Visible-light-driven Ag-decorated g-C₃N₄/Bi₂WO₆ Z-scheme composite for high photocatalytic activity

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Abstract: A novel Z-scheme Ag-decorated g-C₃N₄/Bi₂WO₆ composite is successfully synthesized by introducing Ag NPs on the interface of g-C₃N₄/Bi₂WO₆ composite. The Ag-decorated g-C₃N₄/Bi₂WO₆ sample exhibits much higher photocatalytic activity than g-C₃N₄/Bi₂WO₆ composite on the degradation of Rhodamine B under visible light. The significantly enhanced catalytic efficiency could be attributed to the Z-scheme transfer mechanism of photogenerated electron-hole pairs, which was confirmed by investigating the morphology, structure, optical properties and photocatalytic activities.

Keywords: Z-scheme; Ag-decorated g-C₃N₄/Bi₂WO₆; Nanocomposites; Microstructure; Photocatalysis

Introduction

Visible-light-driven catalysts are considered as the most promising green approach to degrade environmental pollution [1]. In the past decades, single-component

photocatalysts have been widely used, especially for TiO_2 [2]. While high photogenerated carrier combination rate and low visible light utilization efficiency restrict their further application. Graphitic carbon nitride ($\text{g-C}_3\text{N}_4$), with a narrow band gap of 2.7 eV, is considered as a promising metal-free polymeric photocatalyst [3]. Constructing of $\text{g-C}_3\text{N}_4$ based heterogeneous photocatalysts is one of the effective methods to improve the photocatalytic performance by effective separation of photogenerated electron-hole pairs [4, 5]. However, the separation process inevitably accompany with the decline of redox ability [6, 7]. Therefore, more mechanisms are still need to be explored to explain and improve the performance of photocatalysts.

Inspired by the photosynthesis of chloroplast in nature, a new Z-scheme photocatalytic mechanism was proposed [8, 9]. The Z-scheme photocatalysts can retain the strong redox ability by recombining the weak reduction ability electrons with weak oxidizing ability holes, electrons and holes can also be spatially separated. For instance, Zhu's group reported that the superior photocatalytic activity of CdS-Au-TiO_2 composite benefits from its Z-scheme transfer of photogenerated electron-hole pairs [10]. Besides, some recent studies also point that the electron transfer mediators can influence the photocatalytic process. For example, Iwase et al. demonstrated that the effectiveness of reduced graphene oxide as a solid electron mediator for a Z-scheme photocatalytic water splitting system [11]. Ye et al. reported that the role of metal Ag was SPR effect and the Z-scheme bridge for Ag/AgCl/BiOCl and Ag/AgBr/BiOBr , respectively [12].

In this work, we successfully synthesized Ag-decorated $\text{g-C}_3\text{N}_4/\text{Bi}_2\text{WO}_6$ (denoted

as Ag-CN/BW) composite. Bi_2WO_6 was chosen as the desirable candidate for its excellent photocatalytic effect and suitable valence band (VB) and conduction band (CB) position, metal Ag here acts as electron mediator. The optimal mass ratio between g- C_3N_4 and Bi_2WO_6 refer to the previous report [13]. The photocatalytic activities of Ag-CN/BW composite photocatalyst with different doping content were also discussed.

2. Experimental

The g- C_3N_4 was prepared by the polymerization method [14]. The g- $\text{C}_3\text{N}_4/\text{Bi}_2\text{WO}_6$ composite was prepared by adding g- C_3N_4 into the precursor solution of Bi_2WO_6 , then the suspension solution was transferred to Teflon-lined stainless steel autoclave and maintained at 160°C for 20 h. The Ag-decorated g- $\text{C}_3\text{N}_4/\text{Bi}_2\text{WO}_6$ composites were obtained using the photodeposition method. Synthetic details can be found in Supporting Information.

