Constructing BiVO₄/Graphene/TiO₂ nanocomposite photoanode for photoelectrochemical conversion applications

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Abstract

BiVO₄/Graphene/TiO₂ as a novel nanocomposite photoanode was designed, synthesized and characterized for photoelectrochemical application. BiVO₄/Graphene nanocomposite was initially synthesized by photocatalytic process and then, BiVO₄/Graphene/TiO₂ nanocomposite thin film was prepared by deposition of the BiVO₄/Graphene solution onto the surface of sol-gel derived TiO₂ thin film. Morphology, crystal structure, surface chemical composition and optical properties of the synthesized BiVO₄/Graphene/TiO₂ nanocomposite thin film were characterized and compared with the BiVO₄/Graphene and pure TiO₂ samples. Observations of scanning electron microscopy (SEM) images revealed that the surface of the TiO₂ thin film was modified by the BiVO₄/Graphene with high surface area. According to X-ray diffraction (XRD) analysis, formation of anatase and monoclinic phase was confirmed for crystalline structure of TiO₂ and BiVO₄, respectively. UV–visible absorption spectra of the samples showed that the absorption edge and intensity of the BiVO₄/Graphene/TiO₂ nanocomposite film were increased with respect to the TiO₂ film. The BiVO₄/Graphene/TiO₂ nanocomposite photoanode yielded a photocurrent density of ~1.30 A/m² as compared to 0.27 A/m² for the TiO₂ at 0.8 V vs Ag/AgCl under UV-

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visible irradiation in similar condition. The improved photoelectrochemical activity is believed due to the enhanced light absorption and higher surface area of BiVO₄/Graphene as well as better charge transfer of the photogenerated carriers at the BiVO₄/Graphene/TiO₂ interfaces via Graphene.

Keywords: BiVO₄/Graphene/TiO₂ nanocomposite; photocurrent density; photoconversion efficiency; electron lifetime; charge transfer

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 TiO₂ [3, 4]. TiO₂ 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, addition of metal [6], nonmetal [7], carbon-based material [8-10] or narrow band gap semiconductor [11, 12] to TiO₂ has been implemented to improve its PEC properties of TiO₂. Among these approaches, coupling of narrow band gap semiconductors such as Bi₂S₃ [13], Ag₂S [14], CdS [15], Fe₂O₃ [16] and BiVO₄ [17, 18] to TiO₂ can efficiently improve the photosensitivity of TiO₂ into the visible region as well as facilitate charge transfer. In particular, BiVO₄ with monoclinic crystalline structure has shown activities for water splitting under visible light irradiation [19, 20]. Therefore, BiVO₄-TiO₂ 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 $\text{BiVO}_4\text{-TiO}_2$ 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, 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 - reducing 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 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, $8 \Omega/\square$)) 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 $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ 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, 400 W, 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 $\text{Cu-K}\alpha$ radiation source ($\lambda=1.5410 \text{ \AA}$) 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 K₂SO₄ 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/m² (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 BiVO₄/Graphene (front side irradiation) and the BiVO₄/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 0.01–10⁵ 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 BiVO₄/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 BiVO₄/Graphene nanocomposite (Fig. 1(b)), suggesting that GO in BiVO₄/Graphene has been reduced. The broad absorptions at low frequency (below 1000 cm⁻¹) were associated with $\nu_1(\text{VO}_4)$ and $\nu_3(\text{VO}_4)$ [24].

Figure 2 shows SEM images of surface morphology of the TiO₂ and BiVO₄/Graphene/TiO₂ nanocomposite thin films. Typically, Fig. 2(a) indicates top view of TiO₂ thin film synthesized by sol-gel method on FTO substrate and the inset of Fig. 2(a) shows FTO substrate without any TiO₂ thin film. It is clear that the TiO₂ sol has covered interspace of grains on FTO surface. Also, cross section image of the TiO₂ thin film has been shown in Fig. 2(b) that the thickness of the sol–gel deposited TiO₂ (determined by two dash lines) was measured about 100 nm consistent with the other

published reports [26]. Moreover, Fig. 2(c and d) illustrates morphology and cross section of the BiVO₄/Graphene/TiO₂ nanocomposite thin film. As indicated in Fig. 2(c), BiVO₄/Graphene thin film has uniformly covered on the surface of TiO₂ thin film. Also, according to the cross sectional image (Fig. 2(d)), the thickness of BiVO₄/Graphene/TiO₂ nanocomposite thin film was estimated about 300 nm which has increased as compared with the pure TiO₂ thin film. It should be noted that the effective surface area of the BiVO₄/Graphene/TiO₂ nanocomposite thin film increased due to presence of Graphene possessing high surface area in the BiVO₄/Graphene nanocomposite thin film. The increase in surface area was also confirmed by the corresponding AFM images (not shown here). Based on AFM image analysis, surface ratio (the ratio of real 3D surface to the 2D projected area) was calculated and the results showed the ratio at about 1.12 and 1.50 for pure TiO₂ and BiVO₄/Graphene/TiO₂ nanocomposite thin films, respectively. Role of surface area on its PEC activity for different photoelectrodes will be discussed in section 3.2.

