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Preparation of Ag-Sm Co-doped TiO2 Catalyst by Microwave Hydrothermal Method and Its Photocatalytic Activity

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Abstract. The optimum conditions for the preparation of TiO_2-Ag-Sm photocatalysts by microwave hydrothermal method are as follows: n(Ag^+): n(Ti^{4+})=0.3%, microwave power 600 W, reaction temperature 150 ℃, reaction time 3 h, calcination temperature 650 ℃ and calcination time 3h. The structure of the catalyst was characterized by XRD, SEM-EDS, ICP-AES, UV-Vis, IR and BET. The photocatalytic degradation activity of TiO_2-Ag-Sm catalyst was investigated under the conditions of microwave, ultraviolet, microwave-ultraviolet and microwave-ultrasonic-ultraviolet under methyl orange solution as simulated pollutant. The results showed that methyl orange was almost degraded completely when the methyl-orange solution was degraded by microwave-ultrasonic-ultraviolet irradiation for 25 min.

Introduction

Compared with other semiconductor photocatalysts CdS, ZnO, ZnS and so on, TiO_2 photocatalyst possesses high oxidation potential, stable chemical property, no secondary pollution and low price, so TiO_2 photocatalyst has been extensively studied[1,2].However, TiO_2 has some defects in photocatalysis. Its forbidden band is wide (Eg=3.2 eV), and it can only be stimulated by ultraviolet. However, most of the sunlight is composed of visible light and ultraviolet light only 3-5%, so its utilization of solar light is low, resulting in its low photocatalytic activity. In addition, the use of time-resolved spectroscopy found that most photoionization-hole (e^-/h^+) pairs in TiO_2 have a high rate of anaplastic recombination after excitation, which is also a reason for the low efficiency of most semiconductor-based photocatalytic reactions[3,4].In view of TiO_2 photocatalytic defects, it needs to be modified. Numerous studies have shown that doping metal ions can extend the photocatalytically active region of TiO_2 to the visible region while doping can inhibit recombination of photogenerated electron-hole (e^-/h^+) pairs and promote the transfer of photogenerated electrons, thereby increasing photocatalytic activity of TiO_2 [5-7].

Using microwave heating method combined with hydrothermal synthesis method can be prepared in a short time with small size and high purity uniform particles. The microwave can heat the solution in a short time, which can largely eliminate the influence of the temperature gradient on the synthesis. In the meantime, it is possible to crystallize the TiO_2 colloidal particles rapidly during the preparation of the catalyst to obtain the ultrafine TiO_2 particles[8-10]. In this paper, silver-samarium co-doped TiO_2 photocatalyst was prepared by microwave hydrothermal method. The photocatalytic activity of the prepared catalyst was investigated with methyl orange solution as a simulated pollutant to further improve the photocatalytic activity of the doped TiO_2 catalyst.

Experimental Part

The Main Reagent. Tetra-n-butyl titanate (AR, Sinopharm Chemical Reagent Co., Ltd.); silver nitrate (AR, Aladdin reagent); samarium nitrate (AR, Aladdin reagent); absolute ethanol (CP, Shanghai Chemical Reagent Factory); methyl orange (AR, Sinopharm Chemical Reagent Co., Ltd.);

ultrapure water.

Preparation of TiO_2-Ag-Sm catalyst and Photocatalytic Activity Test. Respectively, a certain amount of anhydrous ethanol and tetra-n-butyl titanate were mixed, the mixture was stirred magnetically for a certain time to get A solution; Weigh a certain amount of silver nitrate and samarium nitrate dissolved in dilute nitric acid and added dropwise to A solution stirred for a certain time to get B solution; The solution B was placed in a microwave hydrothermal parallel synthesizer (microwave power 600 W, the reaction temperature 150 ℃, the reaction time 3 h) to obtain a TiO_2 sol, filtered, vacuum dried, milled, placed in a muffle furnace temperature calcined 3h get TiO_2-Ag-Sm photocatalyst, bottling spare. The photocatalytic activity of the catalyst test methods are described in the literature[11,12].

