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Article

Amorphous TiO₂-modified CuBi₂O₄ Photocathode with enhanced photoelectrochemical hydrogen production activity

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ABSTRACT

In this study, CuBi₂O₄ photocathodes were prepared using a simple electrodeposition method for photoelectrochemical (PEC) hydrogen production. The prepared photocathodes were modified with amorphous TiO₂ and a Pt co-catalyst, which resulted in the formation of CuBi₂O₄/TiO₂ p-n heterojunctions, and enhanced the activities of the as-prepared photocathodes. The novel Pt/TiO₂/CuBi₂O₄ photocathode exhibited a photocurrent of 0.35 mA/cm² at 0.60 V vs. Reversible Hydrogen Electrode (RHE), which was nearly twice that of the Pt/CuBi₂O₄ photocathode. The present study provides a facile method for increasing the efficiency of photocathodes and provides meaningful guidance for the preparation of high-performance CuBi₂O₄ photocathodes.

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1. Introduction

Recently, due to increasing energy and environment problems, the development of energy-saving and emission-reducing technology has become urgent. The most efficient method which can solve the current dilemma is the development and implementation of cleaner energy. Solar energy has attracted significant attention for its green, widespread, and inexhaustible characteristics. In recent years, photocatalytic technology has become an increasingly popular research topic due to its capability of converting solar into chemical energy, degrading organic pollutants, and producing organic fuel [1–8]. In the field

of photocatalysis, photoelectrochemical (PEC) water-splitting is considered to be a promising solution which could provide enough clean energy and satisfy the increasing energy demands of modern society [11,12]. The biggest challenge to date for PEC water-splitting is the preparation of highly active photoanodes and photocathodes. Though a large number of n-type semiconductor materials, such as BiVO₄, ZnO, and Fe₂O₃, have been developed for preparing photoanodes [13–15], only a few candidates including p-Si, Cu₂O, Cu₂ZnSnS₄, and CuIn_xGa_{1-x}Se [16–19] have been reported as p-type semiconductors for photocathodes. However, these materials have some unavoidable problems which limit their applications and include high

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cost, difficult preparation, and instability. The exploration of photocathode materials is crucial for further developments in the field of PEC water-splitting.

CuBi₂O₄ is a p-type semiconductor which is naturally stable and exhibits a band gap of approximately 1.70 eV with excellent visible light responses, allowing it to utilize a significant part of light energy [20–23]. The conduction band minimum (CBM) of CuBi₂O₄ is estimated to be at a more negative potential than the thermodynamic potential for H₂ production, and its valence band maximum (VBM) at a more positive potential than that of p-type Si or Cu₂O. This appropriate band gap structure makes it a promising photocathode material. Few studies have been reported for PEC hydrogen production using CuBi₂O₄ photocathodes. However most of them focused on synthetic methods and theoretical calculations [21–23], and not on promoting interfacial carrier separation.

In this study, the p-type CuBi₂O₄ photocathodes were prepared using a simple electrochemical synthesis method. The CuBi₂O₄/TiO₂ p-n heterojunction was first prepared by spin-coating a TiO₂ layer on the surface of the CuBi₂O₄ photocathodes. The experiment results showed that the activity of the prepared CuBi₂O₄ photocathode was substantially improved by the formation of the CuBi₂O₄/TiO₂ heterojunction. It is believed that the successful construction of Pt/CuBi₂O₄/TiO₂ will act as a guide for future modification studies of CuBi₂O₄ photocathodes.

2. Experimental

2.1. Chemicals

All chemicals were of analytical grade and were used without further purification.

2.2. Preparation of the photocathodes

A typical three-electrode system composed of an F-doped Tin Oxide (FTO) working electrode, Ag/AgCl (saturated KCl) reference electrode, and Pt counter electrode was used. Preparation of the Cu/Bi metal film was achieved via electrodeposition in a dimethyl sulfoxide (DMSO) electrolyte solution containing 20 mmol/L Bi(NO₃)₃, 10 mmol/L Cu(NO₃)₂, and 100 mmol/L KClO₄. Deposition was performed for 10 cycles at 0.05 C/cm² ($E = -1.5$ V vs Ag/AgCl) for each cycle. A total charge of 0.50 C/cm² was applied. Subsequently, the Cu/Bi films were heated at 500 °C for 3 h in air (ramping rate = 3 °C/min) to form CuBi₂O₄ [27]. After annealing, the organic residue from DMSO was removed from the surface.

