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Fabrication and Enhanced Visible-light Photocatalytic Activity of Pt/Bi$_2$WO$_6$ Composite with Hierarchical Flower-like Structure

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Abstract: Visible light activated Bi$_2$WO$_6$ was synthesized by the precipitation method with hydrothermal techniques firstly. And then a series of Pt/Bi$_2$WO$_6$ composite micro-flowers (Pt mass concentration: 0.5%, 1.0%, 1.5%, 2.0%) assembled by Bi$_2$WO$_6$ nano-sheets were synthesized by photo-deposition method. The products were characterized by X-ray diffraction (XRD), UV-vis diffusion absorption spectroscopy (DRS), high resolution scanning electron microscopy (HRSEM), energy dispersive spectroscopy (EDS), and X-ray photoelectron spectroscopy (XPS). The photocatalytic activity of the products was evaluated by degradation of rhodamine B (RhB) under a Xenon lamp irradiation ($\lambda$>420nm). The results showed that sample synthesized at 180°C for 12h (pH=4) had a 3D hierarchical flower-like structure and excellent photocatalytic activity. After photo-deposition of Pt on the surface, the morphology of the sample did not change obviously. However, its photocatalytic activity was greatly enhanced. The products with 1.0% mass ratio of Pt to Bi$_2$WO$_6$ exhibited the highest RhB degradation of 86.5% under visible light irradiation in 120 min, much higher than that of pure Bi$_2$WO$_6$ with RhB degradation of 36.4%. The stability test showed that no obvious loss of photocatalytic activity of the product was detected after four cycles.

1. Introduction
Environmental pollution and energy shortages are two very serious problems for human survival currently. Semiconductor photocatalysis technology is a promising alternative to solve these problems, having potential applications in the field of pollution remediation and new energy exploitation [1]. Bismuth tungstate (Bi$_2$WO$_6$) has received much attention as a visible-light photocatalyst because of its narrow bandgap (~2.8 eV), chemical inertness, photo-stability, and environment friendly features [2-4]. However, the rapid recombination of photogenerated carriers weakens its photocatalytic activity seriously. Especially, the low conduction band bottom potential of Bi$_2$WO$_6$ leads to the inefficient reaction of photo-induced electrons with electron acceptors and promotes the recombination of photogenerated electron-hole pairs. To improve the photocatalytic performance, various Bi$_2$WO$_6$ nanostructures such as nanoparticles [5], nanoplates [6], porous thin film [7], nest-like structures [8], flower-like structures [9], clew-like microspheres [10], multilayered disk-like architecture [11], and octahedron-like structures [12] have been successfully fabricated. Although great progress has been made in this field, the photocatalytic activity of Bi$_2$WO$_6$ is still limited by the fast recombination of...
photogenerated hole-electron pairs. In order to improve the photocatalytic activity of Bi$_2$WO$_6$, many efficient methods have been reported, metal deposition, semiconductor coupling, etc [13-15].

In this work, Pt/Bi$_2$WO$_6$ is selected as the target to investigate the influence of combination of several modification strategies on photocatalytic property of Bi$_2$WO$_6$ under visible light. Firstly, Bi$_2$WO$_6$ with 3D flower like hierarchical structure self-assembled by nanosheets was synthesized by hydrothermal method with Na$_2$WO$_4$·2H$_2$O and Bi(NO$_3$)$_3$·5H$_2$O as raw materials. Then, the flower like Bi$_2$WO$_6$ was surface modified with Pt by photo-deposition method. The synthesized samples were characterized by XRD, UV-vis, SEM, EDS and XPS. The photocatalytic activity of the resulting material was investigated by photocatalytic degradation of RhB under xenon lamp (λ>420nm).

2. Experimental

2.1 Preparation of photocatalyst

All raw materials and reagents used were of analytical grade without further purification. Firstly, 10 mmol bismuth nitrate was dissolved in 4.5mL nitric acid solution with a concentration of 2mol·L$^{-1}$ under magnetic stirring to obtain a clear solution A; 5mmol sodium tungstate was fully dissolved in 40mL deionized water to obtain solution B. Then, solution B was added dropwise into solution A under strong magnetic stirring. And then the mixture was continued to stir for 30 min to form a uniformly mixed suspension C at room temperature. The pH value of C was adjusted to 4 with nitric acid solution and sodium hydroxide. The above mixture was transferred to a Teflon-lined miniature magnetic stirring autoclave, and then submitted to hydrothermal treatment at 180 ºC. After 12h of reaction, the autoclave was naturally cooled down to room temperature. The resultant yellowish precipitate was collected by centrifuge and washed several times with deionized water and absolute ethanol. And then the filter cake was dried under vacuum at 80℃ for 6 h to obtain pure Bi$_2$WO$_6$.

