BiVO₄/TiO₂(N₂) Nanotubes Heterojunction Photoanode for Highly Efficient Photoelectrocatalytic Applications

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Abstract We report the development of a novel visible response BiVO₄/TiO₂(N₂) nanotubes photoanode for photoelectrocatalytic applications. The nitrogen-treated TiO₂ nanotube shows a high carrier concentration rate, thus resulting in a high efficient charge transportation and low electron–hole recombination in the TiO₂–BiVO₄. Therefore, the BiVO₄/TiO₂(N₂) NTs photoanode enabled with a significantly enhanced photocurrent of 2.73 mA cm⁻² (at 1 V vs. Ag/AgCl) and a degradation efficiency in the oxidation of dyes under visible light. Field emission scanning electron microscopy, X-ray diffractometry, energy-dispersive X-ray spectrometer, and UV–Vis absorption spectrum were conducted to characterize the photoanode and demonstrated the presence of both metal oxides as a junction composite.

Graphical Abstract Visible-light response BiVO₄/TiO₂(N₂) nanotubes photoelectrode was fabricated for photoelectrochemical water splitting and organic degradation in this paper.

1 Introduction

The extreme shortage of natural resources and severe environmental problems caused by burning fossil fuels are pressing global concerns. In the past decades, many efforts
were made to explore alternate energy sources. Photo-electrocatalytic (PEC) technology is widely recognized as an alternative energy source because it provides a highly efficient and eco-friendly route to produce renewable energy, and it degrades organic pollutants by the direct use of sunlight [1–4]. It can be achieved using a semiconductor photoanode/liquid junction, which drives an oxidation reaction. Therefore, in most PEC cells, the overall performance is primarily determined by the photoanode. However, it is still a challenge to synthesize a photoanode material that is chemically stable and has reasonably high incident light-to-current conversion efficiency in the visible range.

In recent years, Bi3+-based complex oxides that could absorb visible light effectively and with the advantage of price beneficial have been produced as alternative energy materials [5–8]. BiVO4 is a promising high efficient photoanode and photocatalysis material, with advantages of small optical band gaps (2.4 eV) and high stability, and low conduction band edges that overcome traditional photoanode materials, such as ZnO, TiO2, WO3, and Fe2O3 [9–13]. However, BiVO4 has the shortages of poor carrier transport properties and a substantially less efficient physical photoconversion rate [8].

One approach for alleviating these limitations is to use another semiconductor as support material to form a heterojunction that not only facilitates carrier transport but also enhances light absorption. Among various semiconductors, TiO2 has been intensively studied as a promising photoanode because it is stable, cost-effective, and has a negative flat band potential (~0.2 V vs. RHE) (RHE, reversible hydrogen electrode) [14–18]. Recently, Xie et al. [19] found an unusual spatial transfer of visibly excited high-energy electrons of BiVO4 to TiO2, which indicated enhanced photoactivity in the heterojunction of BiVO4/TiO2 nanoparticles. Li et al. [20] demonstrated that a proper facet contact between BiVO4 and TiO2 nanoparticles was the key to improving the photoactivity of BiVO4. Recently, we studied one-dimensional (1D) nanostructured TiO2 coupled with a BiVO4 heterojunction with straight channels for electron transportation that reduced carrier diffusion lengths and improved charge collection efficiencies [21]. However, TiO2 has an intrinsically low mobility that limits the enhancement of photoactivity of the BiVO4–TiO2 heterojunction. Therefore, increasing the carrier concentration and also the conductivity in TiO2 is crucial to constructing a BiVO4–TiO2 heterojunction for a high-performance PEC cell.

In this study, we pre-treated TiO2 nanotubes in the nitrogen gas (TiO2(N2) NTs) and then coupled them with BiVO4 to form a BiVO4/TiO2(N2) NTs heterojunction. We find that the photocurrent is increased by approximately 30 % compared to those obtained by previously reported BiVO4/TiO2 NTs heterojunction [21]. Our PEC experiments further demonstrate the improved performance in the degradation of dyes. These results are attributed to the high carrier concentration of TiO2 NTs after annealing in a non-oxidizing atmosphere, as observed by Mott–Schottky spectra. In this case, the defects presented in the TiO2(N2) NTs increase the charge transfer kinetics, along with the reduced recombination losses due to trap filling. Thus, the charge transport between BiVO4 and TiO2 is enhanced to produce a higher photoactivity. This heterojunction provides useful insight into the design and fabrication of BiVO4-based photoanodes for potentially cost-effective and highly efficient PEC applications in large-scale applications.