Preparation of Pt/CuBi₂O₄ photocathodes. Pt was deposited onto the CuBi₂O₄ films through photoelectrochemical reduction in 20 vol% methanol aqueous solution containing 0.3 mmol/L H₂PtCl₆. A 300 W Xe arc lamp was used as the light source and was equipped with an AM 1.5G filter. CuBi₂O₄ photoelectrodes were used as working electrodes. The deposition amount was approximately 0.02 C/cm² at $E = 0$ V vs Ag/AgCl.

Deposition of TiO₂. The sol-gel precursor was prepared by adding 0.3 mL of isopropyl titanate to 20 mL ethanol under

stirring. Subsequently, 250 μ L of the precursor was dropped on the CuBi₂O₄ photoelectrodes for spin-coating (1000 r/min, 30 s) several times and the photoelectrodes were annealed at different temperatures for 1 h.

Preparation of TiO₂ powder. The sol-gel precursor was dried in glass beakers and annealed at different temperatures. The preparation of the Pt/TiO₂/CuBi₂O₄ photocathodes was performed using the same method as that of the Pt/CuBi₂O₄ photocathodes.

2.3. Characterization of the photocathodes

Morphology observation was performed using an S-4800 field emission scanning electron microscope (FE-SEM, Hitachi, Japan). The purity and crystallinity of the CuBi₂O₄ and TiO₂/CuBi₂O₄ electrodes were examined by X-ray diffraction (XRD) using a Bruker AXS D8 ADVANCE diffractometer (Cu K_{α} X-ray radiation, $\lambda = 0.154056$ nm). The light source was a 300 W Xe arc lamp (PLS-SXE 300, Beijing Trusttech Co. Ltd.) equipped with an AM 1.5 filter (100 mW/cm²). UV-vis diffuse reflectance spectra were recorded using a Shimadzu UV 2550 spectrophotometer equipped with an integrating sphere, and BaSO₄ was used as a reference. The X-ray photoelectron spectroscopy were got through Thermo Scientific ESCALAB 250.

Photoelectrochemical measurements were performed using an electrochemical analyzer (CHI660C, CH Instruments) with a standard three-electrode system in 0.1 mol/L NaOH electrolyte solution. The reference electrode was Ag/AgCl (saturated KCl), the counter electrode was a Pt plate, and the prepared photocathodes were used as working electrodes.

3. Results and discussion

XRD was used to investigate the phase structure of the samples. Fig. 1 shows the XRD of the CuBi₂O₄ sample prepared without a spin coated TiO₂ layer. The observed diffraction peaks at 20.87°, 28.01°, 29.68°, 30.74°, and 33.26° arose from (200), (211), (220), (002), and (310), respectively which cor-

Fig. 1. XRD patterns of the TiO₂/CuBi₂O₄ sample.

respond to JCPDS No. 72-493. The obvious peak at approximately 26.4° is characteristic of the FTO substrate. The XRD patterns of the $\text{TiO}_2/\text{CuBi}_2\text{O}_4$ photocathodes treated at different temperatures are shown in Fig. S1 and exhibited no obvious TiO_2 peaks.

To clarify the status of the TiO_2 on CuBi_2O_4 , we prepared TiO_2 using the same sol-gel precursor under different temperature heat treatment conditions, as shown in Fig. S2. Only when the temperature was raised over 400°C did the reaction products show good crystallinity, indicating that the TiO_2 obtained at 200°C on CuBi_2O_4 was amorphous.

