AgI/AgCl/H₂WO₄ Double Heterojunctions Composites: Preparation and Visible-Light Photocatalytic Performance

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AgI/AgCl/H₂WO₄ double heterojunctions photocatalyst was prepared via deposition-precipitation followed by ion exchange method. The structure, crystallinity, morphology, chemical content and other physical-chemical properties of the samples are characterized by X-ray diffraction (XRD), electron microscopy (SEM), energy dispersive x-ray spectra (EDX), UV–vis diffuse reflectance spectroscopy (DRS), and photoluminescence (PL). The photocatalytic activity of the AgI/AgCl/H₂WO₄ was evaluated by degrading methyl orange (MO) under visible light irradiation (λ > 400 nm). The double heterojunctions photocatalyst displayed more efficient photocatalytic activity than pure AgI, AgCl, H₂WO₄ and AgCl/H₂WO₄. Based on the reactive species and energy band structure, the enhanced photocatalytic activity mechanism of AgI/AgCl/H₂WO₄ was discussed in detail. The improved photocatalytic performance of AgI/AgCl/H₂WO₄ double heterojunctions could be ascribed to the enhanced interfacial charge transfer and the inhibited recombination of electron-hole pairs, which was in close relation with the AgI/AgCl/H₂WO₄ heterojunctions formed between AgI, AgCl and H₂WO₄.

Key Words: AgI/AgCl/H₂WO₄, Heterojunctions, Preparation, Visible light photocatalytic

Introduction

Photocatalytic oxidation (PCO) technique has been used in the field of environmental pollution control because it can effectively destroy many non-biodegradable pollutants with structural stability. In addition, compared to the traditional water treatment techniques via physical methods, PCO process possesses obvious advantages of energy-saving, high-efficiency, thoroughly degrading, less secondary pollution, etc. Therefore, it has been considered to be a very promising approach of wastewater treatment. Up to now, a variety of semiconductor photocatalysts have been developed and investigated in detail. TiO₂ with large band gap (3.0-3.2 eV) is one of the most widely studied photocatalysts due to its high efficiency, low cost, non-toxicity, and high stability. However, TiO₂ only responds to ultraviolet light which only occupies about 4% of the solar spectrum. The limited utilization of solar energy hinders the applicability of single semiconductor photocatalyst. Thus, it is essential to develop visible light photocatalysts with high photocatalytic activity.

Previously, many coupled semiconductor systems have been extensively studied as efficient visible light photocatalysts that showed higher photocatalytic efficiencies than single semiconductors, such as Bi₂O₃/TiO₂, CuO/ZnO, BiOCl/Bi₂O₃, BiOCl/Bi₂O₃Cl, WO₃/BiOCl, SrO/CuBi₂O₄, CuO/TiO₂, ZnMn₂O₄/TiO₂, AgBr/WO₃, AgI/BiOCl, AgI/TiO₂, WO₃/TiO₂, AgBr/AgNbO₄, AgBr/H₂WO₄, and so on. In these systems, two semiconductors with matching band potentials are combined and a heterojunction is constructed simultaneously between the two components, which can suppress the recombination of the electron-hole pairs, increase lifetime of the charge carriers, promote quantum efficiency, and further effectively improve the photocatalytic activity of semiconductor photocatalysts. It should be noted that most coupled semiconductor systems only focused on two components, and three components semiconductor composites with double heterojunctions are rarely reported. Wang et al. reported that ZnO/ZnWO₄/WO₃ composites with double heterojunctions displayed higher activity than ZnO/WO₃ and proposed that the formed double heterojunctions in ZnO/ZnWO₄/WO₃ system presented high efficient separation of electron-hole pairs. We have also constructed a AgI/AgCl/TiO₂ three-component system with double heterojunctions and proved that the novel photocatalyst was efficient for the improvement of photocatalytic activity of AgX and TiO₂ which implied that the construction of double heterojunctions in composite photocatalysts may be a promising way for the enhancement of photocatalytic performance.

