On the improvement of photoelectrochemical performance and finite element analysis of reduced graphene oxide–BiVO₄ composite electrodes

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ABSTRACT

Incorporation of thermally reduced graphene oxide (RG-O) into the metal oxide semiconductor BiVO₄ improves its photoactivity by about three times for sulfite oxidation. The enhancement of photoactivity is attributed to reduced electron–hole recombination of BiVO₄ using the RG-O as a conductive matrix in the composite photocatalyst. Photoelectrochemical behavior of the BiVO₄ and RG-O/BiVO₄ composite electrodes were simulated using finite element analysis to obtain the carrier mobility and its lifetime in the photoelectrodes. In contrast with sulfite oxidation, the improvement of photocurrent for water oxidation of RG-O/BiVO₄ composite electrode was not significant because of the slower kinetics for water oxidation. To address the kinetic limitations, platinum (Pt) as an effective electrocatalyst was photodeposited on the RG-O/BiVO₄ electrode. Addition of the Pt significantly improved water oxidation photocurrent of the Pt/RG-O/BiVO₄ electrode. RG-O/W–Mo-doped BiVO₄ composite electrodes were also prepared to investigate a further enhancement of photoactivity of W–Mo-doped BiVO₄. The behavior obtained from RG-O/W–Mo-BiVO₄ and RG-O/BiVO₄ electrodes provides a valuable insight into the role of RG-O as a conducting additive and the role of W and Mo as dopants into BiVO₄.

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1. Introduction

Metal oxide semiconductors, e.g., TiO₂, Fe₂O₃, WO₃ and BiVO₄, have been extensively studied as water oxidation photocatalysts for the possible solar photolysis of water [1]. Metal oxide semiconductors are chemically stable, cheap and abundant, and their semiconductor properties, such as the size of band-gap, the band-edge locations, and the carrier mobility, can be significantly modified by the addition of dopant, e.g., Si-doped Fe₂O₃ [2], N-doped WO₃ [3], and W-doped BiVO₄ [4,5]. However, significant electron–hole recombination, indicated by the short minority carrier-lifetime and short carrier-diffusion length of metal oxide semiconductors, remains a major barrier to achieving a high conversion efficiency of sunlight to chemical energy, i.e., for hydrogen production by water splitting [6–8]. Methods of increasing the carrier mobility, e.g., by doping or the addition of conductive or electron accepting materials into the metal oxide semiconductor have been recently attempted to address the rapid electron–hole recombination of the photocatalysts. For example, conductive TiSi₂ was incorporated into TiO₂ [9,10], WO₃ [11], and α-Fe₂O₃ [12] to improve the electron transport through the electrodes. Also, composite photocatalysts with carbon based conducting materials, such as carbon nanotube or reduced graphene oxide (RG-O), have also been suggested for TiO₂ [13–15] and BiVO₄ [16] to overcome the rapid recombination of excited electron–hole pairs; the addition of conductive materials into semiconductors increases the rate at which electrons are transported from the semiconductor/solution interface and hence the separation of electron–hole pairs. However, conductive materials can also act as traps, i.e., recombination centers for the electron–hole pairs [17].

The chemistry of graphite oxide (GO) and later graphene oxide (G-O) has been extensively studied for its properties and synthesis since the first report of GO in 1859 [18]. G-O is intrinsically an insulator, but it is used as a precursor for graphene-like material, i.e., reduced graphene oxide (RG-O). G-O is a possible source for the mass production of RG-O, and chemical derivatives of G-O and RG-O are promising materials for such applications as polymer nanocomposites, ultracapacitors, rechargeable batteries, sensors, and thin films [19–23]. Among such applications, RG-O (or G-O) composites with semiconductor photocatalysts have been reported to enhance photoactivity with the RG-O as a conductive additive to improve the bulk conductivity and facilitate electron–hole separations in photocatalysts as described above [14–16]. Here, we report the facile preparation and photoelectrochemical (PEC) behavior of RG-O/metal oxide composite photocatalysts based on BiVO₄ and W–Mo-doped BiVO₄. We also report a simulation (finite element analysis) of the PEC properties [24–26]. BiVO₄, with a band gap...
of 2.4 eV, is a visible light water oxidation photocatalyst. Moreover, W-doped BiVO₄ or W–Mo-doped BiVO₄ produces a photocurrent for water oxidation that is more than 10 times higher than undoped BiVO₄ [4,5]. BiVO₄ or W–Mo-doped BiVO₄ were employed in a simple two-step process to fabricate composite electrodes in which G-O is exfoliated and homogeneously dispersed ultrasonically in ethylene glycol solution and then thermally reduced during metal oxide formation by thermal annealing of drop-cast electrodes in air. In addition, in some experiments a Pt electrocatalyst was photodeposited onto the composite electrodes to decrease kinetic limitations of the water oxidation reaction on the composite electrodes; the effect of reduced electron–hole recombination by incorporation of RG-O clearly results in an increased photocurrent after the surface treatment.

