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Facile Synthesis of Bismuth Oxide/Bismuth Vanadate Heterostructures for Efficient Photoelectrochemical Cells

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Herein, we report a facile approach to synthesize the Bi$_2$O$_3$/BiVO$_4$ heterostructures for photoelectrochemical (PEC) cells. Due to the fast separation of the electron-hole pairs as a result of the p-n junction, the Bi$_2$O$_3$/BiVO$_4$ heterostructures achieved a remarkable photocurrent of 2.58 mA cm$^{-2}$ at 1.2 V vs. Ag/AgCl, which is about 5 times than the pristine BiVO$_4$.

Due to ever-growing environmental concerns and increasing energy demands, hydrogen is considered as a key energy of the future because of its clean, renewable, carbon-free, and high energy density properties. Inspired by natural photosynthesis, artificial photoelectrochemical (PEC) water splitting is a promising pathway to produce economically hydrogen. The efficiency of PEC water splitting is largely determined by the properties of the photoanode, and considerable efforts have been devoted to exploring the highly active photoanode materials. Semiconductor metal oxides such as TiO$_2$, ZnO, Fe$_2$O$_3$, In$_2$O$_3$, and WO$_3$ have been extensively studied as photoanodes for PEC water splitting and numerous successes have achieved. Among various metal oxides, binary metal oxide BiVO$_4$ hold great promise for its significant advantages of the photoactive phase i.e. the monoclinic scheelite phase with a band gap of ~2.36 eV and high theoretical efficiency of 9.1%, which is capable of harvesting visible light. Nevertheless, the efficiency of the BiVO$_4$ is still low as a result of its relatively poor light-harvesting ability and rapid recombination of photo-generated carriers. Therefore, it is highly desirable and important to improve the photoactivity and of BiVO$_4$ by increasing the efficiency of absorption of the BiVO$_4$ and the separation of the electron-hole pairs.

To improve the PEC activity of BiVO$_4$ photoanodes, some strategies including element-doping, hydrogenation and composites have been proposed. Another effective strategy is to develop BiVO$_4$-based heterostructures. For example, various heterostructures such as WO$_3$/BiVO$_4$, CaFe$_2$O$_4$/BiVO$_4$, TiO$_2$/BiVO$_4$, and BiVO$_4$/Bi$_2$S$_3$ have been reported and enhanced PEC activity of these photoanodes have been achieved as a result of the increased carrier density, reduced electron-hole recombination and the narrow band gap of the semiconductor. However, the present PEC performance of these heterostructures is still unsatisfactory. Therefore, the development of new BiVO$_4$-based heterostructure photoanodes with high PEC activity and excellent stability is very desirable.

In this work, we firstly reported the design and synthesis of the Bi$_2$O$_3$/BiVO$_4$ p-n heterostructures for efficient PEC cells. α-Bi$_2$O$_3$ is an intrinsic p-type semiconductor with good PEC water splitting and photocatalytic activity. When the p-type Bi$_2$O$_3$ and n-type BiVO$_4$ are integrated together, a number of p-n junctions will be formed. Then, the holes in the valence band (VB) of the p-type Bi$_2$O$_3$ will combine with the electrons in the conduction band (CB) of the n-type BiVO$_4$ due to the p-n junctions. As a consequence, the photoexcited electron-hole pairs are effectively separated by this novel n-p junction structure, which is crucial for the enhancement of PEC activity. Our results show that the Bi$_2$O$_3$/BiVO$_4$ p-n heterostructures achieved a remarkable photocurrent density of 2.58 mA cm$^{-2}$ at 1.2 V vs. Ag/AgCl, which is about 5 folds that of pristine BiVO$_4$. The Incident-photon-to-current-conversion efficiency (IPCE) of Bi$_2$O$_3$/BiVO$_4$ reaches 35.6% at 440 nm, which is much higher than that of the pristine BiVO$_4$ (about 10% at 440 nm). The Mott-Schottky analysis supports that the Bi$_2$O$_3$/BiVO$_4$ electrode possesses one order of magnitude improvement on donor density compared to the bare BiVO$_4$ electrode. This high photocatalytic activity makes Bi$_2$O$_3$/BiVO$_4$ a promising and an active photoanode.