The CN bottom and the VB top of H₂WO₄ lie below the CB bottom and VB top of AgI and AgCl, respectively, which will result in the highly efficient separation of photoinduced electrons and holes. Inspired by this, in this work, we introduced H₂WO₄ as a substrate and synthesized a novel visible light composite photocatalyst AgI/AgCl/H₂WO₄ with double heterojunction structure via a simple deposition-precipitation method followed by ion exchange between AgCl and KI solution. XRD, SEM, EDX and UV-Vis spectrometry were used to characterize the as-prepared AgI/AgCl/H₂WO₄ double heterojunctions photocatalyst. The photodegradation of methyl orange (MO) was carried out to study the photocatalytic activity of the AgI/AgCl/H₂WO₄ double heterojunctions.
under visible light irradiation ($\lambda > 400$ nm). Moreover, in attempt to explore the roles of different reactive species and the reaction mechanism, various scavengers were introduced to the photocatalytic reaction system.

Experimental

Materials. Sodium tungstate dihydrate ($\text{Na}_2\text{WO}_4\cdot 2\text{H}_2\text{O}$), nitric acid (HNO$_3$), ethanol, silver nitrate (AgNO$_3$), potassium chloride (KCl), potassium iodide (KI) and methyl orange (MO) were of analytical grade without further purification. They were purchased from Sinopharm Chemical Reagent Co., Ltd. Deionized water was used throughout this study.

Samples Preparation. H$_2$WO$_4$ was prepared in advance. $\text{Na}_2\text{WO}_4\cdot 2\text{H}_2\text{O}$ was dissolved in ethanol-water solution (1:2, V/V). After the pH of the solution was adjusted to 2.0 with HNO$_3$ solution, the reaction mixture was subsequently stirred for 12 h at 60 $^\circ$C. Finally, yellow H$_2$WO$_4$ precipitate was centrifuged, collected, washed with deionized water for 3 times, and dried at 65 $^\circ$C for 24 h.

The procedure of AgCl/H$_2$WO$_4$ substrate prepared via a deposition-precipitation method was depicted as follows. H$_2$WO$_4$ (10.0 g) was homogeneously dispersed in deionized water (500 mL) and sonicated for 20 min. Subsequently, a quantity of AgNO$_3$ (1.70 g) solution was added to the H$_2$WO$_4$ suspension and stirred for 20 min. Then a stoichiometric amount of KCl (0.745 g) was dropwise added into the suspension and the resulting suspension was strongly stirred at room temperature for 2 h. The product was centrifuged, washed and dried at 60 $^\circ$C for 14 h. Finally, AgCl/H$_2$WO$_4$ substrate with theoretical Ag/W molar ratio of 0.25:1 was obtained.

AgI/AgCl/H$_2$WO$_4$ photocatalyst was synthesized by iodine ion exchange of AgCl/H$_2$WO$_4$ substrate. In a typical synthetic route, a stoichiometric amount of KI solution was dropped into the AgCl/H$_2$WO$_4$ (1.0 g) suspension that dispersed in deionized water (100 mL) and then stirred magnetically for 20 min. After that, the product was filtered, washed and dried at 65 $^\circ$C for 24 h. The corresponding AgI/AgCl/H$_2$WO$_4$ samples with different molar percentage of AgI to initial AgCl (10%, 30%, 50% and 80%) were obtained by changing the KI amounts, respectively.

Sample Characterization. The phases of the products were identified using X-ray diffractometer (XRD) (BRUKER D8 ADVANCE X-ray powder diffractometer) with Ni-filtered Cu Kα radiation ($\lambda = 1.5406$ Å) at a scanning rate of 10° s$^{-1}$ from 10° to 60°. The accelerating voltage and emission current were 40 kV and 40 mA, respectively. FEI Sirion 200 field emission scanning electron microscope (SEM) with 5.00 kV scanning voltages was employed to observe the morphologies of the as-prepared catalysts. Energy-dispersive spectroscopy (EDS) was observed by using an Oxford instruments INCA X-ray detector. UV–vis diffuse reflectance spectroscopy measurements were carried out to calculate the energy band gaps of the composites using a TU-1901 UV-VIS spectrophotometer (Beijing Purkinje General Instrument Co., Ltd.) equipped with an integrating sphere attachment.

The scanning wavelength range was from 350 to 600 nm and BaSO$_4$ was used as a reflectance standard. Fluorescence emission spectra were recorded on a JASCO FP-6500 type fluorescence spectrophotometer with 315 nm excited source over a wavelength range of 350-600 nm.

Photocatalytic Activity Measurements. In order to evaluate the photocatalytic activity of samples, the process of MO degradation was carried out in a batch reactor under visible light irradiation ($\lambda > 400$ nm). The initial concentration of MO solution was 10 mg/L. The reactor and procedure were referred to the previous study.$^{23}$ The MO concentration collected at each specific irradiation time interval was determined from the absorbance at a wavelength of 464 nm using 722s spectrophotometer, with deionized water as a reference sample.