2. Experimental

2.1. Chemicals

Bi(NO₃)₃·5H₂O (99.999%) and (NH₄)₂C₂H₃O₂·xH₂O·yH₂O (99.99%) were obtained from Strem Chemicals (Newburyport, MA). H₂SO₄ (98%), HCl (Technical grade), KMnO₄ (99.6%), Na₂HPO₄ (99.9%), NaH₂PO₄ (99.5%), MeOH (99.8 %), and ethylene glycol were purchased from Fisher Scientific (Pittsburg, PA). Na₂(SO₄)₅·10H₂O (99.0%) were purchased from Sigma–Aldrich (St. Louis, MO). VCl₃ (99%, Alfa-Aesar, Ward Hill, MA) and Na₂SO₃ (99.6%, Mallinckrodt Baker, Phillipsburg, NJ) were used as received. Fluorine-doped tin oxide (FTO, TECE 15, Pilkington, Toledo, OH) was used as a substrate of the electrodes. Deionized (DI) Milli-Q water was used as the solvent in electrochemical experiments.

2.2. Graphene oxide (G-O) preparation

Graphite oxide (GO) was synthesized by a modified Hummer’s method [27]. Briefly, 100 mg of natural graphite (SP-1, Bay Carbon, Bay City, MI) was mixed with 50 mL concentrated H₂SO₄ in a flask, followed by the addition of 500 mg of KMnO₄. After addition of KMnO₄, the mixture was heated at 35 °C and stirred for 2 h. Excess DI water (50 mL) was added to the flask (placed in an ice bath), and then more water (100 mL) was added followed by stirring in the ice bath for 1 h. H₂O₂ (30 wt% in water) was then added to the mixture until no further gas evolution was observed, followed by stirring for 2 h. The final suspension was filtered and washed with HCl (10% in water) and dried in air. Suspensions of G-O platelets were prepared by sonication of GO in DI water or ethylene glycol for 1 h.

2.3. Electrodes

Thin film electrodes of the BiVO₄ (or BiVO₄ with 2 atomic% (at%) W and 6 at% Mo, ‘W–Mo-doped BiVO₄’) and RG-O/BiVO₄ (or RG-O/ W–Mo-doped BiVO₄) composites were prepared on an FTO substrate by drop casting the precursor solution. The metal oxide films were cast using 100 μL of a precursor solution with a total concentration of 20 mM in ethylene glycol. For RG-O/metal oxide composite electrodes, the targeted amount of GO powder was suspended in the metal oxide precursor solution and the solution was ultrasonicated for 1 h before drop casting. Then, the film was annealed in air for 3 h at temperatures from 400 °C to 550 °C, ramped from room temperature at a rate of 1 °C per min.

Photodeposition of Pt on photoelectrodes was conducted in aqueous solution of 10 mM H₃PO₄ and 0.2 M MeOH. BiVO₄ (and W–Mo-doped BiVO₄) and its RG-O composite electrodes on FTO were placed in the Pt precursor solution in a borosilicate glass cell. UV–visible irradiation was then performed at full output with a Xenon lamp (XBO 150 W, Osram, Munich, Germany) for 30 min, and a beam intensity was about 200 mW cm⁻². During the irradiation, photoreduction of Pt occurred on the thin film electrodes while MeOH was oxidized by the photoexcited electron and hole [28].

2.4. Instruments

A CH Instruments Model 630D electrochemical analyzer (Austin, TX) was used as a potentiostat for the experiments with the thin film electrodes. Illumination was with a Xenon lamp (XBO 150 W, Osram) at full output for UV–visible irradiation or using a 420 nm cut-off filter (WBF-3, Oriel, Darmstadt, Germany) for visible irradiation. A Pt gauze counter electrode and Ag/AgCl reference electrode in a saturated KCl solution were used to complete the three-electrode configuration. However, all potentials reported here are with respect to the normal hydrogen electrode (NHE). X-ray diffraction (XRD) measurements were performed using a Bruker–Nionius D8 advanced powder diffractometer (Madison, WI) operated at 40 kV and 40 mA with Cu Kα radiation (λ = 1.54 Å). Grazing incidence XRD (GIXRD) with incidence angle of 1° in detector scan mode was performed to obtain diffractograms from the thin film electrodes on FTO. The scan rate was 12° per minute in 0.02° increments of 2θ from 15° to 80°. Scanning electron microscopy (SEM) images were obtained with a LEO 1530 SEM at a working voltage of 10 kV and working distance of 5 mm. Thermogravimetric analysis (TGA) was conducted from room temperature to 800 °C with a Perkin–Elmer TGA 4000 with a ramp rate of 1 °C per min under dry air flow. X-ray photoelectron spectroscopy (XPS) was performed on a Kratos Axis Ultra DLD instrument (Manchester, UK) with a monochromatic Al Kα X-ray source with 180° hemispherical electron energy analyzer.

