



Preparation and Photocatalytic Properties of $\text{Sr}_{2-x}\text{A}_x\text{FeMoO}_6$ ($X = 0, 0.1$; $A = \text{Li, Na, K}$)

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In this paper, the sol-gel method is used to synthesize a series of double perovskite oxides $\text{Sr}_2\text{FeMoO}_6$ and $\text{Sr}_{1.9}\text{A}_{0.1}\text{FeMoO}_6$ ($A = \text{Li, Na, K}$). The crystal structure was investigated by X-ray powder diffraction. The results show that all the as-synthesized samples have tetragonal crystal structure, small amount of substitution has little effect to the structure of $\text{Sr}_2\text{FeMoO}_6$, and they can keep double perovskite structure. Their photocatalytic activities were evaluated by degradation of dye acid black 10 B. The effects of the dosage of photocatalyst, irradiation time, irradiation source, initial concentration of dye solutions and alkali metal ions doping on the photocatalytic activity of samples were investigated. The results show that all the samples present high photocatalytic activities. In the dye concentration range of 20-150 mg/L, the decolorizing rate of acid black 10 B can reach above 95 % when the dosage of photocatalyst $\text{Sr}_2\text{FeMoO}_6$ is 100 mg under UV irradiation for 40 min. Moreover, the photocatalytic activity of Li-doped sample is lower than that of the un-doped sample, but the photocatalytic activity of the Na- or K-doped samples are much better than the un-doped sample and the decolorizing rate is nearly 100 %.

Keywords: $\text{Sr}_2\text{FeMoO}_6$, Alkali metal doping, Sol-gel method, Photocatalytic performance, Decolorizing rate.

INTRODUCTION

Perovskite oxides ABO_3 have attracted a great interest, mainly due to their potential applications in extensive fields, such as recording media, field sensors or heads for hard drives^{1,2}. In recent years, many researchers focused on the photocatalytic degradation of ABO_3 with semiconductor properties for wastewater treatment. For example, Fu *et al.*³ synthesized the perovskite-type oxide $\text{LaFe}_{1-x}\text{Cu}_x\text{O}_3$ and found that trace doped Cu could improve photocatalytic activities. Jianlin *et al.*⁴ synthesized the perovskite ReFeO_3 ($\text{Re}: \text{La, Sm, Eu, Gd}$) photocatalyst and investigated the photocatalytic degradation activity for Rhodamine B aqueous solution under visible light irradiation.

At present, double perovskite-type oxides $\text{A}_2\text{B}'\text{B}''\text{O}_6$ have attracted great interests because A, B' and B'' atoms can be adjusted within a large range, which makes $\text{A}_2\text{B}'\text{B}''\text{O}_6$ show various special performances^{5,6}. Some double perovskite-type oxides exhibits semiconductor behaviour, so this type of materials, as a candidate for photocatalysts in degrading the wastewater, should have good potential application. Recently, Hatakeyama *et al.*⁷ succeeded in synthesizing Ba_2RBiO_6 ($\text{R} = \text{La, Ce, Nd, Sm, Eu, Gd}$ and Dy) with a double perovskite structure and found they showed high photocatalytic activities for degradation of methylene blue solution and gaseous 2-propanol (IPA) under visible light irradiation.

$\text{Sr}_2\text{FeMoO}_6$ (SFMO) is one kind of double perovskite-type oxides and has attracted considerably scientific and technological interest in recent years owing to its giant magneto-resistance under low field at the room-temperature^{8,9}. Our previous study shows that $\text{Sr}_2\text{FeMoO}_6$ also exhibits typical semiconductor behaviour^{10,11}, so it may be a very promising photocatalyst in degrading wastewater.

In this paper, double perovskite-type oxides $\text{Sr}_2\text{FeMoO}_6$ and a series of alkali metal ions doped $\text{Sr}_{1.9}\text{A}_{0.1}\text{FeMoO}_6$ ($A = \text{Li, Na, K}$) were synthesized by sol-gel method with active carbon as reducing agent and their photocatalytic degradation activity for dye acid black 10 B were investigated.