The surface morphologies and elemental distributions of the CuBi_2O_4 and $\text{TiO}_2/\text{CuBi}_2\text{O}_4$ photocathodes were characterized by SEM, as shown in Fig. 2. From the images of the CuBi_2O_4 photocathodes shown in Fig. 2(a)–(c), we can see that the CuBi_2O_4 film was composed of uniform nanoparticles with a diameter of 100–150 nm. Fig. 2(d)–(f) show the SEM images of the $\text{TiO}_2/\text{CuBi}_2\text{O}_4$ photocathodes after modification with a TiO_2 layer and annealing at 200°C . The boundary of the nanoparticles was blurred and the dispersibility deteriorated. The elemental distribution in the $\text{TiO}_2/\text{CuBi}_2\text{O}_4$ photocathodes is shown in Fig. 2(g)–(i). The mapping results indicate that the TiO_2 layer was uniformly deposited on the surface of the CuBi_2O_4 film. The morphologies of photocathodes treated at other temperatures are shown in Fig. S3, and no obvious difference was observed. The thickness of the $\text{TiO}_2/\text{CuBi}_2\text{O}_4$ - 200°C photocathode was determined as shown in Fig S4. From the results, we can see that the thickness of the $\text{TiO}_2/\text{CuBi}_2\text{O}_4$ layer was approximately 350 nm.

The optical properties of the prepared samples were characterized by UV-vis diffuse reflectance spectroscopy, as shown in Fig. 3. From their light absorption properties, it can be concluded that the CuBi_2O_4 samples showed excellent light response in the visible region. The light absorption of the CuBi_2O_4 photocathode was not influenced after modifying the TiO_2 layer. The outstanding light response of CuBi_2O_4 highlights its potential as an outstanding photocathode material.

Herein, the coating of the TiO_2 layer was used to promote the transmission of electrons generated from CuBi_2O_4 . The effect of TiO_2 layer thickness is a key factor for photocathode

Fig. 3. UV-visible light absorption spectra of the CuBi_2O_4 and $\text{TiO}_2/\text{CuBi}_2\text{O}_4$ - 200°C photocathodes.

activity. The $\text{TiO}_2/\text{CuBi}_2\text{O}_4$ samples with different thicknesses were fabricated using different spin-coating times, as shown in Fig. 4(a). From the current-potential curves, it is clear that the photoelectric activity initially increases and then decreases with increasing spin-coating times. The $\text{Pt}/\text{TiO}_2/\text{CuBi}_2\text{O}_4$ photocathodes showed the best performance at four cycles of spin-coating. Fig. 4(b) shows the photocurrent-time curves of the $\text{Pt}/\text{CuBi}_2\text{O}_4$ and $\text{Pt}/\text{TiO}_2/\text{CuBi}_2\text{O}_4$ photocathodes prepared with four cycles of spin-coating. Fig. 4(a) shows that the photocurrent onset potentials of the $\text{Pt}/\text{CuBi}_2\text{O}_4$ and $\text{Pt}/\text{TiO}_2/\text{CuBi}_2\text{O}_4$ photoelectrodes are approximately 1.15 and 1.20 V, respectively, and that the TiO_2 layer did not significantly affect the onset potential. The photocurrent densities of the $\text{Pt}/\text{CuBi}_2\text{O}_4$ and $\text{Pt}/\text{TiO}_2/\text{CuBi}_2\text{O}_4$ electrodes at 0.60 V vs RHE were 0.22 and 0.35 mA/cm^2 , respectively. The comparison of the Photocurrent-time curves of $\text{Pt}/\text{CuBi}_2\text{O}_4$ and $\text{Pt}/\text{TiO}_2/\text{CuBi}_2\text{O}_4$ at 0.60 V vs RHE showed a more significant effect of the TiO_2 layer (Fig. 4(b)). For the Cu-based photocathodes, photoinduced corrosion is commonly encountered and difficult to solve. In these experiments, the pristine $\text{Pt}/\text{CuBi}_2\text{O}_4$ photocathode showed an initial photocurrent density of 0.22 mA/cm^2 , which decreased to 0.20 mA/cm^2 over 100 s of reaction, corresponding to a 9% decrease. In contrast, $\text{Pt}/\text{TiO}_2/\text{CuBi}_2\text{O}_4$ exhibited a pristine photocurrent density of 0.39 mA/cm^2 , which is 1.77 times that of the $\text{Pt}/\text{CuBi}_2\text{O}_4$ photocathode. In addition, the crystallinity of TiO_2 was examined, and the results are shown in Fig. 4(c). The activity of the $\text{Pt}/\text{TiO}_2/\text{CuBi}_2\text{O}_4$ photocathodes decreased with increasing annealing temperature, and the amorphous TiO_2 modified photocathodes prepared at 200°C showed the best activity. Compared to that of the crystalline TiO_2 , amorphous TiO_2 has a disordered structure resulting in a larger surface and more active sites [30,31]. This leads to better contacting both for the CuBi_2O_4 and Pt and more efficient carrier separation. The Faradic efficiency and stability of the photocathode in photoelectrochemical H_2 generation was also measured, as shown in Fig S5. The total Faradic efficiency over 60 min was approximately 96%, and the normalized current indicated the high stability of