2.5. Simulations

Finite element analysis was performed using COMSOL Multiphysics v.3.5 software (Burlington, MA) to study the photoanode properties. The steady state Poisson equation (Eq. (1)) and Nernst–Planck equations (Eqs. (3) and (4)) were used to calculate the potential distribution and the electron–hole transport in the semiconductor electrodes. The physics and reactions used in the simulations are schematically summarized in Fig. 1.

\[
d(-\varepsilon_0 e \psi / dx) / dx = \rho
\]

where \(\varepsilon_0\) is the vacuum permittivity, \(\varepsilon_r\) is the relative permittivity, \(\psi\) is the potential (of Fermi level vs vacuum level), and \(\rho\) is the excess charge density. The simulation domain and constants were set as shown in Supporting information Fig. 51; \(\rho\) was defined as

\[
\rho = (C_p + C_n - N_s) q
\]

where \(q\) is the electron charge, \(N_s\) is the fixed electron doping density at thermal equilibrium, and \(C_p\) and \(C_n\) is the local carrier density of electrons and holes, respectively. \(C_p\) and \(C_n\) were determined using the Nernst–Planck equations as shown below.

\[
d(-D_p \partial \psi / \partial x + \mu_p C_p q / dx) / dx = -R + G \quad \text{for} \quad C_p
\]

\[
d(-D_n \partial \psi / \partial x + \mu_n C_n q / dx) / dx = -R + G \quad \text{for} \quad C_n
\]

where \(D_p\) and \(D_n\) are the diffusion coefficients of electron and hole, and \(\mu_n\) and \(\mu_p\) are the mobilities for electrons and holes, respectively. The diffusion coefficient and mobility are related by the Einstein relation.

\[
D_{np} = \mu_{np} k T / q
\]

where \(k\) is the Boltzmann constant and \(T\) is the temperature. \(R\) is the electron–hole recombination rate in the bulk semiconductor and
the trap-assisted Shockley–Read–Hall recombination equation was used in the simulations [29].
\[
R = \left( C_n C_p - n_i^2 \right) / \left( \tau_n (C_n + n_i) + \tau_p (C_p + n_i) \right) \tag{6}
\]
where \( n_i \) is the intrinsic doping density and \( \tau_n \) and \( \tau_p \) is the recombination lifetime of electrons and holes. Also, the surface recombination of electrons and holes was considered as
\[
dC_n / dt = dC_p / dt = -k_{\text{SurRec}} C_n C_p \tag{7}
\]
where \( k_{\text{SurRec}} \) is the rate constant of the surface trap recombination. \( G \) in Eqs. (3) and (4) is a generation rate of the charge carriers by the absorbed photon energy.
\[
G = I_0 \alpha \exp(-\alpha x) \tag{8}
\]
where \( \alpha \) is the absorption coefficient of the photoanode, and \( I_0 \) is the incidence rate of photon. \( x \) is the penetration depth of the photon into the electrode. Initial conditions for \( \psi \), \( C_n \), and \( C_p \) were
\[
\psi_0 = kT / q \left( \ln(C_{n0} / n_i) - \chi_{\text{semi}} - 0.5 E_g \right) \tag{9}
\]
\[
C_{n0} = n_i / 2 + (n_i^2 / 4 + n_i^2)^{0.5} \tag{10}
\]
\[
C_{p0} = n_i^2 / C_{n0} \tag{11}
\]
where \( \chi_{\text{semi}} \) is the electron affinity of semiconductor electrode, and \( E_g \) is the band gap energy of the semiconductor. The density of available states \( (n_i) \) was set to obtain the intrinsic doping density \( (n_i) \) of photoelectrodes (Eq. (12)). The donor density \( (n_d) \) of BiVO_4 was determined from the previously reported experimental values [5].
\[
n_i = n_i \exp(-qE_g / 2kT) \tag{12}
\]
Boundary conditions for \( \psi \), \( C_n \), and \( C_p \) at the solution/electrode interface and at the electrode/metal contact were
\[
\psi_{\text{solution}} = \psi_0 - E_{\text{app}} \tag{13}
\]
\[
dC_n_{\text{solution}} / dx = -k_B C_a C_b - k_{\text{SurRec}} C_n C_p \tag{14}
\]
\[
dC_p_{\text{solution}} / dx = -k_B C_a C_b - k_{\text{SurRec}} C_n C_p \tag{15}
\]
\[
\psi_{\text{metal}} = \psi_0 \tag{16}
\]
\[
C_{n_{\text{metal}}} = C_{n0} \tag{17}
\]
\[
C_{p_{\text{metal}}} = C_{p0} \tag{18}
\]
where \( E_{\text{app}} \) is the applied potential, and \( k_l \) and \( k_b \) are the hole and electron transfer rate constants of reactions (19) and (20). \( C_a \) and \( C_b \) are the molecular concentrations of A and B in the solution.
\[
A + h^+ \rightarrow C \quad (k_l) \tag{19}
\]
\[
B + e^- \rightarrow D \quad (k_b) \tag{20}
\]
The chemical species, i.e., A and B, were treated as the sulfite and the dissolved oxygen in the solution. \( C_a \) and \( C_b \) were assumed as a constant and the reaction rates of (19) and (20) were limited by the electron and hole fluxes at the electrode surface. Then, linear sweep voltammograms (LSVs) of the photoelectrode were simulated as the \( E_{\text{app}} \) was changed from 0 to 1 V. The photocurrent \( (i) \) was calculated from the electron and hole flux at the electrode/metal interface.
\[
i = q (dC_p / dx - dC_n / dx) \tag{21}
\]

