Degradation of benzene on TiO$_2$/SiO$_2$/Bi$_2$O$_3$ photocatalysts under UV and visible light

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Graphical Abstract

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Abstract: The TiO$_2$/SiO$_2$/Bi$_2$O$_3$ photocatalysts have highly activity for the degradation of benzene under UV and visible light irradiation via different reaction pathways.
Figure Mechanism of photocatalytic benzene on the TiO$_2$/SiO$_2$/Bi$_2$O$_3$ photocatalysts

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Abstract: TiO$_2$/SiO$_2$/Bi$_2$O$_3$ photocatalysts were prepared from TiOSO$_4$, SiO$_2$ sol and Bi(NO$_3$)$_3$ by the co-precipitation method and were characterized by X-ray diffraction (XRD), N$_2$ adsorption/desorption (BET), UV–vis diffuse reflectance spectroscopy (DRS), X-ray photoelectron spectroscopy (XPS), photoluminescence spectroscopy (PLS) and fourier transform infrared spectroscopy (FT-IR) techniques. In the as-prepared samples, except for pure Bi$_2$O$_3$, only anatase-TiO$_2$ was observed, and no diffraction peaks of SiO$_2$ and Bi$_2$O$_3$ came up in XRD pattern. The surface areas of TiO$_2$/SiO$_2$ and the TiO$_2$/SiO$_2$/Bi$_2$O$_3$ were obviously larger than that of pure TiO$_2$. The addition of Bi$_2$O$_3$ improved the absorption of the TiO$_2$/SiO$_2$/Bi$_2$O$_3$ samples under
ultraviolet and visible light. The hydroxyl peak areas of the TiO$_2$/SiO$_2$, TiO$_2$/Bi$_2$O$_3$ and TiO$_2$/SiO$_2$/Bi$_2$O$_3$ were higher than those of pure TiO$_2$ and Bi$_2$O$_3$. The TiO$_2$/Bi$_2$O$_3$ heterojunction structure enhanced separation of photogenerated electrons and holes under UV and visible light. The TiO$_2$/SiO$_2$/Bi$_2$O$_3$ containing 2.5% of Bi$_2$O$_3$ has the highest activity in all of the samples under UV or visible irradiation.

**Keywords:** photocatalytic; TiO$_2$; SiO$_2$; Bi$_2$O$_3$; microstructure; benzene

1. **Introduction**

The photocatalysis is a feasible method for the removal of indoor air pollutants at low concentrations (at ppb levels) [1]. Outstanding stability and strong oxidation power make TiO$_2$ the photocatalysts as a choice for environmental remediation. It is essential to enhance the photocatalytic activity of TiO$_2$ for high concentrations of pollutants abatement (as ppm levels). An approach is that improves the textural properties and surface hydroxyls of photocatalysts by adding SiO$_2$ [2-4] or ZrO$_2$ [2, 5, 6] to TiO$_2$ photocatalysts. Other method is that restrains the recombination of the photo-generated electron-hole pairs via coupling TiO$_2$ with narrow band gap semiconductors, such as Bi$_4$Ti$_3$O$_{12}$/TiO$_2$ [7], CdS/TiO$_2$ [8], BiVO$_4$/TiO$_2$ [9] and WO$_3$/TiO$_2$ [10] composite catalysts.

Bi$_2$O$_3$ is a significant metal-oxide semiconductor with a direct band gap from 2.1~2.8 eV [11], which can be excited by visible light, but the photocatalytic activity of Bi$_2$O$_3$ is low due to the photocorrosion and fast recombination of photogenerated electron–hole pairs [12]. In recent years, the development of Bi$_2$O$_3$/TiO$_2$ composite
photocatalyst that can work effectively under visible irradiation is a very hot topic in photocatalysis research. Liu et al. [13] prepared Bi$_2$O$_3$/TiO$_2$ composite photocatalysts with a no aqueous sol–gel method. Xu et al. [14] reported that the Bi$_2$O$_3$/TiO$_2$ composite films exhibited higher photocatalytic activity as compared to pure TiO$_2$ under solar irradiation.

TiO$_2$/SiO$_2$ photocatalysts were prepared using a precipitation method in our experiments [3, 4], being an easy and inexpensive technique. For improving the activity of the TiO$_2$/SiO$_2$ photocatalysts under ultraviolet irradiation and extending to visible light, the TiO$_2$/SiO$_2$/Bi$_2$O$_3$ samples were synthesized in this paper. The effect of Bi$_2$O$_3$ on the physicochemical properties and activities of the TiO$_2$/SiO$_2$/Bi$_2$O$_3$ would be discussed. The photocatalytic activities of the as-prepared samples were evaluated by the degradation of benzene under UV and visible light irradiation. The synthesis and characteristics of the composites would provide interesting candidates for photocatalytic applications.

