Photocatalytic degradation of ibuprofen by base-modified Bi$_2$WO$_6$ under visible light

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The Structure and Chemistry of Bismuth Tungstate (Bi₂WO₆)

- Aurivillius family, \((\text{Bi}_2\text{O}_2)(\text{A}_{n-1}\text{B}_n\text{O}_{3n+1})\)

- Alternating \((\text{Bi}_2\text{O}_2)_{n}^{2n^+}\) layers and \((\text{WO}_4)_{n}^{2n^-}\) layers, W is 6-coordinated and occupies octahedral sites

- \(\text{Bi}_2\text{WO}_6\) can be considered as a mixed oxide of \(\text{Bi}_2\text{O}_3\) and \(\text{WO}_3\), shares similarity with them in terms of structure and chemistry

- pH plays a significant role when determine the main species of Bi and W in the synthesis solutions

- Schematic structure of \(\text{Bi}_2\text{WO}_6\).
  - red: O; magenta: Bi; white: W
  - yellow plane: (010)

\[
\text{WO}_3\text{·H}_2\text{O} \leftarrow [\text{H}_2\text{W}_{12}\text{O}_{42}]^{10^-} \leftarrow [\text{W}_7\text{O}_{24}]^{6^-} \quad \ldots \quad \leftarrow \text{WO}_4^{2^-}
\]

Acidic: \(\text{Bi}^{3+} \rightarrow \text{Bi oxynitrate} \rightarrow \ldots \rightarrow \text{Bi}_2\text{O}_3\)
Base Modification of Bi$_2$WO$_6$ for Enhanced Photocatalytic Activity under Visible Light

❖ **Pristine Bi$_2$WO$_6$**

Hydrothermal approach with feeding ratios Bi:W =1 (BWO-1) and Bi:W =2 (BWO-2), pH was adjusted with NaOH to 7 before heating at 200 °C for 20 h.

❖ **Novelty: Base-modified Bi$_2$WO$_6$**

1 mmol (0.7 g) of pristine Bi$_2$WO$_6$ was dispersed in 80 ml of NaOH solution with concentrations ranging from 0.5 M to 10 M. The dispersion was sonicated for 15 min. The obtained samples were denoted as X-BWO-1 or X-BWO-2, X is the concentration of NaOH solution.

❖ **Test of photocatalytic performance**

Light source: 300 W Xenon arc lamp with optical filter (420-690 nm)

Total of 50 ml reaction matrix with different parameters was kept in dark for 30 min before irradiation. Initial pH was adjusted with 0.1 M H$_2$SO$_4$ or NaOH when necessary.
Characterization of Base-Modified of Bi₂WO₆

- XRD patterns of samples (0.5/1/2.5/5-BWO-1, BWO-1, and BWO-2).
Characterization of Base-Modified of Bi$_2$WO$_6$

- Nanoplates less than 50 nm aggregated and stacked for BWO-1
- Nanoplates with around 500 x 100 nm (length x thickness) for BWO-2
- Edges of the nanoplates of 1-BWO-1 were rounded and smoothened after base modification

SEM images of BWO-1 (a), BWO-2 (b), and 1-BWO-1 (c)

- Table: properties of synthesized Bi$_2$WO$_6$.  

<table>
<thead>
<tr>
<th>Property</th>
<th>1-BWO-1</th>
<th>BWO-1</th>
<th>BWO-2</th>
</tr>
</thead>
<tbody>
<tr>
<td>$D_{(131)}$ (nm)</td>
<td>235</td>
<td>238</td>
<td>526</td>
</tr>
<tr>
<td>W:Bi (EDS)  c</td>
<td>0.46</td>
<td>0.67</td>
<td>0.65</td>
</tr>
</tbody>
</table>
Characterization of Base-Modified of Bi₂WO₆

- BET surface areas are 15.4, 18.8, and 3.0 m²/g for 1-BWO-1, BWO-1, and BWO-2, respectively.
- Type III isotherm for BWO-2, nonporous solid.
- Type II isotherm for 1-BWO-1 and BWO-1, macroporous materials; Type H3 hysteresis loops, which are given by aggregates of plate-like particles.
- Small amount of mesopores were eliminated by base modification.

❖ N₂ adsorption-desorption isotherm of 1-BWO-1, BWO-1, BWO-2
❖ Pore size distribution of 1-BWO-1, BWO-1, BWO-2
Characterization of Base-Modified of Bi$_2$WO$_6$

- Base modifications with 0.5 to 5 M NaOH had no effects on optical absorbance.
- Band gaps of 0.5/1/2.5/5-BWO-1 and BWO-1 are roughly the same, 2.8 eV.
- Bi$_2$O$_3$ has higher absorbance of visible light, with smaller band gap, 2.7 eV.
- BWO-2 has similar visible light absorbance to that of BWO-1, but slightly stronger absorbance of UV.

❖ UV-vis reflectance spectrum for Bi$_2$WO$_6$ samples.

❖ Tauc plots of the Kubelka–Munk function for Bi$_2$WO$_6$ samples.
Photocatalytic Degradation of Ibuprofen (IBP) by Bi$_2$WO$_6$ under Visible Light

❖ Enhanced Photocatalytic Activity of Base-modified Bi$_2$WO$_6$

![Graph showing photocatalytic degradation of IBP](image)

Ibuprofen (IBP)

❖ BWO-1 has the highest specific surface area.

❖ The band gap of 0.5~5-BWO-1 and BWO-1 are similar, 2.8 eV.