3. Results and discussion

3.1. Experiments with RG-O/BiVO_4

The photoactivity of BiVO_4 and RG-O/BiVO_4 composite electrodes were compared under the same conditions for sulfite oxidation as shown in Fig. 2a. For the RG-O/BiVO_4 electrode, 5 wt% of G-O was added to the precursor solution of BiVO_4 during electrode preparation. The optimum concentration of RG-O in the composite electrode was determined by varying the amount of G-O in the precursor solution and the results are shown in Fig. 3a. 5 wt% G-O in the precursor solution corresponds to 14 \( \mu \)g cm\(^{-2} \) of G-O in the prepared BiVO_4 electrode. As shown in Fig. 3, the photoactivity of the resulting RG-O/BiVO_4 was greatly affected by small changes in the G-O concentration in the precursor solution. Note that the weight ratio of G-O is based on the amount of G-O prepared in the precursor solution of the metal salts, and is the ratio of G-O to the total amount of G-O and resulting metal oxide from the metal salts. The amount of RG-O in the resulting electrode is reduced after the thermal annealing process used for electrode fabrication (see TGA results in Supporting information Fig. S2). However, the RG-O/BiVO_4 electrode prepared from 5 wt% G-O precursor solution showed several times higher photocurrent for sulfite oxidation both under UV-visible and visible light irradiation compared to that of BiVO_4 (see Supporting information Fig. S3 for response to visible light irradiation). As shown below in the finite element analysis, thermally reduced G-O facilitates the transfer of photoex-
Cited electrons to the back contact, conductive FTO, so the incorporation of RG-O into the photocatalyst results in an improved separation of the excited electron–hole pairs \[15\].

As known from earlier studies \[5\], the annealing in air oxidatively converts the metal salts to BiVO\(_4\). However, in this case it also leads to reduction of G-O with either the ethylene glycol or C acting as the reducing agents. The annealing temperature used for the preparation of RG-O/BiVO\(_4\) composite electrodes was also varied (from 400 °C to 550 °C) to observe the effect on the photoactivity of RG-O/BiVO\(_4\) for sulfite oxidation (Fig. 3b). The results show that RG-O/BiVO\(_4\) or BiVO\(_4\) fabricated at 400 °C has a far lower photoactivity, i.e., three times lower photocurrent at 0.5 V compared to those annealed at temperatures above 450 °C. The lower photocurrent of the composite electrodes prepared at 400 °C originated from the low photoactivity of tetragonal scheelite-like BiVO\(_4\). The XRD pattern, shown in Supporting information Fig. S4, indicates that tetragonal scheelite-like BiVO\(_4\) is formed in RG-O/BiVO\(_4\) for the annealing temperature of 400 °C, but the peaks from this tetragonal phase are not observed in RG-O/BiVO\(_4\) at annealing temperatures above 450 °C as shown in Fig. 4. Monoclinic scheelite-like BiVO\(_4\) with a smaller band gap of 2.4 eV, is much more photoactive than the tetragonal scheelite-like BiVO\(_4\) (band gap of 2.9 eV) \[30\]. In addition, TGA analysis in Supporting information

![Fig. 2. LSV of (a) BiVO\(_4\) (yellow) and RG-O/BiVO\(_4\) (blue) and (b) W–Mo-doped BiVO\(_4\) (blue) and RG-O/W–Mo-doped BiVO\(_4\) (yellow) for sulfite oxidation in 0.1 M Na\(_2\)SO\(_3\) and 0.1 M Na\(_2\)SO\(_4\) aqueous solution (pH 7, 0.2 M sodium phosphate buffered). Scan rate was 20 mV s\(^{-1}\) and photocurrent was measured under chopped UV–visible irradiation. Beam intensity was about 120 mW cm\(^{-2}\). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