Catalyst structure testing and characterization. The catalyst was scanned by X-ray diffractometer (XRD) to get the crystal form and grain size of the catalyst by data processing. The surface morphology of the catalyst was observed by scanning electron microscope (SEM), and the EDS was selected by specific microscopic region. To explore the elemental content in the catalyst, ICP-AES analysis of the utilization of the preparation of the catalyst in the process of chemical and elemental loading; UV-Vis spectrophotometer was used to measure its UV-Vis spectrum in the wavelength range of 200-800 nm. The specific surface area analyzer was used to analyze the catalyst surface area, pore volume and pore size. The infrared spectrometer was used to measure the catalyst in the range of 4000-400 cm^{-1} Infrared spectrum.

Results and Discussion

Silver and Samarium Co-doped Amount of TiO_2-Ag-Sm Photocatalytic Activity. Fixed other preparation conditions were unchanged, respectively, change the amount of silver or samarium doping in order to investigate the amount of silver or samarium doped TiO_2-Ag-Sm prepared by microwave hydrothermal photocatalytic activity, the results shown in Fig. 1 and Fig. 2.

The doping amount of element in the TiO_2 catalyst can make it become the center of separation, and then reduce the photogenerated electron-hole recombination rate. As can be seen from Fig. 1 and Fig. 2, when the values of $n(Ag^+):n(Ti^{4+})$ and $n(Sm^{3+}):n(Ti^{4+})$ are 0.3%, the degradation rate of methyl orange reaches 99.84% When the catalyst has a high photocatalytic activity, the optimal doping amount of Sm and Ag is 0.3%, when the microwave hydrothermal method is used to prepare the TiO_2-Ag-Sm catalyst.

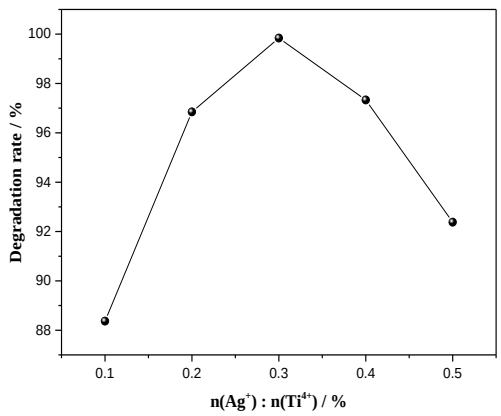


Figure 1. Finite The influence of $n(Ag^+)/n(Ti^{4+})$ mole ratio on photocatalytic activity of TiO_2-Ag-Sm

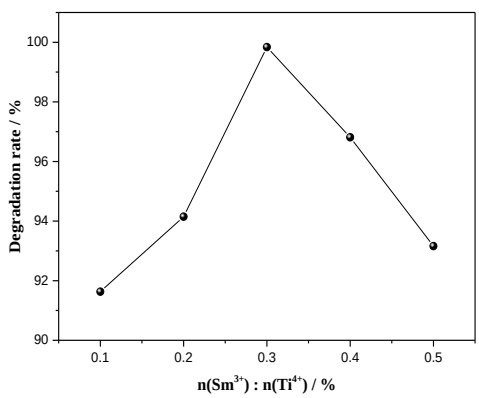


Figure 2. Finite The influence of $n(Sm^{3+})/n(Ti^{4+})$ mole ratio on photocatalytic activity of TiO_2-Ag-Sm

Fig. 3 shows the XRD patterns of TiO_2-Ag-Sm and pure TiO_2 prepared under the optimal conditions. By combining jade5 software phase retrieval analysis shows: pure TiO_2 catalyst and anatase and rutile characteristics of the peak, which shows pure TiO_2 from anatase and rutile two structures; calculated by RIR method two-phase formula can be two-phase, and the mass percentages are 32.95% and 67.05% respectively. The match between TiO_2-Ag-Sm catalyst and anatase is very high, and no other peaks appear in the spectrum, indicating that the TiO_2-Ag-Sm catalyst has a single crystal form. The size of the catalyst is calculated as follows: TiO_2 (28.27 nm)>

