Synthesis and Characterization of Heterostructure Pd/Bi₂WO₆ Nanocomposites with Enhanced Properties of Visible-Light-Driven Photocatalyst

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Abstract

Heterostructure Pd/Bi₂WO₆ nanocomposites were successfully synthesized in ethylene glycol by microwave-assisted deposition method at 300 W for 10 min. Effect of the loaded Pd on phase, composition, morphology and visible-light-driven photocatalytic properties of Bi₂WO₆ was investigated by X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), Fast-Fourier-Transform (FFT) diffraction, UV-visible absorption and X-ray photoelectron spectroscopy (XPS). In this research, good distribution of cubic phase of spherical Pd nanoparticles with particle size of 15–20 nm supported on orthorhombic Bi₂WO₆ thin nanoplates. The 10% Pd/Bi₂WO₆ nanocomposites reveal major metallic Pd⁰ species containing in Bi₂WO₆ sample. Microwave can be used to synthesize metallic Pd nanoparticles supporting on top of Bi₂WO₆ nanoplates. Photocatalytic activities of Bi₂WO₆ loaded with different weight contents of Pd were monitored through photodegradation of cationic rhodamine B (RhB) dye under visible light irradiation of a xenon lamp. The 10% Pd/Bi₂WO₆ nanocomposites have the highest photocatalytic activity because Pd nanoparticles as electron acceptors promote interfacial charge-transfer through Pd/Bi₂WO₆ heterojunction.

1. Introduction

In recent years, semiconductor based photocatalysis as green method is a candidate degradation of harmful organic pollutants in water and air to CO₂, H₂O and other small molecules at room temperature [1–5]. However, the practical applications of visible-light-driven semiconductor based photocatalysts are still restricted by fast rate of photo-induced charge recombination [1–3, 6, 7]. Bi₂WO₆ as a member of the Aurivillius oxide family is composed of perovskite [WO₄]²⁻ layers sandwiched between [Bi₂O₂]²⁺ layers to form internal electric field between the slabs which can lead to enhance the efficient separation of charge carrier and photocatalytic activity [3, 7–9]. Bi₂WO₆ with narrow band gap of 2.7 eV has been studied as an efficient visible-light-driven photocatalyst due to its high physical and chemical stability and high photostability [1, 8, 10]. Moreover, the photocatalytic activity of bare Bi₂WO₆ is limited by fast recombination of photo-induced charge carriers and low efficiency of photo-induced charge transfer [1, 9, 10]. Thus, improving the photocatalytic performance of Bi₂WO₆ as photocatalyst is worth to be investigated.

Noble metals have been used as electronic acceptor from conduction band of semiconductor to enhance the separation of photo-induced electrons and holes and to promote photocatalytic activity of the semiconductor [1, 11–13]. There are reports of Pd nanoparticles loaded on semiconductor with enhanced visible-light-driven photocatalytic activity by surface plasmon resonance (SPR) effect, Mott–Schottky interface and increase of valence band edge [12–15]. It is of great significance for synthesizing Pd nanoparticles supported on top of Bi₂WO₆ for photodegradation of dye in wastewater under visible light irradiation.

The present investigation deals with a facile synthesis of novel Pd/Bi₂WO₆ photocatalyst by microwave method. This method consumes short reaction time and cost effective which can lead to fast reduction rate of Pd²⁺ ions to Pd⁰ nanoparticles supported on top of Bi₂WO₆. Effect of Pd content on phase, morphology and photocatalytic performance of Pd/Bi₂WO₆ for decomposition of rhodamine B (RhB) under visible light irradiation was investigated and discussed according to the experimental results.