![Fig. 3. Photocurrent dependence of RG-O/BiVO\(_4\) composite electrode on the weight ratio of G-O to BiVO\(_4\) for sulfite oxidation (a) and on the annealing temperature on photocurrent of RG-O/BiVO\(_4\) composite electrode for sulfite oxidation (b). RG-O/BiVO\(_4\) composite electrodes were drop-casted on FTO and annealed at 500 °C for 3 h in air in (a). The amount of G-O in the precursor solution was 5 wt% of the resulting BiVO\(_4\) in (b) and RG-O/BiVO\(_4\) composite electrodes were annealed at various temperatures for 3 h in air. The photocurrent was measured at 0.5 V (vs. NHE) in 0.1 M Na\(_2\)SO\(_3\) and 0.1 M Na\(_2\)SO\(_4\) aqueous solution under UV–visible irradiation. Note that the weight ratio of G-O is based on the G-O prepared in the precursor solution of metal oxide, and the weight ratio of RG-O in the resulting electrode is likely changed during the thermal process used for fabricating the electrodes.)

![Fig. 4. XRD patterns of RG-O/BiVO\(_4\) (yellow) and RG-O/W–Mo-doped BiVO\(_4\) (blue). The reference patterns of the monoclinic scheelite-like BiVO\(_4\) (PDF#14-0688, bottom line) and patterns from FTO substrate (*) are also indicated. Dotted lines indicate the characteristic shift of peaks from undoped BiVO\(_4\) to the W–Mo-doped BiVO\(_4\). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)]
Fig. 5. XPS spectra for C1s of RG-O/BiVO4 composite electrodes. The RG-O/BiVO4 was prepared from 5 wt% G-O precursor solution on the FTO substrate. The drop-cast film was annealed at 500 °C for 3 h in air. Note that peaks are shifted (+1 eV) to compensate the sample charging effect in the XPS.

Fig. S2 shows that G-O is thermally reduced at temperatures of about 150 °C and both 400 °C and 450 °C are well above the temperature required for thermal reduction of G-O. XPS spectra for C1s of RG-O/BiVO4 shown in Fig. 5 indicate that the G-O in the precursor solution is being reduced at the elevated temperatures (see Supporting information Fig. S5 for survey scan) [31]. However, further work is needed to study the chemistry of thermal reduction of G-O in air atmosphere and chemical environments used here, i.e., ethylene glycol. In summary, the photoactivity of RG-O/BiVO4 composite is greatly affected by the properties of the host BiVO4. Also, XRD measurements show that RG-O does not disrupt the formation of the BiVO4 crystal structure for the simple drop-casting method. With properly prepared BiVO4, the increased photoactivity of the RG-O composite electrodes indicates that RG-O is an excellent additive for the drop-cast BiVO4 to improve the photocatalytic activity.

3.2. Experiments with RG-O/W–Mo-doped BiVO4

RG-O composite electrodes with W–Mo-doped BiVO4 were also prepared. W–Mo-doped BiVO4 is a photocatalyst with several times greater photoactivity for water oxidation than undoped BiVO4 [5]. Enhanced separation of excited electron–hole pairs has been suggested as a reason for the improved photoactivity of W–Mo-doped BiVO4. Briefly, the modified electronic structure of BiVO4 by doping W and Mo with a small shift of the flat band potential increases the electron (or hole) transfer in BiVO4 [5]. To determine if a further improvement of photoactivity of the W–Mo-doped BiVO4 could be realized, an RG-O composite electrode of W–Mo-doped BiVO4 (RG-O/W–Mo-doped BiVO4) was prepared from a solution of 5 wt% G-O and metal salts in ethylene glycol. Again note, RG-O does not affect the crystal formation of drop-cast W–Mo-doped BiVO4 as shown by the XRD (Fig. 4). In other words, XRD patterns of RG-O/W–Mo-doped BiVO4 show the peaks from monoclinic scheelite-like BiVO4 along with characteristic peak shifts caused by the tetragonal deformation of the monoclinic scheelite-like BiVO4 by the doping with W and Mo at 35, 47, and 59° in Fig. 4. However, the observed photoactivity of RG-O/W–Mo-doped BiVO4 was smaller than that of W/Mo-doped BiVO4 without RG-O (Fig. 2b). Photocurrent for sulfite oxidation measured at 0.5 V decreased about 40% from 1.7 mA cm−2 to 1.0 mA cm−2 by the addition of WG–O to W–Mo-doped BiVO4 under UV–visible irradiation (see Supporting information Fig. S3 for visible response). The effects of the annealing temperature on the photoactivity were also studied for the RG-O/W–Mo-doped BiVO4 at temperatures ranging from 450 °C to 550 °C (Supporting information Fig. S6) and RG-O/W–Mo-doped BiVO4 shows lower photocurrent than W–Mo-doped BiVO4 at all temperatures. The decrease of photoactivity of RG-O/W–Mo-doped BiVO4 may imply that RG-O generates a recombination center or electron trap in W–Mo-doped BiVO4. Also, the results indicate that the increased photocurrent of RG-O/BiVO4 from BiVO4 is not due to the increased electrode area or morphological changes of the photoelectrode; if the enhanced photoactivity of RG-O/BiVO4 was due to the increased surface area of BiVO4 as shown in the SEM images (Supporting information Fig. S7), a similar effect would also be seen for RG-O/W–Mo-doped BiVO4.

