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Constructing $BiVO_4$/Graphene/TiO_2 nanocomposite photoanode for photoelectrochemical conversion applications

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ABSTRACT

$BiVO_4$/Graphene/TiO_2 as a novel nanocomposite photoanode was designed, synthesized and characterized for photoelectrochemical application. $BiVO_4$/Graphene nanocomposite was initially synthesized by photocatalytic process and then, $BiVO_4$/Graphene/TiO_2 nanocomposite thin film was prepared by deposition of the $BiVO_4$/Graphene solution onto the surface of sol–gel derived TiO_2 thin film. Morphology, crystal structure, surface chemical composition and optical properties of the synthesized $BiVO_4$/Graphene/TiO_2 nanocomposite thin film were characterized and compared with the $BiVO_4$/Graphene and pure TiO_2 samples. Observations of scanning electron microscopy (SEM) images revealed that the surface of the TiO_2 thin film was modified by the $BiVO_4$/Graphene with high surface area. According to X-ray diffraction (XRD) analysis, formation of anatase and monoclinic phase was confirmed for crystalline structure of TiO_2 and $BiVO_4$, respectively. UV–visible absorption spectra of the samples showed that the absorption edge and intensity of the $BiVO_4$/Graphene/TiO_2 nanocomposite film were increased with respect to the TiO_2 film. The $BiVO_4$/Graphene/TiO_2 nanocomposite photoanode yielded a photocurrent density of ~1.30 A/m^2 as compared to 0.27 A/m^2 for the TiO_2 at 0.8 V vs Ag/AgCl under UV–visible irradiation in similar condition. The improved photoelectrochemical activity is believed due to the enhanced light absorption and higher surface area of $BiVO_4$/Graphene as well as better charge transfer of the photogenerated carriers at the $BiVO_4$/Graphene/TiO_2 interfaces via Graphene.

1. Introduction

Energy production from harvesting sunlight is one of the main approaches for solving energy problem with minimum environmental impact. Hydrogen production by using solar energy is one of the feasible candidates for replacing fossil fuels that can be generated from photoelectrochemical (PEC) water splitting process [1,2]. The working electrode in PEC water splitting cell typically consists of a semiconductor such as TiO_2 [3,4]. TiO_2 is the most widely used in this field as a result of its low cost, non-toxicity, high chemical stability but low efficiency, high recombination rate of the photoinduced charges, high energy band gap (3.2 eV for anatase) as well as its activity in UV region of solar spectrum are the main drawbacks of using this material [3,5]. In order to overcome these limitations, the addition of metal [6], nonmetal [7], carbon-based material [8–10] or narrow band gap semiconductor [11,12] to TiO_2 has been implemented to improve its PEC properties of TiO_2. Among these approaches, coupling of narrow band gap semiconductors such as Bi_2S_3 [13], Ag_2S [14], CdS [15], Fe_2O_3 [16] and $BiVO_4$ [17,18] to TiO_2 can efficiently improve the photosensitivity of TiO_2 into the visible region as well as facilitate charge transfer. In particular, $BiVO_4$ with monoclinic crystalline structure has shown activities for water splitting under visible light irradiation [19,20]. Therefore, $BiVO_4$-TiO_2 composite can be an interesting candidate for water splitting reaction from theoretical viewpoint. Till now, a few experimental papers have been reported the use of a $BiVO_4$–TiO_2 composite photoanode for photoelectrochemical applications with enhanced activity [17,18]. But, some experimental studies show that the PEC performance of $BiVO_4$ is limited by poor carrier transport properties [21,22]. In search for a new method to enhance its photoactivity, the addition of Graphene as two dimensional carbon based material with high electrical conductivity and carrier mobility can be considered to enhance transfer of photogenerated electrons in the $BiVO_4$ leading to increase photoconversion efficiency of the system [23–25]. Y. Ng et al. [23] have reported enhanced photoelectrochemical water splitting of the $BiVO_4$-reduced Graphene oxide (RGO) composite as a photocatalyst where they show its improved charge transport properties, leading to a remarkable enhancement in visible light response as compared with pure $BiVO_4$.

