

# Insight into the photocatalytic mechanism of the optimal $x$ value in $\text{BiOBr}_{x}\text{I}_{1-x}$ , $\text{BiOCl}_{x}\text{I}_{1-x}$ and $\text{BiOCl}_{x}\text{Br}_{1-x}$ series varying with pollutant type

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**Figure S1** EDS spectra of  $\text{BiOBr}_{0.5}\text{I}_{0.5}$  (a) and  $\text{BiOBr}_{0.95}\text{I}_{0.05}$  (b)

**Table S1** Apparent rate constant ( $k$ ) of MG photodegradation on  $\text{BiOBr}_{x}\text{I}_{1-x}$  with different  $x$  values

$x$ values	0	0.05	0.25	0.4	0.5
$k$ (min <sup>-1</sup> )	0.01286	0.01634	0.01803	0.02050	0.03145
$x$ values	0.6	0.75	0.875	0.95	1
$k$ (min <sup>-1</sup> )	0.01871	0.01723	0.01060	0.00661	0.00630

**Table S2** Apparent rate constant ( $k$ ) of TC photodegradation on  $\text{BiOBr}_{x}\text{I}_{1-x}$  with different  $x$  values

$x$ values	0	0.05	0.25	0.4	0.5
$k$ (min <sup>-1</sup> )	0.00251	0.00452	0.00582	0.00735	0.01096
$x$ values	0.6	0.75	0.875	0.95	1
$k$ (min <sup>-1</sup> )	0.01193	0.02535	0.03283	0.03739	0.01048

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**Figure S2** Photocatalytic activity of  $\text{BiOBr}_{x}\text{I}_{1-x}$  for the degradation of  $20 \text{ mg L}^{-1}$  TC (a),  $10 \text{ mg L}^{-1}$  BPA (b),  $10 \text{ mg L}^{-1}$  MV (c) and  $20 \text{ mg L}^{-1}$  RhB (d) under visible light irradiation

**Figure S3** Photocatalytic activity of  $\text{BiOCl}_{x}\text{Br}_{1-x}$  for the degradation of  $20 \text{ mg L}^{-1}$  TC (a),  $20 \text{ mg L}^{-1}$  RhB (b),  $20 \text{ mg L}^{-1}$  MG (c) and  $20 \text{ mg L}^{-1}$  MV (d) under visible light irradiation

**Figure S4** Photocatalytic activity of  $\text{BiOCl}_{x}\text{I}_{1-x}$  for the degradation of  $20 \text{ mg L}^{-1}$  RhB (a),  $20 \text{ mg L}^{-1}$  TC (b),  $30 \text{ mg L}^{-1}$  MG (c) and  $20 \text{ mg L}^{-1}$  MV (d) under visible light irradiation

**Figure S5** Time-resolved spectral changes of TC (a), RhB (b) and MG (c) over  $\text{BiOBr}_{x}\text{I}_{1-x}$

**Table S3** Equilibrium adsorption capacity ( $q_e$ ) for MG adsorption by fresh and used  $\text{BiOBr}_{x}\text{I}_{1-x}$

$x$ values	0	0.25	0.5	0.75	0.95	1
$q_e$ (Fresh, $\text{mg g}^{-1}$ )	32	35	29	28	25	21
$q_e$ (Used, $\text{mg g}^{-1}$ )	20	21	19	16	14	13

**Table S4** Equilibrium adsorption capacity ( $q_e$ ) for TC adsorption by fresh and used  $\text{BiOBr}_{x}\text{I}_{1-x}$

$x$ values	0	0.25	0.5	0.75	0.95	1
$q_e$ (Fresh, $\text{mg g}^{-1}$ )	15	20	27	28	26	23
$q_e$ (Used, $\text{mg g}^{-1}$ )	5	11	18	19	18	14

**Fig. S6** Photocatalytic activity of fresh  $\text{BiOBr}_x\text{I}_{1-x}$  and  $\text{BiOBr}_x\text{I}_{1-x}$  after desorption for the degradation of  $20 \text{ mg L}^{-1}$  MG (a) and  $20 \text{ mg L}^{-1}$  TC (b)

