# Preparation, Characterization and Photocatalytic Activity of Nanometer SnO<sub>2</sub>

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Abstract-Nanometer oxides SnO<sub>2</sub> were prepared by constant temperature hydrolysis, microwave hydrolysis, chemical precipitation and solid state reaction, respectively. The oxides were characterized by X-ray diffraction (XRD), transmission electron microscope (TEM), UV absorb spectrum **Brunauer–Emmett–Teller** and (BET) measurement. Photocatalytic properties of nanometer SnO<sub>2</sub> were studied in detail. The photocatalytic activities of nanometer oxides were studied using methyl orange (MO) as a mode organic pollutant. The influences of quantities of photocatalysts, photocatalysts doped with different metal ions and pH of MO liquid were studied. It shows that well-crystalled SnO<sub>2</sub> with the particle size of 30-40 nm can be prepared by constant temperature hydrolysis sintered at 800 °C, and the decoloration of MO reaches 97% at 120min, which shows higher photocatalytic activity for methyl orange (MO) than those made from other methods.

*Index Terms*—photocatalysis, tin oxide, methyl orange, organic pollutants, nanometer.

### I. INTRODUCTION

Photoinduced hydrophilicity was discovered in 1995[1], soon after the time that conventional applications of TiO<sub>2</sub> as a photocatalyst began to be developed. In the past two decades, photocatalytic degradation of various kinds of organic and inorganic pollutants using semiconductor powders as photocatalysts has been widely studied. UV irradiation of TiO<sub>2</sub> generates electron-hole pairs, which reduce and oxidize adsorbates on the surface, respectively, thereby producing radical species, such as OH radicals and O2<sup>-</sup>. These radicals can decompose most organic compounds and bacteria. It had been clearly demonstrated that a wider separation of the electron and the oxidized dye enhances the catalytic action by suppression of recombination. A photocatalytic process is based on the generation of electron-hole pairs by means of band-gap radiation that can give rise to redox reactions with the species adsorbed on the surface of the photocatalysts. Sensitization of wide gap semiconductors such as TiO<sub>2</sub> and ZnO[2] has gained significant attention largely owing to their photostability. And the composite photocatalysts such as ZnO/TiO<sub>2</sub>/SnO<sub>2</sub>[3], ZnO/SnO<sub>2</sub>[4,5], tin-doped TiO<sub>2</sub>[6] and  $SnO_2/TiO_2$  [7][8] have been extensively studied[9][10] for their high photocatalytic activities. But the study about  $SnO_2[11] \sim [15]$  is especially less.

In this paper much attention has been focused on  $SnO_2$ , which was investigated as a potential photocatalyst in the sensitized degradation of dye. For the present study, we synthesized of pure SnO<sub>2</sub> powders by using the constant temperature hydrolysis method and determined the photocatalytic degradation rate of MO solutions. Photocatalytic activity was characterized based on photocatalytic degradation of methyl orange under UV-light illumination, and the maximum activity was observed for the powder sintered at 800°C. Finally, an explanation for the increase in the photocatalytic activity of SnO<sub>2</sub> is proposed based on the results of XRD, SEM, TEM, UV absorb spectrum and BET.

## II. EXPERIMENTAL

## A. Preparation of SnO<sub>2</sub> nanometer powders

### 1) Constant temperature hydrolysis

In this paper, SnO<sub>2</sub> nanocrystal was synthesized by constant temperature hydrolysis. The tin tetrachloride [SnCl<sub>4</sub>·5H<sub>2</sub>O, analytical grade] was used as the starting material without further purification, it was dissolved into distilled water to form a transparent solution with the concentration of 0.02 mol/L. Ammonia (NH<sub>3</sub>·H<sub>2</sub>O) solution was added dropwise into the tin tetrachloride solution under magnetic stirring until the pH was 1.0. Then the solution was put into thermostat water bath, in which the temperature was kept about 80°C, for 15 minutes until white depositions came out. The depositions were filtered, washed using distilled water until there was no impurity ions presence and dried at 103 °C. The product was calcined at 600 °C, 700 °C, 800 °C and 900°C for 1h. And coated SnO<sub>2</sub> were also synthesized by this method, the coating mass fractions are all 0.5%, the only difference was that different metal ions such as Ti<sup>2+</sup>, In<sup>3+</sup>,  $Zn^{2+}$  and  $Fe^{3+}$ , which were included raw materials as following, Ti(SO<sub>4</sub>)<sup>2</sup>, InCl<sub>3</sub>, ZnSO<sub>4</sub> and FeCl<sub>3</sub>, respectively. 2) Solid state reaction

Put the raw materials  $n(SnCI_4 \cdot 5H_2O) : n(Na_2CO_3)=1:2$ into carnelian mortar, mix them and mill the mixture for 2 hour, wash, dry and calcine the powder, the following steps are as above.

