Research Article

Ag/AgCl Loaded Bi_2WO_6 Composite: A Plasmonic Z-Scheme Visible Light-Responsive Photocatalyst

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Hierarchical flower-like Bi_2WO_6 was successfully synthesized by facile hydrothermal method at low pH. And Ag/AgCl was loaded by photoreduction on its surface. As-prepared photocatalysts were characterized by various techniques. Bi_2WO_6 was successfully synthesized at a size of 2–3 μm . Depositing Ag/AgCl did not destroy the crystal structure, and both Ag^+ and metallic Ag^0 were found. The band gap of the composite was 2.57 eV, which indicates that visible light could be the activating irradiation. In the photocatalytic activity test, the composite with 10 wt% Ag/AgCl boasted the highest removal efficiency (almost 100%) in 45 min. The significant enhancement can be attributed to the surface plasmon resonance (SPR) effect and the establishment of heterostructures between Ag/AgCl and Bi_2WO_6 . A possible mechanism of photocatalytic oxidation in the presence of Ag/AgCl- Bi_2WO_6 was proposed. This work sheds light on the potential applications of plasmonic metals in photocatalysis to enhance their activities.

1. Introduction

Surface plasmon resonance (SPR) has been widely applied in the conversion of solar to chemical energy. It may be described as the resonant photon-induced collective oscillation of valence electrons when the frequency of photons matches the natural frequency of surface electrons oscillating against the restoring force of positive nuclei [1]. The wavelength of a resonant photon depends on the type of metal. For silver nanoparticles, surface electrons may be activated by ultraviolet (UV) and visible (Vis) photons.

Ag/AgCl was first reported by Wang et al. to exhibit an excellent photocatalytic activity due to the SPR effect [2]. This study shed light on the potential implementation of Ag/AgCl for the photocatalytic oxidation of organic pollutants. To date, researchers have designed composites by depositing Ag/AgCl on photocatalysts, such as Ag/AgCl- TiO_2 [3, 4] and Ag/AgCl-BiOX ($\text{X}=\text{Cl}, \text{Br}$) [5], aiming to enhance their performances. Meanwhile, numerous novel photocatalytic materials have also been reported. Among these materials, Bi_2WO_6 , with a band gap of 2.70 eV, has been found to exhibit a high visible-light-driven photocatalytic activity with regard to the degradation of organic contaminants [6]. This is due to the valence

band of bismuth-based photocatalysts consisting of not only O 2p orbits but also Bi 6s orbits. It has been confirmed that moderately well-dispersed orbits are able to accelerate the mobilities of photogenerated carriers and narrower band gap [7]. However, one of the main problems surrounding Bi_2WO_6 implemented in the degradation of organic pollutants in wastewater is the high recombination rate of photogenerated carriers. One of the most effective approaches to deal with this issue is to establish heterostructures such as BiOBr- Bi_2WO_6 [8, 9], $\text{WO}_3/\text{Bi}_2\text{WO}_6$ [10, 11], and $\text{Bi}_2\text{O}_3/\text{Bi}_2\text{WO}_6$ [10]. At present, there is still no published work establishing the Ag/AgCl- Bi_2WO_6 heterostructure applied in the degradation of organic pollutants.

Based on the above analysis, depositing Ag/AgCl on Bi_2WO_6 should enhance its photocatalytic activity due to the SPR effect and the heterostructure. The depositing method (the photoreduction method) can be implemented as reported [12]. In this work, a facile method of preparing an Ag/AgCl- Bi_2WO_6 composite was developed. As-synthesized photocatalysts were investigated in terms of their crystal structures, morphologies, optical properties, and visible-light-induced photocatalytic activities with regard to the degradation of the organic contaminant Rhodamine B (RhB).

A possible mechanism of the photocatalytic oxidation process in the presence of the Ag/AgCl-Bi₂WO₆ composite was also explored and proposed. The enhanced photocatalytic activity may be regarded as solid evidence of the potential application of Ag/AgCl in photocatalytic oxidation processes.

