Editor's choice paper

Ag/Bi$_{12}$O$_{17}$Cl$_2$ composite: A case study of visible-light-driven plasmonic photocatalyst

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In this investigation, novel Ag/Bi$_{12}$O$_{17}$Cl$_2$ plasmonic composites with different Ag contents were constructed through a solvothermal and subsequent photoreduction route and fully characterized by a collection of analytical techniques. Spectroscopic results confirmed the presence and uniform dispersion of Ag nanoparticles on the 2D nanosheets of Bi$_{12}$O$_{17}$Cl$_2$. The Ag content in composites exerted considerable influence on the extension of light-adsorption range and the enlargement of specific surface areas. The photocatalytic abilities of these Ag/Bi$_{12}$O$_{17}$Cl$_2$ composites were evaluated toward the degradation of rhodamine B (RhB) and 2,4-dichlorophenol (2,4-DCP) under the visible-light irradiation. The results demonstrated that the Ag/Bi$_{12}$O$_{17}$Cl$_2$ composites showed much higher photocatalytic efficiencies than that of pure Bi$_{12}$O$_{17}$Cl$_2$, especially the sample with an optimal Ag content showing the best photocatalytic behavior among all tested samples. The remarkable enhancement of Ag/Bi$_{12}$O$_{17}$Cl$_2$ photocatalytic efficiency could be mainly attributed to the efficient charge separation that was induced by the localized surface plasmon resonance effect of metallic Ag, strong visible-light adsorption and the favorable morphology with enlarged specific surface areas. Eventually, the photocatalysis mechanism over Ag/Bi$_{12}$O$_{17}$Cl$_2$ composites was preliminarily proposed on the base of reactive species trapping experiments.

1. Introduction

Over the past several decades, heterogeneous photocatalytic processes have drawn ever growing interest since they are able to find potential applications in energy storage and environmental remediation by means of absorbing and converting solar to chemical energy [1–3]. Bismuth oxychloride, a group of V–VI–VII ternary semiconductors, featured with a lamellar structure composed of [Cl–Bi–O–Bi–Cl] slices packed together with van der Waals force through chlorine atoms along the c-axis [4]. The laminated structure induces the generation of internal electric field that promotes the separation of photoproduced electron-hole pairs, thus favoring the improvement of photocatalytic performance [5]. However, the bare BiOCl is merely sensitive to UV light due to the large band gap and thus exhibits poor photocatalytic capability in visible-light region [6]. Under specific conditions, the wide band gap can be tuned by simply changing the chemical composition of BiOCl to form chlorine-deficient and oxygen-rich analogues, such as Bi$_{12}$O$_{17}$C$_{22}$, a typical bismuth oxychloride candidate with suitable band structures, thus attracting enormous attention in terms of photocatalytic degradation and selective oxidation under the visible-light illumination [7–9].

The photocatalytic efficiency of bare Bi$_{12}$O$_{17}$C$_{22}$ can be improved by the morphological tailoring or the integration with other appropriate components [10–12]. Adequate morphologies such as nanowires, nanobelts, nanoplates, and three-dimensional hierarchical microflowers achieved by various synthetic protocols, are beneficial to shorten diffusion pathways, strengthen interfacial charge separation, and enhance light harvesting, therefore promoting photocatalytic degradation ability. The latter is relevant to the generation of heterojunction structures by coupling several semiconductor components with appropriate electronic structures, which endows the obtained composites with the prolonged lifetime of carries and extended adsorption in visible-light region [13,14]. He et al. prepared Bi$_{12}$O$_{17}$C$_{22}/\beta$-Bi$_2$O$_3$ composites that exhibited excellent catalytic performance towards degradation of...
4-tert-butylphenol upon visible-light illumination [11]. A heterojunction composite BiO(Bi)2O3C2 was synthesized by Bi et al. and displayed outstanding photocatalytic behavior over methyl orange and phenol under visible light [13]. Quite recently, the Bi2O3C2/MoS2 Janus bilayer junctions could efficiently steer the charge flow by the internal electric field and thus showed superior visible-light hydrogen evolution efficiency [14].

