Supplementary Information for

Refining the band structure of BiOBr nanosheets through the synergetic effects of VO$_4^{3-}$ ions replacement and oxygen vacancies for the promoted visible-light-driven photocatalysis

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3. References
1. Tables

Table S1. General experimental conditions and resulted phase of final products.

<table>
<thead>
<tr>
<th>No.</th>
<th>BiOBr (mmol)</th>
<th>NH$_4$VO$_3$ (mmol)</th>
<th>NH$_4$VO$_3$/BiOBr</th>
<th>Phase of products</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>0.05</td>
<td>0.05</td>
<td>BiOBr</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>0.1</td>
<td>0.1</td>
<td>BiOBr/BiVO$_4$</td>
</tr>
<tr>
<td>3</td>
<td>1</td>
<td>0.5</td>
<td>0.5</td>
<td>BiOBr/BiVO$_4$</td>
</tr>
<tr>
<td>4</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>BiOBr/BiVO$<em>4$/BiV$</em>{1.025}O_{4+x}$</td>
</tr>
<tr>
<td>5</td>
<td>1</td>
<td>2</td>
<td>2</td>
<td>BiVO$<em>4$/BiV$</em>{1.025}O_{4+x}$</td>
</tr>
<tr>
<td>6</td>
<td>1</td>
<td>3</td>
<td>3</td>
<td>BiVO$<em>4$/BiV$</em>{1.025}O_{4+x}$</td>
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Table S2. ICP results of products obtained by adding 0.05 mmol of VO$_3^-$

<table>
<thead>
<tr>
<th>Sample weight (g)</th>
<th>Bi</th>
<th>Amount of element in solution (mg/L)</th>
<th>Percentage of element (%)</th>
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<tr>
<td>0.0451</td>
<td></td>
<td>3.39</td>
<td>75.21%</td>
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<tr>
<td>0.0451</td>
<td>V</td>
<td>0.70</td>
<td>1.56%</td>
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Table S3. Parameters of band structure of BiOBr without and with oxygen vacancy, and BiOBr with oxygen vacancies and VO$_3^-$ ions replacement.

<table>
<thead>
<tr>
<th>BiOBr</th>
<th>BiOBr (V$_O$)</th>
<th>BiOBr (V$_O$ + VO$_3^-$ ions replacement)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cell parameters</td>
<td></td>
<td></td>
</tr>
<tr>
<td>a = 7.875504 Å, b = 7.875504 Å, c = 8.146860 Å, α = β = γ = 90°</td>
<td></td>
<td></td>
</tr>
<tr>
<td>a = 7.873221 Å, b = 7.873221 Å, c = 8.257360 Å, α = β = γ = 90°</td>
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<tr>
<td>a = 7.947960 Å, c = 8.449130 Å, α = 90.091141°, β = 90.823715°, γ = 90.161331°</td>
<td></td>
<td></td>
</tr>
<tr>
<td>bandgap (E$_g$, eV)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.155</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.483</td>
<td></td>
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<td>2.403</td>
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2. Results and discussions

**Fig. S1.** (a) XRD patterns, (b) DRS spectra and corresponding photographs of products obtained at different concentration of NH$_4$VO$_3$ but without BiOBr. (c), (d) and (e) were SEM images of products obtained at 0.5 mmol of NH$_4$VO$_3$ but without BiOBr, (f), (g) and (h) were SEM images of products obtained at 3.0 mmol of NH$_4$VO$_3$ but without BiOBr.