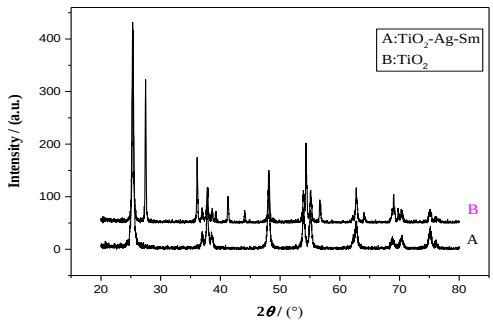


Figure 3. Finite XRD spectra of TiO_2-Ag-Sm and TiO_2 photocatalyst(A:TiO_2-Ag-Sm B:TiO_2)

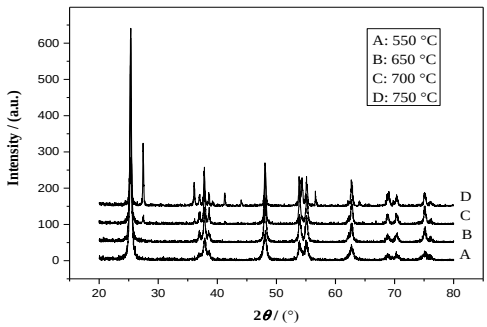


Figure 4. Finite Photocatalytic activity of TiO_2-Ag-Sm catalyst under different degradation conditions

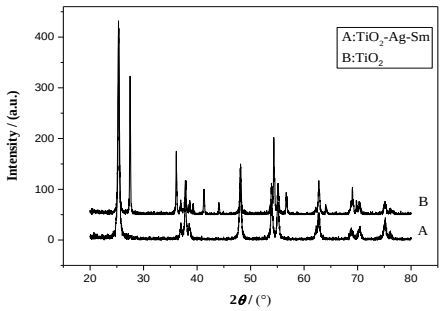


Figure 5. Finite TiO_2-Ag-Sm and pure TiO_2 catalyst XRD patterns

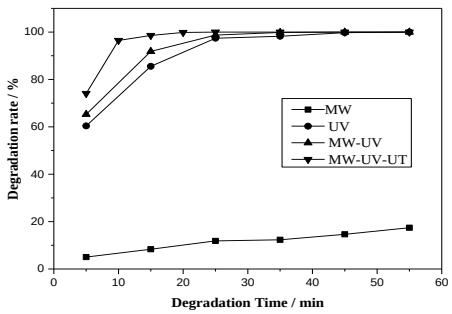


Figure 6. Finite XRD pattern of TiO_2-Ag-Sm catalyst calcined at different temperatures

TiO_2-Ag-Sm (19.36 nm), which shows that the Ag and Sm co-doped TiO_2 catalyst can effectively inhibit the transformation from anatase to rutile phase , but also to some extent inhibit grain growth[13].

TiO_2-Ag-Sm Photocatalytic Activity of the Catalyst. In order to examine the effects of microwave and ultrasonic on the photocatalytic activity, the best conditions for the preparation of TiO_2-Ag-Sm by microwave (MW), ultraviolet (UV), microwave and ultraviolet (MW-UV) and microwave ultraviolet-ultrasound (MW-UV-UT) of four kinds of degradation conditions are used for degradation of methyl orange solution. The result is shown in Fig. 4. As can be seen from Fig. 4, the degradation of methyl orange by TiO_2-Ag-Sm is not obvious under microwave irradiation alone. The degradation rate of methyl orange is only 11.87% when the degradation time is 25 min. In UV, MW-UV and MW-UV-UT three kinds of degradation conditions, the effect of TiO_2-Ag-Sm on the degradation of methyl orange are more obvious, when the treatment time is 25min, the degradation rate of methyl orange are 97.40%, 98.72% and 99.90%; when the treatment time is 55min, almost complete degradation of methyl orange. This shows that microwave and ultrasound can enhance the photocatalytic degradation activity of TiO_2-Ag-Sm.