Besides, another strategy to attain excellent visible-light photocatalytic performance is to incorporate plasmonic metal nanoparticles onto the semiconductors surface [15–17]. These plasmonic metal nanoparticles, like Ag a low cost and toxicity metal, induce the localized surface plasmonic resonance (LSPR) effect that boosts photocatalytic processes through the extension of light adsorption scope, increase of incident light scattering, and efficient transfer of plasmonic energy from metal nanoparticles to semiconductors to produce more charge carriers. Besides, these metal nanoparticles can role as sinks to trap electrons flowed from semiconductors upon excitation, which facilitates the separation of photogenerated electron-hole pairs. Till now, several cases of Ag/bismuth oxyhalide plasmonic photocatalysts have been reported [18–20]. However, to the best of our knowledge, the synthesis and photocatalytic evaluation of Ag/Bi2O17Cl2 composites have never been investigated.

Herein, in this study, a facile photoreduction method was adopted to fabricate Ag/Bi2O17Cl2 plasmonic composites that were systematically characterized by a collection of analytical techniques. The existence of crystalline metallic Ag nanoparticles was recognized by the XPS, SEM, EDS, and UV–vis DRS spectra. With the raise of Ag content, the extension of light absorption range and the enhancement of visible-light harvesting were achieved. These Ag/Bi2O17Cl2 plasmonic composites showed much higher photocatalytic degradation efficiency over both organics RhB and 2,4-DCP than bare Bi2O17Cl2, primarily ascribing to the synergistic effect of the favorable textural, optical, and electronic properties. Finally, a possible photocatalysis mechanism was proposed according to the active species trapping experiments.

2. Experimental

2.1. Chemicals

Bismuth (III) nitrate pentahydrate (Bi(NO3)3·5H2O, AR), hydrochloric acid (HCl, 36 ~38%, AR), sodium hydroxide (NaOH, AR), silver nitrate (AgNO3, AR), isopropanol alcohol (IPA, AR), disodium ethylenediaminetetraacetate dihydrate (EDTA-2Na, AR), nitroblue tetrazolium (NBT, AR), 2,4-dichlorophenol (2,4-DCP, AR) and other chemical reagents involved were supplied by Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Rhodamine B (RhB, AR) was purchased from Shanghai SSS Reagent Co., Ltd. (Shanghai, China). All chemicals were used as received without further purification and deionized water was used throughout the experimental.

2.2. Materials preparation

2.2.1. Synthesis of sample Bi2O17Cl2

The sample Bi2O17Cl2 was synthesized in the light of a reference with a small modification [10]. Typically, Bi(NO3)3·5H2O (3.84 mmol) was dissolved into a HCl aqueous solution (2 M, 25 mL) and the resultant transparent mixture was dropped with a NaOH aqueous solution (4 M, 20 mL). The obtained suspension was allowed to vigorously stir for 0.5 h at room temperature and subsequently transferred into a 100 mL stainless-steel Teflon-lined autoclave. After staying at 160 °C for 6 h and then cooling to room temperature, the yellow precipitate was finally collected, washed with deionized water and absolute ethanol for several times, and dried at 60 °C overnight to give Bi2O17Cl2 as a yellow powder.