2. Experiment

Bismuth (III) nitrate pentahydrate (Bi(NO₃)₃·5H₂O, ACS reagent, ≥ 98.0%), sodium tungstate dihydrate (Na₂WO₄·2H₂O, ACS reagent, ≥ 99%) and palladium (II) chloride (PdCl₂, ≥ 99.9%) were purchased from Sigma-Aldrich Chemical Corporation. Rhodamine B (RhB, C₂₈H₃₁ClN₂O₃, ≥ 95%) was purchased from Loba Chemie Pvt. Ltd. They were used without further purification.

Pure Bi₂WO₆ nanoplates were synthesized by hydrothermal method. Typically, 0.01 mol Bi(NO₃)₃·5H₂O and 0.005 mol Na₂WO₄·2H₂O were dissolved in 100 ml reverse osmosis (RO) water with continued stirring at room temperature. The pH of solution was adjusted to 6 by 3 M NaOH to form white suspension and put in a 200 ml Teflon-lined stainless steel autoclave. The stainless steel autoclave was sealed, heated at 180 °C for 20 h in an electric oven and left cooling down to room temperature. The as-prepared Bi₂WO₆ precipitates were collected, washed and dried for further preparation of Pd/Bi₂WO₆ nanocomposites by microwave-assisted deposition method.

To prepare Pd/Bi₂WO₆ nanocomposites by microwave-assisted deposition method, each of 1%, 5% and 10% PdCl₂ by weight was dissolved in 100 ml ethylene glycol as a reducing reagent. Then, 2.50 g as-prepared Bi₂WO₆ nanoplates were added with continued stirring for 30 min. The whole system was transferred in a microwave oven and heated at 300 W for 10 min. In the end, heterostructure 1%, 5% and 10% Pd/Bi₂WO₆ nanocomposites were separated, washed by water and ethanol several times and dried for further characterization by X-ray diffraction (XRD), scanning electron microscopy (SEM) connected with energy dispersive X-ray spectrometer (EDS), transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS), Fast-Fourier-Transform (FFT) diffraction and UV-visible absorption spectroscopy.

Photocatalytic activities of heterostructure Pd/Bi₂WO₆ nanocomposites with different weight contents of Pd were investigated by photodegradation of RhB under visible light irradiation (λ ≥ 420 nm) from a xenon lamp with a 420 nm cutoff filter. 0.2 g heterostructure 0–10% Pd/Bi₂WO₆ nanocomposites were suspended in 200 ml of 1×10⁻⁵ M RhB solutions (pH = 5.2) with being stirred in the dark for 30 min. During visible light illumination, 5 ml RhB solution was sampled at a given time interval and spun around to separate heterostructure Pd/Bi₂WO₆ nanocomposites by forcing the heavier solid to the outer edge. The residual concentration of RhB was measured at an absorption peak of 554 nm by UV–visible spectroscopy. The decolorization efficiency has been calculated by the following.

$$\text{Decolorization efficiency (\%)} = \frac{C_o - C_t}{C_o} \times 100 \quad (1)$$

C_o is the initial concentration of RhB and C_t is the concentration of RhB after light irradiation within a period of time (t).

3. Results And Discussion

3.1 Characterization of Bi_2WO_6 and $\text{Pd}/\text{Bi}_2\text{WO}_6$

X-ray diffraction (XRD) patterns of Bi_2WO_6 and $\text{Pd}/\text{Bi}_2\text{WO}_6$ are shown in Fig. 1. The XRD pattern of pure Bi_2WO_6 sample exhibits diffraction peaks at 28.36° , 32.96° , 47.22° , 55.88° and 58.64° which correspond to the (131), (200), (202), (331) and (262) planes of orthorhombic Bi_2WO_6 phase comparing to the JCPDS No. 39–0256 [16]. The XRD patterns of $\text{Pd}/\text{Bi}_2\text{WO}_6$ nanocomposites show addition diffraction peaks at 40.11° which can be identified to the (111) plane of metallic cubic Pd phase (JCPDS No. 46-1043 [16]). There is no change in orthorhombic structure of Bi_2WO_6 phase in the $\text{Pd}/\text{Bi}_2\text{WO}_6$ nanocomposites. These results indicate that metallic Pd nanoparticles deposited on top of Bi_2WO_6 nanoplates. No other diffraction peaks were detected in both XRD patterns of Bi_2WO_6 and $\text{Pd}/\text{Bi}_2\text{WO}_6$. The crystallite size of Pd in $\text{Pd}/\text{Bi}_2\text{WO}_6$ nanocomposites was calculated from the Scherrer's equation as follows.