It is established in sulfite oxidation that the incorporation of RG-O into BiVO4 improves the photoactivity of undoped BiVO4 as described above. There has also been a report of the improved PEC water oxidation on RG-O/BiVO4 composite electrodes [16]. However, we found that the photocurrent measured for water oxidation showed that the increase of photocurrent by RG-O addition to BiVO4 is less marked for water oxidation than that for sulfite oxidation (Fig. 6a). The enhancement of photocurrent for water oxidation by RG-O addition to BiVO4 was only about 30% at the potential of 0.6 V from 30 μA cm−2 to 40 μA cm−2. Although there is a report of very large increases in photocurrent by addition of RG-O to BiVO4 from a few μA cm−2 to tens of μA cm−2 for water oxidation [16], we have not seen such a large effect. The smaller improvement of photocurrent with RG-O addition to BiVO4 can be caused

Fig. 6. LSVs of (a) BiVO4 (blue) and RG-O/BiVO4 (yellow) and (b) Pt/BiVO4 (black) and Pt/RC-O/BiVO4 (blue under visible and yellow under UV–visible irradiation) with photodeposited Pt electrocatalyst for water oxidation in 0.1 M Na2SO4 aqueous solution (pH 7, 0.2 M sodium phosphate buffered). Scan rate was 20 mV s−1. Photocurrent was measured under chopped UV–visible irradiation. Beam intensity was about 120 mW cm−2. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)
by the slower kinetics of inner-sphere reactions of water oxidation compared with the fast and irreversible sulfite oxidation. In other words, slow charge transfer at the surface from the photocatalyst to the adsorbate is the rate-determining step of photo-induced water oxidation. Improvement in bulk carrier mobility does not help in the effective separation of electron–hole pairs of RG-O/BiVO₄ for water oxidation; yet is obvious for the fast sulfite oxidation. In addition, for W–Mo-doped BiVO₄ the negative effect of RG-O on the photoactivity of W–Mo-doped BiVO₄ was also confirmed in water oxidation (not shown here).

3.3. Experiments with Pt Electro catalyst on RG-O/BiVO₄

To increase the kinetics of water oxidation on BiVO₄ and RG-O/BiVO₄, a Pt electrocatalyst was photodeposited onto the electrodes [32]. The results in Fig. 6b shows that for water oxidation the photooxidation current of RG-O/BiVO₄ increased about five times by the addition of Pt catalyst from 40 µA cm⁻² to 200 µA cm⁻² at 0.6 V. In contrast to RG-O/BiVO₄, BiVO₄ without RG-O exhibited no improvement from the catalyst. Pt/BiVO₄ actually showed slightly lower currents than the film without the electrocatalyst. This suggests that BiVO₄ without G-O still suffers from severe electron–hole recombination that limits the overall rate of the reactions. However, it is also possible that the Pt electrocatalysts were not properly photodeposited on BiVO₄ without G-O as the BiVO₄ shows poorer photoactivity than RG-O/BiVO₄ under the given experimental conditions.

3.4. Digital simulations

Finite element analysis was performed to study the effects of addition of RG-O to BiVO₄. Experimental results shown in Fig. 2 for sulfite oxidation of BiVO₄ were used to fit the simulation parameters, i.e., the hole and electron transfer rate constants (k_f and k_b in Eqs. (14) and (15)), the surface recombination rate constants (k_{SurRec}), the electron and hole mobility (ν_n and ν_p), and the electron and hole recombination lifetimes (τ_n and τ_p) of BiVO₄. The simulated LSVs of BiVO₄, R-GO/BiVO₄ and W–Mo-doped BiVO₄ electrodes are shown in Fig. 7 with the experimental results. The fitting parameters obtained from simulations are summarized in Tables 1 and 2. The parameters were assigned for the model used and the values are largely determined by the specific calculations in this study. Thus, experiments that are independent of the PEC ones that can provide accurate parameters, such as mobility, are still required to ensure a unique set of properties in the given model. To show the sensitivity of fitting parameters in the model used, simulated LSVs for BiVO₄ are shown with varied values for four different parameters in Supporting information Fig. S8. In the calculations for the BiVO₄, carrier mobility and lifetime affected the photocurrent densities over wide potential ranges where the rate constants for surface recombination reaction (7) and electro-