2.2.2. Synthesis of Ag/Bi2O17Cl2 plasmonic composites

An aqueous suspension (40 mL) containing as-prepared sample Bi2O17Cl2 (1 g) was sonicated for 0.5 h and then was added with a desired amount of AgNO3. After continuously stirred for 4.5 h at room temperature and dropwise added with methanol (20 mL) in dark, the resultant mixture was subjected to an exposure to a 400 W halogen lamp (Institute for Electric Light Source, Beijing) equipped with a NaNO3 solution (2 M) to remove ultraviolet light (<400 nm). After 20 min irradiation, the photo-reduction reaction was stopped and the precipitate was collected by centrifugation, rinsed with deionized water and absolute ethanol for several times, and dried at 60 °C for 12 h to give a target composite Ag/Bi2O17Cl2. For convenience, the as-prepared Ag/Bi2O17Cl2 series were named as ABx and x hereafter referred to a theoretical mass percentage of Ag versus Bi2O17Cl2. N-doped TiO2 (N-TiO2) was also constructed according to a previous report for comparison [21].

The exact Ag content was measured by an ICP-OES apparatus using a procedure described as follows: 0.1 g ABx sample was added into a Teflon digestion tank and a concentrated nitric acid (65~68%, 15 mL) was subsequently added. The mixture was heated and digested at 200 °C until a suspension around 0.5 mL was obtained. Afterwards, a concentrated nitric acid (85~68%, 5 mL) was added and the resultant mixture was undergone a same digestion protocol to ensure the complete dissolution. The remained clear solution (0.5 mL) was diluted with the nitric acid solution (7.6%) to 500 mL and then was analyzed. The Ag content in sample AB2, AB4, AB6, and AB8 was 0.70%, 0.90%, 1.26%, and 0.80%, respectively. Since the content of samples quite differentiated to the theoretical amount, the Ag content remained in mother liquid was further checked by using ICP-OES and was 1.10%, 2.82%, 4.80%, and 6.71%. The total Ag content by the integration of target sample and mother liquid was approximately in accordance with the initial addition amount. We speculated that with the increase of Ag initial concentration, the generated Ag nanoparticles tended to agglomerate to a separate phase from the surface of Bi2O17Cl2 substrate and were thus easily removed along with the mother liquid, which were supported by the mother liquid as a grey suspension and ICP-OES results.

2.3. Characterization

The crystalline structures and compositions of samples were measured by powder X-ray diffraction (XRD) patterns on a Bruker DB Advance X-ray diffractometer (Bruker AXS, Germany) using a Cu Kα radiation source (λ = 1.5406 Å). The valence-band X-ray photoelectron spectroscopy (VB XPS) spectrum and X-ray photoelectron spectroscopy (XPS) measurements were conducted on a Thermo Scientific ESCALAB 250-i system. Binding energies were calibrated with the adventitious carbon (C1s = 284.6 eV). The morphology and microstructure of obtained samples were recorded by a transmission electron microscope (TEM, JEOL JEM-2011) and a scanning electron microscope (SEM, Hitachi S-4700) equipped with an X-ray energy dispersion spectroscopy (EDS). The specific surface areas were evaluated by nitrogen adsorption-desorption isotherms at 77 K by using a Micromeritics 3Flex apparatus. Before measurements, all samples were degassed at 423 K under vacuum over 6 h. UV–vis diffuse reflectance spectra (UV–vis DRS) were obtained on a Shimadzu UV-2600 spectrophotometer using BaSO4 as a reference. Photoluminescence (PL) spectra were recorded on a Shimadzu RF-5301 PC Fluorescence spectrophotometer with an excitation wavelength of 324 nm. The Ag content was evaluated by an ICP-OES apparatus (PerkinElmer Optima 8000)
2.4. Photocatalytic activity measurement

Photocatalytic evaluations were performed toward the degradation of dye RhB and 2,4-DCP under visible-light irradiation using a 300 W xenon lamp (CEL-HXF300, Aulight, Beijing) equipping with a 420−780 nm cut-off filter. 40 mg of the photocatalyst was added to and dispersed in 80 mL RhB (15 mg L\(^{-1}\)) or 2,4-DCP (10 mg L\(^{-1}\)) aqueous solutions. The distance between the light source and the surface of reaction solution was fixed as 20 cm. Prior to irradiation, the suspension was vigorously stirred in dark for 1 h to reach an adsorption−desorption equilibrium between contaminant molecules and surface of photocatalysts. At the irradiation time intervals of every 30 min, a 3 mL aliquot was collected and the residue concentration of RhB and 2,4-DCP was analyzed by using the ESR technique on a FA200 spectrometer.