The Bi$_2$O$_3$/BiVO$_4$ heterostructure nanospheres were prepared on FTO substrates via a two-step process, as schematically illustrated in Figure 1. Metallic Bi nanobelts were firstly grown on FTO substrates by electrodeposition (experimental section). As shown in Figure 1b, the deposited film is black in colour and consisting of nanobelts with a 300 nm wide dendritic structure. XRD spectrum confirms that the deposited film is rhombohedral Bi (Figure S4a and Figure S5). To obtain the Bi$_2$O$_3$/BiVO$_4$ heterostructures, the as-prepared Bi nanobelts were impregnated in the solution of 0.1 mol L$^{-1}$ NH$_4$VO$_3$ for 6 h and then annealed at 550 $^\circ$C in air (experimental section). Interestingly, the colour of the film has been changed from black to yellow (inset in Figure 1c) and XRD studies clearly demonstrate the successful
transformation from metallic Bi to Bi$_2$O$_3$/BiVO$_4$ (Figure S4d). As shown in Figure 1c, the dendritical structure is basically retained after formed the Bi$_2$O$_3$/BiVO$_4$ heterostructures. Additionally, it should be noted that the Bi nanobelts have been transformed into some connected nanospheres with a dendritical structure. Furthermore, the composition of the Bi$_2$O$_3$/BiVO$_4$ heterostructures can be readily adjusting the immersion time in the NH$_4$VO$_3$ solution. For example, Bi$_2$O$_3$/BiVO$_4$ heterostructures was obtained when the immersion time was fixed to 6 h, as shown in Figure S1. When the immersion time increased to 12 h, pure BiVO$_4$ nanospheres were obtained (Figure S2 and Figure S4c). In addition, pure Bi$_2$O$_3$ nanobelts could be formed by directly annealed the as-prepared Bi nanobelts in air (Figure S3 and Figure S4b). All these results clearly show that our present method is an effective method to synthesize the heterostructures with controllable composition. More XRD details of Bi$_2$O$_3$, BiVO$_4$, and composite were shown in Figure S4.

Figure 1. (a) Schematic diagrams for the growth process of Bi$_2$O$_3$/BiVO$_4$ heterostructures, SEM images of (b) Bi, (c) Bi$_2$O$_3$/BiVO$_4$ heterostructures.

