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Artificial all-solid-state system by RGO bridged Cu_2O and Bi_2WO_6 for Z-scheme H_2 production and tetracycline degradation

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ABSTRACT

With the development of visible-light-driven photocatalytic systems, the Z-scheme system has been paid more attention for water-splitting and contaminants degradation in an effort to the full utilization of superior band potential between two different semiconductors. Here we present systemic investigation of the reduced graphene oxide (RGO)-based composites, including RGO-Cu_2O, RGO-Bi_2WO_6, RGO-Cu_2O/Bi_2WO_6, Cu_2O/Bi_2WO_6 heterojunction and physical mixed RGO + Cu_2O + Bi_2WO_6, to give a clear demonstration of the Z-scheme photocatalytic mechanism. The three-component RGO-Cu_2O/Bi_2WO_6 composite showed the highest photocatalytic activity on water splitting, which is about 3 times and 4 times that of RGO-Cu_2O and Cu_2O respectively. And it also exhibited an excellent photocatalytic performance with a 86% degradation rate for tetracycline that is about 3 (6) times as high as that of pure Cu_2O (Bi_2WO_6). These results demonstrate that the construction of RGO-Cu_2O/Bi_2WO_6 Z-scheme system is beneficial to water splitting and pollutant degradation for which the superior band potential of Cu_2O and Bi_2WO_6 are fully utilized. This work not only reports a new Z-scheme system of RGO-Cu_2O/Bi_2WO_6 but also provides a guide to the design of RGO-based photocatalysts.

1. Introduction

The conversion from the endless solar energy to the clean hydrogen energy with the photocatalytic technology is a potential task [1–3]. a variety of photocatalytic systems have been developed to enhance energy conversion efficiency for which the most hydrogen-generating semiconductors are inefficient. Among them, the Z-Scheme photocatalytic system rooting from the photosynthesis in natural green plants has attracted more and more attention in recent years for the preeminent charge transfer efficiency and excellent redox potential, which is composed of two distinct narrow-bandgap semiconductors and a shuttle redox medium [4–7]. The donor/acceptor pair, such as IO_3^-/I^- [8–11], Fe^{3+}/Fe^{2+} [12–15] and etc., is usually used as the conventional redox medium for overall water splitting. Yasuyoshi et al. built a Z-scheme photocatalytic system made up of of Ru/$SrTiO_3$:Rh and $BiVO_4$ powders for water-splitting, in which $[Co(bpy)_3]^{3+/2+}$ and $[Co(phen)_3]^{3+/2+}$ were used as the electron mediators [16]. However, the traditional Z-scheme system using the donor/acceptor pair cannot be applied to the degradation of pollutants and is also restricted by to the pH of reaction solution. Since the all-solid-state TiO_2-Au-CdS system was reported [17], more and more solid conductive substances are used as the charge-transferred medium to overcome those defects of traditional system, such as metals (Au [18–20], Ag [21–24], Cu [25,26] and Pt [27,28]) and non-metals (graphene [29–33] and carbon nanotubes [34,35]). For instance, the Z-Scheme Ag_3PO_4/Ag/WO_{3-x} photocatalyst prepared by Bu et al. via an in situ deposition method exhibited the enhanced photocatalytic degradation performance than the single Ag_3PO_4 and WO_{3-x} [24], where the Ag nanoparticles served as carrier-transfer centers, prolonging the carrier lifetime of Ag_3PO_4 and WO_{3-x}. Iwase et al. built a Z-scheme system employing a H_2-evolving component (Ru/$SrTiO_3$:Rh) and a O_2-evolving component ($BiVO_4$), which were combined with reduced graphene oxide [31]. The system showed a huge improvement in water-splitting under visible-light irradiation, resulting from greater consumption of electron-hole pairs throughout the photocatalysis process. However, the selection and development of semiconductors with enhanced hydrogen generation and oxygen evolution are quite important to the photocatalysis.