2. Experimental

2.1. Catalyst preparation

The TiO$_2$/SiO$_2$/Bi$_2$O$_3$ photocatalysts were prepared by a co-precipitation method. The SiO$_2$ aqueous sol and Bi(NO$_3$)$_3$·5H$_2$O were dissolved in TiOSO$_4$ aqueous solution. The mixed solutions and concentrated NH$_3$·H$_2$O were added dropwise under vigorous stirring, and pH of the suspension was adjusted to 10. The mixture was stirred and kept in a water bath at 70 °C for 5 hours. Subsequently, the precipitates
were filtered off, rinsed with distilled water until the complete removal of \( \text{SO}_4^{2-} \), and then dried at 100 °C and calcined at 600 °C for 3 h. The amount of \( \text{SiO}_2 \) was 5 wt % for the \( \text{TiO}_2/\text{SiO}_2 \) and \( \text{TiO}_2/\text{SiO}_2/\text{Bi}_2\text{O}_3 \) samples. The mass fractions of the \( \text{Bi}_2\text{O}_3 \) dopant in the samples varied from 0, 0.5, 0.8, 1.2, 2.5 to 5 wt %, respectively. The as-prepared samples with different \( \text{Bi}_2\text{O}_3 \) amounts were denoted as TSBN. Herein, N represents \( \text{Bi}_2\text{O}_3 \) percents (for example, 0, 0.5, 0.8, 1.2, 2.5 and 5).

2.2. Catalyst characterization

The XRD analysis was conducted on DX-1000 X-ray diffractometer, using Cu \( \text{K}\alpha \) radiation (\( \lambda =0.15406 \) nm), scanning mode with 0.05°/second. X-ray patterns were measured from 20 to 80°. The average crystallite size of anatase can be estimated by the Scherrer equation: 

\[
D = \frac{0.89\lambda}{\beta \cos \theta}
\]

Herein, \( \beta \) is the half-height width of the (101) diffraction peak and \( \theta \) is the Bragg angle of the (101) diffraction peak.

\( \text{N}_2 \) adsorption/desorption isotherms were collected on QUADRA SORB SI, an Automated Surface Area and Pore Size Analyzer (Uuantachrome Instruments) at -196 °C. UV–vis diffuse reflectance spectroscopy was recorded on Pgeneral TU-1901 spectrometer, operated in the diffuse reflectance mode, for the wavelength within the range of 200-800 nm. Fourier transform infrared spectroscopy was obtained from a Thermo Nicolet 6700 unit, operated in the wave numbers from 4000 to 400 cm\(^{-1}\). The X-ray photoelectron spectra of the samples were acquired at room temperature using a Vacuum Generator Scientific XSAM800 system from Kratos Co. (U.K). The photoluminescence emission spectra of the samples were measured at room temperature by F-7000 FL Spectrophotometer (Hitachi) over a wavelength range of...
300–700 nm. The excitation wavelength was 210 nm.

2.3. Catalysts activity studies

The photocatalytic activities of the as-prepared TiO$_2$/SiO$_2$/Bi$_2$O$_3$ catalysts were evaluated in a 165 L of home-made batch reactor via the gas-phase photocatalytic oxidation with benzene. Germicidal lamps (3×8 W, 254 nm, F8T5BLB lamp, PHILIPS) were used as the ultraviolet irradiation source. U-type compact fluorescent lamps (Philips Genie energy saving lamp, 3×23 W, 390 nm < \( \lambda \) < 700 nm) were as visible light source. A thin layer of powder sample (0.3 g) was distributed evenly onto an aluminum foil (12 cm×24 cm). A specific amount of liquid benzene was injected into the system. Before illumination, the benzene in the reactor was diffused using a minifan in the dark for over 2 h to ensure the establishment of an adsorption/desorption equilibrium between the photocatalysts and benzene. Once the equilibrium has been reached, turn on the lamps (UV or visible) and the photocatalysis was started. The initial concentration of benzene was 80 mg·m$^{-3}$ and the concentration was monitored every 0.5 hour by GC 2000-II gas-phase chromatogram equipped with FID detector and GDX101 column. The determination of CO$_2$ concentration in the reactor was performed with a gas chromatograph (GC 2000-II) equipped with a FID and a methane converter.

3. Results and discussion

3.1. XRD analysis of catalysts
Fig. 1 XRD patterns of the TiO$_2$, Bi$_2$O$_3$, TiO$_2$/SiO$_2$ and TiO$_2$/SiO$_2$/Bi$_2$O$_3$ samples with different Bi$_2$O$_3$ amounts.

Figure 1a displays the XRD patterns of the TiO$_2$, TiO$_2$/SiO$_2$, TiO$_2$/Bi$_2$O$_3$, TiO$_2$/SiO$_2$/Bi$_2$O$_3$ and Bi$_2$O$_3$ samples. In these samples, except for the pure Bi$_2$O$_3$, only anatase-TiO$_2$ was present, which the principal diffraction peak was around 25.35° corresponding to crystal plane (101) of anatase TiO$_2$. The characteristic diffractive peaks of SiO$_2$ and Bi$_2$O$_3$ did not come up. The shift of the main diffraction peaks of TiO$_2$ was not observed. The SiO$_2$ is possibly an amorphous phase existing in the TiO$_2$/SiO$_2$ and TiO$_2$/SiO$_2$/Bi$_2$O$_3$ samples [15, 16]. Moreover, no significant shifts of
the principal diffraction peaks of TiO$_2$ were observed, indicating that Bi$_2$O$_3$ was present in a separate phase adsorbed by TiO$_2$ rather than incorporated into the TiO$_2$ lattice, which is in accordance with the reports by Liu et al. [13], Bian et al.[17] and Hong et al. [18]. And the Bi$_2$O$_3$ is possibly highly dispersed in the TiO$_2$/Bi$_2$O$_3$ and TiO$_2$/SiO$_2$/Bi$_2$O$_3$ samples [17,19]. However, Bagwasi and co-workers [20] suggested that Bi$^{3+}$ substituted for Ti$^{4+}$ in bismuth and boron co-doped TiO$_2$, which is different from our observation. It may be due to the difference of precursors, preparation method and photocatalyst systems. The characteristic peaks of the pure Bi$_2$O$_3$ sample could be indexed to cubic Bi$_2$O$_3$, corresponding to crystal planes (111), (200), (220), (311), (222), (400), (331), (420) (JCPDS card no. 76-2478). When 5% of SiO$_2$, both 5% of SiO$_2$ and 2.5% of Bi$_2$O$_3$ were incorporated into TiO$_2$, respectively, the intensities of TiO$_2$ diffraction peaks obviously became weak. However, when only 2.5% of Bi$_2$O$_3$ added into TiO$_2$, the intensities of TiO$_2$ diffraction peaks were slightly changed as compared to pure TiO$_2$. It meant that 5% of SiO$_2$ dopant obviously impeded the growth of TiO$_2$ crystallite, as shown in Table 1.

