

# Hexagonal Ferrite $MFe_{12}O_{19}$ (M=Sr, Ba, Cu, Ni, Pb) Based Photocatalysts: Photoluminescence, Photocatalysis and Applications

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**Abstract:** Hexagonal ferrite ( $MFe_{12}O_{19}$ , M=Sr, Ba, Cu, Ni, Pb) is a kind of semiconductor material with excellent performance and an important magnetic material, with high chemical and thermal stability, low cost, simple preparation process, excellent optical, magnetic, wave-absorbing, dielectric, photoluminescence properties and catalytic activities have been widely used in broadcast communication, information storage, aerospace, automatic control, catalytic synthesis, medicine and biology and many other fields. This paper focuses on the application of  $MFe_{12}O_{19}$ -based ferrite in the field of photocatalysis, and further discusses the effect of preparation method on the photocatalytic activity of  $MFe_{12}O_{19}$ -based photocatalysts. The application of  $MFe_{12}O_{19}$ -based photocatalysts in the degradation of dyes, drugs and persistent organic pollutants (POPs) was deeply revealed, and the photocatalytic mechanisms of single-phase  $MFe_{12}O_{19}$ , ion-doped  $MFe_{12}O_{19}$  and  $MFe_{12}O_{19}$ -based composite photocatalysts were also explored. The relationship between photocatalytic activity and photoluminescence properties of  $MFe_{12}O_{19}$ -based photocatalysts have also been investigated. This review points out the direction for further research on the application of  $MFe_{12}O_{19}$ -based photocatalysts in the field of photocatalysis.

**Keywords:** Hexagonal ferrite, Photocatalytic activity, Photocatalytic mechanism, Photoluminescence properties, Photocatalysts.

## 1. INTRODUCTION

The great development of the world economy is the development at the expense of the environment, which has been widely concerned by all countries. [1-4] The clothes people wear in daily life, drugs, textiles, paper will use a large number of dyes, antibiotics and other persistent organic pollutants (POPs), these pollutants directly discharged into the environment, will cause fatal harm to the environment, thus affecting human production and life. [5-8] Therefore, the degradation of dyes, drugs and POPs at source will greatly reduce their harm to the environment. The common practice of scientific researchers is to select appropriate photocatalysts for the photocatalytic degradation of dyes, drugs and POPs by reasonable use of sunlight, and unprecedented progress has been made. [9-18] In spite of this, photocatalyst cannot be recovered in water, which will cause secondary pollution to water body.

Recently,  $MFe_{12}O_{19}$  (M=Sr, Ba, Cu, Ni, Pb), as a class of strong magnetic material with high photocatalytic

activity, has entered the attention of researchers engaged in photocatalytic research. [19-21] The magnetic field is used to recover the photocatalyst, which greatly reduces the secondary pollution caused by the photocatalyst to water. [22-25] Figure 1(a) shows the crystal structure of  $MFe_{12}O_{19}$  photocatalysts. The unit cell of  $MFe_{12}O_{19}$  is composed mainly of two building blocks of 'S' block ( $Fe_6O_8$ )<sup>2+</sup> and 'R' block ( $MFe_6O_{11}$ )<sup>2+</sup> has a spinel unit cell and hexagonal closed packing of oxygen ions and M ions, respectively. [26] Figure 1(b) shows the related energy level diagram of  $MFe_{12}O_{19}$  photocatalysts. Conduction band potential ( $E_{CB}$ ) and valence band potential ( $E_{VB}$ ) of  $MFe_{12}O_{19}$  can be calculated by equations (1) and (2).

$$E_{CB} = X - E^e - 0.5E_g \quad (1)$$

$$E_{VB} = E_{CB} + E_g \quad (2)$$

Where  $E^e=4.5$  eV,  $E_g$  is the optical band gap value of  $MFe_{12}O_{19}$ .  $X$  is the absolute electronegativity of  $MFe_{12}O_{19}$ . According to formula (3),  $X(MFe_{12}O_{19})$  can be obtained.

$$X(MFe_{12}O_{19}) = \sqrt[3]{X(M)X(Fe)^{12}X(O)^{19}} \quad (3)$$

Based on the above formula, the  $E_{CB}$  and  $E_{VB}$  of  $MFe_{12}O_{19}$  photocatalysts are given in Table 1. With the

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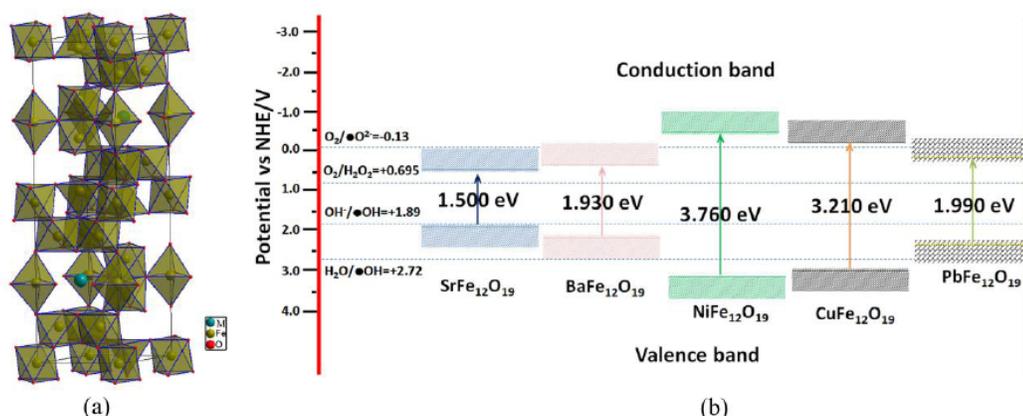


Figure 1: (a) Crystal structure and (b) the related energy level diagram of  $MFe_{12}O_{19}$  photocatalysts.

Table 1: The  $E_{CB}$  and  $E_{VB}$  of  $MFe_{12}O_{19}$  Photocatalysts

Samples	$E_g$ (eV)	$X$ (V)	$E_{CB}$ (V)	$E_{VB}$ (V)	References
$SrFe_{12}O_{19}$	1.500	5.735	0.485	1.985	[27]
$BaFe_{12}O_{19}$	1.930	5.768	0.303	2.233	[28]
$NiFe_{12}O_{19}$	3.760	5.878	-0.502	3.258	[20]
$CuFe_{12}O_{19}$	3.210	5.882	-0.233	2.987	[29]
$PbFe_{12}O_{19}$	1.990	5.856	0.361	2.351	[30]

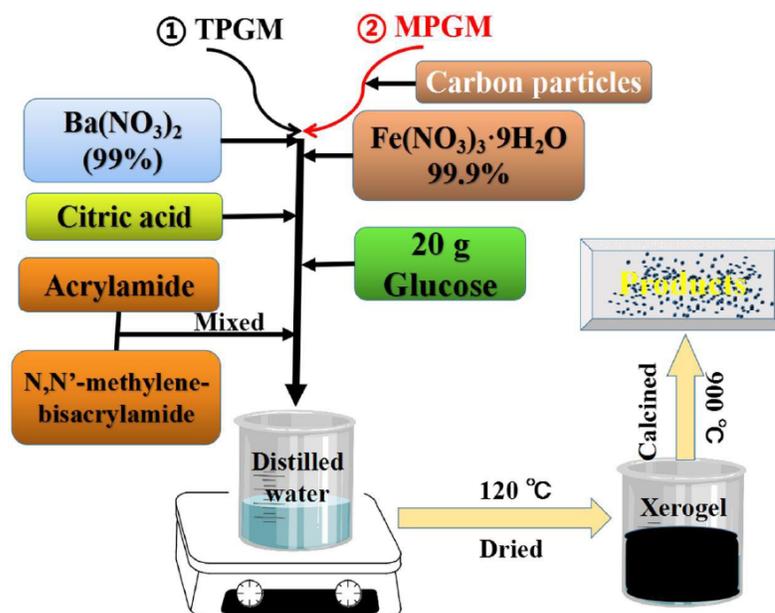
difference of M ions, the optical band gap of  $MFe_{12}O_{19}$  is different, which leads to the difference of conduction band potential and valence band potential, and thus affects the photocatalytic activity of  $MFe_{12}O_{19}$ . [20, 27-30] Therefore, the design of  $MFe_{12}O_{19}$ -based photocatalysts for pollutant degradation can be based on the above theory.