Among the known photocatalysts, the p-type Cu_2O has drawn significant attentions in the realm of photocatalysis due to its low toxicity, rich reserve and simple preparation [36–39]. The Cu_2O possesses a

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narrow band gap of ~2.2 eV with a higher conduction band position than the standard hydrogen electrode. Thus, the conduction band potential of Cu_2O is negative enough to have a strong reducing capability for hydrogen production and pollutants degradation [40–45]. Bi_2WO_6 is a typical n-type semiconductor with a band gap of ~2.7 eV and is wildly accepted as a promising candidate photocatalyst owning to its nontoxicity, well chemical stability, visible-light response [46–48]. Bi_2WO_6 is also one of the reported oxygen evolution materials because of its positive valence band potential [47,48]. Moreover, the H_2-evolving Cu_2O matches well with the O_2-evolving Bi_2WO_6 in terms of the energy band structure to artificially design a Z-scheme photocatalytic system. Besides, due to excellent transparency, large surface area and electron mobility, reducing graphene oxide (RGO) is naturally selected as a solid medium for conducting electrons between Cu_2O and Bi_2WO_6.

In this paper, Cu_2O and Bi_2WO_6 were selected to build an all-solid-state Z-scheme system with RGO as a carrier medium. Those RGO-Cu_2O/Bi_2WO_6 composites were prepared through a simple ethanol-thermal method. The photocatalytic performance of RGO-Cu_2O/Bi_2WO_6 composites was investigated on water-splitting and tetracycline (TC) degradation by regulating the mass ratio between Cu_2O, Bi_2WO_6 and RGO. Moreover, the corresponding Z-scheme-based electron transfer route was further discussed.

2. Experimental section

2.1. Chemicals and materials

Flake graphite, P_2O_5, $K_2S_2O_8$, H_2O_2, H_2SO_4, HCl, $KMnO_4$, Bi$(NO_3)_3{\cdot}5H_2O$, Cu$(NO_3)_2{\cdot}3H_2O$, $Na_2WO_4{\cdot}2H_2O$, NaOH, HNO_3 and C_2H_5OH were purchased from Sinopharm Chemical Reagent Co., Ltd (Beijing, China).

2.2. Synthesis of graphene oxide (GO)

GO was synthesized via a modified Hummer's method.

2.3. Synthesis of Bi_2WO_6

Pure Bi_2WO_6 was synthesized by the hydrothermal method as following: First, 5.0×10^{-3} mmol of Bi$(NO_3)_3{\cdot}5H_2O$ and 2.5×10^{-3} mmol of $Na_2WO_4{\cdot}2H_2O$ were separately stirred and dissolved in two 10 mL of distilled water, forming solution A and solution B, respectively. Then, solution B was dropwisely added into solution A to form a mixture suspension. The pH of the obtained suspension was adjusted to 3 using the HNO_3 solution (1 M). The acid mixture was transferred to a 50 mL Teflon-lined stainless steel autoclave and maintained at 150 °C for 12 h. Afterwards, the white product was filtered, washed repeatedly with water and dried in vacuum.

2.4. Synthesis of RGO-Cu_2O/Bi_2WO_6

The RGO-Cu_2O/Bi_2WO_6 nanocomposites were prepared via a simple solvothermal reduction process, as illustrated in Scheme 1. First, 50 mg of GO sheet was dissolved in 15 mL of pure ethanol by ultrasound for 2 h. Second, 0.4728 g of Cu$(NO_3)_2{\cdot}3H_2O$ was dissolved in the black GO solution by stirring constantly. Then the pH of mixed solution was slowly adjusted to 8 using NaOH aqueous solution (6 M), forming a uniform dark blue suspension. Subsequently, 10 mL of Bi_2WO_6 (0.06 g) ethanol solution was slowly added to the above suspension, and the whole mixture was moved to a 50 mL Teflon-lined stainless steel autoclave and maintained at 180 °C for 12 h. Finally, the product was filtered, washed repeatedly with water and ethanol, and dried in vacuum. The product was denoted by G50-7/3, since the GO dosage was 50 mg and the mass ratio of Cu_2O to Bi_2WO_6 was7:3. In this way, the different RGO-Cu_2O/Bi_2WO_6 photocatalysts were synthesized by controlling the mass ratio of Cu_2O, Bi_2WO_6 and the content of RGO.