In here, we have synthesized TiO_2 thin film by sol–gel method and then, $BiVO_4$/Graphene nanocomposite synthesized by a facile via photocatalytic process. Then, the $BiVO_4$/RGO nanocomposite was loaded onto the surface of the deposited TiO_2 thin film by spin coating method. To

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the best of our knowledge, the synthesized $BiVO_4$/Graphene/TiO_2 nanocomposite thin film has not been studied for PEC application, yet. Physical and chemical properties as well as photoelectrochemical activity of the synthesized $BiVO_4$/Graphene/TiO_2 nanocomposite thin film were investigated by different analytical techniques and compared the results with pure TiO_2 and $BiVO_4$/Graphene thin films. Moreover, by using PEC measurements, photocurrent density and its stability, photoconversion efficiency, charge transfer resistance and electron life time were also studied in order to understand mechanism of photoenhancement under UV–visible irradiation.

2. Material and methods

2.1. Preparation of $BiVO_4$/Graphene/TiO_2 film

First, sol–gel derived TiO_2 thin film was prepared using the method explained in our recent work group [26]. In brief, 2.3 mL titanium (n) butoxide (98%, Merck) was mixed with 23 mL ethanol and stirred for 0.5 h. Then, 8 drops of nitric acid as a catalyst were added to the solution. After 2 h stirring and 1 day aging, the sol was deposited on substrates (cleaned microscope slide glass and fluorine-doped tin oxide coated glass (FTO, 8 Ω/☐) by dipping into TiO_2 sol and pulling them up at a rate of 5 mm/s for two times. In the second step, for preparation of $BiVO_4$/Graphene nanocomposite, Graphene oxide (GO) was obtained by the modified Hummers method [27]. $BiVO_4$ was prepared by mixing 10 mmol of $Bi(NO_3)_3.5H_2O$ and 5 mmol of V_2O_5 in 50 mL of 0.75 M HNO_3 solution [23,28] and the suspension stirred for two days at room temperature. Then, the obtained greenish $BiVO_4$ was collected by filtration and dried at 110 °C for 6 h. The $BiVO_4$ powder was suspended in ethanol and GO powder with 5 wt.% of $BiVO_4$ was added to the solution. The $BiVO_4$/GO suspension was sonicated for 10 min to produce $BiVO_4$/GO dispersion. The dispersion was irradiated by UV lamp (ULTRA-MED FDA, 400W, OSRAM) under Argon stream and stirring for 3 h to obtain a uniform $BiVO_4$/Graphene nanocomposite solution. The solution was dried to obtain a proper powder. Then, the resultant powder was added to ethanol solution, then, it was sonicated to obtain a 0.5 mg/mL concentration. The final suspension was deposited on both FTO and TiO_2 coated FTO electrodes by spin coating with a constant rotation speed of 1500 rpm for 8 times to make a desire thickness.

2.2. Characterization

Fourier transform infrared (FTIR) spectra were recorded on a Bruker VERTEX 70 spectrometer using the KBr pellet technique. Morphology of all samples was investigated by scanning electron microscopy SEM (JEOL, JSM7001). Philips PW 3710 profile X-ray diffractometry (XRD) with a Cu-Kα radiation source ($\lambda = 1.5410$ Å) with a step size of 0.05° (conventional θ–2θ diffractometer) was utilized to determine the phase formation and crystalline structure of the nanocomposite thin films. Surface chemical composition of the thin films was also investigated by X-ray photoelectron spectroscopy (XPS) equipped with an Al-K_α X-ray source at an energy of 1486.6 eV. For all measurements, the concentric hemispherical energy (CHA) analyzer (Specs EA 10 Plus) operating in a vacuum better than 10^{-7} Pa was used. All binding energy values were calibrated by fixing the C(1s) core level to the 285.0 eV. All of the XPS peaks were deconvoluted using SDP software (version 4.1) with 80% Gaussian-20% Lorentzian peak fittings. The absorption spectra of the samples were investigated by UV–visible diffuse reflectance spectroscopy (DRS) from 200 to 1000 nm wavelength with resolution of 1 nm.

