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Photocatalytic activity of mixture of SnS_2 and TiO_2 powders in destruction of metyhyl orange in water

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Nano-SnS_2 and TiO_2 powders were synthesized with chemical solution method and sol-gel method respectively. XRD and AFM and spectrophotometry were used for characterization of the powders. Experiment results indicated that the mixture of SnS_2 and TiO_2 powders consist of uniform anatase TiO_2 crystals of 9.9 nm with hexagonal SnS_2 nanocrystals of 9.6nm. The degradation rates of methyl orange on the mixed powders were increased with increasing SnS_2 content. The degradation rates of a methyl orange solution under sunlight for 3h were increased from 22% to 90% with increasing SnS_2 content from 0mol% to 30mol%. Substitution groups on benzene and benzene can be further photodecomposed in a condition of micro-alkaline solution.

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1. Indroduction

Nano-TiO_2 materials as a photocatalyst were studied widely for potential application in decontamination of environment. Photocatalytic properties of TiO_2 powders are dependent on light absorption, however TiO_2 is activated only in the ultraviolet region, which restricted its application in nature light condition. To improving the photocatalytic properties of TiO_2 some attempts have been made to increasing the light absorption, such as adopting CdS [1-5], CdSe [6], PbS [7], and Fe_2O_3 [8], V_2O_5 [9], Bi_2S_3 [10], SnO_2 [11-13] et al as short bandgap semiconductors and doping nitrogen [14] and sulfur [15] to lower the bandgap energy of TiO_2 and doping noble metal catalyst Pt-Ru [16] and Au [17,18] et al. The semiconductor doping have the advantages of full use of natural light and low cost of materials and convenience in syntheses technology and were widely studied in form of mixed colloid suspensions [3,4,7,11] and films [5,6,10,12,13] and compound powders [1,2,8-10]. In semiconductor doping, CdS and CdSe and PbS are detrimental to human health and the environment although remarkable increase effect in photocatalytic properties, Fe_2O_3, V_2O_5, and SnO_2 are large bandgap semiconductors, SnS_2 is a short bandgap semiconductor (~1.1eV) and non-poisonous and were not reported previously as a semiconductor doping in TiO_2 materials. In present paper we report photocatalytic properties and synthesis of mixture of SnS_2 and TiO_2 powders.

2.Experimental section

2.1 Preparation of SnS_2 and TiO_2 powders

TiO_2 particles were prepared with sol-gel method. Titanium isopropoxide was dissolved in ethanol and stabilized with little acetylaccetone and adjusted pH=5 with HCl with constant stirring and stable for a period of 3d. Concentration of Ti^{4+} ion in the solution was 0.5M. The solution was then dried for 48h at 60-80°C. The gel was changed from yellowish to yellow in color and maintained transparent. As

-dried precursor was calcined for 1h at 400°C in air.

SnS_2 powders were prepared with chemical solution method. $SnCl_4·5H_2O$ and $Na_2S·9H_2O$ were respectively dissolved in HCl solution with pH=1 and distill water. These $SnCl_4$ and Na_2S solutions were respectively of ion concentration of 2M and 1M. 50ml Na_2S aqueous solution was dropwise added to 25ml $SnCl_4$ solution with constant stirring. Brown precipitation was then formed in mixed solution and filtered, washed with water, and dried for1h at 80 °C.

2.2 Characterization of powders

The phase identification of the TiO_2 and SnS_2 powders were respectively conducted at room temperature using X-Ray diffractometry (XRD, $CuK_{\alpha 1}$, λ = 0.15406 nm, Model No: D/Max-2200PC, Rigaku, Japan). The phases and particle sizes of the powders were determined with the Jade5 analytic software carried with X-Ray diffractometer. The morphologies of the powders were analyzed using atomic force microscopy (AFM, Model No: SPI3800N, Japan).

In this study, methyl orange was used as a photocatalytic substrate to study photodegradation on the mixed powders of TiO_2 and SnS_2. Photodecomposition experiments were performed in glass beaker. In each experiment, 50ml methyl orange solution were added to 100mg mixed TiO_2 and SnS_2 powders at molar ratio of 10: 0, 9: 1, 8: 2, and 7: 3 and dispersed with KQ-50E ultrasonic generator respectively. Sunlight at noon and 40W-fluorescent lamp were used as light resources. Two pH values and four concentrations of methyl orange solution and two illustration conditions were used. The pH values of solutions were adjusted with NH_4OH and HCl and measured on 2C-digitel pH meter. The conditions for each experiment are shown in Table 1. The absorption spectra of methyl orange solutions before and after irradiation were measured on UV-265FW spectrophotometer. The rates of photodegradation (R) were calculated using absorption intensities before and after irradiation (I_o and I) according to

$$R = \frac{I_o - I}{I_o} \cdot 100\%$$

Table 1. Conditions of photodegradation experiments.