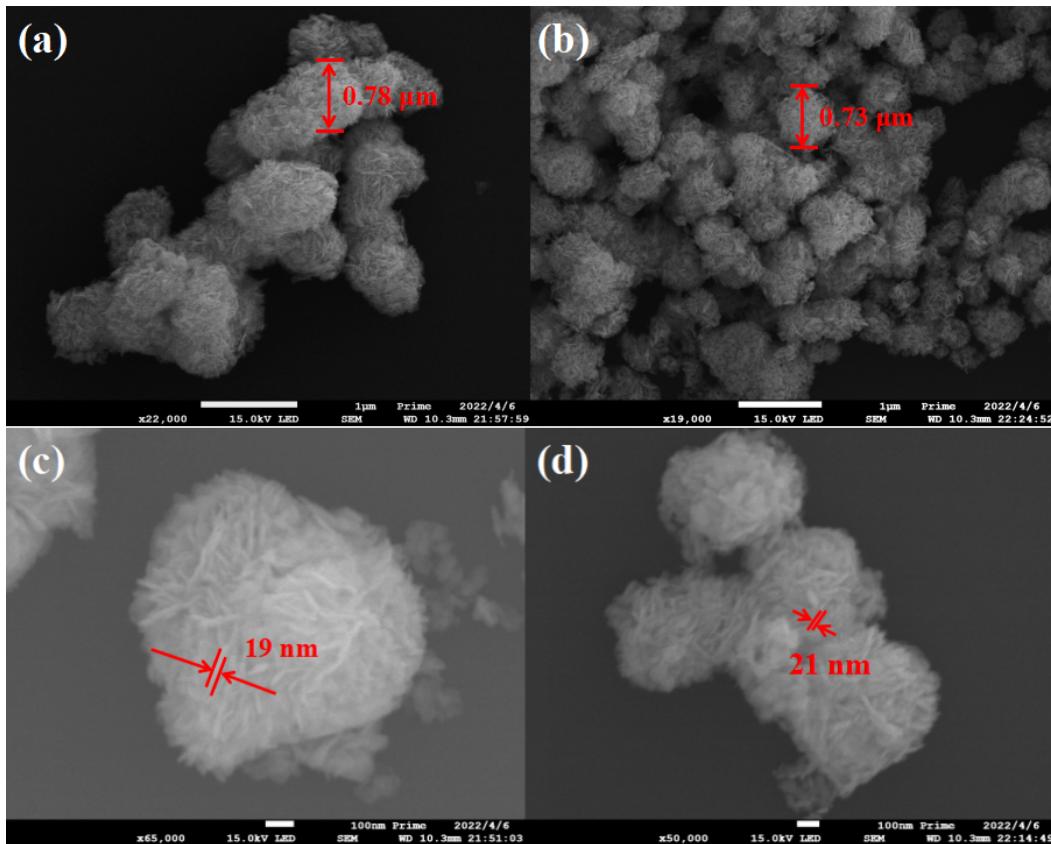
**Fig. S7** Effect of contact time on the removal of  $20 \text{ mg L}^{-1}$  MG (a, b) and  $20 \text{ mg L}^{-1}$  TC (c, d) over fresh  $\text{BiOBr}_x\text{I}_{1-x}$  (a, c) and used  $\text{BiOBr}_x\text{I}_{1-x}$  (b, d)

**Figure S8** Recycling experiments of TC and MG on  $\text{BiOBr}_{0.95}\text{I}_{0.05}$  and  $\text{BiOBr}_{0.5}\text{I}_{0.5}$ , respectively

**Figure S9** XRD pattern of  $\text{BiOBr}_{0.5}\text{I}_{0.5}$  (a) and (b)  $\text{BiOBr}_{0.95}\text{I}_{0.05}$  before and after cycles

**Figure S10** Active species trapping experiments of  $20 \text{ mg L}^{-1}$  TC photodegradation over  $\text{BiOBr}_{0.95}\text{I}_{0.05}$  under visible light irradiation

