



# Effects of calcination temperatures and additives on the photodegradation of methylene blue by tin dioxide nanocrystals

Xia Wan<sup>a</sup>, Rui Ma<sup>a</sup>, Shaolong Tie<sup>a,\*</sup>, Sheng Lan<sup>b</sup>

<sup>a</sup> School of Chemistry and Environment, South China Normal University, Guangzhou 510006, PR China

<sup>b</sup> School of Information and Optoelectronic Science and Engineering, South China Normal University, Guangzhou 510006, PR China

## ARTICLE INFO

Available online 6 September 2014

### Keywords:

SnO<sub>2</sub> nanocrystal  
Photocatalysis  
Calcination temperature  
Additive

## ABSTRACT

The tin dioxide (SnO<sub>2</sub>) nanocrystals were synthesized by direct precipitation method and a series of SnO<sub>2</sub> samples were obtained via calcining SnO<sub>2</sub> at different temperatures. The characteristics of SnO<sub>2</sub> samples were investigated by scanning electron microscope (SEM), X-ray diffraction (XRD), fourier transform infrared spectroscopy (FT-IR), Brunauer Emmett Teller (BET), photoluminescence spectroscopy (PL), and UV–vis diffuse reflectance spectroscopy (DRS). The effects of calcination temperatures and additives on the photodegradation of methylene blue (MB) on SnO<sub>2</sub> samples under UV-light irradiation have been researched. The results showed that the SnO<sub>2</sub> sample with low temperature-treated ( $T \leq 200$  °C) exhibits the highest degradation efficiency, while with increasing temperature-treated (from 400 °C to 1000 °C) SnO<sub>2</sub> samples show decreasing degradation activities. The additives, such as methanol, sodium fluoride, Fe(III), Ag<sup>+</sup>, and terephthalic acid showed different influences on MB degradation in UV/SnO<sub>2</sub> systems. It has been demonstrated that in SnO<sub>2</sub>-MB systems both hydroxy radicals (OH<sup>•</sup>) generated on the surface of SnO<sub>2</sub> and photogenerated holes ( $h_{vb}^+$ ) in the valence band (VB) of SnO<sub>2</sub> jointly control the photo-oxidation process of MB. In SnO<sub>2</sub> system with increasing temperature-treated ( $T \geq 400$  °C) the contribution of OH<sup>•</sup> to MB degradation gradually decreased due to the diminution of surface-bonding hydroxyl groups (–OH) and chemisorbed water (H<sub>2</sub>O) molecules on the surface of SnO<sub>2</sub>, by comparison, the contribution of  $h_{vb}^+$  increased. The effects of Ag<sup>+</sup> and Fe(III) species on MB degradation and the formation of OH<sup>•</sup> were investigated in detail and the mechanisms have been discussed. The presence of Ag<sup>+</sup> ion at low concentration promotes the degradation of MB by capturing the photogenerated electrons ( $e_{cb}^-$ ) on the surface of SnO<sub>2</sub> catalyst, suppressing the recombination of photogenerated electrons and holes. The presence of Ag<sup>+</sup> ion at high concentration observably reduces the degradation in catalyst system which the photodegradation process is controlled by OH<sup>•</sup>, conversely, it intensively promotes the degradation in which the photodegradation process is controlled by  $h_{vb}^+$ . The effects of Fe(III) species on the degradation are similar to those of Ag<sup>+</sup> ions.

© 2014 Elsevier Ltd. All rights reserved.

## 1. Introduction

Semiconductor oxides, such as titanium dioxide (TiO<sub>2</sub>) and zinc oxide (ZnO), have been widely used as photocatalysts

\* Corresponding author. Tel./fax: +86 20 39310187.  
E-mail addresses: [waxia@scnu.edu.cn](mailto:waxia@scnu.edu.cn) (X. Wan),  
[tiesl@scnu.edu.cn](mailto:tiesl@scnu.edu.cn) (S. Tie).

<http://dx.doi.org/10.1016/j.mssp.2014.07.048>

1369-8001/© 2014 Elsevier Ltd. All rights reserved.

owing to their high activities, low costs, and environmentally friendly features [1,2]. SnO<sub>2</sub> is a direct wide band-gap semiconductor with n-type conductivity. In comparison with TiO<sub>2</sub> and ZnO in which the band gap energies are about 3.2 eV and 3.3 eV, respectively, the band gap energy ( $E_g$ ) of SnO<sub>2</sub> lies at about 3.8–4.0 eV. The reduction potential of hole ( $h_{vb}^+$ ) in the VB of SnO<sub>2</sub> lies at about +3.7 V (vs. a standard hydrogen electrode (SHE) with pH=7) and situates at the deepest level in comparison with TiO<sub>2</sub> at +2.7 V and ZnO at +2.7 V [3], indicating that the photogenerated holes ( $h_{vb}^+$ ) in the VB of SnO<sub>2</sub> have super strong oxidative power to decompose most organic compounds [4,5]. On the other hand, the reduction potential of photogenerated electron ( $e_{cb}^-$ ) in the conduction band (CB) of SnO<sub>2</sub> locates at +0.14 V (vs. SHE), which is lower than that of one electron reduction for the surface-adsorbed oxygen (−0.046 V vs. SHE) [6]. This situation causes the fact that  $e_{cb}^-$  cannot be captured by one electron reduction process, so the accumulated electrons result in the fast recombining with  $h_{vb}^+$  and the resulting reduction of photocatalytic activity. Therefore, suppressing the recombination of electron–hole pair in SnO<sub>2</sub> system is an effective pathway to improve the photocatalytic efficiency. Doping other elements in SnO<sub>2</sub> is regarded as a very useful way to enhance the charge separation of electron–hole pair [7,8]. Coupling two or three semiconductor oxides with different band gap energies has been demonstrated as one of the most effective ways to enhance the photocatalytic efficiency, such as SnO<sub>2</sub>/TiO<sub>2</sub> [9], SnO<sub>2</sub>/ZnO [10], and SnO<sub>2</sub>/ZnO/TiO<sub>2</sub> [11].

