Construction and characterization of Ag/AgI/Ag₃BiO₃ heterojunction and its photocatalytic mechanism

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ABSTRACT
In this work, a new ternary Ag/AgI/Ag₃BiO₃ photocatalyst was fabricated by an in-situ precipitation method, where Ag⁰ nanoparticles, serving as a mediator, implanted on the surface of glossy AgI, quantum efficiency being improved attributed to the surface plasmon resonance (SPR) effect. The composites showed superior photocatalytic performance to methylene blue (MB) degradation under visible illumination (λ > 420 nm). The Kobs values of Ag/AgI/Ag₃BiO₃-3 were 7.4 and 3.6 times compared with that of pristine Ag₃BiO₃ and AgI, respectively. Based on the series of experimental results, a Z-scheme heterojunction has formed in preparations. The electron-hole pairs maintained a transferable cycle, which efficiently inhibited the recombination of electron-hole pairs. According to active species analysis, holes were determined the predominant work-function in photocatalytic degradation system. The feasible mechanism has proposed to illustrate the photocatalytic decomposition of MB on Ag/AgI/Ag₃BiO₃. Our work has important implication for the management and practical application of catalysts.

1. Introduction
For decades, photocatalyst has always been exploited as a promising tool to alleviate increasing environment crisis. Including TiO₂, ZnO, CdS, Fe₂O₃, Bi₂O₃ and AgX (X = Cl, Br, I) were studied by researchers as semiconductor photocatalyst [1–6]. AgX that is a photosensitive material has always caught many eyes in photocatalytic field [7–9]. The defect electronic structure of semiconductor results in highly recombination of photo-stimulated carriers, limiting the practical applications, but adulteration is greatly beneficial to the transmission of carriers, which may lead to a heterojunction formation [10–12]. Using polyvinylpyrrolidone (PVP) as a surfactant, Zhang and colleagues [13] controlled AgI/g-C₃N₄ heterojunction photocatalysts by a deposition-precipitation method, and the photocatalysts exhibited higher oxidation than initial AgI and g-C₃N₄. Parallelly, due to the powerful separation and migration of interfacial charge...
carries, AgX (X = I, Br)/CuBi₂O₄ heterojunction composites exhibited excellent photocatalytic performance [14]. Fang et al. [15] developed a WO₃/Ag/AgCl film on glass by an impregnating–precipitation–photoreduction method, and Z-scheme was proposed to explain its excellent photocatalytic activity. A group [16] constructed AgI nanoparticle-functionalized reduced graphene oxide aerogels, which not only exhibited better photocatalytic activity and stability, but were active catalysts for the synthesis of bis(indolyl)methane under solvent-free conditions. Studies on AgX are sufficient to demonstrate the importance of it in the field of photocatalysis.

Recently, Bi-based photocatalyst is a rising star at photocatalytic materials, and it has attracted extensive attention. For instance, (BiO)₂CO₃ [17], Bi₂MoO₆ [18] and BiVO₄ [19] etc. were found extensive applications in photocatalytic oxidations and reductions. Li et al. [20] designed double-shell Bi₂O₃/Bi₂WO₆ hollow microspheres to rhodamine B degradation under visible-light irradiation. Li et al. [21] prepared Z-scheme ternary g-C₃N₄/Bi₂O₃/BiPO₄ heterostructure which extremely restrained the recombination of photo-generate electron and hole pairs, thus exhibiting outstanding oxidation and reduction abilities for methyl orange. As we all know, ABO₃ is a perovskite oxide structure compound, and it can adopt majority of metallic ions. Gong and coworkers [22] synthesized the AgBiO₃ NPs and found that it could be rejected for mineralization including phenols and rhodamine B owe to AgBiO₃ NPs self-produced amount of the main reactive oxygen species (ROS). M. Rurtz and M. Jansen [23] fabricated Ag₃BiO₃ inorganic compound for the first time and proposed its structural model, considering Ag₃BiO₃ comprises of Ag₂O and Bi₂O₃. To our best knowledges, there are hardly any reports about the optical properties of Ag₃BiO₃ up to now.

It is well-known that noble metal loading can improve quantum efficiency resulting from the observably surface plasmon resonance (SPR) effect under visible-light illumination [24,25]. Sellappan et al. [26] designed, fabricated, and examined Ag/TiO₂ and Au/TiO₂ nanocomposites, and studied that interfacial charge transfer is the crucial cause of the activity enhancement where particles are in direct to contact with TiO₂. Besides, since the SPR effect of noble metal loading, the absorption edge of composites can be enlarged in visible-light region [27,28].