The product obtained above was dispersed in a certain amount of H$_2$PtCl$_6$ solution, magnetically stirred in the dark for 1h to achieve adsorption-desorption equilibrium. 5% volume methanol was added into the mixture as a sacrifice reagent. Then the above mixture was illuminated under a HSX UV-300 Xe lamp in the N$_2$ atmosphere with a vigorous magnetic stirring for 120min. The resultant precipitate was collected by centrifuge and washed three times with distilled water and absolute ethanol until no Cl$^-$ could be detected. And then the filter cake was dried under vacuum at 98℃ for 4h to obtain xwt% Pt/Bi$_2$WO$_6$ (xwt% is the mass ratio of Pt to Bi$_2$WO$_6$).

2.2 Characterization

The crystal structures of the samples were characterized by X-ray diffraction (XRD, 6100, Rigaku) with Cu K$_{α1}$ radiation scanning from 2θ=10-80° at a rate of 2 °·min$^{-1}$. The morphologies and microstructures characterizations were performed on the field emission scanning electron microscopy (SEM, JSM-7800F, JEOL). The surface chemical composition was determined by energy dispersive X-ray spectroscopy (EDS, Quantera SXM, Oxford Instruments). X-ray photoelectron spectroscopy (XPS) measurements were conducted using a Quantera SXM spectrometer (Physical Electronics), and the radiation was provided by a monochromatized Al Kα X-ray source. The binding energies were referenced to the C1s line at 284.8eV from adventitious carbon. The photo-absorption performance was characterized by a UV-vis diffuse reflectance spectroscopy (DRS, UV-2600, Shimadu) using BaSO$_4$ as the reference.

2.3 Measurement of photocatalytic activities

Photocatalytic activities of the as-prepared samples for degradation of RhB were evaluated under visible light irradiation. A HSX UV-300 Xenon arc lamp with a 420 nm cut-off filter was used as the light source. All experiments were carried out in a photoreaction apparatus. For each experiment, 0.20 g photocatalyst was added into 100mL RhB solution with a concentration of 20 mg·L$^{-1}$. Before illumination, the suspensions were stirred in dark for 60 min to reach adsorption-desorption equilibrium. Afterwards, 3.0mL suspension was withdrawn and centrifuged to remove the
photocatalyst particles at regular intervals. And then the concentration of the RhB solution was determined by a UV-2600 spectrophotometer at 554 nm. The degradation efficiency $D$ is defined as:

$$D = \frac{A_0 - A}{A_0} \times 100\% = \frac{C_0 - C}{C_0} \times 100\%$$  

where, $C_0$ is the concentration of the RhB solution after the adsorption/desorption equilibrium established and $C$ is the concentration after various intervals of the irradiation.

3. Characterization results and discussion

3.1. XRD and UV-vis DRS analysis

Fig. 1(a) shows the XRD patterns of Bi$_2$WO$_6$ and xwt% Pt/Bi$_2$WO$_6$. Four strong diffraction peaks at $2\theta$=28.31°, 32.61°, 47.11° and 55.81° can be observed in both samples, which are assigned to (103), (200), (220) and (303) planes of the orthorhombic Bi$_2$WO$_6$ (JCPDS no. 39-0256), respectively. It is seen that all the diffraction peaks of xwt% Pt-Bi$_2$WO$_6$ particles can be indexed in terms of the orthorhombic Bi$_2$WO$_6$ phase, and no traces of other impurity phases are detected in the XRD patterns. It was probably due to the little addition of Pt and Pt attached to the surface of Bi$_2$WO$_6$.

The optical absorption properties of pure Bi$_2$WO$_6$ and Pt/Bi$_2$WO$_6$ composites were measured by UV-vis spectrometry, as shown in Fig.1(b). Pure Bi$_2$WO$_6$ displays photo-absorption property from the UV light region to the visible light absorption shorter than 450nm. However, after loading of Pt, the absorption intensity in the visible light region is improved. And the powder color shifts from yellowish to light grey with the increase of Pt species content. The observed red shift could be attributed to the surface plasmon resonance absorption effect of Pt nanoparticles.