2. Experimental

2.1. Preparation of Bi₂WO₆ and Ag/AgCl-Bi₂WO₆ Composites. All of the reagents were purchased from the Sigma-Aldrich Company, were of analytical purities, and were used as received. Bi₂WO₆ was synthesized by a hydrothermal method. In a typical process, 0.9702 g Bi(NO₃)₃·5H₂O were dissolved in 20 mL acetic acid, termed solution A, which was magnetically stirred for 10 min. Next, 0.3298 g Na₂WO₄·2H₂O were dissolved in 40 mL distilled deionized water (DDW), termed solution B. Solution B was added dropwise into solution A and stirred magnetically for 30 min. The suspension was then transferred to a 100 mL Teflon-lined stainless steel autoclave (approximately 60% of its maximum volume) and heated at 180°C for 20 h. After the autoclave was allowed to cool to room temperature, the precipitate was separated by centrifugation and washed once with ethanol and then twice with DDW. The precipitate was then dried at 60°C for 12 h.

The Ag/AgCl-Bi₂WO₆ composite was prepared by the photoreduction method. Typically, 0.32 g Bi₂WO₆ were dispersed in 40 mL DDW and sonicated for 30 min. Next, 0.24 g NaCl (excess amount) was added to the suspension, which was termed solution C. Meanwhile, 0.0421 g AgNO₃ were added to 20 mL DDW, termed solution D. Solution D was added dropwise to solution C with vigorous stirring for 30 min. Products were separated by centrifugation and dispersed in 40 mL DDW and then illuminated under a 300 W halogen tungsten projector lamp (Ushio) for 30 min. Final products were separated via centrifugation, washed twice with DDW, and dried at 60°C for 12 h. The sample was then collected and labelled as Ag/AgCl (10 wt%)-Bi₂WO₆. Similarly, Ag/AgCl (1 wt%)-Bi₂WO₆, Ag/AgCl (2 wt%)-Bi₂WO₆, Ag/AgCl (4 wt%)-Bi₂WO₆, Ag/AgCl (8 wt%)-Bi₂WO₆, and Ag/AgCl (20 wt%)-Bi₂WO₆ were also prepared.

2.2. Characterization. X-ray diffraction (XRD) analysis was performed using a Rigaku Ultima IV Diffractometer with CuK α radiation ($\lambda = 0.15418$ nm) at 40 kV and 44 mA. Surface elements and the chemical states of samples were tested using a XSAM-800 X-ray Photoelectron Spectroscopy (XPS). A field-emission scanning electron microscope (FE-SEM, JEOL JSM-7500F) using energy dispersive X-ray spectroscopy (EDS) and transmission electron microscopy (TEM, JEM-2100F) were applied to explore the morphologies of samples. Acceleration voltages of the SEM and TEM were 3.00 kV and 200 kV, respectively. The Thermo Evolution 300 spectrophotometer was used to evaluate the ultraviolet-visible (UV-Vis) diffuse reflectance spectra (DRS) of the photocatalysts.

2.3. Photocatalytic Activity Test. The target organic pollutant was Rhodamine B (RhB). The characteristic peak

in UV-Vis spectroscopy of RhB is found at a wavelength of 554 nm, which was used to calculate its concentration based on the Beer-Lambert law. A 500 mL beaker with a cooling jacket maintaining the system at 20°C served as the photocatalytic reactor. The visible-light source was a 300 W halogen tungsten projector lamp (Ushio) with a cut-off (Kenko Zeta, transmittance > 90%) to filter out irradiation with a wavelength below 400 nm. The distance between the irradiation source and the top of the beaker was 10 cm, and the irradiation intensity was measured by a quantum meter (Biospherical QSL-2100, 400 nm < λ < 700 nm) to be 1.1×10^{-2} Einsteins m⁻² s⁻¹. In each batch, 100 mL fresh solution with a concentration of RhB at 10 mg/L (10 ppm) was added to the reactor and mixed with as-prepared photocatalysts in the absence of light for 30 min to ensure that adsorption-desorption equilibrium was achieved. The quantity of photocatalyst added was 0.5 g/L. After mixing, the light was turned on to begin the photocatalytic process. An aliquot of 1 mL suspension was taken every 3 min for 45 min and tested using a Genysys 10-UV spectrophotometer (Geneq Inc.). To explore the roles of radical species, EDTA-2Na and 2-Butanol with concentrations of 0.01 mol/L were added to the reactor.

