



# Review of the Current Advances of Silver Halides-Based Composites as Photocatalysts for the Degradation of Organic Pollutants

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## Paper History:

**Received:** 1<sup>st</sup> May. 2024

**Revised:** 28<sup>th</sup> Jan. 2025

**Accepted:** 9<sup>th</sup> Feb. 2025

## Abstract

Industrial activities significantly affect the environment by releasing many organic pollutants, including industrial dyes, phenols and antibiotics, which produce wastewater. Effective removal of these substances from wastewater has appeared as a noticeable research field owing to its environmental significance. Exorbitant operational expenses and the potential generation of supplementary pollutants load conventional techniques like adsorption, membrane separation, and coagulation. Semiconductor-based photocatalysis has effectively degraded organic contaminants into less toxic or biodegradable compounds. The construction of robust visible-light-sensitive photocatalytic hybrids for environmental decontamination is an inspiring task for researchers. The exceptional photocatalytic performance of silver halides (AgX, where X is I, Cl, and Br) has recently attracted significant consideration as photocatalysts. Moreover, the combination of silver halides with other photo-active semiconductors to create efficient visible-light-driven photocatalyst heterojunctions has significantly promoted the broader application of the photocatalysis process with enhanced efficiency. Ag-silver halides/semiconductors heterojunctions have developed as crucial components in efficient composites for photocatalysis through surface plasmonic actions, helping with visible light absorption. The current study overviews the most recent Ag and silver halide-based composite photocatalysts. Additionally, it provides an essential understanding of their promoted photocatalytic performances and their main applications in organic pollutant degradation. Moreover, the photocatalytic mechanisms and environmental applications of AgI and composites were discussed.

**Keywords:** AgX, Heterojunctions, Photocatalytic Mechanism, Organic Pollutants, Photocatalytic Degradation.

مراجعة التطورات الحالية للمركبات القائمة على هاليدات الفضة كمحفزات ضوئية  
لتحلل الملوثات العضوية

حنان هاشم عبد ، سعد حنش عمار

الخلاصة:

تؤثر الأنشطة الصناعية بشكل كبير على البيئة من خلال إطلاق العديد من الملوثات العضوية، بما في ذلك الأصباغ الصناعية والفينولات والمضادات الحيوية، مما يؤدي إلى تكوين مياه الصرف الصحي. لقد برزت الإزالة الفعالة لهذه المواد من مياه الصرف الصحي كجال بحثي بارز بسبب أهميتها البيئية. إن التقنيات التقليدية مثل الامتزاز وفصل الأغشية والتخثر ذات نفقات التشغيل الباهظة والتوليد المحتمل للملوثات الإضافية. أكد التحفيز الضوئي المعتمد على أشباه الموصلات فعاليته في تحليل الملوثات العضوية إلى مركبات أقل سمية أو قابلة للتحلل. يعد بناء محفزات ضوئية هجينة قوية حساسة للضوء المرئي لإزالة التلوث البيئي محط اهتمام للكثير من الباحثين. في الآونة الأخيرة، اجتذب أداء التحفيز الضوئي الاستثنائي لهاليدات الفضة (AgX، حيث X هو I و Cl و Br) اهتمامًا كبيرًا كمحفزات ضوئية. علاوة على ذلك، فإن دمج هاليدات الفضة مع أشباه الموصلات الضوئية الأخرى لإنشاء تقاطعات غير متجانسة فعالة محفزة

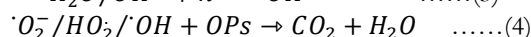
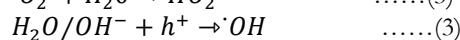
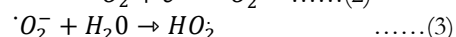
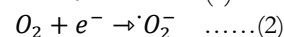
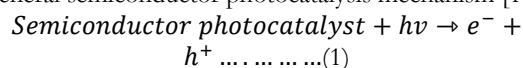
ضوئياً بالاعتماد على الضوء المرئي، قد عزز بشكل كبير من التطبيق الأوسع لعملية التحفيز الضوئي بكفاءة محسنة. لقد تطورت الوصلات المتغايرة بين هاليدات الفضة وأشباه الموصلات كمكونات حاسمة في المركبات الفعالة للتحفيز الضوئي من خلال الإجراءات البلازمية السطحية، والتي تعمل على امتصاص الضوء المرئي. في هذه الورقة، تم تقديم مراجعة عامة عن المحفزات الضوئية المركبة المعتمدة على هاليدات الفضة والفضة، والفهم الأساسي لأداء التحفيز الضوئي المعزز وتطبيقاتها الرئيسية في تحليل الملوثات العضوية. علاوة على ذلك، تم مناقشة آليات التحفيز الضوئي والتطبيقات البيئية لـ AgI ومركباتها.

