Enhanced photocatalytic performance of Au nanoparticles-modified rose flower-like Bi$_2$WO$_6$ hierarchical architectures

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1. Introduction

Metal oxide semiconductors that contain the Bi element are widely known to be an important class of visible-light-responsive photocatalysts and have become a research hotspot in the field of photocatalysis. Different from other oxide semiconductors, whose valence band consists of merely O 2p states, Bi-containing oxide semiconductors have a valence band composed of O 2p and Bi 6s hybrid orbitals. Due to this unique band structure, Bi-containing oxide semiconductors exhibit high oxidative activity and charge-carrier mobility. Bismuth tungstate (Bi$_2$WO$_6$) is one of the most extensively studied Bi-containing oxide semiconductors as visible light photocatalysts. Bi$_2$WO$_6$ belongs to the Aurivillius family and has a layered two-dimensional crystal structure with perovskite-like units (WO$_4$)$^{2-}$ sandwiched between (Bi$_2$O$_2$)$_{2+}$ layers. Moreover, Bi$_2$WO$_6$ has relatively small bandgap energy of 2.9 eV compared to the most famous TiO$_2$ photocatalyst with bandgap energy of 3.2 eV, implying that it can largely absorb the visible part of the solar spectrum. Recently, a great deal of work has been devoted to the photocatalytic property of Bi$_2$WO$_6$ toward the degradation of organic dye pollutants. However, to incorporate Bi$_2$WO$_6$ into practical photocatalytic application, further efforts are required to improve its photocatalytic performance. Thus two crucial points need to be taken into account, i.e., the efficient light absorption and the efficient separation of photogenerated electron–hole pairs.

Three dimensional (3D) self-assembled hierarchical architectures commonly exhibit superior light absorption efficiency compared with solid particles because they are able to largely harvest light by multiple scattering. This indicates that 3D self-assembled hierarchical architectures are quite attractive for the application as photocatalysts. To address the morphology-mediated tailoring of the photocatalytic performance of Bi$_2$WO$_6$, considerable efforts have been made to fabricate Bi$_2$WO$_6$ nano/microstructures with different morphologies including caddice clew-, octahedron-, flower-, nest-, and square plate-like structures. In our previous work, we demonstrated that self-assembled 3D rose flower-like Bi$_2$WO$_6$ hierarchical architectures synthesized via a hydrothermal route exhibited a highly superior photocatalytic activity toward the dye degradation. On the other hand, decoration of photocatalysts with metallic nanostructures including Au, Ag and Pt nanoparticles has been established as a promising strategy to promote the electron–hole pair separation and hence improve their photocatalytic performance. It is generally accepted that metal nanoparticles can act as efficient electron sinks to capture photogenerated electrons, leaving behind photogenerated holes on the photocatalyst surface. This electron transfer process leads to a significant inhibition of electron–hole pair recombination, and more charge carriers are therefore available to participate in the photocatalytic reactions. Moreover, electrons on the surface of metal nanoparticles will undergo a collective oscillation under visible light irradiation, which is known as the surface plasmon resonance (SPR) effect. The SPR on metal nanoparticles can enhance the local electric field of neighboring semiconductors, which will facilitate the separation of photogenerated electrons and holes. Alternatively, SPR-induced electrons and holes could also act as redox centers to initiate the photocatalytic reactions. In previous work, Au nanoparticles were decorated onto Bi$_2$WO$_6$ nanosheets to form semiconductor/metal hybrid system with enhanced photocatalytic performance. However, little work has been devoted to the assembly of Au nanoparticles on Bi$_2$WO$_6$ with 3D self-assembled hierarchical
architectures. In this work, we attempted to assemble Au nanoparticles on rose flower-like Bi2WO6 hierarchical architectures to achieve an excellent Au–Bi2WO6 nanocomposite photocatalyst with superior photocatalytic performance.

2. Experimental

2.1 Synthesis of Bi2WO6 flower-like hierarchical architectures

Bi2WO6 flower-like hierarchical architectures were synthesized via a hydrothermal route as described in literature. All raw materials and reagents used in the experiment are of analytical grade without further purification. 3.0025 g of glacial acetic acid was dissolved in 20 mL distilled water, to which was dissolved 0.9702 g (0.002 mol) of Bi(NO3)3·5H2O (solution A). 0.3298 g (0.001 mol) of Na2WO4·2H2O was dissolved in 20 mL distilled water (solution B). Then the solution B was slowly added to the solution A drop by drop under constant magnetic stirring. After another 30 min of stirring, the mixture solution was made up to 70 mL by adding distilled water, and was transferred and sealed in a stainless steel autoclave with a Teflon liner of 100 mL capacity, followed by hydrothermal treatment at 200°C. After 24 h of reaction, the autoclave was naturally cooled down to room temperature. The produced precipitate was collected by centrifugation at 4000 rpm for 10 min, washed several times with distilled water and absolute ethanol, and dried in a thermostat drying oven at 60°C for 8 h to obtain final Bi2WO6 product.