No	methyl orange solution		Illumination condition	
	concentration (10^{-5}M)	pH	light resource	time(h)
T_1	4.9	5.0	sunlight at noon	3
T_2	7.6	5.0	40W-fluorescent lamp	4
T_3	12.2	5.0	sunlight at noon	3
T_4	24.4	8.0	sunlight at noon	3

3. Results and discussion

The TiO_2 and SnS_2 powders prepared by Sol-gel method and chemical solution method were soft powders and white and brown in color respectively. The XRD patterns of TiO_2 and SnS_2 powders are shown in Fig. 1 that indicated that TiO_2 powder had anatase and little rutile phase and was of a particle size of 9.9nm determined with strong peak (101) at $2\theta \approx 25.3^o$ and SnS_2 powders had hexagonal phase and was of particle size of 9.6nm determined with strong peak (001) at $2\theta \approx 15.04^o$. SET surface area of powders (S_{BET}) were approximately calculated using the particle size (s) and bulk density (d), $4.1 g/cm^3$ for TiO_2 and $4.5 g/cm^3$ for SnS_2, according to

$$S_{BET} = \frac{6}{s \cdot d}$$

As-calculated S_{BET} were $148 m^2/g$ and $139 m^2/g$ for TiO_2 and SnS_2 respectively. In AFM photograghs of TiO_2 and SnS_2 powders as shown in Fig. 2, both powders were of similar particle sizes as results of XRD analyses and SnS_2 powders had aggregated morphology.

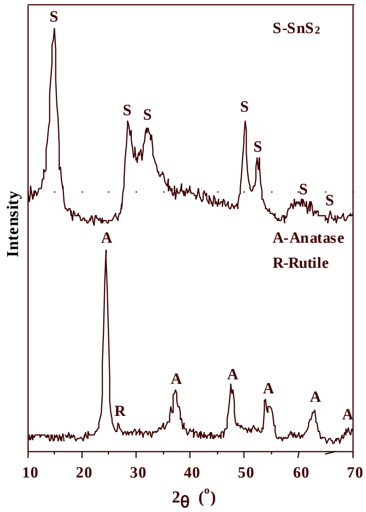

Fig. 1. XRD patterns of TiO_2 and SnS_2 powders.

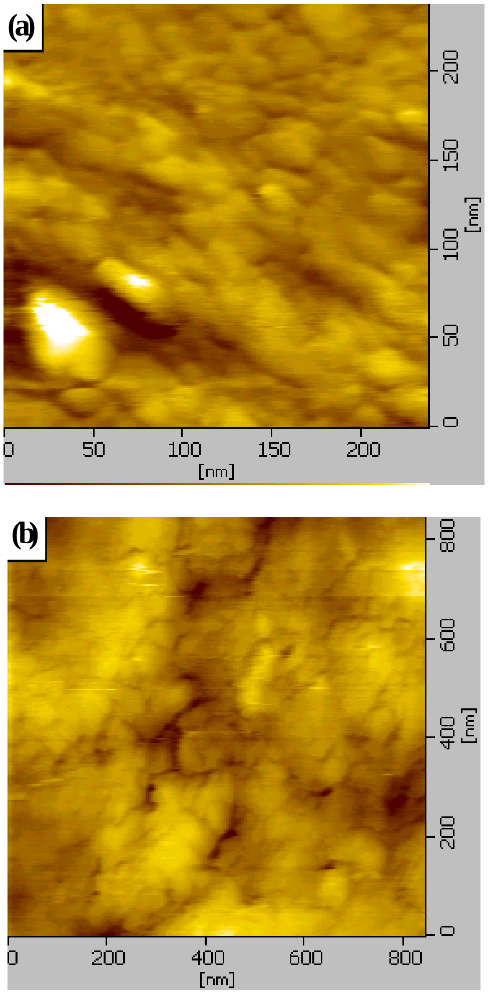

Fig. 2. AFM micrograghs of (a) TiO_2 and (b) SnS_2 powders.

Fig. 3 shows dependences of photodegradation rate of methyl orange on SnS_2 content in mixed powders in four test conditions. In experiment condition of T_1, due to lower concentration of methyl orange, photodegradation rate was close to hundred percent on mixture of SnS_2 and TiO_2 powders, in fact, color was eliminated in 20min, 50min, and 150min as SnS_2 content of 30mol%, 20mol% and 10mol% respectively. In conditions of higher concentrations of methyl orange, photodegradation rate were increased successively with increasing SnS_2 content from 0 to 30mol%, under either sunlight or fluorescent lamp. In contrast, increase of degradation rate as increase content of SnS_2 was less in illumination condition of fluorescent lamp, indicating large light intensity mad more contribution to the photodegradation of methyl orange on short bandgap semiconductor. Shiragami and co-workers[19] similarly reported that photocatalytic reductions of some organic compounds on CdS suspensions were increased with increasing the light intensity.

