Supplementary data for

Engineering Z-scheme TiO$_2$-OV-BiOCl via oxygen vacancy for
photocatalytic degradation of imidaclorpid

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The calculation of intensity-average lifetime of samples:

In this work, the time-resolved photoluminescence (TRPL) decay spectra was applied to study the effective transfer of photo-generated electrons intuitively. As shown in Fig. 5(d), all of the TRPL spectra is consistent with a multi-exponential decay process. And their decay dynamics can be obtained through fitting to a biexponential function [1,2]:

\[ I(t) = A_1 \exp\left(\frac{-t}{\tau_1}\right) + A_2 \exp\left(\frac{-t}{\tau_2}\right) \]  

(1)

where \( I(t) \) indicates the PL intensity, \( A_1 \) and \( A_2 \) are used to represent the amplitude (or weighting factors). the \( \tau_1 \) and \( \tau_2 \) represent the corresponding lifetime. The average lifetime \( (\tau_m) \) is often used to evaluate carrier separation efficiency of photogenerated charges, and the \( \tau_m \) was calculated according to the following equation:

\[ \tau_m = \frac{(A_1\tau_1^2 + A_2\tau_2^2)}{(A_1\tau_1 + A_2\tau_2)} \]  

(2)

The short lifetime component \( (\tau_m) \) stems from the nonradiative recombination of the \( \tau_1 \) photogenerated electrons with the surface defects. And, the long lifetime component \( (\tau_2) \) is derived from the interband recombination of the free-excitons [3]. The experimental decay profiles of TiO\(_2\)-OV-BiOCl samples are listed in Table. S1. For TiO\(_2\)-OV-BiOCl, the two exponential constants \( (\tau_1 \) and \( \tau_2 \)) are 2.207 ns and 2.261 ns, which are longer than that of TiO\(_2\)/BiOCl \( (\tau_1 = 3.779 \text{ ns and } \tau_2 = 8.059 \text{ ns}) \) and BiOCl \( (\tau_1 = 2.207 \text{ ns and } \tau_2 = 0.245 \text{ ns}) \). Therefore, TiO\(_2\)-OV-BiOCl possess a longer average lifetime \( (\tau_m = 5.83 \text{ ns}) \) than that of TiO\(_2\)/BiOCl \( (\tau_m = 4.76 \text{ ns}) \) and BiOCl \( (\tau_m = 4.33 \text{ ns}) \).
### Table S1. The fitted parameters of the TRPL decay profiles.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$A_1$</th>
<th>$\tau_1$ (ns)</th>
<th>$A_2$</th>
<th>$\tau_2$ (ns)</th>
<th>$\tau_{ave}$ (ns)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO$_2$-OV-BiOCl</td>
<td>0.6348</td>
<td>5.978</td>
<td>0.276</td>
<td>2.261</td>
<td>5.83</td>
</tr>
<tr>
<td>TiO$_2$/BiOCl</td>
<td>0.624</td>
<td>3.799</td>
<td>0.803</td>
<td>8.050</td>
<td>4.76</td>
</tr>
<tr>
<td>BiOCl</td>
<td>0.363</td>
<td>2.207</td>
<td>0.276</td>
<td>6.245</td>
<td>4.33</td>
</tr>
</tbody>
</table>

**Fig. S1.** The prepared TiO$_2$/BiOCl using F127 as the surfactant in other solvents (a) and in the methanol solvent using other surfactants (b).
Fig. S2. SEM images of TiO$_2$-OV-BiOCl (a, b) and TiO$_2$/BiOCl (c, d); HRTEM images of TiO$_2$-OV-BiOCl (e-f).
Fig. S3. The survey spectra of TiO$_2$-OV-BiOCl (a); The BET of prepared TiO$_2$/BiOCl and TiO$_2$-OV-BiOCl (b).

Fig. S4. Photocatalytic degradation of IMD by TiO$_2$-OV-BiOCl under different the additive amount of titanium trichloride solution (a), solvent systems (b) and types of surfactants (c); The change in colour of TiO$_2$-OV-BiOCl and BiOCl (d) before and after illumination under simulated sunlight.
Fig. S5. (a) HPLC graph of IMD and by-products within 35 minutes retention times in IMD undergoing photocatalytic degradation (a) and photo-degradation (b) at varies reaction time; (c) HPLC graph of IMD and by-products (d) undergoing photocatalytic degradation over TiO$_2$-OV-BiOCl and photo-degradation by simulated sunlight at varies reaction time.
Fig. S6. The iron spectra at different retention time of photocatalytic degradation for IMD under irradiation at 40 min.

Reference:
