Effect of calcination temperature and reducing agent used in the synthesis of black titanium dioxide on photocatalytic degradation of methyl orange

Saran Saensook and Akawat Sirisuk*

Center of Excellence in Catalysis and Catalytic Reaction Engineering, Department of Chemical Engineering, Faculty of Engineering, Chulalongkorn University, Bangkok 10330, Thailand

*E-mail: akawat.s@chula.ac.th

Abstract:

This research studied the synthesis of black titanium dioxide for the photocatalytic degradation of methyl orange in aqueous solution. First, titanium dioxide was synthesized via a sol-gel method. Then sodium borohydride powder was used as the reducing agent to carry out the chemical reduction of TiO$_2$ in order to obtain black TiO$_2$. A $2^2$ factorial experimental design was employed to evaluate the significance of the following two factors: (1) calcination temperature and (2) the amount of reducing agent. The calcination temperature was varied at 400 and 500 °C, while the molar ratio of NaBH$_4$ to TiO$_2$ was varied at 0:1 and 1:1. In this experiment, the catalysts were used for photocatalytic degradation of an aqueous solution of 10 ppm methyl orange. The solution and the catalyst were placed in the annular photoreactor in the absence of light for 60 minutes and were then irradiated by either UV or visible light bulbs for 180 minutes. XRD results of TiO$_2$ that were calcined at 400 and 500 °C indicated that they consisted of anatase, rutile, and brookite. Furthermore, the reduction of TiO$_2$ by NaBH$_4$ improved its photocatalytic activity because it introduced oxygen vacancies, which trapped photoexcited electrons on the surface of TiO$_2$.

1. Introduction

Water pollution is still an increasingly dangerous problem that affects people around the world.$^1$ Toxic and chemical waste in water can cause illness in humans and poison the aquatic animals.

Heterogeneous photocatalysis has been considered as one of the most effective methods for the degradation of organic pollutants because it has many benefits over the conventional method, such as no generation of polycyclic products, and fast oxidation of polluting compounds up to the minimum level.$^2$

Methyl Orange (MO) is one of azo dyes which are widely used, especially in textiles industries. It is the polluting compound that can lead to the serious environmental problems.$^2$

TiO$_2$ have been the most studied semiconductor photocatalysts for pollutant removal due to its good photocatalytic activity, low cost, nontoxicity, and high stability. Its drawback is the large band gap about 3.2 eV (for anatase) that limits the catalyst can be activated under UV irradiation only. Therefore, its application under direct solar light or visible light is limited.$^3$

Black TiO$_2$ nanomaterials have been developed because of its ability to utilize the visible light, leading to markedly enhanced photocatalytic activity towards photocatalytic pollution removal and hydrogen generation from water.$^3$

Sodium borohydride (NaBH$_4$) is a commonly used reducing reagent that was chosen to synthesize black TiO$_2$ because of its high ability in reducing Ti$^{4+}$ to Ti$^{3+}$. Also it increases the density of oxygen vacancies, which consequently enhances the charge transportation in semiconductors as well as the electrical conductivity.$^4$

In this study, we investigated the photocatalytic degradation of methyl orange in aqueous phase over white and black TiO$_2$.
catalysts that were synthesized in different conditions. Factorial experimental design was employed to study the main effects and the interaction effects of the two factors.

2. Materials and Methods
2.1 Materials
The chemicals used in the preparation of the catalyst include titanium tetraisopropoxide (Ti(OC\textsubscript{2}H\textsubscript{5})\textsubscript{4}; TTIP 97%), nitric acid (HNO\textsubscript{3} 70%), sodium borohydride (NaBH\textsubscript{4} 99%) and ethanol (C\textsubscript{2}H\textsubscript{5}OH 99.5%) were purchased from Sigma-Aldrich Inc.