To study the degradation of phenol, 100 mL phenol solution with a concentration of 10 mg/L (ppm) was mixed with an Ag/AgCl-Bi₂WO₆ composite. Samples taken during the photocatalytic process were tested using UV-Vis spectroscopy with the peak absorption at a wavelength of 270 nm. Other procedures used the same process as that of the degradation of RhB.

To recycle the photocatalysts, photocatalysts were separated by centrifugation between experiments and then used in the following experiment without a wash. The final used products were separated via centrifugation and dried at 60°C for 12 h. Products were collected and tested using XRD to measure their crystal stabilities.

3. Results and Discussions

3.1. XRD and XPS. The X-ray diffraction (XRD) patterns of as-prepared Ag/AgCl-Bi₂WO₆ composites and pure Bi₂WO₆ and Ag/AgCl are shown in Figure 1. The diffraction peaks of pure Bi₂WO₆ agreed well with the orthorhombic structure (space group: Pbc_a (61), PDF card number 00-039-0256) [13]. Specifically, peaks at $2\theta = 28.3^\circ$, 32.7° , 47.1° , 55.8° , and 58.54° were assigned to the (131), (060)/(200)/(002), (260)/(202), (191)/(331)/(133), and (262) planes of Bi₂WO₆, respectively. Samples with deposit amounts of Ag/AgCl larger than and including 4 wt% showed characteristic peaks of Ag and AgCl. As for the small amount of Ag⁰, the peak was weak. In Figure 2, the XRD pattern of Ag/AgCl (10 wt%)-Bi₂WO₆ was enlarged and each species in the composite was identified. Excluding peaks from Bi₂WO₆, peaks at $2\theta = 27.8^\circ$ (Figure 2(a)), 32.2° , 46.2° , 54.8° , and 57.5° (Figure 2(c)) were found, indicating the existence of AgCl (cubic structure, space group Fm-3m (225), PDF card number 00-006-0480). Meanwhile, the peak at $2\theta = 38.2^\circ$ (Figure 2(b)) was attributed to the (111) crystal plane of Ag (PDF card number 01-087-0719). The lattice parameters of Bi₂WO₆ are $a = 5.4513$ Å, $b = 16.4192$ Å, and $c = 5.4587$ Å. In regard to these parameters

TABLE 1: Lattice parameters of Bi_2WO_6 and $\text{Ag}/\text{AgCl}-\text{Bi}_2\text{WO}_6$ composites.

Amount of Ag/AgCl (wt%)	<i>a</i>	<i>b</i>	<i>c</i>
0 (pure Bi_2WO_6)	5.4513 ($\pm 0\%$)	16.4192 ($\pm 0\%$)	5.4587 ($\pm 0\%$)
1	5.4381 (-0.2%)	16.4363 ($+0.1\%$)	5.4434 (-0.3%)
2	5.4274 (-0.4%)	16.4413 ($+0.1\%$)	5.4490 (-0.2%)
4	5.4378 (-0.2%)	16.4205 ($+0.01\%$)	5.4445 (-0.3%)
8	5.4381 (-0.2%)	16.4392 ($+0.1\%$)	5.4534 (-0.1%)
10	5.4399 (-0.2%)	16.4473 ($+0.2\%$)	5.4561 (-0.05%)
20	5.4361 (-0.3%)	16.4432 ($+0.1\%$)	5.4600 ($+0.02\%$)

FIGURE 1: XRD patterns of as-prepared samples: pure Bi_2WO_6 , Ag/AgCl , and $\text{Ag}/\text{AgCl}-\text{Bi}_2\text{WO}_6$ composites.

shown in Table 1, negligible differences between them were observed. This indicates that loading of Ag/AgCl may not destroy the main structure of Bi_2WO_6 and merely laid upon its surface as opposed to covalently anchoring to its lattice [14].