3.2 SEM and EDS analysis

The morphologies of Bi$_2$WO$_6$ and 1wt% Pt/Bi$_2$WO$_6$ samples were characterized by SEM and EDS. The SEM images and EDS analyses of pure Bi$_2$WO$_6$ and 1wt% Pt/Bi$_2$WO$_6$ samples are shown in Fig. 2. Typical flower-like microspheres of pure Bi$_2$WO$_6$ with the diameters of 3.0-6.0μm are clearly observed as shown in Fig.2 (a). The higher magnification SEM image shown in Fig.2 (b) demonstrates the detailed surface information of pure Bi$_2$WO$_6$. It can be seen clearly that each Bi$_2$WO$_6$ flower-like hierarchical microsphere is constructed by many petals or nanosheets, which are closely packed. Such flower-like hierarchical structure with 3D microspheres is formed by self-assembly of nanosheets due to the anisotropic properties of Bi$_2$WO$_6$. It seems like that two-dimensional sheet of Bi$_2$WO$_6$ is accumulated by produced nanoparticles initially, then with the extension of reaction time, many nanosheets can self-assemble into three-dimensional sphere with lower surface energy and larger surface area. This flower-shaped porous structure is not only beneficial to the adsorption of pollutants,
but also to absorption and diffuse of light, thus useful for photocatalysis. Fig.2 (c, d) clearly shows that 1wt% Pt/Bi₂WO₆ sample has a similar structure with the pure Bi₂WO₆. The surface morphology of Bi₂WO₆ sample did not change significantly after deposition of 1wt% Pt on the surface, indicating that the morphology and hierarchical structure of the sample have not been destroyed in the photo-deposition process.

In order to further confirm the existence of Pt on the surface of the sample, EDS analyses were conducted, as shown in Fig.2 (e). It can be seen that a series of peak signals corresponding to Bi, W, O, Pt were detected on the surface of 1wt% Pt/Bi₂WO₆, proving the existence of Pt on the surface of Bi₂WO₆ after photo-deposition.

3.3 XPS analysis

X-ray photoelectron spectroscopy (XPS) is a very sensitive instrument for the analysis of surface composition and chemical state of the materials. The binding energy obtained in the XPS analysis was corrected for specimen charging by referencing C1s to 284.50eV. As shown in Fig.3, the Bi4f7/2 and the Bi 4f5/2 peaks of the Pt/ Bi₂WO₆ appear at 159.26 and 164.43 eV, respectively. The W4f7/2 and the O1s of the Pt/ Bi₂WO₆ are 34.63 and 531.89 eV, respectively. These above results are in agreement with the conventional Bi₂WO₆ nanomaterials [16]. The existence of Pt has a great influence on the photocatalytic properties of the photocatalyst. The characteristic peaks of platinum at the binding energies of 71.9eV and 75.1eV ascribed to Pt 4f5/2 and Pt 4f7/2, respectively, indicating that the Pt on the surface of Bi₂WO₆ existed in metallic state [17].
3.4 Photocatalytic activity
The photocatalytic activity of pure Bi$_2$WO$_6$ and Pt/Bi$_2$WO$_6$ composite samples was evaluated by the photocatalytic degradation of RhB under visible light ($\lambda$ > 420 nm). As shown in Fig.4 (a), compared with pure Bi$_2$WO$_6$, the photocatalytic activity of Pt/Bi$_2$WO$_6$ samples was improved more or less, and 1.0wt%Pt/Bi$_2$WO$_6$ exhibited the highest photocatalytic activity among all the samples, with degradation rate of RhB for 86.5% in 120min, which is far higher than that of pure Bi$_2$WO$_6$ with 37.4%. Maybe a small Schottky barrier was formed between Pt and Bi$_2$WO$_6$, which can effectively trap electrons. Thus the separation efficiency of the light generated electron-hole pairs was increased, and the photocatalytic activity was improved. However, when an excess of Pt (higher than 1.0 wt%) was deposited on the surface of Bi$_2$WO$_6$, its photocatalytic activity was reduced gradually, as clearly shown in Fig.4 (b). On the one hand, aggregates of the excess Pt may be formed on the surface of Bi$_2$WO$_6$, which may act as the recombination centers of electron-hole pairs; on the other hand, the surface activity centers of Bi$_2$WO$_6$ may be covered by an excessive amount of Pt particles, which result in a "light shielding effect", thus the reduced photocatalytic activity. 1.0wt% Pt/Bi$_2$WO$_6$ was selected for further investigation.