Based on the band arrangement theory, a variety of  $MFe_{12}O_{19}$ -based photocatalysts have been designed to degrade pollutants. [31] In order to promote the degradation of pollutants by  $MFe_{12}O_{19}$ , Valero-Luna *et al.* [32] enhanced the visible photocatalytic activity of  $BaFe_{12}O_{19}$  by adding  $H_2O_2$  to methyl blue dye solution. To reduce the optical bandgap value of  $MFe_{12}O_{19}$ , ion doping  $MFe_{12}O_{19}$  was used to preserve its strong magnetic properties and enhance the photocatalytic activity of the system. [33] Due to the limitation of synthesis methods, most researchers still focus on the construction of heterojunction. [34-42] Based on different synthesis methods of  $MFe_{12}O_{19}$ -based photocatalysts to construct a recyclable magnetic photocatalyst with high photocatalytic activity, this paper studied the application of  $MFe_{12}O_{19}$ -based photocatalysts in the degradation of dyes, drugs and POPs, and then summarized the photocatalytic

mechanism of different  $MFe_{12}O_{19}$ -based photocatalysts. Meanwhile, the internal mechanism of photoluminescence and photocatalysis of  $MFe_{12}O_{19}$ -based photocatalyst is also deeply understood. With the development of science and technology,  $MFe_{12}O_{19}$ -based photocatalysts are developing towards diversification and optimized performance, with a view to industrial application in the near future.

## 2. SYNTHESIS OF $MFe_{12}O_{19}$ ( $M=SR, BA, CU, NI, PB$ ) BASED PHOTOCATALYSTS

Although  $MFe_{12}O_{19}$  photocatalyst has high magnetic properties, the metal salt used for synthesis is weak in magnetically, so it is suitable for wet chemical synthesis of this kind of ferrite. Simultaneously, hexagonal ferrite has a high optical absorption coefficient, but its charge carrier transfer and separation efficiency is low, which is not conducive to photocatalytic degradation of pollutants. Therefore, researchers are forced to use special preparation methods to improve the charge carrier transfer and separation efficiency of pure phase  $MFe_{12}O_{19}$ , and at the same time to enhance the charge carrier transfer and separation efficiency of  $MFe_{12}O_{19}$  photocatalyst through ion doping and multi-component semiconductor coupling. The photocatalytic activity of



**Figure 2:** The synthetic path diagram of BaFe<sub>12</sub>O<sub>19</sub> nanoparticles prepared by different polyacrylamide gel methods. Adapted from ref. [48]. Copyright © 2021 Trans Tech Publications Ltd.

MFe<sub>12</sub>O<sub>19</sub> photocatalyst will be greatly affected by different preparation methods. It is worth noting that different ion doping and different semiconductor coupling of MFe<sub>12</sub>O<sub>19</sub> photocatalyst will lead to different photocatalytic activity of MFe<sub>12</sub>O<sub>19</sub> photocatalyst.

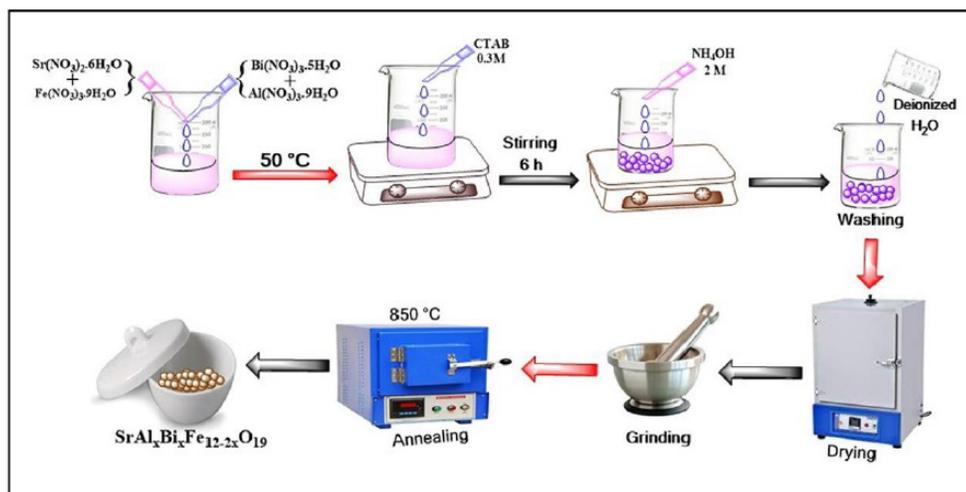
### 2.1. Synthesis of Single Phase MFe<sub>12</sub>O<sub>19</sub> Photocatalysts

There are many methods to synthesize MFe<sub>12</sub>O<sub>19</sub> photocatalyst, including solid phase reaction method, hydrothermal method, coprecipitation method, electrospinning method, sol-gel method and so on. Solid phase reaction method uses simple raw materials, not easy to introduce impurities, but its high synthesis temperature, the equipment requirements are relatively harsh, and the synthesized particle size is large, limiting the application of MFe<sub>12</sub>O<sub>19</sub> in the field of photocatalysis. [43] High temperature reaction method can use oxides as raw materials, but it is exothermic reaction, the heat generated is easy to harm the equipment and human body, so this method limits its application in the preparation of MFe<sub>12</sub>O<sub>19</sub>. [44] Hydrothermal method has relatively low requirements on temperature and equipment, and only requires a reactor to generate pressure below 300 °C to generate the target product. However, the yield is very low and the synthesis time is long, which makes the preparation of MFe<sub>12</sub>O<sub>19</sub> photocatalyst often need to spend a lot of time and raw materials. [45] Similar to hydrothermal method, coprecipitation method has low synthesis temperature but low yield, so its application in the

synthesis of photocatalysts is limited. [46] It is easy to obtain nanowire or nanorods by electrospinning method, but the high pressure is dangerous and the improper operation can easily cause injury. [47] Sol-gel method is a kind of method which can adjust experimental parameters to obtain different morphology, phase purity and physical and chemical properties of MFe<sub>12</sub>O<sub>19</sub> photocatalysts. It is the mainstream method for the synthesis of MFe<sub>12</sub>O<sub>19</sub> photocatalysts. [19] Recently, the MFe<sub>12</sub>O<sub>19</sub> nanoparticles have been synthesized by our group using both traditional polyacrylamide gel method (TPGM) and modified polyacrylamide gel method (MPGM), as shown in Figure 2. By adjusting the sintering temperature, MFe<sub>12</sub>O<sub>19</sub> with different morphologies can be obtained easily. [26, 48-50] The highly dispersed MFe<sub>12</sub>O<sub>19</sub> particles were easily obtained by introducing glucose into the precursor solution.

### 2.2. Synthesis of Ion Doped MFe<sub>12</sub>O<sub>19</sub> Photocatalysts

In the process of synthesizing ion-doped MFe<sub>12</sub>O<sub>19</sub> photocatalyst, it is necessary to consider the content of doping ions, too much will form impurity oxides of doping ions, so that doping ions cannot occupy the position of MFe<sub>12</sub>O<sub>19</sub> lattice. To obtain the best doping ratio, researchers are constantly improving synthesis methods to synthesize ion-doped MFe<sub>12</sub>O<sub>19</sub> photocatalysts. The synthesis of ion-doped MFe<sub>12</sub>O<sub>19</sub> photocatalyst is far more complex than that of single-



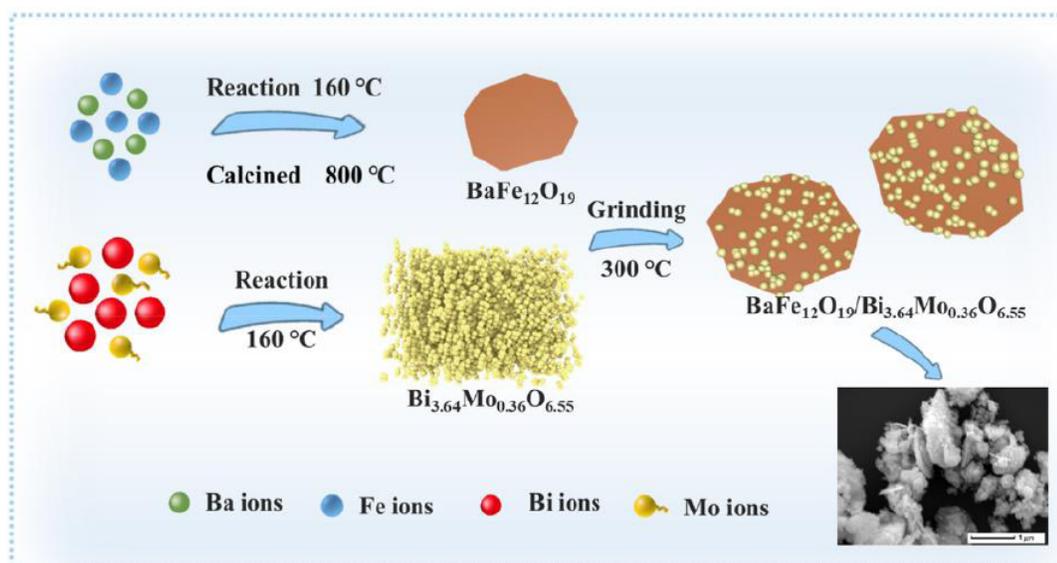
**Figure 3:** Preparation flow chart for the synthesis of  $SrAl_xBi_xFe_{12-2x}O_{19}$  nanoparticles prepared via facile micro-emulsion method. Adapted from ref. [58]. Copyright © 2022 The Korean Society of Industrial and Engineering Chemistry. Published by Elsevier B.V.