Altering the concentration of NH$_4$VO$_3$ but without BiOBr nanosheets as templates, the resulted XRD patterns were recorded (**Fig. S1**). Apparently, the products obtained by adding 0.5 mmol of NH$_4$VO$_3$ were not indexed to BiVO$_4$ because the excessive Bi(NO$_3$)$_3$·5H$_2$O hindered the formation of BiVO$_4$. While, increasing the concentration of NH$_4$VO$_3$ to 3.0 mmol, the characteristic peaks of resulted products were assigned to BiVO$_4$ (JCPDS No. 14-0688) and BiV$_{1.025}$O$_{4+\delta}$ (JCPDS No. 44-0081). Accordingly, the
products obtained by adding 0.5 mmol of NH$_4$VO$_3$ only exhibited absorbance edge of
~450 nm due to the absence of BiVO$_4$ (Fig. S1b). While, with and without BiOBr, the
products obtained by adding 3.0 mmol of NH$_4$VO$_3$ showed similar optical absorbance
region covering the whole violet and visible light region owing to the presence of
BiV$_{1.025}$O$_{4+x}$. The morphology of products produced by adding 0.5 mmol of NH$_4$VO$_3$
were mixed with nanosheets and irregular polyhedron (Fig. S1c to S1e). Comparatively, the products resulted by adding 3.0 mmol of NH$_4$VO$_3$ were stacked
with assembled sheets and assembled particles (Fig. S1f to S1h).

The Raman shifts reflect the structure variation of different samples (Fig. S2).
According to the dimensionless intensity of different products (Fig. S2a), the vibration
and stretching mode assigned to BiOBr and BiVO$_4$ were evolved gradually, when
increasing the concentration of VO$_3^-$ . Furthermore, when increasing the concentration
of VO$_3^-$ , the Raman intensity of different products increased firstly (until 0.5 mmol of
VO$_3^-$ ), and then diminished subsequently (from 0.5 to 3.0 mmol). This change of
Raman intensity suggested that the vibrations and stretches of BiOBr and BiVO$_4$ were
weakening. As examined the local magnified Raman spectra, the shifts of different
bonds were exploited. For the BiOBr nanosheets, strong peaks of 92.8 and 112.8 cm$^{-1}$
ascribed to the $A_{1g}$ first-order vibration modes of Bi-metal and $A_{1g}$ internal Bi-Br
stretching mode, respectively.$^{1,2}$ While, a weak peak located at 161.4 cm$^{-1}$ assigned to
the $E_g$ Bi-Br stretching mode (Fig. S2b). When increasing the concentration of VO$_3^-$ ,
the $A_{1g}$ vibration mode of Bi-metal and $E_g$ Bi-Br stretching mode were gradually
depleted and diminished (Fig. S2c). When increasing the concentration of VO$_3^-$ over
0.1 mmol, the peaks located at 210.8, 321.6, 368.1, and 829.1 cm$^{-1}$ assigned to BiVO$_4$
were observed (Fig. S2d-e).$^{3,4}$ Particularly, Raman shifts of 321.6 and 368.1 ascribed
to the asymmetric and symmetric bending modes of the VO$_4^{3-}$ tetrahedra units could
be observed (Fig S2d). Raman peak of 829.1 cm\(^{-1}\) attributed to the V–O bond and 210.8 cm\(^{-1}\) produced by the BiVO\(_4\) external vibration modes were also present (Fig S2d and S2e). Notably, the Raman shifts assigned to BiVO\(_4\) were red-shifting gradually, indicating that the phonon energy was decreased probably due to structure distortion caused by the VO\(_4^{3-}\) ion exchange.\(^5\)

Fig. S2. (a) Raman shifts, local magnified Raman shifts of different marked numbers, (b) 1#, (c) 2#, (d) 3#, and (e) 4#.
According to survey spectra of products obtained by adding 0.5 and 3.0 mmol of VO$_3^-$, the concentration of V 2p was continuously increased when increasing the concentration of VO$_3^-$ (Fig. S3a). The binding energies located at 524.5 and 517.2 eV respective ascribed to V 2p$_{1/2}$ and V 2p$_{3/2}$ for products obtained by adding 0.5 mmol of VO$_3^-$, which were shifted to lower binding energies for products by adding 3.0 mmol of VO$_3^-$ (Fig. S3b). Accordingly, the Bi–O band, Bi 4f$_{5/2}$ and Bi 4f$_{7/2}$ binding energies for products obtained by adding 3.0 mmol of VO$_3^-$ were also shifted to lower binding energies (Fig. S3c and S3d), indicating that the electronegativity of Bi and O increased due to the excessive VO$_4^{3-}$ units, compared with products obtained by adding 0.5 mmol of VO$_3^-$. 

