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TiO₂ nanoparticles anchoring on Two-dimensional Bi₂Se₃ nanosheet as an enhanced visible light catalyst

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Abstract

Titanium dioxide (TiO_2) has been widely studied in the field of photocatalysis. However, the development of TiO_2 was limited by the photoresponse only in the ultraviolet region and the rapid recombination of photogenerated electron-hole pairs. In this work, TiO_2 and two-dimensional (2D) bismuth selenide (Bi_2Se_3) hybrid nanosheets ($\text{TiO}_2/\text{Bi}_2\text{Se}_3$ HNs) have been prepared via a simple ultrasonic route. X-ray diffraction pattern and Raman spectra were carried out to confirm that as-prepared samples were pure and well crystalized. Besides, the microstructure characterization proves that 2D Bi_2Se_3 nanosheets have high specific surface area and can serve as a stable platform to construct the intimate interaction with TiO_2 . Furthermore, photoelectrochemical (PEC) measurements demonstrate that the $\text{TiO}_2/\text{Bi}_2\text{Se}_3$ HNs exhibit excellent photocatalytic performance under visible light, which were much better than pure TiO_2 and Bi_2Se_3 . More importantly, the photocurrent density was quite stable and only dropped by 10% after 125 cycles. In summary, the improved photocatalytic activity is due to the unique characteristic of 2D Bi_2Se_3 nanosheets, such as maximized reaction sites and good electrical conductivity, and the positive coupling effect of the $\text{TiO}_2/\text{Bi}_2\text{Se}_3$ heterojunction. This study indicates that $\text{TiO}_2/\text{Bi}_2\text{Se}_3$ HNs photocatalysts have excellent potential for photocatalytic application.

Keywords: TiO_2 ; Bi_2Se_3 ; Photocatalysis; heterojunction;

1. Introduction

In many renewable energy sources, solar energy has become the direction of research attention with the characteristics of being clean and pollution-free. The development of photocatalysis has been the focus of widespread concern in recent years owing to photocatalysis is widely used in various research fields, including environmental and energy related fields[1-4]. Since the first report from Fujishima et al.[5] in 1972, the photocatalytic properties of TiO_2 have been used to solar cells[6], photoelectric sensors[7] and photohydrolysis electrodes[8] due to its hydrophilicity, chemical stability, long life, non-toxicity and low cost. However, TiO_2 with the bandgap of 3.2 eV has photoresponse only in the ultraviolet region, which significantly decreases the utilization rate of solar energy[9, 10]. Meanwhile, the photocatalytic activity of it is usually limited by amounts of active sites for surface reactions and the rapid recombination of photogenerated electron-hole pairs[11-13]. In order to improve the photocatalytic performance, G. Sanzone et al.[14] successfully demonstrated the use of an Ag- TiO_2 nano-engineered film for visible-driven photocatalysis. Besides, Wang et al.[15] reported a plasmonic coupling Au/ TiO_2 /Au photocatalyst, and the photocurrent density of this favorable nanostructure exhibiting a significant improvement in the visible region compared with the pure TiO_2 . Nevertheless, the high cost of rare resources promoted us to explore low-cost and high-performance alternatives without precious metals. Recently, Ren et al.[16] reported a co-catalyst by TiO_2 loading on MoS_2 , in which the photo-generated charges will be trapped on the surface of MoS_2 , thereby effectively decreasing the electron-hole pairs recombination rate and

representing higher efficiency than pure TiO_2 . Therefore, building an efficient electron-hole transporter opens up novel perspective for enhancing photocatalytic performance.