2.3. Photoelectrochemical measurements

To investigate PEC properties of all samples, a cell with a three-electrode configuration and galvanostat/potentiostat (Autolab PGSTAT302) equipment were used to evaluate and compare the results. The PEC measurements were carried out in a compartment cell (two glass vessels connected with a porous silicon sinter (ion exchange membrane) with 0.1 M K_2SO_4 aqueous solution as electrolyte. A platinum wire was used as counter electrode and reference electrode was Ag/AgCl. The synthesized samples were used as working electrodes with an equal surface area (10 mm × 20 mm) for all measurements in order to keep conditions similar for comparing their activity. Xenon short arc lamp (OSRAM, HBM/OFR) with a natural daylight was used as the irradiation source. Intensity of the lamp was adjusted at 1000 W/m^2 (AM 1.5) by varying the input power. It should be noted that a quartz window was installed for transmittance of UV light. The working electrode was irradiated from the side of $BiVO_4$/Graphene (front side irradiation) and the $BiVO_4$/Graphene side of photoanode was the electrode/solution interface. Also, the ohmic contact was connected through FTO. All PEC measurements have been performed at room temperature (~25 °C) and in air. Electrical properties of the prepared samples have been studied using electrochemical impedance spectroscopy (EIS) with an alternating current signal (10 mV) in the frequency range between 0.01–10^5 Hz under illumination with the same Autolab instrument and electrolyte. Mott–Schottky plots were also measured at a frequency of 1 kHz in the dark to obtain information on flat band potential and donor density of the thin films.

3. Results and discussion

3.1. Physical and chemical characterizations

To investigate the reduction of GO during photocatalytic reduction process in $BiVO_4$/Graphene nanocomposite, FTIR analysis was conducted. Fig. 1(a) displays the characteristic bands of GO at 1047, 1394, 1621 and 1727 cm^{-1}, corresponding to the C–O–C stretching vibration, the C–OH stretching mode, the O–H deformation of the C–OH groups as well as the C = C stretching mode in –COOH group and the C = O stretching vibrations of the –COOH group, respectively. The broad band at ~3413 cm^{-1} was assigned to O–H stretching vibration of adsorbed water molecules on GO. As compared to the peaks of functional groups of GO, the bands featuring oxygen-containing functional groups disappeared for the $BiVO_4$/Graphene nanocomposite (Fig. 1(b)), suggesting that GO in $BiVO_4$/Graphene has been reduced. The broad absorptions at low frequency (below 1000 cm^{-1}) were associated with $\nu_1(VO_4)$ and $\nu_3(VO_4)$ [24].

Fig. 2 shows SEM images of surface morphology of the TiO_2 and $BiVO_4$/Graphene/TiO_2 nanocomposite thin films. Typically, Fig. 2(a) indicates top view of TiO_2 thin film synthesized by sol–gel method on FTO substrate and the inset of Fig. 2(a) shows FTO substrate without any TiO_2 thin film. It is clear that the TiO_2 sol has covered interspace of grains on FTO surface. Also, cross section image of the TiO_2 thin film has been shown in Fig. 2(b) that the thickness of the sol–gel deposited TiO_2 (determined by two dash lines) was measured about 100 nm

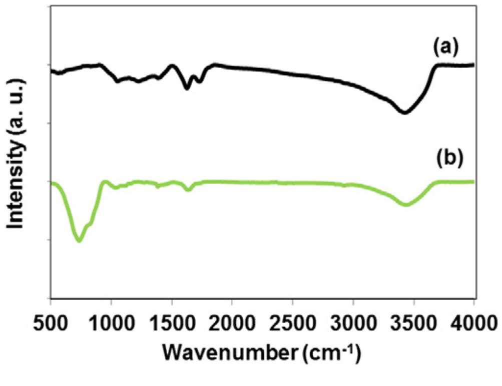

Fig. 1. FTIR spectra of (a) graphene oxide (GO) and (b) $BiVO_4$/Graphene nanocomposite.