2.2 Synthesis of titanium dioxide
Titanium dioxide was synthesized via a sol-gel method by mixing titanium tetraisopropoxide (TTIP) in deionized water (DI) containing nitric acid (70%) as the volume ratio of TTIP:DI water: HNO\textsubscript{3} was 1:12:0.087. After adding TTIP, white precipitate formed instantaneously. The mixture was stirred for three days until clear sol was obtained. Then the clear sol was dialyzed in cellulose membrane with a molecular weight cutoff of 3500. The distilled water used in dialysis was changed daily until a pH of sol reached 3.5. Finally, the sol was dried and calcined at 400 or 500 ºC for 5 hours in air atmosphere as T400-5 and T500-5, respectively.

2.3 Synthesis of black titanium dioxide
Typically, 3.0 g of TiO\textsubscript{2} nanoparticles powder (from Section 2.2) and NaBH\textsubscript{4} (99%) (0 and 1.42 g corresponding to the molar ratio NaBH\textsubscript{4}/ TiO\textsubscript{2} of 0:1 and 1:1, respectively) were mixed and ground thoroughly for at least 30 minutes. Then the mixtures were charged in a porcelain boat, and placed in a tubular furnace, and heated to 400 or 500 ºC with a heating rate of 10 ºC min\textsuperscript{-1} for 5 hours under an N\textsubscript{2} atmosphere. After cooling down to room temperature, the resulting black powder was washed with deionized water and ethanol and dried at 70 ºC in drying oven. The products were BT400-5-1 and BT500-5-1.

2.4 Characterization techniques
X-ray diffractometry (XRD) analysis was conducted using a SIEMENS D5000 X-ray diffractometer with a CuK\textalpha radiation source at a scan rate of 0.50 min\textsuperscript{-1} in the 20 range of 20-80º. BET specific surface area of the catalysts was measured using Micromeritics ASAP 2020 surface area analyzer. X-ray photoelectron spectroscopy (XPS) was executed on a Kratos Amicus/ESCA 3400 with AlK\textalpha X-ray source. The UV-visible diffuse reflectance spectra of the samples in the wavelength range of 200-800 nm were obtained using Perkin Elmer Lambda 650 spectrophotometer. The concentration of methyl orange was also measured by Perkin Elmer Lambda 650 spectrophotometer at the wavelength of 464 nm. Photoluminescence measurement was carried out in a Horiba Fluoromax Spectrofluorometer by using a Xenon lamp as the excitation source at room temperature.

2.5 Photocatalytic experiment
The photocatalytic activity of the catalyst was studied for the photo-degradation of methyl orange under both UV and visible light irradiations at ambient temperature. Initially, 0.40 g of catalyst was dispersed in 400 mL of an aqueous solution of 10 ppm methyl orange. The mixture was stirred in the absence of light for one hour to achieve adsorption equilibrium. After that, the mixture was exposed to either UV irradiation using 75W Philips UV-C lamps or visible light irradiation using 18W Philips TL-D standard colors lamp. During 180 minutes of irradiation, 5 mL of the solution was extracted every 15 minutes to measure the concentration of methyl orange using UV-visible spectrophotometer. The conversion (η) was calculated as follows:

\[ \eta(\%) = \frac{c_0 - c_t}{c_0} \times 100\% \quad (1) \]

where η is the conversion (%) of reaction, \( c_0 \) and \( c_t \) are the concentrations of
methyl orange at initial and different irradiation time, respectively.

### 2.6 Experimental Design

A 2² factorial experimental design was employed in this study. The two factors are calcination temperature (Factor A) and the molar ratio of reducing agent to catalyst (Factor B). Each factor was varied at two levels (as seen in Table 1). Four factorial points was run with two replicates, resulting in 8 batches of photocatalysts in total. The photocatalytic experiments were run under both UV and visible light irradiation and the conversion of methyl orange was the response used in statistical analysis.