$$D = K\lambda/\beta\cos\theta \quad (2)$$

D is the crystallite size (nm), K is the shape factor and equals 0.94 for spherical particle, λ is the wavelength of Cu K_α line ($\lambda = 0.154056$ nm), β is the full width at half maximum (FWHM) in radian and θ is the Bragg's angle [3, 17, 18]. The crystallite size of Pd nanoparticles containing in 10% $\text{Pd}/\text{Bi}_2\text{WO}_6$ nanocomposites is 8.53 nm.

SEM images of Bi_2WO_6 and $\text{Pd}/\text{Bi}_2\text{WO}_6$ are shown in Fig. 2. The as-prepared Bi_2WO_6 sample was composed of nanoplates with 100–200 nm in diameter and an average thickness of about 20 nm. The surface of Bi_2WO_6 nanoplates is smooth. Upon being loaded with Pd, the morphologies of 1%, 5% and 10% $\text{Pd}/\text{Bi}_2\text{WO}_6$ nanocomposites remain unchanged. SEM image of 10% $\text{Pd}/\text{Bi}_2\text{WO}_6$ nanocomposites presents clear Pd nanoparticles with particle size of < 20 nm deposited on the surface of Bi_2WO_6 synthesized by microwave-assisted precipitation method. The elemental constituents containing in 10% $\text{Pd}/\text{Bi}_2\text{WO}_6$ nanocomposites were analyzed by energy dispersive X-ray spectroscopy (EDS) and the elemental distribution was analyzed by EDS mapping as the results shown in Fig. 3. The EDS spectrum of 10% $\text{Pd}/\text{Bi}_2\text{WO}_6$ nanocomposites contains Pd, Bi, W and O. The EDS analysis shows that Pd in 10% $\text{Pd}/\text{Bi}_2\text{WO}_6$ nanocomposites is 8.57% by weight. The EDS mapping of 10% $\text{Pd}/\text{Bi}_2\text{WO}_6$ nanocomposites shows uniform distribution of metallic Pd nanoparticles across the whole sample.

Figure 4 shows TEM images of the as-prepared Bi_2WO_6 sample and $\text{Pd}/\text{Bi}_2\text{WO}_6$ nanocomposites with different contents of metallic Pd particles loaded on top. As shown in Fig. 4a, the Bi_2WO_6 sample exhibits nanoplates with edge of 200×100 nm. The SAED pattern of single phase of orthorhombic Bi_2WO_6 nanoplate (Fig. 4b) shows spots of electron diffraction pattern, certifying a single crystalline nanoplate. The pattern can be indexed to the (200), (220) and (020) planes of orthorhombic Bi_2WO_6 which is in good agreement with the XRD standard [19, 20]. A set of diffraction spots was specified as the [001] zone axis of orthorhombic Bi_2WO_6 . Thus, the exposed facet of Bi_2WO_6 nanoplate is (001) plane [19, 20]. Figure 4c and d of 5% and 10% of $\text{Pd}/\text{Bi}_2\text{WO}_6$ samples shows Pd fine dispersive nanoparticles with size of 15–20 nm on top of Bi_2WO_6 nanoplates. They should be noted that a number of Pd nanoparticles were increased with the progressive increase of PdCl_2 content. The average particle sizes of Pd counted for 100 particles were 9.97 ± 2.17 and 11.22 ± 2.53 nm for 5% $\text{Pd}/\text{Bi}_2\text{WO}_6$ and 10% $\text{Pd}/\text{Bi}_2\text{WO}_6$, respectively. Figure 4e shows a high-resolution TEM image of 10% $\text{Pd}/\text{Bi}_2\text{WO}_6$ nanocomposites which revealed the Schottky barriers between metallic Pd nanoparticles and Bi_2WO_6 nanoplates and enhanced the photocatalytic performance of heterostructure $\text{Pd}/\text{Bi}_2\text{WO}_6$ nanocomposites [1, 6, 8, 9]. Obviously, the lattice fringe spaces of 3.18 Å and 2.25 Å were well-indexed to the (131) plane of orthorhombic Bi_2WO_6 structure and the (111) plane of cubic Pd structure. The Fast-Fourier-Transform (FFT) diffraction pattern of a Pd nanoparticle as shown in Fig. 4f appears as clear diffraction spots with systematic alignment of the single crystalline nanoparticle.