✓ The ratio of W to Bi significantly affects the photocatalytic activity of Bi$_2$WO$_6$.

❖ Photocatalytic removal of IBP by Bi$_2$WO$_6$ under visible light

$C_{Cata} = 0.1 \text{ g/L, } C_{0-IBP} = 5 \mu\text{M, } pH_i = 5.6, V= 50 \text{ ml.}$
Photocatalytic Degradation of Ibuprofen by Bi$_2$WO$_6$ under Visible Light

❖ Effect of pH on photocatalytic degradation of IBP by 1-BWO-1

- pH$_{pzc}$ of base-modified samples were dramatically increased
- Optimal pH value is 5.6 where 1-BWO-1 and IBP bear opposite charges
- Photocatalytic efficiency as well as adsorption of IBP decreased when pH <5.6 or pH >5.6

\[ pK_{a_{IBP}} = 5.2 \]

<table>
<thead>
<tr>
<th>pH$_{pzc}$</th>
<th>1-BWO-1</th>
<th>BWO-1</th>
</tr>
</thead>
<tbody>
<tr>
<td>9.2</td>
<td></td>
<td>5.1</td>
</tr>
</tbody>
</table>

❖ Effect of pH on IBP degradation with 1-BWO-1 under visible light

\[ C_{Cata} = 0.1 \text{ g/L} \]
\[ C_{0-IBP} = 5 \text{ μM} \]
\[ V = 50 \text{ ml} \]

❖ First-order rate constants of degradation of IBP under different pH values
Photocatalytic Degradation of Ibuprofen by Bi$_2$WO$_6$ under Visible Light

❖ Effect of ionic strength and phosphate on photocatalytic degradation of IBP by 1-BWO-1

- Complete inhibition of IBP degradation by 1-BWO-1 with presence of phosphate

- Phosphate ions have strong affinity for the surface of 1-BWO-1 by forming BiPO$_4$, which inhibit the adsorption of IBP

- Adding 10 mM NaClO$_4$ only caused slight decrease to the degradation of IBP

- Independence of ionic strength indicates there is a strong inner-sphere complexation between IBP and active sites on the surface of 1-BWO-1

❖ Effect of ionic strength and phosphate on IBP degradation with 1-BWO-1 under visible light,

\[ C_{\text{Cata}} = 0.1 \text{ g/L}, \quad C_{0-\text{IBP}} = 5 \mu\text{M}, \quad V = 50 \text{ ml}. \]
Photocatalytic Degradation of Ibuprofen by $\text{Bi}_2\text{WO}_6$ under Visible Light

❖ Identification of reactive species in the degradation of IBP by 1-BWO-1

- Isopropanol (IPA) —— $\cdot$OH
  minor contribution

- $p$-benzoquinone ($p$BQ) —— $O_2^{\cdot-}$
  minor contribution

- Triethanolamine / Formic acid
  (TEOA/FA) —— $h^+$
  complete inhibition, primary species

- $\text{AgNO}_3$ —— $e^-$
  facilitate $h^+$/e$^-$ separation

Photocatalytic removal of IBP by 1-BWO-1 with presence of various scavengers under visible light.

$C_{\text{Cata}} = 0.1$ g/L, $C_{0-\text{IBP}} = 5 \mu\text{M}$, $pH_i = 5.6$, $V = 50$ ml.
$C_{0-\text{TEOA}} = C_{0-\text{FA}} = C_{0-\text{IPA}} = C_{0-\text{AgNO}_3} = 5$ mM, $C_{0-p\text{BQ}} = 0.5$ mM.
Possible mechanism for the photocatalytic reaction of base-modified Bi$_2$WO$_6$

![Diagram showing energy levels and charge transfer in a photocatalytic process.]

- $E_g = 2.8$
- CB at $-0.55$
- VB at $2.25$
- $\text{O}_2^-$ at $-0.3$
- $\text{O}_2^-$ to $\text{H}_2\text{O}_2$ to $\cdot\text{OH}$

Mechanism of Bi$_2$WO$_6$ photocatalytic process:

- Higher affinity towards molecular oxygen and contaminant molecules;
- Positions of VB and CB shift to more positive side
Photocatalytic Degradation of Ibuprofen by Bi$_2$WO$_6$ under Visible Light

❖ Reusability and stability of 1-BWO-1 during the degradation of IBP

- Catalysts were collected and washed with ethanol for three times, and then dried at 40 °C overnight
- Removal efficiency dropped slightly from 90 % to 82 % after 5 runs
- Good stability of 1-BWO-1 suggests that base modification is also able to create structural changes on the surface

❖ Photocatalytic removal of IBP in five cycles by 1-BWO-1 under visible light

$C_{\text{Cata}} = 0.1 \text{ g/L, } C_{0-\text{IBP}} = 5 \mu\text{M, } pH_i = 5.6, V= 50 \text{ ml.}$
Conclusions

- NaOH was used to successfully modified the surface of Bi$_2$WO$_6$.

- After base modification, band gap and BET surface area did not change significant, the ratio of W to Bi decreased and the pH$_{pzc}$ increased from 5 to 9.

- Besides, base modification improved the removal efficiency of ibuprofen by Bi$_2$WO$_6$ under visible light.

- Photo-generated h$^+$ plays a significant role for the degradation of ibuprofen by 1-BWO-1 under visible light.

- XPS, FTIR, Raman, and EPR will be analyzed to further understand the mechanisms of improved photocatalytic activity of Bi$_2$WO$_6$ by base modification.
ACKNOWLEDGEMENT

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