Supplementary Material

Insight into the origin of photoreactivity of various well-defined Bi$_2$WO$_6$ crystals: exposed heterojunction-like surface and oxygen defect

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<table>
<thead>
<tr>
<th>Sample</th>
<th>X</th>
<th>$E_g$ (eV)</th>
<th>$E_{CB}$ (eV)</th>
<th>$E_{VB}$ (eV)</th>
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</thead>
<tbody>
<tr>
<td>Nanosheet-assembled microspheres</td>
<td>6.36</td>
<td>2.51</td>
<td>0.61</td>
<td>3.12</td>
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<tr>
<td>Nanoparticle-assembled microspheres</td>
<td>6.36</td>
<td>2.41</td>
<td>0.66</td>
<td>3.07</td>
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<tr>
<td>Single-crystalline nanosheets</td>
<td>6.36</td>
<td>2.51</td>
<td>0.61</td>
<td>3.12</td>
</tr>
</tbody>
</table>

**Table S1** The valence band (VB) edge and the conduction band (CB) edge positions of Bi$_2$WO$_6$.

The valence band (VB) edge and the conduction band (CB) edge positions of the prepared Bi$_2$WO$_6$ can be calculated from the following formula:

$$E_{VB} = X - E_g + 0.5E_g$$ (1)
\[ E_{CB} = E_{VB} - E_g \]  \hspace{1cm} (2)

where \( E_{VB} \) is the VB edge potential, \( E_{CB} \) is the CB edge potential, \( E_g \) is the band gap energy of the semiconductor, \( X \) is the electronegativity of the semiconductor that is the geometric mean of the electronegativity of the constituent atoms, \( E^e \) is the energy of free electrons on the hydrogen scale (about 4.5 eV). The \( X \) values of \( \text{Bi}_2\text{WO}_6 \) is 6.36 eV. 

**Fig. S1** Emission spectrum of the 300W Xe lamp with a 420 nm cutoff filter.
**Fig. S2** TEM images of as-prepared Bi$_2$WO$_6$ samples: (a-b) nanosheet-assembled microspheres, (c-d) nanoparticle-assembled microspheres and (e) single-crystalline nanosheets.

**Fig. S3** (a) Schematic illustration of the crystal orientation of the nanosheets with exposed (020) facets. (b) The crystal structure of orthorhombic Bi$_2$WO$_6$. Atomic structure of the (020) facets: (c) side view and (d) top view. W, O and Bi atoms are represented as blue, red and yarrow spheres, respectively.
**Fig. S4** Enlarged profile of the XRD patterns of the prepared Bi$_2$WO$_6$ samples between angles 10-30 °: (a) nanosheet-assembled microspheres, (b) nanoparticle-assembled microspheres and (c) single-crystalline nanosheets.

**Fig. S5** Photocatalytic degradation of MO under visible light irradiation over various Bi$_2$WO$_6$ samples: (a) nanosheet-assembled microspheres, (b) nanoparticle-assembled microspheres and (c) single-crystalline nanosheets.
Fig. S6 N$_2$ absorption-desorption isotherms of the prepared Bi$_2$WO$_6$ samples: (a) nanosheet-assembled microspheres, (b) nanoparticle-assembled microspheres and (c) single-crystalline nanosheets.

Fig. S6 describes typical N$_2$ adsorption-desorption isotherms of the prepared samples. Both Bi$_2$WO$_6$ nanosheet-built microspheres and nanosheets showed a typical II adsorption-desorption isotherms. In addition, the weak adsorption-desorption hysteresis demonstrated monolayer absorption. However, the nanoparticle-assembled microspheres displayed IV-type isotherm character, indicating the existence of mesopores. The specific surface areas of nanosheet-assembled microspheres, nanoparticle-assembled micropsheres and single-crystalline nanosheets are 26.97±1, 40.72±1 and 13.56±1 m$^2$ g$^{-1}$, respectively.

Supplementary reference