## B. Characterization

The crystal structure of the samples was characterized by an X-ray diffraction (XRD, Bluker D8-Advance) with a CuK<sub> $\alpha$ </sub> radiation (wavelength  $\lambda$ =0.15406 nm) operating at 40



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mA and 40 kV. The specific surface area of  $SnO_2$  was measured by the gas adsorption analyzer (Model 3H-2000) according to the Brunauer-Emmett-Teller method using nitrogen absorption. The size distribution and morphology of the samples were measured by transmission Electron Microscopy (TEM model JEM-100CX II, JEOL Corporation). The surface of the nanoparticles were observed by Hitachi S-4800 Field Emission Scanning Eelectron Microscopy (FE-SEM).

## C. Photocatalytic experiment

The photocatalytic activities of SnO<sub>2</sub> photocatalysts were evaluated by the degradation of methyl orange water-soluble dyestuff. Experiments were performed in the SGY-1 multifunctional photocatalytic reactor with a 300-W high pressure mercury lamp ( $\lambda_{max}$ = 365 nm). Running water was passed through the two-double wall to cool the reaction solution and remove the IR fraction of the beam. The suspensions for the photocatalytic reactor were prepared by adding various nanopowders to a certain concentration of MO solution. All experimental conditions were kept constant as following: 250ml of the suspension, 20mg/L of initial MO concentration, continuous magnetic stirring and illumination with a 300-W high pressure Hg lamp. The photocatalytic reaction lasted 2h. All experiments were carried out at room temperature. Samples (10ml) for analysis were extracted through pipette every 20 minutes and centrifuged immediately. Absorbance of the suspension and initial solution was determined, respectively. 752UV-vis spectrophotometer was used at the maximum absorption wavelength ( $\lambda_{max}$ =449nm) of MO. Degradation rate D was calculated as D = (A0-A)/A0, where A0 shows initial absorbance and A shows the sample absorbance. Comparison experiments were carried out under the same condition, but one was done without catalyst and another was in the dark.

#### III. RESULTS AND DISCUSSION

## A. characterizations

X-ray diffraction patterns of the samples of  $SnO_2$  are shown in Fig.1. The powder diffraction patterns matched very well with that of the PDF (JCPDS powder diffraction file) number 41-1445, it shows that the particles were cubic, the unit cell parameter: a=b=4.738A, c=3.187A, and they were crystalline powders with narrow grain size-distribution and high purity. The mean grain size was calculated by Deby-Scherrer equation:  $D=0.89\lambda/\beta cos\theta$ , where D is the mean grain size. The results showed that the mean grain size is about 20.7 nm. Surface area of the as-prepared materials after calculated according to the Brunauer-Emmett-Teller (BET) method was  $16.57m^2/g$ . The lager surface area may benefit the contact between dyestuff and catalysts, and can absorb larger numbers of dyestuff as well as increase photoactivities.



Figure 1. (a) SnO<sub>2</sub> calcined at 800°C by solid state reaction(b) SnO<sub>2</sub> calcined at 800°C by constant temperature hydrolysis



Figure 2. IR spect ra of different SnO<sub>2</sub> samples



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Figure 3. The TEM photograph of the oxide  $SnO_2$  calcined at 800  $^{\circ}C$  by constant temperature hydrolysis



Figure 4. The SEM images of SnO<sub>2</sub> calcined at 800°C

The TEM photograph of the oxide  $\text{SnO}_2$  is given in Fig.3 and the SEM image shows on Fig.4. The photograph shows that the oxide powder is of an equable distribution except for a few aggregated particulates. The average grain size calculated by proportion of the photograph is about 20-30 nm, which is uniform with the result of the XRD patterns.

To further understand the nano structure of  $SnO_2$ composite nanoparticles, their N<sub>2</sub> adsorption and desorption The isotherms were measured. typical  $N_2$ adsorption-desorption isotherms and pore size distributions of SnO<sub>2</sub> are shown in Fig.5. They exhibited a type IV isotherms with type H<sub>3</sub> hysteresis when the relative pressure P/Po is in the range of 0.6-1.0 according to the IUPAC nomenclature. This is a characteristic process between adsorption into and desorption from the mesopores. The insets in Fig.3 are the corresponding pore size distribution (PSD) curves, which were derived by the Barret-Joyner-Halenda (BJH) method. In addition, the Brunauer-Emmett-Teller (BET) analysis showed that the surface areas of the SnO<sub>2</sub> was  $16.57 \text{ m}^2 \text{ g}^{-1}$ , respectively, indicating that the surface areas decreased with the increasing of the calcination temperature.