The chemical states of Pd nanoparticles on top of Bi_2WO_6 nanoplates were investigated by XPS. The survey XPS spectrum of 10% $\text{Pd}/\text{Bi}_2\text{WO}_6$ (Fig. 5a) shows that the heterostructure 10% $\text{Pd}/\text{Bi}_2\text{WO}_6$ nanocomposites are composed of Pd 3d, Bi 4f, O 1s and W 4f elements corresponding to the above EDS results. The Pd 3d spectrum of 10% $\text{Pd}/\text{Bi}_2\text{WO}_6$ (Fig. 5b) contained two signals of Pd $3d_{5/2}$ and Pd $3d_{3/2}$ at 335.27 eV and 340.60 eV, respectively. The signals certified that Pd species in the catalyst mainly existed as metallic Pd nanoparticles [12, 13, 21–23]. Moreover, the peaks at higher binding energies are assigned to Pd^{2+} (Pd $3d_{5/2}$ at 335.96 eV and Pd $3d_{3/2}$ at 341.92 eV), Pd^{3+} (Pd $3d_{5/2}$ at 336.88 eV and Pd $3d_{3/2}$ at 342.49 eV) and Pd^{4+} (Pd $3d_{5/2}$ at 337.93 eV and Pd $3d_{3/2}$ at 343.24 eV) [13, 21–23]. Figure 5c shows two binding energy peaks of 159.42 eV and 164.76 eV in accordance with the Bi $4f_{7/2}$ and Bi $4f_{5/2}$ levels, respectively. Thus, Bi species in Bi_2WO_6 are attributed to the typical Bi^{3+} ions [1, 8, 9, 12, 19, 20]. The XPS spectrum of W 4f (Fig. 5d) shows two main binding energies at 35.67 eV for W $4f_{7/2}$ and 37.83 eV for W $4f_{5/2}$, certifying the existence of W^{6+} oxidation state [1, 8, 9, 19, 20]. The O 1s core level (Fig. 5e) can be de-convoluted into three peaks, which include bonds of Bi–O at 530.33 eV, W–O at 531.11 eV and O–H on top of Bi_2WO_6 at 532.37 eV [1, 19, 20].

The optical properties of photocatalysts were analyzed by UV-visible spectroscopy as the results shown in Fig. 6. UV-visible absorption of pure Bi_2WO_6 sample (Fig. 6a) shows an excellent absorption in UV-visible region due to the intrinsic energy gap of Bi_2WO_6 [24–26]. Comparing to Bi_2WO_6 , 10% $\text{Pd}/\text{Bi}_2\text{WO}_6$ shows higher absorption in visible light because of the localized SPR effect of Pd nanoparticles

supported on top of Bi₂WO₆ nanoplates [27–29]. The results indicate that heterostructure Pd/Bi₂WO₆ nanocomposites absorbed visible light which can lead to generate more charge carriers and to improve photocatalytic activity [26–29]. Figure 6b shows the plot of $(\alpha h\nu)^2$ versus $h\nu$ of pure Bi₂WO₆ and 10% Pd/Bi₂WO₆ samples by Kubelka–Munk equation [24, 26]. The band gaps of pure Bi₂WO₆ and 10% Pd/Bi₂WO₆ samples are 2.48 eV and 2.54 eV, respectively.

