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Enhancement of photoelectrochemical water splitting response of WO_3 by Means of Bi doping

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ABSTRACT

Doping is a very effective strategy for tailoring the electronic band structure and improving the charge transport properties of WO_3, which could in turn enhance its photoelectrochemical (PEC) activity. In this work, we report a facile hydrothermal route to synthesize Bi doped WO_3 thin films on fluoride-doped tin oxide (FTO) glass substrate and investigated the insights of its band alignment. Systematic doping of Bi into WO_3 was achieved during the condensation of peroxopolytungstic acid (PTA) in the course of hydrothermal synthesis. The effect of Bi doping on the morphology and crystal structure was investigated and the approximate amount of Bi incorporated into WO_3 was estimated using energy dispersive spectroscopy (EDS). Results of UV–Vis spectroscopy, Mott-Schottky analysis and valence-band (VB) X-ray photoelectron spectroscopy revealed that the insertion of Bi into the lattice of WO_3 changes the band gap, valence band maximum, and the conduction band minimum of WO_3. PEC measurements displayed remarkable enhancement in photocurrent values from 0.401 mA cm^{-2} for un-doped WO_3 to ~1.511 mA cm^{-2} (*ca.* 4-fold increase) for optimized Bi doped WO_3 samples at 1.23 V vs. RHE under simulated AM 1.5 G sunlight without the addition of catalysts. The results of electrochemical impedance spectroscopy confirmed that doping WO_3 with Bi lead to low charge transfer resistance across the electrode/electrolyte interface and an increase in charge-carrier density. This work suggests that Bi doping has the potential to significantly improve the PEC water splitting efficiency of WO_3.

1. Introduction

The continuously increasing energy demand and global warming force mankind to move towards renewable and environmentally friendly energy sources that could fulfill the global energy needs and significantly reduce the environmental impact and climate change [1]. Hydrogen is considered to be an ideal energy carrier that might be able to satisfy the global energy requirements owing to being a clean, renewable, carbon-free, and high-energy density energy source. The light reaching the surface of the earth from the sun is considered to be the largest and the most abundant energy resource available [2] and this light energy can be effectively used to produce H_2 (in addition to O_2) from water via photoelectrochemical (PEC) and photocatalytic water splitting [3]. Hence, the production of H_2 via solar water splitting is one of the most promising solutions to the existing energy demands and environmental concerns. Photocatalytic water splitting was first demonstrated by Fujishima and Honda using a TiO_2 semiconductor under UV light irradiation [4]. Since then, numerous other semiconductor materials have been investigated for their potential to increase the solar-to-hydrogen (STH) conversion efficiency. However, fabricating a system consisting of semiconductors for efficient PEC water splitting still remains a scientific and technical challenge.

Metal oxide semiconductors are considered as the most promising materials for PEC production of hydrogen owing to their electrical properties, ease of fabrication and stability. In particular, WO_3 is one such n-type semiconducting metal oxide, which has received considerable attention in solar water splitting applications as a result of its earth-abundance, highly tunable composition, high chemical stability at the relevant pH, and excellent electrical conductivity [5]. WO_3 is comprised of perovskite units and is one of the most attractive candidates for photocatalysis and photo-electrocatalysis, as it exhibits absorption of approximately 12% of the solar spectrum ($E_g = 2.5–2.8$ eV), a moderate length of hole diffusion (~150 nm) in comparison to α-Fe_2O_3 (2–4 nm), and better electron transport (*ca.* 12 $cm^2\ V^{-1}\ s^{-1}$) than TiO_2 (0.3 $cm^2\ V^{-1}\ s^{-1}$) [6–8]. As a photoanode in a PEC water split-

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ting device, WO_3 can achieve a theoretical maximum conversion efficiency of solar energy into H_2 of about 4.8% [9]. Hence, WO_3 is considered to be a more suitable material than TiO_2 and Fe_2O_3 for PEC water splitting applications. However, despite the aforementioned advantages, WO_3 would benefit considerably from further improvements in its efficiency as a photoanode in PEC water splitting devices.

Recently, many efforts have been directed at improving the PEC solar water splitting efficiency of WO_3, including its morphological modification, doping with transition metals, loading of noble-metals, sensitization with narrow band gap materials and fabrication of composite materials. Among these strategies, doping with transition metals represents an effective strategy for tailoring the electrical and optical properties of WO_3 [10]. However, such doping can also introduce various changes such as phase segregation of different oxides, low solubility of dopant species, presence of interstitials instead of substitutional impurities, diffusion of defects to surfaces and grain boundaries, and structural instabilities [10]. For example, doping WO_3 with isovalent elements does not result in charge mismatch problems, thus limiting the formation of other defects like anion or cation vacancies, whereas doping with non-isovalent elements is usually compensated for by the creation of oxygen vacancies [10]. Therefore, it is highly desirable to design an efficient synthetic route for the fabrication of systematically doped WO_3 thin films without introducing the above-mentioned problems.