Fig. 2. SEM images of the CuBi_2O_4 (a–c) and $\text{TiO}_2/\text{CuBi}_2\text{O}_4$ - 200°C samples, and the mapping results of $\text{TiO}_2/\text{CuBi}_2\text{O}_4$.

Fig. 4. (a) Current-potential curves with different TiO₂ layer thicknesses (annealed at 200 °C, scanning rate of 10 mV/s). (b) Photocurrent-time curves of the Pt/TiO₂/CuBi₂O₄ and Pt/TiO₂/CuBi₂O₄ photocathodes at 0.60 V vs. RHE in 0.1 mol/L NaOH. (c) Current-potential curves of the Pt/TiO₂/CuBi₂O₄ photocathodes annealed at different temperatures. (d) IPCE curves of the Pt/CuBi₂O₄ and Pt/TiO₂/CuBi₂O₄-200 °C photocathodes measured at 0.60 V vs. RHE in 0.1 mol/L NaOH.

the photocathode.

The incident photon to current efficiency (IPCE) of the photoelectrodes was characterized at 0.60 V vs. RHE in 0.1 mol/L NaOH electrolyte (Fig. 4(d)). The IPCE of the CuBi₂O₄ photocathode at different wavelengths shows similar tendencies and increased significantly after decorating TiO₂ on the photocathode. The prepared Pt/CuBi₂O₄ and Pt/TiO₂/CuBi₂O₄-200 °C photocathodes showed their highest IPCE values of 1.4% and 2.9%, respectively, at 400 nm. These photoelectrochemical tests indicated that modifying amorphous TiO₂ improved the activity of the CuBi₂O₄ photocathode.

To further understand the role of TiO₂ in the improved PEC performance, electrochemical impedance spectroscopy (EIS) analysis and Mott-Schottky experiments were used to investigate the interfacial properties of the Pt/CuBi₂O₄ and Pt/TiO₂/CuBi₂O₄ photocathodes. The diameter of the semicircle in the EIS measurements reflects the resistance of electron transfer, which can directly indicate the photogenerated electron transfer efficiency at the interface between the electrodes and electrolyte solution [24,25]. Fig. 5(a) shows the EIS curves of the Pt/CuBi₂O₄ and Pt/TiO₂/CuBi₂O₄ photocathodes measured in 0.1 mol/L NaOH under light illumination. The Pt/TiO₂/CuBi₂O₄-200 °C photocathode exhibited a smaller EIS

curve diameter compared to that of the Pt/CuBi₂O₄ photocathode. This indicates that the resistance between the Pt/TiO₂/CuBi₂O₄-200 °C photocathode and electrolyte interface is smaller than that of the Pt/CuBi₂O₄ photocathode and electrolyte interface, allowing photogenerated electrons to transfer more efficiently upon modification with TiO₂. Mott-Schottky analysis was used to confirm the flat band potential (E_{fb}) and understand the changing interface, using a 1 kHz frequency and 10 mV amplitude. For p-CuBi₂O₄, a negative slope was obtained, as shown in Fig. 5(b), and the intersection point with the x-axis represents the E_{fb} which was approximately 1.47 V. A negative shift of 0.11 V was observed after deposition of amorphous TiO₂. From previous reports regarding the band gap structure of CuBi₂O₄ [20–23], we can conclude that n-TiO₂ and p-CuBi₂O₄ construct a single kind of p-n heterojunction at the interface, which promotes carrier separation.

