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Gallium-doped tungsten trioxide thin film photoelectrodes for photoelectrochemical water splitting

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ABSTRACT

A sol–gel method was used to synthesise different compositions of Ga-doped tungsten trioxide thin films using tungstic acid and gallium(III) nitrate as starting materials. The precursor solutions were drop-casted on FTO glass and annealed at 500 °C for 30 min, and the resulting materials were characterised with SEM, XRD, UV/Vis spectrophotometry and photoelectrochemical analysis. The Ga-doped WO_3 samples exhibited a greater grain than undoped WO_3, and a monoclinic structure was observed for all WO_3 samples. The band gap reduction of WO_3 from 2.74 to 2.60 eV indicated the red-shift of light absorption towards the visible light region in the solar spectrum. The donor carrier density for the doped WO_3 increased, and the conduction band edge position exhibited a positive shift. The photoactivity of WO_3 increased threefold when the photoanode was 20% doped with gallium.

1. Introduction

Due to their photocatalytic activity and stability during long-term irradiation in acidic and basic media, metal oxides are commonly used as photocatalysts for the decomposition of water to hydrogen and oxygen from photoelectrochemical (PEC) path [1]. The widely used TiO_2 is one of the wide band gap semiconductors that mainly use ultraviolet irradiation which is only about 5% of the solar energy reaching earth to achieve photoexcitation and charge separation and this makes it very inefficient [2]. Current research is moving towards the use of small-band-gap photocatalysts that can promote photocatalytic reactions using ultraviolet and also visible light which is about 45% of the terrestrial solar energy [3–5].

A relatively smaller band gap semiconductor, tungsten trioxide (WO_3), plays an important role in electrochromic, photochromic and sensor applications [6–8]. Because of its band gap between 2.4 and 2.8 eV, WO_3 can absorb the blue part of visible light and the ultraviolet region in the solar spectrum, making it highly attractive for photocatalysis research. Although it has a positive conduction band of E_{CB} (+0.4 V versus NHE) at pH 0 and low light energy conversion efficiency [9], this material is attractive for photocatalytic research because of its ease of preparation at high purity, its absorption at longer wavelengths and its stability during irradiation in various aqueous electrolytes.

The performance of WO_3 can be further enhanced by doping with suitable metal. Recently, gallium has been used as a dopant for TiO_2 thin films in DSSC applications [10],

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photocatalysts for water purification [11] and water splitting for hydrogen production [12]. The powder form Ga-doped TiO_2 photocatalyst is able to absorb a longer wavelength than pure TiO_2 in water purification and water splitting reactions which indicates reduction in the band gap energy of the doped photocatalyst. The hydrogen generation rate has been improved with Ga-doping and the 2 mol% Ga-doped TiO_2 powder photocatalyst has the highest hydrogen production rate. Although the Ga-doped TiO_2 thin films for DSSC application show a blue-shift in the UV/Vis spectrum, which represents an increase in the band gap energy of the films, the power conversion efficiency of the 0.5% Ga-doped TiO_2 (4.57%) is higher compared to pure TiO_2 (2.51%). The short-circuit current density produced by the Ga-doped TiO_2 is higher. Generally, Ga-doped TiO_2 samples have a higher photocatalytic activity than undoped TiO_2 samples. Similar improvement is expected in the Ga-doping into WO_3 which will enhance the light absorption and hence will improve PEC water splitting performance.

The purpose of this study is to investigate the effect of Ga-doping into WO_3 based on its morphology, crystal structure and photoelectronic properties, and also to examine the performance of the thin film for photoelectrochemical water splitting. The properties of these films are studied in detail and discussed in terms of potential applications.

