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Performance Promotion of Ag₂O Photocatalyst by Particle^vSize^{Le Online} DOI: 10.1039/DONJ00255K and Crystal Surface Regulation

Jian He, Hongyan Fu, Pan Wu, Zehao Lin, Ya Zeng, Wei Jiang*

The insufficient photocatalytic performance of Ag₂O makes it hard to be applied to actual industrial printing and dyeing waste water treatment system, which contains a variety of organic pollutants. Therefore, it is urgent to promote the photocatalytic performance of Ag₂O. In this study, the main factors affecting the properties of Ag₂O photocatalysts were screened out by single factor experiments. Then, the optimum conditions for the preparation of Ag₂O were simulated by response surface design. The prepared Ag₂O showed good photodegradation performance to methyl orange and phenol, but the degradation of rhodamine B was significantly delayed. After that, the pyridine was introducZZed to adjust the crystal plane structure of Ag₂O. The results showed that the photocatalytic oxidation capacity of Ag₂O was greatly improved. Ninety percent of rhodamine was removed within 25 minutes. Moreover, the mechanism of controlling photocatalytic performance has also been studied through fine characterizations.

1. Introduction

Since the discovery of photocatalytic splitting of water on a TiO₂ electrode in 1972¹, photocatalytic technology has been attracting massive research interest in the field of energy and environment owning to its excellent performance in water splitting or pollutants decomposition, low energy consumption, non-toxic harmless, no secondary pollution^{2, 3}. However, the photocatalytic material represented by TiO₂ has a wide band gap and can only utilize 4% ~ 6% of the ultraviolet light in the sunlight⁴, which results in low quantum efficiency and narrow application range. To effectively utilize the visible light which accounts for 43% of the total sunlight, it is important to find an appropriate photocatalyst.

Silver(I) oxide (Ag₂O), a brown powder with a narrow band gap of 1.3 eV, has been widely used as photosensitive materials, optical memory materials, and photoelectric conversion devices ⁵⁻⁷. Recently, it has been studied as an excellent photocatalyst because of its low band-gap energy^{8, 9}. Under the visible light, the methyl orange(MO) in the solution can be degraded completely in about 120 $s^{10},$ and about 70% of methylene blue(MB) can be oxidatively decomposed within 60 minutes¹¹. Compared with traditional photocatalytic materials, these reports show that Ag₂O has high visible light utilization efficiency and broad application prospects. However, the excellent degradation efficiency of Ag₂O is not working for all types of organic pollutants. For instance, it can degrade MO in 2 minutes, but it has to spend two hours to degrade rhodamine B (RhB)¹². In fact, the components of actual industrial printing and dyeing waste water system are complex and contain a variety of organic pollutants. Therefore, it is urgent to improve the photocatalytic performance of Ag_2O and improve the degradation ability to refractory organic materials.

The strategy to optimize photocatalytic performance involves constructing heterojunction¹³⁻¹⁵, doping noble metal^{16, 17}, and adjusting the crystal face^{18, 19}. Among these methods, constructing heterojunction and doping noble metal are often used to control the width of the forbidden band and reduce the

compound rate of the electron and cavity²⁰⁻²². However, the band gap of Ag₂O is 1.3 ev, which can make good use of the ultraviolet-visible or even near-infrared region. The light response range of Ag₂O is wide enough for photocatalytic degradation of organic pollutants, and to improve the photocatalytic efficiency of Ag₂O by reducing the gap width is not significant. Thus, improving the total surface area and increasing the ratio of high-efficiency crystal face of Ag₂O is a better approach to improve the performance. Generally, the total surface area can be increased by controlling the particle size and increasing the grain boundary. Crystal size is closely related to nucleation and crystal growth kinetics, which is determined by the supersaturated degree and the crystallization condition, such as reactant concentration and temperature. The grain boundary can be increased by adding H_3BO_3 to form tiny grains. Then, the crystal face can be optimized by adding the crystal structure regulator to control the crystallization process^{23, 24}.

In this research, a single factor test was used to confirm the impact factors and identify the factors that need to be optimized. Then, we obtained the best preparation condition based on the response surface method. AgNO₃ and NaOH are used as reactants and H_3BO_3 as a crystallization additive. The photocatalytic performance of Ag₂O was optimized by controlling the amount of pyridine. The photocatalytic activity of photocatalyst was investigated with RhB, MO, and phenol. The kinetics and mechanism of photocatalytic degradation were also analyzed.