phase  $MFe_{12}O_{19}$  photocatalysts, and the conventional synthesis method is easy to introduce impurities, and it is difficult to obtain the desired target products, which will enable researchers to constantly develop new methods to synthesize ion-doped  $MFe_{12}O_{19}$  photocatalysts. A simple microemulsion method was developed to synthesize a variety of ion-doped  $MFe_{12}O_{19}$  photocatalysts, including  $Ba_{1-x}Nd_xFe_{12-y}Cu_yO_{19}$ , [51]  $Ba_{1-x}Co_xFe_{12-y}Cr_yO_{19}$ , [52]  $BaNi_xFe_{12-x}O_{19}$ , [53]  $Ba_{1-x}Zn_xFe_{12-y}Cr_yO_{19}$ , [54]  $BaCr_xFe_{12-x}O_{19}$ , [33]  $Ba_{1-x}Zn_xFe_{12-y}Mn_yO_{19}$ , [55]  $Sr_{1-x}Zn_xFe_{1-y}Ni_yO_{19}$ , [56] and  $Ba_{1-x}Mg_xFe_{12-y}Mn_yO_{19}$  [57]. Raza *et al.* [58] reported the  $SrAl_xBi_xFe_{12-2x}O_{19}$  nanoparticles prepared via facile micro-emulsion method exhibits high photocatalytic activity and antibacterial properties. The preparation flow chart for the synthesis of  $SrAl_xBi_xFe_{12-2x}O_{19}$  nanoparticles as shown in Figure 3. First, the corresponding metal salts are dissolved in deionized water in molar ratio. Subsequently, cetyltrimethylammonium bromide was added to reduce superficial tension and reduce rapid agglomeration between particles. After all reagents are completely dissolved, the pH value is adjusted with ammonia water, and the final product is obtained after several times of cleaning, drying, ball milling and sintering. Ashraf *et al.* [59] also synthesized  $Ba_{0.4}Sr_{0.6}Al_{0.4-x}Sm_xFe_{11.60}O_{19}$  photocatalysts by the sol-gel method, which showed high photocatalytic activity in the degradation of methylene blue.

### 2.3. Synthesis of $MFe_{12}O_{19}$ Based Composite Photocatalysts

For the  $MFe_{12}O_{19}$ -based multi-element composite photocatalysts, in addition to obtaining single-phase

matrix material, it is necessary to construct multi-element composite photocatalysts. There are three common methods. First, each single-phase catalyst is synthesized in a different way, and then a variety of single-phase materials are coupled together by a special synthesis method. [27, 28, 60, 61] Zhang *et al.* [36] synthesized  $BaFe_{12}O_{19}/Bi_{3.64}Mo_{0.36}O_{6.55}$  composite photocatalysts by the low temperature sintering technology combined with hydrothermal method, the photocatalyst shows a high photocatalytic activity for the degradation of pollutants. Figure 4 shows the synthetic process of  $BaFe_{12}O_{19}/Bi_{3.64}Mo_{0.36}O_{6.55}$  composite photocatalysts. By this method, the fine particles of  $Bi_{3.64}Mo_{0.36}O_{6.55}$  were successfully interacted on the lamellar  $BaFe_{12}O_{19}$  photocatalysts. Such binding mode promotes the transfer and separation of charge carriers at the interface of  $BaFe_{12}O_{19}$  and  $Bi_{3.64}Mo_{0.36}O_{6.55}$ , thus enhancing the photocatalytic activity of the system. The second is to synthesize a single phase material and then coupled another single phase material together in the same way. [34, 62, 63] This method is simpler and more efficient than the previous method and reduces the influence of the intermediate process on the properties of the final product. The third method is one-step synthesis method. [64-66] This method is to add different metal salts to the precursor solution at one time according to the molar ratio, and obtain the final product through gel, drying and sintering. Although the one-step synthesis method is very simple compared with the previous two methods, the composition is difficult to control, so there are not many researchers who use this method to synthesize  $MFe_{12}O_{19}$ -based composite photocatalysts.



**Figure 4:** The synthetic process of  $\text{BaFe}_{12}\text{O}_{19}/\text{Bi}_{3.64}\text{Mo}_{0.36}\text{O}_{6.55}$  composite photocatalysts. Adapted from ref. [36]. Copyright © 2022 Elsevier Ltd.

### 3. PHOTOCATALYTIC APPLICATIONS

With high optical absorption coefficient and magnetic properties,  $\text{MFe}_{12}\text{O}_{19}$  has important applications in the field of magnetic separation recyclable photocatalysis. However, as a photocatalyst,  $\text{MFe}_{12}\text{O}_{19}$  is not the most excellent photocatalytic semiconductor materials due to its high charge carrier recombination rate. In terms of magnetic separation and recovery,  $\text{MFe}_{12}\text{O}_{19}$ 's high magnetic properties make it better than other semiconductor magnetic materials in this field. Due to the application of  $\text{MFe}_{12}\text{O}_{19}$  photocatalyst in magnetic separation and recovery, many types of photocatalysts have been gradually developed, including ion-doped  $\text{MFe}_{12}\text{O}_{19}$  photocatalysts, multi-heterojunction  $\text{MFe}_{12}\text{O}_{19}$ -based composite photocatalysts, etc. These new magnetic separation photocatalysts have been widely used in the degradation of dyes, drugs and POPs.

#### 3.1. Applications in the Degradation of Dyes

Most of the  $\text{MFe}_{12}\text{O}_{19}$ -based photocatalysts for the degradation of pollutants are mainly concentrated in the degradation of dye, especially the color dye to the river pollution is shocking. Table 2 shows the photocatalytic activity of  $\text{MFe}_{12}\text{O}_{19}$ -based composite photocatalysts toward the photodegradation of dyes. Single-phase  $\text{MFe}_{12}\text{O}_{19}$  photocatalyst can degrade dyes, but the degradation effect is not as good as that of ion-doped  $\text{MFe}_{12}\text{O}_{19}$  photocatalysts and multiplex  $\text{MFe}_{12}\text{O}_{19}$  composite photocatalysts. Compared with

the  $\text{MFe}_{12}\text{O}_{19}$  photocatalyst, the optical band gap value of the ion-doped  $\text{MFe}_{12}\text{O}_{19}$  photocatalyst is significantly reduced, which also makes the ion-doped  $\text{MFe}_{12}\text{O}_{19}$  show more excellent photocatalytic activity. However, due to the presence of Fe ions, the photocatalytic mechanism of  $\text{MFe}_{12}\text{O}_{19}$  based photocatalyst is unclear. After years of unremitting research, the photocatalytic mechanism of  $\text{MFe}_{12}\text{O}_{19}$  based photocatalyst was finally revealed. Simultaneously, the photocatalytic activity of  $\text{MFe}_{12}\text{O}_{19}$ -based photocatalysts is affected by the type of dye, light time, dye concentration, catalyst content, light source and other factors, so that they show different photocatalytic activity. [67-104] The photocatalytic activity of ion doped  $\text{MFe}_{12}\text{O}_{19}$  photocatalysts is affected by doping ions, which contribute a lot to photocatalysis, which makes the analysis of its photocatalysis mechanism also greatly affected. In the construction of multi-heterojunction  $\text{MFe}_{12}\text{O}_{19}$  composite photocatalysts, its photocatalytic activity is affected by other semiconductor materials, so the selection of semiconductor materials is very careful. Researchers have combined oxides, sulfides, polymers, metal-organic framework materials, carbon nanotubes, noble metal particles with  $\text{MFe}_{12}\text{O}_{19}$  to construct  $\text{MFe}_{12}\text{O}_{19}$ -based composite photocatalysts, which have been widely used in the degradation of organic dye wastewater. [40, 46, 67, 73, 74] To make  $\text{MFe}_{12}\text{O}_{19}$ -based photocatalyst practical, researchers have been trying to combine  $\text{MFe}_{12}\text{O}_{19}$  with other substances to obtain  $\text{MFe}_{12}\text{O}_{19}$ -based composite photocatalysts with excellent photocatalytic activity.