To detect active radical species generated in photocatalytic process, 1.0 mM IPA and EDTA-2Na were introduced in the presence of composite AB4 during photocatalytic experiments for capturing hydroxyl radicals (*OH) and holes (*h\(^{+}\)), respectively [22, 23]. The formation of superoxide radicals (*O\(_2^-\)) was checked by adding 25 μM NBT in the place of RhB in solution [24]. The presence of *OH and *O\(_2^-\) radicals was further examined by 5,5-dimethyl-1-pyrroline-N-oxide (DMPO) capture under deionized water for DMPO−*OH and methanol for DMPO−*O\(_2^-\) by using the ESR technique on a FA200 spectrometer.

The reusability and durability of composite AB4 were evaluated under a same condition as above. Specifically, after each run, the photocatalyst was carefully collected from the reaction medium by centrifugation, rinsed by deionized water and ethanol for several times, then dried at 60 °C overnight for the next cycling experiment.

3. Results and discussion

XRD patterns of plasmonic composites Ag/Bi\(_{12}\)O\(_7\)Cl\(_2\) and pure Bi\(_{12}\)O\(_7\)Cl\(_2\) are displayed in Fig. 1. Clearly, all diffraction peaks of sample AB0 are well-resolved and can be unambiguously assigned to the pure tetragonal-phase Bi\(_{12}\)O\(_7\)Cl\(_2\) (JCPDS No. 37-0702). After the decoration of Ag, those composites exhibit quite similar diffraction patterns to pure Bi\(_{12}\)O\(_7\)Cl\(_2\), revealing that the existence of Ag species exerts insignificant influence on the crystallinity. Besides, the negligible variety of all peak positions and lattice parameters of Bi\(_{12}\)O\(_7\)Cl\(_2\) in composites confirms that the Ag species deposit on the surface, instead of into the Bi\(_{12}\)O\(_7\)Cl\(_2\) lattice. In addition, a slight change of peak intensity ratio (117)/(00 12) is clearly observed and can be attributed to the variation of preferred orientation induced by the sonication treatment during the photo-reduction synthesis [25]. The absence of corresponding diffraction peaks of metallic Ag may possibly assigned to the low content and good dispersion of Ag species onto the surface of Bi\(_{12}\)O\(_7\)Cl\(_2\). Besides, characteristic peaks assigning to impurities or other phases are undetectable, demonstrating the high purity of these as-prepared composites.

To verify the presence of metallic Ag and check surface valence states of AB composites, XPS analysis of the composite AB4 was carried out and shown in Fig. 2. The survey spectrum in Fig. 2A identifies the presence of several elements Bi, O, Ag, Cl and adventitious C, as expected. Fig. 2B displays the valence-band X-ray photoelectron spectroscopy (VBXPS) spectra, revealing that the position of valence-band maximum (E\(_{VBM}\)) of composite AB4 is located at 2.02 eV that is quite close to the reported value [8]. Both prominent peaks with binding energies at about 159.31 eV and 164.64 eV in Fig. 2C are ascribed to Bi 4f\(_{7/2}\) and Bi 4f\(_{5/2}\) of chemical states of Bi\(^{3+}\) in lattice, which is in good accordance with the previous reports [20]. The high resolution spectrum of the Ag 3d in Fig. 2D displays two peaks with binding energies located at 373.63 eV and 367.63 eV, corresponding to Ag 3d\(_{3/2}\) and Ag 3d\(_{5/2}\) respectively. The presence of both abovementioned peaks and the separation of 6.0 eV between binding energies ensure the formation of zero-valence Ag instead of Ag cations in composite AB4 [19]. The banding energy of Ag 3d\(_{5/2}\) is much smaller than that of metallic Ag (368.2 eV) and quite close to those in composites Ag/ZnO (367.6 eV) [26], Ag/g-C\(_3\)N\(_4\) (367.8 eV) [27], and Ag/AgCl/NaTaO\(_3\) (367.4 eV) [28], mainly attributing to the special interaction between metallic Ag and semiconductor Bi\(_{12}\)O\(_7\)Cl\(_2\). Lu et al. attributed the low binding energy of Ag 3d\(_{5/2}\) to the evident positive charge of Ag induced by the efficient migration of electrons from Ag to ZnO that was driven by the relatively small work function of Ag in comparison to that of ZnO [26]. Similarly, it is reasonable to speculate that the work function of Ag herein may be smaller than that of another component Bi\(_{12}\)O\(_7\)Cl\(_2\), which should be researched in detail in the future.