Terephthalic acid photoluminescence probing technique (TA-PL) was introduced to detect the formation of ·OH radicals, in which a basic TA solution set at 5 × 10$^{-3}$ M in 2 × 10$^{-3}$ M NaOH solution was added to the reactor instead of MO. Then the suspension was collected every 60 min to measure on a JASCO FP-6500 type fluorescence spectrophotometer after centrifugation. The excitation wavelength used was 315 nm.

Furthermore, the effects of main reactive species involved in the PCO process were investigated using a quantity of appropriate species quenchers. A series of comparison experiments were carried out between the original degradation of MO by AgI/AgCl/H$_2$WO$_4$ and those obtained after addition of quenchers in the initial solution, under other identical conditions. The dosages of the species quenchers were all 1 mmol/L.

Results and Discussion

Characterization of AgI/AgCl/H$_2$WO$_4$. XRD is used to investigate the changes of structure and the composition of the AgI/AgCl/H$_2$WO$_4$ double heterojunctions photocatalysts obtained at different AgI contents. Figure 1 shows the XRD patterns of the samples obtained at various AgI contents. The analysis of XRD patterns reveals that AgCl with the characteristic peaks of (111), (200) and (220) is of cubic structure (JCPDS 31-1238), while AgI has both β-AgI (JCPDS 85-0801) and γ-AgI (JCPDS 09-0399) structures, assigned to β-(100), (110) and γ-(111) diffraction peak, respectively. The characteristic peaks of H$_2$WO$_4$ (020), (111) and (131), are in good agreement with the standard card of orthorhombic structure (JCPDS 43-0679). With the increase of AgI contents in AgI/AgCl/H$_2$WO$_4$ composites, the intensity of peaks of AgI gradually increased, whereas those of AgCl decreased simultaneously due to its consumption, and that no other peaks of impurity were detected. Based on this result, AgI, AgCl and H$_2$WO$_4$ are confirmed to coexist in AgI/AgCl/H$_2$WO$_4$ double heterojunctions may be formed in the composites.

Figure 2 shows the comparison of XRD pattern of AgI/AgCl/H$_2$WO$_4$ before and after 180 min irradiation for the degradation of MO. It is observed that the crystal structure of
the used AgI/AgCl/H₂WO₄ had no obvious changes except that two small peaks at 38.16° was detected and identified as the main peaks of metal silver (JCPDS 04-0783), as shown in the inset of Figure 2. This suggests that a trace amount of metal silver was formed in AgI/AgCl/H₂WO₄ after degradation of MO, which may affect the stability and the photocatalytic activity of AgI/AgCl/H₂WO₄.

The typical microstructure of the pure H₂WO₄ and 50% AgI/AgCl/H₂WO₄ were analyzed by SEM and the results are shown in Figure 3(a) and (b). It can be observed that pure H₂WO₄ and AgI/AgCl/H₂WO₄ consisted of anomalous particles with diameters less than 250 nm, respectively. Moreover, the surfaces of these anomalous particles were modified with some nanoparticles (Fig. 3(b), inset). But the quantity of the nanoparticles on the surface of AgI/AgCl/H₂WO₄ sample decreased, which may be attributed to the aggregation of AgCl and AgI particles that deposited on the surface of H₂WO₄. Higher resolution images can not be obtained because AgI and AgCl are decomposed by the high energy electron beam. To further confirm the element components of the composite, the EDS of pure H₂WO₄ and AgI/AgCl/H₂WO₄ composites were obtained on an Oxford instruments INCA X-act detector, respectively. Since H element can not be detected, only W and O elements could be observed in pure H₂WO₄ (Fig. 3(c)). Similarly, five elements including Ag, I, Cl, W and O was appeared in AgI/AgCl/H₂WO₄ (Fig. 3(d)), and no other impurity element was found.

