Research Article

Enhancement in Photoelectrochemical Efficiency by Fabrication of BiVO$_4$@MWCNT Nanocomposites

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An enormous enhancement in the photo-to-current conversion efficiency over the nanocomposite material composed by BiVO$_4$ on the surface of MWCNTs, with respect to electrode of pure BiVO$_4$, was observed. The heterojunction formed between MWCNTs and nano-BiVO$_4$ is beneficial for the separation of photogenerated electrons and holes, resulting in more electrons that are able to transport efficiently to the surface and therefore enhance the photoefficiency.

1. Introduction

Since the photoelectrochemical water splitting (the Honda-Fujishima effect) was reported in 1972 [1], great progresses have been made on the research and application of photocatalysis and photoelectrochemistry both in energy and environmental fields.

Up to date, the design and development of visible-light-responsive photocatalysts is one of the research directions, because the utilization of visible light, which accounts for more than half of the solar spectrum, is significant. For this goal, it is utmost important to develop photocatalysts with a narrow band gap. One of the efforts consists of creating an electron donor level between the valence band and conduction band of TiO$_2$ by doping with metallic or nonmetallic elements such as such as Ag, Cu, Fe, Co, V, Cr, and Pd and rare earth element or N, S, and C [2–10]. However, although the doping of foreign elements extends the absorption to visible-light ranges, it increases the defects of semiconductor photocatalysts, which therefore is a part of the ultraviolet light-responsive performance that the titanium oxide originally possessed was occasionally ruined [11–17]. Another effort is the exploring of complex compounds that containing Bi$^{3+}$, In$^{3+}$, Sn$^{2+}$ (s$^2$ configuration), or Ag$^+$ (d$^{10}$ configuration) ions in an oxide system. Thus, it is able to elevate the valence band by means of the hybridization of their respective orbitals with the O$_{2p}$ orbital, and also narrowing the band gap of the semiconductor [18].

BiVO$_4$ is one of such complex oxides with narrow band gap. BiVO$_4$ shows not only excellent visible-light photocatalytic properties, but also a high photo-to-current conversion efficiency [19–27]. Almost a decade ago, the high activity of BiVO$_4$ for photocatalytic O$_2$ evolution from aqueous suspensions containing Ag$^+$ as a sacrificial electron acceptor under visible-light irradiation was observed [19]. It was then discovered that nanocrystalline BiVO$_4$ thin-film electrodes show high photocurrent yields for oxygen evolution in neutral aqueous electrolytes [25–27]. Therefore, BiVO$_4$ might be a good visible-light photovoltaic material. However, at the present stage, it is still necessary to explore strategies to improve the visible-light photoelectrochemical reactivity and efficiency of BiVO$_4$.

The photoelectrochemical properties can be enhanced if the photogenerated electrons or holes are transmitted effectively, in which the recombination of electrons and holes is avoided. As we have known, the rate of electron-hole
recombination is a decisive factor for photoelectrochemical properties. Thus, to form a heterojunction with semiconductor called a Schottky barrier, where there is a space-charge separation region, is an effective method of increasing recombination times for electron-hole pairs. Traditionally, this method of extending recombination times was established with platinum and other noble metal interfaces. CNTs have a variety of electronic properties, similar to the metals above mentioned, and they may also exhibit metallic conductivity as one of the many possible electronic structures [28]. The physical and chemical characteristics of semiconductor photocatalysts as well as the high conductivity along the tube axis of carbon nanotubes (CNTs) produced a great deal of incentive to disperse CNTs into the photoactive layer in order to obtain more efficient photoelectrochemical devices [29, 30]. However, the fabrication of nanosized BiVO₄ on the surface of MWCNTs to form a nanocomposite of BiVO₄@MWCNT was not reported in the literatures.

In this work, the photoelectrochemical property of the BiVO₄@MWCNT thin-film photoelectrode was studied, and an enhancement in the photo-to-current conversion efficiency was observed. The heterojunction formed between BiVO₄ and CNTs as well as the direct electron transportation effect of carbon nanotube is proposed to charge for the enhancement of photocatalytic efficiency.

2. Experimental Section

2.1. Fabrication of BiVO₄@MWCNTs Nanocomposites. BiVO₄-MWCNTs nanocomposite was prepared by co-precipitation method. First, required amounts of Bi(NO₃)₃·5H₂O and NH₄VO₃ were separately dissolved in 2.0 mol/L of nitric acid solution. The pretreated MWCNTs (provided by Chengdu Organic Chemical Co. Ltd.) were dispersed into PEG in ultrasonic for 1 h. Then, the mixture of MWCNTs and PEG were added into Bi(NO₃)₃ and NH₄VO₃. Meantime, 5 g of urea was added into the above mixture. The solution was stirred at 353–363 K for 12 h. At last, the mixture was filtered, washed, and dried, and the BiVO₄@MWCNTs nanocomposite was received. For comparison, pure BiVO₄ was also prepared according to the procedure reported in the literature [23]. The electrodes were prepared using the above-synthesized powders by dip-coating on the ITO conductive glass.