2. Experimental

2.1 Preparation of Ag_2O

All analytical grade reagents, including $AgNO_3$, $H3BO_3$, NaOH, Pyridine, MO, RhB, Phenol, were purchased from Cheng Du Kelong Chemical Reagent Co. Ltd, and used directly without further purification. Ag_2O crystals were prepared by the ionexchange method. In the single-factor and multi-factor test, an aqueous solution containing a certain amount of H_3BO_3 and NaOH is added to the $AgNO_3$ solution. The mixture was stirred for 2.5 h. Then, the solution was filtrated and washed with deionized water. Finally, the obtained dark brown powders

^{*} Low-carbon Technology and Chemical Reaction Engineering Laboratory, School of Chemical Engineering, Sichuan University, Chengdu, 610065, China.

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were dried at 60 °C in ambient air for more than 12 h. All the above operations were carried out in the darkness.

To optimize the crystal morphology, a mixed solution containing 6 mmol of AgNO₃ aqueous solution and a certain amount of pyridine was prepared, and then a mixed solution of NaOH and H₃BO₃ was added into the AgNO₃ aqueous solution. The other experimental procedures are the same as the above experiment.

2.2 Photocatalytic activity experiment

The photocatalytic activities were evaluated by the photodegradation of MO, RhB, and phenol under the irradiation of visible light, respectively. Simulate visible light irradiation was provided by a 500 W xenon lamp (OCRS-IV) with a 380 nm cut off filter. Before the photocatalytic degradation experiment, the self-degradation property of organic pollutants was tested. The result in Fig. 1 shows that all the organic dyes in the water are hard to decompose under irradiation of visible light without photocatalyst.



Then, 0.03 g of Ag₂O powder was suspended in the solution with different organic dyes in the photo-degradation experiment. The solution was magnetically stirred during the reaction. Before irradiation, the suspension was stirred in the darkness for 30 min to establish an adsorption-desorption equilibrium of dyes on the surfaces of Ag₂O. After illumination, suspensions were sampled from the same tube at a fixed time interval. Then the sample powders were separated by centrifuging, and the clarified dye solutions were analyzed with a TU-1901 UV–Vis spectrophotometer to determine the concentration of the organic dyes by monitoring the height of the maximum of the absorbance peak in ultraviolet-visible spectra of the solution.

2.3. Characterization

49 The crystal structures of as-prepared Ag₂O were determined by 50 glancing angle X-ray diffraction (DX-2007 SSC) with a Cu K α 40 k 51 V/30 m A X-ray source. The surface morphology was observed 52 with field-emission SEM (JSM-7500F, JEOL). The specific surface 53 area of the samples was tested by the SSA-3500 automatic 54 surface area analyser. The concentrations of MO, RhB, and 55 phenol in the degradation process were analyzed by a TU-1901 56 UV-Vis spectrophotometer at a wavelength of 464nm, 553nm, 57 and 270 nm. Fourier transform infrared spectra (FT-IR) were 58 recorded on a Spectrum Two Li10014 from 4000 to 500 cm⁻¹ 59 with a resolution at 0.5 cm⁻¹.

3. Results and Discussion

3.1 Single fact experiment

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In the preparation of Ag_2O , the formation of Ag_2O precipitation is a crystallization process. The crystal particle size and specific surface area are usually affected by nucleation and growth rate. The rate of nucleation is controlled by temperature and reactant concentration, and factors related to the growth rate are main the solution viscosity and temperature. The crystal structure and surface morphology can directly affect photocatalyst performance. Therefore, to optimize Ag_2O preparation conditions and improve the photocatalytic activity is necessary. In this section, the effect of reactants concentration, H_3BO_3 concentration, and temperature on the photocatalytic activity of Ag_2O is investigated by single-factor experiments. At this stage, the photocatalytic activity of the obtained Ag_2O was evaluated by degrading 10 mL of 16 mg/L MO solution under the visible light.

First of all, the effect of reactants concentration on photocatalytic activity of Ag₂O was discussed. From Fig. 2a and Fig. 2b, the concentration of AgNO₃ has a little effect on Ag₂O photocatalytic performance, while the photocatalytic activity of Ag₂O can be significantly changed by the concentration of NaOH. When the concentration of NaOH increased from 0.05mol/L to 0.3 mol/L, the activity of photocatalytic degradation of MO gradually increased. While the concentration of NaOH was further increased, and the photocatalytic activity decreased. This is because a low concentration of the reactant leads to a low supersaturation and form a large particle Ag₂O, which possesses a small surface area and a weak photocatalytic activity. However, when the concentration gets higher, the crystal growth rate is far less than the nucleation rate. A large number of crystal nucleus are tending to appear in the reaction system instantly. This makes the crystal form a small particle. Small particles usually have high surface free energy and are easily form aggregates. Hence, we get the optimized reactant concentration is 0.3mol/L.