**Fig. S3.** (a) XPS survey spectra, high-resolution XPS spectra of (b) V 2p, (c) O1s, and (d) Bi 4f of products obtained by adding 0.5 and 3.0 mmol of VO$_3^-$. 


**Fig. S4.** SEM images of different products generated by adding different concentration of VO$_3^-$, (a) BiOBr nanosheets, (b) 0.05, (c) 0.5, (d) 1.0, (e) 2.0, (f) 3.0 mmol of VO$_3^-$ (a$_1$, b$_1$, c$_1$, d$_1$, e$_1$ and f$_1$ were the low magnification SEM images of products, a$_2$, b$_2$, c$_2$, d$_2$, e$_2$ and f$_2$ were the high magnification SEM images).

The initial BiOBr showed irregular square sheet-like morphology, and the thickness was ~20 nm (**Fig. S4a**). When gradually increasing the concentration of VO$_3^-$, the sheet-like morphology of products was maintained but showed slightly
difference (Fig. S4b-f). Some nanosheets were broke into small pieces, while some nanosheets were grew up with jagged edges by adding 0.05 mmol of VO$_3^-$ (Fig. S4b).

When elevating the concentration of VO$_3^-$ to 1.0 mmol, small piece of nanosheets disappeared, and the nanosheets were tended to aggregate (Fig. S4c and S4d). These aggregated nanosheets continuously shifted to more irregular nanosheets at 3.0 mmol of VO$_3^-$ (Fig. S4e and S4f).

In terms of the BiOBr nanosheets, the thickness was ~20 nm (Fig. S5a). The TEM image confirmed the sheet-like morphology (Fig. S5b). And the clear perpendicular interplanar lattice spacing of 0.277 nm assigned to (110) planes of BiOBr were observed (Fig. S5c). The products obtained by adding 0.1 mmol of NH$_4$VO$_3$ also showed sheet-like morphology (Fig. S5d). According to the HRTEM image, clear and perpendicular interplanar lattice spacings of 0.277 nm were observed, which were assigned to the (110) atomic planes of BiOBr (Fig. S5e). This result indicated that 0.1 mmol of VO$_3^-$ affected the structure of BiOBr barely due to the lower concentration of VO$_3^-$, which was confirmed by the EDS results (Fig. S5f–g).

The products obtained by adding 0.5 mmol of NH$_4$VO$_3$ still maintained sheet-like morphology, and the thickness of the resulted nanosheets was ~16.3 nm to 90.7 nm (Fig. S5h). Based on the lateral HRTEM image, clear and continuous interplanar lattice spacing of 0.817 nm assigned to the (001) planes of BiOBr were observed (Fig. S5i). Compared to the theoretical value of interplanar lattice spacing of 0.810 nm, this value was slightly expanded, indicating that the VO$_3^-$ ions exchange caused the expansion of crystal lattices of initial BiOBr. Furthermore, the component of V was higher than that of Br in the final products based on the EDS spectrum (Fig. S5j–k), suggesting that the percentage of VO$_3^-$ replacing the Br of BiOBr increased.
**Fig. S5.** (a) SEM, (b) TEM and (c) HRTEM images of BiOBr nanosheets. (d) TEM, (e) HRTEM images of products obtained by adding 0.1 mmol of VO$_3^-$, (f) SEM image and (g) EDS spectrum of the mark in (f) (inset with EDS element percentage). (h) TEM, (i) lateral HRTEM, (j) SEM images, and (k) corresponding elements mapping of products obtained by adding 0.5 mmol of VO$_3^-$, and EDS spectrum of (j) (inset with EDS element percentage).
Fig. S6. (a) Photodegradation of RhB over different samples under solar light irradiation, (b) the ratio of BiOBr and NH$_4$VO$_3$, the adsorption percentage of RhB and the final phase of products obtained at different concentration of NH$_4$VO$_3$. (c) Schematic illustration of oxygen vacancies diminishing and forming VO$_4^{3-}$ tetrahedral unit.