The elemental compositions and chemical states of $\text{Ag}/\text{AgCl}-\text{Bi}_2\text{WO}_6$ composites were determined by X-ray photoelectron spectroscopy. In Figure 3(a), survey spectra and high-resolution scans of typical orbits in Ag/AgCl (10 wt%)- Bi_2WO_6 are illustrated. Specifically in the survey spectra, all elements of the composite (Bi, W, O, Ag, and Cl) were demonstrated. The spectra were calibrated using C 1s, the binding energy of which was 284.6 eV. As for high-resolution XPS spectra in Figure 3(b), two strong peaks centered at 164.50 eV and 159.19 eV indicate that the valence of Bi in the composite was +2 [15]. Furthermore, binding

energies of 37.57 eV and 35.41 eV for W $4f_{5/2}$ and W $4f_{7/2}$, respectively, were found in Figure 3(c), which were confirmed W in the composite with valence of +6 [15, 16]. The largest peak in Figure 3(d) could be separated into 3 smaller peaks which are corresponding well with O in the composite with forms of Bi_2WO_6 at 530.28 eV, $-\text{OH}$ at 531.28 eV, and H_2O at 531.96 eV. The existence of a negligible fraction of hydroxyl anion and H_2O in the composite may be attributed to the reaction of atmospheric water with the oxide surface and the chemisorbed water vapor on top of the oxide surface [17]. Silver peaks at 373.39 eV and 367.30 eV in Figure 3(e) were ascribed to binding energies of Ag $3d_{3/2}$ and Ag $3d_{5/2}$, respectively, in the presence of Ag^+ in AgCl [18]. Smaller peaks located at 374.39 eV and 368.32 eV for binding energies of Ag $3d_{3/2}$ and Ag $3d_{5/2}$ were assigned to that of metallic Ag^0 [18]. This may suggest that metallic Ag^0 can be found in the composite.

3.2. SEM, EDS, and TEM. Morphologies of as-prepared samples were measured by SEM and TEM, the results of which are shown in Figure 4. Bi_2WO_6 synthesized by the hydrothermal method described in this work exhibited a nanoplate-built hierarchical flower-like structure (Figure 4(a)). Similar structures were also reported in the literatures [19, 20]. A potential mechanism for the formation of this superstructure is shown in Scheme 1. The scheme shows that an irregular structure is formed through self-aggregation at the first step. As for the low pH (<1), $\text{Bi}_2\text{O}_2^{2+}$ and WO_4^{2-} ions are generated in solution and may be nucleated onto protuberances on the surface of solid spheres. This dissolution-recrystallization process is called Ostwald ripening. The plate-like structure is owed to the intrinsic anisotropic growth habits of Bi_2WO_6 [21]. According to the Gibbs-Thomson law, larger particles grow at the cost of small particles as for the energy difference in solubility. Flower-like superstructures eventually self-organize after sufficient duration of hydrothermal treatment. The size of each hierarchical microsphere was around 2-3 μm . Ag/AgCl growing on the surface of Bi_2WO_6 is shown in Figure 4(b). Smaller plate-like AgCl could be observed as randomly loaded on its surface and metallic silver (Ag^0) was not observed. However, Ag^0 was shown to be present in the composite based on TEM imaging results (Figure 4(c)). In the inset of Figure 4(c), nanoparticles with a size of no more than 5 nm could possibly be identified as metallic silver (Ag^0). Furthermore, EDS was performed on the composite and is illustrated in Figure 5. Characteristic peaks of all elements

SCHEME 1: Potential mechanism of forming the hierarchical flower-like superstructure of Bi_2WO_6 .

FIGURE 2: XRD pattern of Ag/AgCl (10 wt%)- Bi_2WO_6 .

in the composite were found, which further confirms the successful synthesis of Ag/AgCl- Bi_2WO_6 in this work.