Figure 3 shows XRD spectra for various samples. Fig. 3(a) demonstrates low diffraction intensity of the TiO₂ thin film due to its low layer thickness. It was found that the TiO₂ thin film possessed two main peaks at 25.30° and 37.70° (overlapped with FTO peak) due to diffraction from the (101) and (004) planes of its anatase phase [17, 29]. Therefore, the samples contain TiO₂ with anatase crystalline phase. Peak intensity of the Graphene appeared at about 2θ = 24.70° is overlapped with the FTO peak [30]. The XRD pattern of the BiVO₄/Graphene nanocomposite thin film (as shown in Fig. 3(b)) displays diffraction peaks (2θ) at around 18.91°, 28.80°, 30.60°, 34.50°, 47.10° which could be indexed to the characteristic peaks (011), (112), (004), (200) and (024) of monoclinic BiVO₄, respectively [19, 31]. Moreover, the BiVO₄/Graphene nanocomposite on TiO₂ thin film does not cause any change in the XRD peak positions as compared with the pure TiO₂ thin film indicating that the BiVO₄/Graphene/TiO₂ nanocomposite thin film

prepared by this method retains the crystalline structure of TiO_2 and BiVO_4 components (see Fig. 3(c)).

The surface chemical composition of the pure TiO_2 and $\text{BiVO}_4/\text{Graphene}/\text{TiO}_2$ nanocomposite thin films was studied by the XPS technique. By comparing survey curve (not shown here) of the $\text{BiVO}_4/\text{Graphene}/\text{TiO}_2$ nanocomposite thin film with pure TiO_2 thin film, Bi and V elements were found on the surface of the $\text{BiVO}_4/\text{Graphene}/\text{TiO}_2$ nanocomposite thin film. Fig. 4(a) depicts the Ti(2p) core level binding energy of the TiO_2 thin films sample. The two peaks located at about 459.0 and 464.5 eV are attributed to the $\text{Ti}(2p_{3/2})$ and the $\text{Ti}(2p_{1/2})$ in the Ti^{4+} chemical state, respectively [26, 32]. Fig. 4(b) shows the Bi(4f) for the $\text{BiVO}_4/\text{Graphene}/\text{TiO}_2$ nanocomposite. The two peaks (A and B) located at about 159.5 and 164.8 eV are attributed to the $\text{Bi}(4f_{7/2})$ and $\text{Bi}(4f_{5/2})$ binding energies, respectively. This is confirming that the bismuth species are mainly in Bi^{3+} cations, contributing to the Bi-O bonds. In addition, peaks C and D at 158.8 and 164.1 eV binding energies are indicating formation of C-Bi bonds. Also, Fig. 4(c) indicates that the core level binding energies of the vanadium peaks (A and B) are centered at 516.5 and 523.5 eV related to the $\text{V}(2p_{3/2})$ and the $\text{V}(2p_{1/2})$ core-level binding energy, respectively. All these information are characteristic of the V^{5+} oxidation state in BiVO_4 . Furthermore, the peaks C and D at 518.1 and 522.0 eV are assigned to the formation of C-V bonds in the nanocomposite [19, 33]. Therefore, the XPS spectra provide evidence for the chemical interaction between the BiVO_4 and Graphene, which will facilitate charge transfer between the BiVO_4 and Graphene in the nanocomposite sample [33]. According to our XPS data analysis, the Bi:V ratio was measured at about 0.94 that indicated formation of nearly stoichiometric BiVO_4 .

Figure 5 illustrates the UV-visible diffuse reflectance spectra (DRS) of the different thin films. Based on DRS analysis, the absorption edge of the pure TiO_2 sample occurred in the UV region at about 389 nm whereas the absorption edge of the

BiVO₄/Graphene thin film was occurred at about 525 nm. Thus, it was found that the absorption edge of the BiVO₄/Graphene/TiO₂ thin film extended toward visible region relative to the pure TiO₂ thin film. The presence of the BiVO₄/Graphene in the BiVO₄/Graphene/TiO₂ nanocomposite photoanode can improve the PEC performance as a result of visible light absorption as compared to the pure TiO₂ photoanode.

3.2. Electrochemical/Photoelectrochemical studies

It is well established that impedance measurements conducted on all synthesized photoelectrodes by potential scan in 0.1 M K₂SO₄ electrolyte in the dark allowed the construction of Mott-Schottky (MS) plots. The MS plot ($1/C^2$ vs. V) provides information on position of the flat-band potential (V_{fb}) from the V-axis intercept that indicate electron transfer in a composite structure. In addition, slope of the MS plot has an inverse relationship with the donor density (N_D) of semiconductor film. The MS plot also describes the semiconductor depletion layer capacitance (C) depending on the applied bias potential (V) and is expressed by equation below [34, 35]:

$$1/C^2 = (2/e\epsilon\epsilon_0 N_D A^2) (V - V_{fb} - k_B T/e) \quad (1)$$

where ϵ is the dielectric constant of the semiconductor in use ($\epsilon = 95$ in this study), ϵ_0 is the vacuum permittivity (8.85×10^{-12} C²/Nm²), e is the electron charge (1.602×10^{-19} C), N_D is the donor density, A is surface area of photoelectrode, V_{fb} is the flat band potential and $k_B T/e$ is a temperature dependent correction term. The above equation can be used for both n- and p-type semiconductors. In n-type semiconductor with electrons as the majority carriers, the MS plot has positive slope whereas the n-type semiconductor possess negative slope.

