Progress in Synthesis and Photocatalytic Activity of MAI₂O₄(M=Mg, Sr, Ba) Based Photocatalysts

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Photocatalysis is regarded as a green technology to degrade organic dyes driven by light energy. The selection of photocatalyst restricts the development of photocatalytic technology. Aluminate is a kind of potential broad-gap semiconductor photocatalyst and also an excellent phosphor substrate materials. The physical and chemical properties of aluminate are strongly dependent on the preparation method. Insight into the influence of synthesis methods on photocatalytic activity of aluminate based photocatalysts is helpful for the development of novel aluminate based photocatalysts. In this paper, the typical synthesis methods of aluminate photocatalysts, ion-doped aluminate based photocatalysts and heterojunction type aluminate photocatalysts, and their photocatalytic activities are reviewed. Based on the energy band theory, the photocatalytic mechanisms of single component aluminate photocatalyst, ion-doped aluminate based photocatalyst, and heterojunction type aluminate photocatalyst were reviewed. The future development of aluminate based photocatalyst will give priority to the salinization of aluminate modified by silver and other metal particles and the photocatalytic application of activated ion modified aluminate based phosphors.

Keywords: photocatalysis, aluminate, heterojunction, photocatalytic mechanism, photocatalytic application

INTRODUCTION

The economic development of all countries in the world has a great impact on the environment, especially human beings' thirst for necessities such as leather, textiles, medicines, food and so on, and the increasing demand for dyes, thus causing different degrees of pollution to the environment. (Wang et al., 2021a; Piriyanon et al., 2021; Ibrahim et al., 2022; Lahiri et al., 2022). Since water is needed for all kinds of necessities, and these factories are built along rivers, direct discharge of organic dyes into rivers will cause devastating pollution to the environment. This forces mankind to consider the problem of environmental pollution while developing. To deal with the pollution of organic dyes to water resources, the countries all over the world have invested a lot of money to solve this problem. Many mature methods have been developed to solve the problem of organic dye contamination, including: 1) Thermocatalytic technique driven by thermal energy. (Bao et al., 2020; Forouzesh et al., 2021) 2) Electrochemical technique driven by electric field or magnetic field. (Li et al., 2017; Szroeder et al., 2019). 3) Piezoelectric catalytic technique driven by mechanical energy. (Cheng et al., 2021a; Cheng et al., 2021b) 4) Biodegradation technique (Ghalei and Handa, 2022; Mathew et al., 2022). 5) Adsorption technique (Gao et al., 2021; Liu et al., 2022). 6) Photocatalytic technique
driven by light energy (Pu et al., 2021; Gao et al., 2022; Zhang et al., 2022). 7) Multi - technology hybrid degradation of organic matter. (Wang et al., 2021b). Among these technologies, the catalyst is the key factor affecting the degradation rate of dyes.

Recently, a series of photocatalysts have been developed to degrade organic dyes. There are three main types of photocatalysts (Wang et al., 2017; Wang et al., 2020a; Rajabathar et al., 2020; Shiwa Wang et al., 2020; Cheng et al., 2021c; Wang et al., 2021c; Ivashchenko et al., 2021; Kim et al., 2021; Kumar and Luxmi, 2021; Musa et al., 2021; Taazayet et al., 2021). 1) Single-component photocatalysts 2) Photocatalyst of two components 3) Ternary or multi-component photocatalysts. For a long time, single-component photocatalysts have been widely favored by researchers because of their advantages of simple composition and easy synthesis. Spinel aluminate is a kind of such single component photocatalyst, which has wide application prospect in the field of photocatalysis due to its high chemical and thermal stability, high catalytic activity, high specific surface area, and high surface defects and active sites. (Kharlanov et al., 2019; Boudiaf et al., 2020; Chen et al., 2021). Spinel aluminate generally has the structure of MB2O4, A is generally Mg, Ca, Sr, Ba, Co, Ni, Cu, Mn, and other bivalent metal ions, B is Al, Fe, Ga, Cr, and other trivalent metal ions. (Sharma et al., 2014; Sriram et al., 2020). Among these spinel aluminates, MAl2O4 (A = Mg, Sr, and Ba) has attracted extensive attention from researchers due to its excellent physicochemical properties make it can be used as long afterglow phosphor base materials, lightweight helmets, photoelectric devices, microwave dielectric capacitors, and high temperature windows, etc. (Han et al., 2018; Takebuchi et al., 2020; Basyrova et al., 2021; Kiryakov et al., 2021).

Simultaneously, MAl2O4 is a kind of environmental friendly material, in the photocatalytic field, especially in the degradation of organic dyes has a good application. (Wang et al., 2019a; Shifa Wang et al., 2020; Liu et al., 2022). Therefore, the work of MAl2O4 and MAl2O4 based photocatalysts in the degradation of organic dyes is reviewed, which has important research significance for the development of new aluminate based photocatalysts.

It is well known that the photocatalytic activity of aluminate based photocatalysts is strongly dependent on the preparation method. Different preparation methods will produce aluminate with different morphology, which may have special defect structure, thus enhancing the photocatalytic activity of aluminate. Ion doping and heterostructure construction will accelerate the transfer and separation of electrons and holes, and improve the photocatalytic activity of the system. Therefore, the influence of ion doping and heterostructure construction on the photocatalytic activity of aluminate photocatalyst should not be underestimated. In this paper, we start from the preparation of aluminate based photocatalysts, reviewed the preparation of single-component aluminate, metal ion doped aluminate and multiple heterojunction aluminate based photocatalysts, and their applications in the field of photocatalysis. Based on electron hole pair transfer, separation and energy band theory, the photocatalytic mechanism of single component aluminate and heterojunction aluminate photocatalysts was reviewed, and which provided technical support for the development of aluminate based photocatalysts.

### SYNTHESIS OF MAl2O4(M = MG, SR, AND BA) BASED PHOTOCATALYSTS

The photocatalytic activity of catalysts strongly depends on morphology, size, dimension, specific surface area, defect and impurity. Ultimately, these parameters affect the electron hole pair transfer and separation efficiency of the photocatalyst, which in turn accelerates the oxidation or reduction capacity of the electrons and holes. The dye is oxidized or reduced to form non-toxic small organic molecules. To regulate these parameters, the special synthesis methods are necessary. Currently, the MAl2O4(M = Mg, Sr, and Ba) based photoatalysts have been synthesized in a number of ways to construct specific defect structures.

### Synthesis of MAl2O4(M = Mg, Sr, and Ba) Photocatalysts

Spinel aluminate is a wide-gap semiconductor, such as BeAl2O4 (6.450 eV) (Ching et al., 2001), MgAl2O4 (3.923 eV) (Wang et al., 2019a), CaAl2O4 (7.400 eV) (Moirangthem et al., 2019), SrAl2O4 (3.984 eV) (Shifa Wang et al., 2020), BaAl2O4 (3.910 eV) (Shang-Pan et al., 2020), NiAl2O4 (4.030 eV) (Bhavani et al., 2018), FeAl2O4 (1.780 eV) (Mu et al., 2017), CoAl2O4 (1.948 eV) (Gao et al., 2018), NiAl2O4 (3.000 eV) (Chellammalgayathri et al., 2021), CuAl2O4 (2.920 eV) (Pothiare et al., 2019), and ZnAl2O4 (3.800 eV) (Shang-Pan et al., 2020). Based on the obtained optical band gap value and band theory, the conduction band potential and valence band potential of MAl2O4 were calculated.

\[
E_{CB} = X - E^* - 0.5E_g \tag{1}
\]
\[
E_{VB} = X + E^* + 0.5E_g \tag{2}
\]

Where, \( X \) of MAl2O4 was estimated by Eq. 3, \( E^* \) is 4.5 eV and \( E_g \) is optical band gap value.