3. Results and Discussion

3.1 Microstructure and morphology

Fig.1a shows the XRD patterns of g- C_3N_4 , Bi_2WO_6 , g- $\text{C}_3\text{N}_4/\text{Bi}_2\text{WO}_6$ and Ag-CN/BW composite. All the diffraction peaks of g- C_3N_4 and Bi_2WO_6 match well with graphite carbon nitride (JCPDS card no. 87-1526) [15] and orthorhombic phase Bi_2WO_6 (JCPDS card no. 73-1126) [16], respectively. Meanwhile, it can be found that, no characteristic peaks of g- C_3N_4 were observed in the pattern of g- $\text{C}_3\text{N}_4/\text{Bi}_2\text{WO}_6$ and Ag-CN/BW composite. This could be ascribed to the overlapping of the two peaks of g- C_3N_4 and Bi_2WO_6 at 2.75° .

Fig.1. (a) XRD patterns and (b) FTIR spectra of as-prepared samples; XPS spectra of (c) survey spectrum, (d) C 1s, (e) Bi 4f, (f) Ag 3d.

The FTIR spectra of as-prepared samples are shown in Fig.1b. The sharp peak at $\sim 810\text{ cm}^{-1}$ belongs to a breathing mode of s-triazine units of g-C₃N₄ [17]. Whereas the absorption bands in the region of $1200\sim 1750\text{ cm}^{-1}$ are attributed to aromatic C–N stretching vibration mode [17, 18]. The broad band centered at $\sim 3150\text{ cm}^{-1}$ can be ascribed to the stretching mode of N–H bond. Pure Bi₂WO₆ sample shows main absorption bands at $400\sim 800\text{ cm}^{-1}$, which are attributed to Bi–O, W–O stretching and W–O–W bridging stretching modes [19]. Furthermore, all characteristic absorption

bands of $\text{g-C}_3\text{N}_4$ and Bi_2WO_6 appear in the spectra of $\text{g-C}_3\text{N}_4/\text{Bi}_2\text{WO}_6$ and Ag-CN/BW composite, indicating that no structure change appears during the hybridization process. However, no peaks of Ag were found due to the low loading quantity.

XPS was carried out to analyze the surface elementary composition and chemical states. Only C, N, Bi, W, O and Ag elements were detected in the survey spectrum in Fig.1c, which could confirm the presence of $\text{g-C}_3\text{N}_4$, Bi_2WO_6 and Ag in the composite. The high resolution C 1s spectrum (Fig.1d) could be deconvoluted into three peaks at 288.6, 286.4 and 284.8 eV, the former two peaks could be attribute to the C-(N)_3 and N-C=N in $\text{g-C}_3\text{N}_4$, the latter one could be attribute to adventitious hydrocarbon from the instrument. In the Bi 4f spectrum (Fig 1e), two main peaks at 164.6 and 159.3 eV can be assigned to Bi^{3+} in Bi_2WO_6 [20]. Additionally, in the Ag 3d orbits scan (Fig.1f), the peaks located at 368.5 and 375.4 eV could be attributed to Ag^0 [21], indicating that Ag NPs was formed on the surface of $\text{g-C}_3\text{N}_4/\text{Bi}_2\text{WO}_6$ composite.

Fig.2. SEM of (a) $\text{g-C}_3\text{N}_4$, (b) Bi_2WO_6 and (c) Ag-CN/BW; (d) TEM of Ag-CN/BW.

The morphologies of as-prepared samples were collected by SEM and TEM. A typically aggregated morphology with a large size and lamellar structure is found in the pure g-C₃N₄ (Fig.2a). The flower-like Bi₂WO₆ microspheres (Fig.2b) with the diameter about 3 μm were in fact composed of numerous tiny two-dimension nanoplates by self-assembly. When g-C₃N₄, Bi₂WO₆ and Ag NPs were assembled together to form synergetic system, flower-like Bi₂WO₆ were broke up into pieces and dispersed uniformly on the surface of g-C₃N₄ nanosheets, as shown in Fig.2c. Furthermore, some dark dots can be observed in the TEM image of Ag-CN/BW composite (Fig.2d), suggesting that the silver ions were successfully reduced and deposited on the surface of g-C₃N₄/Bi₂WO₆ composite.