EXPERIMENTAL

Synthesis of samples: Polycrystalline $\text{Sr}_2\text{FeMoO}_6$ and Li, Na or K-doped samples were prepared by sol-gel method. Stoichiometric powders of $\text{Sr}(\text{NO}_3)_2$, $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$, LiNO_3 (NaNO_3 or KNO_3) were mixed with citric acid and then dissolved with distilled water. The pH of the solution was adjusted to 3 by aqueous ammonia in concentration of 5 mol/L under consecutively stirring. A slight green gel was formed after several hours under the condition of water bath at 60 °C. Then the gel was put into oven and dried at 90 °C. Subsequently, the dry gel was pyrolyzed at 180 °C. The dry gel was frothed, fumed and finally formed a dry black

sponge (which was called precursor). Then the precursor was pre-sintered for 5 h at 600 °C. Finally, the powder was mixed with appropriate active carbon powder and then sintered for 3 h at 1000 °C in the reducing atmosphere provided by active carbon particles to obtain the final product.

Degradation reaction: The degradation reaction was carried out in 250 mL beaker containing 50 mL dye acid black 10 B solution and a certain amount of sample. The suspension was stirred for some time and then filtered. With distilled water as reference solution, the absorbance of the filtrate was measured at the maximum absorption ($\lambda_{\max} = 619$ nm) of the dye to calculate the decolorizing rate (De %).

$$\text{Decolorizing rate (\%)} = \left(1 - \frac{A}{A_0}\right) \times 100$$

where A shows final absorbance and A_0 shows initial absorbance of dye solution. The decolorization rate of dye was used to characterize the photocatalytic activity of sample.

With different dosage of the sample, the degradation reaction time and light sources, the influence on decolorization rate of the acid black 10 B dye was investigated in order to determine an appropriate condition of wastewater treatment.

Characterization: The crystal structure and the phase purity of the samples were investigated by X-ray powder diffraction (XRD) with $\text{CuK}\alpha$ radiation (30 kV \times 20 mA) on a Y2000 diffractometer at room temperature. XRD was performed on powdered samples over the 2θ range of 15 to 75°. A step scan mode was employed with a step width of $2\theta = 0.06^\circ$ and a sampling time of 1s. Absorption curve and absorbance of dye solution were measured by a TU-1810 UV-visible spectrophotometer.

RESULTS AND DISCUSSION

Analysis of phase structure: Fig. 1 shows the XRD patterns of as-synthesized samples $\text{Sr}_2\text{FeMoO}_6$ and $\text{Sr}_{1.9}\text{A}_{0.1}\text{FeMoO}_6$ ($A = \text{Li, Na, K}$). It can be seen that all the reflections of $\text{Sr}_2\text{FeMoO}_6$ can be indexed in a tetragonal system with space group I4/mmm by the Jade5 program and unit cell parameter is $a = 5.580 \text{ \AA}$, $c = 7.882 \text{ \AA}$. The appearance of the superstructure reflection peak (Fig. 1) of (101) indicates part of Fe^{3+} and Mo^{5+} ions orderly occupy on B and B' sites¹², respectively.

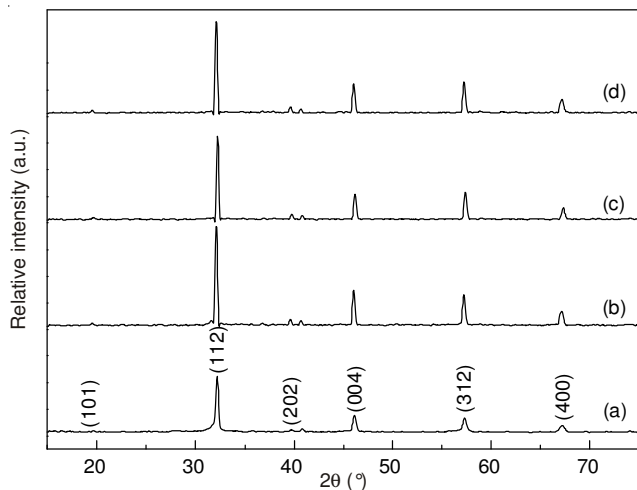


Fig. 1. XRD patterns of $\text{Sr}_{2-x}\text{A}_x\text{FeMoO}_6$ ($x = 0, 0.1$) (a) $x = 0$; (b) $x = 0.1$, $A = \text{Li}$; (c) $x = 0.1$, $A = \text{Na}$; (d) $x = 0.1$, $A = \text{K}$

From Fig. 1, it also can be found the intensity of diffraction peaks for doped compounds $\text{Sr}_{1.9}\text{A}_{0.1}\text{FeMoO}_6$ ($A = \text{Li, Na, K}$) is higher than that of the undoped $\text{Sr}_2\text{FeMoO}_6$, but the position of diffraction peaks does not change obviously. It indicates that appropriate doping of alkali metal ions has little effect on the crystal structure of samples. These samples still have tetragonal crystal structure with space group I4/mmm. In addition, the intensity of the (101) superstructure reflection around 19° of the doped compounds increases compared with the parent compound $\text{Sr}_2\text{FeMoO}_6$, indicating that the ordering degree of Fe and Mo cations is increased by the doping with univalent alkali metal ions.