## 1. Introduction

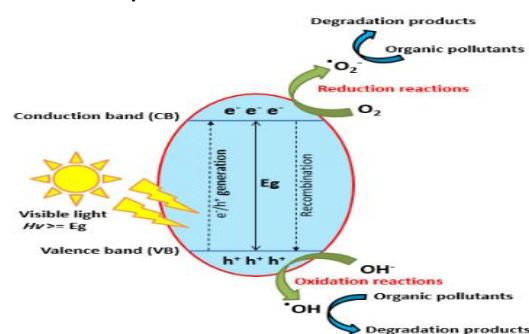
Industrial facilities produce larger quantities of wastewater, leading to significant environmental problems. Numerous industrial operations produce wastewater, which often contains dangerous organic chemicals that are ineffective for treating using traditional biological techniques. With the development of industries, the contamination of the environment by organic and inorganic substances has increased, causing potential risks to both the environment and human health [1], [2]. Many organic pollutants exist in large numbers, excluding phenols, organic dyes, pesticides, fertilizers, detergents, hydrocarbons, oils, antibiotics, plasticizers, carbohydrates, and many others. Several methods for removing pollutants from water-soluble pollutants are currently developing to solve this problem [3], [4].

Traditional water decontamination techniques include adsorption, reverse osmosis, filtration sedimentation, biological and chemical treatments, coagulation, and more [5]. However, various techniques, such as chemical, physical, and biological ones, are used to manage contamination. Advanced oxidation processes (AOPs), like the Fenton process, photocatalysis, ozonation, sonolysis, and their combinations, have gained significant popularity for decomposing organic contaminants. The reasons for using these techniques are their exceptional efficacy, ease of use, consistency, and simplicity [6]. Photocatalysis has revealed promise as an AOP for removing various organic pollutants at normal conditions without producing harmful substances, mostly due to its insignificant effectiveness, economy, recyclability, and simplicity of use [7]. The use of heterogeneous photocatalysts has gained acceptance in various processes due to their advantages, such as easy separation, reusability, and moderate operating conditions [8]. There are three separate stages for categorizing photocatalytic reactions. During the initial stage, photons possessing an energy equivalent to or greater than the band gap energy of the photocatalyst stimulate the material, forming photoinduced electrons ( $e^-$ ) and holes ( $h^+$ ). (Eq. (2.1)). Hole formation is caused by unfilled electron vacancies. When the transfer of electrons occurs from the valence band (VB) to the conduction band (CB). The CB generates photoinduced electrons through this process, whereas the VB generates photoinduced holes. Additionally, the photoinduced electrons ( $e^-$ ) and holes ( $h^+$ ) undergo a reaction with  $O_2$  and  $H_2O$ , forming hydroxyl radicals and superoxide radicals, which exhibit high reactivity. (Eqs. (2.2)-(2.4)). When ( $\cdot O_2^-$ ) radicals combine with water, they produce hydroperoxyl radicals ( $\cdot HO$ ). Another way that holes contribute to

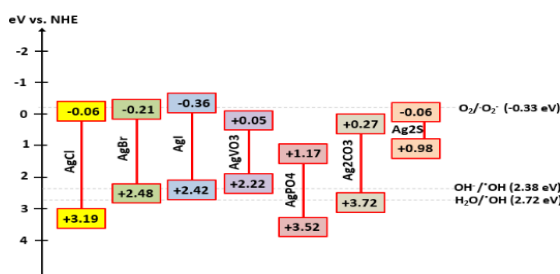
the production of hydroxyl radicals ( $\cdot OH$ ) is by oxidizing  $H_2O$  or adsorbed  $OH^-$  on the surface, contaminating organic compounds into carbon dioxide ( $CO_2$ ) and water ( $H_2O$ ) without producing secondary pollution [9]. Fig. 1 shows a diagram representing a general semiconductor photocatalysis mechanism [10].