#### 3. Results and Discussion

#### 3.1 Phase Analysis (XRD)

XRD results of the photocatalysts are presented in Figure 1. The characteristic diffraction peaks of anatase phase in TiO₂ at 20 values of 25.3°, 37.9°, 48.1°, 53.8°, 62.9°, 69.0°, and 75.3° were observed, while diffraction peaks at 27.4°, 36.1°, and 41.3° corresponded to rutile phase and the peak at 30.8° was assigned to brookite phase. These diffraction peaks were clearly observed in white TiO₂ (see Figures 1a and 1b), suggesting high crystallinity in the sample. When the calcination temperature was increased from 400 to 500 °C, the anatase phase was transformed to the rutile phase and the crystallite size increased (see Table 2) due to the crystal growth and agglomeration. From Figures 1c and 1d, XRD patterns of black TiO₂ had the characteristic diffraction peaks appeared different than those of white TiO₂.

During the NaBH₄ reduction process to synthesize black TiO₂, TiO₂ could undergo the crystalline lattice deformation, resulting in oxygen vacancies and a shell of amorphous TiO₂ was formed.

#### Table 1. Preparation parameters for the synthesis of black TiO₂ used in the 2² factorial design study.

<table>
<thead>
<tr>
<th>Factor</th>
<th>Operating variables</th>
<th>Low</th>
<th>High</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Calcination temperature (°C)</td>
<td>400</td>
<td>500</td>
</tr>
<tr>
<td>B</td>
<td>Molar ratio of NaBH₄/TiO₂</td>
<td>0:1</td>
<td>1:1</td>
</tr>
</tbody>
</table>

#### 3.2 Specific surface area and pore structure

BET specific surface area, pore volume, and pore size of various TiO₂ nanoparticles are listed in Table 2. The specific surface area of TiO₂ that was calcined at 400 °C was larger than that at 500 °C due to the sintering or phase transformation occurring in TiO₂. However, the specific surface areas of black TiO₂ were not different from white TiO₂, which was calcined at the same temperature. So the reduction process did not affect the surface of TiO₂ but the pore structure of black TiO₂ may have been altered during the second calcination during the reduction.

#### Table 2 Specific surface area, total pore volume, average pore size, and crystallite size of various TiO₂.

<table>
<thead>
<tr>
<th>Sample</th>
<th>BET Surface area (m² g⁻¹)</th>
<th>Total Pore volume (cm³ g⁻¹)</th>
<th>Average pore size (nm)</th>
<th>Crystal size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>T-400-5</td>
<td>104.95</td>
<td>0.250</td>
<td>9.5</td>
<td>8.8</td>
</tr>
<tr>
<td>T-500-5</td>
<td>59.59</td>
<td>0.183</td>
<td>12.3</td>
<td>13.2</td>
</tr>
<tr>
<td>BT-400-5-1</td>
<td>105.36</td>
<td>0.224</td>
<td>8.5</td>
<td>9.8</td>
</tr>
<tr>
<td>BT-500-5-1</td>
<td>58.40</td>
<td>0.154</td>
<td>10.5</td>
<td>12.9</td>
</tr>
</tbody>
</table>

*a Calculated by the Debye-Scherer equation and based on (101) diffraction peak.
3.3 UV-Vis diffuse reflectance spectra

To determine the optical absorption properties of the photocatalysts, UV-Vis spectra were obtained in the range of 200 to 800 nm. White TiO$_2$ (see Figures 2a and 2b) had essentially no absorption in visible light region (420-800 nm), but mainly absorbed in UV light region (< 420nm). When they were converted to black TiO$_2$, the absorption spectra in the visible light region improved significantly, which agreed with the change to a darker color after NaBH$_4$ treatment with increasing temperature because they were capable to absorb more light and produce more electron carriers (O$_V$).\textsuperscript{12-13}

![Figure 2](image-url) **Figure 2** UV-vis absorption spectra of various TiO$_2$ nanoparticles. The insets are photographs of actual TiO$_2$ nanoparticles.