 H_3BO_3 works as crystallizing auxiliaries, nucleating stabilizer, and it can improve the quantum efficiency of Ag_2O precipitation. As is shown in Fig. 2c, changing the concentration of H_3BO_3 has a great influence on the photocatalytic activity of Ag_2O . With the increase of H_3BO_3 concentration, the Ag_2O photocatalytic activity was gradually enhanced. When the concentration of H_3BO_3 reached 0.08 mol/L, the photocatalytic performance is the best.

Temperature is another important factor that can influence the nucleation rate and crystal growth rate. As is shown in Fig. 2e, when the temperature was raised from 10 $^\circ\!C$ to 50 $^\circ\!C$, the photocatalytic activity increased until the temperature reached 20 $^\circ\!C$. At low temperature (10 $^\circ\!C$), the migration and movement of ions or molecules were slow, and the rate of nucleation in solution was also relatively small. Hence, the obtained Ag_2O had a larger particle size. With the increase of temperature (20 $^\circ\!C$), both the rate of nucleation and crystal growth in solution was enhanced due to the improvement of reactants diffusive ability, which was an advantage in producing smaller particles. When the temperature continued to increase,

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the product diminishes and agglomeration also became serious. According to the experiment, the best reaction temperature is 20° C.

As a result, the single factor experiments showed that call the factors influence the catalytic activity of Ag2O in the probabilities process. Through the single factor experiments, we obtained the optimal reaction condition.



Fig. 2 Effect of different operating parameters on photocatalytic activity of Ag₂O: (a) concentration of AgNO₃; (b) concentration of NaOH; (c) concentration of H₃BO₃; (d) temperature

3.2 Multi-factor experiment

It can be seen from the single factor experiments that multiple factors may also interact with each other. Therefore, we must consider the interaction between various factors to determine the best technical conditions. The response surface analysis test of the tri-factor and tri-level was designed based on the response surface method Box-Behnken central composite design principle²². The reaction rate constant of the photodegradable MO was treated as the response value. The concentration of NaOH, H_3BO_3 , and temperature were the influencing factors. All the selected factors are listed in Table 1. Input the data range of each factor into the simulation software and then the software independently designed 17 different experimental schemes (Table 2). The rate constant K works as the response value, and the photocatalytic activity of Ag₂O produced by different experimental conditions were obtained through the photocatalytic activity test.

Table 1 Levels of parameters of different factors				
	factors	levels		
Influencing factors		-1	0	+1
H ₃ BO ₃ concentration	А	0.06	0.08	0.1
NaOH concentration	В	0.20	0.25	0.3
temperature	С	15	20	25

Table 2 Scheme and results of the response experiment					
	Factor 1	Factor 2	Factor 3	Response	
Number	A:H ₃ BO ₃ (mol/L)	B:NaOH(mol/L)	C:T(°C)	R1:K	
1	0.1	0.3	20	0.1206	
2	0.1	0.25	25	0.1399	
3	0.08	0.2	25	0.1447	
4	0.06	0.25	15	0.162	
5	0.08	0.25	20	0.1681	
6	0.06	0.3	20	0.1699	
7	0.08	0.3	15	0.1539	
8	0.06	0.25	20	0.1077	
9	0.08	0.25	20	0.1903	
10	0.08	0.2	15	0.1109	
11	0.1	0.25	15	0.1418	
12	0.08	0.3	25	0.1445	
13	0.06	0.2	20	0.1382	
14	0.08	0.25	20	0.1932	
15	0.08	0.25	20	0.1906	
16	0.1	0.2	20	0.1746	
17	0.08	0.25	20	0.1945	

Based on the relationship between the response value and different parameters, simulation software presents four fitting schemes, which are linear model, quadratic model, 2FI model, and third power model. Through the quadratic model, P =

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0.0317 < 0.05 effect is remarkable, loss of quasi P = 0.1076 > 0.05 was not significant, F = 4.40, multiple correlation number R2 = 0.8499, the fitting effect is superior to other models. So the model shows high reliability. According to the experimental results, the quadratic equation fitting model is obtained by regression fitting. The fitting equation is as follows R=-1.48417 + 10.16362A + 6.21575B + 0.048977C - 21.42500AB + 0.13100AC - 0.043200BC - 46.45625A² - 7.17300B² - 1.2363E-003C². In the formula, A stands for H₃BO₃ concentration, B stands for NaOH concentration, C stands for T, and R is the response value. The variance analysis of each factor is shown in Table 3.