Fig.4 (a) Photocatalytic degradation of RhB by different samples under visible light irradiation; (b) Effect of Pt deposition on the photocatalytic activity of Bi$_2$WO$_6$; (c) UV-vis absorption spectra of RhB in the photocatalytic degradation process; (d) Recycle test of 1.0wt% Pt/Bi$_2$WO$_6$
The UV-vis curve of RhB with time photocatalytic degraded by 1.0wt% Pt/Bi₂WO₆ was shown in Fig. 4 (c). A dramatic intensity decrease of the RhB absorption peak at 554 nm with time is observed. And the RhB maximum absorption peak shifts to shorter wavelength from 554 nm to 500 nm. Similar blue shifts have also been reported by Song et al. [18]. As is known, the absorption peaks of 554, 552, 539, 522 and 510 nm are respectively corresponding to N, N, N, N- tetraethyl rhodamine, N, N, N- triethyl rhodamine, N, N- diethyl rhodamine, N- ethyl rhodamine and rhodamine absorption peaks. It is generally considered that the blue shift is due to the fact that RhB transforms into rhodamine after being deethylated and the conjugated structure of rhodamine was correspondingly destroyed. It can be confirmed by the color change during the degradation process. The color of solution is faded from pink, light green into yellow, and finally nearly colorless.

The photocatalytic stability of 1.0wt% Pt/Bi₂WO₆ was investigated and the results were shown in Fig.4 (d). It can be seen clearly that the sample showed good recyclability without loss of apparent photocatalytic activity even after four cycles.

4. Conclusions
(a) The orthorhombic type Bi₂WO₆ was synthesized by hydrothermal method without using any surfactant. The results showed that sample synthesized at 180°C for 12h (pH=4) had a 3D hierarchical flower-like microsphere structure.

(b) The structure of Bi₂WO₆ does not change significantly after photo-deposition of platinum on the surface. But the photocatalytic activity improved significantly. XPS results showed that platinum existed in the form of a metallic state on the surface of the sample. 1.0wt%Pt/Bi₂WO₆ exhibited the highest photocatalytic activity among all the samples under visible light (λ>420nm). The photocatalytic degradation rate of RhB with initial concentration of 20mg·L⁻¹ reached 86.5% in 120min with catalyst dosage of 2.0g·L⁻¹.

(c) The stability test showed the sample 1.0wt%Pt/Bi₂WO₆ had good recyclability without apparent loss of photocatalytic activity after four cycles.

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References
[1] Yu C.L., Yu J.C., Chan M., J. Solid State Chem., 2009, 182, 1061-1069.
[2] Tayade RJ, Surolia PK, Kulkarni RG, etal., Sci Technol Adv Mater, 2007, 8:455-462.
[3] Wu L., Bi J. H., Li Z., et al., Catal Today, 2008, 131: 15-20.
[4] Huang Y., Ai Z. H., Ho W.K., etal., J. Phys. Chem. C, 2010, 114, 6342-6349.
[5] Phu N. D., Hoang L. H., Chen X. B., etal., J Alloys Compd, 2015, 647:123-128.
[6] Zhou Y., Tian Z.P., Zhao Z.Y., etal., ACS Appl. Mater. Interfaces, 2011, 3,3594-3601.
[7] Zhang L. W., Wang Y.J., Cheng H.Y., etal., Adv. Mater. 2009, 21, 1286-1290.
[8] Wu J, Duan F, Zheng Y, et al. J Phys Chem C, 2007, 111: 12866-12871.
[9] Zhao Q., Gong M., Liu W. P., etal., Appl Surf Sci, 2015, 332:138-146.
[10] He D., Wang L., Li, H., etal., Cryst. Eng. Comm., 2011, 3, 4053-4059.
[11] Tang P., Chen H., Cao F., Mater. Lett., 2012, 68, 171-173.
[12] Li Y., Liu J., Huang X., Nanoscale Res. Lett. 2008, 3, 365-371.
[13] Yu Y. N., Lu S. Y., Bao S. J., J Nanopart Res, 2015, 17:323.
[14] Huang H., Liu K., Chen K., et al, J Phys Chem C, 2014, 118:14379-14387.
[15] Zhang Z. J., Wang W. Z., Wang L., et al, Appl. Mater. Interfaces, 2012, 4:593-597.
[16] Xiao Q., Zhang J., Xiao C., etal., Catal. Commun., 2008, 9, 1247-1253.
[17] Fleisch T.H., Zajac G.W., Schreiner J.O., etal., Appl. Surf. Sci., 1986, 26:488-497.
[18] Song J. M., Wang H., Li Y. P., etal., Sci. China Chem., 2012, 42(1):1-8.