In recent years, researchers have received much attention to finding new novel materials that exhibit excellent photocatalytic performance when exposed to visible light or sunlight. Ag-based compounds have developed promising preferences among these materials due to their exceptional photoelectrochemical properties, demonstrating strong responsiveness to visible light [11]. Ag-based semiconductors, such as  $Ag_2S$  [12],  $AgX$  ( $X = Br, Cl, I$ ) [13],  $Ag_2O$  [14],  $AgVO_3$  [15],  $Ag_3PO_4$  [16], and  $Ag_2CO_3$  [17], have received significant studies up to the present time. Ag ion's filled  $d_{10}$  electronic state, which influences the creation and bonding of energy band structures, gives Ag-based semiconductors unique properties [18]. Fig.2 illustrates the band structures of several semiconductors and halides based on silver that are commonly studied.



**Figure (1):** Illustrates photocatalysis, which decomposes water pollutants by photocatalyst activation and significant surface reactions.



**Figure(1):** Illustration of the energy band diagram of semiconductors based on Ag.

## 2. Photocatalytic heterojunctions

A heterojunction generally refers to the interface between two semiconductors with different band structures, resulting in band positions [19]. There are five primary types of semiconductor heterojunctions: straddling alignment (type-I), staggered alignment (type-II), Schottky Junction, p-n heterojunctions, and Z-scheme system. Fig.3 shows a variety of heterojunctions often found in photocatalysts.

### 2.1. Type-I heterojunctions

Type I heterojunction in which semiconductor 1 has a lower (VB) and a more significant (CB) than semiconductor 2. The light absorbed by the semiconductor boosts the kinetic energy of electrons and holes. This means that the holes generated by the light in one semiconductor will move to the valence band of the second semiconductor. Likewise, photoexcited electrons may transfer from the conduction band (CB) of Semiconductor 1 to the conduction band (CB) of Semiconductor 2 [20].

### 2.2. Type-II heterojunctions

In this type, the conduction and valence bands of the first semiconductor appear higher than Semiconductor 2, as shown in Fig.3. When photoexcited, electrons and holes transfer in various directions because of the intrinsic field. The first and second Semiconductors have different chemical potentials, which results in this field. Therefore, electron-hole pairs on opposing sides of the heterojunction may be correctly separated before recombination occurs [21], [22].

### 2.3. p-n Heterojunctions

While a type-II heterojunction can allow electron-hole pairs to be spatially separated, the actual increase in electron-hole separation across such a junction is not enough to overcome. The fast electron and hole recombination occurs within the semiconductor. Therefore, a photocatalyst with a p-n junction can improve the transfer of electrons and holes across a heterojunction. The objective of this technique is to enhance the efficiency of photocatalysis through the addition of an advanced electric field [23].

