Solar Energy 144 (2017) 604–611

Contents lists available at ScienceDirect

Solar Energy

journal homepage: www.elsevier.com/locate/solener

Brief Note

A facile one-step strategy for in-situ fabrication of WO_3-$BiVO_4$ nanoarrays for solar-driven photoelectrochemical water splitting applications

Naseer Iqbal [a,b], Ibrahim Khan [a,c], Zain Hassan Abdallah Yamani [a,d], Ahsanulhaq Qurashi [a,c,*]

[a] Center of Research Excellence in Nanotechnology, King Fahd University of Petroleum and Minerals, Dhahran 31261, Saudi Arabia
[b] Department of Biosciences, COMSATS Institute of Information Technology, Park Road, Chak Shahzad, Islamabad 45550, Pakistan
[c] Department of Chemistry, King Fahd University of Petroleum and Minerals, Dhahran 31261, Saudi Arabia
[d] Department of Physics, King Fahd University of Petroleum and Minerals, Dhahran 31261, Saudi Arabia

ARTICLE INFO

Article history:
Received 26 September 2016
Received in revised form 18 January 2017
Accepted 24 January 2017

Keywords:
Heteronanostructures
Solar water splitting
Nanorods
Tungsten oxide bismuth vanadate
Hydrothermal

ABSTRACT

This paper presents a facile single step strategy for fabrication of tungsten, bismuth and vanadium mixed metal oxide nanoarrays. WO_3-$BiVO_4$ heteronanostructure was obtained hydrothermally with reaction time of two hrs at low temperature 110 °C. The morphology of as prepared WO_3-$BiVO_4$ heterostructure revealed uniform and prominent nanorods like architectures under FE-SEM. These heteronanostructures were of variable sizes i.e., width ⩽100 nm and length 200–400 nm respectively. The energy dispersive X-ray analysis (EDX) and elemental mapping of heteronanostructure further confirmed W, Bi, V and O entities in good elemental composition. The purity and crystalline nature of as synthesized WO_3-$BiVO_4$ were confirmed from X-ray crystallographic (XRD) analysis. UV–Visible spectroscopy and Raman analysis were also carried out to investigate optical properties of WO_3-$BiVO_4$. The band gap energy of WO_3-$BiVO_4$ calculated from UV–Visible absorption and diffused reflectance spectroscopy's was observed to be 2.1 eV respectively. The photoelectrochemical (PEC) studies of FTO coated WO_3-$BiVO_4$ showed a stable and repeatable photocurrent response under 1 SUN solar irradiation source. The linear sweep voltammetry (LSV) and Cyclic Voltammetry (CV) also corroborated substantial photocurrents at different oxidation and reduction potentials. Consequently, it is envisioned that this one-step strategy for in-situ fabrication of WO_3-$BiVO_4$ heteronanostructures have potential applications in solar-driven photoelectrochemical water splitting reactions.

1. Introduction

Since the advent of solar water splitting techniques (Fujishima and Honda, 1972) the research in development of photoelectrocatalysts gained utmost attention (Liao et al., 2014; Reece et al., 2011; Kuang et al., 2016; Qurashi et al., 2015; Iqbal et al., 2016). Fabrication of an optimal material for emergent alternative or green energy resources such as H_2 and O_2 evolution from photoelectrochemical water splitting through a simple and cost effective strategy is a drastic challenge (Avasare et al., 2015; Maeda and Domen, 2010). Various factors on materials standpoint are decisive in order to fabricate a reliable photocatalyst system for solar light driven water splitting which include solar-to- hydrogen conversion (STH) efficiency (May et al., 2015), morphology of the materials (Lai, 2015), photocorrosion (Guo et al., 2010), high charge carrier recombination (Abdi et al., 2013; Appavoo et al., 2015), and band gap energies (Sivula and van de Krol, 2016), etc. Nevertheless, researchers explored many semiconducting heteronanostructures as shown in table 1 that demonstrated remarkable photoelectrochemical activities (Osterloh and Parkinson, 2011; Pihosh et al., 2014; Khan et al., 2016; Ibrahim et al., 2016). Apart from these, several other factors which include a simple or facile strategy of photocatalyst fabrication, cost effectiveness, low temperature, reaction time, etc. are also imperative in evaluating a photocatalyst in real life applications as well as for commercialization.

In recent years, several materials such as TiO_2 and $BiVO_4$ are among the extensively used materials in solar water splitting (Fujishima and Honda, 1972; Yang et al., 2013; Kuang et al., 2016; Pihosh et al., 2014). The wide band gap energy of TiO_2 (3.2 eV) (Pihosh et al., 2014) restricted its photoelectrochemical

* Corresponding author at: Center of Research Excellence in Nanotechnology, and Chemistry Department, King Fahd University of Petroleum and Minerals, Dhahran 31261, Saudi Arabia.
E-mail address: ahsanulhaq@kfupm.edu.sa (A. Qurashi).

http://dx.doi.org/10.1016/j.solener.2017.01.057
0038-092X/

Table 1
Different $WO_3/BiVO_4$ semiconducting nanostructures recently used in solar driven water splitting applications.