The UV–vis diffuse reflectance spectra of AgI, AgCl, H₂WO₄, AgCl/H₂WO₄ and 50% AgI/AgCl/H₂WO₄ are compared in Figure 4. It can be seen that the absorption edge of AgI was located at about 475 nm while AgCl only absorbed visible light slightly, whereas H₂WO₄ exhibited an absorption edge near 540 nm. However, AgCl/H₂WO₄ and 50% AgI/AgCl/H₂WO₄ composites had the similar absorption edges that were just a little shorter than H₂WO₄. The result indicates that the dominant factor for the enhanced photocatalytic performance of AgI/AgCl/H₂WO₄ may be not due to the light absorption ability but the role of AgI-AgCl-H₂WO₄ double heterojunctions that will facilitate the transfer of the photoinduced electrons and holes. Besides, the used AgI/AgCl/H₂WO₄ displayed much stronger absorption in the visible region than fresh AgI/AgCl/H₂WO₄, which may result from the formation of metal silver on the surface of AgI/AgCl/H₂WO₄ according with the result of Figure 2.

In addition, the energy band gap (E₉) of a semiconductor can be calculated using Eq. (1):  

$$\alpha h \nu = A(h \nu - E_g)^{n/2}$$  

where $\alpha$, $\nu$, $E_g$ and $A$ are absorption coefficient, light freqe-
ency, band gap energy, and a constant, respectively. Among them, \( n \) depends on the type of optical transition of a semiconductor (\( n = 1 \) for direct transition and \( n = 4 \) for indirect transition). The values of \( n \) for AgI, AgCl, and H\(_2\)WO\(_4\) are 1, 4 and 1, respectively.\(^{15,19,23,28}\) According to Eq. (1), the \( E_g \) of AgI, AgCl and H\(_2\)WO\(_4\) are determined from the plot of \((\alpha h \nu)^{1/n} \) vs. \( h \nu \) based on their absorption spectra and obtained to be 2.78 eV, 2.93 eV and 2.47 eV, separately, which are shown in Figure 5.

Photocatalytic activity of AgI/AgCl/H\(_2\)WO\(_4\). Methyl orange (MO) that commonly existed in dyeing effluent is a non-biodegradable azo dye and often selected as a model pollutant to evaluate the photocatalytic performance of photocatalytic materials. The degradation of MO was used to evaluate the photocatalytic performance of the prepared catalysts under visible light irradiation (\( \lambda > 400 \) nm). MO was not degraded after 180 min illumination in the absence of photocatalyst, or in the dark with the photocatalyst. The results presented in Figure 6(a) demonstrate that H\(_2\)WO\(_4\) did not possess photocatalytic activity for MO and AgCl/H\(_2\)WO\(_4\) only decomposed 2.5% of MO. However, the composites AgI/AgCl/H\(_2\)WO\(_4\) (10%-80%) exhibited much higher degradation efficiencies than pure H\(_2\)WO\(_4\) and AgCl/H\(_2\)WO\(_4\). Furthermore, it can be seen that the degradation efficiency of the composites increased first as the content of AgI increased to 50%, then decreased with the persistent increase of AgI content in the AgI/AgCl/H\(_2\)WO\(_4\). That is to say, 50% AgI/AgCl/H\(_2\)WO\(_4\) showed the best photocatalytic activity, at which 62.2% of MO was decomposed. This is because fewer interfaces of AgI/AgCl and AgCl/H\(_2\)WO\(_4\) heterojunctions will be formed when the content of AgI is too low or excessive, which leads to limitations in separating the electron-hole pairs and further impedes the photocatalytic activity. Therefore, with an appropriate ratio of heterojunctions (50% AgI/AgCl/H\(_2\)WO\(_4\)), the composites can exhibit perfect performance in photocatalysis. In this case, the effect of AgI/AgCl/H\(_2\)WO\(_4\) double heterojunctions on the enhancement of photocatalytic activity is the key factor. What’s more, the changes of UV-vis spectra of MO photodegradation over 50% AgI/AgCl/H\(_2\)WO\(_4\) under visible light irradiation were carried out to test the photocatalytic performance of 50% AgI/AgCl/H\(_2\)WO\(_4\), shown in Figure 6(b). It can be observed that the intensity of the typical absorption peak of MO at 464 nm decreased gradually with increasing irradiation time, which indicates that AgI/AgCl/H\(_2\)WO\(_4\) could exhibit excellent visible light photocatalytic activity for the
MO degradation.

The photocatalytic activity of the powders can be quantitatively evaluated by comparing their apparent reaction rate constants. Most of the photocatalytic oxidation of organic pollutants in aqueous suspensions follows the classical Langmuir–Hinshelwood kinetic model,26 which is described as follows:29,30

\[ \ln\left( \frac{C_0}{C} \right) = k_{app}t \]  

(2)

where \( k_{app} \) is the apparent pseudo-first-order rate constant (\( \text{min}^{-1} \)); \( C \) is MO concentration in aqueous solution at time \( t \) (mg/L); \( C_0 \) is initial MO concentration (mg/L).