Figure 6 shows MS plots for different synthesized samples. The electron densities (N_D) of different electrodes were measured 536.03, 120.80 and 232.18 ($\times 10^{20}$ m⁻³) for the BiVO₄/Graphene/TiO₂, BiVO₄/Graphene and TiO₂ electrodes, respectively. Higher

electron density of the BiVO₄/Graphene/TiO₂ electrode was related to role of electrons from the BiVO₄ as an n-type semiconductor and Graphene as an inhibitor of the electron-hole recombination [36]. In addition, the flat band potential (V_{fb}) of the BiVO₄/Graphene/TiO₂, BiVO₄/Graphene and TiO₂ electrodes were also measured at about -1.10, -0.50 and -0.75 V, respectively. The difference in the V_{fb} values for both BiVO₄/Graphene and TiO₂ electrodes measured under identical conditions showed that electron transfer from the BiVO₄/Graphene to TiO₂ can occur because location of its V_{fb} is situated just under the conduction band of n-type semiconductors [37]

Considering the obtained results from the MS plots and in order to understand the charge transfer and separation processes under photoirradiation, photoelectrochemical (PEC) measurements of the samples were studied. These experiments were performed in 0.1 M K₂SO₄ (pH=6.7) electrolyte under UV-visible light irradiation with three electrode PEC cell. The linear sweep voltammetry (LSV) method was utilized to measure generated photocurrent density in a potential range from 0 to 1.5 V versus Ag/AgCl reference electrode. Fig. 7(A) illustrates the photocurrent density of different samples as a function of applied potential at a constant illumination intensity (1000 W/m²). It is clear that a dark scan linear sweep voltammogram of all samples shows an almost negligible photocurrent density. Under illumination, the BiVO₄/Graphene/TiO₂ nanocomposite photoanode exhibits the highest photocurrent about 2.7 A/m² at 1.5 V potential versus Ag/AgCl which was about 1.3 and 2.9 fold higher than the BiVO₄/Graphene and TiO₂ photoelectrode at bias voltage 1.5 V, respectively. The photocurrent density did not reach saturation and the enhancement of photocurrent density was likely due to more photoelectron transfer from the BiVO₄/Graphene/TiO₂ nanocomposite photoelectrode to the counter electrode via the external circuit. When applied potential increased from 0 to 0.33 V, the photocurrent density of the BiVO₄/Graphene/TiO₂ nanocomposite photoanode increased gradually until reaching a value of approximately 1.30 A/m² at about 0.33 V, then the photocurrent density

decreased slightly. Then, the photocurrent density increased monotonically with the applied bias potential (Fig. 7(A)). In general, BiVO_4 and TiO_2 are n-type semiconductors, but under photoillumination, the electrons move more freely from BiVO_4 to TiO_2 via Graphene interlayer, this leaves an excess of holes in valence band of the BiVO_4 . Thus, the $\text{BiVO}_4/\text{Graphene}/\text{TiO}_2$ structure acts as a p-n junction. Increase and subsequent decrease of photocurrent density was related to the fact that the generated space charge region of the $\text{BiVO}_4/\text{Graphene}/\text{TiO}_2$ nanocomposite photoanode improved the separation of photogenerated electrons and holes by the internal electrostatic field in junction of $\text{BiVO}_4/\text{Graphene}$ and TiO_2 and more holes participated in water oxidation reaction instead of recombination with electrons [38, 39]. It is well known that internal electrostatic field and thickness of space charge layer (W) of p-n junction are decreased with applying forward bias voltage [39]. Thus, further increasing the bias potential ($V > 0.33$ V), the internal electrostatic field weakened due to reduction of space charge layer thickness (W) with the applied bias voltage, leading to decrease in photocurrent density [39, 40]. This change in energy band diagram of the $\text{BiVO}_4/\text{Graphene}/\text{TiO}_2$ has been illustrated in Fig. 7(B). After this step, the photocurrent density increased sharply with higher bias potential. Although, the internal electrostatic field was changed, the shape of photocurrent density curve did not affect by increasing of bias potential due to the relative minor effect. This phenomenon was consistent with the results reported by others [39, 41]. The photocurrent density of $\text{BiVO}_4/\text{Graphene}/\text{TiO}_2$ nanocomposite photoanode was improved as compared to the pure TiO_2 photoanode can be due to the following effects: (i) enhanced light absorption under visible irradiation, (ii) increased effective surface area and interface between photoanode and electrolyte by presence of $\text{BiVO}_4/\text{Graphene}$, (iii) improved charge separation and transport of carriers via existence of Graphene.