Nanomaterial type	Methodology	Reaction conditions	Morphology	Current density	Band Gap (eV)	Year/ Reference
$WO_3/BiVO_4$ thin film	Wet synthesis: Step wise spin coating From precursor solutions	Annealing at 550 °C for 1 h	Grains like	120 μA·cm^2	2.43	2009/ Chatchai et al. (2009)
$WO_3/BiVO_4$ heterojunction films	Solvothermal(ST) growth of WO3 nanorods on FTO followed by $BiVO_4$ spin coatings	180 °C for 24 h (ST) and annealing at 500 °C for 2 h	Nanorods	1.6 mA/cm^2	2.4	2011/Su et al. (2011)
WO_3-NRs, WO_3-NRs/$BiVO_4$ and WO_3-NRs/$BiVO_4$ photoanodes modified with Co-Pi	Reactive magnetron sputtering and Glancing Angle Deposition (GLAD)	Annealing in air at 500 °C for 4.5 h.	Nanorods	WO_3-NRs = ~0.4 mA/cm^2 WO_3-NRs/$BiVO_4$ = ~ 2 mA/cm^2 WO_3-NRs/$BiVO_4$-Co-Pi = 3.2 mA/cm^2	2.4	2014/ Pihosh et al. (2014)
$WO_3/BiVO_4$ heterojunctions	Solution processed method	1 h at 80 °C and annealed for 1 h at 500 °C	Aggregated network of particles/sequential layering of WO_3 and $BiVO_4$	1 mA/cm^2	–	2015/ Grigioni et al. (2015)
$WO_3/BiVO_4$ core/shell nanorods in photovoltaic–photoelectrochemical (PV–PEC) tandem device based on GaAs/InGaAsP (PV cell) and $WO_3/BiVO_4$ core/shell nanorods (PEC cell)	Combination of GLAD and electrochemical deposition (ED)	500 °C for 2 h	Nanorods	PV–PEC tandem device = 6.56 mA/cm^2	–	2016/ Sonya et al. (2016)
Single phase WO_3-$BiVO_4$ heteronanostructure composites	Hydrothermal reaction	110 °C for 2 h and annealed in air for 2 h for 80 °C	Nanorods	0.5 mA·cm^2	2.1	This work

properties (Fujishima and Honda, 1972; Sivula and van de Krol, 2016). However, low band gap photocatalyts are suitable for capturing visible light spectrum but they are mostly susceptible to photocorrosion as compared to their larger band gap counterparts. Furthermore, it is studied (Su et al., 2011) that on coupling a larger band gap photocatalytic material with a smaller band gap material, a more negative conduction band is expected. Thus the electrons in conduction band can move from smaller band gap photocatalytic material into the larger band gap material. Consider $BiVO_4$ which has a narrow band gap of (2.4 eV) in monoclinic phase, it has excellent stability against photocorrosion and its preparation is cost effective too. Theoretically, under the standard AM 1.5G solar irradiation, STH efficiency of $BiVO_4$ approaches 9.2% with the photocurrent of 7.5 mA cm^{-2}. Despite of being a good photon absorber with a direct bandgap, $BiVO_4$ has poor electron transport properties (Abdi and van de Krol, 2012) that is attributed to high recombination rate of photogenerated carriers. Henceforth, $BiVO_4$ is characterized by a short carrier diffusion length (L_d) of around 70 nm^3, which is the main reason of $BiVO_4$ photo anodes to generate small photocurrents (Pihosh et al., 2015). In this scenario, the incorporation of different metallic centers or oxides such as WO_3 with $BiVO_4$ could enhance their photoelectrochemical properties. As the conduction band of $BiVO_4$ is more negative than that of WO_3 (Pihosh et al., 2015) so when coupled with photocorrosion resistant WO_3, the photo anodes (Long and Kisch, 2008; Luo et al., 2011), thus fabricated could be employed for reliable and effectual photoelectrochemical applications under visible irradiation.

In the present research work, we are successfully reporting a new facile and single step strategy where in-situ impregnation of photocorrosion resistant WO_3 is carried out with $BiVO_4$ in a hydrothermal reaction. The most exciting features of this strategy were one step fabrication of WO_3-$BiVO_4$ nanorods like heterostructure at low temperature 110 °C in 2 h. The as synthesized WO_3-$BiVO_4$ heteronanostructures were fully characterized via UV–VIS, Raman, XRD, FE-SEM, EDX, etc. techniques and also investigated for photoelectrochemical (PEC) water splitting studies.

2. Materials and methods

All the chemicals and reagents such as Tungsten hexachloride (WCl_6), Bismuth trinitrate penta hydrate [$Bi(NO_3)_3{\cdot}5H_2O$] and vanadium pentoxide (V_2O_5) precursors were purchased from Sigma Aldrich and used as received unless otherwise stated.

2.1. Preparation of WO_3-$BiVO_4$

Equal amounts of each precursor Tungsten hexachloride (WCl_6), Bismuth trinitrate penta hydrate ($Bi(NO_3)_3{\cdot}5H_2O$) and vanadium pentoxide (V_2O_5) were mixed in deionized water and stirred for 30 min. at room temperature until a homogenous mixture is obtained. The reaction mixture was further sonicated for 30 min. at room temperature. The resulting reaction mixture was poured into a Teflon vessel enclosed with a steeliness steel autoclave Jacket in order to proceed a hydrothermal reaction. This autoclave reactor was then placed into oven at 110 °C for 2 h. Later on, reaction mixture was centrifuged at 4000 rpm for 5 min. The yellowish brown product (WO_3-$BiVO_4$) was collected and dried at 100 °C in vacuum oven.

2.2. Characterization of WO_3-$BiVO_4$ heteronanostructures

The crystalline phases of as-synthesized WO_3-$BiVO_4$ heteronanostructures were identified by X-ray diffraction (XRD) technique using a Benchtop MiniFlex -X-ray Diffraction instrument (Mini-XRD) from Rigaku (40 kV and 15 mA) in the range of 10–70° (2θ) at a scanning rate of 3° min^{-1}. The morphology of the WO_3-$BiVO_4$ heteronanostructures were investigated by Tescan Lyra 3 Field Emission Dual Beam (Electron/Focused Ion Beam)