Topological insulator is a kind of quantum materials with a conductive gapless surface state on the surface or edge of an insulating bulk, which bring broad prospects in basic research on the topological ordering of condensed matter systems and applications for spintronic devices[17-19]. Recently, the VA-VIA compound semiconductor[20-22] has received great attention from researchers as a third-generation semiconductor sensitizer due to its suitable electronic and optical properties. Among them, bismuth selenide (Bi_2Se_3) is a typical topological insulator and an important member of the V_2VI_3 compound family[23], thereby it has excellent application prospects in many fields. As a direct band gap (0.3-1.2 eV) layered semiconductor[24], Bi_2Se_3 has been extensively used in various fields, such as thermoelectrical devices[25], electrical transport devices[26], optical recording system and strain gauges[27], due to its appreciable thermoelectric property, high electrical conductivity, photosensitivity and electrochemical property. In addition, the morphology of 2D nanosheets is easy to be formed[28], which can provide a beneficial load platform for combining with other semiconductors to form a heterojunction. The surface of Bi_2Se_3 has the characteristics of the metals surface state with great amounts of itinerant electrons, which is particularly beneficial to the charge transfer of the active site platform[26, 29]. Thereby, it can effectively inhibit the recombination of electron-hole pairs. Meanwhile, the surface of Bi_2Se_3 also provides more additional active sites to enhance photocatalytic performance. For example, M. Baitimirova et al.[30] reported

the deposition of ZnO nanolayers with different thicknesses (10-150 nm) on nanostructured Bi₂Se₃, and the result showed that the photoluminescence of the Bi₂Se₃/ZnO heterostructure was greatly enhanced compared with pure ZnO nanolayer. Besides, Zhang et al.[31] reported a near-infrared SnTe/Bi₂Se₃ heterostructure photodetector, which exhibits a higher light response rate of 145.74 mA W⁻¹ and a maximum detection rate. This heterostructure not only utilizes the effective charge transfer of topological insulators, but also provides an ideal platform for studying the energy-band coupling effect of surface states between topologies and semiconductors. All in all, three complementary advantages are proposed to prove that the optical properties of photosensitive materials can be obviously enhanced in the heterostructure, namely, increased charge separation between the interface of two nanomaterials, improvement of the photosensitive crystals and surface plasmon-photon coupling of semiconductors[30-34]. However, the excellent characteristics of Bi₂Se₃ in the direction of photocatalysis have rarely been studied.

In this work, powder/2D TiO₂/Bi₂Se₃ heterojunction hybrid nanosheets (HNs) with different mass ratios were prepared by a simple ultrasonication. The surface of TiO₂ and Bi₂Se₃ nanosheets can be tightly and stably connected via the ultrasonic system. The PEC tests demonstrate that the photocatalytic efficiency of TiO₂ is greatly improved by the hybridization with Bi₂Se₃ nanosheets. The excellent performance of TiO₂/Bi₂Se₃ HNs can be attributed to the type-II heterojunction formed between the interfaces, which can effectively inhibit the recombination of photogenerated electron-hole pairs and accelerate the transport efficiency of carriers. In addition, more additional

active sites are provided by the Bi_2Se_3 nanosheets, and it can effectively prevent the agglomeration of TiO_2 . Meanwhile, the photocatalytic performance of the $\text{TiO}_2/\text{Bi}_2\text{Se}_3$ HNs can be further improved under full-spectrum light irradiation due to the synergistic effect of heat transferred by visible light and near-infrared light. All results indicate that the obtained hybrid nanosheets exhibit excellent PEC performance and probably play a potential advantage in practical applications.

2. Experimental section

2.1 Sample preparation

Bi_2Se_3 bulk (99.99%) and TiO_2 powder (anatase, 99.8%) were purchased from Aladdin Co., Inc. All of the other reagents were of analytical purity and were used as received without further purification.

Bi_2Se_3 nanosheets were obtained by liquid phase lift-off process[28]. Briefly, an appropriate amount of Bi_2Se_3 (200 mg) was dissolved to 80 ml N-Methyl pyrrolidone solution, then sonicated for 24 hours at room temperature. Afterwards, the obtained homogeneous solution was washed several times with acetone and ethanol, and the acquired powder was evenly dispersed in deionized water and allowed to stand for 6 hours. Eventually, Bi_2Se_3 nanosheet powder was acquired after drying in a vacuum oven.

Typically, a certain amount of original Bi_2Se_3 nanosheets (10 mg) and TiO_2 (100 mg) were dissolved in 30 ml deionized water at room temperature. The above experiment was carried out under vigorous stirring. After that, the above solution was sealed in a 50 ml glass bottle and sonicated in an ultrasonic machine for 6 h. Finally, dry in a freeze-

drying oven for 24 hours to obtain a homogeneous mixture.