Figure 1b demonstrates the XRD patterns of the TiO$_2$/SiO$_2$/Bi$_2$O$_3$ samples with different Bi$_2$O$_3$ amounts. All were presented crystallized the diffraction peaks of Bi$_2$O$_3$ were not observed due to the low

<table>
<thead>
<tr>
<th>Sample</th>
<th>$D$ nm</th>
<th>$S_{BET}$ $m^2$·g$^{-1}$</th>
<th>$V_{pore}$ cm$^3$·g$^{-1}$</th>
<th>$D_{mean}$ nm</th>
<th>BE eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO$_2$</td>
<td>10.2</td>
<td>106</td>
<td>0.201</td>
<td>10.2</td>
<td>3.21</td>
</tr>
<tr>
<td>TS</td>
<td>8.1</td>
<td>162</td>
<td>0.273</td>
<td>6.8</td>
<td>3.18</td>
</tr>
<tr>
<td>TB 2.5</td>
<td>9.6</td>
<td>102</td>
<td>0.217</td>
<td>9.2</td>
<td>3.15</td>
</tr>
<tr>
<td>Bi$_2$O$_3$</td>
<td>12.1</td>
<td>27</td>
<td>0.073</td>
<td>10.6</td>
<td>2.80</td>
</tr>
<tr>
<td>TSB 0.5</td>
<td>7.2</td>
<td>153</td>
<td>0.256</td>
<td>6.0</td>
<td>3.17</td>
</tr>
<tr>
<td>TSB 0.8</td>
<td>6.8</td>
<td>156</td>
<td>0.262</td>
<td>5.2</td>
<td>3.15</td>
</tr>
<tr>
<td>TSB 1.2</td>
<td>6.6</td>
<td>164</td>
<td>0.278</td>
<td>6.4</td>
<td>3.13</td>
</tr>
<tr>
<td>TSB 2.5</td>
<td>7.2</td>
<td>166</td>
<td>0.289</td>
<td>6.5</td>
<td>3.11</td>
</tr>
<tr>
<td>TSB 5</td>
<td>7.0</td>
<td>166</td>
<td>0.273</td>
<td>6.5</td>
<td>3.07</td>
</tr>
</tbody>
</table>
amount and high dispersion. Bian et al. [17] reported that no significant diffractional peaks of Bi$_2$O$_3$ could be observed even at Bi/Ti molar ratio up to 5.0%, indicating that the Bi$_2$O$_3$ species were highly distributed in the TiO$_2$. And Wang et al. [19] impregnated bismuth over the zeolite, no characteristic peaks of crystalline Bi$_2$O$_3$ phase are observed even at high loadings of Bi$_2$O$_3$ (20%), suggesting that the dispersed Bi$_2$O$_3$ species over HZSM-5 are nanosized particles that escape the XRD detection. However, Shamaila et al. [21] reported that characteristic peaks of Bi$_2$O$_3$ were present when 5 % of Bi$_2$O$_3$ loaded on TiO$_2$ using the wet impregnation method. It is possible that doping method resulted in the difference of Bi$_2$O$_3$ dispersion in the TiO$_2$.

3.2. Textural properties of catalysts

Table 1: Microstructure and textural properties of the TiO$_2$, Bi$_2$O$_3$, and TiO$_2$-based composites

<table>
<thead>
<tr>
<th>Property</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$D$</td>
<td>Mean crystallite size estimated by the Scherrer formula for anatase TiO$_2$</td>
</tr>
<tr>
<td>$S_{\text{BET}}$</td>
<td>Specific surface area determined from the linear of the BET plot</td>
</tr>
<tr>
<td>$V_{\text{pore}}$</td>
<td>Total pore volume of samples</td>
</tr>
<tr>
<td>$D_{\text{mean}}$</td>
<td>Average pore diameter of samples</td>
</tr>
</tbody>
</table>
BE- Band gap energy of the samples