**Table 2: The photocatalytic activity of  $MFe_{12}O_{19}$ -based composite photocatalysts toward the photodegradation of dyes. MB -Methylene Blue, ABU Acid blue, ABA-Acid black, AV-Acid violet, ABR-acid brown, ES -Eosin, CR-Congo red, CV-Sulphur blue, AR -Acid red, MG -Malachite green, MO -Methyl orange, MR-Methyl red, MW-Methylene white, TB-Toluidine blue, MX-5B - Procion red, BR46-Basic Red 46, RhB - Rhodamine B**

Samples	Dye	Lamp	$C_{Catalyst}$ ( $g \cdot L^{-1}$ )	$C_{Drug}$ ( $mmol L^{-1}$ )	t (h)	D (%)	SA ( $mmol/g/h$ )	Reference
$Ba_{1-x}Sm_xFe_{12-x}Co_xO_{19}$	MB	Visible light	2.00	0.031	1	87.12%	0.0135	[63]
$BaFe_{12}O_{19}$	MB	Visible light	0.75	0.031	6	70.8%	0.0048	[32]
$Ba_{0.4}Sr_{0.6}Al_{0.4-x}Sm_xFe_{11.60}O_{19}$	MB	UV light	0.25	0.031	2.34	99%	0.0525	[59]
$BaFe_{12}O_{19}/Sm_2Ti_2O_7/Ag$	MB	Osram lamp	/	0.031	2	99.03%	/	[67]
$BaFe_{12}O_{19}$	MB	Xenon lamp	2.00	0.031	3	78%	0.0041	[68]
$BaFe_{12}O_{19}$	MB	Sun light	0.80	0.125	3	73%	0.038	[69]
$CuFe_{12}O_{19}$ -CNT	MB	UV light	0.02	0.063	0.83	54.1%	2.0531	[40]
$SrFe_{12}O_{19}$	MB	Xenon lamp	1.00	0.031	4.5	95%	0.0065	[70]
$ZnFe_2O_4/SrFe_{12}O_{19}$	MB	Xenon lamp	2.00	0.031	2	96.6%	0.0075	[64]
$SrFe_{12}O_{19}/MoS_2$	MB	Visible light	0.40	0.063	1	86%	0.1354	[46]
$SrFe_{12}O_{19}$	MB	Visible light	4.00	0.016	3	84%	0.0011	[71]
$SrFe_{12}O_{19}/ZnFe_2O_4$	MB	Visible light	1.00	0.016	4	90%	0.0036	[65]
$SrFe_{12}O_{19}$	MB	UV light	/	0.156	2	46%	/	[72]
MIL-88A (Fe)/BiOBr/ $SrFe_{12}O_{19}$	MB	Xenon lamp	1.00	0.031	1.5	90.1%	0.0186	[73]
$Sr(CeNd)_xFe_{12-2x}O_{19}$ /polythiophene	MB	Mercury lamp	2.00	0.031	0.5	98%	0.0304	[74]
$La_{0.2}Sr_{0.7}Fe_{12}O_{19}$	MB	Xenon lamp	1.00	0.031	6	88%	0.0045	[75]
$SrFe_{12}O_{19}/SiO_2/TiO_2$	MB	UV light	/	0.156	3	83%	/	[76]
$SrFe_{12}O_{19}/SiO_2/TiO_2$	MB	UV light	/	0.156	3	80%	/	[77]
15% $SrFe_{12}O_{19}/BiVO_4$	MB	Xenon lamp	2.00	0.016	5	93%	0.0015	[78]
$ZnFe_2O_4$ - $SrFe_{12}O_{19}$	MB	Halogen lamp	2.00	0.031	5	100%	0.0031	[66]
$TiO_2$ -coated- $SrFe_{12}O_{19}$	MB	UV light	0.18	0.078	7	98.19%	0.0625	[79]
25% $SrFe_{12}O_{19}/SrTiO_3$	MB	Xenon lamp	0.67	0.013	2	98.6%	0.0096	[80]
$Bi_2O_3/SrFe_{12}O_{19}$	MB	Halogen lamp	2.00	0.013	4/6	97.7%	0.0016	[41]
BiOCl- $SrFe_{12}O_{19}$	MB	UV light	2.00	0.013	0.83	99%	0.0077	[81]
$TiO_2/SrFe_{12}O_{19}$	MB	UV light	2.00	0.013	5	94.7%	0.0012	[82]
$BaFe_{12}O_{19}-TiO_2$	AB	UV light	10.00	0.021	1	/	/	[83]
$PbFe_{12}O_{19}-TiO_2$	ABU	UV light	20.00	0.021	1	75%	0.0009	[24]
$PbFe_{12}O_{19}-PbS$	ABU	UV light	10.00	0.042	1	97%	0.0041	[25]
$SrFe_{12}O_{19}@Ag$	ABU	Tungsten lamp	1.00	0.011	2	58.1%	0.0032	[84]
$BaFe_{12}O_{19}-ZnO$	ABA	UV light	10.00	0.016	1	81%	0.0013	[85]
$SrFe_{12}O_{19}-SrTiO_3$	ABA	UV light	10.00	/	0.5	95%	/	[86]
$CoFe_2O_4/BaFe_{12}O_{19}$	CR	Xenon lamp	5.00	/	0.83	84.5%	/	[38]
$SrFe_{12}O_{19}$	CR	Visible light	0.50	0.028	3	90%	0.0168	[87]
$Ba_{1-x}Co_xFe_{12-y}Cr_yO_{19}$	CV	Sun light	0.10	0.024	1	64.23%	0.1541	[52]
$BaNi_xFe_{12-x}O_{19}$	CV	Xenon lamp	0.07	0.024	1.7	97%	0.2044	[53]
$BaCr_xFe_{12-x}O_{19}$	CV	Argon lamp	0.10	0.024	1.5	91%	0.1456	[33]

$\text{SrBi}_x\text{Al}_y\text{Fe}_{12-2x}\text{O}_{19}$	CV	Sun light	1.00	0.024	2	83%	0.0099	[58]
$\text{SrMn}_x\text{Fe}_{12-x}\text{O}_{19}$	CV	Sun light	0.10	0.024	1.67	96%	0.1497	[88]
$\text{SrNi}_x\text{Fe}_{12-x}\text{O}_{19}$	CV	Visible light	0.02	0.024	1.5	91%	0.728	[89]
$\text{CuFe}_{12}\text{O}_{19}$ /CNT	AR	UV light	0.02	0.023	0.83	21.6%	0.2953	[29]
$\text{Ba}_{1-x}\text{Nd}_x\text{Fe}_{12-y}\text{Cu}_y\text{O}_{19}$	MG	Sun light	0.05	0.011	1	92.6%	0.2	[51]
$\text{BaFe}_{12}\text{O}_{19}/\text{Bi}_{3.64}\text{Mo}_{0.36}\text{O}_{6.55}$	MO	Visible light	0.20	0.062	1	84.5%	0.2619	[36]
$\text{BaFe}_{12}\text{O}_{19}$	MO	Visible light	0.50	0.031	0.67	97%	0.0898	[90]
$\text{BaFe}_{12}\text{O}_{19}$	MO	Hg lamp	2.00	/	3.3	95%	/	[91]
$\text{PbFe}_{12}\text{O}_{19}$	MO	UV light	/	/	1.17	29.41%	/	[22]
$\text{SrFe}_{12}\text{O}_{19}/\text{MoS}_2$	MO	Visible light	0.40	0.062	1	61%	0.0946	[92]
$\text{SrFe}_{12}\text{O}_{19}$	MO	Hg lamp	2.00		3.67	95%		[93]
$\text{SrFe}_{12}\text{O}_{19}$	TB	Tungsten lamp	5.00	0.100	20h	100%	0.001	[94]
$\text{TiO}_2/\text{BaFe}_{12}\text{O}_{19}$	MX-5B	UV light	0.01	/	5	96%	/	[95]
$\text{SrFe}_{12}\text{O}_{19}/\text{ZnO}$	BR46	Visible light	0.75	0.025	1.5	99%	0.022	[96]
16.8%of $\text{BaFe}_{12}\text{O}_{19}/\text{g-C}_3\text{N}_4$	RhB	Visible light	1.00	0.021	1.7	95.8%	0.0118	[61]
10% $\text{BaFe}_{12}\text{O}_{19}/\text{AgBr}$	RhB	Xenon lamp	0.50	0.042	0.5	98.2%	0.1649	[62]
$\text{Ba}_{1-x}\text{Zn}_x\text{Fe}_{12-y}\text{Cr}_y\text{O}_{19}$	RhB	Sun light	/	/	1.5	81.8%	/	[54]
$\text{BaFe}_{12}\text{O}_{19}$	RhB	Xenon lamp	20.00	0.021	3	100%	0.0004	[97]
$\text{Ba}_{1-x}\text{Mg}_x\text{Fe}_{12-y}\text{Mn}_y\text{O}_{19}$	RhB	Sun light	0.10	0.021	0.83	85%	0.2151	[57]
$\text{BiOC}/\text{SrFe}_{12-x}\text{Co}_x\text{O}_{19}/\text{rGO}$	RhB	Sun light	1.00	0.021	1.33	94%	0.0148	[98]
$\text{Bi}_3\text{O}_4\text{Cl}/\text{SrFe}_{12}\text{O}_{19}$	RhB	Sun light	1.00	0.021	1.33	99.7%	0.0157	[40]
$\text{Bi}_4\text{O}_5\text{Br}_2/\text{SrFe}_{12}\text{O}_{19}$	RhB	Xenon lamp	1.00	0.021	1	99.3%	0.0209	[99]
$\text{ZnO}/\text{SrFe}_{12}\text{O}_{19}$	RhB	Xenon lamp	1.00	0.021	1.17	99.5%	0.0178	[100]
$\beta\text{-Bi}_2\text{O}_3/\text{SrFe}_{12}\text{O}_{19}$	RhB	Xenon lamp	2.00	0.021	2.5	92.97%	0.0039	[41]
$\text{ZnO}/\text{Bi}_{24}\text{O}_{31}\text{Br}_{10}/\text{SrFe}_{12}\text{O}_{19}$	RhB	Xenon lamp	0.50	0.042	0.5	96.8%	0.1626	[101]
$\text{Sr}_{1-x}\text{Co}_x\text{Fe}_{12-y}\text{Cr}_y\text{O}_{19}$	RhB	Sun light	0.10	0.021	0.75	87.6%	0.2453	[102]
$\text{BiOBr}/\text{SrFe}_{12}\text{O}_{19}$	RhB	Visible light	0.50	0.021	0.5	97%	0.0814	[103]
$\text{BiOCl}/\text{SrFe}_{12-x}\text{Co}_x\text{O}_{19}$	RhB	Xenon lamp	1.00	0.021	1.67	98%	0.0123	[104]

