The High Photocatalytic Activity of SnO$_2$ Nanoparticles Synthesized by Hydrothermal Method

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Tin oxide nanoparticles (SnO$_2$ NPs) were prepared at low temperature by hydrothermal method. Synthesized SnO$_2$ NPs were confirmed via characterization techniques such as UV-visible spectroscopy (UV-vis), X-ray diffraction (XRD), and Transmission Electron Microscope (TEM). The synthesized nanoparticles were in the size of 3 nm and they have high photocatalytic activity. The result showed that SnO$_2$ NPs degraded 88.88% MB solution after 30 minutes of UV illumination and reached 90.0% for 120 minutes (2 hours) of UV illumination. Moreover, they degraded 79.26% MB solution after 90 minutes (1.5 hours) under assisted sunlight illumination.

1. Introduction

In recent years, nanomaterials attracted much attention due to their high surface-to-volume ratio, enhanced characteristics of quantum size effects, and the high fraction of chemically similar surface sites [1]. Among metal oxide semiconductor materials, tin dioxide (SnO$_2$) has been attracting a great deal of research interest owing to its outstanding physical and chemical properties [2–4]. SnO$_2$ is an n-type semiconductor with a wide band gap of 3.6 eV at room temperature, having excellent optical and electrical properties such as peculiar optical transparency, low resistivity, and high theoretical specific capacity [5, 6]. Moreover, SnO$_2$ possesses a high electron mobility (∼100–200 cm$^2$ V$^{-1}$ s$^{-1}$), indicating a faster transport of photoexcited electrons [7–9]. In the last decade, SnO$_2$ has been studied as promising material with many unique surface properties including luminescence and photocatalytic activity [2]. In particular, as the diameter of SnO$_2$ is smaller than excitons and carriers are confined in all three dimensions to a nanometer size region, the high band gap energy and high stability of SnO$_2$ nanoparticles (SnO$_2$ NPs), unique properties such as the blue shift of the band edge transition energy, and unusual structural and optical properties take place [10, 11]. Moreover, the high degradation rate of the organic dye on the as-synthesized SnO$_2$ NPs with size below 10 nm can be attributed to the small size of SnO$_2$ NPs because the large surface area helps to increase the photocatalytic reaction sites and promotes the efficiency of the electron-hole separation [12–14].

There are many methods to synthesize SnO$_2$ NPs, such as sol-gel [2, 15], hydrolysis [16], electrochemical oxidation of tin metal sheet in a nonaqueous electrolyte containing NH$_4$F [17], the chemical coprecipitation route [18, 19], dropping ammonium hydroxide into tin salt solution under sonication [20], and a microwave irradiation method [21, 22]. However, the hydrothermal method with an aqueous solvent as a reaction medium is environmentally friendly because the reactions are carried out in a closed system. Hydrothermal synthesis involves use of water as a solvent at elevated temperatures and pressures in a closed system and certain properties of the solvents such as density, viscosity, and diffusion coefficient change [23, 24]. Furthermore, hydrothermal synthesis is often used due to its simple processes and equipment, without high temperature sintering, allowing the control of the grain size, morphology, and degree of crystallinity by easy changes in the experimental procedure [25].
In the present work, we synthesize SnO$_2$ NPs powder via a simple hydrothermal method from tin chloride, sodium hydroxide, and hydrazine hydrate. The trick in the hydrothermal method presented here is the application of hydrazine hydrate (N$_2$H$_4$-H$_2$O), which served as both the alkali and the ligand to coordinate with Sn ions to form a complex cluster. Furthermore, the hydrothermal process is desirable for the large-scale fabrication of other ultrafine oxide nanoparticles [1]. Besides, the photodegradation of dye organics by solar irradiation is a comparatively greener approach than by UV-light [26]. Previous publications on the photocatalytic activity of SnO$_2$ NPs often use UV-light as excited source for photoreactions. Herein, we synthesized SnO$_2$ particles with diameters <10 nm, which presents excellent photocatalytic degradation using MB as a model pollutant in the presence of UV-light and direct sunlight.

2. Experimental

2.1. Materials. Tin chloride (SnCl$_2$·5H$_2$O, Merck, 99.99% pure), hydrazine hydrate (N$_2$H$_4$-H$_2$O, 99% pure), sodium hydroxide (NaOH, 99%), methanol (CH$_3$OH, 99% pure), and methylene blue (C$_{16}$H$_{18}$N$_2$Cl, JHD Fine Chemicals, China, 99%) were used. Deionized (DI) water was obtained from a laboratory water purifier. In the experiment, 0.9028 g SnCl$_2$·5H$_2$O was added into 25.75 mL DI water and 1.14 mL hydrazine hydrate (N$_2$H$_4$·H$_2$O). After that, solutions were adjusted to pH = 12 by the addition of the NaOH solution and transferred to a stainless autoclave. Finally, it is heated at 135°C for 24 hours and cooled naturally to room temperature. The product was centrifuged, filtered out, rinsed with methanol and DI water several times, and then dried at 120°C for an hour in the air.