An in-depth observation for these plasmonic composites was further performed by SEM and TEM images, as shown in Fig. 3. Fig. 3A and B depict the typical morphological and microstructural images of samples AB0 and AB4. Evidently, numerous irregular two-dimensional nanosheets with a thickness of approximately 80 nm in sample AB0 tend to randomly aggregate to large clusters with smooth surfaces exposed. After the decoration of metallic Ag species through a photoreduction process, some brilliant cubic dots in a size ranging from several nanometers to 250 nm appear on surface of large clusters in sample AB4 in Fig. 3B, as marked by yellow arrows. To identify the chemical composition of these brilliant dots, two microregions without and with a dot labeled respectively by the sonication treatment during the photoreduction synthesis can be attributed to the variation of preferred orientation induced by the sonication treatment during the photoreduction synthesis [25]. The absence of corresponding diffraction peaks of metallic Ag may possibly assigned to the low content and good dispersion of Ag species onto the surface of Bi\(_{12}\)O\(_7\)Cl\(_2\). Besides, characteristic peaks assigning to impurities or other phases are undetectable, demonstrating the high purity of these as-prepared composites.

The optical property of as-prepared samples was evaluated by UV−vis diffuse reflectance spectra (UV−vis DRS). As displayed in Fig. 4A, the photoresponse of the sample AB0 ranges from the UV-light to visible-light region and the adsorption edge approaches up to 530 nm. After the integration of metallic Ag nanoparticles, these
composites show a similar absorption ability in UV-light region while an enhanced absorption in visible-light region in comparison to sample AB0, mainly attributing to the LSPR effect of plasmonic Ag species with the wide nanoparticles size distribution[29], as also represented in Fig. 3 and Fig. S1. Furthermore, the visible-light absorption of these composites strengthens with the increase of Ag

Fig. 2. XPS analysis of the composite AB4: (A) survey spectra, (B) VBXPS, (C) Bi 4f, and (D) Ag 3d.

Fig. 3. SEM images of composites AB0 (A) and AB4 (B), and the corresponding EDS spectra (C) and (D), TEM of the samples AB0 (E) and AB4 (F).
content and then decrease when mass percentage of Ag/Bi$_{12}$O$_{17}$Cl$_2$ is beyond 4%, revealing that sample AB4 is of the strongest visible-light harvesting ability among all candidates and may potentially display excellent photocatalytic ability. The band gap energies of these samples were calculated following the formula: 
\[
\alpha = A \left( \frac{h \nu-E_g}{n/2} \right)
\]
where \(h\), \(\nu\), \(E_g\), and \(A\) are the absorption coefficient, light frequency, band gap energy, and a constant, respectively. \(n\) is a constant that depends on the characteristic of transition in semiconductors, that is, direct transition (\(n = 1\)) or indirect transition (\(n = 4\)). The Bi$_{12}$O$_{17}$Cl$_2$ with the indirect transition was reported by previous literatures [7,8], and thus its band gap energy was estimated to be 2.41 eV in Fig. 4B. The variation trend of estimated band-gap energies is similar to that of visible-light absorption ability of these composites, as seen in Table 1.