Table 3 Analysis of variance

Source	Sum of	df	Mean Square	F Value	P Value
Model	0.011	9	4.752E-004	4.40	0.0317
А	1.013E-007	1	1.013E-007	3.741E-004	0.9851
В	5.253E-005	1	5.253E-005	0.19	0.6728
С	1.264E-004	1	1.264E-004	0.47	0.5163
AB	1.836E-003	1	1.836E-003	6.78	0.0352
AC	6.864E-004	1	6.864E-004	2.54	0.1553
BC	4.666E-004	1	4.666E-004	1.72	0.2306
A ²	1.454E-003	1	1.454E-003	5.37	0.0536
B ²	1.354E-003	1	1.354E-003	5.00	0.0604
C ²	4.022E-003	1	4.022E-003	14.86	0.0063
Residual	1.894E-003	7	2.706E-004		
Lack of Fit	1.419E-003	3	4.731E-004	3.98	0.1076
Pure Error	4.752E-004	4	1.188E-004		

The experimental conditions and results were analyzed by software. The optimized preparation conditions are as follows: 0.08 mol/L H_3BO_3 , 0.25 mol/L NaOH and 20 °C. The corresponding photocatalytic rate constant (K) is 0.1873.

To verify the optimal scheme, Ag_2O was prepared based on the optimized parameters, and the photocatalytic performance was tested by degrading the MO (Fig. 3). According to the tests, the actual reaction rate constant is 0.1835. The absolute deviation and relative deviation to the theoretical value are all less than 1%. Thus, the optimized parameters obtained from response surface are reliable.



3.3 The crystal face adjusting

Ag₂O was prepared by the above optimum conditions and used to degrade 8mg/L RhB, 50mg/L phenol respectively. As shown in Fig. 3, it takes 4 and 7 minutes for Ag₂O to degrade MO and phenol respectively, but less than 40% of RhB was removed within 10 minutes. Although the preparation conditions of the Ag₂O were optimized, it is still not effective in degrading RhB. To solve practical industrial problems, it is necessary to further improve the photocatalytic performance. Based on the experiment above, we try to add pyridine in the preparation process to sort out the high active crystal surface of Ag₂O and improve the photocatalytic oxidation performance of Ag₂O. The amount of pyridine added to the reactants is shown in Table 4.

Table 4 The reagents of the experiment					
No.	AgNO₃	NaOH	H ₃ BO ₃	Pyridine	Datia
	(mmol)	(mmol)	(mmol)	(mmol)	Ratio
1	6	6	2	0	3:3:1:0
2	6	6	2	1	3:3:1:0.5
3	6	6	2	2	3:3:1:1
4	6	6	2	6	3:3:1:3

3.3.1 photocatalytic activity and kinetic analysis

The photocatalytic activity of Ag_2O was tested by degrading 10 mL RhB solution with a concentration at 8 mg/L (Fig. 4a). Compared to the samples obtained without pyridine (the ratio of reactants was 3: 3: 1: 0), a small amount of pyridine added to the reactants can significantly increase the photocatalytic performance of Ag_2O . When the ratio of reactants was 3: 3: 1: 0.5, 90% RhB was decomposed after 25 min reaction. Compared with Ag_2O prepared without H_3BO_4 and pyridine, the degradation efficiency was increased by $35\%^{25}$. For the Ag_2O prepared by Bi et. al without pyridine, the degradation efficiency was 10% lower than that of the sample prepared in this paper²⁶. However, the results also showed that the addition of more pyridine did not improve the photocatalytic efficiency of Ag_2O .