2.5. Characterization

The X-ray diffraction (XRD) measurement was measured though a D/MAX-2500 X-ray powder diffractometer. The transmission electron microscope (TEM) and high-resolution transmission electron microscope (HRTEM) were obtained a JEM-2100 electron microscope (JEOL, Japan). The UV–vis diffused reflectance spectroscopy (DRS) analysis was recorded on an UV–vis spectrophotometer (UV-2450, Shimadzu, Japan). The X-ray photoelectron spectroscopy (XPS) were obtained using a Thermo ESCALAB 250X (America) electron spectrometer. The photoluminescence (PL) spectra were performed on a Perkin-Elmer LS 55. The electrochemical impedance spectroscopy and Mott–Schottky measurements were operated in a standard three-electrode system with Ag/AgCl electrode as the reference electrode and Pt wire as the counter electrode. The as-prepared products were used as the working electrodes. The electrolyte was adopted with 1 M Na_2SO_4 solution (PH = 7) and the working electrodes were prepared by FTO plate, where the samples (30 mg) is uniformly rotated using absolute ethanol (0.5 mL), polyvinylpyrrolidone (50 mg) and oleic acid (15 μl). The electrochemical impedance spectra were achieved by a CHI 760E electrochemical workstation at a frequency from 1000 kHz to 0.01 Hz. Mott–Schottky measurement was conducted from −1.5 V to 1.5 V

2.6. TC degradation

TC was used for the test of the photocatalytic performance over RGO-Cu_2O/Bi_2WO_6 composites with visible light illumination. The 300 W xenon lamp was used as a light source and the UV cut-off filter was equipped for visible light. 50.0 mg of photocatalyst was dissolved in 90 mL of distilled water by ultrasound in a quartz glass bottle and then 10 mL of TC solution (100 mg/L) was add. Then the whole suspension solution was stirred in a dark place for 30 min until the adsorption–desorption equilibrium between the catalyst and TC was reached. Next, 5 mL of the suspension was collected before the light was turned on and every 20 min after the light was turned on. And the TC concentration of those suspensions was analyzed by a UV–vis spectrophotometer after centrifugation. During the degradation, the whole system was maintained at 20 °C through water cooling device.

2.7. Hydrogen production

The water-splitting experiments were operated in a customized hydrogen production system. The visible light was selected as an illumination light and obtained from a xenon lamp with a 420 nm cut-off filter. In this paper, 50 mg catalyst was dissolved in 100 mL of distilled water by ultrasound in reactor. Then, the whole system was slowly vacuumed and was maintained at this negative pressure throughout the reaction. After the light source was placed above the reactor, the xenon lamp was turn on. The photogenerated gas samples were collected every 1 h and analyzed by a gas chromatograph (GC-7900, AuLight, China, TCD, N_2 as a carrier gas). Moreover, the whole hydrogen production system was was maintained at 5 °C via a condensing machine.

3. Results and discussion

XRD analysis was used for the investigation on crystalline phase of the samples. Fig. 1a displays the XRD patterns of RGO-Cu_2O, RGO-Bi_2WO_6 and RGO-Cu_2O/Bi_2WO_6 composites. As shown in Fig. 1a, the diffraction peaks of RGO-Cu_2O at 29.6°, 36.5°, 42.4°, 61.5° and 73.7° were respectively ascribed to the (1 1 0), (1 1 1), (2 0 0), (2 2 0) and (3 1 1) crystal planes of Cu_2O, according with JCPDS No. 75-1531 [43–45]. The main characteristic peaks of RGO-Bi_2WO_6 at 28.3°, 32.7°, 47.1° and 55.8° assigned to the (1 1 3), (2 0 0), (2 2 0) and (3 1 3) crystal planes of Bi_2WO_6, corresponding to JCPDS No. 39-0256 [46–48]. And those of RGO-Cu_2O/Bi_2WO_6 were well consistent with the JCPDS (75-1531) and JCPDS (39-0256). Owing to the low content of RGO, there