\[
X(MAl_2O_4) = \sqrt{(X(M)(Al)^2X(O))}^4 \tag{3}
\]
Table 1 shows the X value, conduction band potential and valence band potential of MAI₂O₄ photocatalyst. The related energy level diagram of MAI₂O₄ photocatalyst can be described in Figure 1. As can be seen from Figure 1, the band gap value of MAI₂O₄ (M = Fe, Co, and Cu) is less than 3, which can easily respond to visible light and degrade organic dyes under visible light conditions (Gholami et al., 2016; Mu et al., 2017; Feng et al., 2021).

Other aluminate photocatalysts must adopt special preparation methods to introduce impurities or defects if they are to respond to visible light. Wang et al. (Wang et al., 2019b) used amorphous alumina and α-alumina to modify MnAl₂O₄ spinel type oxides exhibits high visible light photocatalytic activity. However, these mainly introduce impurities in the form of doping or coupling to enhance the photocatalytic activity of single component aluminate. In particular, the band gap values of MAI₂O₄ (M = Mg, Sr, and Ba) are close to 4, making it difficult to respond to visible light. Traditional methods such as the solid state reaction method, (Ganesh et al., 2004; Canaza-Mamani et al., 2021), the sol-gel method, (Habibi et al., 2017; Salehadi et al., 2017), the solvothermal method, (Zhu et al., 2012), the hydrothermal method (Sera et al., 2021), and the coprecipitation method (Zawrah et al., 2007) are difficult to make its have special defect structure. In order to make a single component aluminate photocatalytic activity, special preparation methods must be used to enhance the electron and hole pairs transfer and separation ability. Wang et al. (Wang et al., 2019a) synthesized MgAl₂O₄ photocatalyst with special defective structure by gamma ray irradiation assisted polyacrylamide gel method, which showed that it had high visible light photocatalytic activity for the degradation of methylene blue. However, the extreme conditions such as high energy, high pressure and high temperature are often needed to prepare aluminate photocatalyst with defective structure by special preparation process, which are very difficult to achieve in general laboratory. Therefore, other means must be found to enhance the photocatalytic activity of single component aluminate photocatalyst.

### Synthesis of Metal Ion Doped MAI₂O₄(M = Mg, Sr, and Ba) Photocatalysts

Ion doping is an effective way to enhance the photocatalytic activity of a single component semiconductor photocatalyst. Generally, ion doping can change the band gap value of a single component semiconductor photocatalyst. For the MAI₂O₄ doping can choose A site substitution and Al site substitution, A site substitution of ion radius should be close to the A site ion. In the synthesis of dense ceramics, the solid state reaction method is relatively better, and the high temperature, and high pressure conditions are easy to doping ions into the lattice of a single component aluminate. However, due to the small specific surface area and porosity of dense ceramics, the photocatalytic degradation of organic dyes is not favorable, which will greatly limit the application of solid phase reaction method in the synthesis of ion doped aluminate photocatalysts. Alam et al. (Alam et al., 2022) synthesized the Cr³⁺-doped MgAl₂O₄ nanoparticles by the solution combustion method exhibits excellent photocatalytic activity against Acid Red-88 (AR-88) dye. Solution combustion method is easy to control the morphology of Cr³⁺-doped MgAl₂O₄, adjust the doping ratio, reduce the particle size, resulting in a single component of MgAl₂O₄ exhibit novel physicochemical properties. Chen et al. (Chen et al., 2009) synthesized MgAl₂O₄:Eu³⁺ phosphors by hydrothermal method exhibits high photoluminescence properties. Different morphologies of MgAl₂O₄:Eu³⁺ phosphors can be obtained by changing the ratio of precursor salts. The SEM images of MgAl₂O₄:Eu³⁺ phosphors as shown in Figure 2.