The N$_2$ adsorption-desorption isotherms were measured to investigate the textural property of obtained samples. As represented in Fig. 5, the isotherms of AB series belong to the Type IV with a Type H3 hysteresis loop at a high relative pressure between 0.5 and 1.0, revealing the presence of slit-like pores that may possibly be formed from the inter-nanosheet stacking morphology [11]. The specific surface area values and pore volumes increased slightly and then decreased along with the increase of Ag precursor addition.

The above phenomenon can be explained as follows. The introduction of appropriate amount of external Ag nanoparticles may cause the creation of new exposed surface and thus improve the specific surface area. However, the excess amount of Ag nanoparticles may inversely reduce the surface area by means of blocking stacking pores. As can be seen, the composite AB4 has the largest specific surface area among all samples, which is beneficial to adsorb organic contaminants around active sites and thus maximize the photocatalytic performance [30].

It is well realized that the photoluminescence (PL) spectroscopy is able to reflect the migration, transfer, and separation efficiency of photoinduced electron-hole pairs that directly affect the photocatalytic performance of semiconductors [31]. PL spectra of samples AB0, AB4, and AB8 were hereafter recorded and shown in Fig. 6. A broad intensive band with several weak peaks ranging from 400 to 600 nm is observed and ascribed to charge-transfer transitions between valance and conduction band, the surface-defect like oxygen vacancies generated from the fast growth rate, and different valence states of bismuth ions in Bi$_{12}$O$_{17}$Cl$_2$ [10,12]. The existence

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**Table 1**

<table>
<thead>
<tr>
<th>Samples</th>
<th>(S_{\text{BET}}) (m$^2$ g$^{-1}$)</th>
<th>Pore volume ((10^{-2}) cm$^3$ g$^{-1}$)</th>
<th>Band gap (eV)</th>
<th>Apparent reaction rate constants</th>
</tr>
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<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>For RhB (10$^{-3}$ min$^{-1}$)</td>
</tr>
<tr>
<td>AB0</td>
<td>6.4</td>
<td>3.3</td>
<td>2.41</td>
<td>1.93</td>
</tr>
<tr>
<td>AB2</td>
<td>7.1</td>
<td>3.3</td>
<td>2.43</td>
<td>5.72</td>
</tr>
<tr>
<td>AB4</td>
<td>7.6</td>
<td>4.0</td>
<td>2.46</td>
<td>10.3</td>
</tr>
<tr>
<td>AB6</td>
<td>5.2</td>
<td>2.4</td>
<td>2.36</td>
<td>6.76</td>
</tr>
<tr>
<td>AB8</td>
<td>5.8</td>
<td>2.3</td>
<td>2.37</td>
<td>7.63</td>
</tr>
<tr>
<td>N-TiO$_2$</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>1.25</td>
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</tbody>
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**Fig. 4.** (A) UV–vis diffuse reflectance spectra of Ag/Bi$_{12}$O$_{17}$Cl$_2$ series; (B) a plot of \((\alpha h \nu)^{1/2}\) vs. photon energy \((h \nu)\) of corresponding samples.

**Fig. 5.** Nitrogen adsorption–desorption isotherms of Ag/Bi$_{12}$O$_{17}$Cl$_2$ series.

**Fig. 6.** The photoluminescence spectra of samples AB0, AB4, and AB8 at room temperature \((\lambda_{\text{ex}} = 324\ \text{nm})\).
of deposited Ag can inhibit the radiative recombination of generated charge carriers [32]. Accordingly, the emission band intensity of the sample AB4 is weaker than those of samples AB0 and AB8, suggesting that the presence of appropriate amount of Ag is crucial to the efficient separation of photogenerated charge carriers. Therefore, sample AB4 with the lowest band intensity is expected to show an excellent photocatalytic degradation efficiency basing upon UV-vis DRS and PL analyses.