Photoactivity of different synthesized photoelectrodes was also investigated by chronoamperometry technique (photocurrent transient). Fig. 8(A) shows the

photocurrent density of the samples increased by illumination, exhibiting a good sensitivity and it decreased when lights off. In addition, the photoresponse of the photoelectrodes showed a slight reduction in current density in the first few seconds of each illumination time interval due to the charge carrier recombination process as also seen by others [34, 42]. As shown in Fig. 8(A), the transient photocurrent density of the BiVO₄/Graphene/TiO₂ nanocomposite photoanode was about 1.30 A/m², whereas for the BiVO₄/Graphene and TiO₂ photoanodes were measured lower at about 0.51 and 0.27 A/m², respectively. The measured photocurrent density of the BiVO₄/Graphene/TiO₂ nanocomposite photoanode was higher than the BiVO₄/Graphene and TiO₂ photoanode by a factor of 2.54 and 4.81, respectively. It was believed that the photocurrent enhancement of the BiVO₄/Graphene/TiO₂ photoanode was due to its higher surface area, more visible light absorption efficiency and better charge separation of photogenerated electron–hole pairs in this system. To assure photostability of the BiVO₄/Graphene/TiO₂ photoanode under long illumination time, its photocurrent density was investigated as a function of time for 2 hours. Fig. 8(B) shows photocurrent density of about 1.1 A/m² after two hours illumination indicating its good photostability under PEC condition.

Another method to evaluate PEC cell activity is by measuring the ratio of collected photocurrent to input light intensity at different bias voltages. This quantity is called the applied bias photon-to current efficiency (ABPE) (η), defined by the following equation [36]:

$$\eta(\%) = J(1.23 - V)/I_0 \quad (2)$$

where J is the current density under photoirradiation, V is the applied bias voltage versus reversible hydrogen electrode (RHE) and I₀ is the input light intensity (1000 W/m²). As shown in Fig. 9, a maximum photoconversion efficiency of 0.12% was measured for the BiVO₄/Graphene/TiO₂ nanocomposite photoanode at bias voltage of 0.30 V (0.90 V vs

RHE) that was higher than the photoconversion efficiency of 0.037% for the BiVO₄/Graphene nanocomposite at 0.68 V (1.28 V vs RHE) and TiO₂ (0.0001% at 0.37 V (0.97 V vs RHE)), respectively.

To study and compare the electrical properties and charge transfer resistance of the different samples, the electrochemical impedance spectroscopy (EIS) was implemented using the same electrolyte. EIS technique of the prepared electrodes presented as Nyquist plots are shown in Fig. 10. Fig. 10(A) shows Nyquist plots for the BiVO₄/Graphene/TiO₂ photoanode in dark condition and compared it with its activity under illumination. As observed in the Figure, the impedance spectrum is affected by the light intensity onto the PEC cell. In fact, the internal resistance corresponding to the overall charge transfer process (including the BiVO₄/Graphene/TiO₂ nanocomposite components and electrode/electrolyte) under illumination is significantly lower than in dark conditions. In addition, the Nyquist plots obtained in the dark shows a higher semicircle in the overall frequency range indicating that the impedance behavior relates to charge transfer resistances in the electrode/electrolyte interface. Therefore, upon illumination, the semicircle corresponds to the charge-transfer resistance in the nanocomposite components and the electrode/electrolyte interface, suggesting that charge transfer controls the kinetics in all interfaces. Moreover, under illumination, photoelectrons are able to transfer to the external circuit and cause an increase in photocurrent density. On the other hand, in the dark condition, there is only an equilibrium of charges and consequent electron accumulation in the electrodes, responsible for the higher charge transfer resistance. Also, Fig. 10(B) illustrates the Nyquist plots for the TiO₂ and BiVO₄/Graphene/TiO₂ nanocomposite photoanodes under illumination. The radius of the Nyquist plots changes in the order of TiO₂ and BiVO₄/Graphene/TiO₂ nanocomposite samples and decreased in resistance for the BiVO₄/Graphene/TiO₂ nanocomposite photoanode relative to the pure TiO₂. The Nyquist plots were fitted with an equivalent circuit (inset of Fig. 10(B)) to identify and

quantify resistive elements corresponding to the photoanodes in the electrolyte. Based on our data analysis, the charge transfer resistances of the TiO_2 and $\text{BiVO}_4/\text{Graphene}/\text{TiO}_2$ photoelectrodes were determined about 30.5 and 7.0 k Ω , respectively. The lower electrical resistance of the $\text{BiVO}_4/\text{Graphene}/\text{TiO}_2$ photoelectrode in the Nyquist plot suggested that charge transfer resistance was controlling the kinetics at the electrode interface and showed attenuation in charge recombination, stepwise and ease of charge transfer with the help of Graphene in the $\text{BiVO}_4/\text{Graphene}/\text{TiO}_2$ nanocomposite photoelectrode.

To better understand the mechanism of the lower charge transfer resistance of the $\text{BiVO}_4/\text{Graphene}/\text{TiO}_2$, Bode plots were also used to study and compare frequency response of the investigated photoanodes. Fig. 11 shows the Bode plots of the different samples indicating the longer and efficient electron lifetime in the $\text{BiVO}_4/\text{Graphene}/\text{TiO}_2$, as compared to other synthesized photoanodes. The electron lifetime (τ_e) can be obtained by using the following equation [43, 44]:

$$\tau_e = 1/(2\pi f_{\max}) \quad (3)$$

where the $f_{\max}$ is frequency at which the low frequency peak appears in the Bode plot. The value of τ_e was determined at about 440 ms for the $\text{BiVO}_4/\text{Graphene}/\text{TiO}_2$ nanocomposite photoelectrode which was much longer than that of the $\text{BiVO}_4/\text{Graphene}$ (11 ms) and TiO_2 (5 ms) photoanodes. Therefore, the electron-hole recombination rate was greatly reduced leading to increase in electron lifetime due to presence of Graphene as an efficient charge carrier transporter. Table 1 summarized and compared data measured for the types of photoanodes.