In order to better understand the microstructure of Bi$_2$O$_3$/BiVO$_4$ heterostructures, transmission electron microscopy (TEM) analysis was carried out. Figure 3a is a typical TEM image of the as-prepared Bi$_2$O$_3$/BiVO$_4$ heterostructures, showing that a lot of nanoparticles of 5 nm in diameter are uniformly covered onto the surface of the spheres. Figure 3b shows the high-resolution TEM (HRTEM) image of the sample, suggesting the Bi$_2$O$_3$/BiVO$_4$ heterostructure nanospheres are well crystalline. The well-resolved lattice fringes of 0.32 nm that corresponding to the (120) plane of monoclinic Bi$_2$O$_3$ are well observed. The lattice fringes of 0.29 nm that corresponding to the (040) plane of monoclinic BiVO$_4$ are also observed. Therefore, the Bi$_2$O$_3$/BiVO$_4$ heterostructures are successfully prepared. As shown in Figure 3c-f, distributions of Bi, V and O are clearly presented by the STEM EDS elemental maps, which indicate that the Bi, V and O are uniformly embedded in the nanospheres, and high combining degree of each other.
To study the effect of the p-n heterojunction on the PEC activity of BiVO$_4$ photoanode, PEC measurements were performed on the pristine BiVO$_4$, Bi$_2$O$_3$/BiVO$_4$ and Bi$_2$O$_3$ samples in a three-electrode electrochemical cell with 0.1 mol L$^{-1}$ Na$_2$SO$_4$ solution as the electrolyte. Figure 4a compares the current vs. potential (i-E) curves for the pristine BiVO$_4$, Bi$_2$O$_3$/BiVO$_4$ heterostructures and Bi$_2$O$_3$ photoelectrodes in the dark and under visible light ($\lambda > 420$ nm) irradiation. As expected, the Bi$_2$O$_3$/BiVO$_4$ electrode exhibited the best photocurrent density compared to the BiVO$_4$ and Bi$_2$O$_3$. The photocurrent density of Bi$_2$O$_3$/BiVO$_4$ achieved a current density of 2.58 mA cm$^{-2}$ at the potential of 1.2 V vs. Ag/AgCl, which is about 5 times higher than those of pristine BiVO$_4$ (0.47 mA cm$^{-2}$). This present value is also higher than recent reported BiVO$_4$-based photoanodes, such as Co-Pt Modified BiVO$_4$/ZnO (2.0 mA cm$^{-2}$ at 1.2V vs. Ag/AgCl) 23, WO$_3$/BiVO$_4$ (0.55 mA cm$^{-2}$ at 1.23V vs. Ag/AgCl) 24, BiVO$_4$-TiO$_2$ (0.53 mA cm$^{-2}$ at 1.2V vs. Ag/AgCl) 25, macro-mesoporous Mo:BiVO$_4$ (2.0 mA cm$^{-2}$ at 1.0 V vs. Ag/AgCl) 26. Furthermore, the current vs. potential (i-E) curves for the pure p-type Bi$_2$O$_3$ is shown in Figure S6. Incident-photon-to-current-conversion efficiency (IPCE) measurements were further performed to investigate the PEC performances of the as-prepared photoelectrodes. Figure 4b shows the IPCE spectra of the pristine Bi$_2$O$_3$, BiVO$_4$ and Bi$_2$O$_3$/BiVO$_4$ photoelectrodes measured at 0.6 V vs. Ag/AgCl as a function of incident light wavelength. Obviously, the Bi$_2$O$_3$/BiVO$_4$ photoanode showed substantially enhanced IPCE values compared to the pristine Bi$_2$O$_3$ and BiVO$_4$ at all measured wavelengths, which agree well with their J-V characteristics. The maximum IPCE value of the Bi$_2$O$_3$/BiVO$_4$ reaches 35% at 440 nm, which is much higher than that of pristine BiVO$_4$ (about 10% at 440 nm) and pure Bi$_2$O$_3$ (about 0.16% at 440 nm). This result conveniently supports our hypothesis that the PEC performance of BiVO$_4$ can be greatly improved by forming Bi$_2$O$_3$/BiVO$_4$ p-n type heterostructures.

The PEC stability of a photoelectrode is another crucial point for a PEC cell to produce hydrogen. The stability of the Bi$_2$O$_3$/BiVO$_4$ photoanode was also evaluated, and the photocurrent-time (i-t) curves of Bi$_2$O$_3$/BiVO$_4$ photoanode collected at 1.2 V vs. Ag/AgCl are shown in Figure 4c. The photocurrent of Bi$_2$O$_3$/BiVO$_4$ is initially about 2.58 mA cm$^{-2}$ and the photocurrent only decreases to 2.28 mA cm$^{-2}$ within the initial 20 minutes and then photocurrent decreases slowly to 1.91 mA cm$^{-2}$ within 120 min of illumination. This demonstrates that the Bi$_2$O$_3$/BiVO$_4$ heterostructures are very stable during the long time irradiation and extreme voltage, which is due to the separation of electron-hole pairs in the p-n heterostructures.