To date, a variety of dopants have been introduced into WO_3 in order to improve its PEC water splitting ability. In particular, doping of Bi into WO_3 is known to increase the photocatalytic activity of WO_3 as reported by Zou et al. [11]. The valence band of Bi inserted WO_3 material consists of O 2p and Bi 6p with a small contribution from Bi 6s hybrid orbitals, and the bottom conduction band is formed by W 5d orbitals with a minor contribution from Bi 6p orbitals. The hybridization of Bi 6s and O 2p levels causes the valence band to become largely dispersed, that favors the mobility of photoinduced holes and promotes the oxidative reactions [12–16]. Therefore, it is higly desirable to dope WO_3 with Bi for improved PEC water splitting applications. Despite some reports, [11–16] no clear study has been carried out to investigate the effect of Bi doping on the band structure and alignment of WO_3 and its influence on the PEC activity, which could give very crucial information regarding further improvement in the PEC water splitting activity. Therefore, in this article, we have investigated the influence of Bi doping on the band structure of WO_3. Furthermore, the effects of Bi doping on the morphology, crystal structure, optical response, and charge-transfer properties of WO_3 films are investigated and EDS is used for the quantitative analysis of Bi doped WO_3 samples. Spectroscopic analysis shows that the insertion of Bi into WO_3 affects the conduction band minimum, valence band maximum, as well as the band gap of WO_3. The optimized Bi doped WO_3 photoanode displays a photocurrent density of 1.511 mA cm^{-2} at 1.23 V vs. RHE under AM 1.5 G sunlight illumination. In addition, the effect of doping on the electrical properties of the prepared thin films is extensively studied by electrochemical impedance spectroscopy and Mott–Schottky analysis.

2. Experimental

Bi doped WO_3 thin films on a fluorine-doped tin oxide (FTO) glass substrate were fabricated by a modified facile hydrothermal method [17,18]. 0.824 g (0.05 M) of sodium tungstate dihydrate ($Na_2WO_4{\cdot}2H_2O$, Junsei ≥99.0%) was added to 47.5 mL of deionized water and stirred for 5 min. After the dissolution of sodium tungstate dihydrate, 1 mL of concentrated hydrochloric acid (HCl, Sigma Aldrich) was added at room temperature (23 °C) and the mixture was stirred for 1 h to give a yellow precipitate of tungstic acid. To this, 1.5 mL of hydrogen peroxide (H_2O_2, 30% w/w in H_2O, Sigma Aldrich) was added (at room temperature, 23 °C) and the mixture was stirred for 2 h to give a stable solution of peroxopolytungstic acid (PTA). To this transparent solution of PTA, different quantities of bismuth nitrate pentahydrate ($Bi(NO_3)_3{\cdot}5H_2O$, Sigma Aldrich ≥98.0%) were added and the resulting mixtures were stirred for 30 min. The doped samples with different Bi contents, resulting from the addition of different molar concentrations of bismuth nitrate pentahydrate, are given in Table S1. In each case, a previously cleaned FTO substrate was subsequently placed at an angle against the wall of a Teflon-liner, with the conducting side facing down. The synthesis solution was transferred to a Teflon-lined autoclave, filling it 70% of its capacity. The hydrothermal synthesis was carried out at 150 °C for 3 h. After this time, the autoclave was allowed to cool to room temperature and the samples were removed, rinsed with deionized water (~100 ml), and annealed at 500 °C for 2 h in air. The un-doped WO_3 thin films were synthesized using the same procedure without the addition of bismuth nitrate pentahydrate.

The crystalline structure of the samples was characterized by X-ray diffraction (XRD, MiniFlex desktop XRD instrument) using Cu Kα radiation (wavelength 0.15418 nm) at a diffraction angle (2θ) between 10° and 90°. The morphologies of the thin films were analyzed using a Hitachi S4800 (Japan) scanning electron microscope (SEM) and a JEOL JEM-2100F (USA) transmission electron microscope (TEM). EDS measurements are carried out during TEM measurements. UV–Vis absorption spectra were recorded using a Varian Cary 5000 spectrophotometer (Australia). Thermo Fisher Scientific Co., (USA) Theta probe angle-resolved X-ray photoelectron spectrometer with a monochromatic micro-focused Al Kα (1486. 6 eV) source was used for XPS analysis. The X-ray emission energy was 150 W with a 15 kV accelerating voltage, typical operating pressures were 10e-7 Pa, the energy resolution for each point was 0.05 eV, and the peak energy was self-calibrated to C1s and O1s reference peak states. A spot size of X-ray emission energy is 15 μm × 15 μm for each sample. An ABET Technologies Sun 2000 solar simulator (ABET Technologies, USA) calibrated to AM 1.5 G sunlight irradiance conditions was used as the light source. Incident photon to current conversion efficiency (IPCE) measurements were performed using a 1000 W xenon arc lamp (Thermo Oriel 66902, USA) combined with a monochromator (Thermo Oriel Cornerstone 7400 1/8).

The PEC properties were characterized using a standard three-electrode cell in an aqueous 0.1 M Na_2SO_4 electrolyte at room temperature (25 °C) with an electrochemical analyzer (Iviumstat electrochemical interface, Netherland). The as-prepared doped and un-doped WO_3 thin films were used as the working electrode, while a saturated Ag/AgCl electrode and Pt sheet were used as reference and counter electrodes, respectively. The photocurrents were measured using linear sweep voltammograms in a potential range from −0.5 to 1.7 V (vs. Ag/AgCl) at a scan rate of 10 mV s^{-1} under AM 1.5 G sunlight illumination from the front side of the sample. The samples were masked with an O-ring in the PEC cell, exposing 0.12 cm^2 of each sample to the incident light source. Transient photocurrents (for stability) of the photoanodes were measured at a bias of 1.23 V (vs. RHE). Electrochemical impedance spectroscopy (EIS) was conducted in the frequency range 0.1–10^5 Hz at 1.23 V (vs. RHE) and an AC voltage perturbation of 5 mV.

3. Results and discussion

In order to effectively modify the band gap and band edges of WO_3 and to introduce impurity states in the band gap, a systematic approach to doping is required. Therefore, it is important to adopt