2.2. Synthesis of SnO$_2$ NPs by the Hydrothermal Method. SnO$_2$ NPs were prepared using the hydrothermal method. Firstly, 0.9028 g SnCl$_2$·5H$_2$O was introduced into a mixed solution of 25.75 mL DI water and 1.14 mL hydrazine hydrate (N$_2$H$_4$·H$_2$O). After that, solutions were adjusted to pH = 12 by the addition of the NaOH solution and transferred to a stainless autoclave. Finally, it is heated at 135°C for 24 hours and cooled naturally to room temperature. The product was centrifuged, filtered out, rinsed with methanol and DI water several times, and then dried at 120°C for an hour in the air.

2.3. Characterization of SnO$_2$ NPs. The size and morphology of SnO$_2$ NPs were characterized by TEM (JEM 1400 Instrument, JEOL). XRD analysis was carried out (Bruker D8-Advance 5005) at a voltage of 45 kV with Cu Kα radiation (λ = 1.5406 Å) to examine the crystalline phase of synthesized nanoparticles. The Fourier transform infrared spectroscopy (FT-IR) spectrum was recorded on a FT-IR spectrometer (Vertex 80, Bruker, Germany) over the range of 400 to 4000 cm$^{-1}$ in transmission mode at room temperature to identify the functional group present on SnO$_2$ NPs and responsible for the stability of nanoparticles.

2.4. Photocatalytic Activity of SnO$_2$ NPs for Degradation of the MB Solution. In order to determine the photocatalytic activity of the SnO$_2$ NPs, we use the MB dye solution as a model of contamination to characterize their photocatalytic activity. In the experiment, 30 mL of the MB solution (10 mg/L) and 0.03 grams of catalyst were used. This solution was stirred for 10 minutes in dark for the equilibrium of the adsorption and desorption process of MB with NPs. After stirring, the solution was irradiated by UV lamp (Osram, Germany) and direct sunlight conditions. The UV lamp has radiation of 350 nm with 7 W of lamp power. Concentrations of the MB solution initially and after every 15 minutes of irradiation of UV-light were taken by using UV-visible spectrophotometer (U2910, Hitachi, Japan). In case these solutions irradiated by sunlight, the experiments were carried out on a sunny day at Ho Chi Minh City between 10 a.m.–1 p.m. with outside temperature from 35°C to 40°C and these experiments were tested 3 times.

3. Results and Discussion

3.1. X-Ray Diffraction (XRD) Pattern Analysis. The XRD pattern of the product is shown in Figure 1. The peaks at 2θ values of 26.6°, 33.8°, 51.8°, and 65.9° can be associated with (110), (101), (211), and (301), respectively. A matching of the observed and standard planes confirmed that the product is of SnO$_2$ having a tetragonal structure, which are in good agreement with the literature values (JCPDS card number 41-1445). The average particle size ($D$) was estimated using the following Scherrer equation [30, 31]:

$$D = \frac{0.9\lambda}{\beta\cos\theta},$$

where $D$ is the crystallite size, $\lambda$ is the X-ray wavelength, $\beta$ is the full width at half maximum of the diffraction peak, and $\theta$ is the Bragg diffraction angle of the diffraction peaks. The average particle size of SnO$_2$ calculated using Scherrer equation of SnO$_2$ is 3 ± 0.1 nm.

Comparison of the XRD pattern of the as-synthesized samples is as follows: the samples calcined at 300°C in flowing air for 2 hours (Figure 1(b)) do not change characterization peaks of SnO$_2$ peaks and the intensity of peaks do not increase significantly. Therefore, we only use the as-synthesized samples for survey continuously.

3.2. Transmission Electron Microscopic Analysis (TEM). The morphology and the particles size of the samples were obtained by TEM images (Figure 2(a)). The image shows that spherical shaped nanoparticles have been formed and they were uniformly distributed except for a few aggregated.

![Figure 1: XRD patterns of the (a) as-synthesized and (b) thermally treated SnO$_2$.](image-url)
3.3. Fourier Transform Infrared Spectroscopy. The FT-IR spectroscopy was recorded at room temperature for determination of the functional group of materials available in the nanopowders. The FT-IR spectrometer was used for the analysis in a range between 4000 and 380 cm\(^{-1}\), as shown in Figure 3. The band around 3454.29 to 3539.64 cm\(^{-1}\) and 1612.43 cm\(^{-1}\) indicates the presence of O-H group due to stretching vibrations of water molecules or hydroxyl groups absorbed at the surface of SnO\(_2\) and also to stretching vibrations of Sn-OH groups [26, 32]. The band around 3196.74 cm\(^{-1}\) and 2928.99 cm\(^{-1}\) indicates the presence of C-H group. The peak around 608.14 cm\(^{-1}\) is assigned to Sn-O-Sn stretching mode of surface bridging oxide formed by the condensation of adjacent surface hydroxyl groups [25, 26, 32]. Therefore, the presence of these bands confirmed the formation of SnO\(_2\).