**Figure S11** NBT transformation efficiency on  $\text{BiOI}$ ,  $\text{BiOBr}_{0.5}\text{I}_{0.5}$ ,  $\text{BiOBr}_{0.95}\text{I}_{0.05}$  and  $\text{BiOBr}$  under visible light irradiation



**Figure S12** SEM images of  $\text{BiOBr}_{0.5}\text{I}_{0.5}$  (a, c) and  $\text{BiOBr}_{0.95}\text{I}_{0.05}$  (b, d)

**Fig. S13**  $\text{N}_2$  adsorption-desorption isotherms of  $\text{BiOBr}_{0.25}\text{I}_{0.75}$  (a),  $\text{BiOBr}_{0.5}\text{I}_{0.5}$  (b),  $\text{BiOBr}_{0.75}\text{I}_{0.25}$  (c) and  $\text{BiOBr}_{0.95}\text{I}_{0.05}$  (d), insets showing the corresponding pore size distribution curves and calculated surface areas and mean pore diameters

**Fig. S14** Plots of  $\Delta(\text{pH})$  vs. pH measured for  $\text{BiOBr}_{0.25}\text{I}_{0.75}$  (a),  $\text{BiOBr}_{0.5}\text{I}_{0.5}$  (b),  $\text{BiOBr}_{0.75}\text{I}_{0.25}$  (c) and  $\text{BiOBr}_{0.95}\text{I}_{0.05}$  (d)

**Figure S15** Mott-Schottky curves of  $\text{BiOBr}_{0.95}\text{I}_{0.05}$  at different frequency (a) and  $\text{BiOBr}_x\text{I}_{1-x}$  samples with different  $x$  values (b)

**Figure S16** UV-vis diffuse reflectance spectra (DRS) and the plots of the  $(\alpha h\nu)^{1/2}$  vs. photon energy ( $h\nu$ ) of BiOCl<sub>0.25</sub>Br<sub>0.75</sub>, BiOCl<sub>0.75</sub>Br<sub>0.25</sub> (a) and BiOCl<sub>0.25</sub>I<sub>0.75</sub>, BiOCl<sub>0.8</sub>I<sub>0.2</sub> (b)

**Figure S17** Mott-Schottky curves of BiOCl<sub>0.25</sub>Br<sub>0.75</sub>, BiOCl<sub>0.75</sub>Br<sub>0.25</sub> (a) and BiOCl<sub>0.25</sub>I<sub>0.75</sub>, BiOCl<sub>0.8</sub>I<sub>0.2</sub> (b)

**Table S5** The fitting values of each component in the equivalent circuit diagram

$x$ values	0	0.5	0.95	1
R <sub>1</sub> (Ω)	29.13	8.766	13.41	16.43
R <sub>2</sub> (Ω)	10334	2116	779.2	3694
CPE-T	3.94E-5	2.2E-3	1.64E-4	6.9E-4
CPE-P	0.86	0.35	0.71	0.79

**Table S6** The band potentials and band gap energy of BiOCl<sub>0.25</sub>Br<sub>0.75</sub>, BiOCl<sub>0.75</sub>Br<sub>0.25</sub> BiOCl<sub>0.25</sub>I<sub>0.75</sub> and BiOCl<sub>0.8</sub>I<sub>0.2</sub>

Samples	$E_g$ (eV)	$E_{CB}$ (V)	$E_{VB}$ (V)
BiOCl <sub>0.25</sub> Br <sub>0.75</sub>	2.48	-0.57	1.91
BiOCl <sub>0.75</sub> Br <sub>0.25</sub>	2.89	-0.61	2.28
BiOCl <sub>0.25</sub> I <sub>0.75</sub>	1.97	-0.18	1.79
BiOCl <sub>0.8</sub> I <sub>0.2</sub>	2.29	-0.11	2.18

**Figure S18** Band structures of BiOCl<sub>0.25</sub>I<sub>0.75</sub>, BiOCl<sub>0.8</sub>I<sub>0.2</sub>, BiOCl<sub>0.25</sub>Br<sub>0.75</sub>, BiOCl<sub>0.75</sub>Br<sub>0.25</sub> and the oxidation potential of MG, MV, TC and RhB