3.3. UV-Vis Diffused Reflectance Spectra (DRS). The optical absorbent properties of the Ag/AgCl- Bi_2WO_6 composite were measured using UV-Vis diffused reflectance spectroscopy. Spectra of pure Bi_2WO_6 , Ag/AgCl, and Ag/AgCl (10 wt%)- Bi_2WO_6 are illustrated in Figure 6(a). After loading Ag/AgCl onto Bi_2WO_6 , the absorbent ability of the photocatalyst in the visible-light range was enhanced. This is mainly due to the plasmon resonance of photoreduced silver (Ag^0) from AgCl [2], which could also be evidence for the existence of Ag^0 in the composite. To further explore the band gap (E_g)

of samples, the classical Tauc equation (1) was employed as follows:

$$\alpha E_{\text{photon}} = K (E_{\text{photon}} - E_g)^{n/2}, \quad (1)$$

$$E_{\text{photon}} = h\nu,$$

where α , h , ν , and K are the absorption coefficient, the Planck constant, the irradiation frequency, and the constant for semiconductors (usually equal to 1), respectively. The constant n depends on the type of band gap, where $n = 1$ is for direct transition and $n = 4$ is for indirect transition. The band gap of the as-prepared Bi_2WO_6 in this work is characteristic of a direct transition (Figure 7), so n is equal

FIGURE 3: XPS spectra of Ag/AgCl (10 wt%)-Bi₂WO₆ composite: (a) survey spectra, and high-resolution orbits scan of (b) Bi 4f, (c) W 4f, (d) O 1s, (e) Ag 3d, and (f) Cl 2p.

FIGURE 4: SEM images of pure Bi_2WO_6 (a) and Ag/AgCl (10 wt%)- Bi_2WO_6 composite (b), and TEM images of Ag/AgCl (10 wt%)- Bi_2WO_6 composite (c).

FIGURE 5: EDS of Ag/AgCl (10 wt%)- Bi_2WO_6 composite.

to 4. By plotting $(\alpha E_{\text{photon}})^{1/2}$ versus E_{photon} as illustrated in Figure 6(b), the intercept at the horizontal axis is the band gap value. This indicates that Ag/AgCl in composites narrowed the band gap from 2.70 eV to 2.57 eV compared to pure Bi_2WO_6 , which could widen the edge wavelength of incidence from 459.3 nm to 482.5 nm. This indicates that

Ag/AgCl - Bi_2WO_6 composites could be effectively activated under visible-light irradiation.

3.4. Photocatalytic Activity Test under Visible Light. Photocatalytic activities of as-prepared samples were tested by degrading RhB (10 mg/L). All of the screening test results are plotted in Figure 8. The removal efficiencies for pure Bi_2WO_6 and Ag/AgCl were 38.8% and 65.3% in 45 min, respectively. By increasing the loading amount of Ag/AgCl in the composites from 1 wt% to 10 wt%, removal efficiencies of the composites were increased up to 100% after 45 min under visible light. This enhancement effect may be attributed to the establishment of a heterojunction between Ag/AgCl and Bi_2WO_6 [3, 14, 23]. However, further increasing the amount of Ag/AgCl in the composites deteriorates the photocatalytic degradation performances. This may be interpreted as larger nanoparticles which are loaded onto Bi_2WO_6 possibly weakening the anchoring forces between them and destroying the heterostructure.

Langmuir-Hinshelwood kinetic analysis was applied to RhB degradation in the presence of as-prepared photocatalysts. Trials performed with diluted concentrations of RhB ($c_0 < 10^{-3}$ mol/L) showed that the Langmuir-Hinshelwood

FIGURE 6: (a) UV-Vis diffused reflectance spectra and (b) $(\alpha E_{\text{photon}})^{1/2} - E_{\text{photon}}$ curves of as-prepared pure Bi₂WO₆, Ag/AgCl, and Ag/AgCl-Bi₂WO₆ (10 wt%)-Bi₂WO₆.

