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Photocatalytic activity of WO_3/Fe_2O_3 nanocomposite photoanode

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ARTICLE INFO

Article history:
Received 31 March 2015
Received in revised form
4 May 2015
Accepted 5 May 2015
Available online 29 May 2015

Keywords:
Photo-catalysis
Iron oxide
Tungsten trioxide
Composite nano-particle

ABSTRACT

The $(WO_3)_{1-x}$–$(Fe_2O_3)_x$ ($0 \leq x \leq 1$) nano-particle thin films with various compositions have been deposited onto the fluorine thin oxide (FTO) coated glass substrate using sol-gel, spin-coating technique. An electrode/electrolyte interface has been formed between an n-type $(WO_3)_{1-x}$–$(Fe_2O_3)_x$ composite semiconductor and a 0.5 mol L^{-1} Na_2SO_4 aqueous solution. The photo-catalytic activity of the films has been investigated through the photocurrent-voltage. UV-visible spectroscopy, SEM and XRD have been used to characterize solar absorption, surface morphology and the crystallinity of samples, respectively. The photo-electrochemical (PEC) experiments were performed under solar irradiation to evaluate the amount of electron-hole generation in different samples. All the composite nano-particles indicated higher efficiency compared to pristine iron and tungsten oxides. A clear relationship was also confirmed between band gap energy and photo-catalytic activity of thin films. The band-gap energy of mixed thin films decreased linearly with the increasing Fe_2O_3 content in the film samples. The maximum photocurrent density of 2.34 mA cm^{-2} has been obtained for sample with $x = 0.25$ at 1.4 V vs. RHE. The result revealed that the sample also has the highest photon-to-current efficiency (0.87%), and solar absorption.

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Introduction

Semiconductors have been of significant interest due to their extraordinary electrical, magnetic, optical and mechanical properties [1]. Having these suitable properties, semiconductors have found to be useful in a wide variety of industrial areas such as electronics, catalysis, ceramics, magnetic and structural components [2]. Recently, these materials are of significant interest in photo-catalytic hydrogen production. Clean and renewable source of energy (hydrogen fuel) can be produced by utilizing abundant solar radiation by photo-catalytic splitting of water into hydrogen and oxygen. In order to achieve great amount of hydrogen fuel, photoelectrode semiconductors need to be of high efficiency and stability. In fact, a target efficiency of 10% is required to achieve commercialised hydrogen fuel [3]. However, the efficiency and stability of photo-catalytic semiconductors have not been reached to commercial applications yet [4,5].

Stable single crystal photo-electrodes (PEs) made from metal oxide have shown low efficiency [6]. In contrast, multi-junction conventional semiconductor PEs have demonstrated

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http://dx.doi.org/10.1016/j.ijhydene.2015.05.016
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Table 1 – List of chemicals used in this study.

Name	Formula	Grade (%)	Supplier
Tungsten powder	W	99	Sigma Aldrich
Iron (III) nitrate	$Fe(NO_3)_3.9H_2O$	99.9	Chem. supply
Hydrogen peroxide	H_2O_2	30	AMRESCO
Ethanol	C_2H_6O	70	Sigma Aldrich
Platinum black powder	Pt	99	Sigma Aldrich
Propan-2-ol	C_3H_7OH	70	Chem. Supply
Triton X-100	$(C_2H_4O)_{9.5}C_{14}H_{22}O$	99	Sigma Aldrich

a high efficiency, >10% [7,8], but degraded within a short time (low stability). The type of PEs as well as electrolytes and experimental conditions are important factors that can affect the efficiency and stability of semiconductors [9].

Various semiconductive metal oxides have been widely used as photo-anode with such photo-catalytic properties as band gap, flat band potential, over potential and stability against corrosion [10,11]. Later on, multi-junction electrodes had been investigated to improve the stability and efficiency of PEs [12–14]. Despite of numerous efforts, the efficiency and stability of semiconductors are still far from being commercialised. Recently, composite nano-materials are being of significant interest to develop a better pathway to produce stable and efficient semiconductors. For instance, WO_3/TiO_2 nanocomposite material was synthesised and tested for photocurrent generation by Shiyanovskaya group [15]. Their produced nanocomposite exhibited enhanced photocurrent generation compare to pristine WO_3 and TiO_2. However, since both WO_3 and TiO_2 have large band gaps, WO_3/TiO_2 nanocomposite was not able to absorb light in the visible region.