2.2. The Photoelectrochemical Measurements. The photoelectrochemical properties were carried by CHI760C electrochemical work station (Shanghai Chenhua instrument Co., Ltd.) in a three-electrode cell setup with a flat circular quartz window (diameter = 2 cm) opposite the working electrode, and platinum wire and Ag/AgCl were used as counter and reference electrodes, respectively. The light source was a 300-W Xe arc lamp (PLS-SXE300, Beijing Changtuo Co. Ltd.), and the electrodes were illuminated from the back electrode of the ITO side with a 420 nm bandpass filter in front of a quartz window to remove the light of wavelength less than 420 nm. The electrolyte was 0.5 mol/L Na₂SO₄ solution without pH control.

3. Results and Discussions

3.1. The Enhanced Photoefficiency of BiVO₄@MWCNTs Nanocomposites. Figure 1 shows the photoelectrochemical behaviors of the thin-film photoelectrodes fabricated by pure BiVO₄, a mixture of BiVO₄ and MWCNTs, and BiVO₄@MWCNTs nanocomposite, which were measured by transient photocurrent-time curves. As can be seen from the current-time (I-t) curves, pure BiVO₄ thin-film electrode showed an intensive photocurrent density of about 30 μA/cm² under visible light (λ ≥ 420 nm) irradiation. The photocurrent over the photoelectrode prepared from a mixture of BiVO₄ and CNT is increased in a certain extent with comparison to that over pure BiVO₄ photoelectrode, getting to 42 μA/cm². While it is interesting that the photocurrent intensity on BiVO₄@MWCNTs nanocomposite electrode is much higher than that over the above two electrodes, reaching to over 140 μA/cm². It should be noted that the amount of photoactive BiVO₄ in BiVO₄@MWCNTs nanocomposite and mixture of BiVO₄-MWCNTs is much lower than that of pure BiVO₄. So, it is unambiguously that the photocurrent over BiVO₄@MWCNTs nanocomposite photoelectrode was enhanced greatly with comparison to the pure BiVO₄ as well as BiVO₄-MWCNTs electrodes. As all of the semiconductors were prepared by coprecipitation method, while the only difference is just whether or not formation of nanocomposites of BiVO₄ with the MWCNTs, the enhanced photocurrents over photoelectrodes of BiVO₄@MWCNTs suggested that the formation of nanocomposite structure of BiVO₄@MWCNTs is the major factor for improving the photo-to-current conversion efficiency.

3.2. The Structure of BiVO₄@MWCNTs Nanocomposites. The crystalline structure of BiVO₄ and the morphologies of the formatted composites with carbon nanotube were characterized by X-ray diffraction pattern and electron microscopy. Figure 2 shows the XRD patterns of pure BiVO₄, BiVO₄@MWCNTs nanocomposite, and MWCNTs, respectively. The diffraction peaks of pure BiVO₄ prepared...
Intensity (a.u.) 2
θ (deg) 10 20 30 40 50 60 70

Figure 2: XRD patterns of (a) pure BiVO₄ nanoparticles, (b) BiVO₄@MWCNTs nanoparticles, (c) MWCNTs, and (d) JCPDS card no. 14-0688.

Intensity (a.u.) 2
θ (deg) 18 19 20

Figure 3: FE-SEM image of BiVO₄-MWCNTs. The insert shows the limited bulk BiVO₄ formed between MWCNTs.

by a coprecipitation process are in good agreement with the standard JCPDS card no. 14-0688. This structure is the typical monoclinic scheelite BiVO₄ (Figure 2(a)). No impurity peaks were observed, indicating that the sample is a pure phase BiVO₄ with a monoclinic scheelite structure. The XRD patterns of the BiVO₄@MWCNTs composites exhibit diffraction peaks much similar to the pure BiVO₄ powders except that two small peaks at 26.06° and 44.46° (indicated by dots in Figure 2), which are attributed to the characteristic peaks of MWCNTs (Figure 2(c)). These results suggested that the BiVO₄ particles in BiVO₄@MWCNTs composites sample are also of monoclinic scheelite phase.

In the three main crystal forms of BiVO₄ (tetragonal zircon type and monoclinic and tetragonal scheelite structure), monoclinic scheelite BiVO₄ is much more active than the tetragonal scheelite for O₂ evolution from aqueous AgNO₃ solution under visible-light irradiation [21]. The photovoltaic current properties of monoclinic scheelite BiVO₄ was also found much intensive than the other two structures. This is because the tension in the microstructure of monoclinic scheelite BiVO₄ is more intensive than that of tetragonal scheelite, due to the presence of a 6s² lone pair of Bi³⁺ resulted in the lone-pair distortion of the former one is much higher than the later one [21, 23]. These distinctive differences in the structure can be conveniently distinguished by XRD patterns, in which the monoclinic scheelite BiVO₄ with a high distortion generally shows well splitting of peaks at 18.5°, 35°, and 46° of 2θ. The widened part of XRD patterns near 19° of pure BiVO₄ and BiVO₄@MWCNTs composites are distinguished shown in the section of Figure 2(b). It can be observed that both samples showed two peaks with well resolution at this area. This observation suggested that both of the pure BiVO₄ and the BiVO₄@MWCNTs composites are of monoclinic scheelite type with a high distortion.