The visible-light-driven photocatalytic performance of pure Bi₂WO₆ and Bi₂WO₆ doped with different contents of Pd was investigated for photodegradation of RhB. Figure 7 shows UV–visible spectra of RhB solution over 10% Pd/Bi₂WO₆ for different lengths of irradiation time. They can be seen that $\lambda_{\max}$ of RhB at 554 nm was significantly decreased with increasing in irradiation time and was slightly blue shifted because of deethylation of ethyl group and decomposition of RhB [20, 30, 31].

The photocatalytic performance of pure Bi₂WO₆ and Bi₂WO₆ doped with different contents of Pd under visible light irradiation was estimated through the change of RhB concentration as a function of irradiation time (Fig. 8a). The photolysis of pure RhB solution was carried out under visible-light irradiation. The RhB solution was highly stable and was not degraded under visible light irradiation within 120 min. Clearly, the degradation efficiency of Bi₂WO₆ was improved by being loaded with Pd. The degradation efficiencies of Pd/Bi₂WO₆ samples were improved with increasing in Pd content from 1–10% by weight. Bi₂WO₆ could degrade 48.71% RhB under light irradiation within 120 min. In contrast, 10% Pd/Bi₂WO₆ sample could degrade almost 100% of RhB under visible light irradiation within 120 min. This sample has the highest activity for RhB degradation.

The kinetic degradation of RhB over Bi₂WO₆ and Pd/Bi₂WO₆ nanosamples was also investigated by the pseudo-first-order equation as follows.

$$\ln(C_0/C_t) = kt \quad (3)$$

, where k is the first-order rate constant, C_0 is the initial concentration and C_t is the concentration at a time (t) [1, 3, 11, 13, 14, 17, 20]. The photodegradation of RhB by Bi₂WO₆ and Pd/Bi₂WO₆ follows the pseudo-first order kinetics (Fig. 8b). The degradation rate constant over 10 wt% Pd/Bi₂WO₆ nanocomposites (0.0270 min^{-1}) is 4.79 times that over pure Bi₂WO₆ nanoplates ($5.64 \times 10^{-3} \text{ min}^{-1}$). These results were suggested that 10% Pd/Bi₂WO₆ nanocomposites exhibited the highest photocatalytic performance for RhB degradation. The photostability of reused 10% Pd/Bi₂WO₆ nanocomposites was further investigated for five recycles as the results shown in Fig. 9. There is no obvious decline in photodegradation of RhB after five reaction runs. Thus, 10% Pd/Bi₂WO₆ nanocomposites have excellent photostability and photocorrosion resistance under visible light irradiation.

During photodegradation of RhB solutions containing 10% Pd/Bi₂WO₆ nanocomposites under visible light irradiation, isopropanol (IPA), benzoquinone (BQ) and ethylenediaminetetraacetic acid disodium salt (EDTA-2Na) were also added for scavenging hydroxyl radical ($\bullet\text{OH}$), superoxide radical ($\bullet\text{O}_2^-$) and

photogenerated hole (h^+), respectively [32–35]. The photodegradation of RhB (Fig. 10) was significantly decreased to 35.78% and 25.35% for the addition of IPA and BQ. But for the addition of EDTA-2Na, the photodegradation of RhB was still quite high. According to the results, $\bullet OH$ and $\bullet O_2^-$ are the main active species for RhB degradation over 10% Pd/Bi₂WO₆ nanocomposites.