2.2 Preparation of Au-decorated Bi2WO6

The as-synthesized Bi2WO6 flower-like hierarchical architectures were decorated with Au nanoparticles via a photocatalytic reduction route. 0.1 g of Bi2WO6 was loaded in 100 mL distilled water. 0.025 g of ammonium oxalate was dissolved in the Bi2WO6 suspension, followed by magnetic stirring for 60 min. Then to the suspension was slowly added 0.76 mL of HAuCl4 solution with concentration of 0.029 mol L−1 (M). After magnetically stirred for 30 min, the mixture was irradiated with a 15W low-pressure mercury lamp for 30 min under mild stirring. During the irradiation, Au3+ ions were reduced to form Au nanoparticles onto Bi2WO6 architectures. The involved reactions can be described by Eqs. (1) and (2). The precipitate was collected by centrifugation, washed with distilled water several times, and dried in a thermostat drying oven at 60°C for 12 h to obtain final Au–Bi2WO6 composite.

\[ \text{Bi}_2\text{WO}_6 + h\nu \rightarrow \text{Bi}_2\text{WO}_6 (e^- + h^+) \]  
(1)

\[ \text{Au}^{3+} + 3e^- \rightarrow \text{Au}_{\text{metal}} \]  
(2)

2.3 Sample characterization

The crystal structure of the samples was examined by means of X-ray powder diffraction (XRD) with Cu Kα radiation (λ = 0.15406 nm). The morphology and microstructure of the samples was investigated by field-emission scanning electron microscopy (SEM) and field-emission transmission electron microscopy (TEM). The chemical state of elements in the samples was determined by X-ray photoelectron spectroscopy (XPS). The optical absorption and bandgap energy of the samples was investigated by ultraviolet–visible diffuse reflectance spectroscopy (UV–vis DRS) on a UV–vis spectrophotometer with an integrating sphere attachment.

2.4 Photoelectrochemical measurement

The electrochemical impedance spectroscopy (EIS) and photocurrent response of the samples were measured on a CST 350 electrochemical workstation using a three-electrode cell configuration consisting of a standard calomel electrode (SCE) as the reference electrode, a platinum foil as the counter electrode, and the working electrode. The working electrode was prepared as follows. 15 mg of the samples (Bi2WO6 or Au–Bi2WO6), 0.75 mg of carbon black and 0.75 mg of polyvinylidene fluoride were mixed together using 1-methyl-2-pyrrolidione as solvent. The formed slurry was uniformly coated on fluorine-doped tin oxide glass substrate with area of 1 × 1 cm2, and submitted to drying at 60°C for 5 h in a thermostat drying oven. 0.1 M Na2SO4 aqueous solution was used as the electrolyte. During the photoelectrochemical measurement, a 200 W xenon lamp was used as the light source. The EIS measurement was carried out by applying the sinusoidal voltage pulse of amplitude of 5 mV over a frequency range from 0.01 Hz to 100 kHz. The transient photocurrent response was measured at a bias potential of 0.2 V.

2.5 Photocatalytic evaluation

Rhodamine B (RhB) in aqueous solution was chosen as the target organic pollutant to investigate its degradation behavior over the samples under simulated sunlight irradiation from a 200 W xenon lamp. The initial concentration of RhB solution was 5 mg L−1 and the photocatalyst loading was 0.1 g in 100 mL of RhB solution. Before photocatalysis, the mixture was magnetically stirred in the dark for 30 min to establish the adsorption/desorption equilibrium of RhB onto the photocatalyst surface. During the photocatalysis process, the reaction solution was kept at room temperature by cooling the water-jacketed reactor with a water-cooling system. At intervals of 30 min, 3 mL of the reaction solution was taken out from the reactor to examine the RhB concentration by measuring the absorbance of the reaction solution at 554 nm on a UV–vis spectrophotometer. Before the absorbance measurement, the reaction solution was centrifuged at 4000 rpm for 10 min to remove the photocatalyst.