The results further show that it is easy to synthesize different morphologies of ion doped aluminate photocatalysts by hydrothermal method. Wang et al. (Wang et al., 2019c) reported that the Mg₁₋ₓCoₓAl₂O₄ photocatalysts synthesized by the irradiation assisted polyacrylamide gel route exhibits high photocatalytic activity. The method can be used to synthesize aluminate photocatalysts with different proportions and morphologies, which is beneficial to improve the photocatalytic activity of single component aluminate photocatalysts.

### Synthesis of MAI₂O₄(M = Mg, Sr, and Ba) Based Multivariate Heterojunction Photocatalysts

Another way to enhance the photocatalytic activity of semiconductor photocatalysts is to construct multiple photocatalysts with special heterojunction structure. Similarly, the aluminate based phosphors can be used in a similar way to enhance...
the photoluminescence properties of a single component aluminate (Wang et al., 2020b; Liu et al., 2020). Surface modification of MgAl2O4 with metal particles can enhance its photoluminescence properties due to plasma resonance effect. With the increase of sintering temperature, the metal particles are oxidized, which affects the band gap value of the system. The MgAl2O4: M (M = Mg, Ti, Mn, Co, and Ni) phosphors exhibits wide visible light absorption, suggesting that they have high photocatalytic activity under visible light. Mkhalid et al. (Mkhalid, 2022) synthesized the Ag2O/SrAl2O4/CNT ternary photocatalyst by the sol-gel method exhibits high visible-light-responsive for H2 production. The construction of multiple heterojunctions is benefical to enhance the electron transport, transfer and separation efficiency of SrAl2O4, and thus improving the photocatalytic activity of the system under visible light irradiation. Sol-gel method has more advantages than solid phase method and coprecipitation method because of its easy composition control and simple synthesis. Hydrothermal method is easy to synthesize the aluminate products with different morphologies, but its application in the construction of multiple heterojunctions is less. Therefore, the sol-gel method is commonly used to synthesize aluminate-based multielement heterostructures.

PHOTOCATALYTIC ACTIVITY OF MAL2O4(M = Mg, Sr, and Ba) PHOTOCATALYSTS

The photocatalytic activity of aluminate photocatalyst is strongly dependent on the preparation method, ion doping and heterostructure construction. 

Photocatalytic Activity of MAL2O4(M = Mg, Sr, and Ba) Photocatalysts

Due to the large band gap value of MAL2O4(M = Mg, Sr, and Ba) aluminate photocatalyst, there are relatively few studies on its use as photocatalyst alone. Except for MgAl2O4 and BaAl2O4, single component SrAl2O4 has not been used as a photocatalyst to degrade organic dyes. Table 2 shows the photocatalytic activity of MAL2O4 and BaAl2O4 photocatalyst. Nassar et al. (Nassar et al., 2014) reported the MgAl2O4 photocatalyst prepared by the sol–gel–auto combustion method exhibits high photocatalytic activity for the degradation of Reactive Red Me 4BL dye. Qian et al. (Qian et al., 2017) synthesized MgAl2O4 photocatalyst by a simple hydrothermal route exhibits high photocatalytic activity for the degradation of Methylene blue. However, MgAl2O4 synthesized by this method is inadequate in degrading phenol. Li et al. (2011) prepared the mixed amorphous and crystalline MgAl2O4 nanopowders by a simple solution combustion method using glycine and urea as fuel mixtures exhibits high visible light-induced photocatalytic activity for the degradation of Methylene bule. Jiang et al. (2014) synthesized the MgAl2O4 photocatalyst by a sol–gel–method exhibits a poor photocatalytic activity for the degradation of various dyes including methyl orange, acid red B and reactive brilliant red K-2G. Parvarinezhad et al. (2019) synthesized the MgAl2O4 nanopowders by one-step solid state reaction method possessed strong light absorption properties in the ultraviolet-visible region. Wang et al. (2019d) synthesized the MgAl2O4 and BaAl2O4 photocatalysts by the polyacrylamide gel method exhibits high photocatalytic activity. The results
show that the photocatalytic activity of MAI₂O₄ synthesized by different preparation methods is different.