Textural properties of the TiO$_2$, Bi$_2$O$_3$ and composites are listed in Table 1. Surface areas of the composites such as TiO$_2$/SiO$_2$ and TiO$_2$/SiO$_2$/Bi$_2$O$_3$ are obviously larger than that of pure TiO$_2$ owing to incorporation of SiO$_2$ with netlike and porous structure [3, 4]. The TiO(OH)$_2$ precipitates deposited on the surface of SiO$_2$ particles during preparation, retarding the growth of TiO$_2$ particles, and the netlike structure of SiO$_2$ promoted the formation of porous structure TiO$_2$. However, the addition of Bi$_2$O$_3$ has hardly effect on the surface area of the TiO$_2$/Bi$_2$O$_3$ and TiO$_2$/SiO$_2$/Bi$_2$O$_3$ due to the compact structure of Bi$_2$O$_3$, its surface area being $27 \text{ m}^2 \cdot \text{g}^{-1}$. As shown in Table 1, the pore size of the pure oxides such as TiO$_2$ and Bi$_2$O$_3$ is larger than that of the composites due to their large particle size. Pore volume of the composites increased when SiO$_2$ added into TiO$_2$, and more reactant molecules would be adsorbed on the active sites on the surface of catalysts, which is in favorable of degradation of benzene.

3.3. UV-vis diffuse reflectance spectroscopy
Fig. 2 UV-visible absorption spectroscopy of the TiO$_2$, Bi$_2$O$_3$ and TiO$_2$-based composites

The optical properties of the as prepared samples were measured by using UV-visible diffuse reflectance spectroscopy. Figure 2a represents the UV–vis DRS of the TiO$_2$, TiO$_2$/SiO$_2$, TiO$_2$/Bi$_2$O$_3$, TiO$_2$/SiO$_2$/Bi$_2$O$_3$ and Bi$_2$O$_3$ samples. It can be clearly seen that there is an intense adsorption band with a steep edge in visible region for
pure Bi$_2$O$_3$. And the Bi$_2$O$_3$ clearly enhanced the photo-adsorption of the TiO$_2$/Bi$_2$O$_3$ and TiO$_2$/SiO$_2$/Bi$_2$O$_3$ samples in UV light region, and slightly improved the photo-adsorption of the samples in visible regions. Among the samples, the absorption intensity for the TiO$_2$/SiO$_2$/Bi$_2$O$_3$ is the largest in UV light region. According to the spectra in Figure 2b, a shift to long wavelength was markedly observed for the TiO$_2$/SiO$_2$/Bi$_2$O$_3$ samples containing 2.5 % and 5 % of Bi$_2$O$_3$ in comparison with the pure TiO$_2$. The band-gap energies of the as-prepared samples were obtained in Table 1.

3.4. FT-IR spectra analysis of catalysts
Fig. 3 FT-IR spectra of the TiO<sub>2</sub>, Bi<sub>2</sub>O<sub>3</sub> and TiO<sub>2</sub>-based composites

Figure 3 depicts the FT-IR spectra of the TiO<sub>2</sub>, TiO<sub>2</sub>/SiO<sub>2</sub>, TiO<sub>2</sub>/Bi<sub>2</sub>O<sub>3</sub> and TiO<sub>2</sub>/SiO<sub>2</sub>/Bi<sub>2</sub>O<sub>3</sub> catalysts in the wave number range from 400 to 4000 cm<sup>-1</sup>. Broad absorption bands in the range of 400–600 cm<sup>-1</sup> are attributed to the stretching vibration of Ti–O bonds in Ti–O–Ti [22]. The peak at 1630 cm<sup>-1</sup> corresponds to the bending vibrations of the O–H bond of chemisorbed water, and the broad absorption peak appearing around 3440 cm<sup>-1</sup> are assigned to the stretching mode of the O–H bond of the surface hydroxyl groups or adsorbed water strongly bound to the catalyst surface [23, 24]. As shown in Figure 3a, pure Bi<sub>2</sub>O<sub>3</sub> and pure TiO<sub>2</sub> have small hydroxyl peak, whereas the composites such as the TiO<sub>2</sub>/SiO<sub>2</sub>, TiO<sub>2</sub>/Bi<sub>2</sub>O<sub>3</sub> and TiO<sub>2</sub>/SiO<sub>2</sub>/Bi<sub>2</sub>O<sub>3</sub> have larger hydroxyl peaks, and among the composites, the TiO<sub>2</sub>/SiO<sub>2</sub>/Bi<sub>2</sub>O<sub>3</sub> has the largest hydroxyl peak. As demonstrated in Figure 3b, the hydroxyl group peaks of the TiO<sub>2</sub>/SiO<sub>2</sub>/Bi<sub>2</sub>O<sub>3</sub> samples increased with the increase of Bi<sub>2</sub>O<sub>3</sub> amounts, apart from the sample of 5 % Bi<sub>2</sub>O<sub>3</sub>. More surface hydroxyl groups are beneficial to the photocatalytic reactions [2-4, 25].

