Hafnium oxide (HfO₂) overlayer was reported to be loaded on the surface of WO₃ nanoparticles by a simple solvothermal method for the first time. HfO₂ powders were dissolved in the concentrated sulfuric acid as raw material. The physicochemical properties of WO₃ nanoparticles with and without HfO₂ passivation layer were characterized by X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS) and Fourier transform infrared spectroscopy (FTIR). For the film electrode prepared with doctor-blade method, scanning electron microscopy (SEM) and UV–vis absorbance spectroscopy (UV–vis) were used to determine the morphological and optical properties. Meantime, the photoelectrochemical properties of two samples were evaluated by means of liner sweep voltammogram, electrochemical impedance spectroscopy (EIS), intensity modulated photocurrent spectrum (IMPS) and incident photon to current conversion efficiency (IPCE). The WO₃ film with HfO₂ passivation layer showed better photoelectrochemical performance which could be ascribed to the inhibition of the recombination of electron-holes.

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Introduction

Recently, photoelectrochemical (PEC) water splitting, as an effective solution to solve the current energy and environmental crises in the modern industrial societies, has triggered enormous research activities [1]. Since Honda and Fujishima's work was reported, various kinds of semiconductors have been investigated as photocatalysts [2–11]. Among them, TiO₂ and ZnO are highly reactive, excellently photocorrosion resistive, non-toxic and inexpensive materials [2,3]. But the band gaps of both semiconductors are too large to have a

response in the visible light region, and the wide band gap (3.2 eV for anatase phase or 3.3 eV for ZnO) is a fatal shortcoming so that limits the photoresponse ability and the light to chemical (stored energy) conversion efficiency [4]. CdS and Cu₂O have great responses under visible light. However, the photocorrosion influences the stability of photocatalysts [5,6]. After striking a balance among the above advantages, WO₃ is a promising candidate due to its suitable band gap, great chemical stability, and environmental friendliness [12,13].

It has been reported to further increase the light to chemical conversion efficiency of WO₃ with a series of methods. Besides controlling particle size or morphology [14–18], noble

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metal depositon [19,20], doping [21–26] and semiconductor coupling [7,27–29], loading passivation layer on the surface of semiconductor is also a good solution because of two reasons. One is that the passivation layer can affect surface defect sites so as to inhibit the electron-hole recombination on the surface of semiconductor. The other is that the passivation layer can provide chemical resistance to the electrolyte for the photo-active semiconductor. Owing to the above benefits, passivation layers were fabricated by various kinds of techniques, such as atomic layer deposition (ALD) [30,31], electron beam evaporation [32], spin coating [33], electrochemical deposition [34], floating transfer [35] and chemical bath [36]. Among these, Wonyong Choi et al. [30] had deposited Al_2O_3 on the surface of WO_3 via ALD. The Al_2O_3 overlayer had an influence on the surface states so that the WO_3 film with the Al_2O_3 overlayer had an improvement in the photocurrent.

HfO_2 is a wide band gap material, which is widely used in the dye-sensitised solar cell (DSSC) [37–39] and metal-oxide-semiconductor high-electron-mobility transistor (MOS-HEMTs) [40] as a passivation layer. It can be coated on the surface of materials via sputtering with pure Hf target [40], atomic layer deposition with hafnium tetrachloride gas and water vapor [37], or hydrolyze with hafnium chloride and hafnium isopropoxide [38]. Kim et al. coated the HfO_2 layer over TiO_2 films, and the photo conversion efficiency of the solar cell was improved from 5.67 to 9.59% [38]. Even though the enhancement of photo conversion efficiency is interesting, the precursors of HfO_2 (hafnium chloride and hafnium isopropoxide) are more instable and expensive than the HfO_2 powder. When Hf target is used as raw material, the cost of sputtering also needs to be considered. So we believe that preparing the passivation layer with HfO_2 powders via a less costly method is a nice choice. To the best of our knowledge, there is no report to fabricate HfO_2 passivation layer with common HfO_2 powders in DSSC and photolysis of water.

In this paper, we loaded HfO_2 overlayer on the surface of WO_3 nanoparticles in the concentrated sulfuric acid with HfO_2 powders by solvothermal method for the first time. The nanoparticles were prepared into photoanodes to evaluate the photoelectrochemical properties by various methods, such as linear sweep voltammetry, electrochemical impedance spectroscopy (EIS) and incident photon to current conversion efficiency (IPCE). Surely, the effects of HfO_2 overlayer on the physical properties and photoelectrochemical performances were then discussed in detail.