**Photocatalytic Activity of Metal Ion Doped MAI₂O₄ (M = Mg, Sr, and Ba) Photocatalysts**

Metal ion doping can effectively change the band gap value of aluminate photocatalyst so as to enhance its photocatalytic activity. Different doping ions have different regulation on the band gap of aluminate, so different metal ions doped aluminate show different photocatalytic activity. Table 3 shows the photocatalytic activity of metal ion doped MAI₂O₄ (M = Mg, Sr, and Ba) photocatalyst. Li et al. 2(016) synthesized the Mg₁₋ₓZnxAl₂O₄ spinel nanoparticles by the chemical coprecipitation method have a high photocatalytic activity. The photocatalytic activity of Mg₁₋ₓZnxAl₂O₄ spinel nanoparticles increased with the increasing of x value as shown in Figure 3. When Cu²⁺ ions were engrafted onto MgAl₂O₄ nanoparticles by a highly adaptable and energy efficient chemical process, the photocatalytic activity of the system was greatly improved (Mukherjee et al., 2020). The photocatalytic activity of MgAl₂O₄ can also be improved by introducing Co (Wang et al., 2019c) or Ce (Chen et al., 2019).

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**Table 2 | The photocatalytic activity of MAI₂O₄ photocatalyst.**

| Samples | Dye | Lamp | C_{catalyst} (g L⁻¹) | C_{dye} (mg L⁻¹) | Irradiation time (min) | D% (%) | References |
|---------|-----|------|----------------------|-----------------|----------------------|-------|------------|
| MAI₂O₄ | Red Me | Reactive UV illumination | 2 | 10 | 350 | 90.00 | Nassar et al. (2014) |
| Amorphous Earth-abundant | Red Me | Sunlight | 1 | 10 | 240 | 81.01 | Qian et al. (2017) |
| MAI₂O₄ | Phenol | 300 w Xe lamp | 0.75 | 50 | 100 | 40.01 | Li et al. (2011) |
| MAI₂O₄ | Methyl orange | high pressure mercury lamp | 5 | 12 | 100 | 40.01 | Jiang et al. (2014) |
| MAI₂O₄ | Malachite green | lamp (300 W) | 0.3125 | 5 | 100 | 100 | Parvarinezhad et al. (2019) |
| MAI₂O₄ | Methylene blue | 150 W Xe-lamp | 1 | 5 | 180 | 99.6 | Wang et al. (2019a) |
| MAI₂O₄ | Methyl orange | high pressure mercury lamp | 1 | 5 | 240 | 79 | Wang et al. (2019c) |

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**Table 3 | The photocatalytic activity of metal ion doped MAI₂O₄ (M = Mg, Sr, and Ba) photocatalyst.**