The band gap energy of black TiO$_2$ became narrower than that of white TiO$_2$, as shown in Figure 3. Consequently, the photoexcitation of electrons from the valence band to the conduction band was easier, resulting in the enhancement of the photocatalytic degradation rate.\textsuperscript{14}

![Figure 3](image-url) **Figure 3** A Tauc plot of the Kubelka-Munk function versus photon energy for various TiO$_2$ nanoparticles.

3.4 PL spectra

To study the behavior of the electron and holes recombination in white and black TiO$_2$, photoluminescence measurement were performed in the wavelength range of 350-600 nm with the excitation wavelength at 325 nm (see Figure 4). The main emission peaks of all samples appeared around 467 nm. Black TiO$_2$ had the lower peak intensities than white TiO$_2$, suggesting that the recombination rate of electron and holes was slow. This was attributed to the formation of O$_V$, which can act as electron traps, leading to higher photocatalytic activity.\textsuperscript{15}

![Figure 4](image-url) **Figure 4** PL spectra for various TiO$_2$ nanoparticles

3.5 XPS analysis

X-ray photoelectron spectroscopies were employed to determine the presence of Ti$^{3+}$ and oxygen vacancies on the surface of white TiO$_2$ and black TiO$_2$. The characteristic peaks in Figures 5a and 5c at 458.4 - 458.7 eV and 464.1 - 464.3 eV were assigned to Ti$^{4+}$-O bonds for Ti$^{4+}$ 2p$_{3/2}$ and 2p$_{1/2}$, respectively, while the peaks at 456.1 - 456.6 and 459.8 - 460.4 eV corresponded to the formation of Ti$^{3+}$. The O 1s spectra (as seen in Figures 5b and 5d) consisted of two oxygen peaks: Ti-O bonds or oxygen lattice (O$_L$) at 529.6 - 530.0 eV and a hydroxyl group (O-H) or oxygen vacancies (O$_V$) at 531.9 - 532.5 eV. When compared white TiO$_2$ to black TiO$_2$, the peak area ratio of Ti$^{3+}$/Ti$^{4+}$ increased as well as the proportion of oxygen vacancies (see Table 3).
During the reduction process, the decomposition of NaBH\textsubscript{4} generated the active hydrogen and reacted with the oxygen lattice in TiO\textsubscript{2}, leading to the formation of oxygen vacancies and larger amounts of Ti\textsuperscript{3+}. The greater proportion of a hydroxyl group, which was related with O\textsubscript{v}, increased with the addition of reducing agent or temperature possibly due to the effect of the distortion of black TiO\textsubscript{2} surface.\textsuperscript{12,16}

**Table 3** The peak area ratios of titanium and oxygen for various TiO\textsubscript{2} from XPS.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Ti 2p Peak area ratio</th>
<th>O 1s peak area ratio</th>
<th>Ti\textsuperscript{3+}/Ti\textsuperscript{4+} peak area ratio</th>
<th>O\textsubscript{L}</th>
<th>O\textsubscript{V}</th>
</tr>
</thead>
<tbody>
<tr>
<td>T400-5</td>
<td>0.111</td>
<td>77.46</td>
<td>22.54</td>
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<td></td>
</tr>
<tr>
<td>T500-5</td>
<td>0.072</td>
<td>80.90</td>
<td>19.10</td>
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<tr>
<td>BT400-5-1</td>
<td>0.162</td>
<td>68.19</td>
<td>31.81</td>
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</tr>
<tr>
<td>BT500-5-1</td>
<td>0.223</td>
<td>52.97</td>
<td>47.03</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

During the reduction process, the decomposition of NaBH\textsubscript{4} generated the active hydrogen and reacted with the oxygen lattice in TiO\textsubscript{2}, leading to the formation of oxygen vacancies and larger amounts of Ti\textsuperscript{3+}. The greater proportion of a hydroxyl group, which was related with O\textsubscript{v}, increased with the addition of reducing agent or temperature possibly due to the effect of the distortion of black TiO\textsubscript{2} surface.\textsuperscript{12,16}