Herein, we prepared a new ternary Ag/AgI/Ag₃BiO₃ photocatalyst via an in-situ precipitation method and investigated the activity of ternary composites on photocatalytic degradation of MB. The new composites exhibited higher quantum efficiency and outstanding photocatalytic performance under visible-light illumination. The stability of the composites was also investigated. Finally, the feasible mechanism was determined through various technical characterization and analysis.

2. Experimental
2.1. Materials
Bi(NO₃)₃·5H₂O, NaOH, NH₃·H₂O, KI, concentrated nitric acid and absolute ethyl alcohol were purchased from Beijing Chemistry Company, China. AgNO₃ was purchased from Shanghai Chemical reagent Co. Ltd. Melamine was obtained from Sinopharm chemical reagent Co. Ltd. The deionized water (resistivity > 18.0 MΩ cm) was used throughout the experiments. All the reagents were bought from commercial sources of AR range and all of this without further purification.
2.2. Preparation of Ag₃BiO₃, AgI and Ag/AgI/Ag₃BiO₃ samples

The Ag₃BiO₃ nanoparticles were prepared as follows. Firstly, 3 mmol of AgNO₃ was dissolved in 30 mL of deionized water forming colorless solution. Secondly, 1 mmol of Bi(NO₃)₃·5H₂O reagent was dissolved in 10 mL of deionized water containing 2 mL of concentrated nitric acid. Then, the two solutions were mixed, and then 10 mL of 5 M NaOH solution was added slowly drop by drop in the mixing solution at the same time. Next, the suspensions were transferred into a Teflon-lined stainless steel autoclave (filled 70 percent) of 100 mL capacity and heated at 453 K for 12 h, cooled to room temperature naturally and collected all depositions. Finally, Ag₃BiO₃ powder was obtained after several washings with distilled water and absolute ethanol and drying at 333 K for 12 h.

Ag/AgI/Ag₃BiO₃ was prepared by an in-situ precipitation method. Initially, in order to form silver ammonia solution, a set amount of AgNO₃ solution was introduced moderate ammonia. Secondly, as-obtained Ag₃BiO₃ were added into abovementioned silver ammonia solution with magnetic stirring. Then, ratable AgI solution was instilled the abovementioned suspension and kept stirring for another 0.5 h. Finally, all sediments (Ag/AgI/ABO-X) were desiccated at 333 K for 12 h. These Ag/AgI/ABO-X (X = 1, 2, 3, 4, 5, the molar ratios of AgI to Ag₃BiO₃, Ag is trace) were collected for further use. For comparison, pure AgI was prepared under similar experimental conditions.

2.3. Apparatus

The crystalline structure of as-obtained composites was characterized by an X-ray diffractometer (2θ ranged from 10° to 80°). The morphological features of composites were characterized by a scanning electron microscope (SEM). An X-ray photoelectron spectroscopy (XPS) was also employed to detect the elements of compositions and its chemical state on a KRATOA XSAM800 with Mg Kα irradiation. UV–vis diffuse reflectance spectra (UV-DRS) was carried out on a UV2401 spectrophotometer to analyze the light absorption performance of samples. The photoluminescence (PL) spectra result of samples were performed with the excitation wavelength of 225 nm by a Varian Cary Eclipse spectrometer. The electrochemical impedance spectra (EIS) of all of samples were carried out on a Zahner electrochemical workstation. 300 W Xe arc lamp was occupied in the simulated solar-light.

2.4. Photocatalytic experiments

In typically, the photocatalytic activities of as-obtained samples were evaluated through removing MB dye under visible-light illumination. One 300 W Xe arc lamp acts as the illuminant to offer energies. The illuminated area is about 33.18 cm², and the distance between the liquid level and light source is around 10 cm. In this work, 0.05 g of as-prepared samples and 100 mL MB solution (pristine absorbance is 2.50) were added into a glass reactor which kept room temperature inside. The suspensions were continuously stirred for 0.5 h absenting illumination before embarking on photocatalytic indeed works to get the adsorption or desorption equilibrium of MB dye on catalyst’s surface. Then, 3 mL of suspension was collected from reaction system at the given time interval. All collections were separated together via centrifugation at 5,000 rpm.
for 10 min. After that, UV-vis spectrophotometer (UV-1600) was employed to analyze these supernatants. For comparison, the original MB solution (not participate in any manage) also was judged with the same parameters. Degradation efficiency could be calculated by the way [29]:

\[
\eta(\%) = \left(1 - \frac{A}{A_0}\right) \cdot 100,
\]

or

\[
\eta(\%) = \left(1 - \frac{C}{C_0}\right) \cdot 100,
\]

(1)

Where \(\eta\) is the degradation efficiency of catalysts toward MB dye. \(C\) and \(C_0\) are the concentrations while \(A\) and \(A_0\) donate the absorbance at irradiation time \(t\) and 0, respectively.