3.5. XPS analysis of catalysts

<table>
<thead>
<tr>
<th>Sample</th>
<th>Binding energy/eV</th>
<th>Ti 2p&lt;sub&gt;3/2&lt;/sub&gt;</th>
<th>O 1s</th>
<th>Si 2p</th>
<th>Bi 4f&lt;sub&gt;7/2&lt;/sub&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>458.6</td>
<td>530.0</td>
<td>531.6</td>
<td>532.9</td>
<td>—</td>
</tr>
<tr>
<td>TiO&lt;sub&gt;2&lt;/sub&gt;/SiO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>458.6</td>
<td>530.0</td>
<td>531.2</td>
<td>532.6</td>
<td>102.1</td>
</tr>
<tr>
<td>TiO&lt;sub&gt;2&lt;/sub&gt;/Bi&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;</td>
<td>458.5</td>
<td>529.7</td>
<td>530.9</td>
<td>532.6</td>
<td>— 159.0</td>
</tr>
<tr>
<td>TiO&lt;sub&gt;2&lt;/sub&gt;/SiO&lt;sub&gt;2&lt;/sub&gt;/Bi&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;</td>
<td>458.6</td>
<td>529.8</td>
<td>531.1</td>
<td>532.9</td>
<td>102.2 159.1</td>
</tr>
<tr>
<td>Bi&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;</td>
<td>—</td>
<td>530.0</td>
<td>531.2</td>
<td>532.5</td>
<td>— 158.9</td>
</tr>
</tbody>
</table>
Table 3 Surface atomic concentrations of O 1s in the TiO$_2$, Bi$_2$O$_3$ and TiO$_2$-based composites

<table>
<thead>
<tr>
<th>Sample</th>
<th>O$_{\text{lattice}}$ /%</th>
<th>O 1s</th>
<th>OH$^-$/%</th>
<th>H$_2$O /%</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO$_2$</td>
<td>69.1</td>
<td>21.9</td>
<td>9</td>
<td></td>
</tr>
<tr>
<td>TiO$_2$/SiO$_2$</td>
<td>63.6</td>
<td>23.2</td>
<td>13.2</td>
<td></td>
</tr>
<tr>
<td>TiO$_2$/Bi$_2$O$_3$</td>
<td>68.5</td>
<td>22.7</td>
<td>8.8</td>
<td></td>
</tr>
<tr>
<td>TiO$_2$/SiO$_2$/Bi$_2$O$_3$</td>
<td>55.1</td>
<td>32.4</td>
<td>12.5</td>
<td></td>
</tr>
<tr>
<td>Bi$_2$O$_3$</td>
<td>79.4</td>
<td>17.6</td>
<td>3</td>
<td></td>
</tr>
</tbody>
</table>

High-resolution XPS was used to elucidate the detailed surface chemical compositions and their electronic states of samples. As shown in Table 2, the binding energy of Ti 2p$_{2/3}$ for pure TiO$_2$ and the TiO$_2$-based composites is approximately 458.6 eV, which is attributed to Ti$^{4+}$ [13]. However, Bagwasi et al. [19] reported that the binding energy of Ti 2p$_{3/2}$ was around 458.0 eV lower than the results, which the Bi species increased the electron density around Ti due to Bi incorporated to TiO$_2$ lattices. The binding energies of O 1s were 529.9, 531.2 and 532.6 eV could be attributed to the lattice oxygen, hydroxyl groups and surface adsorbed water for the crystallites of the TiO$_2$, Bi$_2$O$_3$ and TiO$_2$-based composites, respectively [26]. Clearly, the surface hydroxyl concentration of the TiO$_2$-based composites is much higher than that of pure TiO$_2$ and Bi$_2$O$_3$ listed in Table 3. Linsebigler et al. [27] reported that hydroxyl groups on the surface of TiO$_2$ would accept holes generated by illumination, and produce hydroxyl radicals which have strong oxidizability. The binding energy of Si 2p in the TiO$_2$/SiO$_2$ (102.1 eV) and TiO$_2$/SiO$_2$/Bi$_2$O$_3$ (102.2 eV) was lower than that of pure SiO$_2$ being 103.4 eV due to an oxygen loss in SiO$_2$ [28]. Since Ti has greater affinity for oxygen than Si, some Si–O bonds disappeared to promote the formation of Ti–O bonds on the surface of the
TiO$_2$/SiO$_2$ [29]. The XPS spectra demonstrates the binding energies (BE) of 158.9, 159.0 and 159.1 eV in Bi4f$_{7/2}$ levels corresponding to the Bi$_2$O$_3$, TiO$_2$/Bi$_2$O$_3$ and TiO$_2$/SiO$_2$/Bi$_2$O$_3$ samples, respectively. The BE values were almost the same as those obtained from pure Bi$_2$O$_3$. Meanwhile, the Bi$_2$O$_3$ exerted did not significantly influence the XPS spectra either the Ti 2p$_{3/2}$ level or the O 1s level. The results showed that the Bi$_2$O$_3$ was present in a separate oxide in the TiO$_2$/Bi$_2$O$_3$ and TiO$_2$/SiO$_2$/Bi$_2$O$_3$ samples, i.e., the Bi species were not incorporated into the TiO$_2$ lattice, which was in good accordance with the conclusion from aforementioned XRD patterns. It was possibly that Ti$^{4+}$ (0.068 nm) was difficult to be replaced by big size of Bi$^{3+}$ (0.096 nm).