Photocatalytic activity of $\text{Sr}_2\text{FeMoO}_6$ for dye acid black 10 B solution

Effect of the dosage of $\text{Sr}_2\text{FeMoO}_6$ on decolorizing rate:

Several groups of 50 mL dye acid black 10 B solution with the initial concentration 20 mg/L were taken. Degradation test was carried out under ultraviolet irradiation for the same time 40 min. The effect of dosage of $\text{Sr}_2\text{FeMoO}_6$ on decolorizing rate is shown in Fig. 2. It can be seen that the dosage of $\text{Sr}_2\text{FeMoO}_6$ has great effect on the decolorizing rate of acid black 10 B solution. The decolorizing rate increases with the dosage of $\text{Sr}_2\text{FeMoO}_6$ and the decolorizing rate reaches up to about 97% when the dosage increases to 100 mg. After that, the decolorizing rate is basically the same. Thus, the appropriate dosage of $\text{Sr}_2\text{FeMoO}_6$ is 100 mg for 50 mL dye solution.

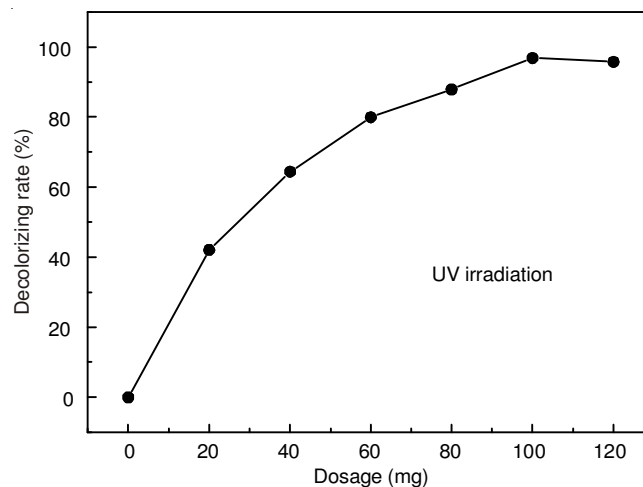


Fig. 2. Relationship between dosage of $\text{Sr}_2\text{FeMoO}_6$ and decolorization rate

Effect of light sources and reaction time on decolorizing rate:

Degradation test was carried out under different light sources, ultraviolet lamp and daylight lamp condition, with the same dosage 100 mg of $\text{Sr}_2\text{FeMoO}_6$. The effect of irradiation time under different light sources on the decolorizing rate is shown in Fig. 3. It indicates that the trend of decolorizing rate is basically consistent under two different light sources. The reaction rate is all fast in the first 20 min and the decolorizing rate can reach above 80%. After 20 min, decolorization rate increases slowly. But, the decolorization effect under UV irradiation is better than that under daylight lamp irradiation at the same time. The decolorizing rate is close to 100% when the irradiation time is 40 min under UV irradiation. So the

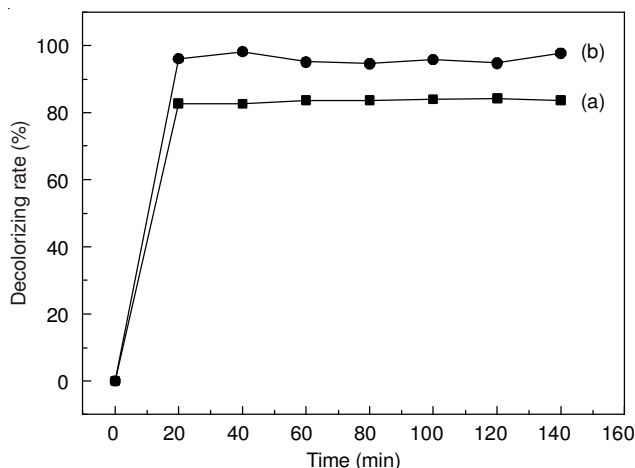


Fig. 3. Relationship between irradiation time and decolorization rate (a) under daylight lamp irradiation, (b) under UV-light irradiation

condition of irradiation time of 40 min and UV irradiation is the better choice.