2 Experimental Procedures

2.1 Preparation of BiVO4/TiO2(N2) NTs

Photoanodes

TiO2 NTs were prepared by a template method in which ZnO nanowires (NWs) were transformed during a liquid-phase deposition (LPD) process. ZnO NWs were synthesized on FTO glass (2 × 2 cm2) after a hydrothermal treatment [22]. Next, a LPD treatment was conducted by placing ZnO NW substrates in a mixed solution of 50 mm (NH4)2TiF6 and 150 mm H3BO3 for 20 min at 25 °C [23]. After the LPD treatment, the sample was further annealed at 500 °C for 2 h in nitrogen gas, and nitrogen-treated TiO2 NTs were obtained and marked as TiO2(N2) NTs. For the fabrication of the BiVO4/TiO2(N2) NTs photoanode, a yellow precursor solutions of 300 mM Bi(NO3)3 and 300 mM NH4VO3 in 2 M HNO3 were deposited on the TiO2 NTs by spin coating [24]. Finally, the samples were sintered at 450 °C for 2 h in room air and yielded a yellow BiVO4/TiO2(N2) NTs film. For the control, the TiO2 NTs annealed in room air were used to prepare the BiVO4/TiO2 NTs photoanodes and bare BiVO4/FTO photoanodes were also prepared using the same procedure without the TiO2 NTs substrate.

2.2 Structural Characterization

The morphologies of the samples were characterized using field emission scanning electron microscopy and a microscope equipped with an energy-dispersive X-ray spectrometer (EDX) (FEL, Sirion200) and TEM (JEM-2100F, JEOL, Japan). The crystalline phase of the samples was characterized by X-ray diffractometry (XRD) (AXS-8 Advance, Bruker, Germany). X-ray photoelectron spectroscopy (XPS) measurements were performed on an ESCALAB250 XPS measuring system with a Mg Kα
X-ray source. Optical absorption measurements were conducted in a Lambda 750 UV–Vis–IR spectrophotometer using an integrating sphere.

2.3 Photoelectrochemical Measurements

The photo responses of the BiVO$_4$/TiO$_2$ NTs photoanode were conducted using a three-electrode system with the Ag/AgCl electrode as the reference, platinum foil as the auxiliary electrode, and the samples as the working electrode. The working electrode potential and current were controlled by an electrochemical workstation (CHI 660c, CH Instruments Inc., TX, USA). A 350-W Xe lamp was used as a simulated light source, without further description, and all experiments were conducted under visible light (light intensity, 100 mW cm$^{-2}$). The electrolyte was a 0.1 M Na$_2$SO$_4$ solution. The linear sweep voltammograms (LSV) were conducted under chopped light irradiation. The scan rate for the linear sweep voltammetry was 10 mV s$^{-1}$. Photoluminescence (PL) measurements were conducted using an OmniPL-LF325 system with a 325 nm laser at room temperature. The incident photon-to-charge conversion efficiency (IPCE) was measured by a system comprising a monochromator (Zolix, P.R. China), a 500-W xenon arc lamp, a calibrated silicon photodetector, and a power meter. Mott–Schottky (impedance) spectra were recorded in 0.2 M Na$_2$SO$_4$ without light at a frequency of 1 kHz and a scan rate of 10 mV s$^{-1}$.

Intensity modulated photocurrent spectroscopy (IMPs) was determined using an electrochemical workstation (ZENNIUM, ZAHNER-elektrik GmbH & Co. KG, Germany) equipped with a controlled intensity modulated photospectroscopy setup (CIMPS, PP211, ZAHNER-elektrik GmbH & Co. KG, Germany) after a two-electrode configuration. A white light lamp (WLC02, ZAHNER-elektrik GmbH & Co. KG, Germany) was used as the light source. The modulated light in the frequency range of 0.1 Hz–1 kHz superimposed on a steady dc light with an intensity of 60 mW cm$^{-2}$ was also used as a light source.

