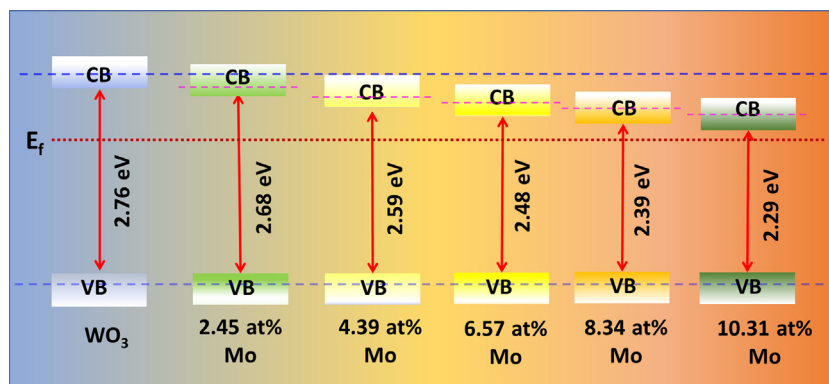


Regular Article

Influence of molybdenum doping on the structural, optical and electronic properties of WO_3 for improved solar water splittingShankara S. Kalanur^a, Hyungtak Seo^{a,b,*}^a Department of Materials Science and Engineering, Ajou University, Suwon 443-739, Republic of Korea^b Department of Energy Systems Research, Ajou University, Suwon 443-739, Republic of Korea

GRAPHICAL ABSTRACT



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ABSTRACT

Doping WO_3 with foreign atoms is a very efficient strategy to modify the structural, optical and electronic properties which could influence its photoelectrochemical (PEC) water splitting activity. In this study, we report a simple and efficient single-step strategy for the fabrication of molybdenum (Mo)-doped WO_3 thin films. The characterization results show that doping Mo into WO_3 leads to a significant change in the morphology without changing its crystal structure. Elemental mapping and EDS analysis revealed that Mo was homogeneously doped into the crystal lattice of WO_3 in the at.% range of 0–10.31. The incorporation of Mo into WO_3 reduced the band-gap of WO_3 and increased its light absorption ability. Notably, X-ray photoelectron spectroscopic valence band-edge analysis confirmed that substitution of Mo into WO_3 led to a downward shift in the conduction band minimum without any significant change in the valence band maximum with respect to Fermi level. The fabricated Mo-doped WO_3 electrodes exhibited a higher photocurrent compared to undoped WO_3 samples under simulated 1.5 AM sunlight without the addition of a water oxidation catalyst. The procedure proposed herein provides a simple and systematic approach for the fabrication of band-gap-tailored WO_3 photoanodes by Mo doping for efficient PEC water splitting.

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1. Introduction

Recently, much scientific research has been devoted towards finding new and renewable energy sources to offset the depletion

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of fossil fuels and the serious environmental problems and global warming caused by the increasing content of atmospheric CO₂. Hydrogen is considered as one of the most efficient, renewable, and promising clean energy sources for the future that can replace fossil fuels and decrease the environmental damage associated with it. At present, industrial production of hydrogen is largely achieved by steam reforming of natural gas (methane), followed by the water–gas shift reaction [1]. However, steam reforming of methane produces a large amount of the greenhouse gas CO₂ and therefore an alternative, new, efficient, and cleaner approach is required for hydrogen production [2]. PEC water splitting is a promising approach for generating clean and storable fuel (hydrogen) directly from sunlight and water. Direct photo-electrolysis during PEC water splitting is a more elegant and potentially cheaper approach because it offers the simultaneous functions of light-harvesting and electrolysis in a single device [3]. PEC water splitting was first successfully demonstrated by Fujishima and Honda in 1972 using TiO₂. Since then, much effort has devoted in this field to find a suitable semiconductor material for efficient PEC solar water splitting. In particular, the use of oxide semiconductors for PEC water splitting is considered more reasonable as these materials are easily synthesized, inexpensive, and generally very stable in aqueous solutions [4]. To achieve efficient PEC solar water splitting, an ideal semiconductor material must fulfill all necessary requirements, such as high visible-light absorption, efficient charge carrier separation, efficient catalysis, and chemical stability [5]. Therefore, designing a suitable system based on semiconductor photoelectrodes is crucial for achieving efficient PEC solar water splitting.

WO₃ is an indirect band-gap semiconductor ($E_g \approx 2.6\text{--}2.8$ eV) capable of capturing approximately 12% of the solar spectrum [6]. Due to its band-gap, WO₃ is considered as a more suitable material than TiO₂ for PEC water splitting application. The WO₃ photoanode has a theoretical maximum solar-to-H₂ energy conversion efficiency of about 4.8% in PEC water-splitting devices [6]. The advantages of the WO₃ photoanode include the high resistance against photocorrosion, good chemical stability in acidic aqueous solutions, moderate hole diffusion length, and inherently good electron transport properties under illumination [7–11]. Despite these advantages, WO₃ still may not be considered as an ideal material for water splitting due to its band-gap that permits absorption of only a small portion of incident sunlight. Therefore, band-gap modification (narrowing the band-gap) is required to allow WO₃ to absorb a sufficient portion of solar light to enhance the PEC water splitting efficiency.