Fig. 4 shows that the UV-visible spectra of initial acid black 10 B solution (constitutional formula is shown in the inset of Fig. 4) and the filtrates after decolorizing for 40 min under UV irradiation. It can be seen that there are two obvious absorption peaks in curve (a). Based on spectrum theory, the strong absorption peak at 619 nm in visible region is caused by the conjugated system of azo bond; the absorption peak at 322 nm in ultraviolet region is due to naphthalene and benzene rings connected with the azo bond. It can be seen from curve (b) that characteristic absorption peaks of the dye solution have disappeared completely after the degrading reaction.

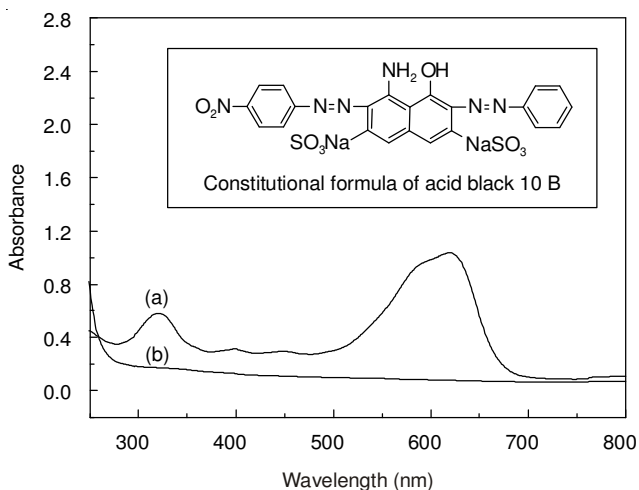


Fig. 4. UV-visible spectra of (a) the initial acid black 10 B, (b) the filtrate after degrading for 40 min (the inset is constitutional formula of acid black 10 B)

Effect of initial dye concentration on decolorizing rate:

With the appropriate conditions (the dosage of $\text{Sr}_2\text{FeMoO}_6$ is 100 mg under UV irradiation, the reaction time is 40 min), the effect of initial dye concentration on the decolorizing rate were investigated and the result is shown in Fig. 5. It can be seen that the decolorizing rate decreases gradually with the increase of the initial dye concentration. But, in the concentration range of 20-150 mg/L, the decolorizing rate is all above 95 %. It

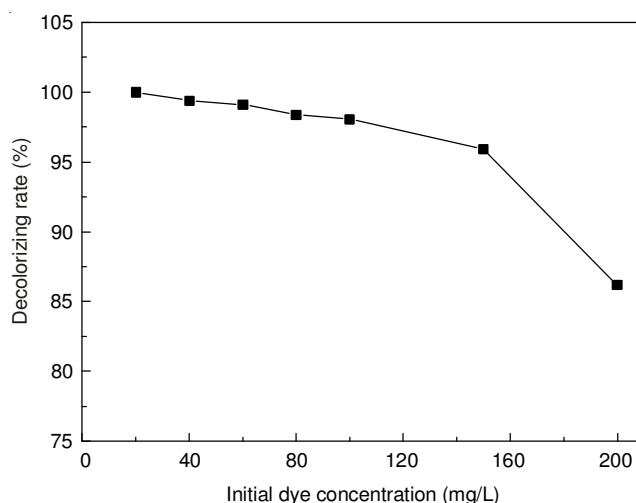


Fig. 5. Dependence of the decolorization rate on initial concentration of acid black 10 B

indicates that $\text{Sr}_2\text{FeMoO}_6$ has high degradation activity for dye acid black 10 B in a wide concentration range. When the initial dye concentration increases to 200 mg/L, the decolorizing rate decreases to 86.2 %. So, the more dosage of $\text{Sr}_2\text{FeMoO}_6$ is needed.

Effect of doping Li^+ , Na^+ or K^+ on photocatalytic activity of $\text{Sr}_2\text{FeMoO}_6$: In order to compare the photocatalytic activity of doped samples $\text{Sr}_{1.9}\text{A}_{0.1}\text{FeMoO}_6$ ($A = \text{Li, Na, K}$) with undoped sample more distinctly, the lower dosage (about 60 mg) was chosen. After degrading for 20 and 40 min under UV irradiation, the decolorizing rate of dye acid black 10 B (initial concentration is 20 mg/L) under different photocatalyst $\text{Sr}_{2-x}\text{A}_x\text{FeMoO}_6$ ($x = 0, 0.1$) were investigated and the results are shown in Table-1. From Table-1, it can be seen that the photocatalytic activity of Li-doped sample is slightly lower than that of the un-doped sample, but the photocatalytic activity of Na- or K-doped samples are much better than the un-doped sample and the decolorizing rate is nearly 100 %.