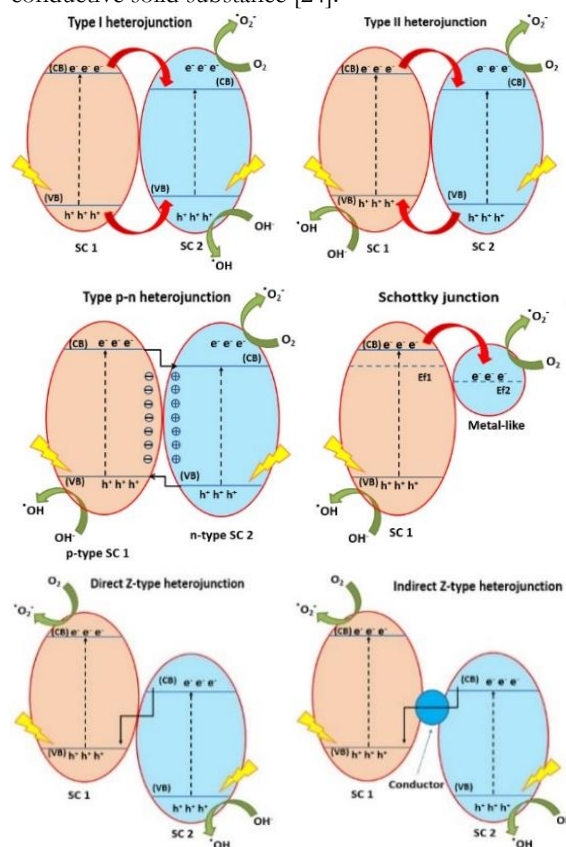
### 2.4. Schottky Junction

The formation of a Schottky junction involves the chemical combination of semiconductors with metal-like materials. This combination plays a crucial role in developing the region of space-charge separation (as shown in Fig. 3). Due to its remarkable characteristics, the electrons efficiently move between the two components at the junction of the joined materials. Consequently, the alignment of Fermi energy levels can

significantly reduce the recombination of charge carriers. Consequently, this significantly enhances the photocatalytic activity. [20]

## 2.5. Z-scheme Heterojunction

Although the heterojunction photocatalysts discussed earlier can improve the efficiency of electron-hole separation, they often face a limitation in terms of their redox capabilities. This occurs because the semiconductor undergoes oxidation and reduction processes with lower oxidation and reduction potentials, respectively [20]. In 1979, Bard et al. suggested an innovative solution to overcome these problems by inventing a Z-scheme photocatalytic system. The goal of this system was to facilitate the direct transfer of photogenerated electrons from the second semiconductor's lower conduction band (CB) to the valence band (VB) of the first semiconductor. This junction is known as a direct Z-scheme heterojunction. Another alternative is the application of an indirect Z-scheme photocatalyst heterojunction, which combines an electron mediator consisting of a conductive solid substance [24].



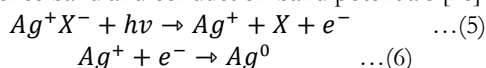
**Figure(2):** Different types of heterostructured photocatalytic heterojunctions

## 3. Silver halides as potential photocatalysts

In recent years, there has been a growing attraction to AgX-based photocatalysts due to their ability to respond to visible light and the enhanced photochemical reactions facilitated by the presence of Ag nanoparticles, known as the plasmonic enhancement effect [25]. A plasmon-enhanced photocatalyst, composed of plasmonic metal nanoparticles and a semiconductor, exhibits significant superiority in two features of photocatalytic



enhancement. Firstly, the plasmonic metal nanoparticles serve as an antenna, efficiently localizing and transmitting energy from the incident radiation to the semiconductor material. As a result, the photocatalyst exhibits a high absorption coefficient, enhancing light absorption [29]. Additionally, bigger metal particles on the semiconductor surface cause the irradiation light to throw quickly. Consequently, there is a significant increase in the transmission of light through the semiconductor, resulting in improved interaction between the light and the photocatalytic material [26]. Silver halide particles absorb photons and generate an electron/hole pair. The photoelectrons subsequently interact with the silver ions, making  $\text{Ag}^0$  atoms. (Eq 6 and 7) show an excellent representation of this reaction [27]. Additionally, table 1 shows the band gaps for AgCl, AgBr, and AgI, as well as their valence band and conduction band potentials [28].



**Table( 1):** The potential values of AgCl, AgBr, and AgI valence and conduction bands, as well as the corresponding positions of their band gaps.