3.4. Photocatalytic Activity of SnO\(_2\) NPs. The photocatalytic activity of SnO\(_2\) NPs was examined by the changes in the absorption spectra of the MB dye solution during their photodegradation process. Figure 4(a) shows that commercial SnO\(_2\) degraded of 20.49\% MB solutions after 30 minutes of UV lamp illumination and it mostly does not degrade when increasing illumination time. Figures 4(b) and 4(c) show the change of the absorption of MB solution when it obtained SnO\(_2\) NPs under different UVA irradiation times. Figure 4(b) shows that the degradation activity of SnO\(_2\) NPs is better than the commercial SnO\(_2\). Figure 4(c) is a magnified image of Figure 4(b). It shows that the typical absorption peak of MB at 664 nm wavelength is significantly decreased. However, when the irradiation time increases from 15 minutes to 180 minutes, the decline of the absorption peak of MB is insignificant. Besides, Figures 4(b) and 4(c) indicate that SnO\(_2\) NPs degraded 88.88\% MB solution after 30 minutes of UV illumination and reached 90.0\% for 120 minutes (2 hours) of UV illumination. These results show that the more the illumination time increases, the more the concentration of MB dye decreases, which is shown by the decrease in UV-absorbance spectra. It can be seen that the intensity of the absorption peak gradually decreases with increasing UV illumination time.

Figure 5 shows the photocatalytic activity of SnO\(_2\) NPs according to UV illuminated times condition. After 15 minutes of UV illumination, SnO\(_2\) NPs degraded strongly MB solutions and nearly saturated during the time from 30 minutes to 180 minutes. Whereas, the degradation of commercial SnO\(_2\) is weak and unstable.

The mechanism for photodegradation of MB dye can be explained as follows [33, 34]. Because SnO\(_2\) NPs are synthesized by hydrothermal method, there are the generated oxygen vacancies in SnO\(_2\) crystal, and these can induce the formation of new energy levels in the band gap. After the heat treatment of Sn(OH)\(_4\), the hydroxyls remaining in the structure will generate molecular water, while releasing the lattice oxygen and producing a neutral oxygen vacancy (V\(_O\)) in its position. Also the high pressure produced in the hydrothermal process is in favor of
Figure 4: UV-visible absorbance spectra for photodegradation of MB dye according to illumination time under UVA irradiation: using commercial SnO$_2$ (a) and using SnO$_2$ NPs (b) and a magnified image (c).

The process can be expressed as follows:

$$\text{SnO}_2 \leftrightarrow \text{SnO}_{2-n} + \frac{n}{2}\text{O}_2(g)$$  \hspace{1cm} (2)$$

$$\text{O}_x^+ \leftrightarrow \frac{1}{2}\text{O}_2(g) + V_0$$  \hspace{1cm} (3)$$
These neutral vacancies may be singly ionized vacancies as \( V_0^* \) or \( V_0^- \). Semiconductor photocatalytic activity has attracted great interest due to its potential applications in the degradation of environmental pollutants and organic pollutant transformation.

So, electron (\( e^- \)) is excited from the valence band into the conduction band, generating hole (\( h^+ \)) when a photon with energy of \( hv \) matches or exceeds bandgap energy, \( E_g \), of semiconductor \( \text{SnO}_2 \):

\[
\text{SnO}_2 + hv \rightarrow e^- + h^+ \tag{4}
\]

\[
h^+ + \text{H}_2\text{O} \rightarrow \text{OH} + \text{H}^+ \tag{5}
\]

\[
\text{OH}^- + h^+ \rightarrow \cdot \text{OH} \tag{6}
\]

\[
\text{O}_2^- + e^- \rightarrow \cdot \text{O}_2^- \tag{7}
\]

\[
\cdot \text{O}_2^- + \text{H}^+ \rightarrow \cdot \text{OOH} \tag{8}
\]

\[
\text{MB} + hv \rightarrow \text{MB}^* \tag{9}
\]

\[
\text{MB}^* + \text{SnO}_2 \rightarrow \text{MB} + \text{SnO}_2 (e^-) \tag{10}
\]

\[
\text{SnO}_2 (e^-) + \text{O}_2 \rightarrow \text{SnO}_2 + \text{O}_2^- \tag{11}
\]

\[
\text{SnO}_2 (e^-) + \cdot \text{O}_2^- + 2\text{H}^+ \rightarrow \text{SnO}_2 + \text{H}_2\text{O}_2 \tag{12}
\]

\[
\text{SnO}_2 (e^-) + \text{H}_2\text{O}_2 \rightarrow \text{SnO}_2 + \cdot \text{OH} + \text{OH}^- \tag{13}
\]

\[
\text{MB}^* + \text{O}_2 \text{ or } \cdot \text{O}_2^- \text{ or } \cdot \text{OH} \rightarrow \text{degradation compounds} \tag{14}
\]