To further investigate the effect of heterojunction formed between AgI, AgCl and \( \text{H}_2\text{WO}_4 \), the control experiments for MO degradation were carried out with different catalysts that contained the same weight of active component. The \( k_{app} \) values of different catalysts calculated from the Langmuir-Hinshelwood kinetics model are presented in Figure 7.

Obviously, the photocatalytic activity of heterojunction AgI/AgCl was much higher than that of the single AgI and AgCl. And the photocatalytic activity of AgCl/H\( \text{H}_2\text{WO}_4 \) was also superior to the pure AgCl and \( \text{H}_2\text{WO}_4 \). Among the different samples, the 50% AgI/AgCl/H\( \text{H}_2\text{WO}_4 \) had the highest activity with \( k_{app} \) of 5.52 \( \times 10^{-3} \text{ min}^{-1} \). The rate constants of the AgI/AgCl/H\( \text{H}_2\text{WO}_4 \) double heterojunctions photocatalyst exhibit strong photocatalytic activity for MO decomposition under visible-light irradiation.

The activity enhancement of AgI/AgCl/H\( \text{H}_2\text{WO}_4 \) was likely to result from a synergistic effect of several factors, including the light absorption intensity, morphology, recombination rate of the electron-hole pairs, crystallite size, and so on. Based on the comprehensive analysis of above, the decrease in the recombination rate of the electron-hole pairs was finally regarded as the key factor for the highest photocatalytic activity of AgI/AgCl/H\( \text{H}_2\text{WO}_4 \), which can be attributed to the function of double heterojunctions between AgI, AgCl and \( \text{H}_2\text{WO}_4 \) formed in the composite. That is to say, the existence of heterojunctions in the composites can facilitate the separation of the electrons and holes.

The reuse and stability of the highly efficient AgI/AgCl/H\( \text{H}_2\text{WO}_4 \) composites were evaluated by recycled runs in the photocatalytic degradation of MO under visible light irradiation. The catalysts were separated from the reaction mixture by centrifugation after each reaction cycle. It is found that the photocatalytic activity of AgI/AgCl/H\( \text{H}_2\text{WO}_4 \) declined and the used catalyst became darker than the newly prepared catalyst, which demonstrates that metal silver was formed after irradiation. The comparative XRD patterns of the used AgI/AgCl/H\( \text{H}_2\text{WO}_4 \) with the newly one in Figure 2 show that two small peaks of metal Ag were detected at 38.16° and 44.07° whereas the crystal structures of AgI and AgCl were well maintained. However, the trace amount of silver has decreased the photocatalytic activity of AgI/AgCl/H\( \text{H}_2\text{WO}_4 \) in the cyclic experiments. Similar phenomenon has also been observed in previous studies,17,31,32 which is different from the Ag/AgX plasmonic photocatalysts,33-35 because the promotion or inhibition role of photoinduced Ag to the photocatalytic activity of the photocatalysts is based on many parameters of the Ag particles, such as morphology, position, size, etc.35-37 Herein, the stability of AgI/AgCl/H\( \text{H}_2\text{WO}_4 \) should be further improved in this study.

**Photocatalytic Mechanism of AgI/AgCl/H\( \text{H}_2\text{WO}_4 \).** In order to investigate the mechanism of photocatalysis of AgI/AgCl/H\( \text{H}_2\text{WO}_4 \), the effect of active radical species (h\(^+\), ·OH and ·O\(_2^-\)) suspected to be involved in the PCO process were examined under visible light.

Generally, the formation of ·OH can be detected by terephthalic acid photoluminescence probing technique (TA-PL).38 Figure 8 shows the PL emission spectra excited at 315

**Figure 7.** The comparison of degradation efficiency of MO by different photocatalysts containing the same weight of each active component.

**Figure 8.** ·OH trapping PL spectral changes observed during irradiation of AgI/AgCl/H\( \text{H}_2\text{WO}_4 \) in a 5 \( \times 10^{-4} \text{ M} \) terephthalic acid solution (excitation at 315 nm).
nm from TA solution, which were measured every 60 min of illumination. Apparently, the PL intensity of ·OH at about 425 nm did not increase gradually with the irradiation time, which signifies that no ·OH radicals were formed during the PCO process. This confirms that ·OH radicals are not the dominant active species for the degradation of MO.