Based on the above results, a possible PEC activity mechanism was proposed and the steps are shown in Scheme 1. When TiO_2 and $\text{BiVO}_4/\text{Graphene}$ are in contact with each other on the surface of FTO substrate, the band structure of components is rearranged (Scheme 1(b)). Work function energy level of Graphene and Fermi levels of

the metal oxides have tendency to reach a balanced value due to the system thermal equilibrium [38, 45]. Upon photoirradiation, the TiO_2 and BiVO_4 are excited and photogenerated holes and electrons appear in the valence bands and conduction bands of both TiO_2 and BiVO_4 , respectively. The role of Graphene sheet as an electron conductor is to enhance the electron–hole separation and easily transfer the electrons from the conduction band of BiVO_4 to the conduction band of the TiO_2 [17]. Then, electrons flow to the FTO substrate and ultimately transfer to the Pt counter electrode to reduce water and form H_2 under the external electrostatic field. This action of Graphene is also supported by recent studies on the BiVO_4 /Graphene systems [24, 39]. Moreover, the holes at the valence band of TiO_2 migrate to the valence band of BiVO_4 leading to participate in oxidation of water to form O_2 via Graphene [46]. A similar mechanism has been also proposed for the Fe_2O_3 -Nano rod Array/Reduced Graphene Oxide/ $\text{BiV}_{1-x}\text{Mo}_x\text{O}_4$ heterojunction by Hou et al. [35]. Therefore, we believe that the introduction of BiVO_4 /Graphene to TiO_2 resulted in photoenhancement in the efficiency of PEC reaction can be due to the following actions: i) increasing both surface area and interface between photoanode and electrolyte, ii) more visible light absorption, iii) faster electron-hole transport and iv) better charge separation. In other words, Graphene and BiVO_4 act as a charge transporter and sensitizer, respectively. These materials which can efficiently increase visible light absorption, decrease the charge-transfer resistance, increase the electron density and as a result, improve the PEC performance of the BiVO_4 /Graphene/ TiO_2 photoanode.

4. Conclusions

In summary, we have designed and constructed a novel nanocomposite BiVO_4 /Graphene/ TiO_2 as a photoanode for PEC application. The TiO_2 thin film was fabricated on FTO substrate using sol-gel method. Then, BiVO_4 /Graphene nanocomposite was synthesized by photocatalytic process followed by deposition on the

TiO₂ film. SEM images showed presence of TiO₂, BiVO₄ and Graphene as well as morphological structure and thickness of the BiVO₄/Graphene/TiO₂ nanocomposite thin films. Anatase phase of TiO₂ and monoclinic crystalline structure of the BiVO₄ as visible active phase have been determined by XRD analysis. The UV–visible absorption spectra of the samples showed that the absorption edge and its intensity of the BiVO₄/Graphene/TiO₂ increased in visible region as compared with the pure TiO₂ thin film. Based on PEC measurements, high photocurrent density of 1.30 A/cm² was achieved under solar simulation conditions. A maximum photoconversion efficiency of 0.12% for the BiVO₄/Graphene/TiO₂ nanocomposite photoanode was measured under irradiation, which was higher than those of BiVO₄/Graphene and TiO₂. The observed enhancement in PEC activity was due to higher absorption of light and surface area, role of high interface between the photoanode and electrolyte as well as a better charge carrier separation and transportation. The constructed BiVO₄/Graphene/TiO₂ nanocomposite can open a promising avenue for design and fabrication of novel Graphene-based nanocomposite device in hydrogen generation and other solar energy applications.

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References

- [1] A. Fujishima, K. Honda, Electrochemical photolysis of water at a semiconductor electrode, Nature 238 (1972) 37-38.

- [2] M. Yousefi, M. Amiri, R. Azimirad, A.Z. Moshfegh, Enhanced photoelectrochemical activity of Ce doped ZnO nanocomposite thin films under visible light, *J. Electroanal. Chem.* 661 (2011) 106-112.
- [3] M. Wang, J. Iocozia, L. Sun, C. Lin, Z. Lin, Inorganic-modified semiconductor TiO₂ nanotube arrays for photocatalysis, *Energy Environ. Sci.* 7 (2014) 2182-2202.
- [4] Z. Hu, J.C. Yu, T. Ming, J. Wang, A wide-spectrum-responsive TiO₂ photoanode for photoelectrochemical cells, *Appl. Catal. B: Environ.* 168–169 (2015) 483-489.
- [5] S.G. Kumar, L.G. Devi, Review on modified TiO₂ photocatalysis under UV/visible light: selected results and related mechanisms on interfacial charge carrier transfer dynamics, *J. Phys. Chem. A.* 115 (2011) 13211-13241.
- [6] M.M Momeni, Y. Ghayeb, Fabrication, characterization and photoelectrochemical behavior of Fe–TiO₂ nanotubes composite photoanodes for solar water splitting, *J. Electroanal. Chem.* 751 (2015) 43-48.
- [7] T. Lin, C. Yang, Z. Wang, H. Yin, X. Lu, F. Huang, J. Lin, X. Xie, M. Jiang, Effective nonmetal incorporation in black titania with enhanced solar energy utilization, *Energy Environ. Sci.* 7 (2014) 967-972.
- [8] S.Y. Chae, P. Sudhagar, A. Fujishima, Y.J. Hwang, O.-S. Joo, Improved photoelectrochemical water oxidation kinetics using a TiO₂ nanorod array photoanode decorated with graphene oxide in a neutral pH solution, *Phys. Chem. Chem. Phys.* 17 (2015) 7714-7719.
- [9] D. Jariwala, V.K. Sangwan, L.J. Lauhon, T.J. Marks, M.C. Hersam, Carbon nanomaterials for electronics, optoelectronics, photovoltaics and sensing, *Chem. Soc. Rev.* 42 (2013) 2824-2860.
- [10] B. Zhou, M. Schulz, H.Y. Lin, S.I. Shah, J. Qu, C.P. Huang, Photoelectrochemical generation of hydrogen over carbon-doped TiO₂ photoanode, *Appl. Catal. B: Environ.* 92 (2009) 41-49.