| Samples | Dye | Lamp | C_{catalyst} (g L⁻¹) | C_{dye} (mg L⁻¹) | Irradiation time (min) | D% (%) | References |
|---------|-----|------|----------------------|-----------------|----------------------|-------|------------|
| Mg₁₋ₓZnxAl₂O₄ | Methylene blue | A Hg lamp | 2 | 10 | 240 | 99 | Li et al. (2016) |
| Cu²⁺ engrafted | Methylene blue | Sunlight | 1.5 | 10 | 240 | 98.5 | Mukherjee et al. (2020) |
| MAI₂O₄ | Methylene blue | 150 W Xe-lamp | 1 | 5 | 120 | 98 | Wang et al. (2019c) |
| Mg₁₋ₓCoₓAl₂O₄ | Rhodamine B | 150-W/m² xenon lamp | 1.5 | 5 | 180 | 88.2 | Chen et al. (2019) |
| Mn-codoped | Methylene blue | 150-W/m² xenon lamp | 1 | 5 | 180 | 85 | Wang et al. (2019e) |
| MAI₂O₄: Ce | Methylene blue | 1 | 400 ml | 100 | 0.78 mmol/h | Park. (2018) |
| Bismuth doped | Methylene blue | high pressure mercury lamp | 0.428 | 25 | 120 | 78 | García et al. (2018) |
| SrAl₂O₄ | Congo red | high pressure mercury lamp | 0.6 | 15 | 120 | 100 | Berlanga et al. (2017) |
| SrAl₂O₄:CxCu | Congo red | lamp (300 W) | 0.5 | 10 | 300 | 80 | Shifa Wang et al. (2020) |
| SrAl₂O₄: Ce: Mn | Congo red | 200 W/m² xenon lamp | 0.5 | 10 | 300 | 80 | Deepika and Kumar, (2020) |
| Rare earth doped | Methylene blue | Solar | 1 | 25 | 240 | 22.8 | Mumanga et al. (2021) |
| SrAl₂O₄ | Congo orange | 100 mW/cm² Newport solar simulator | 1 | 15 | 180 | 99% | |
| Nd³⁺ doped BaAl₂O₄ | Methylene blue | 150 W/m² xenon lamp | 1 | 5 | 240 | 79.85 | Wang et al. (2020c) |
ions into MgAl₂O₄. Ce and Mn co-doped MgAl₂O₄ can further improve the photocatalytic activity of MgAl₂O₄ (Wang et al., 2019e). Metal ion doping in SrAl₂O₄ has also been widely used, through Eu²⁺ and Dy³⁺ (Park, 2018), Cu (Berlanga et al., 2017), Ce and Mn (Shifa Wang et al., 2020), and rare earth ion (Deepika and Kumar, 2020) doping SrAl₂O₄, all enhance the photocatalytic activity of SrAl₂O₄. Similarly, Nd³⁺ (Mumanga et al., 2021) and Ce and Mn (Wang et al., 2020c) ions are also used in the doping of BaAl₂O₄, and their photocatalytic activity is greatly improved compared with that of single-phase BaAl₂O₄.

**Photocatalytic Activity of MAI₂O₄ (M = Mg, Sr, and Ba) Based Multivariate Heterojunction Photocatalysts**

The construction of multiple heterojunction composite is beneficial to combine the advantages of multiple semiconductor materials and enhance the photocatalytic activity of the system. The MAI₂O₄ (M = Mg, Sr, and Ba) photocatalyst has a relatively large band gap, which makes it difficult to respond to visible light. Therefore, the semiconductor materials that can respond to visible light are preferentially selected for the construction of heterojunction. **Table 4** shows the photocatalytic activity of MAI₂O₄ (M = Mg, Sr, and Ba) based multivariate heterojunction photocatalysts. MgAl₂O₄ based photocatalyst was constructed by combining various semiconductor materials, and its photocatalytic activity was confirmed to be enhanced (Abbasi Asl et al., 2019; Abbasi Asl et al., 2020; Wang et al., 2021d). Meanwhile, MgAl₂O₄/CeO₂/Mn₃O₄ ternary heterojunction photocatalyst was constructed by combining CeO₂ and Mn₃O₄, showing high photocatalytic activity for the degradation of methylene blue dye (Li et al., 2021). Aluminate is a very good phosphor base material, the introduction of activated ions will make aluminate luminescence as phosphor. Recently, researchers have found that aluminate activated by metal ions as photocatalysts also have high photocatalytic activity. The photocatalytic activity of SrAl₂O₄ was greatly enhanced by the construction of multi-component composite SrAl₂O₄ photocatalysts (García et al., 20162016; Xiao et al., 2018; Liu et al., 2019; Zargoosh and Moradi Aliabadi, 2019; Mavengere and Kim, 2020; Aliabadi et al., 2021). The construction of the heterojunction provides a technical advantage.
reference for the subsequent study of other aluminate photocatalysts. The photocatalytic activity of aluminate modified by noble metal particles can be greatly improved by plasma resonance effect. However, the modification of Silver particles on the surface of MgAl₂O₄ easily leads to the hydrolysis of MgAl₂O₄, which greatly affects the application of MgAl₂O₄ as a photocatalyst. Zhu et al. (2015) synthesized the Ag/BaAl₂O₄ photocatalyst shows high photocatalytic activity for the degradation of Gaseous toluene. When the silver content is low, the hydrolysis of BaAl₂O₄ is inhibited and it can be used as a photocatalyst. Li et al. (2009) constructed the TiO₂/BaAl₂O₄:E u²⁺, D y³⁺ photocatalyst exhibits high photocatalytic activity. These successful applications provide a new idea for the use of wide-band gap semiconductors as photocatalysts in future research.