### 3.2. Applications in the Degradation of Drugs

Recently, the research of  $\text{MFe}_{12}\text{O}_{19}$ -based photocatalysts in the degradation of dyes is becoming more and more mature. No new breakthrough can be made in the degradation process, the influence of process parameters or the study of photocatalytic mechanism, which makes researchers have to open up new ways to study the photocatalytic activity of  $\text{MFe}_{12}\text{O}_{19}$ -based photocatalysts. Drugs contain a large number of antibiotics, and only a small part of them are absorbed by human body, animal and aquatic products. Most of them will be discharged through feces and other excretions, thus polluting the environment. Using this as a breakthrough, researchers have made a certain breakthrough in drug

degradation of  $\text{MFe}_{12}\text{O}_{19}$ -based photocatalysts. Table 3 shows the photocatalytic activity of  $\text{MFe}_{12}\text{O}_{19}$ -based composite photocatalysts toward the photodegradation of drugs. Kaur *et al.* [105] decorated different metal ions such as Cr, Mn, Fe, Co, Ni, Cu, Zn on the surface of  $\text{SrFe}_{12}\text{O}_{19}$  and studied the effect of these ions on the degradation of levofloxacin (LVX) and sulfamethoxazole (SFX). The results showed that the  $\text{SrFe}_{12}\text{O}_{19}$ -based photocatalyst was selective to drug degradation, and its photocatalytic activity was affected by metal ions. Other novel  $\text{MFe}_{12}\text{O}_{19}$ -based photocatalysts have also been used to degrade drugs. [20, 34, 36, 37, 106-109] The research on the degradation of drugs is still in the stage of vigorous development. Many photocatalytic mechanisms are unknown, and advanced technologies are needed to

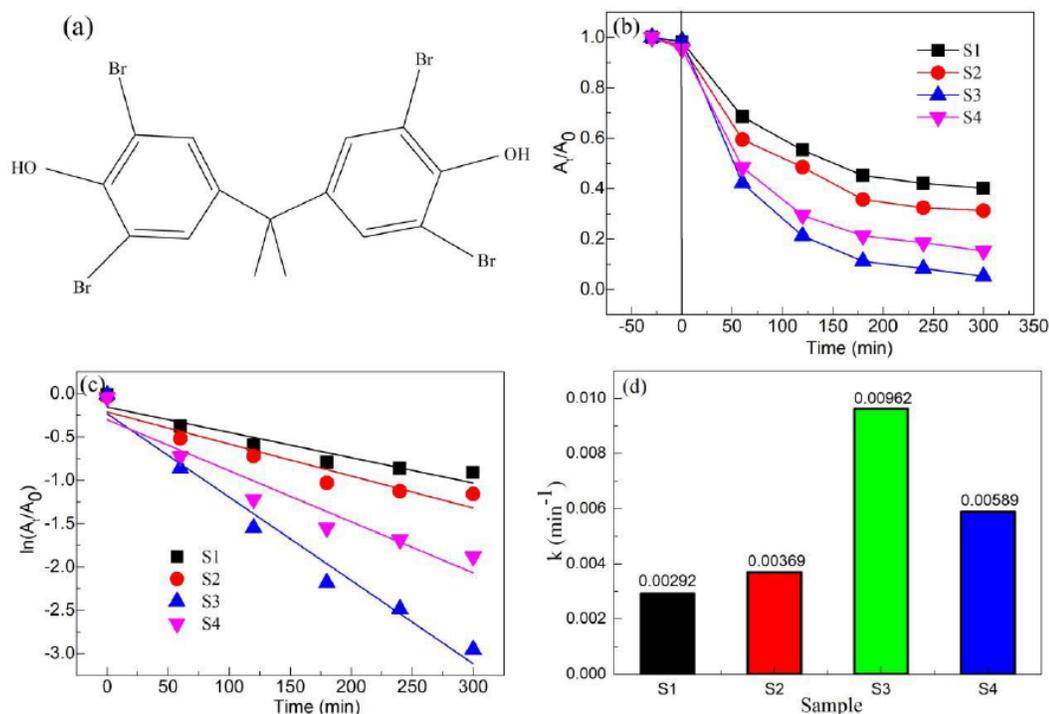
**Table 3: The photocatalytic activity of  $MFe_{12}O_{19}$ -based composite photocatalysts toward the photodegradation of drugs. LVX - Levofloxacin, SFX - Sulfamethoxazole, RDX - hexahydro-1,3,5- trinitro-1,3,5 triazine, OC - Oxytetracycline, CC - Chlortetracycline, TCH - Tetracycline Hydrochloride, TC - Tetracycline, CFX - Ceftriaxone sodium, BPA - bisphenol A, ATZ- Atrazine, 2,4-DCP - 2,4-Dichlorophenol**