3. Results and discussion

3.1. Characterization

First, all as-obtained were analyzed by a powder X-ray diffraction (XRD). Attested in Figure 1, it turns out that all the samples AgI, Ag\(_3\)BiO\(_3\) and Ag/AgI/ABO were synthesized successfully already. The intense diffraction peaks of AgI match with JCPDS card no. 09-0374 and align well with previous reports [30,31]. Located at 28.4\(^\circ\), 33.1\(^\circ\), 33.6\(^\circ\), 34.8\(^\circ\) and 53.4\(^\circ\) of 2\(^\theta\) degree, the characteristic peaks agree with (312), (431), (332), (422) and (372) planes, respectively, of Ag\(_3\)BiO\(_3\)(JCPDS card no. 49-0140). Remarkably, as the increasing contents of AgI, the height of major diffraction peaks of Ag\(_3\)BiO\(_3\) were increasingly lower in the Ag/AgI/ABO composites, indicating the size or clusters of Ag\(_3\)BiO\(_3\) were greatly affected by the AgI contents. Gone were the (101) and (103) peaks of Ag/AgI/ABO, may revealing traces of sliver ions from AgI were reduced to metallic sliver because it is a sensitizer [32].

![Figure 1. XRD pattern of the as-prepared samples.](image)
Second, in order to further prove the existence of metallic sliver and to analyze the elemental compositions and chemical status, Ag/AgI/ABO-3 composite was characterized by XPS. The full-range XPS spectrum (See Figure 2(a)) confirms only I, Ag, O, Bi and a carbon (indicator) peak existence, revealing that the chemical states of all elements are involved. From the high-resolution XPS spectra of O 1s in Figure 2(b), it is resolved into

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**Figure 2.** Survey XPS spectrum (a), high-resolution XPS spectrum of O 1s (b), I 3d (c), Bi 4f (d), and Ag 3d (e).

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a couple of peaks located at 532.6, 531.0 and 529.4 eV. The higher banding energy of 532.6 eV ascribed to oxygen complexes absorbed surface such as OH, H2O, and O2 and the peaks at 531.0 and 529.4 eV respectively stemmed from Ag-O and Bi-O bonds in Ag3BiO3 [33,34]. The high-resolution XPS spectrum (see Figure 2(c)) for I 3d3/2 and 3d5/2 are observed at 631.0 and 619.9 eV respectively, ascribed to the I− in AgI [35,36]. The XPS spectrum of Bi 4f, Figure 2(d) shows that the binding energies of Bi 4f7/2 and 4f5/2 are distinctly observed at 164.0 and 158.7 eV respectively, ascribed to the Bi3+ in Ag3BiO3. As is shown in Figure 2(e), the peaks centered about at 374.8 and 368.7 eV are respectively coincident with the Ag 3d3/2 and 3d5/2, which are ascribed to the Ag+ [37]. Moreover, the Ag 3d5/2 high-resolution XPS spectra is also resolved a slight peak located at 367.9 eV, revealing a bit Ag0 have yielded in Ag/AgI/Ag3BiO3 [38,39] and that is corresponded to the XRD result.

3.2. Morphology analysis

Figure 3 displays the microcosmic morphology features of Ag3BiO3, AgI and Ag/AgI/ABO-3 composites. As is shown in Figure 3(a), Ag3BiO3 with aggregation is a nanoparticle ranged from 200 to 500 nm. Figure 3(b) exhibits that the morphology of pristine AgI is a glossy irregular particle. The formed heterojunction can be found to be comprised by metallic Ag, Ag3BiO3 and AgI (See Figure 3(c)). The morphologies of AgI particles obviously change after imbedding Ag3BiO3 nanoparticles over it. On the one hand, the AgI is surrounded by a mount of nanoparticles and the quantity of its crystallographic planes has increased. On the other hand, there are trace of fine nanoparticles, metallic Ag, implanted on the surface of AgI, which is wonderful to consistent with XRD and XPS. It proves a fact that a heterojunction in Ag/AgI/ABO can promote the separation and transmission efficiency of electron-holes, thereby enhancing the photocatalytic performance.