To further understand the photocatalytic degradation mechanism, Fig. 4b showed the time-dependent absorption spectra of RhB solution in the presence of Ag₂O (the ratio of reactants was 3:3:1:0.5). At the wavelength of λ = 553 nm, an

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obvious absorption peak belonged to RhB was observed, and it was gradually decreasing. Generally, the chromophore of RhB molecular (phenylamino and carbonyl bond) is decomposed into colorless intermediate, which means that the maximum absorption peak in the visible region decreased rapidly in the absorption spectrum. Then, the colorless intermediate product is further degraded, and the maximum absorption peak of the absorption spectrum in the visible region exhibits blue-shifted phenomenon²⁷. However, from Fig. 4b, no blue shift phenomenon was found in the degradation of RhB. This indicates that the reaction is mainly caused by chromophore destruction in the photocatalytic degradation of RhB. The degradation kinetics of RhB was also investigated rand the results are shown in Fig. 4c. The kinetics of the process field degradation process is usually fitted with the Langmuir-Hinshelwood model²⁸, as follows:

$\ln(C_0/C) = kt$

Where k is the pseudo-first-order rate constant, C_0 and C are the RhB concentrations in solution at times 0 (after stirring in the dark for 30 min) and t, respectively. It can be found that when the ratio of reactants is 3: 3: 1: 0.5, the rate constant of Ag₂O is the largest (Fig. 4d).



Fig. 4 The photodegradation of 8 mg/L RhB by Ag₂O prepared by different ratio of reagents:(a) degradation kinetics(b) The UV-Vis absorption spectral(the ratio of reactants is 3: 3: 1: 0.5), (c) Kinetic fit (b) Degradation rate constant of RhB.

Phenol is considered to be a typical organic matter for evaluating the performance of photocatalyst. In this case, Ag₂O was used as a photocatalyst to degrade the phenol under visible light irradiation, as is shown in Fig. 5a. From Fig. 5a, the photocatalytic performance of the optimum sample (No. 2, reactant ratio: 3: 3: 1: 0.5) was not much different from that of Ag₂O without pyridine. With the increase of pyridine, the photocatalytic activity of Ag₂O is gradually deteriorating. Moreover, when the pollutants changed from phenol into MO, it can be seen from Fig. 5b that the optimized Ag₂O (No. 2) shows the best photocatalytic activity. As the number of pyridine increases, the photocatalytic performance gradually deteriorated.

The photocatalytic degradation kinetics of phenol and MO were investigated, and the results were shown in Fig. 5(c, d). The degrading process of phenol and MO follows second-order kinetics. In this case, the mechanism of photocatalytic degradation is the organic pollutants adsorbed on the active center of the catalyst and reacts with the adsorbed organic pollutants approaching to the surface. In this study, this model also can be applied to a lower concentration of RhB. Since the diffusion rate of organic contaminants is slow, and this step is usually considered as a rate control step, at this time: $r_{obs}=KC_{dye}$. For higher concentrations of phenol and OM, the model cannot be used in this situation. The higher the concentration of the organic pollutants is, the more amounts of organic pollutants adhere to the surface of the catalyst. The rates of photogenerated electrons and holes under the visible light irradiation are equal to the adsorption rate of organic pollutants. At this time, the adsorption stage and the diffusion stage are all become the rate control step in the whole reaction processes,

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which affects the reaction rate of the whole reaction. In this situation, $r_{obs} = K C_{dye} C_{active center}$.

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Fig. 5 The photocatalytic degradation of (a) 50 mg/L phenol; (b) 16 mg/L MO by Ag₂O prepared by different ratio of reagents; Kinetic fit for degradation of (c) 50 mg/L phenol (d) 1 mg/L MO by Ag₂O

In summary, the photocatalytic performance of Ag_2O prepared by different reactants to degrade 8mg/L RhB, 50mg/L phenol, and 16mg/L MO has been studied carefully. It can be seen from Fig. 6a, the degradation rate of these three different organic matters showed a consistent rule. The No. 2 Ag_2O sample showed the best photocatalytic activity for all organic pollutants. When the RhB was degraded, the No.1 sample without pyridine showed the worst photocatalytic activity. However, when the organic pollutant was changed from RhB to MO and phenol, the photocatalytic activity of No. 1 was only lower than that of No. 2 and larger than that of No. 3 and No. 4. To further confirm this result, the photocatalytic degradation rate was calculated. The calculation method is as follows:

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$$V = \frac{(C_0 - C) \times V_0}{M \times m \times t}$$
(2)

Where V is the degradation rate (mmol/(g·min)), C_0 and C are the initial and ultimate concentration of organic pollutants (mg/L), M is the relative molecular mass of organic pollutants, m is the mass of the catalyst(g), t is the photocatalytic reaction time (min). As shown in Fig. 6b, the photocatalytic degradation rate results are consistent with the degradation rate constants.