2.4 Organics Compounds Degradation

The PEC degradation of the methylene blue (MB) experiment was conducted under the following conditions: visible light irradiation (100 mW cm$^{-2}$), vigorous stirring, 1.0 V (vs. Ag/AgCl) of electric bias, pH 7, and 0.1 M sodium sulfate as the supporting electrolyte. Before degradation test, the nitrogen was bubbled to remove oxygen from the solution. The initial concentration of MB solution was 10 mg L$^{-1}$ and the reaction solution was 20 mL during the experiment. The degradation rates of the dyes were analyzed with an UV–Vis spectrophotometer (UV2102 PCS, UNICO, Shanghai).

3 Results and Discussion

The main fabrication strategies for the BiVO$_4$/TiO$_2$(N$_2$) NTs photoanodes are conducted in three steps as illustrated in Fig. 1. First, the ZnO NW template is grown on the FTO substrate through a hydrothermal method. Second, the template is transformed to TiO$_2$ NTs after an LPD treatment which involves hydrolysis of ammonium hexafluorotitanate, and leads to the deposition of TiO$_2$ as well as mild etching of ZnO from the formation of HF. Third, BiVO$_4$ is deposited on the TiO$_2$ NTs to form a photoactive composite layer.

Figure 2 shows the top and cross-sectional SEM images of optimized TiO$_2$(N$_2$) NTs and BiVO$_4$/TiO$_2$(N$_2$) NTs, respectively. As shown in Fig. 2a, b, the obtained TiO$_2$(N$_2$) NTs have a vertical geometric shape, although the treatment of the NWs leads to partial connectivity among the constituent wires due to the surface tension during the evaporation of the solvent (Fig. 2a). Compared with the nitrogen-treated TiO$_2$ NTs, the geometry for the air-annealed TiO$_2$ NTs remains unchanged (not presented here). The TiO$_2$ NTs are approximately 400 nm in length with a relatively rough surface (Fig. 2b). Likewise, the side view also confirms the formation of the heterojunction of the BiVO$_4$/TiO$_2$(N$_2$) NTs heterojunction (Fig. 2d). The thickness of the junction is approximately 600 nm, which is thicker than that of pure BiVO$_4$ photoanode (Fig. S1). As shown in Fig. S2, the TEM images also demonstrate the heterojunction structure, where the BiVO$_4$ nanoparticles are clearly observed on the TiO$_2$ NTs.

Fig. 1 Schematic diagram of the main processes for the fabrication of the BiVO$_4$/TiO$_2$ NTs photoanodes
The elemental composition of the BiVO$_4$/TiO$_2$(N$_2$) NTs was also analyzed and their characteristic elements were identified using an EDX detection spectrometer. As shown in Fig. S2, the elements of Bi and V have almost the same percentage of atoms (%), indicating the formation of BiVO$_4$. XRD also measured the crystalline phases of BiVO$_4$ and BiVO$_4$/TiO$_2$ NTs, and the results are shown in Fig. 3. For all samples, the prominent peaks for BiVO$_4$ are likely derived from the monoclinic phase of BiVO$_4$ (PDF 14-0688). The typical peaks at 25.3° and 27.4° are assigned to the (101) and (110) planes of anatase and rutile phases, respectively. In Fig. 3a, the annealed composite has anatase phase and a large amount of rutile phase from the integrated intensity of the peaks associated with the (101) and (110) planes. However, for the BiVO$_4$/TiO$_2$(N$_2$) NTs sample, it contains mostly anatase (Fig. 3b). These results are in accord with the reports by Jin et al. [25] and Mahajan et al. [26], who studied the effects of the atmosphere on the crystalline phase of TiO$_2$ nanotube arrays in the annealing process. Also, the peaks at 26.4° and 37.6° for both samples are ascribed to the FTO substrate. To further study the surface composition and chemical state of TiO$_2$(N$_2$), XPS analysis was also conducted, and the results are illustrated in Fig. 4. The full survey indicates the presence of Sn, O, Ti, and N (Fig. 4a). Figure 4b–d shows the high-resolution XPS spectra of the elements, respectively. For the O 1s (Fig. 4b), the peak at 531.0 eV corresponds to the lattice oxygen, which is related to the Ti–O or Sn–O chemical bonding in the SnO$_2$ or TiO$_2$. Two distinct peaks located at 464.5 and 458.7 eV in Fig. 4c are assigned to the binding energy of Ti 2p$_{1/2}$ and Ti 2p$_{3/2}$, respectively, indicating the presence of Ti$^{3+}$. The peak at 400.1 eV could ascribe to γ-N state, which is molecularly chemisorbed N$_2$ [27].

