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

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Abstract

Heterostructure Pd/Bi$_2$WO$_6$ nanocomposites were successful 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 Bi$_2$WO$_6$ 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 Bi$_2$WO$_6$ thin nanoplates. The 10% Pd/Bi$_2$WO$_6$ nanocomposites reveal major metallic Pd$^0$ species containing in Bi$_2$WO$_6$ sample. Microwave can be used to synthesize metallic Pd nanoparticles supporting on top of Bi$_2$WO$_6$ nanoplates. Photocatalytic activities of Bi$_2$WO$_6$ 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/Bi$_2$WO$_6$ nanocomposites have the highest photocatalytic activity because Pd nanoparticles as electron acceptors promote interfacial charge-transfer through Pd/Bi$_2$WO$_6$ 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 CO$_2$, H$_2$O 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]. Bi$_2$WO$_6$ as a member of the Aurivillius oxide family is composed of perovskite [WO$_4$]$^{2-}$ layers sandwiched between [Bi$_2$O$_2$]$^{2+}$ 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]. Bi$_2$WO$_6$ 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 Bi$_2$WO$_6$ 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 Bi$_2$WO$_6$ as photocatalyst is worth to be investigated.

Noble metals have been used as electronic accepter 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 Bi$_2$WO$_6$ for photodegradation of dye in wastewater under visible light irradiation.
The present investigation deals with a facile synthesis of novel Pd/Bi$_2$WO$_6$ photocatalyst by microwave method. This method consumes short reaction time and cost effective which can lead to fast reduction rate of Pd$^{2+}$ ions to Pd$^0$ nanoparticles supported on top of Bi$_2$WO$_6$. Effect of Pd content on phase, morphology and photocatalytic performance of Pd/Bi$_2$WO$_6$ 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(NO$_3$)$_3$·5H$_2$O, ACS reagent, ≥ 98.0%), sodium tungstate dihydrate (Na$_2$WO$_4$·2H$_2$O, ACS reagent, ≥ 99%) and palladium (II) chloride (PdCl$_2$, ≥ 99.9%) were purchased from Sigma-Aldrich Chemical Corporation. Rhodamine B (RhB, C$_{28}$H$_{31}$ClN$_2$O$_3$, ≥ 95%) was purchased from Loba Chemie Pvt. Ltd. They were used without further purification.

Pure Bi$_2$WO$_6$ nanoplates were synthesized by hydrothermal method. Typically, 0.01 mol Bi(NO$_3$)$_3$·5H$_2$O and 0.005 mol Na$_2$WO$_4$·2H$_2$O 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 Bi$_2$WO$_6$ precipitates were collected, washed and dried for further preparation of Pd/Bi$_2$WO$_6$ nanocomposites by microwave-assisted deposition method.

To prepare Pd/Bi$_2$WO$_6$ nanocomposites by microwave-assisted deposition method, each of 1%, 5% and 10% PdCl$_2$ by weight was dissolved in 100 ml ethylene glycol as a reducing reagent. Then, 2.50 g as-prepared Bi$_2$WO$_6$ 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/Bi$_2$WO$_6$ 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/Bi$_2$WO$_6$ 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/Bi$_2$WO$_6$ nanocomposites were suspended in 200 ml of 1x10$^{-5}$ 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/Bi$_2$WO$_6$ 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.
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\(_2\)WO\(_6\) and Pd/Bi\(_2\)WO\(_6\)**

X-ray diffraction (XRD) patterns of Bi\(_2\)WO\(_6\) and Pd/Bi\(_2\)WO\(_6\) are shown in Fig. 1. The XRD pattern of pure Bi\(_2\)WO\(_6\) 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\(_2\)WO\(_6\) phase comparing to the JCPDS No. 39–0256 [16]. The XRD patterns of Pd/Bi\(_2\)WO\(_6\) nanocomposites show additional 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\(_2\)WO\(_6\) phase in the Pd/Bi\(_2\)WO\(_6\) nanocomposites. These results indicate that metallic Pd nanoparticles deposited on top of Bi\(_2\)WO\(_6\) nanoplates. No other diffraction peaks were detected in both XRD patterns of Bi\(_2\)WO\(_6\) and Pd/Bi\(_2\)WO\(_6\). The crystallite size of Pd in Pd/Bi\(_2\)WO\(_6\) nanocomposites was calculated from the Scherrer’s equation as follows.

\[ D = \frac{K\lambda}{\beta \cos \theta} \quad (2) \]