Samples	Drug	Lamp	$C_{Catalyst}$ ( $g \cdot L^{-1}$ )	$C_{Drug}$ ( $mmol L^{-1}$ )	t (h)	D (%)	SA ( $mmol/g/h$ )	Reference
$SrFe_{12}O_{19}$	LVX	Visible light	0.5	0.05	2	64.5%	0.03225	[105]
$SrFe_{12}O_{19}@Dop$	LVX	Visible light	0.5	0.05	2	71.5%	0.03575	
$SrFe_{12}O_{19}@Dop@Cr$	LVX	Visible light	0.5	0.05	2	68.5%	0.03425	
$SrFe_{12}O_{19}@Dop@Mn$	LVX	Visible light	0.5	0.05	2	98.1%	0.04905	
$SrFe_{12}O_{19}@Dop@Fe$	LVX	Visible light	0.5	0.05	2	92%	0.046	
$SrFe_{12}O_{19}@Dop@Co$	LVX	Visible light	0.5	0.05	2	95.2%	0.0476	
$SrFe_{12}O_{19}@Dop@Ni$	LVX	Visible light	0.5	0.05	2	95.3%	0.04765	
$SrFe_{12}O_{19}@Dop@Cu$	LVX	Visible light	0.5	0.05	2	94.5%	0.04725	
$SrFe_{12}O_{19}@Dop@Zn$	LVX	Visible light	0.5	0.05	2	93.1%	0.04655	
$SrFe_{12}O_{19}$	SFX	Visible light	0.5	0.05	2	66%	0.033	
$SrFe_{12}O_{19}@Dop$	SFX	Visible light	0.5	0.05	2	72.1%	0.0361	
$SrFe_{12}O_{19}@Dop@Cr$	SFX	Visible light	0.5	0.05	2	70.7%	0.0353	
$SrFe_{12}O_{19}@Dop@Mn$	SFX	Visible light	0.5	0.05	2	97.2%	0.0486	
$SrFe_{12}O_{19}@Dop@Fe$	SFX	Visible light	0.5	0.05	2	84.1%	0.0421	
$SrFe_{12}O_{19}@Dop@Co$	SFX	Visible light	0.5	0.05	2	95.6%	0.0478	
$SrFe_{12}O_{19}@Dop@Ni$	SFX	Visible light	0.5	0.05	2	89.2%	0.0446	
$SrFe_{12}O_{19}@Dop@Cu$	SFX	Visible light	0.5	0.05	2	92.9%	0.0465	
$SrFe_{12}O_{19}@Dop@Zn$	SFX	Visible light	0.5	0.05	2	75.2%	0.0376	
$BaFe_{12}O_{19}(800^{\circ}C)$	RDX	UV light	1	0.1801	4	98.1%	0.0441	[106]
$BaFe_{12}O_{19}/Bi_{3.64}Mo_{0.36}O_{6.55}$	OC	Visible light	0.2	0.043	1	86%	0.1849	[36]
$BaFe_{12}O_{19}/Bi_{3.64}Mo_{0.36}O_{6.55}$	CC	Visible light	0.2	0.0417	1	81%	0.1688	
$BaFe_{12}O_{19}/Bi_{3.64}Mo_{0.36}O_{6.55}$	TCH	Visible light	0.2	0.042	1	84.5%	0.1775	[107]
$Bi_2O_3/Bi_2S_3/BaFe_{12}O_{19}$	TC	Visible light	3	0.022	1	83%	0.0061	
$NiFe_{12}O_{19}-ZnO$	CFX	UV light	0.4	0.0523	2	98.5%	0.0644	[20]
$NiFe_{12}O_{19}-TiO_2$	CFX	UV light	0.2	0.0523	2	95.5%	0.1248	
$NiFe_{12}O_{19}$	CFX	UV light	/	/	2	74.7%	/	[37]
1% $BaFe_{12}O_{19}/Ag_3PO_4$	BPA	Xenon lamp	1	0.0876	0.5	53.3%	0.0933	
5% $BaFe_{12}O_{19}/Ag_3PO_4$	BPA	Xenon lamp	1	0.0876	0.5	65.3%	0.1144	
10% $BaFe_{12}O_{19}/Ag_3PO_4$	BPA	Xenon lamp	1	0.0876	0.5	79.9%	0.1399	
15% $BaFe_{12}O_{19}/Ag_3PO_4$	BPA	Xenon lamp	1	0.0876	0.5	79.8%	0.1398	
$Ag_2O/BaFe_{12}O_{19}$	ATZ	Xenon lamp	1	0.2318	1	74%	0.1715	[34]
0.4% $Ag_2O/BaFe_{12}O_{19}$	ATZ	Xenon lamp	1	0.2318	1	79%	0.1831	
0.8% $Ag_2O/BaFe_{12}O_{19}$	ATZ	Xenon lamp	1	0.2318	1	90%	0.2086	
1.2% $Ag_2O/BaFe_{12}O_{19}$	ATZ	Xenon lamp	1	0.2318	1	100%	0.2318	[108]
$TiO_2-SiO_2-BaFe_{12}O_{19}$	2,4-DCP	Sun light	/	/	2.5	100%	/	
$TiO_2/GO/SrFe_{12}O_{19}$	2,4-DCP	Sun light	4	0.3067	3	100%	0.0256	[109]

characterize the degradation processes to gain an in-depth insight into their photocatalytic mechanisms.

### 3.3 Applications in the Degradation of POPs

There are few studies on the degradation of POPs



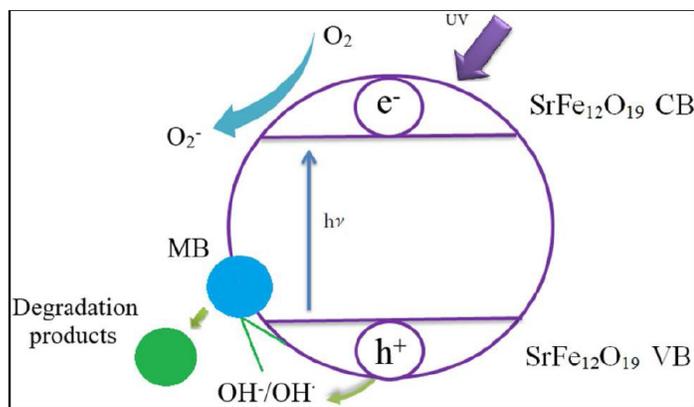
**Figure 5:** (a) Molecular structure of tetrabromobisphenol A. (b) Photocatalytic degradation curve, (c) Plots of  $\ln(A_t/A_0)$  vs. irradiation time and (d) First order kinetic constant ( $k$ ) of tetrabromobisphenol A in the presence of carbon quantum dots (CQDs)/CeO<sub>2</sub>/BaFe<sub>12</sub>O<sub>19</sub> magnetic separation photocatalysts under simulated sunlight radiation. S1-CeO<sub>2</sub>, S2-(15 wt%) CQDs / (5 wt% BaFe<sub>12</sub>O<sub>19</sub>/CeO<sub>2</sub>), S3-(15 wt%) CQDs / (10 wt% BaFe<sub>12</sub>O<sub>19</sub>/CeO<sub>2</sub>) and S4-(15 wt%) CQDs / (15 wt% BaFe<sub>12</sub>O<sub>19</sub>/CeO<sub>2</sub>). Adapted from ref. [28]. Copyright © 2022 The Authors. Publishing services by Elsevier B.V. on behalf of KeAi Communications Co. Ltd.

by MFe<sub>12</sub>O<sub>19</sub>. Tetrabromobisphenol is a type of POPs, which is very harmful to the environment. In our early study, the CQDs/CeO<sub>2</sub>/BaFe<sub>12</sub>O<sub>19</sub> magnetic separation photocatalysts was synthesized by the hydrothermal method combined with the polyacrylamide gel method, and the photocatalytic activity of the magnetic separation photocatalysts for the degradation of tetrabromobisphenol under visible light irradiation was studied. CeO<sub>2</sub> is easily synthesized by wet chemistry and its particle size can be easily controlled. [110] Due to its internal oxygen vacancy, CeO<sub>2</sub> is very popular for photocatalytic degradation of pollutants. The effects of different contents of CQDs and BaFe<sub>12</sub>O<sub>19</sub> on the photocatalytic activity of CQDs/CeO<sub>2</sub>/BaFe<sub>12</sub>O<sub>19</sub> magnetic separation photocatalyst were studied. The photocatalytic activity of CQDs/CeO<sub>2</sub>/BaFe<sub>12</sub>O<sub>19</sub> magnetic separation photocatalyst can be effectively regulated by magnetic field. Figure 5 shows the molecular structure of tetrabromobisphenol A and the photocatalytic activity of CQDs/CeO<sub>2</sub>/BaFe<sub>12</sub>O<sub>19</sub> magnetic separation photocatalysts. It can be seen from Figure 5 that the CQDs/CeO<sub>2</sub>/BaFe<sub>12</sub>O<sub>19</sub> magnetic separation photocatalysts has the best photocatalytic activity to degrade tetrabromobisphenol A when the mass percentage of BAFe<sub>12</sub>O<sub>19</sub> is 10 wt%. Due to the

small content of carbon quantum dots and BaFe<sub>12</sub>O<sub>19</sub> in CQDs/CeO<sub>2</sub>/BaFe<sub>12</sub>O<sub>19</sub> magnetic separation photocatalysts, it is very difficult to detect them by conventional XRD. Therefore, neutron powder diffraction is used to study their composition, phase structure and magnetic structure. The FENGHUANG diffractometer is very suitable for measuring the neutron powder diffraction spectra of magnetic samples at different temperatures. [111] In the study of other low content MFe<sub>12</sub>O<sub>19</sub> composite photocatalysts, it is important to use neutron powder diffraction to understand its phase composition, structure and magnetic structure.

#### 4. PHOTOCATALYTIC MECHANISM

Since MFe<sub>12</sub>O<sub>19</sub> was used as a photocatalyst, the research on it has been non-stop. Due to the high magnetic properties of MFe<sub>12</sub>O<sub>19</sub>, it can be separated from water by magnetic field when it is used as a photocatalyst, without causing secondary pollution to water. However, the charge transfer and separation efficiency of single-phase MFe<sub>12</sub>O<sub>19</sub> is low, which makes its application as a photocatalyst very limited. Therefore, researchers have adopted various methods to improve the photocatalytic activity of MFe<sub>12</sub>O<sub>19</sub>. After



**Figure 6:** Photocatalysis mechanism of  $SrFe_{12}O_{19}$  particles. Adapted from ref. [72]. Copyright © Springer Science+Business Media, LLC, part of Springer Nature 2020.

years of research, a unified theory of photocatalysis mechanism has been preliminarily formed.