TABLE-1 DECOLORIZING RATE OF DYE ACID BLACK 10B UNDER DIFFERENT PHOTOCATALYST $\text{Sr}_{2-x}\text{A}_x\text{FeMoO}_6$ ($x = 0, 0.1$)		
Samples	Decomposition (%)	
	20 min	40 min
$\text{Sr}_2\text{FeMoO}_6$	79.9	87.4
$\text{Sr}_{1.9}\text{Li}_{0.1}\text{FeMoO}_6$	77.7	83.6
$\text{Sr}_{1.9}\text{Na}_{0.1}\text{FeMoO}_6$	96.4	97.5
$\text{Sr}_{1.9}\text{K}_{0.1}\text{FeMoO}_6$	95.9	97.4

Decoloring mechanism: The double perovskite $\text{Sr}_2\text{FeMoO}_{6-\delta}$ exhibits semiconducting behaviour¹¹, the valence and conduction bands are known to consist of O 2p, Fe 3d and Mo 4d states respectively. Due to the narrow gap band, the electrons in the valence band can be excited and hopped to the conduction band under the external light irradiation, generating photoinduced electrons in the conduction band and photoinduced holes (h^+) in the valence band, *i.e.*, forming the electron-hole pairs. Then they are separated and transferred to the surface of particles rapidly by electric field. As the photoinduced holes are positively charged, easily capturing

the electrons with the suited energy and recovering, they show strong oxidative property. Therefore, these photoinduced holes can oxidize the OH⁻ and H₂O adsorbed on the surface of Sr₂FeMoO_{6-δ} particles to highly active hydroxyl radicals (•OH). •OH is a kind of strong oxidants, it can oxidize the adjacent dye molecules and the •OH can also spread to the solution and oxidize other dye molecules, making them degrade into inorganic small molecules, so as to achieve the purpose of decolorization. In addition, Sr₂FeMoO₆ was prepared in reducing atmosphere, so there are some oxygen vacancies. These oxygen vacancies can also play a role of the trap to capture the photoinduced electrons¹³, thus can inhibit the recombination of photoinduced electrons and holes effectively. Therefore, as-synthesized Sr₂FeMoO₆ shows excellent photocatalytic degradation activity.

When the alkali metal ions Na⁺ or K⁺ partially replace Sr²⁺ in Sr₂FeMoO₆, the appropriate defect energy level is formed between the valence and conduction band. Thus, the band gap decreases, the number of electron-hole pairs increases, which make the hydroxyl radical •OH concentration and decolorizing rate increase. As for Li-doped sample, due to the larger radius difference between Li⁺ and Sr²⁺, the doping of Li⁺ causes the lattice distortion, so the transition of electrons is hindered and decolorizing rate decreases.

Conclusion

A series of double perovskite oxide Sr₂FeMoO₆ and Sr_{1.9}A_{0.1}FeMoO₆ (A = Li, Na, K) were prepared successfully by sol-gel method. This method has the advantages of homogeneous components, small particle size, easy operation, etc. All the samples show excellent photocatalytic activity for acid black 10 B. In the dye concentration range of 20-150 mg/L, the decolorizing rate of acid black 10 B can reach above 95 % when the dosage of sample Sr₂FeMoO₆ is 100 mg under UV irradiation only for 40 min. This indicates that the photocatalytic reaction is efficient and fast. The doping of alkali metal ions Li⁺, Na⁺ or K⁺ has a certain influence on photocatalytic activity of Sr₂FeMoO₆. Doping Na⁺ or K⁺ can improve the photocatalytic activity of Sr₂FeMoO₆ effectively. The photocatalytic activity of Sr₂FeMoO₆ and Sr_{1.9}A_{0.1}FeMoO₆ (A = Li,

Na, K) is due to the semiconducting properties. Under UV irradiation, photoinduced holes (h⁺) oxidize H₂O and OH⁻ adsorbed on the surface of sample particles into high activity hydroxyl radicals •OH. Then the •OH oxidize the dye molecules so as to achieve the purpose of decolorization. Partial replacements of Sr²⁺ in Sr₂FeMoO₆ with the alkali metal ions Na⁺ or K⁺ result in the decrease of band gap. Therefore, the number of photoinduced holes (h⁺) increases, which make the hydroxyl radical •OH concentration and decolorizing rate increase.

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