FIGURE 7: Band gap of Bi₂WO₆ (simulated by Quantum Espresso [22]).

model could be simplified to a pseudo-first-order reaction model [24], expressed as follows:

$$\ln\left(\frac{c_0}{c}\right) = k_r \times K \times t = k' t, \quad (2)$$

where t , c_0 , and c are the time, the initial concentration, and concentration at each specific reaction time t of RhB, k_r is the reaction rate constant, K is the adsorption coefficient of the pollutant on the photocatalyst, and k' is pseudo-first-order reaction kinetics constant used as the parameter to evaluate the performances of as-prepared photocatalysts in degrading pollutants. A plot of $\ln(c_0/c)$ as a function t is found in Figure 9, where the slope of the line of best fit is

FIGURE 8: Photocatalytic degradation of RhB (10 mg/L) under visible light with as-prepared pure Bi₂WO₆, Ag/AgCl, and Ag/AgCl-Bi₂WO₆ composites.

the pseudo-first-order kinetics constant, the results of which are summarized in Table 2. The excellent linearity of each line of best fit indicates that the photocatalytic degradation of RhB under visible-light irradiation in the presence of Ag/AgCl-Bi₂WO₆ follows first-order kinetics. The process carried out with pure Bi₂WO₆ as the photocatalyst exhibited

TABLE 2: Pseudo-first-order reaction rate constants for various processes.

	Bi ₂ WO ₆	1 wt%	2 wt%	4 wt%	8 wt%	10 wt%	20 wt%	Ag/AgCl
Pseudo-first-order								
k (10 ⁻² min ⁻¹)	1.047	2.733	3.371	3.930	4.576	5.688	4.508	2.037
R^2	0.9999	0.9961	0.9989	0.9979	0.9989	0.9993	0.9987	0.9939

FIGURE 9: Photocatalytic kinetics of each process.

the lowest reaction constant, while loading of Ag/AgCl onto Bi₂WO₆ increased the constant up to 5.4 times compared to that of pure Bi₂WO₆ at 10 wt% Ag/AgCl. These results confirm that the presence of Ag/AgCl in the composites significantly increases photocatalytic activity with regard to the degradation of organic pollutants.

The stepwise mechanism for the degradation of RhB was observed by taking UV-Vis spectra, which are illustrated in Figure 10. In the inset table, the positions of characteristic peaks for each intermediate species are summarized [25]. It can be concluded that two processes of RhB degradation exist, namely, deethylation and destruction of the aromatic ring. In the deethylation process, RhB is decomposed into N,N,N'-Triethyl-Rhodamine (TER), N,N'-Diethyl-Rhodamine (DER), N-Ethyl-Rhodamine (MER), and Rhodamine, the UV-Vis characteristic peaks of which are located at wavelengths of 539 nm, 522 nm, 510 nm, and 498 nm, respectively. In the first 33 min, peak positions blue-shifted from 554 nm to 498 nm, indicating that RhB degraded into Rhodamine. After that, peak positions stabilized at 498 nm and gradually reduced in intensity. This may be attributed to the degradation of Rhodamine into smaller species such as H₂O and CO₂.

The photocatalytic activity with respect to the degradation of the colourless organic compound, phenol, was investigated and is illustrated in Figure 11. These results aimed to confirm the increased photocatalytic activity in the

FIGURE 10: UV-Vis spectra of solutions taken during the photocatalytic process in the presence of Ag/AgCl (10 wt%)-Bi₂WO₆ (inset table shows characteristic wavelength for each intermediate species in water [25]).

presence of the Ag/AgCl-Bi₂WO₆ composite under visible light attributed to the surface plasmon resonance effect instead of photosensitization of the dye (RhB in this work) [26]. The composite performed well in the degradation of phenol (approximately 30% of phenol was converted in 45 min), which was a better performance than that exhibited by pure Bi₂WO₆ (only about 5% of phenol was converted in 45 min). This confirmed that the enhancement effect of loading Ag/AgCl onto Bi₂WO₆ exists under visible-light irradiation.

3.5. Roles of Radical Species. Holes (h⁺) and free radicals, especially •OH, are regarded as the main oxidative species in photocatalytic degradation of organic pollutants [27]. In this study, EDTA-2Na and 2-Butanol were chosen as the hole and hydroxyl radical scavengers, respectively [28]. When holes were quenched, only 15% of RhB was removed (Figure 12). Comparatively, there was little influence when 2-Butanol was added to quench hydroxyl radicals. This suggests that the hydroxyl radical is not the main oxidative species in

FIGURE 11: Degradation of phenol (10 mg/L) by using Ag/AgCl-Bi₂WO₆ composite.