3.6. Photoluminescence emission spectra of catalysts

![Photoluminescence spectra of the TiO$_2$, Bi$_2$O$_3$ and TiO$_2$-based composites](image)

Fig. 4 Photoluminescence spectra of the TiO$_2$, Bi$_2$O$_3$ and TiO$_2$-based composites

Photocatalysts generate electrons and holes after being irradiated by UV light, and recombination of some electrons and holes can release energy in the form of fluorescence emission. Lower fluorescence emission intensity implies lower recombination rate of electron–hole pairs. Figure 4 shows the comparison of the room
temperature photoluminescence spectra with 210 nm excitation wavelengths in the range of 300–700 nm for the TiO$_2$, TiO$_2$/SiO$_2$, TiO$_2$/Bi$_2$O$_3$, Bi$_2$O$_3$, TiO$_2$/SiO$_2$/Bi$_2$O$_3$ samples. For pure TiO$_2$ and TiO$_2$/SiO$_2$, the emission peaks around 405, 416, 432, 451, and 466 nm were observed. The peaks of the TiO$_2$/Bi$_2$O$_3$ were around 398 and 463 nm. The peak of the Bi$_2$O$_3$ was observed at 452 nm. The peak of the TiO$_2$/SiO$_2$/Bi$_2$O$_3$ appeared at 378 nm. All these peaks are ascribed to surface traps [30]. The PL intensity of these samples decreased in order: TiO$_2$ (TiO$_2$/SiO$_2$) > TiO$_2$/Bi$_2$O$_3$ > Bi$_2$O$_3$ > TiO$_2$/SiO$_2$/Bi$_2$O$_3$. The TiO$_2$ and TiO$_2$/SiO$_2$ have the greatest relative intensity of emission spectra, which their electrons and holes are easy to recombine. The PL intensity of the TiO$_2$/Bi$_2$O$_3$ is lower than that of the TiO$_2$, and the PL intensity of the TiO$_2$/SiO$_2$/Bi$_2$O$_3$ is the lowest. It indicated that coupling TiO$_2$ with Bi$_2$O$_3$ is helpful to inhibit the recombination of electrons and holes, and benefit the photocatalytic reactions [14].

3.7. Photocatalytic activity of catalysts

3.7.1. Photocatalytic activity of catalysts under UV light irradiation
Fig. 5 Photocatalytic activities of the TiO$_2$, Bi$_2$O$_3$ and TiO$_2$-based composites under UV irradiation

Figure 5a shows the photocatalytic degradation of benzene over the composites (TiO$_2$/SiO$_2$, TiO$_2$/Bi$_2$O$_3$ and TiO$_2$/SiO$_2$/Bi$_2$O$_3$) and pure oxides (TiO$_2$ and Bi$_2$O$_3$) as a function of irradiation time under UV light. As indicated in Figure 5a, the activities of the composites (TiO$_2$/SiO$_2$, TiO$_2$/Bi$_2$O$_3$ and TiO$_2$/SiO$_2$/Bi$_2$O$_3$) were better than that of the pure oxides TiO$_2$ and Bi$_2$O$_3$. The activity of the TiO$_2$/SiO$_2$/Bi$_2$O$_3$ was the highest in all of the samples. The activities of the TiO$_2$/SiO$_2$/Bi$_2$O$_3$ composites with different Bi$_2$O$_3$ amounts are shown in Figure 5b. The rates of benzene removal were observed within 3.5 h of irradiation, the conversions of benzene were 87.6% for 0.5% Bi$_2$O$_3$ sample, 90.4% for 0.8% Bi$_2$O$_3$ sample, 93.7% for 1.2% Bi$_2$O$_3$ sample, 99.8% for 2.5% Bi$_2$O$_3$ sample and 84.2% for 5% Bi$_2$O$_3$ sample. Namely, the TiO$_2$/SiO$_2$/Bi$_2$O$_3$ sample with 2.5% of Bi$_2$O$_3$ exhibited the best photoactivity. The rate constant of the TiO$_2$/SiO$_2$/Bi$_2$O$_3$ was 1.8 times of the pure TiO$_2$’s and 1.5 times of the TiO$_2$/SiO$_2$’s (see Table 1).
One hand, the incorporation of SiO$_2$ increased the surface area and surface hydroxyl concentration. Another hand, TiO$_2$ is n-type semiconductor, when the p-Bi$_2$O$_3$ was added into TiO$_2$, a number of micro p–n heterojunction in the TiO$_2$/Bi$_2$O$_3$ and TiO$_2$/SiO$_2$/Bi$_2$O$_3$ photocatalysts would be formed. Bi$_2$O$_3$ region has the negative charge, while TiO$_2$ region has the positive charge due to the formation of inner electric field. Under near UV illumination, the electron–hole pairs may be generated, the holes flow into the negative field, and the electrons move to the positive field. Thus, the photo-generated electron–hole pairs would be effectively separated in the TiO$_2$/Bi$_2$O$_3$ interfaces. Liu et al. [13] reported that it was desirable to prepare heterojunction composite with intimate contact between hetero-phase nanoparticles of Bi$_2$O$_3$ and TiO$_2$ to make inter-particle electron transfer more efficiently and achieve a highly photocatalytic performance. Moreover, the addition of Bi$_2$O$_3$ enhanced markedly the adsorption capability of photocatalysts under ultraviolet irradiation (see Figure 2a) and surface hydroxyl amounts (see Figure 3a), decreased recombination rate of electron–hole pairs (see Figure 4). Therefore, addition of Bi$_2$O$_3$ improved the activity of TiO$_2$ photocatalysts.