From the aforementioned spectroscopic analyses, we can conclude that metallic silver nanoparticles were successfully formed via a photoinduced reduction process and uniformly dispersed on surface of Bi$_{12}$O$_{17}$Cl$_2$. In addition, composite AB4 possesses excellent visible-light harvesting ability and effective separation capability of charge carriers, potentially benefitting the enhancement of photocatalytic degradation of organic contaminants.

Photocatalytic degradation of RhB and 2,4-DCP over as-synthesized samples was evaluated under visible-light irradiation ($\lambda \geq 420$ nm), as shown in Fig. 7A. Dye RhB could not be significantly decomposed in absence of photocatalysts even after an irradiation time of 240 min, suggesting that the direct photolytic degradation can be ignored. Sample N-TiO$_2$ shows fairly low photocatalytic degradation efficiency around 30% after 240 min. Bare Bi$_{12}$O$_{17}$Cl$_2$ displays a moderate catalytic performance, by which around 40% RhB molecules were destroyed after 240 min. However, the deposition of metallic Ag on surface of Bi$_{12}$O$_{17}$Cl$_2$ ensures the significant enhancement of photocatalytic efficiency toward the degradation of RhB. In particular, with the raise of Ag content in plasmonic composites, the photocatalytic performance of as-obtained photocatalysts increases first and then declines when the content of metallic silver species exceeds 4%. As a result, under the identical condition sample AB4 is the best candidate among all samples and provide a maximal catalytic degradation efficiency of 93%. The apparent reaction rate constant were estimated through a pseudo-first-order kinetic equation that was simplified from the Langmuir–Hinshelwood kinetic model in diluted solutions [33], and are listed in Table 1. Correspondingly, the sample AB4 has the largest apparent reaction rate constant value that is almost 5.3 and 8.2 times as high as the samples AB0 and N-TiO$_2$, as also shown in Fig. S2.

To exclude the possibility of dye sensitization, 2,4-DCP as a colorless pollutant, was utilized to identify the visible-light-driven photocatalytic process, as depicted in Fig. 7B. Clearly, after an irradiation time of 180 min the composite AB4 exhibits a satisfactory photocatalytic efficiency about 82% that is much higher than those results from AB0 and N-TiO$_2$. The temporal evolution of the absorbance spectra of 2,4-DCP was recorded and shown in Fig. S3. Accordingly, the apparent reaction rate constant of the composite AB4 is 1.7 and 2.3 times as high as those from samples AB0 and N-TiO$_2$ in Fig. S2, respectively.

The enhancement of photocatalytic behavior of AB plasmonic series is mainly attributed to following aspects. Foremost, the integration of metallic Ag species strengthens the visible-light scattering and harvesting ability in visible-light region, favoring the generation of more electron-hole pairs for oxidative degradations. Second, the Ag nanoparticles are able to role as electron sinks to promote the efficient separation of produced charge carriers [34,35]. A suitable amount of Ag deposits facilitates the migration and transfer of excited electrons from the conduction band of semiconductor to metallic sites through the Schottky barrier generated at the metal-semiconductor interface. However, an excessive content of silver species acts as recombination centers for the photogenerated electron-hole pairs or cover active sites on surface to hinder the accessibility and incoming visible light, thus diminishing the photocatalytic degradation efficiency [18,19]. Thirdly, the LSPR effect of metallic Ag species excited by the absorption of visible light with specific frequency would promote the surface electron excitation and interfacial electron transfer, and thus be propitious to the enhanced photocatalytic efficiency [5,36]. Last but not the least, the suitable electronic property and morphology with enlarged specific surface areas may also contribute to the increased photocatalytic performance. The former ensures the moderate band gap energy that can be easily excited and trigger photocatalytic process and the
Fig. 9. DMPO spin-trapping ESR spectra by the samples AB0 and AB4 for detecting DMPO-•O2− (A) and DMPO-•OH (B) in deionized water and methanol, respectively.