3.3. UV-vis diffuse analysis

In order to obtain the band gap energies of photocatalysts, optical absorption studies in the UV–vis region was carried out, shown in Figure 4. AgI holds a sharp adsorption edge with wavelengths presumably 450 nm, which is in accordance with report [40]. For Ag3BiO3 nanoparticles, its absorption band edge onset about at 600 nm, displays stronger absorption than AgI in visible region. Obviously, compared to intrinsic absorption intensity of AgI, the Ag/AgI/ABO-3 heterojunction shows stronger absorbance in visible region, which coincident with the spread of absorption in visible-light region. Therefore, it features the great enhancement of photocatalytic performance, attributed to the strong light harvesting property of Ag3BiO3. The valence band and conduction band
both of Ag$_3$BiO$_3$ and AgI are estimated by Butler and Ginley model using formula (2) and (3) [41]:

$$E_c = \chi - E_0 - 0.5E_g,$$

$$E_v = E_c + E_g,$$

of which $E_c$, $\chi$, $E_0$, $E_g$ and $E_v$ are conduction band energy, pearson absolute electronegativity of samples, the reduction potential of water, the band energy of as-obtained sample and valence band energy, respectively. Here, $\chi$ values are 5.615 eV and 5.479 eV for Ag$_3$BiO$_3$ and AgI, respectively. According to the above rules, the available $E_g$ of AgI is 2.74 eV, $E_c$ and $E_v$ of Ag$_3$BiO$_3$ are 0.19 eV, 2.05 eV, respectively.

### 3.4. Photocatalytic activity of photocatalyst

At this work, MB dye as an objective contaminant was used for evaluating the as-obtained photocatalytic performance. Control experiments were carried out and it implied that MB dye couldn’t be mineralized in the absence of the as-obtained samples. From the Figure 5(a) it can be seen, every doping sample’s photocatalytic activities for MB dye outperform its individual counterparts. In contrast, Ag/AgI/ABO-3 photocatalyst is the best one to degrade MB dye at all samples exposing visible illumination. For Ag/AgI/ABO-3, it exhibits its highest photocatalytic performance rate of 0.02723 min$^{-1}$ with 80.5 percent degradation, which much exceeded that of bare AgI and Ag$_3$BiO$_3$ (See Figure 5(c)). Accordingly, locating at 664 nm is the characteristic absorbance peak of MB dye [42]. Figure 5(b) describes the time-dependent UV-Vis absorption spectra evolution curves of MB dye in the degradation system that Ag/AgI/ABO-3 involves. It could be seen that slight hypsochromic effects of MB occurred as MB was gradually demethylated [43,44]. The SEM image of Ag/AgI/ABO (See Figure 3(c)) offers an indication that a heterojunction
accelerates the separation of electron hole pairs, thus improving the photocatalytic activities of dopants. Moreover, the mineralization level of the Ag/AgI/ABO-3 photocatalyst to MO was investigated to determine the mineralization ratio of the degraded MB [45]. As total organic carbon (TOC) analysis pattern shows in Figure 5(d), the TOC value fell by 16.48 percent after an hour visible light irradiation. This result indicates that Ag/AgI/ABO-3 photocatalyst was easy to mineralize MB dye solution.

3.5. Active species analysis

Generally, the reactive species on the surface of as-prepared photocatalysts play an active role in photocatalytic process. Therefore, different scavengers were brought in photocatalytic reaction system to affirm which kinds of species at work. Popularly, isopropanol (IPA), ammonium oxalate (AO) and benzoquinone (BQ) were used for capturing hydroxyl (•OH), holes (h⁺) and superoxide (•O²⁻), respectively. As is shown in Figure 6, the photocatalytic performance is slightly reduced when IPA and BQ are introduced into photocatalytic system, which indicates •OH and •O²⁻ made segmental influence on photodecomposition process. On the other hand, the photocatalytic performance is obviously declined when AO is supplied for photodecomposition process, validating that holes are the predominant work-functional species. Therefore, a feasible photocatalytic mechanism can be proposed for the Ag/AgI/ABO photocatalytic reactions.
3.6. Reaction mechanism