The internal elemental composition and the chemical state of the Pt/CuBi₂O₄ and Pt/TiO₂/CuBi₂O₄ photocathodes were further analyzed by X-ray photoelectron spectroscopy (XPS). Fig. 6(a)–(d) show the XPS spectra of Cu 2p, Bi 4f, O 1s, and Ti 2p, respectively. In the XPS spectra of the CuBi₂O₄ photocathode shown in Fig. 6(a), the peaks at 934.3 and 954.1 eV correspond to the binding energies of Cu 2p_{3/2} and Cu 2p_{1/2}, respec-

Fig. 5. (a) Nyquist plots of the $\text{Pt}/\text{CuBi}_2\text{O}_4$ and $\text{Pt}/\text{TiO}_2/\text{CuBi}_2\text{O}_4-200^\circ\text{C}$ photocathodes. The EIS was measured at 0.60 V vs. RHE in 0.1 mol/L NaOH under light irradiation. (b) Mott-Schottky plots of the $\text{Pt}/\text{CuBi}_2\text{O}_4$ and $\text{Pt}/\text{TiO}_2/\text{CuBi}_2\text{O}_4-200^\circ\text{C}$ photocathodes.

Fig. 6. XPS spectra of the CuBi_2O_4 and $\text{TiO}_2/\text{CuBi}_2\text{O}_4$ photocathodes. (a) $\text{Cu } 2p$; (b) $\text{Bi } 4f$; (c) $\text{O } 1s$; (d) $\text{Ti } 2p$.

tively, and the peaks at 942.3 and 962.4 eV correspond to satellite peaks of $\text{Cu } 2p$. The $\text{Cu } 2p$ peak positions and the presence of satellite peaks confirm that the copper in CuBi_2O_4 exists as Cu^{2+} . The $\text{Bi } 4f$ peaks located at 158.8 and 164.1 eV were assigned to the $\text{Bi } 4f_{7/2}$ and $\text{Bi } 4f_{5/2}$, respectively, of Bi^{3+} . The peak at 529.8 eV originates from the oxygen in the crystal lattice and the higher binding energy of 531.6 eV indicates the presence of oxygen defects or absorbed chemical oxygen. Two weak peaks were observed at approximately 458.0 and 464.9 eV, originating from $\text{Ti } 2p$ in TiO_2 [26–28]. The $\text{Cu } 2p$, $\text{Bi } 4f$, and $\text{O } 2p$ peaks

showed negligible changes after TiO_2 layer decorating, which indicates that the TiO_2 deposition did not destroy the CuBi_2O_4 layer and increased the activity of the photocathode. In addition, FTIR spectra were used to investigate the surface of the $\text{TiO}_2/\text{CuBi}_2\text{O}_4$ electrode, as shown in Fig. S6. The peak at approximately 1070 cm^{-1} was attributed to oxygen deficiency, and with increasing annealing temperature, the peak became weaker, indicating the loss of oxygen deficiency at higher temperatures [29].

Based on the above experimental results, we proposed a

Fig. 7. Photoelectrochemical hydrogen production mechanism of the Pt/TiO₂/CuBi₂O₄ photocathode.

possible mechanism to explain the higher efficiency of the Pt/TiO₂/CuBi₂O₄ photocathodes for PEC hydrogen production, as shown in Fig. 7. After modifying with the n-type semiconductor TiO₂, a kind of type II p-n CuBi₂O₄/TiO₂ heterojunction formed. The heterojunction aided in the separation of electrons and holes generated by the CuBi₂O₄ film. As a result, the Pt/TiO₂/CuBi₂O₄ photocathode showed much better performance than that of the Pt/CuBi₂O₄ photocathode.