3.3. The Morphologies of BiVO₄@MWCNTs Nanocomposites. Figure 3 shows the typical morphologies of the BiVO₄@MWCNTs, which were examined by SEM. It is seen that most of the BiVO₄ particles are nanosized that attached to the MWCNTs tightly. On the other hand, there are some bulks BiVO₄ particles that were observed among BiVO₄@MWCNTs nanoparticles, revealing that the particles free from the MWCNTs grow more readily than those on the MWCNTs (shown in the inset of Figure 3), and the diameter bulk particles reach to 1 μm. In the mean time, some of the MWCNTs attached tightly to the surface of the bulk BiVO₄.

Figure 4 shows the typical TEM photographs of pure MWCNTs and BiVO₄@MWCNTs. It is seen that BiVO₄ nanoparticles are attached on the wall of MWCNTs (Figure 4(b)), contrasting to the relative smooth surface of pure MWCNT (Figure 4(a)). The size of BiVO₄ nanoparticles
is less than 10 nm, in the range of 5–10 nm. In addition, the BiVO₄ nanoparticles on the MWCNTs are significantly smaller than the particles of bulk BiVO₄, which should be attributed to the restriction effect of MWCNTs on the growth of attached nanoparticles. To investigate the composition of these tiny particles, EDX spectra analysis was applied to probe the composition of the coated nanoparticles (Figure 4(c)). It was found that V, Bi, O, C, and Cu elements are present on the surface of the nanotubes, revealing the existence of V and Bi on MWCNTs. The Cu signal arises from the copper grid and the C signal comes from the MWCNTs. Furthermore, the interface between MWCNT and BiVO₄ is clearly seen, indicating that BiVO₄ nanoparticles are well attached on the outermost shell of MWCNTs. Besides attaching on the surface of MWCNTs, BiVO₄ nanoparticles were also observed in the inner hollow cavity of nanotubes (shown in Figure 4(d)). It shows that nanosize cylinder in cavity of nanotubes is about 10 nm for the diameter and 40 nm for the length. However, the diameter of MWCNTs is just about 7-8 nm. The expansion force of the crystal growth of BiVO₄ led to the distortion of the nanotubes, while the suppression of the carbon wall resulted in the growth of crystal toward the tube axis, which is free of such hindrance.

3.4. The Structural Effect of Nanocomposites on the Photoefficiency. As we have observed, the photo-to-current efficiency of BiVO₄@MWCNTs nanocomposites has been enhanced enormously. The enhancement should be related to the structure of BiVO₄@MWCNTs nanocomposites. For a semiconductor thin-film electrode, the photocurrent should be controlled by the recombination probability of photogenerated electrons and holes. The higher rate of e⁻–h⁺ recombination will lead to a low photocurrent, and thus a lower photoefficiency. Because the MWCNTs had a high electron
affinity and excellent conductivity, the exited electrons from photactive BiVO₄ were trapped easily by MWCNTs and transferred quickly along CNT to the ITO conductive glass substrate. Consequently, intensive current was observed. Moreover, the observations in the TEM micrographs of BiVO₄@MWCNTs suggested that the BiVO₄ nanoparticles are tightly attached with the surface of MWCNTs, and this tight attachment can form a heterojunction between the photactive materials with CNT and lead to less boundaries exist between the two phases; therefore, less electrons losses occurred in the boundary. The heterojunction formed in the device can achieve charge separation and collection due to the tightly attachment of BiVO₄ with MWCNTs. Due to the introduction of internal junctions of BiVO₄/nanotube within the nanocomposite matrix, the electric field at these junctions can split up the electrons and holes. Therefore, in addition to the MWCNTs acting as a pathway for the electrons collection, electrons and holes can travel toward their respective contacts, avoiding the recombination, and thus, the photo-to-current efficiency is enhanced. However, although in the mixture of BiVO₄ and MWCNTs, the MWCNTs were also participated in the electrons transfer, the heterojunction between BiVO₄ and MWCNTs is not formed and electric field does not exist, so the main photogenerated electrons were lost in the boundary between BiVO₄ and the MWCNTs. Therefore, the photocurrent was not enhanced greatly as expect.

4. Conclusions

The BiVO₄@MWCNTs nanocomposites were successfully fabricated by a soft-chemistry coprecipitation approach. An enhancement in the photocurrent over BiVO₄@MWCNTs composite electrode with respect to electrode of mixture of BiVO₄/MWCNTs as well as pure BiVO₄ was observed. It is concluded that the participation of MWCNTs acts as the electrons transfer media and the combination of BiVO₄ with MWCNTs tightly is beneficial for the electrons collection, resulting in that more electrons are able to transport quickly to the surface, which thus enhance the photo-to-current conversion efficiency.

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