2.2 Characterization

Determine the crystal structure of the prepared sample X-ray diffraction (XRD) via a Rigaku D/max 2500 powder diffractometer equipped with monochromatic high-intensity Cu K α radiation. Raman spectra of the prepared Bi₂Se₃ nanosheets were obtained by using Renishaw InVia Raman microscope at room temperature with an excitation laser wavelength of 532 nm. Transmission electron microscopy (TEM, JEM 2100) and an energy dispersive spectroscope (EDS) were used to characterize the surface morphology and microstructure of the samples.

2.3 Preparation of working electrodes

Indium tin oxide (ITO, 30 mm×10 mm×1 mm) conductor glass was used as the substrate of the working electrode and was ultrasonically cleaned with acetone, ethanol and deionized water. Then, a small portion (3 mg) of the prepared sample was mixed with 1 mL of ethanol solution to obtain a uniformly dispersed slurry. After spreading the above slurry on the ITO substrate, it was dried overnight under 60 °C ambient conditions to obtain the required working electrode.

2.4 Photoelectrochemical (PEC) measurements

The PEC tests were performed in different illumination intensity (60 mW/cm², 80 mW/cm², 100 mW/cm²) and different concentrations of Na₂SO₄ electrolytes (0.1 M, 0.5 M, 1 M). Use a Standard three-electrode system with different anodes (pure TiO₂, TiO₂/Bi₂Se₃, pure Bi₂Se₃), cathode (Pt flake) and an Ag/AgCl reference electrode. Electrochemistry workstation CHI660E (CH Instruments, Inc., Shanghai) was used to

control the bias potential and record the photocurrent generated. A 350 W xenon arc lamp (Beijing Perfect Light Technology Co., Ltd.) was placed at a distance of 20 cm from the reaction vessel, which was used as a light source without filter. The linear sweep voltammograms of the different samples were measured at a scan rate of 10 mV/s. All the experiments were carried out at the same condition.

3. Results and discussion

Figure 1(a) is the powder X-ray diffraction pattern of the as-prepared $\text{TiO}_2/\text{Bi}_2\text{Se}_3$ HNs sample, which was compared with the pure TiO_2 nanoparticles and sole Bi_2Se_3 nanosheets. It is obvious the diffraction peaks at 25.2° , 38.5° , 47.9° , 54.9° , 62.5° , 68.5° , 70.1° , 74.8° and 82.5° observed in the XRD patterns can be ascribed to the (101), (112), (200), (211), (204), (116), (220), (215) and (224) crystal planes, which is consistent with TiO_2 (JCPDS card no.71-1167). And the diffraction peaks at 18.4° , 27.7° , 29.4° , 35.3° , 40.4° , 51.0° , 57.5° , 66.5° , 71.5° , 83.5° can be indexed to the (006), (104), (015), (018), (10 10), (021), (10 16), (11 15), (125), (306) planes of Bi_2Se_3 nanosheets (JCPDS card no.12-0732). All the diffraction peaks are marked with Bi_2Se_3 or TiO_2 , without other impurities, indicating that the sample has higher purity and well crystallinity. In order to further confirm the composition of the sample, Raman spectroscopy (excited with a 532 nm laser) was performed to prove the existence of the characteristic peak of the sample in Figure 1(b). The Raman peak observed at 130 cm^{-1} can be attributed to the in-plane E_g^2 mode, while peaks located at 71 cm^{-1} and 173 cm^{-1} are corresponding to the A_{1g}^1 and A_{1g}^2 vibration modes of Bi_2Se_3 , respectively[35]. The characteristic peak of Bi_2Se_3 can be detected in HNs, which proves that the structure of Bi_2Se_3 will

not be destroyed after combination treatment. However, the peaks of Bi_2Se_3 at 130 cm^{-1} and 173 cm^{-1} were not prominent enough, because it was coincided with the large and sharp peak of TiO_2 at 143 cm^{-1} . Simultaneously, the Raman spectrum of the HNs, as expected, displays an intense and sharp band at 143 cm^{-1} , which can be mainly attributed to the E_g mode in anatase. Moreover, the Raman peaks at 402, 520 and 641 cm^{-1} are assigned to the B_{1g}^1 , A_{1g}^1 and E_g modes of anatase, respectively. Consequently, it is believed that the hybrid treatment will not change the inherent structures of the raw materials.