- [11] J.M. Fang-Xing Xiao, H.-Y. Wang, H. Yang, J. Chen, B. Liu, Electrochemical construction of hierarchically ordered CdSe-sensitized TiO₂ nanotube arrays: towards versatile photoelectrochemical water splitting and photoredox applications, *Nanoscale* 6 (2014) 6727-6737.
- [12] S. Hernández, V. Cauda, A. Chiodoni, S. Dallorto, A. Sacco, D. Hidalgo, E. Celasco, C.F. Pirri, Optimization of 1D ZnO@TiO₂ core-shell nanostructures for enhanced photoelectrochemical water splitting under solar light illumination, *ACS Appl. Mater. Interfaces* 6 (2014) 12153-12167.
- [13] G. Ai, R. Mo, Q. Chen, H. Xu, S. Yang, H. Li, J. Zhong, TiO₂/Bi₂S₃ core-shell nanowire arrays for photoelectrochemical hydrogen generation, *RSC Adv.* 5 (2015) 13544-13549.
- [14] M. Gholami, M. Qorbani, O. Moradlou, N. Naseri, A.Z. Moshfegh, Optimal Ag₂S nanoparticle incorporated TiO₂ nanotube array for visible water splitting, *RSC Adv.* 4 (2014) 7838-7844.
- [15] J. Bai, J. Li, Y. Liu, B. Zhou, W. Cai, A new glass substrate photoelectrocatalytic electrode for efficient visible-light hydrogen production: CdS sensitized TiO₂ nanotube arrays, *Appl. Catal. B: Environ* 95 (2010) 408-413.
- [16] P. Luan, M. Xie, X. Fu, Y. Qu, X. Sun, L. Jing, Improved photoactivity of TiO₂-Fe₂O₃ nanocomposites for visible-light water splitting after phosphate bridging and its mechanism, *Phys. Chem. Chem. Phys.* 17 (2015) 5043-5050.
- [17] S. Ho-Kimura, S.J.A. Moniz, A.D. Handoko, J. Tang, Enhanced photoelectrochemical water splitting by nanostructured BiVO₄-TiO₂ composite electrodes, *J. Mater. Chem. A* 2 (2014) 3948-3953.
- [18] M. Xie, X. Fu, L. Jing, P. Luan, Y. Feng, H. Fu, Long-lived visible-light-excited charge carriers of TiO₂/BiVO₄ nanocomposites and their unexpected photoactivity for water splitting, *Adv. Energy Mater.* 4 (2014) 1-6.

- [19] Q. Jia, K. Iwashina, A. Kudo, Facile fabrication of an efficient BiVO_4 thin film electrode for water splitting under visible light irradiation, *PNAS* 109 (2012) 11564-11569.
- [20] Y. Liang, J. Messinger, Improving BiVO_4 photoanodes for solar water splitting through surface passivation, *Phys. Chem. Chem. Phys.* 16 (2014) 12014-12020.
- [21] D.K. Zhong, S. Choi, D.R. Gamelin, Near-complete suppression of surface recombination in solar photoelectrolysis by “Co-Pi” catalyst-modified W:BiVO_4 , *J. Am. Chem. Soc.* 133 (2011) 18370-18377.
- [22] W. Luo, Z. Yang, Z. Li, J. Zhang, J. Liu, Z. Zhao, Z. Wang, S. Yan, T. Yu, Z. Zou, Solar hydrogen generation from seawater with a modified BiVO_4 photoanode, *Energy Environ. Sci.* 4 (2011) 4046-4051.
- [23] Y.H. Ng, A. Iwase, A. Kudo, R. Amal, Reducing graphene oxide on a visible-light BiVO_4 photocatalyst for an enhanced photoelectrochemical water splitting, *J. Phys. Chem. Lett.* 1 (2010) 2607-2612.
- [24] Y. Fua, X. Sun, X. Wang, BiVO_4 -graphene catalyst and its high photocatalytic performance under visible light irradiation, *Mater. Chem. Phys.* 131 (2011) 325-330.
- [25] H.S. Park, H.-W. Ha, R.S. Ruoff, A.J. Bard, On the improvement of photoelectrochemical performance and finite element analysis of reduced graphene oxide- BiVO_4 composite electrodes, *J. Electroanal. Chem.* 716 (2014) 8-15.
- [26] N. Naseri, P. Sangpour, A.Z. Moshfegh, Visible light active Au:TiO_2 nanocomposite photoanodes for water splitting: Sol-gel vs. sputtering, *Electrochim. Acta.* 56 (2011) 1150-1158.
- [27] W. S. Hummers, R. E. Offeman, Preparation of Graphitic Oxide, *J. Am. Chem. Soc.* 80 (1958) 1339-1339.
- [28] Y.H. Ng, A. Iwase, N.J. Bell, A. Kudo, R. Amal, Semiconductor/reduced graphene oxide nanocomposites derived from photocatalytic reactions, *Catal. Today* 164 (2011) 353-357.