Silver Halide	Band Gap (eV)	Valence band (eV)	Conductive band (eV)	Ref.
AgCl	3.25	+3.19	-0.06	[29]
AgBr	2.69	+2.48	-0.21	[27]
AgI	2.78	+2.42	-0.36	[30]

#### 4. Synthesis methods of silver halides (AgX) semiconductors

AgX exhibits common properties in its synthesis due to its composition of  $\text{Ag}^+$  and halide ions ( $\text{X}^-$ ). They include the ion exchange between silver salt and HX and the precipitation reaction between  $\text{Ag}^+$  and  $\text{X}^-$ . Here, we classify several synthetic methods related to thoroughly examining the reaction process [31] precipitation method [27] deposition-precipitation method [30] Polyvinylpyrrolidone-assisted precipitation [32] template-directed formation [33] hydrothermal method [10] ion-exchange method [34] refluxing method [35]

##### 4.1. Precipitation method

The most straightforward and practical approach to synthesizing AgX crystals involves a chemical precipitation reaction between  $\text{Ag}^+$  and  $\text{X}^-$  ions. This process occurs when their respective solutions are mixed under controlled conditions, leading to the formation of AgX crystals, which are insoluble silver halides that precipitate out of the solution [27], [30].

##### 4.2. Deposition-precipitation method

Among the various methods used to synthesize plasmonic photocatalysts incorporating Au, Ag, and Ag-AgX (where  $\text{X} = \text{Cl}, \text{I}, \text{and Br}$ ), Deposition-precipitation, followed by washing and reduction, is the most commonly used. Typically, this process involves depositing noble metal nanoparticles (NPs), particularly those with relatively small sizes (e.g., less than 5 nm) and narrow size distributions, onto support materials through deposition-precipitation. By adjusting factors like the pH of the solution and

calcination temperature, it is possible to control the size of particles and the amount of loading of noble metals in the resulting photocatalysts[30]

##### 4.3. Polyvinylpyrrolidone-assisted precipitation

Polyvinylpyrrolidone (PVP) is extensively used as an effective capping agent for controlling the morphology of various inorganic crystals, including metal single crystals, metallic salts, and inorganic semiconductors [25], [36]. In the context of silver compositions, PVP has established itself as the leading morphology-controlling agent, facilitating the large-scale production of silver crystals with uniform distribution [31]. The attraction between  $\text{Ag}^+$  and PVP, which forms a PVP- $\text{Ag}^+$  complex, provides selectivity. This complex plays a crucial role in stabilizing  $\text{Ag}^+$  ions [31]. These conventional synthesis procedures involve dissolving  $\text{Ag}^+$  cations and  $\text{X}^-$  anions in viscous solvents and adding PVP. Such solvents include glycerol, ethylene glycol or deionized water with P-tolyl sulfonic acid. PVP acts as a stabilizer for both ions while also potentially forming complexes with  $\text{Ag}^+$ . The next step is thoroughly mixing the liquids, forming milky dispersions containing particles sized in several or tens of nanometers. Alternatively, when conducted at specific temperatures, larger crystals in the micron range with uniform morphologies can be synthesized [36].

##### 4.4. Template-directed formation

Template-based AgX synthesis can be broadly classified into two categories: complex and soft, similar to other composite nanoparticles (NPs). Commonly used templates for this purpose include anodic aluminium oxide (AAO) and water-soluble sacrificial salt crystal templates. In the synthesis process, the sacrificial salts serve as both reactants and templates. When an  $\text{AgNO}_3$  solution is introduced, it triggers an ion exchange diffusion process between  $\text{X}^-$  and  $\text{Ag}^+$ . The reaction leads to the formation of AgX crystals on the surface of the salt crystal. After the completion of AgX crystal development, the salt crystal/AgX samples undergo a water-washing process to eliminate and dissolve the inner core of the salt crystal. This procedure forms AgX structures characterized by hollow interiors [37]. Synthesis of nanoparticles from inorganic crystals frequently requires using soft templates, noble metals, and metal oxides [38]. The method of synthesizing AgX nanoparticles entails the combination of two identical reverse micelles, wherein each micelle contains either silver or halide ions. The formation of AgX nanoparticles within the water pools of reverse micelles occurs through a series of collisions, association, and dissociation processes involving  $\text{Ag}^+$  and  $\text{X}^-$  ions [39].