Figure 5. Nitrogen adsorption isotherms for SnO2 calcined at 800°C

The UV-Vis diffuse reflectance spectra of  $\text{SnO}_2$  powders calcined at 700°C, 800°C and 900°C for 1 h, respectively, is given in Fig.4. From the figure we can find that several absorption bands are observed in the UV region between 200 nm and 450nm at each curve. It is to be noted that absorption peaks in the spectra are blue-shifted by increasing the calcination temperature from 700°C to 900°C. Such shifts may be attributed to the changes of crystallite phase and size of coupled oxides, defects, and so on. There are strong absorption peaks in the UV region between 200 nm and 300 nm, which hints that the SnO<sub>2</sub> powders may have good photocatalytic activity.

The specific surface areas of the  $SnO_2$  powders by different methods are given in Table 1.It shows that specific surface area of  $SnO_2$  calcined at  $800^{\circ}C$  synthesized by constant temperature hydrolysis is the highest one , which may benefit the higher photocatalytic activity. The higher specific surface area at  $800^{\circ}C$  may attribute to more defects in the  $SnO_2$  crystal, which result in the more tiny pores. And at  $900^{\circ}C$  these tiny pores were collapsed, resulting in the decreasing of specific surface area.



Figure 6. UV-Vis diffuse reflectance absorption spectra of SnO<sub>2</sub> calcined at different temperature



TABLE I. THE SPECIFIC SURFACE AREAS OF THE SNO<sub>2</sub> powders by DIFFERENT METHODSA. CONSTANT TEMPERATURE HYDROLYSIS, B. MICROWAVE HYDROLYSIS, C. SOLID STATE REACTION

method	<b>a</b> .1			<b>b</b> .1	<b>C</b> .1
Calcinations temperature/C.,	700.,	800.1	900.1	800.1	800.1
specific surface area/m²/g.1	21.6.	45.7.,	9.6.1	12.7.1	8.9.1

### B. Photocatalytic activities of the nanometer oxide SnO2

We studied the different quality of the photocatalyst to methyl orange solution in this experiment, the results are shown in figures, the concentration of the MO solution is 20 mg/L, the reaction time is 120min, the samplings were collected from the reactor each 20 min.

1) Different syntheses of  $SnO_2$  on the photocatalytic activity

Different syntheses of SnO<sub>2</sub> on the photocatalytic activity to MO are shown in Fig.6. We can know that the photocatalytic activity of SnO<sub>2</sub> prepared by constant temperature hydrolysis has the highest photoactivity, which is 97% after illumination for 2 hours, compared with SnO<sub>2</sub> synthesized by other methods. This may be attribute to the high specific surface area of SnO<sub>2</sub>, which means the more small size of SnO<sub>2</sub>, the diffuse time from bulk of SnO<sub>2</sub> to the surface of the photogenerated electron and hole become short, which makes the complex probability decrease in  $SnO_2$  bulk and makes the enhancement quantity of electron and hole arrived at the surface. At the short time electron and hole react oxidation-deoxidation with the electron donators or acceptors, and the separate efficiency of photoinduced electron is high, thus the photogenerated electron and hole can be effectively used. Furthermore, small particle and high specific surface area benefit the adsorption of oxygen and the degradation organic substance onto the surface of SnO<sub>2</sub>, which make the reaction speed fast, so SnO<sub>2</sub> has more perfect photocatalytic activity.



Figure 7. Different syntheses of SnO<sub>2</sub> on the photocatalytic activity

## *2) Effect of calcination temperature on the photocatalytic activity*

The effect of heat-treating temperature on the photocatalytic activity of  $SnO_2$  is shown in Fig. 7. The final degradation rate of MO after reaction for 120 min is increased with increasing calcination temperature before 800°C and then decreased, which may be attributed to some variation in phase composition and particle size. For samples

calcined at 600 °C, 700 °C, 800 °C and 900 °C, the size of  $\text{SnO}_2$  are 12.2 nm, 15.8 nm, 20.7 nm, 24.1 nm, respectively. The high photocatalytic activity of  $\text{SnO}_2$  was obtained at 800 °C, which was attributed to higher specific surface area, which was according with the result in Table 1. Higher specific surface area benefits the adsorption of reagent on the surface of photocatalysts, which exhibits higher photocatalytic efficiency.