4. Conclusions

In summary, a simple electrodeposition method was used to prepare highly crystalline CuBi₂O₄ films on FTO glass for PEC hydrogen production. The CuBi₂O₄ photocathodes were modified with an amorphous n-TiO₂ layer by spin-coating, and with Pt by PEC reduction. Characterization of the photoelectrodes indicated that the TiO₂ layer played a key role in the separation of the photogenerated electrons and holes because of the p-n heterojunction formed. A suitable thickness of TiO₂ greatly enhanced the activity of CuBi₂O₄ photocathodes. This study provides a reference for the preparation of high-performance CuBi₂O₄ photocathodes.

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Graphical Abstract

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CuBi₂O₄ photocathodes were prepared for PEC hydrogen production. The fabricated photocathodes were modified with amorphous TiO₂ and Pt co-catalysts, which resulted in the formation of p-n heterojunctions, and enhanced the activities.

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非晶TiO₂修饰CuBi₂O₄光阴极增强其光电化学产氢活性

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摘要: 光催化作为太阳能利用领域的研究热点引起了广泛的关注。其中, 光电化学技术能够通过分解水提供清洁的氢能源, 因此被认为是一种潜在的新能源制造方式。在光电化学分解水产氢的过程中, 最重要的是高效光电极的制备。一系列n型半导体材料已被广泛地报道并用作光阳极, 如BiVO₄, ZnO, Fe₂O₃等。然而对于光阴极材料, 其可选择性则较少。CuBi₂O₄是一种天然矿物, 具有廉价易得以及化学性质稳定的特性, 而且是一种p型半导体材料, 因此能够用于制备光阴极; 另外因为其强的可见光响应(1.70 eV), 所以具有广泛的应用前景。目前对于CuBi₂O₄光阴极研究主要集中在合成和理论计算方面, 而对于如何促进界面处的载流子分离研究较少。

本文通过一种简单的电沉积方法成功制备出CuBi₂O₄光阴极, 然后利用非晶TiO₂和助催化剂Pt进行修饰后将其用于光电化学产氢。由于形成了CuBi₂O₄/TiO₂ p-n结, 因此其光阴极活性得到增强。新的Pt/TiO₂/CuBi₂O₄光阴极在0.60 V偏压处的光电流为0.35 mA/cm², 其数值约为Pt/CuBi₂O₄光阴极的两倍。XRD结果表明, 我们制备的CuBi₂O₄为纯相且结晶性较好, 其表面修饰的TiO₂为非晶相的。SEM结果表明, CuBi₂O₄电极层由100–150 nm的颗粒构成。紫外-可见吸收光谱表明, 制备的CuBi₂O₄光电极拥有良好的可见光吸收性质, 而且TiO₂修饰未对CuBi₂O₄的光吸收产生明显的影响。XPS结果表明, 修饰TiO₂并未对CuBi₂O₄电极造成成分上的破坏。光电化学测试表明, 修饰TiO₂层厚度和结晶性会影响光电极的最终活性。修饰四层TiO₂和退火200 °C的样品具有最好的活性。

另外稳定性测试也表明, 修饰非晶TiO₂的CuBi₂O₄光阴极具有良好的稳定性。在IPCE测试中, Pt/TiO₂/CuBi₂O₄光阴极在其光响应范围内均比Pt/CuBi₂O₄光阴极表现出更高的效率。阻抗结果测试中Pt/TiO₂/CuBi₂O₄光阴极具有更小的阻抗, 这表明其载流子传输更加高效。在Mott-Shetty测试中, Pt/TiO₂/CuBi₂O₄和Pt/CuBi₂O₄光阴极都表现出p型半导体性质, 但是Pt/TiO₂/CuBi₂O₄具有更负的平带电位, 这表明修饰的TiO₂仍具有n型半导体材料的特性, 并与p型的CuBi₂O₄形成p-n结, 从而促进了载流子分离效率。

关键词: 光电化学产氢; CuBi₂O₄; 非晶TiO₂; p-n结; 载流子分离

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