The photocatalytic efficiency of catalyst is influenced by intrinsic and extrinsic factors. Except for the intrinsic factors, such as changing the composition of catalyst via doping other elements and coupling different catalysts together, the extrinsic factors, like pH value, irradiation light source, reaction temperature, and the presences of dissolved organic substances and inorganic ions, known as additives, also strongly influence the photocatalytic processes. It has been demonstrated that the presence of alcohol strongly interfered the photocatalytic reaction via capturing hydroxyl radicals (OH<sup>•</sup>) and holes ( $h_{vb}^+$ ) generated during UV and/or visible light irradiation [12], consequently, the photocatalytic mechanism could be inferred. The presences of various dissolved metal ions are common in underground, ground and industrial waste water, and they can influence the efficiency of photocatalytic removal of contaminant. Studying the effects of metal ions on degradation processes is necessary and useful. For example, some metal ions, like Ag<sup>+</sup>, Au<sup>3+</sup> and Pd<sup>2+</sup> ions, can capture photogenerated electron to convert into metal solid and deposit on the surface of catalyst, resulting in the reduction of electron–hole recombining. This phenomenon could be used to synthesize core–shell structure material or to enhance the photocatalytic efficiency of catalyst [13–15].

Although there is a little research on Ag<sup>+</sup> or Fe(III) ions decorated or doped in SnO<sub>2</sub> photocatalysts [5,7,9,16], to the best of our knowledge, there is no report on the effects of Ag<sup>+</sup> and Fe(III) species presenting in SnO<sub>2</sub> suspensions on photocatalytic processes. In this study, we synthesized series of SnO<sub>2</sub> samples with different particle sizes and investigated the effects of additives, including methanol, Ag<sup>+</sup> and Fe(III) species, on the photocatalytic degradation of MB.

The mechanisms of photocatalytic processes in SnO<sub>2</sub>–MB systems were discussed. Since some additives often occur in waste water, the investigation may be helpful for the rational design and application of photocatalyst system.

## 2. Materials and experimental methods

### 2.1. Raw materials

Anhydrous tin tetrachloride [SnCl<sub>4</sub>, A.R.], sodium acetate [CH<sub>3</sub>COONa, A.R.], sodium hydroxide [NaOH, A.R.], hydrochloric acid [HCl, A.R.], ferric nitrate [Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O, A.R.], sodium fluoride [NaF, A.R.], silver nitrate [AgNO<sub>3</sub>, A.R.], and methylene blue (≥98.5%) were purchased from Tianjin Fine Chemicals Development Centre. Methanol (MeOH) is of HPLC grade quality and purchased from Aladdin's Reagent Company Limited. Terephthalic acid (TPA) was purchased from Shanghai Jingchun Industrial Corporation Limited and purified by reprecipitation method [17] to terephthalic acid disodium salt. Except TPA, the other chemicals in this study were used directly without further purification.

### 2.2. Synthesis of SnO<sub>2</sub> nano-catalyst

For obtaining the catalyst with a larger surface-to-volume ratio a direct precipitation method at mild temperature (~92 °C) and normal pressure was chosen to prepare SnO<sub>2</sub> sample. SnCl<sub>4</sub> and NaOH are used as starting reagents. Typically, 0.0133 mol (3.465 g) anhydrous SnCl<sub>4</sub> was dissolved in 100 mL 2 mol L<sup>−1</sup> HCl solution (solution A) and about 10 g NaOH was dissolved in 100 mL deionized water (solution B). The 800 mL deionized water loaded in a 2000 mL three-necked bottle was heated to 92 °C, then solutions A and B were added dropwise into the three-necked bottle with stirring automatically and the adding process lasted for 2 h. After the dropping, the pH value of the suspension was adjusted to 6.0 with NaOH or HCl solution, then continually kept temperature at 92 °C for 1 h, aged at 60 °C for 18 h, then filtered and washed several times with deionized water, dried at 80 °C in an oven for 24 h. Finally, a SnO<sub>2</sub> sample was obtained and denoted by S000. S000 was thermally treated at 200 °C, 400 °C, 600 °C, 800 °C, and 1000 °C in air for 3 h, respectively, so the S200, S400, S600, S800, and S1000 samples were obtained.

### 2.3. Photocatalytic activity testing

In order to evaluate the photocatalytic property of SnO<sub>2</sub>, MB was chosen as a decomposition target. Because the excited energy must be higher or equal to the band gap  $E_g$  of SnO<sub>2</sub> (about 3.8 eV), a 125 W low-pressure mercury lamp predominantly emitting at 254 nm (produced by Philips Electronics Ltd.) was chosen as an irradiation source. For maintaining the ionic strength of degradation solution, sodium acetate (CH<sub>3</sub>COONa) was added in MB solution. The preparative experiments have proved that the presence of 0.1 mol L<sup>−1</sup> CH<sub>3</sub>COONa in 40 mg L<sup>−1</sup> MB solution did not influence the rate constant of MB degradation. For each condition, 0.05 g SnO<sub>2</sub> catalysts were dispersed in 50 mL of

Download English Version:

<https://daneshyari.com/en/article/728483>

Download Persian Version:

<https://daneshyari.com/article/728483>

[Daneshyari.com](https://daneshyari.com)