In light of the discussion above, Figure 7 schematically shows the feasible photocatalytic mechanism to illustrate the superior photocatalytic performance of MB dye over Ag/AgI/ABO material. Nevertheless, photogenic electrons and holes are effortless to recombination due to the narrow band gap level of Ag$_3$BiO$_3$ material. A type-I heterojunction is firstly employed to explain the photocatalytic mechanism on Ag/AgI/ABO. According to the alignment of both Ag$_3$BiO$_3$ and AgI electronic structures, they can be excited synchronously by solar light ($\lambda > 420\text{ nm}$). As is shown in Fig 8(a), photons are absorbed by Ag$_3$BiO$_3$ and AgI under visible-light illumination. Simultaneously, the electron-hole pairs
yield on both Ag₃BiO₃ and AgI interface. In addition, because of Ag⁰ SPR, electrons on the CB of Ag can migrate to that of AgI. Since the CB of Ag₃BiO₃ is more positive than that of AgI, the number of electrons transfers to the CB of Ag₃BiO₃. Unluckily, it is hardly for Ag₃BiO₃ to reduce O₂ into \( \cdot \text{O}_2^- \) as the potential level of it is less negative than that of \( \cdot \text{O}_2^- / \text{O}_2 \) (-0.33 eV vs. NHE) \[46,47\], which against the consequence of trapping experiments. Besides, holes on the VB of AgI can move to that of Ag₃BiO₃, posed the recombination of electrons and holes, which is not beneficial for photocatalytic reaction. The conditions are similar with the report \[48\]. Consequently, it is most possible that Z-Scheme heterojunction plays a significant role in photocatalytic process. As is shown in Fig 8(b), the electrons on the CB of Ag₃BiO₃ migrate to the VB of Ag. Under visible illumination, the electrons on the VB of excited Ag can be transferred to CB of AgI in the help of Ag⁰ SPR. It is well-known that electron possesses powerful reduction ability. The absorbed O₂ is reduced into \( \cdot \text{O}_2^- \) by electrons on the CB of AgI. In line with active species trapping experiments, both \( \cdot \text{O}_2^- \) and \( \cdot \text{OH} \) are considered as secondary radical species, and holes are the dominant active species in photocatalytic process. As we can see, the photo-generated holes of Ag₃BiO₃ transfer to AgI on the VB. The separation of electron-hole pairs maintains a transferable cycle, which effectively inhibits the recombination of electron-hole pairs.

In order to investigate the separation efficiency and transport properties of charge carries, the PL emission spectra shows in Figure 8(a). A weaker PL intensity reflects a higher lifetime of photo-excited charge-carrier \[49,50\]. It can be seen clearly that the PL peak intensity of Ag₃BiO₃ is the strongest, followed by AgI, which indicates that the photogenic electron-hole pairs are easy to recombine. However, the PL peak of Ag/AgI/ABO-3 is significantly weakened, indicating the recombination of photogenic electron-hole pairs over Ag/AgI/ABO-3 can be inhibited validly. In addition, as illustrated in Figure 8(b), the EIS Nyquist plot of samples are semicircles and the radius value of Ag₃BiO₃ is the biggest, followed by AgI, indicating their impedance and capacitive reactance bigger than the composites. Namely, the efficient charges separation both of Ag₃BiO₃ and AgI are poor compared to Ag/AgI/ABO, which conforms to the photocatalytic performance results. It’s worth noting that the radius of Ag/AgI/ABO-3 is the smallest among all samples, revealing that there emerges a significantly efficient charges separation, which attributes to the function of Z-Scheme heterojunction. Moreover, moderate amount of Ag⁰ nanoparticles anchored on AgI surfaces serve as charge carriers separation centers, facilitating the surface electron excitation and interfacial transfer with the effect of SPR, also presented by PL \[51\].

Figure 8. PL spectra (a) and EIS emission spectra (b) of as-prepared samples.
In a word, the Ag/AgI/ABO photocatalyst has formed Z-scheme heterojunction which advanced the electron and hole pairs’ transport property, along with the enhancement of the photocatalytic performance. The feasible mechanism was demonstrated by PL and EIS.

4. Conclusions

The Ag/AgI/ABO photocatalyst was fabricated by an in-situ precipitation method for the first time. Ag\(^0\) nanoparticles yielded during synthetic process. These appreciate metallic Ag\(^0\) nanoparticles acted as charge carrier separation center over SPR which accelerated the interfacial electrons transfer to other electron acceptors. The Z-scheme heterojunction has formed in Ag/AgI/ABO where the electron-hole pairs were able to be separated and migrated efficiently. Thus, the as-prepared exhibited superior photocatalytic performance to the MB dye degradation over Ag/AgI/ABO. Holes that were dominant radical species played an important role in the process degradation of MB dye. Enhancing the stability of the photocatalyst is a huge challenge. In shortly, the Ag/AgI/ABO photocatalyst is a utility material to curb environmental issue.

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Conflicts of interest

The authors declare no conflict of interest.

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