Figures 2(a) and (b) are the TEM images of as-prepared $\text{TiO}_2/\text{Bi}_2\text{Se}_3$ HNs. It is explicit that TiO_2 and 2D Bi_2Se_3 nanosheets had successfully combined together to form composite as expected (Figure. 2(a)), and there have quite a large amount of TiO_2 particles covering the surface of the Bi_2Se_3 nanosheets with a diameter of about 50 nm. The clear crystal lattice fringes with the d-spacing of 0.207 nm could be observed in Figure 2(b), which is well indexed to the (110) planes of Bi_2Se_3 . And the high-resolution TEM image demonstrates that the lattice spacing of TiO_2 is 0.352 nm, corresponding to the (1 0 1) facets of anatase, which is considered to possess high photocatalytic activity[36]. In order to further verify the rationality of the experiment, the elemental mapping (inset in Figure 2(b)) of the composition material obtained by EDS also indicates that the atomic ratios of the elements are close to their feeding molar ratios.

In order to research the PEC performance of the $\text{TiO}_2/\text{Bi}_2\text{Se}_3$ heterostructure, the samples are inspected through a PEC test in comparison to pure TiO_2 and Bi_2Se_3 . Figure 3(a) shows the fast and uniform photocurrent response for each turn-on and turn-off

operation for $\text{TiO}_2/\text{Bi}_2\text{Se}_3$, pure TiO_2 and Bi_2Se_3 at an applied potential 0V. It is interesting that the saturation current density is about $4.3 \mu\text{A cm}^{-2}$ for $\text{TiO}_2/\text{Bi}_2\text{Se}_3$, which is almost 2.5 times that of pure TiO_2 . In addition, the photocurrent is so stable that no significant photocurrent attenuation can be found. Therefore, the high light response performance of $\text{TiO}_2/\text{Bi}_2\text{Se}_3$ HNs can be attributed to the improved electron mobility of Bi_2Se_3 nanosheets and the addition of active sites. At the same time, the electron-hole recombination is inhibited due to the type-II band arrangement in the closed-connected $\text{TiO}_2/\text{Bi}_2\text{Se}_3$ HNs. In addition, the rapid charge migration and transport of Bi_2Se_3 nanosheets further extend the life of photogenerated electrons and holes, thereby increasing the photocurrent density. Obviously, this structure can not only make full use of the coupling between the two materials, but also fully utilize their respective advantages to maximize the photocatalytic performance of the materials. To better understand the improved electron transport performance of Bi_2Se_3 nanosheets, we also performed electrochemical impedance spectroscopy (EIS) in the Figure 3(b), which are displayed to further investigate the photocatalytic activity enhancement mechanism. The resistance between the surface of the electrode material and the interface layer is represented by the arc radius of the EIS spectrum curve. Therefore, the smaller the curve radius, the lower the impedance and the faster the charge transfer rate. It was apparent that with the introduction of Bi_2Se_3 nanosheets, the $\text{TiO}_2/\text{Bi}_2\text{Se}_3$ HNs has minimal electrical resistance due to the high electric conductivity of Bi_2Se_3 , which indicates that the high conductivity of Bi_2Se_3 plays an important role in improving the photocatalytic activity of $\text{TiO}_2/\text{Bi}_2\text{Se}_3$ HNs. In addition, the resistance of

the Bi₂Se₃ nanosheets is smaller than that of the pure TiO₂ probably because the advantage of metallic surface states characteristic on Bi₂Se₃ surface with great amounts of itinerant electrons exists. However, the photoelectric conversion efficiency of TiO₂ is much better than that of Bi₂Se₃. Therefore, the photocurrent increased as the increase of conversion efficiency, which is consistent with the test results of photocurrent density (Figure 3a).