##### 4.5. Ion-exchange method

Similar to synthesis using complex templates, the in situ ion exchange method offers precise control over the positioning of silver halide nanostructures on pre-existing anion or cation salts [34]. The wastewater treatment industry frequently employs ion exchange. This process is environmentally friendly, offers low maintenance costs, and can achieve high flow rates for treated water. Despite these advantages, there are certain limitations associated with this method. These



risks include bacterial contamination, possible chlorine contamination, and the adsorption of organic matter [40]. Many silver-based compounds (Ag-based compounds) are prepared or obtained as templates to streamline the experimental process and save time. Once halide ions ( $X^-$ ) are introduced, an ion-exchange reaction occurs between the anions from the Ag-based compound and  $X^-$ , forming AgX crystals that deposit onto the surface of the substrate precursors. This process of anion exchange allows for precise control over the generation of AgX on the surface of Ag-based compounds in the hybrid system by adjusting the concentration of  $X^-$  ions with high resolution [31].

#### 4.6. Hydrothermal method

This process uses a chemical reaction between reactants at a specific temperature and pressure. This method may readily adjust essential factors, including precursor concentration, temperature, and fabrication time. Hydrothermal conditions may also effectively control the near atmosphere, which helps produce different intermediates and valence compounds and efficient binding processes.

### 5. AgX-based photocatalytic systems

AgX is considered an appropriate semiconductor choice for altering the composition of a photocatalytic system due to its photosensitive properties. These materials can produce extremely strong composite photocatalysts that demonstrate enhanced activity and stability compared to single-component systems [41]. Combining AgX with other metallic semiconductors would significantly improve light absorption efficiency and promote the separation of photoinduced charge carriers through similar transmission pathways [42]. In addition, there has been significant interest in combining AgX and Ag/AgX with materials that are not light-sensitive, especially carbon-based conductive materials [43].

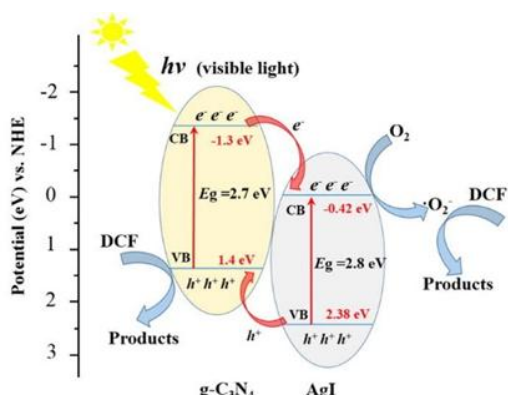
#### 5.1. AgI-based composite as photocatalysts

Silver iodide (AgI) is a photosensitive substance widely employed in photography. Recently, it has gained significant attention due to its outstanding photocatalytic properties [44]. Due to its suitable band edge positions and exceptional photoelectrocatalytic characteristics, Combine silver iodide with a wide range of semiconductors [45]. The benefits of AgI-based composite materials were evident for several reasons. (i) AgI exhibits excellent light photosensitivity and can readily produce metallic Ag NPs. By incorporating AgI into composite materials, It is possible to improve the composite's light-absorbing properties significantly (ii) AgI possesses developed redox potentials compared to most semiconductor-based photocatalytic materials, thereby facilitating enhanced separation of photo carriers and promoting the production of reactive radicals. (iii) the predominant morphological structure of AgI is in the form of nanoparticles, but pure AgI tends to agglomerate easily [45]. Many research works fabricated AgX-g-C<sub>3</sub>N<sub>4</sub> (graphitic carbon nitride)