TiO_2-Ag-Sm Catalyst XRD Analysis. The XRD pattern of TiO_2-Ag-Sm and pure TiO_2 catalyst is shown in Fig. 5. As can be seen from Fig. 5, the characteristic peaks of anatase and the appearance of rutile pure TiO_2 atlas, using RIR method to calculate two crystal quality percentage are 32.95% and 67.05%, which indicates that after high temperature calcination of TiO_2 is composed of anatase and rutile two phases; compared with pure TiO_2, Rutile characteristic peak the catalyst of TiO_2-Ag-Sm do not appear, the average size of calculated by the Scherrer formula [14] of two kinds of TiO_2 particles in the catalyst are 19.36 nm and 28.27 nm, which indicates that doping can effectively inhibit the transformation of anatase phase and the grain growth of rutile, so as to effectively improve the photocatalytic activity of TiO_2 catalyst.

Fig. 6 is a XRD diagram of the TiO_2-Ag-Sm catalyst prepared by calcining at different temperatures. We can see from Fig. 6, when the calcination temperature reaches 700 ℃ when the catalyst appears the characteristic diffraction peaks of rutile phase, as the temperature continues to rise, the rutile phase diffraction peak is more and more strong, the rutile phase content increasing; calculated by RIR method of two-phase formula can be, TiO_2-Ag-Sm at 700 ℃: rutile W_R=2.06%, anatase in W_A=97.94%; 750 ℃: rutile W_R= 19.35%, anatase W_A=80.65%; when the catalyst in the main phase of anatase and rutile phase, its photocatalytic activity is higher, but the proportion of rutile will affect high catalytic activity, therefore the different catalysts in the presence of an optimum ratio of anatase and rutile phases.

SEM and EDS Analysis. The SEM image of TiO_2-Ag-Sm catalyst is shown in Fig. 7. It can be seen from Fig. 7 that the particle size distribution of the TiO_2-Ag-Sm catalyst is relatively uniform, which is favorable for photocatalytic degradation. At the same time, the specific micro-region of TiO_2-Ag-Sm is selected for full-spectrum scanning to determine the element types and their contents. The results are shown in Fig. 8 and Table 1.The results show that the main elements in TiO_2-Ag-Sm are Ti and O, and contain trace Ag and Sm (Ag:0.02%, Sm:0.09%). This indicates that the TiO_2-Ag-Sm catalyst prepared by microwave hydrothermal synthesis is loaded with two elements Ag and Sm.

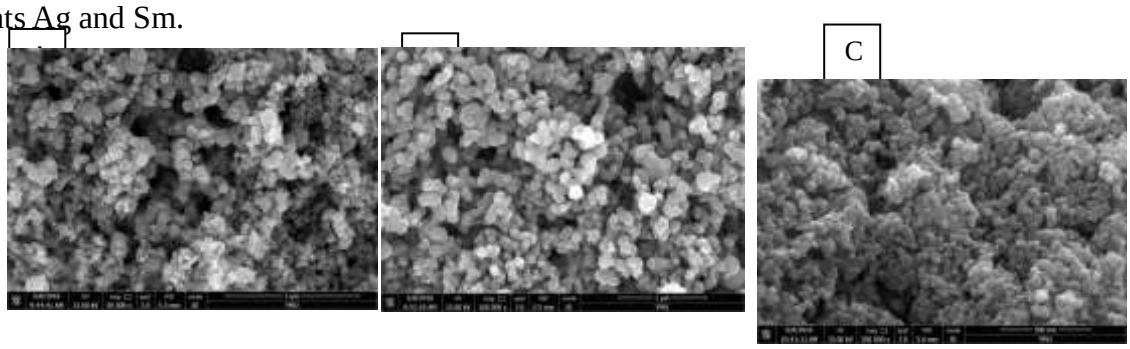


Figure 7. Finite SEM images of TiO2-Ag-Sm catalysts at different magnifications (A: 50,000 times; B: 100,000 times; C: 200,000 times)