The optical absorption spectra of the TiO$_2$ NTs, TiO$_2$(N$_2$) NTs, BiVO$_4$/TiO$_2$ NTs, and the BiVO$_4$/TiO$_2$(N$_2$) NTs are shown in Fig. 5. The TiO$_2$ NTs show an absorption edge at ~360 nm, whereas, the TiO$_2$(N$_2$) NTs with an
absorption tails extend into the visible wavelength regions. The long absorption tail indicates the presence of additional energy states within the band gap of TiO₂. The energy may have resulted from the presence of oxygen vacancies or non-stoichiometric TiO₂ due to annealing in a non-oxidizing atmosphere. On the other hand, the pure BiVO₄ film displayed absorption within the visible region of the spectrum with the edge at ~516 nm, which corresponded to the band gap energy of 2.4 eV and further demonstrated the formation of monoclinic phase BiVO₄ [28]. After the deposition of BiVO₄, both the BiVO₄/TiO₂ NTs and the BiVO₄/TiO₂(N₂) NTs had very similar band gap absorption compared to BiVO₄, although they had enhanced intensities in the visible region. The enhanced absorption intensity was attributed to the thicker BiVO₄ film in the heterojunction as observed in the SEM images.

Figure 6 presents the LSV characteristics of the TiO₂ NTs, TiO₂(N₂) NTs, BiVO₄, BiVO₄/TiO₂ NTs, and the BiVO₄/TiO₂(N₂) NTs, respectively. The TiO₂ NTs sample exhibited a pretty low photocurrent under visible irradiation due to its large band gap, whereas the TiO₂(N₂) NTs sample had a slight photocurrent. The photocurrent for pure BiVO₄ increased steadily with the increasing potential of the working electrode, and a photocurrent density of 1.36 mA cm⁻² (1.0 V vs. Ag/AgCl) was obtained. Compared to that of pure BiVO₄, a significant enhancement in photocurrent, ca. 2.06 mA cm⁻² (1.0 V vs. Ag/AgCl), by the BiVO₄/TiO₂ NTs was observed. The photocurrent was further enhanced by approximately 30 % when using the BiVO₄/TiO₂(N₂) NTs, which obtained the photocurrent of 2.73 mA cm⁻² (1.0 V vs. Ag/AgCl). The BiVO₄/TiO₂(N₂) with the cyclic voltammetry test also shows a stable photocurrent in the measuring range (Fig. S4).

Incident photon-to-current efficiency was measured in order to ascertain the light conversion efficiency of the heterojunction of the BiVO₄/TiO₂(N₂) NTs and was compared to the BiVO₄/TiO₂ NTs, BiVO₄, and TiO₂ in Fig. 6b. Due to a large band gap, both the TiO₂ NTs and TiO₂(N₂) NTs had low efficiencies below 400 nm, although the TiO₂(N₂) NTs exhibited better performances. The IPCE of BiVO₄ was comparatively at ~20 % at 410 nm, whereas heterojunction BiVO₄/TiO₂ NTs had a higher IPCE at nearly 28 % at 410 nm. Comparably, the IPCE of BiVO₄/TiO₂(N₂) NTs further increased to 44 % at 410 nm, which
was more than 100 % higher than the IPCE of bare BiVO₄. This again suggests that the rectifying electron transfer from BiVO₄ to TiO₂ likely inhibits the fast recombination and increases the solar energy conversion efficiency of the junction. The IPCE was nearly zero at 550 nm, which is consistent with the optical absorption of the samples.