It is known that both the light absorption and separation efficiency of photoexcited electron-hole pairs have important influences on the PEC property of the photoelectrode. Diffuse reflectance UV-visible spectra of the Bi$_2$O$_3$, BiVO$_4$ and Bi$_2$O$_3$/BiVO$_4$ heterostructures were collected to understand the influence of p-n heterojunction on the light harvesting capability. As shown in Figure 5a, the band edges of the Bi$_2$O$_3$ and BiVO$_4$ samples were at about 400 nm and 512 nm, respectively, which are consistent with the recent reports. 24, 25 There is only one absorption band edge as the Bi$_2$O$_3$ and BiVO$_4$ distribute so uniformly in the heterostructures, which is consistent with the recent reports, such as BiOI/TiO$_2$ heterostructures, 26 BiVO$_4$/TiO$_2$ heterostructures. 27 Additionally, the band edge of Bi$_2$O$_3$/BiVO$_4$ heterostructures sample (460 nm) lied between the Bi$_2$O$_3$ (400 nm) and BiVO$_4$ (512 nm). As an indirect semiconductor, the band gap of

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**Figure 4.** (a) I-E curves recorded with a scan rate of 25 mV s$^{-1}$ under a full-arc xenon lamp irradiation, (b) IPCE spectra collected at the incident wavelength range from 300 to 700 nm at 0.6 V vs. Ag/AgCl of the Bi$_2$O$_3$, BiVO$_4$, and Bi$_2$O$_3$/BiVO$_4$ heterostructures, (c) Chronoamperometry (i-t) of Bi$_2$O$_3$/BiVO$_4$ heterostructures.

**Figure 5.** (a) UV-Vis diffuses absorption spectra and (b) Mott-Schottky curves of BiVO$_4$ and Bi$_2$O$_3$/BiVO$_4$ heterostructures.
Bi$_2$O$_3$, BiVO$_4$ and Bi$_2$O$_3$/BiVO$_4$ heterostructures could be determined with the formula:

\[
\alpha h \nu = A (h \nu - E_g)^{n/2},
\]

where \(\alpha\), \(h\), \(\nu\), \(A\), \(E_g\), and \(n\) are the absorption coefficient, Planck's constant, the incident light frequency, a constant, the band-gap energy, and an integer, respectively. Among them, \(n\) depends on the characteristics of the optical transition in a semiconductor, i.e., direct transition (\(n = 1\)) or indirect transition (\(n = 4\)). For BiVO$_4$ and Bi$_2$O$_3$, both of them pertain to direct transition and the values of \(n\) are 1. The band-gap energy (\(E_g\)) value of BiVO$_4$ can be thus estimated from a plot of \((\alpha h \nu)^2\) versus the photon energy \((h \nu)\). From the Figure S7, the estimated band gap of Bi$_2$O$_3$ is about 2.32 eV, which is much smaller than those of untreated BiVO$_4$ (2.36 eV) and Bi$_2$O$_3$ (2.85 eV) samples. The conduction band edge of a semiconductor at the point of zero charge can be calculated by the empirical equation:

\[
E_{CB} = X - E' + 0.5E_g^{39},
\]