- [29] N. Alenzi, W.-S. Liao, P.S. Cremer, V. Sanchez-Torres, T.K. Wood, C. Ehlig-Economides, Z. Cheng, Photoelectrochemical hydrogen production from water/methanol decomposition using Ag/TiO₂ nanocomposite thin films, *Int. J. Hydrogen Energy* 35 (2010) 11768-11775.
- [30] Q. Zhang, Y. He, X. Chen, D. Hu, L. Li, T. Yin, L. Ji, Structure and photocatalytic properties of TiO₂-Graphene Oxide intercalated composite, *Chin. Sci. Bull.* 56 (2011) 331-339.
- [31] J. Su, L. Guo, S. Yoriya, C.A. Grimes, Aqueous growth of pyramidal-shaped BiVO₄ nanowire arrays and structural characterization: application to photoelectrochemical water splitting, *Cryst. Growth Des.* 10 (2010) 856-861.
- [32] S. Yousefzadeh, M. Faraji, Y.T. Nien, A.Z. Moshfegh, CdS nanoparticle sensitized titanium dioxide decorated graphene for enhancing visible light induced photoanode, *Appl. Surf. Sci.* 320 (2014) 772-779.
- [33] Z. Sun, C. Li, S. Zhu, M. Cho, Z. Chen, K. Cho, Y. Liao, C. Yin, D. Zhang, Synthesis of BiVO₄@C core-shell structure on reduced Graphene oxide with enhanced visible-light photocatalytic activity, *ChemSusChem*. 8 (2015) 2719–2726.
- [34] A. Hagfeldt, H. Lindström, S. Södergren, S.-E. Lindquist, Photoelectrochemical studies of colloidal TiO₂ films: The effect of oxygen studied by photocurrent transients, *J. Electroanal. Chem.* 381 (1995) 39-46.
- [35] K. Gelderman, L. Lee, S.W. Donne, Flat-band potential of a semiconductor: using the Mott–Schottky equation, *J. Chem. Educ.* 84 (2007) 685.
- [36] X. Wang, J. Xie, C.M. Li, Architecting smart "umbrella" Bi₂S₃/rGO-modified TiO₂ nanorod array structures at the nanoscale for efficient photoelectrocatalysis under visible light, *J. Mater. Chem. A* 3 (2015) 1235-1242.
- [37] K. Sayama, A. Nomura, T. Arai, T. Sugita, R. Abe, M. Yanagida, T. Oi, Y. Iwasaki, Y. Abe, H. Sugihara, Photoelectrochemical decomposition of water into H₂ and

O₂ on porous BiVO₄ thin-film electrodes under visible light and significant effect of Ag ion treatment, *J. Phys. Chem. B* 110 (2006) 11352-11360.

[38] Y. Chen, J.C. Crittenden, S. Hackney, L. Sutter, D.W. Hand, Preparation of a novel TiO₂-based p-n junction nanotube photocatalyst, *Environ. Sci. Technol.* 39 (2005) 1201-1208.

[39] Y. Hou, F. Zuo, A. Dagg, P. Feng, Visible light-driven α -Fe₂O₃ Nanorod/Graphene/BiV_{1-x}Mo_xO₄ core/shell heterojunction array for efficient photoelectrochemical water splitting, *Nano Lett.* 12 (2012) 6464-6473.

[40] H. Yu, X. Quan, S. Chen, H. Zhao, TiO₂-multiwalled carbon nanotube heterojunction arrays and their charge separation capability, *J. Phys. Chem. C* 111 (2007) 12987-12991.

[41] S. Gawęda, R. Kowalik, P. Kwolek, W. Macyk, J. Mech, M. Oszejca, A. Podborska, K. Szaciłowski, Nanoscale digital devices based on the photoelectrochemical photocurrent switching effect: preparation, properties and applications, *Isr. J. Chem.* 51 (2011) 36-55.

[42] S. Yousefzadeh, A. Reyhani, N. Naseri, A.Z. Moshfegh, MWCNT/WO₃ nanocomposite photoanode for visible light induced water splitting, *J. Solid. State. Chem.* 204 (2013) 341-347.

[43] F. Wang, Y. Wang, X. Zhan, M. Safdar, J. Gong, J. He, Pt nanoparticle and CdS quantum dot assisted WO₃ nanowires grown on flexible carbon fibers for efficient oxygen production, *Cryst Eng Comm* 16 (2014) 1389-1394.