The PEC properties of the BiVO₄/TiO₂(N₂) NTs were investigated by treating the organic dye (MB) under visible light illumination. It can be seen that almost no MB or little MB can be directly degraded by only applying electrocatalytic or photolytic reaction, and the TiO₂ NTs only resulted in a removal ratio of only 14.1 % within 80 min, whereas the TiO₂(N₂) NTs had a higher efficiency of 27.2 % under the same conditions. The limited improvement in degradation of MB by TiO₂ NTs was due to a large band gap that limited the use of visible light. Compared to the TiO₂ NTs, the BiVO₄ electrode degraded 52.4 % of the MB within the same time because of good absorption in the visible region. For the BiVO₄/TiO₂ NTs, the removal rate increased to 76.7 % due to fast electron transfers between the BiVO₄ and TiO₂ NTs. However, it is easily observed from Fig. 7a that the BiVO₄/TiO₂(N₂) NTs obtained the removal rate of 91.8 % under the same conditions. The recycle performance of the BiVO₄/TiO₂(N₂) NTs for PEC degradation of MB was investigated in five PEC cycles, and the results are shown in Fig. 7b. These results further suggested that the BiVO₄/TiO₂ NTs were stable for PEC applications, such as treating organic wastewater [29–31].

During all the process in PEC, we use 1 cm² photoanode under visible light illumination.

As previously discussed, the BiVO₄/TiO₂(N₂) NTs exhibited a significant enhancement in photoactivity as verified by higher photocurrent as well as a higher PEC efficiency in the degradation of dyes. Apparently, the TiO₂(N₂) NTs played an important role in the promotion of the charge transfers in the electrode. We concluded that the carrier concentration in the TiO₂ NTs could be increased after annealing in a nitrogen atmosphere. To make sure the impacts of the TiO₂(N₂) NTs, impedance measurements were carried out at a frequency of 1 kHz on both the TiO₂(N₂) NTs and TiO₂ NTs electrodes in 0.2 M Na₂SO₄ electrolytes in the dark. The results are demonstrated by the Mott–Schottky plots in Fig. 8a. From the linear portion of the Mott–Schottky plots, charge carrier densities are calculated using the relation

\[
N_D = \frac{2}{\varepsilon \varepsilon_0 m \varepsilon^2}
\]

where \(N_D\) is the charge carrier density, \(\varepsilon\) is the elementary electron charge (\(\varepsilon = 1.6 \times 10^{-19}\) C), \(\varepsilon\) is the dielectric constant (\(\varepsilon = 48\)), \(\varepsilon_0\) is the permittivity in vacuum (\(\varepsilon_0 = 8.85 \times 10^{-12}\) F m⁻¹), and \(m\) is the slope of the \(1/C^2\) versus potential plot. A charge carrier density of \(2.9 \times 10^{18}\) cm⁻³ was determined for the TiO₂ NTs, but was \(2.1 \times 10^{19}\) cm⁻³ for the TiO₂(N₂) NTs. These results indicated that the charge carrier concentration of the TiO₂
NTs was indeed increased after calcination in the non-oxidizing atmospheres. The higher defect density of the nitrogen-annealed sample also involved a higher electrical conductivity [32] and rapid charge transfer.