Based on the above results and discussion, a mechanism of the enhanced photocatalytic performance of Pd/Bi₂WO₆ was proposed (Fig. 11). Electrons were excited from valence band (VB) to conduction band (CB) while holes were induced in VB of Bi₂WO₆ under visible light irradiation [1, 9, 11, 14, 19, 20]. Subsequently, the excited electrons and photo-induced holes were transferred to the surface of Bi₂WO₆ photocatalyst and reacted with O₂ and H₂O/OH⁻ to produce active superoxide anion radical ($\bullet O_2^-$) and hydroxyl radical ($\bullet OH$) for degradation of RhB molecules [1, 9, 11, 14, 19, 20].

Thus, Pd nanoparticles on top of Bi₂WO₆ nanoplates act as electron acceptors, promote interfacial charge-transfer kinetics through the metal – semiconductor interface [1, 9, 11, 12, 14, 19, 20], improve the separation of electron – hole pairs and enhance the photocatalytic activity of Pd/Bi₂WO₆ nanocomposites.

4. Conclusions

Visible-light-driven Bi₂WO₆ nanoplates containing different weight contents of Pd nanoparticles were successfully synthesized by microwave-assisted deposition method. XRD, TEM, SEM and XPS analyses showed that the products were spherical metallic Pd nanoparticles supported on top of Bi₂WO₆ thin nanoplates. The photocatalytic activities of Bi₂WO₆ and Pd/Bi₂WO₆ were investigated through photodegradation of RhB under visible light irradiation. The 10% Pd/Bi₂WO₆ nanocomposites have photocatalytic degradation of rhodamine B for two times of the pure Bi₂WO₆ phase by forming Pd nanoparticle – Bi₂WO₆ nanoplate Schottky barriers. In this research, 10% Pd/Bi₂WO₆ nanocomposites are very stable and have very high corrosion resistance under visible light irradiation. The 10% Pd/Bi₂WO₆ nanocomposites are considered as a promising photocatalyst for wastewater treatment.

Declarations

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Figures

Figure 1

XRD patterns of 0–10% Pd/Bi₂WO₆ samples.

Figure 2

SEM images of (a) Bi₂WO₆, (b) 1% Pd/Bi₂WO₆, (c) 5% Pd/Bi₂WO₆ and (d) 10% Pd/Bi₂WO₆.

Figure 3

(a) SEM image and (b) EDS spectrum of 10% Pd/Bi₂WO₆ nanocomposites. EDS mapping of (c) Pd, (d) Bi, (e) W and (f) O containing in 10% Pd/Bi₂WO₆ nanocomposites.

Figure 4

TEM images, SAED pattern, HRTEM image and FFT pattern of (a, b) Bi₂WO₆, (c) 5% Pd/Bi₂WO₆ and (d-f) 10 % Pd/Bi₂WO₆.

Figure 5

XPS spectra of (a) full survey scan, (b) Pd 4d, (c) Bi 4f, (d) W 4f, (e) O 1s of as-synthesized heterojunction 10% Pd/Bi₂WO₆ nanocomposites.

Figure 6

(a) UV-visible spectra and (b) the plot of $(\alpha h\nu)^2$ versus $h\nu$ of Bi_2WO_6 and 10% Pd/ Bi_2WO_6 .

Figure 7

UV-visible absorption of RhB solutions photocatalyzed by 10% Pd/Bi₂WO₆ nanocomposites under visible light irradiation within 120 min.

Figure 8

(a) Decolorization efficiency and (b) pseudo-first-order plot for photodegradation of RhB solutions over 0–10% Pd/Bi₂WO₆ samples comparing with decolorization efficiency of RhB solution without a photocatalyst.

Figure 9

Photocatalysis of re-used 10% Pd/Bi₂WO₆ nanocomposites for five recycles.

Figure 10

Photodegradation of RhB solutions containing different active scavengers comparing with that without a scavenger over 10% Pd/Bi₂WO₆ nanocomposites.

Figure 11

Schematic diagram for photocatalytic mechanism of Pd/Bi₂WO₆ nanocomposites.