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3.4 Mechanism and Characterization

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3.4.1 FT-IR spectra analysis

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Based on the above experimental results, it is necessary to explain the reason caused the best photocatalytic activity of sample No. 2 through characterization. To determine whether pyridine was introduced into the catalyst, the composition of Ag₂O was characterized by FT-IR spectroscopy. The results are shown in Fig. 7a. The result shows that there are four characteristic peaks at 614 cm⁻¹, 884 cm⁻¹, 1384 cm⁻¹, 1384 cm⁻¹, and 1652 cm⁻¹ respectively. All the peaks are belong mg 10^{1} Ag 0^{0} With the increase of pyridine in the reactants, there is no additional peak in the spectrum. Thus, from the FT-IR spectroscopy tests, the obtained samples are all pure Ag₂O, and pyridine is only used as a regulator in the crystallization process.



3.4.2 Crystal Structure

Crystal structures of Ag₂O were investigated by XRD measurements (Fig. 7b). All the peaks for the samples correspond to the cubic phase of Ag₂O (PDF# 41-1104) with the lattice constants equal to 4.718 Å. The XPS spectra from Fig. 7c also shows that the photocatalyst obtained from this method is mainly composed of Ag and O. Combined with the XRD tests, the result shows that Ag mainly exists in the form of Ag⁺. There is no metal Ag in the obtained samples. However, the diffraction peaks intensity of these samples on different crystal faces and grain size shows a slight difference. Therefore, the addition of pyridine cannot change the composition of the catalyst. The grain size was calculated with the Debye-Scherrer equation. The content of each crystal face was calculated from each diffraction peak, as shown in Table 5. For the No. 2 sample, the content of (111) crystal face is the lowest, and the content of (200) crystal face is the highest. However, for the No.1 sample, it's the opposite. The content of (111) crystal planes is the highest, and the content of (200) crystal surface is the lowest. Wang $^{\rm 18}$ calculated the surface free energy of Ag_2O crystals based on density functional theory (DFT): the surface of (111) crystal face is 0.65 J/m², and it is 0.94 J/m² for (100) face. As for the (110) face, the surface free energy is 0.76 J / m². Thus, the No.2 sample has the largest surface free energy, and it also shows the strongest adsorption ability to organic pollutants. That is the reason why the sample No.2 has the best photocatalytic activity. However, as can be seen from Fig. 5, sample No. 1 also showed good photocatalytic activity for both MO and phenol. When the organic pollutants changed from MO and phenol to RhB, sample No.1 showed the worst photocatalytic activity. This is because sample No.1 has the highest content of 111 crystal face, and the 111 crystal face is positively charged²⁹. MO and phenol are anionic dyes that can adsorb on the surface of the catalyst to enhance the photocatalytic activity. This also explains why Ag₂O can degrade phenol and MO faster than RhB.

tal face of Ag ₂ O prepared by different ratio of reagents				
nt of (111)	Content of (200)	Content of (220)		
0.72	0.17	0.11		

Ratio	Content of (111)	Content of (200)	Content of (220)
3:3:1:0	0.72	0.17	0.11
3:3:1:0.5	0.65	0.25	0.10
3:3:1:1	0.68	0.23	0.09
3:3:1:3	0.67	0.22	0.11

3.4.3 Morphology

Table 5 Content of crys

The surface morphology of the Ag_2O sample was examined by SEM. As is shown in Fig. 8, the shape of Ag_2O is an irregular sphere, and the average diameter was about 200–400 nm. With the increase of pyridine content, the particle size of the sample gradually increased. Only when a small amount of pyridine (NO.2) is added to the solution, its particle size is smaller than that without adding pyridine.

During the crystallization process, the morphology of the Ag₂O area is usually affected by nucleation and growth rate. In the first step, the mixed reaction of AgNO₃ and pyridine (Py) was performed for 30min. Py and Ag⁺ formed the coordination complex quickly. When the mixture of NaOH and H₃BO₃ added into the premixed solution, Ag⁺ would be released from the coordination complex. The nucleation and growth rates can be controlled by adjusting the rate of the mixed solution. The crystal structure and surface morphology can directly affect photocatalyst performance. However, excessive addition of Py inhibits the release of Ag⁺, which in turn inhibits the growth of Ag₂O crystals.

To further demonstrate the effect of pyridine on the particle size, the particle size distribution of Ag₂O photocatalyst material with different pyridine additions was tested (Fig. 9). These results are consistent with the results observed by SEM. when a small amount of pyridine was added (sample No. 2), the size of the particles is the smallest, and the average particle size is 360 nm. As the amount of pyridine increases, the particle size

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gradually increases. The Ag₂O particles without pyridine are

slightly larger than the particle size of the sample No.2.