Numerous strategies have been employed to enhance the PEC properties of WO₃, such as morphological control, transition-metal-doping, noble-metal-loading, surface sensitization, and the development of composite materials. In particular, doping and co-doping are effective strategies for tailoring the electronic band structure and enhancing the PEC properties of WO₃ [12]. Doping of several metals such as Ti, Zn, Dy, Te, Ta, V, Cu, Ag, Ce, Mg, Mo, and Ni into WO₃ has been reported in the literature [13–24]. Among these approaches, doping WO₃ with Mo improves the photocatalytic properties by narrowing its band-gap [25]. This is because the ionic radius of Mo is close to that of tungsten, which enables Mo to be suitably incorporated into the tungsten lattice [26,27]. Further, doping WO₃ with an isovalent element like Mo does not create charge mismatch problems and thus limits the formation of other defects such as anion or cation vacancies [12]. Therefore, doping WO₃ with Mo is considered an efficient strategy for improving the PEC properties of WO₃. Despite the few reports on Mo doping [23,25,28–30], no clear experimental data has been documented regarding the modification induced in the band-edge position of WO₃ after Mo doping and its influence on PEC water splitting ability.

In view of this, herein, we propose a simple and systematic approach for the fabrication of band-gap-tailored WO₃ photoanodes via Mo doping. The physical properties of the synthesized Mo-doped WO₃ thin films are characterized by scanning electron microscopy (SEM), X-ray diffraction (XRD), transmission electron microscopy (TEM), energy-dispersive X-ray analysis (EDS), UV–Vis absorption spectroscopy, and X-ray photoelectron spectroscopy (XPS). Based on the spectroscopic analysis we present detailed insights of band edge positions of WO₃ after Mo doping for the first time. Most importantly here we show that, Mo doping led to a downward shift in the conduction band minimum of WO₃ without any significant change in the position of valence band maximum with respect to Fermi level. The PEC properties of the undoped and Mo-doped WO₃ photoanodes are studied under 1-sun illumination in 0.1 M Na₂SO₄ aqueous solution. The results confirm that Mo-doped photoanodes show superior PEC activity compared to undoped WO₃ thin films.

2. Materials and methods

Mo-doped WO₃ thin films were directly grown on a fluorine-doped tin oxide glass (FTO) substrate via a facile hydrothermal method. In a typical synthesis, 0.824 g of sodium tungstate dihydrate (Na₂WO₄·H₂O, Junsei $\geq 99.0\%$) was dissolved in 47.5 mL of de-ionized water by stirring for 5 min. To this solution, 1 mL of concentrated hydrochloric acid (HCl, Sigma Aldrich) was added and stirred vigorously for another 1 h to obtain a yellow solution of tungstic acid. Hydrogen peroxide (H₂O₂, 1.5 mL; Sigma Aldrich) was added and further stirred for 3 h to obtain a stable transparent solution of peroxotungstic acid. Different amounts of ammonium molybdate tetrahydrate ((NH₄)₆Mo₇O₂₄·4H₂O, Sigma Aldrich) were added to this solution and stirring was continued for 1 h to obtain a transparent solution for the synthesis. The amount of ammonium molybdate tetrahydrate required for obtaining the dopant loading in atomic percentage (at.%) is given in Table S1. The transparent solution of peroxotungstic acid containing molybdenum was transferred to a Teflon-lined autoclave, filling it to 70%. A previously cleaned FTO substrate was then placed at an angle ($\sim 60^\circ$) against the wall of the Teflon liner with the conducting side facing down. Hydrothermal deposition was conducted at 150 °C for 2 h. After the synthesis, the autoclave was allowed to cool to room temperature and the samples were removed, rinsed with de-ionized water, and annealed at 500 °C for 2 h. The undoped WO₃ thin films were synthesized using the same procedure described above, without the addition of ammonium molybdate tetrahydrate.

The crystalline phases of the as-prepared thin films were characterized by X-ray diffraction (XRD, MiniFlex desktop XRD instrument) at diffraction angles (2θ) between 10° and 90° using Cu-K α radiation. The morphology of the surface and cross-section of the films was analyzed using a Hitachi S4800 (Japan) scanning electron microscope (SEM) and a JEOL JEM-2100F (USA) transmission electron microscope (TEM). EDS measurements were carried out during the TEM measurements via a connection to the TEM instrument. UV–Vis absorption spectra were recorded using a Varian Cary 5000 spectrophotometer (Australia) using integrated ball. XPS analyses of the prepared samples were carried out with a Theta Probe spectrometer from Thermo Fisher Scientific (USA). An ABET Technologies Sun 2000 solar simulator (ABET Technologies, USA) calibrated to AM 1.5G irradiance conditions was used as the light source. Incident photon-to-current conversion efficiency (IPCE) measurement was 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 evaluated with a typical three-electrode system using an electrochemical analyzer (Iviumstat

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