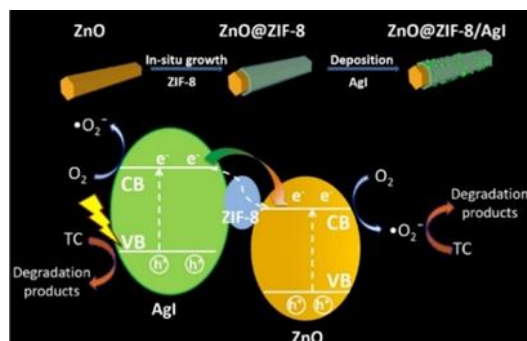
composites as photocatalysts. Therefore, it is essential to review some of these works. g-C<sub>3</sub>N<sub>4</sub> is one of the oldest polymers, as reported in the literature [46]. g-C<sub>3</sub>N<sub>4</sub> is the most mutual metal-free semiconductor in photocatalysis applications due to its simple fabrication, unique electronic structures, high stability, nontoxic, and inexpensive. Xu et al. constructed AgX/g-C<sub>3</sub>N<sub>4</sub> composites (where X = I or Br). The photocatalytic behaviours of AgX/g-C<sub>3</sub>N<sub>4</sub> hybrids were assessed for degradation of methyl orange as an organic contaminant under visible illumination [47]. Zhang et al. stated the assembly of AgI/g-C<sub>3</sub>N<sub>4</sub> heterostructure as a visible-light-promoted photocatalyst. The synthesized AgI/g-C<sub>3</sub>N<sub>4</sub> (45% AgI in the composite) photocatalyst displayed advanced photoactivities through type-II mechanism than those of g-C<sub>3</sub>N<sub>4</sub> and AgI single constituents in the photodegradation of diclofenac under visible lighting, giving reaction rate constant = 0.561 min<sup>-1</sup>, which is 43.2 and 12.5 times greater than that achieved by g-C<sub>3</sub>N<sub>4</sub> and AgI [48]. Fig. 4 shows the charge transfer pathway between AgI and g-C<sub>3</sub>N<sub>4</sub> in the synthesized photocatalyst. Metal-organic frameworks (MOFs) have been extensively used with different semiconductors to produce photocatalytic heterojunctions. MOFs are inorganic-organic porous hybrid materials which have experienced rapid advancements [49]. These requests include catalysis, separation processes, gas storage, and CO<sub>2</sub> capture. Many MOFs exhibit semiconductor-like performance when exposed to light, indicating their potential utility as photocatalysts. Recent research has revealed that MOFs represent a promising new class of photocatalysts, particularly for degrading organic pollutants. This discovery releases exciting possibilities for their application in environmental remediation and pollution control processes. The use of porous MOFs offers excellent potential for developing new composite photocatalysts due to their high specific surface area, customizable porous structure, and exceptional stability [50]. Gao et al. developed a new ternary composite based on Zn-zeolitic imidazolate framework-8 (ZIF-8), ZnO, and AgI [51]. They used ZnO@ZIF-8/AgI photocatalyst for tetracycline photocatalytic decomposition under visible lighting. Their results state that the ternary ZnO@ZIF-8/AgI photocatalyst can improve the immigration and separation rates of generated electron-hole couples through the formed interface. The ZnO<sub>4</sub>@ZIF-8/AgI hybrid showed high adsorption-photocatalytic activities, higher than the single- and binary photocatalysts. Fig. 5 shows the proposed ZnO@ZIF-8/AgI hybrid photocatalyst synthesized by Gao et al. for TC degradation, including carrier transfer pathway in the presence of ZIF-8 as electrons mediator between AgI and ZnO, and thus facilitating the degradation efficiency. Table 2 summarises the other reports., which were shown to improve the photocatalytic behavior of AgI-based heterostructure nanocomposite photocatalysts.