According to previous studies,$^8,^9$ the native oxygen vacancies possessing massive localized electrons are able to capture positive charge molecules or ions. RhB with positive charge groups of $\text{C}^+=\text{N}^-$ could adsorb onto the surface of BiOBr nanosheets with massive oxygen vacancies. Then, the adsorption efficiency of RhB over BiOBr or BiOBr/BiVO$_4$-based photocatalysts could reflect the variation of surface charge. According to the adsorption efficiency of RhB over different samples (Fig. S7a), the RhB adsorption efficiency was gradually decreased when increasing the concentration.
of VO$_3^-$, on the other hand, the templates BiOBr nanosheets was enclosed with (001) facets, which were terminated with [Bi$_2$O$_2$]$_{2}^{2+}$, which could bond with VO$_3^-$ to form unsaturated VO$_4^{3-}$ tetrahedral units as terminated layer on the surface when slightly increasing the concentration of VO$_3^-$. These unsaturated VO$_4^{3-}$ tetrahedral units also could contribute to the adsorption of RhB. Thus, the adsorption efficiency of RhB over different products should be the synergetic effect of oxygen vacancies and unsaturated VO$_4^{3-}$ units. At higher concentration of VO$_3^-$ (2 and 3 mmol), final products with phase of BiVO$_4$/BiV$_{1.025}$O$_{4+x}$ only with unsaturated VO$_4^{3-}$ units on the surface contributed to the adsorption of RhB (Fig. S7b).

The more electronegativity of the O atoms presents in unsaturated V=O bond of VO$_3^-$, resulting in that the electrophilic properties of V ions. The adjacent bismuth ions of oxygen vacancies are considered as being rich in electrons.$^{10,11}$ The unsaturated V=O is opened and the V bond with the O atoms adjacent to oxygen vacancies on the surface of BiOBr nanosheets due to the nucleophilic reagent of reaction. During this process, the electrons rich in Bi atoms are shifted to the O and transferred to the V to form VO$_4^{3-}$ tetragonal units on the surface of BiOBr nanosheets (Fig. S7c).$^{12}$ Bi and O adjacent to oxygen vacancies loss the electrons and the bind length of Bi–O bond become longer, when lower concentration of VO$_3^-$ adsorb and interact with the surface of BiOBr with oxygen vacancies. But when the oxygen vacancies are consumed completely and VO$_3^-$ are excessive, the electrons transfer from V to Bi and O, the electronegativity of Bi and O increase, and the Bi–O bond should get shorter.
Fig. S7. (a) XPS valence band spectra of BiOBr nanosheets and products obtained by adding 0.05 mmol of VO$_3^-$.
(b) Pseudo first-order kinetic fitting of different samples within 8 min visible-light irradiation.

According to the XPS valence band spectra of BiOBr nanosheets and products obtained by adding 0.05 mmol of VO$_3^-$, its VB were 1.83 and 1.76 eV, respectively (Fig. S7a). Correspondingly, the CB of BiOBr nanosheets and products obtained by adding 0.05 mmol of VO$_3^-$ were −0.99 and −1.03 eV, based on the bandgaps (Fig. 5).

The pseudo first-order kinetic fitting of different samples within 8 min visible-light irradiation were plotted and estimated according the equation of

$$-\ln \left( \frac{C}{C_0} \right) = kt$$

$k$ and $t$ are reaction rate constant and irradiation time, respectively. $C$ and $C_0$ are the concentration of solution at $t$ and original concentration of solution) (Fig. S7b).

Apparently, the reaction rate constant of product obtained by adding 0.05 mmol was the superior, while the value of the products obtained at higher concentration of VO$_3^-$ was much lower.

3. References

(1) M. Hu, A. H. Yan, X. Y. Wang, F. Huang, Q. P. Cui, F. Li, J. Huang, Hydrothermal method to prepare Ce-doped BiOBr nanoplates with enhanced carrier transfer and