Previously, pristine Fe_2O_3 and WO_3 nanoparticles have been optimized for hydrogen production applications using different series of surfactants [16,17]. The ultimate goal of this study is to improve the efficiency and stability of semiconductor photo-electrodes by applying the composition of Fe_2O_3 and WO_3 nanoparticles thin films. This composition could be promising due to following reasons: (i) optimal visible spectrum between WO_3 and Fe_2O_3 (ii) less combination of electron hole in the semiconductor (high electron transportation of WO_3 overcomes the low transportation of Fe_2O_3); (iii) higher absorptivity and spectral sensitivity within a wide range of photon energies.

In this study, seven different nanocomposite thin films of $(WO_3)_{1-x}-(Fe_2O_3)_x$, with $0 \leq x \leq 1$, were synthesized and deposited by sol-gel spin-coating method. Consequently, the deposited thin films were examined in a photoelectrochemical cell. The films were also characterized by UV-visible spectroscopy, SEM and XRD. Finally, the photoelectrochemical performance of WO_3/Fe_2O_3 nanostructures were quantified and the optimal composition of $(WO_3)_{1-x}-(Fe_2O_3)_x$ were obtained.

Table 2 – Composite nanomaterial preparation for $(WO_3)_{1-x}-(Fe_2O_3)_x$ samples.

Sample	WO_3 solution (Mole fraction)	Fe_2O_3 solution (Mole fraction)	pH
x = 1.00	0.00	1.00	1.8
x = 0.75	0.25	0.75	1.6
x = 0.50	0.50	0.50	1.3
x = 0.35	0.65	0.35	1.5
x = 0.25	0.75	0.25	1.4
x = 0.15	0.85	0.15	1.2
x = 0.00	1.00	0.00	1.1

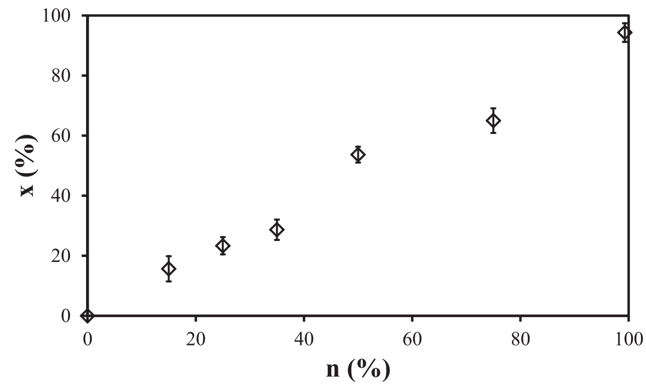

Fig. 1 – The percentage of Fe_2O_3 content in precursor solution (*x*) versus its concentration in the calcinated thin films (*n*) based on EDX analysis.

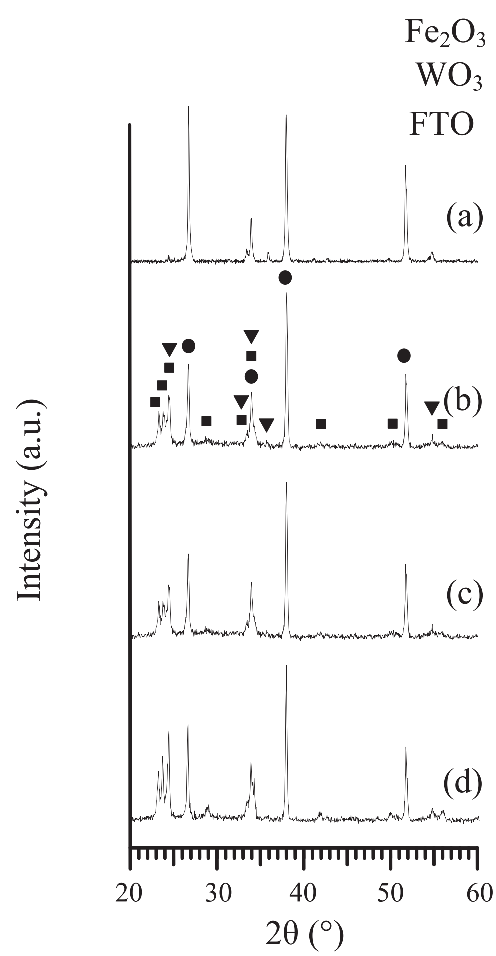

Fig. 2 – X-ray diffraction patterns for annealed samples of (a) x = 1, (b) x = 0.5, (c) x = 0.35, (d) x = 0.

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