Table (2): AgI-based photocatalysts for pollutant degradation

<i>AgI-based composite photocatalysts</i>	<i>Synthesis method</i>	<i>Organic pollutant Degradation</i>	<i>Ref.</i>
MoS <sub>2</sub> /BiOI/AgI composite	Precipitation	Rhodamine B	[52]
AgI/g-C <sub>3</sub> N <sub>4</sub>	Deposition-precipitation	Diclofenac	[48]
AgI/RGO nanocomposites	Ultrasound-assisted	Rhodamine B	[53]
AgI/MIL-53(Fe) composites	Simple grinding	Rhodamine B	[54]
g-C <sub>3</sub> N <sub>4</sub> /Fe <sub>3</sub> O <sub>4</sub> /AgI/Ag <sub>2</sub> CrO <sub>4</sub>	Deposition	Rhodamine B	[55]
Fe <sub>3</sub> O <sub>4</sub> /ZnO/Ag <sub>3</sub> VO <sub>4</sub> /AgI	Ultrasonic irradiation	Rhodamine B	[56]
g-C <sub>3</sub> N <sub>4</sub> /Fe <sub>3</sub> O <sub>4</sub> /AgI/Bi <sub>2</sub> S <sub>3</sub>	Refluxing at 96 °C	Rhodamine B, methylene blue, and fuchsine	[57]
BiOI/Ag@AgI	In-situ grown	Tetracycline	[58]
C-Ag <sub>3</sub> PO <sub>4</sub> @Ag@AgI	Ion-exchange	Rhodamine B, bisphenol A	[59]
AgI/WO <sub>3</sub>	Precipitation	Tetracycline	[60]
AgI/β-Bi <sub>2</sub> O <sub>3</sub>	Facile method	Methyl orange and tetracycline	[61]
AgI/BiOBr	Precipitation	Ciprofloxacin	[62]
AgI/Bi <sub>2</sub> Sn <sub>2</sub> O <sub>7</sub>	Deposition-precipitation route	Tetracycline	[63]
AgI/Bi <sub>12</sub> O <sub>17</sub> Cl <sub>2</sub>	Hydrothermal-precipitation	Sulfamethazine	[64]
CeO <sub>2</sub> -AgI	Precipitation	Rhodamine B	[65]
AgI Ag <sub>2</sub> Mo <sub>2</sub> O <sub>7</sub>	Ion-exchange	Methyl orange	[66]
AgI/Bi <sub>5</sub> O <sub>7</sub> I	Deposition	Methyl orange	[67]
g-C <sub>3</sub> N <sub>4</sub> /BiOI/Ag-AgI	Positive exciton splitting	Tetracycline	[68]



Figure(4): Illustration of the charge transfer pathways in AgI/g-C<sub>3</sub>N<sub>4</sub> hybrid [48]. Reprinting permitted. (License Number: 5592981336014).



Figure(5): the proposed ternary composite of ZnO@ZIF-8/AgI constructed by Gao et al. [51]. Reprinted with permission (License Number: 5593030577259). Copyright 2022 Elsevier

## 6. Conclusion

Photocatalysis holds significant potential for degrading organic pollutants by utilizing semiconducting materials that can absorb light energy to produce reactive species. Silver halides (AgX,

including AgI, AgCl, and AgBr) have attracted attention as promising photocatalysts due to their favorable band structures, stability, and low cost. This paper offers a detailed overview of silver halide-based composite photocatalysts, highlighting their potential due to these properties. Additionally, it explores the possibility of improving photocatalytic efficiency in the degradation of organic pollutants by combining different semiconductors to create photocatalytic heterojunctions. AgX can form heterojunctions with other materials, such as metal oxides, MOFs, or carbon-based materials, which improves charge separation, light absorption, and reactive sites, enhancing photocatalytic performance. Conversely, in heterojunctions formed by two semiconductors, where one's conduction band (CB) or valence band (VB) edge lies between those of the other, photogenerated charges can only migrate from the comprehensive bandgap component to the narrow bandgap. The transfer does not occur in the opposite direction, i.e., from the narrow bandgap semiconductor to the wide bandgap semiconductor. AgX-based composite materials have appeared as efficient photocatalysts for photodegradation of organic pollutants. Their enhanced photocatalytic activity, synergistic effects, visible light responsiveness, and efficient pollutant degradation make them valuable materials for environmental remediation applications. We mainly discussed various synthesis methods for fabricating silver halides and their composite photocatalysts. The choice of fabrication method influences the photocatalyst's morphological, surface, and crystalline properties, ultimately affecting their photocatalytic performance. The contributions of these composites to their performances can be summarized as follows: (i) Enhanced adsorption efficiency of organic compounds, thereby facilitating their degradation during photocatalytic processes. (ii)



The presence of these composites helps to minimize electron and hole recombination rates, leading to increased stability and longer lifetimes of the charge carriers. (iii) The composites assist in effectively separating nanosized photocatalysts, thus preventing the accumulation of these materials, optimizing their interactions and ensuring better utilization of light for photocatalysis. In AgX-based heterojunction photocatalysts, the Z-type heterojunction enhanced by the plasmonic effect has emerged as an effective and widely accepted method to reduce charge carrier recombination and enhance charge separation.

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