3. Results and discussion

Figure 1 shows the XRD patterns of Bi2WO6 and Au–Bi2WO6 orthorhombic structure (PDF#73-2020) and Au cubic structure (PDF#04-0784). For Bi2WO6 sample, the diffraction peaks are seen to be in good agreement with the diffraction lines of the standard XRD pattern of PDF#73-2020, indicating the formation of single Bi2WO6 orthorhombic phase. For Au–Bi2WO6 composite, the XRD pattern presents additional weak diffraction peaks...
assignable to Au cubic phase, implying the formation of Au onto Bi$_2$WO$_6$. The diffraction peaks of Bi$_2$WO$_6$ undergo no obvious change, indicating that Bi$_2$WO$_6$ maintains the single orthorhombic phase.

Figure 2(a) shows the SEM image of Bi$_2$WO$_6$, revealing that the prepared Bi$_2$WO$_6$ sample consists of rose flower-like hierarchical architectures with average diameter of 7 μm. Figures 2(b) and 2(c) show the TEM images of Au–Bi$_2$WO$_6$. It is seen that the Bi$_2$WO$_6$ hierarchical architectures are decorated with spherical Au nanoparticles with size of 20–110 nm, as indicated by arrows. Figure 2(d) shows the selected area electron diffraction (SAED) pattern of Au–Bi$_2$WO$_6$, which presents clearly concentric diffraction rings or diffraction spots. Except for additional diffraction rings assignable to Au, all the diffraction rings can be indexed according to the Bi$_2$WO$_6$ orthorhombic phase. The SAED result suggests that Bi$_2$WO$_6$ maintain a well-crystallized orthorhombic phase when decorated with Au nanoparticles. The selected area electron diffraction (SAED) pattern of Au–Bi$_2$WO$_6$, which presents clearly concentric diffraction rings or diffraction spots. Except for additional diffraction rings assignable to Au, all the diffraction rings can be indexed according to the Bi$_2$WO$_6$ orthorhombic phase. The SAED result suggests that Bi$_2$WO$_6$ maintain a well-crystallized orthorhombic phase when decorated with Au nanoparticles. The energy-dispersive X-ray spectroscopy (EDS) is used to investigate the chemical composition of Au–Bi$_2$WO$_6$ composite. Figure 2(e) shows a typical EDS spectrum of the composite. The signals from Bi, W, O and Au elements are clearly included in the spectrum. From the EDS spectrum, the atomic ratio of Bi to W is obtained as 2/1, which is in good agreement with the Bi/W atomic ratio of Bi$_2$WO$_6$ phase. However, the obtained O content is much lower than the stoichiometric ratio of Bi$_2$WO$_6$, which could be due to the fact that EDS is not sensitive to light elements like O.$^{39}$ Figure 2(f) shows the dark-field scanning TEM (DF-STEM) image of Au–Bi$_2$WO$_6$, and Figs. 2(g)–2(j) give the corresponding elemental mapping images of the region indicated in Fig. 2(f). It is seen that the flower-like hierarchical architectures display clearly the elemental distribution of Bi, W and O, and furthermore these elements have an identical distribution. This implies no obvious chemical composition segregation in the Bi$_2$WO$_6$ phase. The elemental mapping image for Au reveals that Au nanoparticles are uniformly assembled onto Bi$_2$WO$_6$ architectures without aggregation.

The chemical states of the elements in Bi$_2$WO$_6$ and Au–Bi$_2$WO$_6$ were investigated by XPS. Figure 3(a) shows the XPS survey scan spectra of Bi$_2$WO$_6$ and Au–Bi$_2$WO$_6$, both of which present the signals of the elements Bi, W and O. Moreover, additional Au signal is clearly included in the XPS spectrum of the composite. The observed C signal at 284.8 eV arises from adventitious carbon that is used for calibrating the binding energy scale. Figure 3(b)–3(d) show the high-resolution XPS spectra of O 1s, Bi 4f and W 4f, respectively. For bare Bi$_2$WO$_6$, the O 1s XPS signal is deconvoluted into two peaks separately at 530.3
and 531.6 eV, implying two different kinds of O species in the sample. The binding energy at 530.3 eV is attributed to the contribution of the crystal lattice oxygen in crystalline Bi$_2$WO$_6$. The higher binding energy at 531.6 eV could arise due to the chemisorbed oxygen species.$^{13,14}$ On the Bi 4f XPS spectrum, the sharp peaks at 159.2 and 164.6 eV belong to the binding energies of Bi 4f$_{7/2}$ and Bi 4f$_{5/2}$, respectively, which implies that Bi is in the form of Bi$^{3+}$ oxidation state.$^{13,14,17}$ On the W 4f XPS spectrum, the binding energies of W 4f$_{7/2}$ and W 4f$_{5/2}$ are observed at 35.4 and 37.5 eV, respectively, suggesting the presence of W$^{6+}$ oxidation state.$^{13,14,17}$ For Au–Bi$_2$WO$_6$ composite, the O 1s and Bi 4f binding energies are identical with those of bare Bi$_2$WO$_6$. However, the W 4f binding energies exhibit a slight shift of 0.2 eV toward lower energy. The decrease of the W 4f binding energies caused by the decoration of Au nanoparticles could arise due to a possible chemical bonding between Bi$_2$WO$_6$ and Au. The Au 4f XPS spectrum shown in Fig. 3(c) presents two sharp peaks at 83.5 and 87.2 eV, which are assigned to the binding energies for Au 4f$_{7/2}$ and Au 4f$_{5/2}$, respectively, implying the existence of Au$^0$ metal state.$^{40}$ No additional peaks assignable to the oxidation states of Au species are observed on the spectrum.