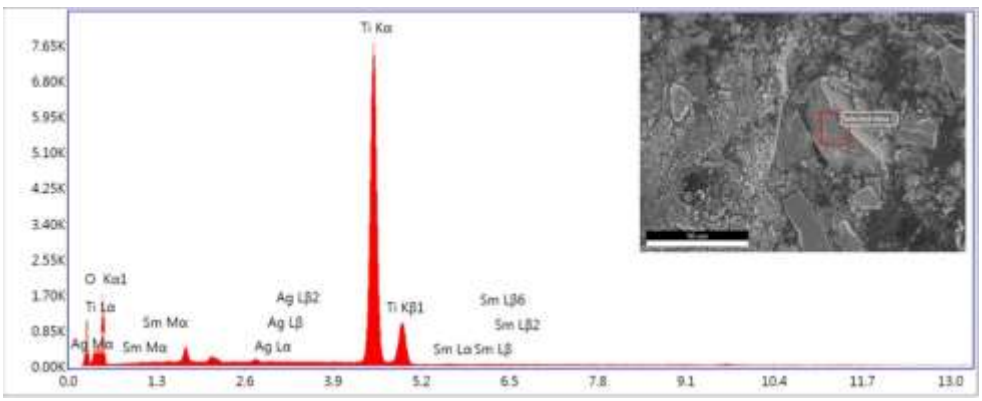


Figure 8. Finite X-ray energy spectrum of TiO_2-Ag-Sm catalyst

Table 1 EDS Elemental Analysis of TiO_2-Ag-Sm Catalyst

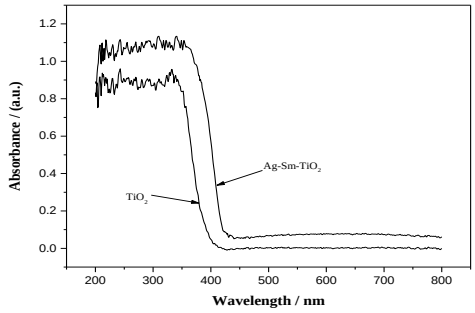
element	*Wt*%	*At*%
OK	41.64	68.27
TiK	57.74	31.62
AgL	0.08	0.02
SmL	0.54	0.09

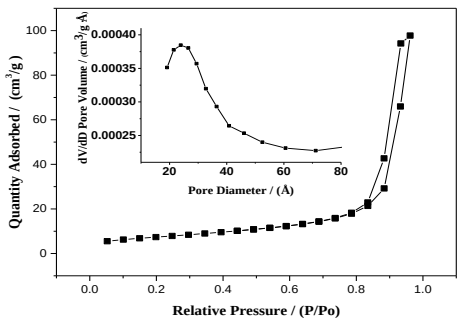
ICP-AES analysis. The contents of Ag and Sm in the TiO_2-Ag-Sm catalyst are quantitatively analyzed by ICP-AES to investigate the loading of the doping elements. The results are shown in Table 2. The theoretical doping amounts of Ag and Sm are 0.30% [n(Ag^+):n(Ti^{4+})=0.3% and n(Sm^{3+}):n(Ti^{4+})=0.3% in the preparation of TiO_2-Ag-Sm, while the actual loadings of the two elements are 0.21% and 0.20%, respectively, indicating that TiO_2 and Ag are indeed loaded in the TiO_2 catalyst during the preparation of TiO_2-Ag-Sm by microwave hydrothermal method.

Table 2. Results of ICP-AES analysis of TiO_2-Ag-Sm catalyst

sample	Doping elements	The actual doping amount /%	Theoretical doping amount /%	Load rate /%
TiO_2-Ag-Sm	Ag	0.21%	0.30%	70.0%
	Sm	0.20%	0.30%	66.7%

UV-Vis Absorption Spectroscopy. Fig. 9 shows the UV-Vis spectra of pure TiO_2 and TiO_2-Ag-Sm prepared by microwave hydrothermal method. It can see from Fig. 9, compared with the pure TiO_2, TiO_2-Ag-Sm of UV and visible light is absorbed, and the light absorption edge red shifted from pure TiO_2 (390nm) to TiO_2-Ag-Sm (443nm) 53nm red shift, which effectively will the optical absorption of TiO_2 extended to the visible. Using the formula Eg=1240 eV lambda can calculate the band gap of pure TiO_2 and TiO_2-Ag-Sm are 3.02 eV and 2.80 eV, which shows the relatively pure TiO_2 doped TiO_2 band gap width is reduced by 0.22 eV, which leads to the





photoinduced electrons more easily across the gap, so as to improve the photocatalytic activity of TiO_2-Ag-Sm catalyst.