The amounts of Bi$_2$O$_3$ can also influence the thickness of the superficial space-charge layer of TiO$_2$. When the space-charge layer thickness approximates the penetration depth of light into the sample, the electron–hole pairs can be effectively separated. When the amount of Bi$_2$O$_3$ is too small, there are no adequate traps for photogenerated electron–hole pairs. However, if the doping quantity is considerably high, Bi$_2$O$_3$ becomes the recombination center of electrons–holes. Hong et al. [18]
reported that Bi (10%)/TiO₂ had lower photocatalytic activity in degrading benzene than that of pure TiO₂ under UV irradiation. It revealed that Bi₂O₃ amount is crucial for the activity of photocatalyst.

3.7.2. Photocatalytic activity of catalysts under visible light irradiation

![Fig. 6](attachment:image.png)

Fig. 6 Photocatalytic activities of the TiO₂, Bi₂O₃ and TiO₂-based composites under visible irradiation

As shown in Figure 6a, the photocatalytic activities of Bi₂O₃-based composites and pure Bi₂O₃ under visible light irradiation followed the order: TiO₂/SiO₂/Bi₂O₃ > TiO₂/Bi₂O₃ > Bi₂O₃, and the photoactivity of the TiO₂/SiO₂/Bi₂O₃ with 2.5% Bi₂O₃
was better than other Bi$_2$O$_3$-based samples in Figure 6b. The Bi$_2$O$_3$ can strongly adsorb visible light and is easily irradiated due to narrow band-gap energy (2.8 eV), and then induces photoelectrons and holes. However, the electron-hole pairs could rapidly be recombined, leading to the quenching of spectral response (see Figure 4). 

For the TiO$_2$/SiO$_2$/Bi$_2$O$_3$ and TiO$_2$/Bi$_2$O$_3$ composites, the conduction band (CB) edge potential of TiO$_2$ (-0.41 eV) is more active than that of Bi$_2$O$_3$ (0.09 eV), hence, the photo-induced electrons on TiO$_2$ particle surface transfer easily to Bi$_2$O$_3$ via interfaces; similarly, the photo-induced holes on the Bi$_2$O$_3$ surface migrate to TiO$_2$ owing to the different valence (VB) edge potentials (2.79 eV for TiO$_2$, 2.89 eV for Bi$_2$O$_3$) [31, 32]. The recombination between photogenerated electrons and holes could be effectively inhibited, leading to the stronger response in visible region. The reports by Li et al. [7], Wu et al. [33], Sun et al. [34] and Min et al. [35] confirmed that heterostructured photocatalysts improved the separation of photogenerated electrons-holes, and enhanced activity under visible light irradiation.

3.7.3. Mineralization of benzene for the TiO$_2$/SiO$_2$/Bi$_2$O$_3$ 2.5% photocatalyst

![Graph showing mineralization of benzene on the TiO$_2$/SiO$_2$/Bi$_2$O$_3$ 2.5% sample](image-url)

Fig. 7 Mineralization of benzene on the TiO$_2$/SiO$_2$/Bi$_2$O$_3$ 2.5% sample
Figure 7 shows that the mineralization of benzene was investigated for the TiO$_2$/SiO$_2$/Bi$_2$O$_3$ 2.5% sample. Although the conversion of benzene was completely carried out in 3.5 h (see Figure 5a), its mineralization reached 96% after 7h under UV light. Furthermore, the conversion of benzene was 33% (see Figure 6a), and its mineralization was only 15% after 7h under visible light. It revealed that the intermediates of benzene degradation were more difficult to be degraded.

3.8. Photocatalytic mechanism on the TiO$_2$/SiO$_2$/Bi$_2$O$_3$ photocatalysts

![Photocatalytic mechanism diagram](image)
Fig. 8 Mechanism of the photocatalytic induction process on the TiO$_2$/SiO$_2$/Bi$_2$O$_3$ photocatalysts: (a) UV induced mechanism and (b) visible induced mechanism

According to the band edge position, as the conduction band of p-Bi$_2$O$_3$ is lower than that of TiO$_2$, the former can act as a sink for the photogenerated electrons. The photogenerated electrons of the TiO$_2$ conduction band will transfer to the conduction band of p-Bi$_2$O$_3$ under light irradiation. Since the holes move in the opposite direction from the electrons, the photogenerated holes of the p-Bi$_2$O$_3$ valence band will transfer to the valence band of TiO$_2$, which makes charge separation more efficiently.

In the most of proposed mechanisms of TiO$_2$-based photocatalytic degradations of organic pollutants, the activated species for photooxidation of benzene mainly include hydroxyl radicals, superoxide radicals and photogenerated holes. The highly
oxidizing hydroxyl radical, which originates from the oxidation of chemisorbed OH or H₂O by photogenerated holes, is regarded as the main oxidative species responsible for the degradation. The strongest evidence for the •OH radical attack mechanism is formation of hydroxylated intermediates through addition of hydroxyl groups to benzene rings [36]. Then, the hydroxylated intermediates continue to react with •OH radical, transform into muconaldehyde product and are finally mineralized [37].

\[
\text{TiO}_2 + \text{UV} \rightarrow h^+ + e^-_{\text{CB}} \quad (1)
\]

\[
\text{H}_2\text{O} \rightleftharpoons \text{OH}^- + \text{H}^+ \quad (2)
\]

\[
\text{OH}^- + h^+ \rightarrow \text{•OH} \quad (3)
\]

\[
\text{•OH} + \text{C}_6\text{H}_6 \rightarrow \text{hydroxylated intermediates} \quad (4)
\]

\[
\text{hydroxylated intermediates} \rightarrow \text{muconaldehyde} \rightarrow \text{CO}_2 + \text{H}_2\text{O} \quad (5)
\]