Fig. 8 SEM image of Ag₂O prepared by different ratio of reagents: (a) The reactant ratio is 3: 3: 1: 0; (b) The reactant ratio is 3: 3: 1: 0.5; (c) The reactant ratio is 3: 3: 1: 1; (d) The reactant ratio is 3: 3: 1: 3



The stability of Ag₂O prepared under the optimized conditions of NaOH: AgNO₃: H₃BO₃: Py equal to 3: 3: 1:0.5 is carefully evaluated. After the photocatalytic experiment, the photo-catalyst is recovered from the solution and washed with ethanol and water respectively

to remove organic matter. From Fig. 10, the photo-degradation efficiency of the recovered photo-catalyst remains stable. After 3 cycles, more than 70% RhB was decomposed after 25 min reaction. According to the XPS analysis, the peaks of Ag and Ag⁺ are close to each other. The binding energy of Ag⁰ is around 368.5 eV and 374.5

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of detection techniques or impurities. There are no obvious peaks of metal Ag in XPS spectra. A slight decrease in Catalytic performance may be caused by crystal structural or size change during the cleaning and drying process.



3.4.5 The specific surface area of the sample

The specific surface area of the photo-catalyst is an important parameter to its photo-catalytic performance. With a larger specific surface area, the recombination rate of photo-generated electrons and holes is lower, and the photocatalytic activity is better. As Fig. 11 showed that when the ratio of reactants is 3: 3: 1: 0.5, the specific surface area is 4.47 m²/g, which is much larger than other samples. Therefore, sample NO.2 has the largest adsorption area, it can provide the most active sites, which shows the best conducive to the photocatalytic reaction.



3.4.6 Quantum efficiency analysis

For the photocatalyst, the recombination rate of photogenerated electron and hole is another indicator of its performance. Quantum yield (QE) is used to determine the utilization ratio of photogenerated electrons and holes in the photocatalytic process. The calculation method is as follows:

$$Q_E = \frac{v \times m \times t}{W \times t \times A} \tag{3}$$

Where v is the photocatalytic degradation rate, m is the mass of the catalyst, t is the photoreaction time, W is the light intensity, A is the reaction area. The mass of the catalyst used in the test is 0.03 g. The light intensity is 16.35 Klux, and its unit can be converted by the following relationship, 1 lux=0.00146 Wm², 1 Wm²=4.57 umol/(m²·s). The area of the reaction was the crosssectional area of the quartz tube which contains 10 mL of the solution, and the diameter is 1.5 cm and the height is 8 cm. The theoretical quantum efficiency is obtained through calculation. As shown in Fig. 12, the results are consistent with the reaction rate constant and the photocatalytic degradation rate. Sample NO. 2 has the highest quantum efficiency.

Thus, the No.2 sample shows the best photocatalytic performance, which is related to the surface area, crystal face content, the surface free energy of the crystal surface, and charge of the crystal surface. The comparison of quantum efficiency also proves that the No.2 sample has the advantage of reducing the combination of photonic electron and hole.



Conclusions

In summary, after the single factor experiments, the photocatalytic performance of Ag_2O is optimized by two

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strategies:(1) the optimum conditions for the preparation of Ag₂O were obtained by response surface experiment; (2) the introduction of pyridine was used to optimize crystallization parameters and expose highly active crystal surfaces. Based on the above two methods, the optimized conditions of the preparation of Ag₂O are as follows: NaOH: AgNO₃: H₃BO₃: Py equal to 3: 3: 1:0.5, Ag₂O showed optimal photocatalytic activity for degradation of RhB, MO and phenol under visible light irradiation. The optimized Ag_2O degradation 90% of RhB within 25 min. By characterizing the analysis, the improvement of