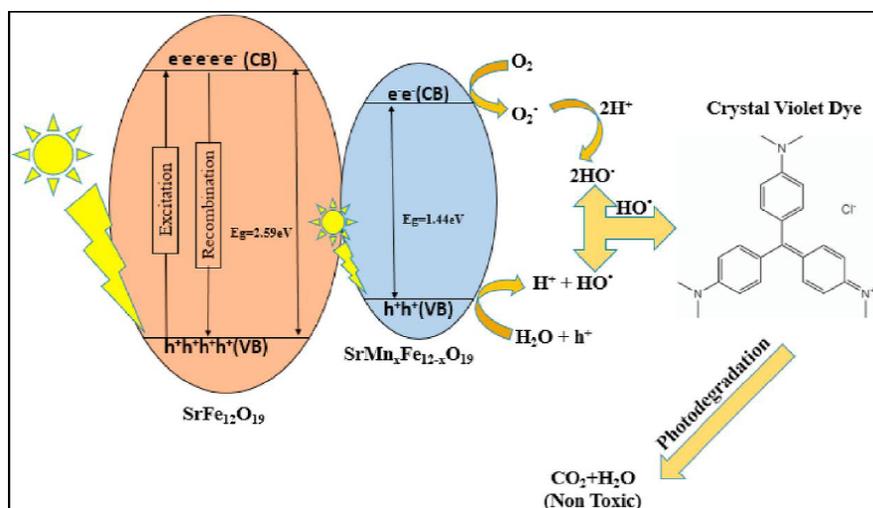
#### 4.1. Photocatalytic Mechanism of Single Phase $MFe_{12}O_{19}$ Photocatalysts

The optical bandgap value of  $MFe_{12}O_{19}$  is affected by M ions, but they have high optical absorption coefficients in both ultraviolet and visible ranges. The high optical absorption coefficient of visible light makes it possible for  $MFe_{12}O_{19}$  to respond to visible light during photocatalytic degradation of pollutants. Figure 6 shows the photocatalysis mechanism of  $SrFe_{12}O_{19}$  particles. [72] When a beam of light with an energy greater than the optical bandgap value of  $MFe_{12}O_{19}$  shines on its surface, electrons in the valence band (VB) of  $MFe_{12}O_{19}$  will transition to its conduction band (CB), leaving holes in the valence band. The holes in the valence band will react with water in the reaction solution to form hydroxyl radicals. The conduction electrons will react with the oxygen in the reaction

solution to form a superoxide radical. Hydroxyl radicals and superoxide radicals react with pollutants to produce non-toxic and harmless products. [93] However, when the optical bandgap value of  $MFe_{12}O_{19}$  is large, it is difficult for  $MFe_{12}O_{19}$  to respond to visible light, which will result in low photocatalytic activity of  $MFe_{12}O_{19}$  in visible light.

#### 4.2. Photocatalytic Mechanism of Ion Doped $MFe_{12}O_{19}$ Photocatalysts

Ion doping  $MFe_{12}O_{19}$  can effectively reduce its optical band gap value and improve its photocatalytic activity. For the photocatalyst with relatively large optical band gap in  $MFe_{12}O_{19}$ , this is undoubtedly good news in terms of enhancing its photocatalytic activity of visible light. Rasheed *et al.* [88] reported the Mn doped  $SrFe_{12}O_{19}$  synthesized by a facile microemulsion route exhibits high solar-light-driven photocatalytic activity for the degradation of crystal violet dye. Figure 7 shows the photocatalysis mechanism of  $SrMn_xFe_{12-x}O_{19}$



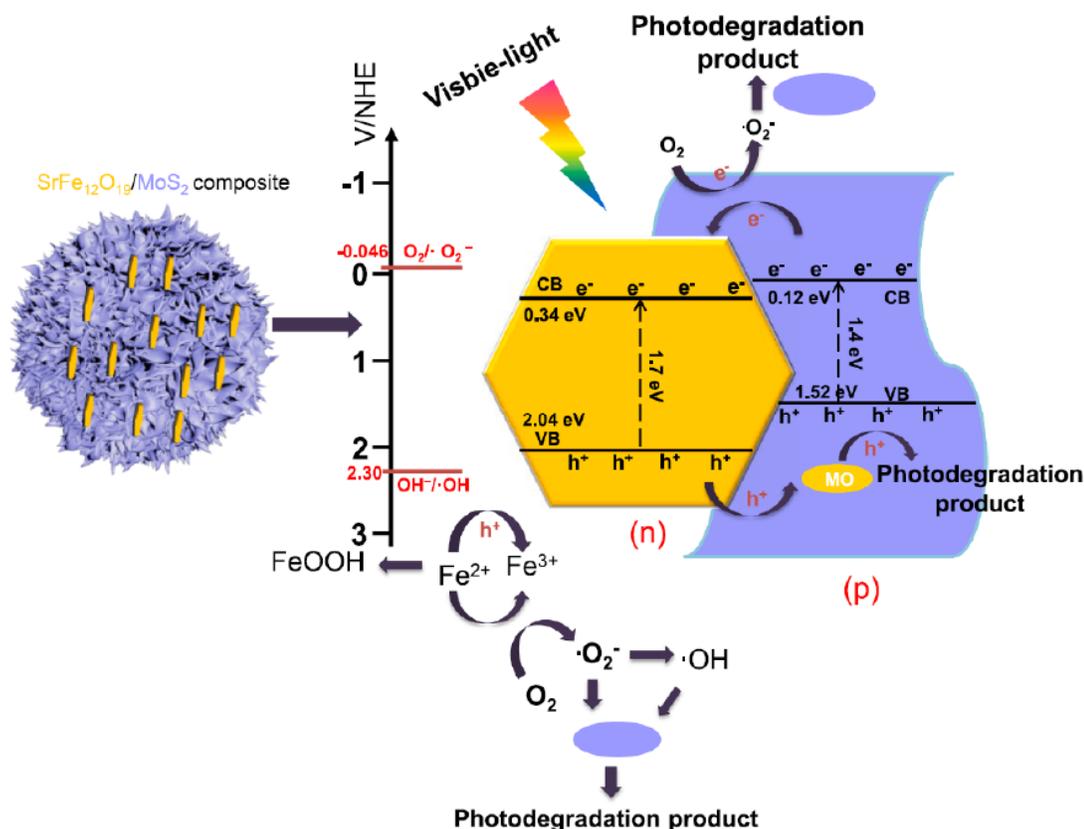
**Figure 7:** Photocatalysis mechanism of  $SrMn_xFe_{12-x}O_{19}$  photocatalysts. Adapted from ref. [88]. Copyright © 2022 Elsevier B.V.

photocatalysts. When Mn ion is not incorporated,  $\text{SrFe}_{12}\text{O}_{19}$  exhibits high charge carrier recombination rate, which makes its photocatalytic activity very poor. When Mn ions were introduced into  $\text{SrFe}_{12}\text{O}_{19}$ , Mn ions occupied part of the position of Fe ions, so that the photocatalyst  $\text{SrMn}_x\text{Fe}_{12-x}\text{O}_{19}$  showed a lower optical band gap value than  $\text{SrFe}_{12}\text{O}_{19}$ , which enhanced the transmission ability between charge carriers. The photocatalytic activity of  $\text{SrMn}_x\text{Fe}_{12-x}\text{O}_{19}$  photocatalyst was significantly higher than that of  $\text{SrFe}_{12}\text{O}_{19}$ . The photocatalytic mechanism of  $\text{MFe}_{12}\text{O}_{19}$  photocatalyst doped with metal ions is similar to that of single-phase  $\text{MFe}_{12}\text{O}_{19}$  photocatalyst except that the optical band gap value is reduced [89, 112, 113].