Figure 3(c) shows the comparison of photoresponsivity under various bias potentials (0-0.5 V) under 100 mW/cm² illumination intensity. It should be noted that all of the curves show that the photocurrent can be effectively switched when the light source is turned on and off with the interval of 20 s. With the increase of external voltage, the photocurrent density of TiO₂/Bi₂Se₃ HNs increases continuously. Generally, the result of increasing of photocurrent density is attributed to the fact that the external potential applied on the photoelectrode promotes the separation of electron-hole pairs, thus their recombination was suppressed. The schematic diagram of photocatalytic hydrogen production process of TiO₂/Bi₂Se₃ HNs is proposed to reveal the possible mechanism of its photocatalytic enhancement, as shown in Figure 3(d). Based on the above analysis, it can be inferred that the enhanced photocatalytic activity of the TiO₂/Bi₂Se₃ HNs may be mainly due to the following factors: (i) the introduction of Bi₂Se₃ nanosheets increased active adsorption sites and photocatalytic reaction centers, (ii) the synergistic effect between TiO₂ and Bi₂Se₃ nanosheets can reduce the recombination of photogenerated electron-hole pairs, (iii) the relatively flat surface of Bi₂Se₃ nanosheets reduces the agglomeration of TiO₂. Under sunlight irradiation, both semiconductors are

excited, whose electrons excited from the valence band (VB) to the conduction band (CB), thus forming photoinduced electron-hole pairs. It is worth noting that the $\text{TiO}_2/\text{Bi}_2\text{Se}_3$ composite is a type-II band gap arrangement, which means that the edge of the conduction band of TiO_2 is located between the CB and the VB of Bi_2Se_3 [37]. When electron-hole pairs were generated by excitation, the photoelectron of Bi_2Se_3 can be transferred to the CB of TiO_2 , and the holes (h^+) of TiO_2 are injected into the VB of Bi_2Se_3 , which prevented the recombination of the electron-hole pairs. In addition, the photogenerated h^+ remaining in the TiO_2 will react with the substances in the surrounding electrolyte. In short, the photogenerated holes in the VB of TiO_2 can be directly transferred to the Bi_2Se_3 nanosheet, thereby effectively separating photogenerated electron-hole pairs, extending the life of charge carriers, as well as expanding more reaction sites[38].

As shown in Figure 4(a), we researched the photocurrent of the $\text{TiO}_2/\text{Bi}_2\text{Se}_3$ HNs under 100 mW/cm^2 illumination intensity and without bias potentials with the different concentrations of the Na_2SO_4 electrolytes. From 0.1 M to 1 M, the photocurrent density is increased from 3.9 to $5.9 \mu\text{A cm}^{-2}$ by more than 25% with good stability. Obviously, the response current increases as the concentration of electrolyte increases[39]. It well known that the photogenerated electrons could be transported to the electrode more efficiently and further reduced the interfacial resistance of materials with electrolyte under high concentration of electrolyte, thus the oxidation process is prevented at some extent which enables the composite sample to maintain both preferable photoresponse activity and environmental stability. In order to give a better understanding on the

factors related to electrochemical properties, such as electrolytes and their concentrations, can also play an important role in the photocatalytic behavior of $\text{TiO}_2/\text{Bi}_2\text{Se}_3$ HNs. The comparison of the photoresponsivity at various bias potentials were presented in Figure 4(b) from 0.1 to 1 M, respectively. From the results that the photocurrent density also increases with the increase of the bias voltage. Simultaneously, this result also verified the conclusion that the photocurrent density increased steadily due to the positive effect of the external potential, which can effectively accelerate the electron-hole separation and transportation. This is consistent with the conclusion of Figure 3(c).

It is well known that incident light intensity is also a vital factor affecting photocurrent density[40]. Figure 4(c) clearly shows that the photocurrent density of $\text{TiO}_2/\text{Bi}_2\text{Se}_3$ HNs increases as the irradiated light intensity increasing under 0.5 M electrolyte without bias potential. It is observed that the photocurrent density increases from 1.2 to 4.3 $\mu\text{A cm}^{-2}$ with the light intensity range from 60 to 100 mW cm^{-2} . Besides that, the comparison of the photoresponsivity at various light intensity are shown in Figure 4(d) from 0 to 0.6 V, respectively. It is noted that with the voltage increasing, the photocurrent density continuously increases, which is similar to the results of Figure 3(a) and 4(b). This phenomenon is in accordance with the fact that the positive potential will help to the separation of photogenerated electron-hole pairs and reduce their rate of recombination, thereby increasing the photocurrent density. The results show that the further improvement of the photocatalytic performance of $\text{TiO}_2/\text{Bi}_2\text{Se}_3$ HNs can be achieved by changing the external bias voltage, light intensity and electrolyte

concentration to obtain the best performance of photocurrent density and charge transfer speed.