![Fig. 7. Comparison of simulated LSVs (yellow solid) to experimental results (blue dash) of (a) BiVO₄, (b) RG-O/BiVO₄ and (c) W–Mo-doped BiVO₄. The experimental results were taken from Fig. 2 for sulfite oxidation under UV–visible irradiation. Scan rate was 20 mV s⁻¹. Parameters used for simulation fitting were summarized in Table 1 and Supporting information Table S1. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)](image-url)
The electron and hole diffusion length of W–Mo- and W–Mo–/C2 electrodes are similar to that reported for electrodes. As the recombination rate decreases, the net flux of minority carrier at the electrode surface in- creases, the net flux of minority carrier at the electrode surface increases from 1 \times 10^{15} \text{cm}^{-2} \text{s}^{-1} (BiVO}_4 to 3 \times 10^{16} (R-GO/BiVO}_4 and 9 \times 10^{15} \text{cm}^{-2} \text{s}^{-1} (W/Mo-doped BiVO}_4 as shown in Fig. 8b. The increased minority carrier flux and reduced recombination rates improves the photoactivity of the RG-O/BiVO}_4 and W–Mo- doped BiVO}_4.

### Table 1

Simulation input parameters for BiVO}_4, R-GO/BiVO}_4, and W–Mo–BiVO}_4 electrodes shown in Fig. 7. (H.S. Park, K.E. Kweon, H. Ye, E. Paek, G.S. Hwang, A.J. Bard, J. Phys. Chem. C, 115 (2011) 17870–17879.)

<table>
<thead>
<tr>
<th>Parameter Value</th>
<th>Units</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \mu_n ) 12</td>
<td>( \text{cm}^2 \text{V}^{-1} \text{s}^{-1} )</td>
<td>Electron mobility</td>
</tr>
<tr>
<td>( \mu_p ) 2</td>
<td>( \text{cm}^2 \text{V}^{-1} \text{s}^{-1} )</td>
<td>Hole mobility</td>
</tr>
<tr>
<td>( \tau_n ) 0.25</td>
<td>( \text{ps} )</td>
<td>Electron lifetime</td>
</tr>
<tr>
<td>( \tau_p ) 0.25</td>
<td>( \text{ps} )</td>
<td>Hole lifetime</td>
</tr>
<tr>
<td>( n_0^+ ) ( 4 \times 10^{19} )</td>
<td>( \text{cm}^{-3} )</td>
<td>Donor doping density</td>
</tr>
<tr>
<td>( k_f ) ( 8 \times 10^{-17} )</td>
<td>( \text{cm}^{-3} \text{s}^{-1} )</td>
<td>Rate constant of reaction (19)</td>
</tr>
<tr>
<td>( k_r ) ( 4 \times 10^{-26} )</td>
<td>( \text{cm}^{-3} \text{s}^{-1} )</td>
<td>Rate constant of reaction (20)</td>
</tr>
<tr>
<td>KeffRec ( 1 \times 10^{-4} )</td>
<td>( \text{cm}^{-3} \text{s}^{-1} )</td>
<td>Rate constant of reaction (7)</td>
</tr>
<tr>
<td>( E_{\text{FlatBand}} ) ( -0.23 )</td>
<td>( \text{V} )</td>
<td>Flat band potential vs NHE at pH 7</td>
</tr>
</tbody>
</table>

### Table 2

Values calculated from input parameters shown in Table 1.

<table>
<thead>
<tr>
<th>Parameter Value</th>
<th>Units</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>( D_n ) ( 3.1 \times 10^{-2} )</td>
<td>( \text{cm}^2 \text{s}^{-1} )</td>
<td>Electron diffusion coefficient</td>
</tr>
<tr>
<td>( D_p ) ( 5.2 \times 10^{-2} )</td>
<td>( \text{cm}^2 \text{s}^{-1} )</td>
<td>Hole diffusion coefficient</td>
</tr>
<tr>
<td>( L_n ) 2.8</td>
<td>nm</td>
<td>Electron diffusion length</td>
</tr>
<tr>
<td>( L_p ) 1.1</td>
<td>nm</td>
<td>Hole diffusion length</td>
</tr>
</tbody>
</table>

The chemical reaction (19) showed limited effects near the onset potentials. However, the values given are still useful as relative measures of the properties of the systems investigated here. Thus the electron and hole diffusion lengths \( \left( L_{n/p} \right) \) calculated from its diffusion coefficient and recombination lifetime was 2.8 and 1.1 nm for BiVO}_4, respectively.