Figure 9. Finite UV-Vis spectra of TiO_2 and TiO_2-Ag-Sm catalyst

Figure 10. Finite N_2 adsorption-desorption isotherms and pore size distribution of TiO_2-Ag-Sm catalyst

Table 3 Specific surface area, pore volume and pore size test results for TiO_2-Ag-Sm catalyst

Sample	$S_{Langmuir}$ [m^2/g]	S_{BET} [m^2/g]	$V_{BJH\text{-}adsorption}$ (cm^3/g)	$V_{BJH\text{-}desorption}$ [cm^3/g]	$D_{BJH\text{-}adsorption}$ [nm]	$D_{BJH\text{-}desorption}$ [nm]
TiO_2-Ag-Sm	90.7853	26.3819	0.044500	0.065716	6.6060	8.9031

N_2 Adsorption-Desorption Analysis. Fig. 10 shows the N_2 adsorption-desorption and pore size distribution of TiO_2-Ag-Sm prepared by microwave hydrothermal method. Table 3 shows the specific surface area, pore volume and pore size of TiO_2-Ag-Sm. As can be seen from Fig. 10 and Table 3, the TiO_2-Ag-Sm catalyst is a spherical mesoporous material with relatively uniform pore size distribution and smaller size. The larger the specific surface area is, the larger the contact area between the catalyst and the organic pollutant is, and the probability of contacting the catalytically active sites increases at the same time, effectively increasing the photocatalytic activity of the catalyst.

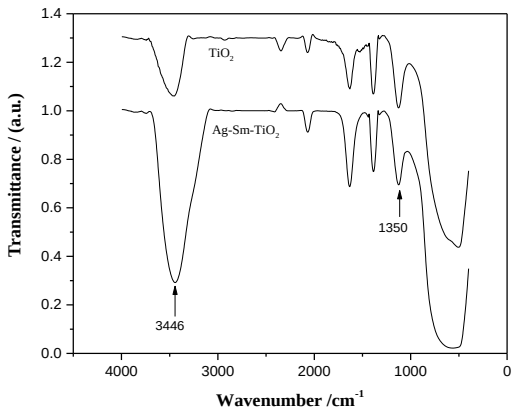


Figure 11. Finite Infrared spectra of TiO_2 and TiO_2-Ag-Sm catalysts

Infrared Spectroscopy. Fig. 11 is an infrared spectrum of TiO_2 and TiO_2-Ag-Sm catalysts. The figure 3446 cm^{-1} around the obvious hydroxyl stretching vibration peak, 1350 cm^{-1} is Ti-OH characteristic absorption peak. Comparing the two IR spectra in Fig. 11, it can be seen that the hydroxyl vibration peak of TiO_2-Ag-Sm is stronger than that of pure TiO_2. Therefore, Ag and Sm doping contribute to the formation of more OH on the surface of TiO_2 catalyst. It is advantageous to improve the catalytic activity.

Conclusion

The optimal conditions for the preparation of TiO_2-Ag-Sm catalyst by microwave hydrothermal method are optimized as follows: silver and samarium doped amount of $n(Ag^+):n(Ti^{4+})=0.3\%$ and $n(Sm^{3+}):(Ti^{4+})=0.3\%$, microwave power 600 W, reaction temperature 150 ℃, reaction time 3 h, calcination temperature 650 ℃ and calcination time 3h. The TiO_2-Ag-Sm catalyst prepared under these conditions degrades methyl orange almost completely when degrading methyl orange solution under UV, MW-UV and MW-UV-UT degradation for 55 min.

The XRD patterns of TiO_2-Ag-Sm catalyst at different calcination temperature show that Ag and Sm doping can make the absorption of TiO_2 extend to the visible region, when the relative mass fraction of the anatase phase and the rutile phase in the catalyst is optimal, this results in higher photocatalytic activity of the catalyst.

Characterization of the catalyst by XRD, SEM, EDS, ICP-AES, UV-Vis, N_2 adsorption-desorption, X-ray energy dispersive spectroscopy and IR show that the TiO_2-Ag-Sm catalyst prepared by microwave hydrothermal method has the advantages of smaller particle size, surface area, pore volume and pore size larger, the surface of the number of high OH, chemical stability and other advantages, resulting in its high photocatalytic activity.

Acknowledgement

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