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Notes and references

- 1. A. Fujishima, . and K. Honda, . *Nature*, 1972, **238**, 37-38.
- 2. J. Moon, C. Y. Yun, K. W. Chung, M. S. Kang and J. Yi, Catalysis Today, 2003, 87, 77-86.
- 3. W. Cui, J. Li, Y. Sun, H. Wang, G. Jiang, S. Lee and F. Dong, Applied Catalysis B: Environmental, 2018, 237, 938-946.
- 4. G. Dong, D. L. Jacobs, Z. Ling and C. Wang, Applied Catalysis B Environmental, 2017, 218, 515-524.
- 5. M. A. Fakhri, Int. J. Nanoelectronics and Materials, 2016, 9, 93-102.
- 6. C. Liu, C. Cao, X. Luo and S. Luo, Journal of hazardous materials, 2015, 285, 319-324.
- 7. A. F. Carroll, K. W. Hang, B. J. Laughlin, K. R. Mikeska, C. Torardi and P. D. VerNooy, Google Patents, 2013.
- 8. X. Wang, S. Li, H. Yu, J. Yu and S. Liu, Chemistry-A European Journal, 2011, 17, 7777-7780.
 - 9. D. Zhang, C. Su, H. Li, X. Pu and Y. Geng, Journal of Physics and Chemistry of Solids, 2020, 139, 109326.
 - 10. W. Jiang, X. Wang, Z. Wu, X. Yue, S. Yuan, H. Lu and B. Liang, Industrial & Engineering Chemistry Research, 2015, 54, 832-841.
- 11. A. Ahmad, J. Liu, X. Liu, L. Li, Y. Xu and X. Guo, e-Polymers, 40 2016, 16, 57-63.
- 12. Z. Wu, Y. Zeng, X. Wang, J. Wei, S. Yuan and B. Liang, 42 Chinese Journal of Environmental Engineering, 2016, 10, 8.
- 43 13. C. Yu, G. Li, S. Kumar, K. Yang and R. Jin, Advanced 44 materials, 2014, 26, 892-898.
- 45 14. M. Wu, J. M. Yan, M. Zhao and Q. Jiang, ChemPlusChem, 46 2012, 77, 931-935.
- 47 15. Y. Tang, X. Zhang, Y. Ma, X. Wang, C. Su, D. Zhang, X. Pu and Y. Geng, Separation and Purification Technology, 2020, 48 230. 115896. 49
- 16. H. Yang, J. Tian, T. Li and H. Cui, Catalysis Communications, 50 2016, 87, 82-85. 51
- 17. H. Li, T. Chen, Y. Wang, J. Tang, Y. Wang, Y. Sang and H. Liu, 52 *Chinese Journal of Catalysis*, 2017, **38**, 1063-1071.
- 53 18. Y.-J. Chen, Y.-W. Chiang and M. H. Huang, ACS applied 54 materials & interfaces, 2016, 8, 19672-19679.
- 55 19. G. Wang, X. Ma, B. Huang, H. Cheng, Z. Wang, J. Zhan, X. 56 Qin, X. Zhang and Y. Dai, Journal of Materials Chemistry, 57 2012, 22, 21189-21194.

photo-catalytic performance owning to the specific risurface area, the content of the crystal plane, the Charge SPCPOStal Pace. This work may provide some valuable information for the development of highly efficient photocatalysts.

Conflicts of interest

There are no conflicts to declare.

- 20. D. Vidyasagar, S. G. Ghugal, A. Kulkarni, P. Mishra, A. G. Shende, Jagannath, S. S. Umare and R. Sasikala, Applied Catalysis B: Environmental, 2018, **221**, 339-348.
- 21. B. Liu, L. Mu, B. Han, J. Zhang and H. Shi, Applied Surface Science, 2017, **396**, 1596-1603.
- 22. Y. Tang, D. Zhang, X. Qiu, L. Zeng, B. Huang, H. Li, X. Pu and Y. Geng, Journal of Alloys and Compounds, 2019, 809, 151855.
- 23. M.-J. Kim, Y.-S. Cho, S.-H. Park and Y.-D. Huh, Crystal Growth & Design, 2012, 12, 4180-4185.
- 24. K. Yetilmezsoy, S. Demirel and R. J. Vanderbei, Journal of Hazardous Materials, 2009, 171, 551-562.
- 25. W. Jiang, Z. Wu, Y. Zhu, W. Tian and B. Liang, Applied Surface Science, 2018, **427**, 1202-1216.
- N. Bi, H. Zheng, Y. Zhu, W. Jiang and B. Liang, Journal of 26. Environmental Chemical Engineering, 2018, 6, 3150-3160.
- H. Fu, S. Zhang, T. Xu, Y. Zhu and J. Chen, Environmental 27. science & technology, 2008, 42, 2085-2091.
- H. Xu, J. Xie, W. Jia, G. Wu and Y. Cao, Journal of colloid and 28. interface science, 2018, 516, 511-521.
- L. M. Lyu, W. C. Wang and M. H. Huang, Chemistry-A 29. European Journal, 2010, 16, 14167-14174.