\[
L_{n/p} = \left( \frac{D_{n/p}}{\tau_{n/p}} \right)^{0.5}
\]

The recombination lifetime (~1 ps) and diffusion length (~2 nm) of BiVO}_4 are similar to that reported for \( \alpha-\text{Fe}_2\text{O}_3 \) which results in poor photoactivity [33]. However, as the RG-O was added to BiVO}_4 it provided a better channel for electron transport that increased the electron and hole mobility and the diffusion length. The electron and hole diffusion length increased about three times from 2.8 and 1.1 nm to 7.3 and 3.5 nm with the addition of RG-O to BiVO}_4 (Table 2). The electron and hole diffusion length of W–Mo-doped BiVO}_4 was even longer than RG-O/BiVO}_4 as expected from the measured photocurrent in Fig. 2 (16 and 9.3 nm). However, the obtained electron/hole recombination lifetime of photoelectrodes is extremely short, ~0.1 to 0.3 ps. For such an extremely short lifetime, the electrodes prepared by drop casting have many grain boundaries (SEM in Supporting information Fig. S7) that can introduce carrier traps and shorten the electron/hole recombination lifetime. The electron and hole diffusion lengths of BiVO}_4, RG-O/BiVO}_4, and W–Mo-doped BiVO}_4 are still much smaller than, for example, that of TiO}_2 (~10 \mu\text{m}) and have low fill factors in the current–potential behavior compared with the TiO}_2 [34]. However, the digital simulations show that improved electron and hole mobility and lifetime by addition of RG-O or W/Mo into BiVO}_4 results in less electron/hole recombination in the bulk semiconductor (Fig. 8a). The peak trap recombination rate of BiVO}_4 electrode at 0.6 V (vs NHE) is 15 \times 10^{20} \text{cm}^{-3} \text{s}^{-1}, and it decreases to 14 \times 10^{20} \text{cm}^{-3} \text{s}^{-1} and 12 \times 10^{20} \text{cm}^{-3} \text{s}^{-1} in the RG-O/BiVO}_4 and W–Mo-doped BiVO}_4 electrodes. As the recombination rate decreases, the net flux of minority carrier at the electrode surface increases from 1 \times 10^{15} \text{cm}^{-2} \text{s}^{-1} (BiVO}_4 to 3 \times 10^{16} (R-GO/BiVO}_4 and 9 \times 10^{15} \text{cm}^{-2} \text{s}^{-1} (W/Mo-doped BiVO}_4 as shown in Fig. 8b. The increased minority carrier flux and reduced recombination rates improves the photoactivity of the RG-O/BiVO}_4 and W–Mo- doped BiVO}_4.

**Fig. 8.** (a) Recombination rate of electron–hole pairs and (b) net hole flux in BiVO}_4 (black dash-dot), RG-O/BiVO}_4 (yellow dash), and W–Mo-doped BiVO}_4 (blue solid) electrodes from the calculation shown in Fig. 7. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)
In summary, RG-O/BiVO₄ exhibited significantly improved photoactivity compared to BiVO₄ by the addition of RG-O. The results indicate that RG-O efficiently facilitates the electron–hole separation in BiVO₄ or reduced electron–hole recombination in the bulk electrodes. Moreover, metal doping of W and Mo into BiVO₄ shows a positive effect on the photoactivity of BiVO₄. The quantitative semiconductor properties were estimated using finite element analysis. In addition, an electrocatalyst, Pt, is required to improve the kinetics of water oxidation to realize the effect of reduced electron–hole recombination of the RG-O/BiVO₄ composite photocatalyst.

4. Conclusions

The photoactivity of the photocatalyst, BiVO₄, for sulfite oxidation was improved by about 3 times by the addition of RG-O. Presumably RG-O as a conductive channel of electrons reduces the electron–hole recombination rate, which is the main factor limiting high photoactivity of metal oxide photocatalysts. The improved carrier diffusion length, mobility, and reduced recombination rate by the addition of RG-O and W and Mo dopants into BiVO₄ were studied by digital simulations. As a result of the addition of RG-O and metal dopants, the electron and hole diffusion length increased from 2.8 and 1.1 nm (BiVO₄) to 7.3 and 3.5 nm (RG-O/BiVO₄) and 16 and 9.3 nm (W/Mo-doped BiVO₄). However, improved electron–hole separation was not significant for water oxidation on RG-O/BiVO₄ probably because of the kinetic limitations of the inner-sphere water oxidation surface reaction. Pt electrocatalyst was thus photodeposited onto RG-O/BiVO₄ to decrease the kinetic limitations. The resulting Pt/RG-O/BiVO₄ electrode showed several times higher photocurrent for water oxidation than Pt/BiVO₄ or BiVO₄.

Acknowledgments

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version at http://dx.doi.org/10.1016/j.jelechem.2013.08.036.

References