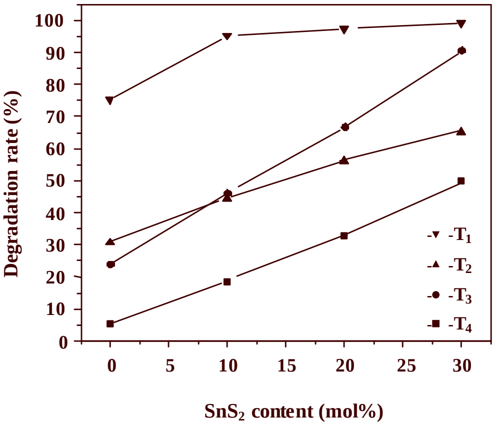

Fig. 3. Dependences of degradation rates of methyl orange on SnS_2 content in mixed powders under different test conditions.

To investigate effect of the pH on photodegradation of methyl orange solution, two pH values of initial solutions were used in the experiments. Fig. 4 shows the absorption profiles of the methyl orange solution with two initial pH values after illumination. In the absorption profiles in an acidic condition (T_3) as shown in figure 4(a), intensity of color peak of methyl orange at ~502nm was decreased with increasing SnS_2 content in mixed powders, indicating degradation rate increased as increase of SnS_2 content. In same time, the intensity of characteristic peak at ~197nm was increased with increasing SnS_2 content, indicating amount of single-ring aromatic produced by preliminary decomposition of methyl orange increased with increasing SnS_2 content. B-absorption bands of single-ring aromatics were of relative large intensities and shift to a short wave of ~243nm, which would be due to the detectable photodecomposed products were mainly various substitution benzenes or solvent effect on spectrophotometry. In alkaline condition (T_4), in fact, pH values of solutions were closed to 7.6, the color peak of methyl orange at ~462nm was also decreased with increasing SnS_2 content, however the intensity of characteristic peak at ~197nm was decreased with increasing SnS_2 content, as shown in Fig. 4(b). This indicated that degradation rate increased as increase of SnS_2 content and the single-ring aromatic as detectable decomposed products of methyl orange can be further reduced on the mixture SnS_2 and TiO_2 photocatalysts in a micro-alkaline condition. B-absorption band was of relative small intensity and in a long wave of ~266nm, which may be due to substitution groups on benzene can be further photodecomposed before decomposition of benzene.

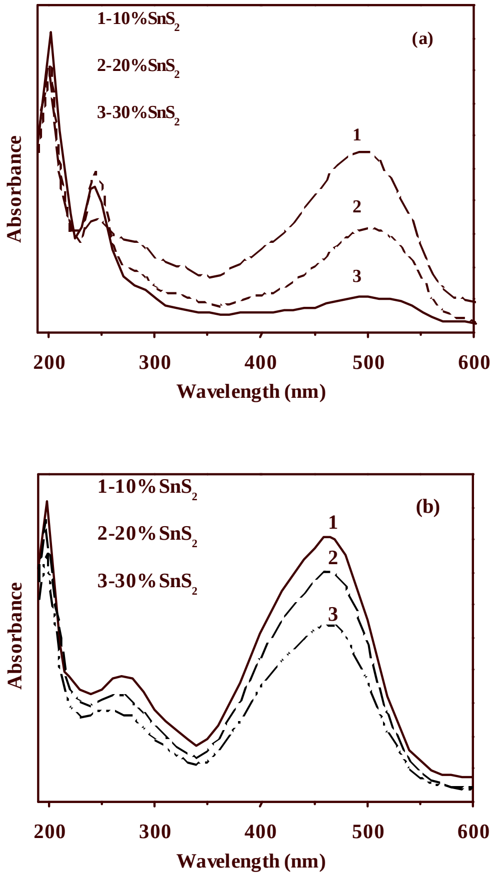

Fig. 4. Absorption profiles of methyl orange solution after illumination under experiment conditions of (a) T_3, (b) T_4.

For many semiconductors, as the pH increases the positions of the banks shift upword with respect to vacuum, i.e., the potential of photogenerated electrons becomes more negative or "more reducing". Decomposition of benzene is easier in reducing catalysis than in oxidic catalysis. These result in that decomposition rate of methyl orange were larger and the benzel ring and substitution groups on benzene can be further decomposed at higher pH condition on semiconductor photocatalyst, specially on the mixture of SnS_2 and TiO_2 powders. In general, product of preliminary photodecomposition of many organic contaminants containing benzyl on the photocatalyst, concluding TiO_2 powders, are benzene and various substituted benzene that are also detrimental to human health and the environment. The more fast photodegradation of the benzyl on mixtures of SnS_2 and TiO_2 powders in comparison with the TiO_2 powders make the mixed powders potential advantage in decontaminant of aquatic environment.

4. Conclusion

Mixture of SnS_2 and TiO_2 photocatalysts were efficiently synthesized with wet chemical methods and have a potential for solar-assisted decomposition of organic compounds. These materials have a large surface area and good photodegradation property. The correlations between activity and SnS_2 content, pH, and light intensity were shown. This, together with narrow bandgap energy of SnS_2, makes the mixed TiO_2 powders able for many photocatalytic reactions. This open new possibility for formation of various narrow bandgap semiconductors mixed TiO_2 materials prepared with various processes that can be used for heterogeneous catalyses and environment decontamination.

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