2. Experimental details

Tungstic acid, H_2WO_4 (Sigma–Aldrich), aqueous ammonia (Merck, 28–30%), gallium(III) nitrate, $Ga(NO_3)_3$ (Sigma–Aldrich) and poly-ethylene glycol 300, PEG 300 (Merck) were used as starting materials for the preparation of Ga-doped WO_3. All other chemicals were of analytic purity grades, and the water used throughout the experiment was double distilled de-ionised water. First, the tungstic acid was added into aqueous ammonia to form an ammonium tungstate solution. Excess ammonia can be eliminated by heating. Appropriate amounts of gallium(III) nitrate and PEG 300 were added into the ammonium tungstate solution to obtain the desired atomic ratio, expressed by $W{:}Ga = x{:}1-x$, where $x = 1$, 0.95, 0.9, 0.85 or 0.8. Before coating, FTO glass was cleaned with acetone, ethanol and iso-propanol for 5 min in each solvent using an ultrasonic cleaner. Then, the gallium(III) nitrate–ammonium tungstate solution was drop-casted on the FTO glass. The resulting samples were calcined and sintered at 500 °C for 30 min at a constant heating rate of 5 °C s^{-1}. The drop-casting and calcination steps were repeated two times to create three layered thin films.

After annealing at 500 °C, the structure and crystallinity of the thin films were studied with an X-ray diffractometer (Bruker D8 Advance diffractometer) using CuKα radiation. The morphology, grain size and thickness of the samples were determined using a scanning electron microscope (Zeiss AM10). Elemental composition was determined by an energy-dispersive X-ray analyser (EDX) attached to the SEM instrument. The light absorption of the thin films was measured using a UV/Vis spectrophotometer (PerkinElmer Lambda 35). The flat band potential (E_{FB}) and the donor carrier density (N_D) were evaluated according to a Mott–Schottky equation in a single compartment electrochemical cell equipped with the WO_3 film-coated FTO working electrode, a saturated calomel reference electrode (SCE) and a platinum wire counter electrode. Photoelectrodes were prepared by attaching copper wire as described by Minggu et al. [13]. The capacitance was tested at a frequency of 100 Hz and 1000 Hz after applying a starting potential for 100 s (by using Gamry Reference 600), and these experiments were performed with a potential step of 100 mV and an equilibrium time of 10 s at each potential. A series combination of a resistor and a capacitor circuit model was used for Mott–Schottky plots [14,15].

The photoelectrochemical (PEC) analyses were carried out using an Ametek Versastat 4 under the irradiation of the 450 W full arc Xenon light source at an intensity of 100 mW/cm^2. The electrolyte in this experiment was 0.5 M Na_2SO_4, and it was purged with nitrogen gas for 30 min before the tests. The scan rate was set to 0.01 V s^{-1}.

3. Results and discussion

3.1. SEM analysis

Fig. 1 presents SEM micrographs of undoped WO_3 and 20% Ga-doped WO_3 on FTO glass. For undoped WO_3, spherical particles with a diameter of 40 nm and a uniform arrangement were observed. The spherical particles suggested that the organic compounds used in the synthesis were successfully eliminated during the calcination process [16].

The morphology of doped WO_3 was different from that of undoped WO_3. Comparing Ga-doped WO_3 samples with undoped WO_3 (Fig. 1b and c) demonstrated that the presence of gallium led to the agglomeration and grain growth of the WO_3 particles, leading to an uneven film surface. The grain size of the Ga-doped WO_3 was larger than that of undoped WO_3. A similar effect can also be observed in Ni-doped WO_3 [17]. The thicknesses of the samples shown in the SEM micrographs are around 1 μm. Taking account of the SnO_2 layer is 900 nm, the WO_3 sample produced in this work is around 100 nm.

The EDX spectra of the undoped and doped WO_3(not shown) confirmed the presence of Ga, W and O. The results demonstrated that the content of Ga and W was in expected values (Table 1). Besides, there was no carbon detected which indicated the PEG 300 added as a binder was fully decomposed.

3.2. XRD analysis

Ga-doped WO_3 thin films with different gallium concentrations as outlined in Table 2 were subjected to X-ray diffraction after annealing at 500 °C for 30 min. All annealed Ga-doped WO_3 samples displayed a monoclinic, polycrystalline WO_3 structure with a main peak at 24.4° corresponding to the (200) plane. The XRD patterns are shown in Fig. 2, and these patterns are in agreement with JCPDS file no. 01-083-0950.

The XRD patterns for the Ga-doped WO_3 samples were found to be the same as those for the undoped WO_3, suggesting that the Ga particles were well incorporated into the WO_3 lattice. No additional peaks were detected even for 20% Ga-doped