Experimental section

Preparation of WO_3 nanoparticles with HfO_2 overlayer

WO_3 nanoparticles were fabricated by a solution method. In a typical experiment, Polyvinyl Pyrrolidone (PVP K-30, 2.0 g) was suspended in deionized (DI) water (15.0 mL). Ammonium metatungstate ($(\text{NH}_4)_6\text{H}_2\text{W}_{12}\text{O}_{40} \cdot x\text{H}_2\text{O}$, 1.478 g, Aldrich) was dissolved in 10.0 mL distilled water and then dropped into the PVP solution under stirring. After ultrasonic treating for 30 min, the solution was stirring for 2 h. Then, 2.0 g polyethylene glycol (PEG1000) was added, and the system was

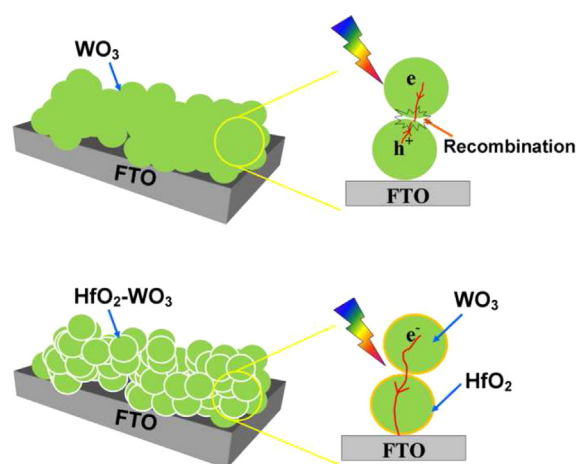
stirred for additional 4 h. The sol-gel was dried at 80 °C, and sintering at 600 °C for 1 h in air.

To synthesize the WO_3 nanoparticles with HfO_2 overlayer ($\text{HfO}_2\text{-WO}_3$), 0.3 g of as-prepared WO_3 nanoparticles were suspended in 30 mL concentrated sulfuric acid solution containing 14 mg HfO_2 . After solvothermal treatment at 110 °C for 2 h, the product was centrifuged, the product was washed with deionized water and absolute ethanol. Then the sample was gained after dried in an oven at 60 °C. For comparison, bare WO_3 nanoparticles were also treated in this way without the addition of HfO_2 .

A nanoporous $\text{HfO}_2\text{-WO}_3$ film-coated FTO electrode was prepared by using a doctor-blade technique [18]. Before coating, the FTO substances were cleaned up in acetone/isopropanol/methanol/DI water, respectively. In detail, 0.175 g $\text{HfO}_2\text{-WO}_3$, 0.05 g PEG20000, 0.025 g ethylcellulose, 0.8 mL terpineol, 0.2 mL acetylacetone and 0.2 mL triton were added to an agate jar. The paste was acquired by ball milling for 8 h. The resulting paste was squeezed over the FTO substrate by a doctor-blade coater and dried at 60 °C for 30 min. Finally, it was calcined at 450 °C for 30 min with a heating rate of 2 °C/min to obtain the $\text{HfO}_2\text{-WO}_3$ film electrode. For comparison, WO_3 film electrode was also fabricated. The ideal structures of the resulting films are shown in Schematic 1.

Characterizations of the samples

Morphological observation of the samples was carried out using a field emission scanning electron microscope (FESEM, JSM-7600F), transmission electron microscopy (TEM, TECNAI G2 F20). The phase structures of the as-prepared films were determined by an X-ray diffractometer (D/Max2250). In addition, the X-ray photoelectron spectroscopy (XPS, ESCALAB 250Xi) was used to examine the element binding environment of the composite. UV–vis absorption spectra measurements



Schematic 1 – Schematic of the structures of WO_3 and $\text{HfO}_2\text{-WO}_3$ electrodes. It is easy for the photo-generated electrons to recombine with photo-generated holes at the surface defect points of the WO_3 nanoparticles. With the passivation layer of HfO_2 , the surface defect points are covered so that the recombination are inhibited at the surface of nanoparticles.

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