When the photo-induced electrons on TiO₂ particle surface transfer to the CB of Bi₂O₃ via interfaces, some photogenerated electrons are captured by O₂ in the air to produce superoxide radicals (O₂⁻⁻) [21, 38, 39], follow on converting into •OH radicals to oxidize benzene.

\[
\text{O}_2 + e^-_{\text{CB}} \rightarrow \text{O}_2^{-\cdot} \quad (6)
\]

\[
\text{O}_2^{-\cdot} + \text{H}_2\text{O} \rightarrow \text{•OH} + \text{OH}^- \quad (7)
\]

Some reactions can also be initiated by direct oxidation of holes on the VB of TiO₂ [14]. Moreover, Zhang et al. [11] considered the holes on the VB of Bi₂O₃ oxidized methyl orange. Fox and Dulay [40] reported that direct hole-organic reactions generate cation radicals, which may be subsequently hydrated to generate
hydroxylated products, which are most of phenol, and some 1,4-benzoquinone and hydroquinone [41].

\[ h^+ + C_6H_6 \rightarrow C_6H_5^+ \]  \hspace{1cm} (8)

\[ C_6H_5^+ + OH^- \rightarrow \text{hydroxylated products (e.g. } C_6H_5OH) \]  \hspace{1cm} (9)

\[ C_6H_5OH + h^+ \rightarrow 1, 4\text{-benzoquinone and/or hydroquinone} \]  \hspace{1cm} (10)

In addition, Hennezel et al. [41] reported that the photocatalytic degradation of benzene proceeds via the direct holes oxidation of benzene. The direct holes oxidation route would produce benzene radical cations, which might react with an incoming benzene molecule, resulting in the polymerization of benzene on the surface of catalysts and the deactivation of catalysts.

\[ h^+ + C_6H_6 \rightarrow C_6H_5^+ \]  \hspace{1cm} (11)

\[ C_6H_5^+ + C_6H_6 \rightarrow \text{polymerization} \rightarrow \text{deactivation} \]  \hspace{1cm} (12)

Reaction intermediates were not detected and the deactivation of catalysts was not observed due to low initial concentration of benzene (80 mg·cm\(^{-3}\)) and high photocatalytic activity in our experiments. Therefore, the above reactions (5), (9), (10) and (12) were only possible reaction pathways.

The photogenerated electrons and holes were generated under visible light irradiation from the valence band (VB) composed of the hybridization orbitals of O2p, Bi6s and Bi6p to the conduction band (CB) of Bi\(_2\)O\(_3\) and TiO\(_2\):

\[ \text{Bi}_2\text{O}_3 + \text{vis} \rightarrow h^+ + e^-_{\text{CB}} \]  \hspace{1cm} (13)

It was suggested that benzene was degraded under visible light via a series of steps from (2) to (13) according to the experimental data in Figures 6 and 7. The
schematic diagrams of energy band matching, electron–holes separation process and possible reaction pathways on the TiO$_2$/SiO$_2$/Bi$_2$O$_3$ photocatalyst are illustrated in Figure 8.

3.9. Photocatalytic stability in degradation reaction

![Fig.9 Cycling runs in the photocatalytic degradation of benzene on the TiO$_2$/SiO$_2$/Bi$_2$O$_3$ under UV and visible light](image)

To test the stability of the prepared photocatalysts, the TiO$_2$/SiO$_2$/Bi$_2$O$_3$ 2.5% as a representative photocatalyst, was used for eight recycles of photodegradation of benzene. As indicated in Figure 9, the catalytic activity of the sample exhibited gradually decrease within six recycles under UV irradiation 3.5 h for every time, and then kept stable, the conversion was approximately 85%. While a stable conversion achieved only 22% for the degradation of benzene under visible irradiation 7 h every time. The decrease of catalytic activity within six recycles may be attributed to the adsorption of intermediates on the surface of the TiO$_2$/SiO$_2$/Bi$_2$O$_3$, resulting in the blockade of active sites. Bui et al. [37] reported that benzene was mineralized by
muconaldehyde and phenol two pathways. Muconaldehyde was easily oxidized to carboxylic acids, and then, was mineralized successively. However, it is rather difficult to oxidize phenol and phenolic compounds. Zhu et al. [42] observed that weakly adsorbed phenol was formed during the reaction, which led to the progressive deactivation of the catalyst in the gas–solid system. It was suggested that benzene was degraded mostly via an approach (5) forming muconaldehyde, and secondly approaches (9) and (10) forming phenol ect under UV light, whereas benzene was decomposed by via reactions (9) and (10) and less reaction (12) under visible light.

4. Conclusions

The activity of the TiO$_2$/SiO$_2$/Bi$_2$O$_3$ 2.5\% photocatalyst is higher than that of the TiO$_2$/SiO$_2$, TiO$_2$/Bi$_2$O$_3$, pure TiO$_2$ and Bi$_2$O$_3$. Highly activity of the composite is attributed to the addition of SiO$_2$, increasing the surface area and hydroxyl groups of the sample, and the formation of heterojunction between TiO$_2$ and Bi$_2$O$_3$, enhancing separation efficiency of photo-generated electrons and holes.

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References


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