In the photocatalytic reaction, \( \cdot \text{O}_2^- \) and \( \cdot \text{OH} \) radicals are the extremely strong reduction and oxidation agent, respectively.

Figure 6 shows the UV-visible absorbance spectra for the photodegradation of MB dye of commercial \( \text{SnO}_2 \) and \( \text{SnO}_2 \) NPs under direct sunlight. Sunlight assisted photodegradation property of \( \text{SnO}_2 \) NPs was investigated and it shows the photodegradation efficiency of 79.26% MB solution after 90 minutes (1.5 hours) under direct sunlight illumination. Otherwise, the commercial \( \text{SnO}_2 \) powder only degrades 36.23% of MB solution. Besides, we compared with previous studies of other researchers for the photocatalytic degradation of MB using \( \text{SnO}_2 \) NPs. These results show that the degradation ability of \( \text{SnO}_2 \) NPs with MB solution is very high under both UV illumination and sunlight. It is indicated that only a very small amount of \( \text{SnO}_2 \) NPs (0.03 grams) was degradable more over 90% MB solution under UV illumination condition (power of lamp is 7 W) for 2 hours.

A comparison between the present study and studies conducted by other researchers is shown in Table 1. The comparison also showed that the synthesized \( \text{SnO}_2 \) NPs in this research have extremely high photocatalytic activity.

4. Conclusion

\( \text{SnO}_2 \) NPs of average size 3 nm synthesized by hydrothermal method from tin chloride, sodium hydroxide, and hydrazine hydrate. The photodegradation efficiency of \( \text{SnO}_2 \) NPs with MB solution is very high under both UV illumination and sunlight. \( \text{SnO}_2 \) NPs degraded strongly MB solutions (>80.0%) after 15 minutes of UV illumination and degraded 79.26% MB solution after 90 minutes under sunlight irradiation.
Table 1: The comparison of the photocatalytic degradation of dyes using SnO₂ NPs.

<table>
<thead>
<tr>
<th>Catalysts (shape and particles size)</th>
<th>Light source</th>
<th>Dye (initial concn)</th>
<th>Volume (mL)</th>
<th>% degradation</th>
<th>Irradiation time (mins)</th>
<th>Catalyst concn (g)</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>SnO₂ NPs (~3 nm)</td>
<td>7 W UV lamp, visible light $\lambda = 350$ nm Direct sunlight</td>
<td>MB, 10 mg/L</td>
<td>60</td>
<td>90.0</td>
<td>120</td>
<td>0.03</td>
<td>This work</td>
</tr>
<tr>
<td>SnO₂ NPs (15–40 nm)</td>
<td>Low pressure 125 W UV lamp, visible light $\lambda = 254$ nm</td>
<td>MB, 20 mg/L</td>
<td>100</td>
<td>93.3</td>
<td>120</td>
<td>0.2</td>
<td>[3]</td>
</tr>
<tr>
<td>SnO₂ NPs (~4 nm)</td>
<td>UV lamp, $\lambda = 365$ nm (power of lamp: nondetermined)</td>
<td>Phenol red, 1 mL, $10^{-4}$ M</td>
<td>1.0</td>
<td>100</td>
<td>120</td>
<td>0.25</td>
<td>[27]</td>
</tr>
<tr>
<td>Microspherical (0.4–1.8 $\mu$m diameter)</td>
<td>Four 8 W UV lamps (Philips UV-A, $\lambda = 350$ nm)</td>
<td>Aniline, 20 mg/L 4-Nitroaniline (20 mg/L) 2,4-Dinitroaniline (20 mg/L)</td>
<td>10</td>
<td>80 70 50</td>
<td>120</td>
<td>0.1</td>
<td>[28]</td>
</tr>
<tr>
<td>Spherical SnO₂ quantum dots (~2.5–4.5 nm)</td>
<td>Direct sunlight</td>
<td>Rhodamine B ($10^{-7}$ M) MB ($10^{-4}$ M)</td>
<td>200</td>
<td>83.9 56.8</td>
<td>420 360</td>
<td>0.01</td>
<td>[26, 29]</td>
</tr>
</tbody>
</table>
Competing Interests

The authors declare that they have no competing interests.

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