[44] J. Chao, Z. Wang, X. Xu, Q. Xiang, W. Song, G. Chen, J. Hu, D. Chen, Tin sulfide nanoribbons as high performance photoelectrochemical cells, flexible photodetectors and visible-light-driven photocatalysts, *RSC Adv.* 3 (2013) 2746-2753.

- [45] Y. Hu, D. Li, Y. Zheng, W. Chen, Y. He, Y. Shao, X. Fu, G. Xiao, BiVO₄/TiO₂ nanocrystalline heterostructure: A wide spectrum responsive photocatalyst towards the highly efficient decomposition of gaseous benzene, Appl. Catal. B: Environ. 104 (2011) 30-36.
- [46] G. Konstantatos, M. Badioli, L. Gaudreau, J. Osmond, M. Bernechea, F.P.G. de Arquer, F. Gatti, F.H.L. Koppens, Hybrid graphene-quantum dot phototransistors with ultrahigh gain, Nat. Nanotechnol. 7 (2012) 363-368.

Figure captions

Fig. 1. FTIR spectra of (a) graphene oxide (GO) and (b) BiVO₄/Graphene nanocomposite.

Fig. 2. SEM images of (a, b) pure TiO₂ and (c, d) BiVO₄/Graphene/TiO₂ nanocomposite thin films. The inset in image (a) is top view of bare FTO without any film on it.

Fig. 3. X-ray diffraction (XRD) pattern of (a) pure anatase TiO₂ thin film, (b) BiVO₄/Graphene and (c) BiVO₄/Graphene/TiO₂ nanocomposite thin films grown on the FTO substrate. Peaks labeled with “*”, “B” and “T” correspond to the FTO, monoclinic BiVO₄ and anatase TiO₂ phases, respectively.

Fig. 4. XPS high resolution spectrum of different core level: (a) Ti (2p) for TiO₂ thin film and (b) Bi (4f) and (c) V (2p) for the BiVO₄/Graphene/TiO₂ nanocomposite thin film.

Fig. 5. UV–vis diffuse reflectance spectra of (a) pure TiO₂, (b) BiVO₄/Graphene and (c) BiVO₄/Graphene/TiO₂ nanocomposite thin films.

Fig. 6. Mott–Schottky (MS) curves of (a) TiO₂, (b) BiVO₄/Graphene and (c) BiVO₄/Graphene/TiO₂ photoelectrode measured in 0.1 M K₂SO₄ at 1 kHz in the dark.

Fig. 7. (A) Linear sweep voltammetry (LSV) plots for (a) TiO₂, (b) BiVO₄/Graphene and (c) BiVO₄/Graphene/TiO₂ nanocomposite photoanodes in dark and (d) TiO₂, (e) BiVO₄/Graphene and (f) BiVO₄/Graphene/TiO₂ nanocomposite photoanode under

photoillumination (1000 W/m^2). (B) Band diagram configuration for the $\text{BiVO}_4/\text{Graphene}/\text{TiO}_2$ in equilibrium state and under applied bias potential.

Fig. 8. (A) Photocurrent density versus time at constant potential (0.8 V vs Ag/AgCl reference electrode) for (a) TiO_2 , (b) $\text{BiVO}_4/\text{Graphene}$ and (c) $\text{BiVO}_4/\text{Graphene}/\text{TiO}_2$ nanocomposite photoanodes under photoillumination (1000 W/m^2). (B) The photostability of $\text{BiVO}_4/\text{Graphene}/\text{TiO}_2$ photoelectrode tested at 0.8 V vs Ag/AgCl for 2 hours under illumination.

Fig. 9. Photoconversion efficiency of the (a) TiO_2 , (b) $\text{BiVO}_4/\text{Graphene}$ and (c) $\text{BiVO}_4/\text{Graphene}/\text{TiO}_2$ nanocomposite photoanodes calculated from LSV plots in Fig. 6.

Fig. 10. (A) Nyquist plots obtained in the dark and under illumination conditions for the $\text{BiVO}_4/\text{Graphene}/\text{TiO}_2$ photoelectrode. (B) Comparison of EIS Nyquist plots of (a) TiO_2 and (b) $\text{BiVO}_4/\text{Graphene}/\text{TiO}_2$ photoelectrodes under irradiation.

Fig. 11. Comparison of Bode phase plots of (a) TiO_2 , (b) $\text{BiVO}_4/\text{Graphene}$ and (c) $\text{BiVO}_4/\text{Graphene}/\text{TiO}_2$ photoanodes.

Table 1. Summary and comparison of PEC measured data for different photoelectrodes

Electrode	$N_D (\times 10^{20} \text{ m}^{-3})$	$V_{fb} \text{ (V)}$	photocurrent density	$\eta \text{ (%)}$	$\tau_e \text{ (ms)}$
			(A/m^2) at 0.8 V vs Ag/AgCl		
TiO ₂	232.18	-0.75	0.27	0.0001	5
BiVO ₄ /Graphene	120.80	-0.50	0.51	0.037	11
BiVO ₄ /Graphene/TiO ₂	536.03	-1.10	1.30	0.12	440

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

(B) **Equilibrium**
Space charge region

Forward bias
Space charge region

Figure 8

Figure 9

Figure 10

Figure 11