In addition, in order to study the durability of $\text{TiO}_2/\text{Bi}_2\text{Se}_3$ HNs, the stability measurement has been evaluated, as shown in Figure 5(a). After illuminating for more than 1000 s, there is no obvious photocurrent attenuation in the primary stage, the photocurrent density even remains stable at the level of $4 \mu\text{A cm}^{-2}$ (nearly 95%). The reason for the decrease in photocurrent density is that the sample dropped slightly from the photoanode during the test. Furthermore, the inset of Figure 5(b) is the comparison of photocurrent at different concentrations before and after 25 cycles. Meanwhile, Figure 5(c) shows that the comparison of the photocurrent before and after the cycle of three kinds of light intensity under various bias. Obviously, the photocurrent of the as-prepared sample electrode has no significant distinction after processing 25 cycles. Immediately, we carried out 125 cycles (Figure 5(d)) of photocurrent test on the prepared samples, and found that only 10% drop of current density of the photocurrent density. The results demonstrate that the as-prepared $\text{TiO}_2/\text{Bi}_2\text{Se}_3$ HNs are conspicuously stable in this electrochemical process, while Bi_2Se_3 nanosheets are expected to be an ideal template for water splitting photocatalysts with excellent activity and stability.

4. Conclusion

In summary, the $\text{TiO}_2/\text{Bi}_2\text{Se}_3$ HNs composite has been successfully prepared by a facile method. The surface of TiO_2 and Bi_2Se_3 nanosheets have a strong inherent interaction in the composite material so that the charge can be effectively transferred

between them. Besides, Bi_2Se_3 nanosheets can provide additional reaction sites and form a type-II heterojunction with TiO_2 . More importantly, the photocurrent density represented excellent stability, maintaining a current density of 90% after 125 cycles. The conclusion can be summarized into the following three points: (i) the positive potential will hinder the recombination of photogenerated electron-hole pairs, (ii) the intensity of light will affect the number of photogenerated electrons, (iii) the solution concentration can increase the rate of charge transfer between electrodes. All in all, $\text{TiO}_2/\text{Bi}_2\text{Se}_3$ HNs exhibit excellent photocatalytic performance under photo-illumination, which are much better than pure TiO_2 and Bi_2Se_3 . This provides a facile route to gain higher photocatalytic efficiency and confirming its potential application as advanced PEC materials.

Conflicts of interest

There are no conflicts of interest to declare.

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Figure Captions

Figure 1. (a) X-ray diffraction pattern of $\text{TiO}_2/\text{Bi}_2\text{Se}_3$ HNs, (b) Raman spectra of $\text{TiO}_2/\text{Bi}_2\text{Se}_3$ HNs.

Figure 2. (a), (b) TEM images of the as-prepared $\text{TiO}_2/\text{Bi}_2\text{Se}_3$ HNs. Inset in (b) is the EDS pattern.

Figure 3. (a) Normalized amperometric $i-t$ cycles for PEC with different photoanodes: pure TiO_2 , pure Bi_2Se_3 and $\text{TiO}_2/\text{Bi}_2\text{Se}_3$ under 100 mW/cm^2 illumination. (b) EIS Nyquist plots of pure TiO_2 , pure Bi_2Se_3 and $\text{TiO}_2/\text{Bi}_2\text{Se}_3$. (c) Photocurrent density of $\text{TiO}_2/\text{Bi}_2\text{Se}_3$ under different biases (0–0.5 V). (d) Schematic diagram of photocatalytic process of the as-prepared $\text{TiO}_2/\text{Bi}_2\text{Se}_3$.

Figure 4. Photocurrent density of $\text{TiO}_2/\text{Bi}_2\text{Se}_3$ under different concentration of Na_2SO_4 (0.1, 0.5, 1 M) (a) at 0 V. (b) at 0–0.6 V; The comparison of the photocurrent density of $\text{TiO}_2/\text{Bi}_2\text{Se}_3$ under different illumination intensity (60, 80, 100 mW/cm^2) (c) at 0 V. (d) at 0–0.6 V.