To further confirm enhanced charge transfers between BiVO<sub>4</sub> and the TiO<sub>2</sub>(N<sub>2</sub>) NTs in the heterojunction material, the transit time (\(\tau_d\)) of the majority carriers in the BiVO<sub>4</sub>/TiO<sub>2</sub> NTs electrode and the BiVO<sub>4</sub>/TiO<sub>2</sub>(N<sub>2</sub>) NTs electrode was measured by IMPS, respectively. The transit time \(\tau_d\) was the average time that the photogenerated charges took to transfer to the back contact, and were estimated from the equation \(\tau_d = (2\pi f_{\text{min}} \text{ (IMPS)})^{-1}\), where \(f_{\text{min}}\) is the frequency at the minimal value in the IMPS plot. The transit time reflects the recombination probability of the photogenerated electrons and holes in the photoelectrode [33]. Figure 8b shows the IMPS plots of the BiVO<sub>4</sub>/TiO<sub>2</sub> NTs electrode and the BiVO<sub>4</sub>/TiO<sub>2</sub>(N<sub>2</sub>) NTs electrode, respectively. According to the previous equation, the transit time \(\tau_d\) for the BiVO<sub>4</sub>/TiO<sub>2</sub> NTs was 11.9, and 3.82 ms for BiVO<sub>4</sub>/TiO<sub>2</sub>(N<sub>2</sub>) NTs electrode, which indicated that the transport speed of the majority of photogenerated charges in the BiVO<sub>4</sub>/TiO<sub>2</sub>(N<sub>2</sub>) NTs electrode was three times faster than that of the BiVO<sub>4</sub>/TiO<sub>2</sub> electrode. In other words, the BiVO<sub>4</sub>/TiO<sub>2</sub>(N<sub>2</sub>) NTs heterojunction could facilitate the majority of the photogenerated charges transported to the counter electrode and likewise, the transport of photogenerated electrons to the electrolyte is enhanced.

The transportation of electrons between the two materials was also certified by PL measurement as shown in Fig. 8c. We observed strong emission from bare TiO<sub>2</sub> NTs and BiVO<sub>4</sub>, whereas the BiVO<sub>4</sub>/TiO<sub>2</sub>(N<sub>2</sub>) NTs heterojunction resulted in a near 90 % reduction in the emission intensity. The obvious quenching of luminescence of BiVO<sub>4</sub> is characteristic of charge transfer between the BiVO<sub>4</sub> and TiO<sub>2</sub> NTs, implying a strong indication of the efficient reduction in recombination of charge carriers in the 1D heterojunction material. In consequence, the separation efficiency of photogenerated electron–hole pairs in BiVO<sub>4</sub>/TiO<sub>2</sub>(N<sub>2</sub>) NTs heterojunction could be improved.

Based on the experiments, We concluded that the improved performance of the BiVO<sub>4</sub>/TiO<sub>2</sub>(N<sub>2</sub>) NTs was...
primarily due to enhanced optical absorption and specific TiO$_2$(N$_2$) NTs. The nanotube structure provides larger surface area than the planar structure so that more BiVO$_4$ photocatalyst was loaded for absorbing more visible light. On the other hand, the presence of oxygen vacancies or non-stoichiometric TiO$_2$ in the TiO$_2$(N$_2$) NTs significantly enhanced the carrier density which favors the separation of photo-introduced electron–hole pairs verified by IMPS test. Thus, the higher photocurrent was obtained. The whole PEC system is shown in Fig. 9. Upon excitation by visible light, electrons were photoexcited from the valence band of BiVO$_4$ to its conduction band. Then electron differences in the positions of the conduction bands which drove to photoelectrons generated in BiVO$_4$ to the tubular TiO$_2$(N$_2$) NTs, where electrons were rapidly separated and directed to the Pt counter electrode via the external circuit. Consequently, the photogenerated electrons were scavenged by hydrogen ions on the Pt foil, and formed hydrogen gas, while the photogenerated holes oxidized water or organics on the surface of the BiVO$_4$. Overall, the BiVO$_4$/TiO$_2$(N$_2$) NTs heterojunction offered remarkable photoconversion efficiency.

4 Conclusions

A visible light response BiVO$_4$/TiO$_2$(N$_2$) NTs photoelectrode was fabricated for photoelectrochemical (PEC) organic degradation. Mott–Schottky plots and IMPS demonstrated the increased carrier concentration in the TiO$_2$(N$_2$) NTs, which enhanced electron transfers between BiVO$_4$ and TiO$_2$. A photoelectrochemical measurement confirmed that the photocurrent was increased approximately 100% using the heterojunction when compared to bare BiVO$_4$ under 100 mW cm$^{-2}$ visible light illumination. Due to its excellent photoactivity and stability, the BiVO$_4$/TiO$_2$(N$_2$) NTs show a promising future in PEC applications.

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