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

SEM images of Bi\(_2\)WO\(_6\) and Pd/Bi\(_2\)WO\(_6\) are shown in Fig. 2. The as-prepared Bi\(_2\)WO\(_6\) sample was composed of nanoplates with 100–200 nm in diameter and an average thickness of about 20 nm. The surface of Bi\(_2\)WO\(_6\) nanoplates is smooth. Upon being loaded with Pd, the morphologies of 1%, 5% and 10% Pd/Bi\(_2\)WO\(_6\) nanocomposites remain unchanged. SEM image of 10% Pd/Bi\(_2\)WO\(_6\) nanocomposites presents clear Pd nanoparticles with particle size of < 20 nm deposited on the surface of Bi\(_2\)WO\(_6\) synthesized by microwave-assisted precipitation method. The elemental constituents containing in 10% Pd/Bi\(_2\)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% Pd/Bi\(_2\)WO\(_6\) nanocomposites contains Pd, Bi, W and O. The EDS analysis shows that Pd in 10% Pd/Bi\(_2\)WO\(_6\) nanocomposites is 8.57% by weight. The EDS mapping of 10% Pd/Bi\(_2\)WO\(_6\) nanocomposites shows uniform distribution of metallic Pd nanoparticles across the whole sample.
Figure 4 shows TEM images of the as-prepared Bi$_2$WO$_6$ sample and Pd/Bi$_2$WO$_6$ nanocomposites with different contents of metallic Pd particles loaded on top. As shown in Fig. 4a, the Bi$_2$WO$_6$ sample exhibits nanoplates with edge of 200x100 nm. The SAED pattern of single phase of orthorhombic Bi$_2$WO$_6$ 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$_2$WO$_6$ 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$_2$WO$_6$. Thus, the exposed facet of Bi$_2$WO$_6$ nanoplate is (001) plane [19, 20]. Figure 4c and d of 5% and 10% of Pd/Bi$_2$WO$_6$ samples shows Pd fine dispersive nanoparticles with size of 15–20 nm on top of Bi$_2$WO$_6$ 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% Pd/Bi$_2$WO$_6$ and 10% Pd/Bi$_2$WO$_6$, respectively. Figure 4e shows a high-resolution TEM image of 10% Pd/Bi$_2$WO$_6$ nanocomposites which revealed the Schottky barriers between metallic Pd nanoparticles and Bi$_2$WO$_6$ nanoplates and enhanced the photocatalytic performance of heterostructure Pd/Bi$_2$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$_2$WO$_6$ 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$_2$WO$_6$ nanoplates were investigated by XPS. The survey XPS spectrum of 10% Pd/Bi$_2$WO$_6$ (Fig. 5a) shows that the heterostructure 10% Pd/Bi$_2$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% Pd/Bi$_2$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$_2$WO$_6$ 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$_2$WO$_6$ 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$_2$WO$_6$ sample (Fig. 6a) shows an excellent absorption in UV-visible region due to the intrinsic energy gap of Bi$_2$WO$_6$ [24–26]. Comparing to Bi$_2$WO$_6$, 10% Pd/Bi$_2$WO$_6$ shows higher absorption in visible light because of the localized SPR effect of Pd nanoparticles.
supported on top of Bi\(_2\)WO\(_6\) nanoplates [27–29]. The results indicate that heterostructure Pd/Bi\(_2\)WO\(_6\) 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 \((a\nu)^2\) versus \(\nu\) of pure Bi\(_2\)WO\(_6\) and 10% Pd/Bi\(_2\)WO\(_6\) samples by Kubelka–Munk equation [24, 26]. The band gaps of pure Bi\(_2\)WO\(_6\) and 10% Pd/Bi\(_2\)WO\(_6\) samples are 2.48 eV and 2.54 eV, respectively.

The visible-light-driven photocatalytic performance of pure Bi\(_2\)WO\(_6\) and Bi\(_2\)WO\(_6\) doped with different contents of Pd was investigated for photodegradation of RhB. Figure 7 shows UV–visible spectra of RhB solution over 10% Pd/Bi\(_2\)WO\(_6\) for different lengths of irradiation time. They can be seen that \(\lambda_{\text{max}}\) 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 Bi\(_2\)WO\(_6\) and Bi\(_2\)WO\(_6\) 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 Bi\(_2\)WO\(_6\) was improved by being loaded with Pd. The degradation efficiencies of Pd/Bi\(_2\)WO\(_6\) samples were improved with increasing in Pd content from 1–10% by weight. Bi\(_2\)WO\(_6\) could degrade 48.71% RhB under light irradiation within 120 min. In contrast, 10% Pd/Bi\(_2\)WO\(_6\) 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 Bi\(_2\)WO\(_6\) and Pd/Bi\(_2\)WO\(_6\) nanosamples was also investigated by the pseudo-first-order equation as follows.

\[
\ln\left(\frac{C_0}{C_t}\right) = kt
\]

, 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 Bi\(_2\)WO\(_6\) and Pd/Bi\(_2\)WO\(_6\) follows the pseudo-first order kinetics (Fig. 8b). The degradation rate constant over 10 wt% Pd/Bi\(_2\)WO\(_6\) nanocomposites (0.0270 min\(^{-1}\)) is 4.79 times that over pure Bi\(_2\)WO\(_6\) nanoplates (5.64 × 10\(^{-3}\) min\(^{-1}\)). These results were suggested that 10% Pd/Bi\(_2\)WO\(_6\) nanocomposites exhibited the highest photocatalytic performance for RhB degradation. The photostability of reused 10% Pd/Bi\(_2\)WO\(_6\) 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/Bi\(_2\)WO\(_6\) nanocomposites have excellent photostability and photocorrosion resistance under visible light irradiation.

During photodegradation of RhB solutions containing 10% Pd/Bi\(_2\)WO\(_6\) nanocomposites under visible light irradiation, isopropanol (IPA), benzoquinone (BQ) and ethylenediaminetetraacetic acid disodium salt (EDTA-2Na) were also added for scavenging hydroxyl radical (\(\bullet\)OH), superoxide radical (\(\bullet\)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, •OH and •O2− 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 (•O2−) and hydroxyl radical (•OH) for degradation of RhB molecules [1, 9, 11, 14, 19, 20].

\[
\begin{align*}
\text{Bi}_2\text{WO}_6 + h\nu &\rightarrow e^-_{CB} + h^+_{VB} \quad (4) \\
Pd + e^-_{CB} &\rightarrow e^-_{Pd} \quad (5) \\
e^-_{Pd} + O_2 &\rightarrow •O_2^- \quad (6) \\
h^+_{VB} + H_2O/OH^- &\rightarrow •OH \quad (7) \\
•O_2^-/•OH + \text{RhB dye} &\rightarrow \text{Degraded products} \quad (8)
\end{align*}
\]

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 Bi2WO6 and 10% Pd/Bi2WO6.
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.