Figure 5. (a) Cycling stability and long-term stability test of $\text{TiO}_2/\text{Bi}_2\text{Se}_3$ HNs. The comparison of the photocurrent before and after the 25 cycles under different concentration of Na_2SO_4 (0.1, 0.5, 1 M) (b) at 0 V. (c) at 0–0.6 V. (d) Photocurrent density of $\text{TiO}_2/\text{Bi}_2\text{Se}_3$ after different cycles.

Figure 1

Figure 1. (a) X-ray diffraction pattern of $\text{TiO}_2/\text{Bi}_2\text{Se}_3$ HNs, (b) Raman spectra of $\text{TiO}_2/\text{Bi}_2\text{Se}_3$ HNs.

Figure 2

Figure 2. (a), (b) TEM images of the as-prepared $\text{TiO}_2/\text{Bi}_2\text{Se}_3$ HNs. Inset in (b) is the EDS pattern.

Figure 3

Figure 3. (a) Normalized amperometric $i-t$ cycles for PEC with different photoanodes: pure TiO_2 , pure Bi_2Se_3 and $\text{TiO}_2/\text{Bi}_2\text{Se}_3$ under $100 \text{ mW}/\text{cm}^2$ illumination. (b) EIS Nyquist plots of pure TiO_2 , pure Bi_2Se_3 and $\text{TiO}_2/\text{Bi}_2\text{Se}_3$. (c) Photocurrent density of $\text{TiO}_2/\text{Bi}_2\text{Se}_3$ under different biases (0–0.5 V). (d) Schematic diagram of photocatalytic process of the as-prepared $\text{TiO}_2/\text{Bi}_2\text{Se}_3$.

Figure 4

Figure 4. Photocurrent density of $\text{TiO}_2/\text{Bi}_2\text{Se}_3$ under different concentration of Na_2SO_4 (0.1, 0.5, 1 M) (a) at 0 V. (b) at 0-0.6 V; The comparison of the photocurrent density of $\text{TiO}_2/\text{Bi}_2\text{Se}_3$ under different illumination intensity (60, 80, 100 mW/cm^2) (c) at 0 V. (d) at 0-0.6 V.

Figure 5

Figure 5. (a) Cycling stability and long-term stability test of $\text{TiO}_2/\text{Bi}_2\text{Se}_3$ HNs. The comparison of the photocurrent before and after the 25 cycles under different concentration of Na_2SO_4 (0.1, 0.5, 1 M) (b) at 0 V. (c) at 0-0.6 V. (d) Photocurrent density of $\text{TiO}_2/\text{Bi}_2\text{Se}_3$ after different cycles.

Figures

Figure 1
(a) X-ray diffraction pattern of TiO₂/Bi₂Se₃ HNs, (b) Raman spectra of TiO₂/Bi₂Se₃ HNs.

Figure 2
(a), (b) TEM images of the as-prepared TiO₂/Bi₂Se₃ HNs. Inset in (b) is the EDS pattern.

Figure 3

(a) Normalized amperometric $i-t$ cycles for PEC with different photoanodes: pure TiO_2 , pure Bi_2Se_3 and $\text{TiO}_2/\text{Bi}_2\text{Se}_3$ under 100 mW/cm^2 illumination. (b) EIS Nyquist plots of pure TiO_2 , pure Bi_2Se_3 and $\text{TiO}_2/\text{Bi}_2\text{Se}_3$. (c) Photocurrent density of $\text{TiO}_2/\text{Bi}_2\text{Se}_3$ under different biases (0–0.5 V). (d) Schematic diagram of photocatalytic process of the as-prepared $\text{TiO}_2/\text{Bi}_2\text{Se}_3$.

Figure 4

Photocurrent density of TiO₂/Bi₂Se₃ under different concentration of Na₂SO₄ (0.1, 0.5, 1 M) (a) at 0 V. (b) at 0-0.6 V; The comparison of the photocurrent density of TiO₂/Bi₂Se₃ under different illumination intensity (60, 80, 100 mW/cm²) (c) at 0 V. (d) at 0-0.6 V.

Figure 5

(a) Cycling stability and long-term stability test of TiO₂/Bi₂Se₃ HNs. The comparison of the photocurrent before and after the 25 cycles under different concentration of Na₂SO₄ (0.1, 0.5, 1 M) (b) at 0 V. (c) at 0-0.6 V. (d) Photocurrent density of TiO₂/Bi₂Se₃ after different cycles.