In addition, the control experiments were performed by adding different scavengers in a manner similar to the photo-degradation experiment. The corresponding dosages were referred to the previous studies.32 The results are displayed in Figure 9. It is clear to observe that the degradation efficiency of MO decreased remarkably to 5.9% with the addition of benzoquinone (BQ, a quencher of ·O2⁻).32 When ammonium oxalate (AO, a quencher of h⁺)39 or isopropanol (IPA, a quencher of ·OH)32 was added to the solution independently, the degradation efficiency of MO decreased slightly compared with the highest efficiency of 62.2% in the absence of quencher. Considering the results of both TA-PL detection of ·OH and quenching effect of scavengers, we can conclude that ·O2⁻ radicals, as the dominating active species, play a more important role than h⁺, while ·OH radicals can be neglected for the degradation of MO under visible light irradiation.

In general, when constructing a composite semiconductor including two or more components with matching band potentials, heterojunction interfaces will be formed between them, which facilitate the transfer of the photogenerated carriers and further enhance the photocatalytic activities of semiconductors. In this experiment, the band potentials of AgI, AgCl and H₂WO₄ can be calculated by the following empirical:38,40,41

\[
E_{VB} = X - E^* + 0.5E_g
\]

\[
E_{CB} = E_{VB} - E_g
\]

where \(E_{VB}\) is the valence band (VB) potential, \(E_{CB}\) is the conduction band (CB) potential, \(X\) is the electronegativity of the semiconductor (which is the geometric mean of the electronegativity of the constituent atoms), \(E^*\) is the energy of free electrons on the hydrogen scale (~4.5 eV), and \(E_g\) is the band gap of the semiconductor. The relative CB edge potentials of AgI, AgCl and H₂WO₄ are ~0.41, 0.11 and 1.16 eV respectively, whereas the VB edge potentials of them are 2.37, 3.04 and 3.63 eV differently. The above results of band calculation indicate that AgI, AgCl and H₂WO₄ have the matching band potentials.

According to the results above, a possible mechanism for MO degradation over AgI/AgCl/H₂WO₄ double heterojunctions photocatalyst was proposed and illustrated in Figure 10. When AgI, AgCl and H₂WO₄ were combined, AgI/AgCl/H₂WO₄ double heterojunctions were formed in the composite. Two corresponding active regions, the area where the three substances intersected each other, emerged along with the double heterojunctions. At the active regions, generation and separation of electron–hole pairs occurred and the charges separated more easily. Under visible light irradiation (\(\lambda > 400\) nm), AgI, AgCl and H₂WO₄ can be simultaneously excited to form electron-hole pairs. Then the photogenerated electrons could sequentially transfer from the CB of AgI to that of H₂WO₄ via the CB of AgCl, which can be further trapped by molecular oxygen adsorbed on the surface of the catalyst to yield ·O₂⁻ that effectively react with dyes, shown as Eq. (5):

\[
e^- + O_2 \rightarrow ·O_2^-
\]

Meanwhile, the holes at the VB of H₂WO₄ migrate to the VB of AgCl, and then to that of AgI, which could directly oxidize a portion of dyes. Through this way, electrons and holes recombined with each other more difficulty and separated more easily in the AgI/AgCl/H₂WO₄ double heterojunctions. In consequence, the photocatalytic activity of AgI/AgCl/H₂WO₄ heterostructure is greatly enhanced.

**Conclusion**

In summary, the AgI/AgCl/H₂WO₄ system developed in this work is a new kind of double heterojunction photocatalyst. It was synthesized by deposition-precipitation method followed by iodine ion exchange of AgCl/H₂WO₄ substrate,
which worked efficiently under visible light irradiation. The AgI/AgCl/H₂WO₄ displayed much higher visible light photocatalytic activity than AgI, AgCl or H₂WO₄ for the degradation of MO. It was also found that the molar ratio of AgI to initial AgCl in the AgI/AgCl/H₂WO₄ composites played an important role in the photocatalytic property and the optimized ratio was obtained at 50%. The studies of photocatalytic mechanism demonstrated that the $\cdot O₂^-$ radicals and $h^+$, especially $\cdot O₂^-$, were regarded as the primary active species that were generated by the charge separation and transfer during the photodegradation process. The contribution of the double heterojunctions AgI/AgCl/H₂WO₄ in the composite, which could depress the recombination of photogenerated electron-hole pairs, was responsible for the enhancement of photocatalytic activity.

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