Fig. 10. Reusability tests of the composite AB4 for degradation of RhB under visible-light irradiation (A), and the Ag 3d XPS of the composite AB4 before and after reusability tests (B).

later ensures the efficient access of contaminant molecules to active sites and the subsequent escape of mineralized products or intermediates [37,38]. As a result, a synergistic effect of the strengthened light harvesting ability, efficient separation of charge carriers by LSPR effect, and the favorable electronic structure and morphology enables these Ag-containing bismuth-based composites to exhibit an excellent photocatalytic performance.

To explore the mechanism of the photocatalytic degradation, trapping experiments of active radical species were conducted over the sample AB4, as depicted in Fig. 8A. It is obvious that the photocatalytic performance becomes quite low after adding the reagent EDTA-2Na, holes trapper, indicating that holes were predominately active species during the photocatalytic process. Nevertheless, the addition of IPA, hydroxyl radical trappers, has almost no effect, revealing that the formation of radicals •OH is a minor factor determining the catalytic efficiency [39]. Generally, the existence of •O2− radicals can be detected by the abatement of NBT concentration during photocatalysis since NBT molecules are apt to react with produced •O2− radicals to yield insoluble intermediate purple formazan [24]. Consequently, an obvious decrease of NBT concentration was observed in experimental and hereby contributed to the presence of •O2− radicals in Fig. 8B. To further demonstrate the presence of both •OH and •O2− species, ESR technique was adopted by using DMPO as a scavenger and represented in Fig. 9. As can be observed, neither composite AB4 nor sample AB0 shows any signals in dark. Under visible irradiation for several minutes, both samples exhibit evident several signals corresponding to •OH and •O2− radicals. The intensity of •O2− species signals of composite AB4 is much stronger than that of sample AB0 in Fig. 9A, revealing the more •O2− species generated by the composite AB4 than the sample AB0 [40]. The similar tendency can be found for the formation of •OH radicals in Fig. 9B. In addition, the variation consistency of both •OH and •O2− species signals reveals the possible conversion of •O2− to •OH radicals under such a circumstance.

On the basis of experimental results, a schematic band alignment between the metallic Ag nanoparticles and Bi12O17Cl2 semiconductor was shown to propose a photocatalysis mechanism upon the degradation of organic contaminants in Scheme 1. According to the speculation in the XPS section, the work function of metallic Ag is smaller than that of semiconductor Bi12O17Cl2 and thus the Fermi level of Bi12O17Cl2 is lower than that of Ag, resulting in the efficient transfer of electrons from Ag to Bi12O17Cl2 through the interface of metal-semiconductor, namely the ohmic contact,
4. Conclusion

A series of Ag-containing Bi$_2$O$_5$Cl$_2$ plasmonic composites were prepared via a simple two-step procedure and systematically characterized by various spectroscopic analyses. It was found that metallic Ag nanoparticles were successfully deposited and uniformly dispersed on the surface of Bi$_2$O$_5$Cl$_2$. In addition, the Ag content in composites played an important role on optical and textural properties, and further on the photocatalytic performances. The composite AB4 with an optimized Ag mass percentage of 4% exhibited the best photocatalytic activity and the corresponding apparent reaction rate constants for degradation of RhB and 2,4-DCP were 5.3 and 1.7 times as high as those of pure Bi$_2$O$_5$Cl$_2$, respectively. The significant enhancement of Ag/Bi$_2$O$_5$Cl$_2$ photocatalytic performance might be ascribed to a synergistic effect of the efficient charge separation caused by the LSPR effect of metallic Ag nanoparticles, strong visible-light harvesting and favorable morphology with enlarged specific surface areas. Finally, the photocatalytic mechanism over the Ag/Bi$_2$O$_5$Cl$_2$ composites was speculated according to the reactive radicals trapping experiments.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.molcata.2016.11.028.

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