**PHOTOCATALYTIC MECHANISM OF MAL₂O₄(M = MG, SR, AND BA) BASED PHOTOCATALYSTS**

Different types of photocatalysts have slightly different photocatalytic mechanisms. The photocatalytic mechanism of single component aluminate photocatalyst, ion doped aluminate photocatalyst and heterogeneous aluminate photocatalyst was compared and analyzed.

**Photocatalytic Mechanism of MAL₂O₄ Photocatalysts**

Due to the large band gap value of a single component aluminate, it is difficult to respond directly to visible light. When single component aluminate is synthesized by a special method, it is easy to introduce defects such as oxygen vacancy into the aluminate, so that it has visible photocatalytic activity.

**Photocatalytic Mechanism of MAL₂O₄ Based Heterojunction Photocatalysts**

During the construction of the multiple heterostructure, the semiconductor material enhancing the photocatalytic activity of visible light is regarded as the defect level, so the other half of the aluminate heterojunction acts as the defect level. However, multiple heterojunction photocatalysts introduce new semiconductor materials and have great influence on the phase purity of the whole system. Therefore, the photocatalytic mechanism is different from that of a single component photocatalyst. Figure 5 shows the photocatalytic mechanism of MgAl₂O₄/BeO₂/Fe₃O₄ heterojunction photocatalyst. MgAl₂O₄, CeO₂, and Mn₃O₄ form a double p-n heterojunction structure among each other, which facilitates the transfer and separation of electron hole pairs, thus enhancing the photocatalytic activity of the system. The separation of electron and hole pairs accelerates the oxidation or reduction reactions of each, which then reacts with the dye to produce non-toxic and harmless products.

Figure 4 shows the photocatalytic mechanism of MgAl₂O₄ photocatalyst. When a beam of light hits the surface of MgAl₂O₄, electrons jump from its valence band to the conduction band, and leaving holes in the valence band. It is difficult for electrons to jump directly to the conduction band without the action of defect levels. Therefore, the defect level plays an important role in the whole photocatalytic process. Combined with the band theory analysis, it is found that the degradation of methylene blue dye is difficult to take place in the photosensitization process. Therefore, the whole process is mainly photocatalytic degradation, the valence band electrons and conduction band holes are involved in the reaction, and the final generation of non-toxic and harmless products. The related chemical reactions can be described as follows (Shifa Wang et al., 2020):

1. The creation of electron hole pairs.
   
   \[
   \text{MAI}_2\text{O}_4 + h \rightarrow \text{MAI}_2\text{O}_4 \rightarrow e^- + h^+ \tag{4}
   \]

2. The production of hydroxyl radicals
   
   \[
   h^+ + \text{OH}^- \rightarrow [\text{MSI}_2\text{O}_4]^- \cdot \text{OH} \tag{5}
   \]