Figure 8. Effect of heat-treating temperature on the photocatalytic activity of  $SnO_2\,$ 

## 3) Effect of different metal ions coated in SnO<sub>2</sub> on the photocatalytic activity

Effect of different metal ions coated in  $SnO_2$  with the coating dosage 0.5% on the photocatalytic activity was shown in Fig.8. Effective coated metal ions should accord with two conditions, one is that the coated metal ions can capture electron and hole to make them separate effectively, and the other is that the captured electron and hole can be released and transfer to the reaction interface. From Fig.7, we know that the photocatalytic activities after coating with different ions are all lower then that of  $SnO_2$ . This may be due to the broadener of surface space charge layer, which results in the less separation of photogenerated electron-hole pairs gained by light inspiring of  $SnO_2$ , thus the life of the photo shortened. This may be also because the coated metal ions became the new center of the coupled electron-hole pairs, which results in the reduction of photocatalytic activity.



Figure 9. Effect of different metal ions coated in SnO<sub>2</sub> on the photocatalytic activity

## 4) Effect of photocatalysts dosage on the photocatalytic activity

The photocatalytic degradation of methyl orange over different quality of SnO<sub>2</sub> sample was investigated and the results were shown in Fig.10. The quality of the photocatalyst in the figure is corresponding with 50mg, 100mg and 150mg, respectively. According to the results, the degradation effect was more obviously with the quality increase, the property quality of photocatalyst is 100 mg to the concentration of the dyestuff is 20mg/L. As shown, with catalyst loading increasing, the photocatalytic reactivity increases but the increasing tendency lows down gradually. When the catalyst loading of  $SnO_2$  is 50 mg, the degradation rate is 35%. While the loading reaches 100 mg, the degradation rate is 97%, and the degradation rate is 100 % when the loading is 150mg. This phenomenon could be explained as following: when the catalyst loading is small, the photon absorbed by catalyst and utilized for the photocatalytic reaction is also few, which results in low photocatalytic activity.



Figure 10. Effect of photocatalysts dosage on the photocatalytic activity

With the increase of the catalyst loading, the number of photon absorbed and active centers on the surface of catalyst increase, resulting in the improvement of the activity. But as the catalyst loading becomes larger, the number of photon tends to a saturation value. When the quality of photocatalyst achieves a certain dosage, it will produce negative influence because of their enveloping each other, which induces not sufficient to use the resource of illumination. The larger loading catalyst probably brings about light blocking which has an impact on the photocatalytic efficiency and also results in the waste of catalyst.

5) Effect of pH of the methyl orange solution on the photocatalytic activity





Figure 11. Effect of pH of the methyl orange solution on the photocatalytic activity

The dependence of the initial pH value of reaction suspensions on the degradation rate of MO containing 100 mg of photocatalysts was investigated in Fig.11. The result showed that the initial pH value of reaction suspensions is about 6 when the degradation rate was the highest. Results show that the initial pH values of reaction suspensions have effect on the photocatalytic activity. Therefore, efficient charge separation increases the lifetime of the charge carriers and reduces the recombination of the nanoparticles, thus increases the quantum efficiency.

The degradation is less high in the alkaline condition, while in the acidic condition, the degradation is correspondingly higher. This is because organic compound in the solution react with the dissolved oxygen into ground state charge transfer compound, which become into inspiring state under light and dissociating into R and O unrestricted radicels in the acidic condition, this accelerate the photo oxidation of organic compound. The pH of solution can change the charges of particle surface, which results in the disperse condition in the solution. When the pH is close to 6, there is no surface charge of SnO<sub>2</sub>, and because of the play of Van Der Waals force, it is not easy to conglomerate between particles, which benefits the disperse. So when the pH of solution is close to 6, the degradation efficiency of the organic solutions is higher.

#### IV. CONCLUSIONS

Nanometer oxide SnO<sub>2</sub> with the structure of cubic-type was gained after sintering the precursor at 800°C for 1h, the precursor was synthesized by constant temperature hydrolysis. The mean grain size is about 20-30nm and specific surface area of 16.57m<sup>2</sup>/g. The photocatalytic activities of SnO<sub>2</sub> were evaluated using the photodegradation of methyl orange as a mode organic pollutant, which were compared with that of SnO<sub>2</sub> prepared by microwave hydrolysis, chemical precipitation and solid state reaction. It showed higher photocatalytic activity for MO than that made from other methods, and the decoloration of MO reached to 97% under illuminating with 300-W high-pressure mercury lamp at 120 min when the concentration of methyl orange is 20 mg/L, the photocatalyst is 100 mg and the solution pH value is 6. As a result, SnO<sub>2</sub> nanopowder has good crystalline, dispersivity and small diameter, and it has good photocatalytic activity to MO under UV irradiation.

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