#### 4.3. Photocatalytic Mechanism of $\text{MFe}_{12}\text{O}_{19}$ Based Composite Photocatalysts

For the  $\text{MFe}_{12}\text{O}_{19}$ -based composite semiconductor photocatalysts, there are mainly three ways: One is the precious metal particles dotted on  $\text{MFe}_{12}\text{O}_{19}$  photocatalysts; The other is the combination of other semiconductor materials and  $\text{MFe}_{12}\text{O}_{19}$  photocatalysts; The other is the construction of multi-heterojunction  $\text{MFe}_{12}\text{O}_{19}$  composite photocatalysts, which can effectively improve the transfer and separation of

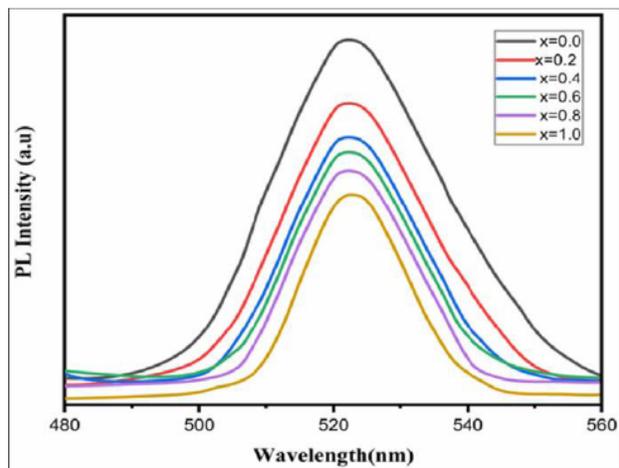
charge carriers between semiconductor interfaces. [64, 84, 98] In fact, these construction strategies are designed based on the theory of band arrangement. The type I band arrangement is conducive to the recombination of charge carriers, the type II band arrangement is conducive to the transfer and separation of charge carriers, and the ultrafine particles such as precious metal ions and carbon quantum dots act as the carriers of charge carrier transport in the process of photocatalyst degradation of pollutants. Figure 8 shows the photocatalysis mechanism of  $\text{MoS}_2/\text{SrFe}_{12}\text{O}_{19}$  heterojunction photocatalysts. [64] A type II band arrangement is formed between  $\text{MoS}_2$  and  $\text{SrFe}_{12}\text{O}_{19}$ , which effectively promotes the transfer and migration of electrons and holes at the interface between  $\text{MoS}_2$  and  $\text{SrFe}_{12}\text{O}_{19}$ , thus improving the photocatalytic activity of  $\text{SrFe}_{12}\text{O}_{19}$ . Meanwhile, the conversion between  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  also greatly improves the transfer and separation of charge carriers, promotes the formation of superoxide free radicals, and thus accelerates the degradation of pollutants. [64, 92] In particular, the formation of p-n junction between  $\text{MFe}_{12}\text{O}_{19}$  and another semiconductor helps to promote the photocatalytic activity of  $\text{MFe}_{12}\text{O}_{19}$  semiconductor photocatalysts. [81] At the same time,



**Figure 8:** Photocatalysis mechanism of  $\text{MoS}_2/\text{SrFe}_{12}\text{O}_{19}$  heterojunction photocatalysts. Adapted from ref. [64]. Copyright © 2021 Elsevier B.V.

the photocatalytic activity of  $MFe_{12}O_{19}$  photocatalysts can also be enhanced by placing  $MFe_{12}O_{19}$  photocatalysts into a metal-organic framework to form double Z-scheme heterojunction materials [73]. In addition to ion doping of  $MFe_{12}O_{19}$ , the researchers introduced a second phase of the semiconductor material for coupling, and also obtained a composite photocatalyst with high photocatalytic activity [74].

## 5. THE MECHANISM OF INTRINSIC CORRELATION BETWEEN PHOTOLUMINESCENCE AND PHOTOCATALYSIS



**Figure 9:** Emission spectra of  $BaCr_xFe_{12-x}O_{19}$  nanoparticles. Adapted from ref. [33]. Copyright © 2022 The Author(s). Published by Elsevier B.V. on behalf of King Saud University.

Generally, the high photocatalytic activity of semiconductor materials is due to the transfer and separation of charge carriers resulting in the formation of a large number of free radicals in the reaction solution. These free radicals interact with pollutants to degrade the pollutants. The high photoluminescence properties of semiconductor materials are mainly due to the recombination of charge carriers, which causes the excess energy in the recombination process to be emitted in the form of photons, thus showing the photoluminescence properties. The photoluminescent properties of  $MFe_{12}O_{19}$  are strongly dependent on the preparation method. A sol-gel autocombustion method has been used to synthesize  $SrFe_{12}O_{19}$  nanomaterials, which exhibit a distinct emission peak at 350 nm under excitation wavelength at 270 nm. [114]  $BaFe_{12}O_{19}$  synthesized by the same method showed a distinct emission peak at 605 nm. [115, 116] It can be seen that the photoluminescence properties of  $MFe_{12}O_{19}$  are obviously different with the same preparation method but different M ions. To gain an insight into the internal correlation between photoluminescence and photocatalysis, Bibi *et al.* [33] synthesized a Cr-doped

$BaFe_{12}O_{19}$  by a facile micro-emulsion route. Figure 9 shows the emission spectra of  $BaCr_xFe_{12-x}O_{19}$  nanoparticles. With the increase of x content, the intensity of emission peak of  $BaCr_xFe_{12-x}O_{19}$  nanoparticles decreased. The photocatalytic activity of  $BaCr_xFe_{12-x}O_{19}$  nanoparticles increased with the increase of x value. It can be seen that the photocatalytic activity of  $MFe_{12}O_{19}$  is inversely proportional to the photoluminescence properties. At the same time, a similar phenomenon has been observed in Gd doped barium hexaferrite. [117, 118] Similar phenomena have been observed in other metal oxides and composites. [119-123]

## 6. CONCLUSIONS AND OUTLOOKS

$MFe_{12}O_{19}$ -based photocatalysts have high magnetic properties, which makes its application in the field of photocatalysis has been unprecedented development. The recycling of  $MFe_{12}O_{19}$ -based photocatalysts by magnetic field can reduce the secondary pollution of photocatalyst to water. The photocatalytic activity of  $MFe_{12}O_{19}$ -based photocatalyst shows high synthesis method dependence, M ion dependence, dopant ion dependence and heterojunction dependence. The photocatalytic mechanism of  $MFe_{12}O_{19}$ -based photocatalyst is subject to the band arrangement theory like other photocatalysts. Simultaneously, due to the presence of Fe ions, part of the photocatalytic mechanism also follows the Z-scheme band arrangement theory. With the increase of photocatalytic activity, the fluorescence emission intensity of  $MFe_{12}O_{19}$  decreased. Based on the current research trends,  $MFe_{12}O_{19}$  photocatalyst can be developed in the following directions:

1. With the development of big data and intelligent artificial intelligence, it is of great research significance to simulate and predict the photocatalytic activity of  $MFe_{12}O_{19}$  based on intelligent optimization algorithm to guide the experiment. This development trend is an effective way to save the cost of time, resources and manpower, and is conducive to making new breakthroughs and achievements. The performance prediction based on intelligence will be a mainstream direction in the synthesis of  $MFe_{12}O_{19}$  photocatalyst in the future.
2. High entropy alloys have been demonstrated to have high photocatalytic activity, and coupling  $MFe_{12}O_{19}$  with high entropy alloys may demonstrate higher photocatalytic activity for pollutant degradation. The photocatalytic mechanism of the coupling of the two is also a

hot topic. Since the photocatalytic mechanism of high entropy alloy itself is immature, the photocatalytic mechanism of high entropy alloy coupled with  $\text{MFe}_{12}\text{O}_{19}$  photocatalyst is more complicated, but it is also a very worthy research topic.

3. The coupling between  $\text{MFe}_{12}\text{O}_{19}$  photocatalyst and other metal-organic framework materials is also worth studying. Although a few literatures have reported the application of  $\text{MFe}_{12}\text{O}_{19}$  coupled metal-organic framework materials in the field of photocatalysis, there are many kinds of metal-organic framework materials, and the photocatalytic activity after coupling with  $\text{MFe}_{12}\text{O}_{19}$  photocatalysts is difficult to predict intuitively, so it is also a fruitful research topic.
4. When  $\text{MFe}_{12}\text{O}_{19}$  is coupled with other types of luminescent materials, the mechanism of the intrinsic correlation between photocatalytic and luminescent properties may be different from the existing mechanism, which is also worthy of investigation. Meanwhile, combined with the study of upconversion luminescence, the photocatalytic mechanism and photoluminescence mechanism of  $\text{MFe}_{12}\text{O}_{19}$  photocatalyst coupled with upconversion luminescence materials become more complicated and unclear.
5.  $\text{MFe}_{12}\text{O}_{19}$ -based photocatalyst has not been reported in any literature on photocatalytic hydrogen production from water and photocatalytic oxidation of heavy metal ions. Therefore, it is of great significance to design  $\text{MFe}_{12}\text{O}_{19}$ -based magnetic separation photocatalysts and study their applications in the decomposition of water to produce hydrogen and the oxidation of heavy metal ions. The calculation of the electronic state density of  $\text{MFe}_{12}\text{O}_{19}$ -based photocatalyst based on first principles will be helpful to the research and development of new  $\text{MFe}_{12}\text{O}_{19}$ -based photocatalysts.

## COMPETING INTERESTS

The authors declare that they have no competing interests.

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