where \(X\) is the valence band-edge potential, \(E'\) is the electronegativity of the semiconductor, \(E_g\) is the absolute electronegativity of the constituent atoms, \(E_g\) is the band-gap energy of the semiconductor, and \(E_{CB}\) can be determined by \(E_{CB} = E_{VB} - E_{eX}\). The \(X\) values for BiVO$_4$ and Bi$_2$O$_3$ are 6.04 and 5.95 eV. The band-gap energies of BiVO$_4$ and Bi$_2$O$_3$ are 2.36 and 2.85 eV, respectively, which are consistent with the recent reports. 34, 35 Given the equation above, the CB and the bottom of the VB of BiVO$_4$ are calculated to be 0.36 and 2.72 eV, the CB and VB of Bi$_2$O$_3$ are calculated to be 0.03 and 2.88 eV, respectively. According to the above results, Scheme 1 was proposed to illustrate a possible charge-separation process. The p-type Bi$_2$O$_3$ is with Fermi energy level close to the valence band while the n-type BiVO$_4$ is with Fermi energy level close to the conduction band (XPS VBM was shown in Figure S8). When the two semiconductors are in contact, the CB potential of Bi$_2$O$_3$ is more negative than that of BiVO$_4$. As shown in Scheme 1, electron–hole pairs will be generated on Bi$_2$O$_3$ and BiVO$_4$ under the irradiation of visible-light. The excited holes on the VB of Bi$_2$O$_3$ transfer to the CB of BiVO$_4$ and combine together. Then, the electrons produced on the CB of Bi$_2$O$_3$ will transfer to Pt electrode to reduce H$^+$ to form H$_2$, while the excited holes on the VB of BiVO$_4$ will oxidize H$_2$O to O$_2$. Furthermore, the migration of photogenerated electrons and holes could be promoted by the internal electric field. Therefore, the formation of Bi$_2$O$_3$/BiVO$_4$ p-n heterojunction on the surface could effectively separate the photogenerated electron–hole pairs and could greatly reduce the recombination of the photogenerated charge carriers.

To elucidate the influence of heterostructure on photoelectrical properties of BiVO$_4$, the electrochemical impedance measurements were carried out. Figure 5b shows the Mott-Schottky plots of the BiVO$_4$ electrodes at a frequency of 1 kHz in the dark, which were generated based on capacitances that were derived from the electrochemical impedance. Both the BiVO$_4$ and Bi$_2$O$_3$/BiVO$_4$ electrodes show positive slopes, as expected for n-type semiconductors. Notably, Bi$_2$O$_3$/BiVO$_4$ shows substantially smaller slope of Mott-Schottky plot compared to bare BiVO$_4$, suggesting significantly increased donor densities based on the following equation:

\[
N_d = (2/e_0\varepsilon_0)[d(1/C^2)/dV],
\]

where \(N_d\) is the donor density, \(e_0\) the electron charge, \(\varepsilon\) the dielectric constant of BiVO$_4$ (\(\varepsilon\approx86\)), \(\varepsilon_0\) the permittivity of vacuum, and \(V\) the applied bias at the electrode. The carrier densities of the BiVO$_4$ and Bi$_2$O$_3$/BiVO$_4$ electrodes are calculated to be 1.85×10$^{19}$ and 3.80×10$^{17}$ cm$^{-3}$, respectively. Notably, Bi$_2$O$_3$/BiVO$_4$ electrode possesses one order of magnitude improvement on donor density compared to the bare BiVO$_4$ electrode. The drastically increasing donor density of Bi$_2$O$_3$/BiVO$_4$ clearly indicated the enhancement of the conductivity. On the other hand, the Mott-Schottky curve of p-type Bi$_2$O$_3$ is shown in Figure S9. All the results clearly verified the assumption that the heterostructures influence the PEC performance deeply.

Conclusions

In summary, the Bi$_2$O$_3$/BiVO$_4$ heterostructures were successfully prepared by a simple electrodeposition method and followed calcination. Raman, TEM and XPS analyses confirm the formation of the p-n heterostructures, which can facilitate the transportation and separation of the photo-generated electron-hole pairs. The Bi$_2$O$_3$/BiVO$_4$ heterostructures exhibited significantly enhanced PEC activity under visible light irradiation. The photocurrent density of Bi$_2$O$_3$/BiVO$_4$ heterostructure photoanode achieved a high photocurrent of 2.58 mA cm$^{-2}$ at 1.2 V vs. Ag/AgCl, which is about 5 times than that of pristine BiVO$_4$. These finding indicates the Bi$_2$O$_3$/BiVO$_4$ heterostructures are very promising candidates for PEC cells.

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Bi$_2$O$_3$/BiVO$_4$ heterostructures with a p-n junction have been successfully synthesized and exhibited enhanced photoelectrochemical activity.