**3.6 Photocatalytic activity**

The photocatalytic activities of white and black TiO\textsubscript{2} were studied for methyl orange (MO) degradation under UV and visible light irradiations. As shown in Figures 6a and 6b, the methyl orange conversion after 180 minutes of UV irradiations with two white TiO\textsubscript{2} photocatalysts were about 41.3% and 38.3%. However, under visible light the conversions over the same catalyst dropped to about 25.7% and 23.3%, respectively. When black TiO\textsubscript{2} were employed in the same condition for MO degradation, the photocatalytic conversions markedly increased under both visible light irradiation (at 49.9% and 60.2%) and UV irradiation (at 59.8% and 70.4%). Black TiO\textsubscript{2} contained surface defects, which acted as the charge carrier traps as well as the adsorption site, thereby preventing the recombination of electron and hole.\textsuperscript{12}

This was attributed to enhanced light absorption in the visible region, higher electron density, and larger amounts of Ti\textsuperscript{3+} on the surface, despite a smaller BET specific surface area.\textsuperscript{13,17}

**Figure 5** XPS spectra for various TiO\textsubscript{2} nanoparticles; (a) Ti 2p and (b) O 1s for T400-5 and BT400-5-1; (c) Ti 2p and (d) O 1s for T500-5 and BT500-5-1

**Figure 6** Photocatalytic degradation of methyl orange results under (a) UV and (b) visible light irradiations
3.7 Factorial experimental design and data analysis

A $2^2$ factorial experimental design was employed to investigate the main effects and the interaction effect on the photocatalytic degradation of MO under UV and visible light irradiations and to evaluate the significance of studied parameters in the synthesis of black TiO$_2$ as mentioned above in Table 1. The analysis of variance (ANOVA) was performed and the result is summarized in Tables 4 and 5. According to the p-values, calcination temperature (Factor A) was not significant statistically. However, reducing agent (Factor B) and the interaction between the two factors were significant at $\alpha = 0.05$. This finding was the same for both photodegradation of MO under UV and visible light irradiations.

Table 4 Analysis of variance (ANOVA) for photocatalytic degradation of MO under UV irradiations.

<table>
<thead>
<tr>
<th>Source of variation</th>
<th>Sum of squares</th>
<th>Degree of freedom</th>
<th>Mean Square</th>
<th>$F$</th>
<th>P-Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>28.01</td>
<td>1</td>
<td>28.01</td>
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<td>0.1185</td>
</tr>
<tr>
<td>B</td>
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<td>1273.86</td>
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<td>0.0018</td>
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<tr>
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<td>93.64</td>
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<tr>
<td>Error</td>
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<td>4</td>
<td>7.12</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>1424.00</td>
<td>7</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 5 Analysis of variance (ANOVA) for photocatalytic degradation of MO under visible light irradiations.

<table>
<thead>
<tr>
<th>Source of variation</th>
<th>Sum of squares</th>
<th>Degree of freedom</th>
<th>Mean Square</th>
<th>$F$</th>
<th>P-Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
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<td>31.05</td>
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<tr>
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<td>24.12</td>
<td>4</td>
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<td></td>
</tr>
<tr>
<td>Total</td>
<td>2001.45</td>
<td>7</td>
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</tr>
</tbody>
</table>

4. Conclusion

In summary, black TiO$_2$ catalysts were successfully synthesized from white TiO$_2$ via NaBH$_4$ reduction process at different calcination temperature. Black TiO$_2$ that was calcined at 500 °C for 5 hours (BT500-5-1) exhibited the highest photocatalytic activities for methyl orange degradation under both UV and visible light irradiations because of slow charge recombination rate compared to white TiO$_2$. This result was in good agreement with the photoluminescence spectroscopy results. The slow recombination rate could be attributed to the greater amount of Ti$^{3+}$ and oxygen vacancies, which were formed during the NaBH$_4$ reduction process.

Acknowledgements

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