3.2 Optical properties

UV-vis diffuse reflectance spectroscopy (DRS) was used to analyze the optical properties of samples. The characteristic absorption edge of Bi₂WO₆ is 441 nm, while g-C₃N₄ presents strong absorption edge at 490 nm. The Ag-CN/BW composite exhibits enhanced light absorption in the visible light region, which might be due to the existence of metal Ag. The band gap energy of g-C₃N₄ and Bi₂WO₆ were estimated to about 2.53 and 2.81 eV (inset of Fig.3a), respectively. The VB and CB of g-C₃N₄ and Bi₂WO₆ can thus be calculated according to the Mulliken electronegativity theory [22].

The photoluminescence (PL) emission spectroscopy was employed to monitors recombination of photoexcited carriers. As shown in Fig.3b, the PL intensity of g-C₃N₄/Bi₂WO₆ and Ag-CN/BW composites shows much lower PL intensity than

pure $g\text{-C}_3\text{N}_4$ and Bi_2WO_6 , indicating that both of them can accelerate the separation of photogenerated electron-hole pairs.

Fig.3. (a) UV-vis diffuse reflectance spectra and (b) photoluminescence spectra of as-prepared samples.

3.3 Photocatalytic activity and photocatalytic mechanism

The photocatalytic activities of as-prepared samples were evaluated by the Rh.B degradation under visible light. As shown in Fig.4a, the $g\text{-C}_3\text{N}_4/\text{Bi}_2\text{WO}_6$ composite exhibited much higher photodegradation efficiency than $g\text{-C}_3\text{N}_4$ and Bi_2WO_6 samples, which can be ascribed to the formation of heterostructure between $g\text{-C}_3\text{N}_4$ and Bi_2WO_6 . However, it cannot explain the high photocatalytic activity of 1.0 wt% Ag-CN/BW using the heterogeneous mechanism. Fig.4b further illustrates the variations of Rh.B absorbance over 1.0 wt% Ag-CN/BW composite. The absorbance obviously decreases with increased irradiation time. No absorbance peak is observed after irradiation for 90 min, which indicates that Rh.B is completely decomposed. The cycling tests in Fig.S1 shows excellent photocatalytic stability of as-prepared photocatalyst.

Z-scheme photocatalytic mechanism can be applied to illustrate the experimental

phenomenon. Under visible light irradiation, $g\text{-C}_3\text{N}_4$ and Bi_2WO_6 are excited simultaneously to form photogenerated electron-hole pairs. The electrons in the CB of Bi_2WO_6 will transfer to Ag NPs, and subsequently transfer to the VB of $g\text{-C}_3\text{N}_4$, as illustrated in Fig.4c. Ag NPs here, acts as the recombination center, can annihilate the weak oxidizing capability holes with weak reductive capability electrons, the redox ability of catalyst can thus be preserved. The reactive oxygen species trapping experiments results indicate that h^+ and $\cdot\text{OH}$ are the main oxidative species as shown in Fig.S2, which will support the Z-scheme mechanism.

Fig.4. (a) C/C_0 versus time curves illustrating photodegradation of Rh.B; (b) UV-vis spectra changes of Rh.B over 1.0 wt% Ag-CN/BW composite; (c) Schematic diagram of degradation process.

4. Conclusion

In this work, a novel Z-scheme Ag-decorated $g\text{-C}_3\text{N}_4/\text{Bi}_2\text{WO}_6$ composite with

enhanced photocatalytic performance was successfully synthesized by a facile hydrothermal synthesis method followed by photo-reduction. The g-C₃N₄/Bi₂WO₆ composite displayed obviously enhanced photocatalytic performance for the degradation of Rh.B after introducing of Ag NPs, and the highest efficiency was observed when using the 1.0 wt% Ag-CN/BW composite as photocatalyst. This study may provide new idea in design of g-C₃N₄ based Z-scheme semiconductor photocatalysts and explore the reaction mechanism of Z-scheme photocatalysts.

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