Figure 4(a) shows the UV–vis DRS spectra of Bi$_2$WO$_6$ and Au–Bi$_2$WO$_6$, and Fig. 4(b) gives the corresponding first-derivative curves of the UV–vis DRS spectra. Compared to bare Bi$_2$WO$_6$, Au–Bi$_2$WO$_6$ exhibits much enhanced absorption in the visible light region, implying an increased utilization rate of sunlight photons for the composite. The absorption edge of the samples ascribable to the electron transition from valence band (VB) to conduction band (CB) can be derived from the peak on the first-derivative curves of the UV–vis DRS spectra. The absorption edge for bare Bi$_2$WO$_6$ is observed at 420.9 nm, indicating that it has a bandgap energy of 2.95 eV. For Au–Bi$_2$WO$_6$, the absorption edge observed at 361.1 nm undergoes a slight blue shift, indicating a minor increase in the bandgap energy of

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Fig. 3. XPS spectra of Bi$_2$WO$_6$ and Au–Bi$_2$WO$_6$. (a) XPS survey scan spectra; (b) O 1s XPS spectra; (c) Bi 4f XPS spectra; (d) W 4f XPS spectra; (e) Au 4f XPS spectra.
Bi₂WO₆ (3.43 eV). This could be interpreted by the chemical bonding between Bi₂WO₆ and Au.

The separation and transfer behavior of photogenerated electrons and holes for Bi₂WO₆ and Au–Bi₂WO₆ was investigated via photocurrent response and EIS. Figure 5(a) shows the transient photocurrent response of the samples measured by several on–off cycles of intermittent irradiation with simulated sunlight. When turning on the simulated sunlight, an obvious photocurrent is observed for both the samples, and the photocurrent drops to an every low level after turning off the light. This effect appears to be very reproducible when the light is repeatedly switched between on and off. Furthermore, it is observed that the photocurrent density for Au–Bi₂WO₆ composite displays much higher than that for bare Bi₂WO₆. This indicates that the decoration of Au nanoparticles on Bi₂WO₆ flower-like hierarchical architectures leads to an increased separation of photogenerated electron–hole pairs. As a result, more photogenerated electrons and holes in Au–Bi₂WO₆ composite are able to participate in the photocatalytic reactions. The charges separation and transfer behavior for Bi₂WO₆ and Au–Bi₂WO₆ can be further verified by the Nyquist plots of their EIS spectra, as shown in Fig. 5(b). It is seen that the Nyquist plots for both the samples display a typical arc shape. The observation of relatively smaller arc diameter for Au–Bi₂WO₆ implies smaller charge-transfer resistance, and hence more efficient electron–hole separation and faster interface charge transfer occurring in the composite.

Based on the EIS measurements in the dark, many other properties of Bi₂WO₆ can be obtained (e.g., the space charge capacitance \( C \), the type of semiconductivity and the flat band potential \( V_{FB} \)). For each applied potential \( V \), the space charge capacitance of Bi₂WO₆ is determined from the capacitive zone of the Nyquist plots according to the following equation:

\[
C = \frac{1}{2\pi f |Z_{im}|}
\]  

where \( 2\pi f \) is the angular frequency corresponding to the value of the imaginary component of the impedance \( Z_{im} \). Figure 6 shows the plots of \( 1/C^2 \) against the applied potential \( V \) (i.e., Mott–Schottky plots) obtained at two frequencies (3000 and 5000 Hz). The Mott–Schottky equation is given by:

\[
\frac{1}{C^2} = \left( \frac{2}{e\varepsilon_r \varepsilon_0 A} \right) \left( V - V_{FB} - \frac{kT}{e} \right)
\]  

where \( e \) is the electron charge, \( \varepsilon_r \) is the relative permittivity, \( \varepsilon_0 \) is the vacuum permittivity, \( N_d \) is the majority carrier density, \( A \) is the electrode surface area, \( k \) is the Boltzmann constant, and \( T \) is the absolute temperature. Generally, the temperature-dependent cor-
semiconductivity of Bi$_2$WO$_6$. Assuming the gap between the CB and VB of Bi$_2$WO$_6$ is 2.95 eV, and calculating the conduction band potential and the bottom edge of the conduction band is about 2.7 times higher than that of bare Bi$_2$WO$_6$. The degradation percentage of RhB reaches 97% after 120 min of irradiation, higher than that of bare Bi$_2$WO$_6$.

The photocatalytic activity of Bi$_2$WO$_6$ and Au–Bi$_2$WO$_6$, was evaluated by the degradation of RhB under simulated sunlight irradiation. Figure 7(a) shows the time-dependent photocatalytic degradation of RhB over Bi$_2$WO$_6$ and Au–Bi$_2$WO$_6$. The degradation percentage of RhB is defined as $(C_0 - C_t)/C_0 \times 100\%$, where $C_0$ represents the initial RhB concentration and $C_t$ represents the remaining RhB concentration after irradiation for time $t$. It is seen that Au–Bi$_2$WO$_6$ exhibits a photocatalytic activity much higher than that of bare Bi$_2$WO$_6$. After 120 min of irradiation, the degradation percentage of RhB reaches 97% for Au–Bi$_2$WO$_6$, compared to 75% for bare Bi$_2$WO$_6$. The plots of $\ln(C_t/C_0)$ vs. irradiation time $t$ for the samples are inserted in Fig. 7(a), displaying a highly linear variation of $\ln(C_t/C_0)$ with $t$. This suggests that the photocatalytic activity for Au–Bi$_2$WO$_6$ is about 2.7 times higher than that of bare Bi$_2$WO$_6$.

The photocatalytic mechanism of Au–Bi$_2$WO$_6$ is schematically illustrated by Fig. 7(b). For bare Bi$_2$WO$_6$, most of the photogenerated electrons and holes tend to recombine quickly, leaving behind only a few carriers participating in the photocatalytic reactions. In contrast, the electron–hole recombination can be significantly inhibited for Au–Bi$_2$WO$_6$ composite due to the electron transfer from Bi$_2$WO$_6$ hierarchical architectures to Au nanoparticles. This electron transfer process is thermodynamically favorable because the CB potential of Bi$_2$WO$_6$ (+0.20 V vs. NHE) is more negative than the Fermi level of Au (+0.45 V vs. NHE). As a result, more carriers are available for the photocatalytic reactions, thus leading to a significantly enhanced photocatalytic activity for Au–Bi$_2$WO$_6$ composite. On the other hand, the SPR on Au nanoparticles could induce a local electric field nearby Bi$_2$WO$_6$, which will promote the separation of photogenerated electron–hole pairs. Moreover, SPR-induced electrons and holes could participate in the photocatalytic reactions. All these could also make a positive contribution in enhancing the photocatalytic performance of Au–Bi$_2$WO$_6$. In most of the photocatalytic systems, photogenerated $h^+$, hydroxyl (OH) and superoxide (O$_2^-$) are generally thought to be the dominant active species responsible for the dye degradation. In the present Au–Bi$_2$WO$_6$ photocatalytic system, the role of OH can be excluded, because when we examined OH by photoluminescence spectroscopy using terephthalic acid as a probe of OH, no OH is found to be produced over the simulated sunlight irradiated Au–Bi$_2$WO$_6$. It is speculated that $h^+$ and O$_2^-$ could be the dominant reaction species causing the dye degradation in the Au–Bi$_2$WO$_6$ photocatalytic system.

4. Conclusions

Au nanoparticles (20–110 nm in size) were successfully assembled onto the surface of rose flower-like Bi$_2$WO$_6$ hierarchical architectures (7 μm in average diameter) via a photocatalytic reduction method. In the obtained Au–Bi$_2$WO$_6$ composite, photogenerated electrons will migrate from Bi$_2$WO$_6$ hierarchical architectures to Au nanoparticles that act as electron sinks. This electron transfer leads to a significant inhibition of electron–hole pair recombination, and as a consequence, more photogenerated holes and electrons are available for participating in the photocatalytic reactions.

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