3. The production of superoxide radicals
   
   \[
   e^- + \text{O}_2 \rightarrow \cdot \text{O}_2^- \tag{6}
   \]
   \[
   \cdot \text{O}_2^- + 2\text{H}^+ \rightarrow \text{H}_2\text{O}_2 \tag{7}
   \]
   \[
   2e^- + \text{O}_2 + 2\text{H}^+ \rightarrow \text{H}_2\text{O}_2 \tag{8}
   \]
   \[
   e^- + \text{H}_2\text{O}_2 \rightarrow \cdot \text{OH} + \text{OH}^- \tag{9}
   \]
   \[
   \cdot \text{O}_2^- + \text{H}_2\text{O}_2 \rightarrow \cdot \text{OH} + \text{OH}^- + \text{O}_2 \tag{10}
   \]

4. Dye degradation
   
   \[
   \cdot \text{OH} + \text{dye} \rightarrow \text{CO}_2 + \text{H}_2\text{O} + \text{non-toxic products} \tag{11}
   \]
Activated ions induce aluminate luminescence, which is its advantage when used as a photocatalyst. Figure 6 shows the photocatalytic mechanism of CdS-sheathed SrAl₂O₄: Eu²⁺, Dy³⁺ heterojunction photocatalysts. When SrAl₂O₄: Eu²⁺, Dy³⁺ is used as phosphors, the recombination of electron and hole pairs in the system is accelerated. However, when it combines with other semiconductor materials to form heterojunction photocatalyst, the energy absorbed by it can promote the electron transition in the whole system, thus accelerating the separation of electron and hole pairs in the system. The non-meeting of electrons and holes on CdS causes each to react with the dye to form CO₂, H₂O and other small molecular organics.

CONCLUSION AND OUTLOOK

Aluminate based photocatalyst is a kind of photocatalyst developed rapidly in recent years. Despite it have a very large band gap, researchers have always found ways to promote the transfer and separation of electrons and hole pairs, and thereby improving their photocatalytic activity. For the single-component aluminate photocatalysts, defects are introduced to provide defect levels to promote electron transition to aluminate conduction band under extreme conditions such as high temperature and high pressure, so as to enhance the photocatalytic activity of visible light. Similarly, impurity ions can be introduced into the lattice of aluminate by ion doping to improve the migration and separation efficiency of electron hole pairs and improve the photocatalytic activity of aluminate. The construction of special heterojunction structure is a simple method with relatively mature technology. By introducing other semiconductor materials with excellent performance, the construction of multiple heterojunction aluminate based photocatalyst has become a hot research field.

There are seven development trends of aluminate based photocatalysts in the future 1) The hydrolysis of aluminate is still one of the key problems to be solved. When silver particles are used to modify aluminate photocatalyst, aluminate will produce different degree of hydrolysis, which has been a difficult problem for researchers. The development of new synthetic pathways may solve this problem. 2) New application of aluminate based heterojunction phosphors in photocatalysis. When aluminate phosphor is combined with other semiconductor photocatalysts, the photocatalytic activity of the whole system will be greatly improved. However, the research of aluminate based phosphor in the field of photocatalysis is still in its infancy, and further research is
The photocatalytic mechanism needs further study. The newly developed aluminate photocatalyst will face the problem that the existing mechanism cannot explain, so it is necessary to develop a new explanation mechanism. 4) The effect of different morphologies of aluminate photocatalysts on photocatalytic activity needs further study. The specific surface area of aluminate photocatalysts with different morphologies was different, and their degradation activity to dyes was obviously different. 5) The photocatalytic activity of aluminate photocatalyst modified by lanthanide metal particles is worth further study. There is no evidence that the modification of aluminate photocatalyst by lanthanide metal particles will lead to hydrolysis, so it is also worth studying. 6) Modification of aluminate photocatalyst by organic macromolecular network. The modification of aluminate photocatalyst by organic macromolecular network is beneficial to provide electron transport carrier for aluminate, thus enhancing the photocatalytic activity of aluminate. 7) New applications of photocatalysts are worth exploring. Novel photocatalysts may induce new interpretation mechanisms, thus promoting the application of these photocatalysts in new fields.

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