FIGURE 12: Photocatalytic activity in presence of Ag/AgCl-Bi₂WO₆ and quenchers.

the degradation of RhB and that holes govern the photocatalytic process. Similar results were also reported in the literature [9, 29]. This phenomenon may be explained knowing that the standard redox potential of Bi₂O₄/BiO⁺ (Bi^V/Bi^{III}) (+1.59 eV) is much more negative than that of [•]OH/-OH (+2.30 eV) [9, 29]. This suggests that “nonselective” [•]OH could not be produced in this photocatalytic oxidation process.

3.6. Reusability. Reusability is a significant parameter used to evaluate photocatalysts implemented in practical

FIGURE 13: Removal efficiencies for 4 runs of 45 min.

FIGURE 14: XRD patterns of Ag/AgCl (10 wt%)-Bi₂WO₆ before and after 4 runs.

applications. As-prepared composites were investigated by taking 4 runs where RhB was degraded. Removal efficiencies after 45 min were plotted in Figure 13. After 4 runs, the removal efficiency decreased slightly from 97.8% to 91.5%, but this relatively high removal efficiency still implies the high stability of the Ag/AgCl-Bi₂WO₆ composite. Furthermore, used photocatalysts were observed by XRD, the patterns of which are shown in Figure 14. Lattice parameters of Bi₂WO₆ after four runs were $a = 5.4577$ Å, $b = 16.3970$ Å, and $c = 5.4505$ Å. All the characteristic peaks of Bi₂WO₆ were found with high intensities, indicating that the main crystal structure of Bi₂WO₆ was stable and was not destroyed during the recycle. However, the characteristic peaks of AgCl were observed with reduced intensities. On the other hand, intensities of other peaks, especially the peak at $2\theta = 38.2^\circ$

FIGURE 15: Schematic of possible mechanism of degrading RhB in the presence of Ag/AgCl-Bi₂WO₆.

(Figure 14(b)), for metallic Ag⁰, became stronger. This may be attributed to the reduction of AgCl to metallic Ag⁰ in the photocatalytic process under visible-light irradiation, as photogenerated electrons are produced and easily react with Ag⁺. This may be an explanation for the decreased removal efficiency of RhB. Another possible explanation is that the intermediate species of RhB were adsorbed on the composite and refractory to be degraded.

3.7. Proposed Mechanism of Photocatalytic Degradation. The band structure of the Ag/AgCl-Bi₂WO₆ composite is illustrated in Figure 15. The proposed mechanism of using the composite to degrade RhB could be summarized as follows: (1) Bi₂WO₆ with a band gap of 2.70 eV is activated by visible-light irradiation, generating electrons and holes; (2) Ag⁰ nanoparticles induced by surface plasmon resonance under visible light could produce electrons and leave holes on the valence band [1], and electrons could rapidly transfer to Bi₂WO₆ or AgCl; (3) RhB could be activated by photons (photosensitization) and generate electrons which could transfer to the conduction band of either Bi₂WO₆ or AgCl; and (4) Cl⁻ could be oxidized into a [•]Cl radical which is supposed to oxidize organic pollutants. Holes on the valence band of Bi₂WO₆ would transfer to that of AgCl, and the separation efficiency of photogenerated electrons and holes would improve [30]. Meanwhile, electrons induced by the surface plasmon resonance and photosensitization effects would be beneficial to produce more oxidative species. The integrated effect results in an enhanced photocatalytic activity to degrade organic pollutants.

4. Conclusion

An Ag/AgCl-Bi₂WO₆ composite was successfully synthesized using a hydrothermal and photoreduced method. Its morphology was hierarchical and flower-like with a size of

2–3 μm. As-prepared photocatalysts were performed with increased photocatalytic activities and high stabilities when degrading RhB under visible-light irradiation. The 10 wt% Ag/AgCl sample exhibited the best performance. A mechanism of photocatalytic oxidation was proposed, and it was deduced that the enhancement effect is mainly due to the establishment of a heterostructure, as well as the surface plasmon resonance and photosensitization effects. This work is evidence for the potential application of plasmonic metals in photocatalytic oxidation processes with enhancement effects.

Competing Interests

The authors declare that they have no competing interests.

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