## **Supporting Information for**

# **Probing the Ring-Opening Pathways for Efficient Photocatalytic**

### **Toluene Decomposition**

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#### **Experimental section:**

**Characterization.** The X-ray diffraction (XRD) was measured to investigate the crystal phased of the as-generated samples with Cu Ka radiation (model D/max RA, Rigaku Co. Japan). The Xray photoelectron spectroscopy (XPS) with Al Ka X-rays (Thermo ESCALAB 250, U. S. A.) was used to study the surface chemical composition. The morphology was investigated via scanning electron microscopy (SEM, JSM-6490, JEOL, Japan) and transmission electrons microscopy (TEM, JEM-2010, Japan). High-resolution TEM (HRTEM) and selected area electron diffraction (SAED) were utilized to verify the exposure of the tailored facets. A scanning UV-vis spectra-photometer (TU-1901, China) was used to characterize the UV-vis diffuse reflectance spectrometry (DRS) spectra. The room-temperature photoluminescence (PL) spectra of the as-prepared samples were investigated using a fluorescence spectrophotometer (Edinburgh Instruments, FLSP-920) equipped with a xenon (Xe) lamp at the excitation wavelength of 360 nm. The surface photovoltage (SPV) was measured on the base of the lock-in amplifier (SR830, Stanford Research Systems, Inc.) and a light chopper (SR540, Stanford Research Systems, Inc.). Steady and ns-level time-resolved fluorescence emission spectra were recorded at room temperature with a fluorescence spectrophotometer (Edinburgh Instruments, FLSP-920). Electron spin resonance (ESR) spectra of chemical radicals were obtained on a JES FA200 spectrometer to determine the involvement of the reactive oxygen species (ROS) under light irradiation. The 5, 5-Dimethyl-1-Pyrroline-N-Oxide (DMPO) was employed as the trapping agent to verify the generation of  $\bullet$ OH and  $\bullet$ O<sub>2</sub><sup>-</sup> respectively in aqueous methanol dispersion. 4oxo-2, 2, 6, 6-Tetramethyl-1-Piperidinyloxy (TEMP) was applied to detect the <sup>1</sup>O<sub>2</sub> and TEMP-1oxyl (TEMPO) was used to characterize the photo-generated electrons.

**Photocatalytic degradation of toluene.** The photocatalytic efficiency was investigated towards the toluene degradation at 1 L/min in a house-customized continuous flow reaction system (Scheme S1 in the Supporting Information). The rectangular reactor was made of polymeric glass and covered by quartz class. The as-prepared sample (0.4 g) was dispersed on four glass sheets for photocatalytic testing. A 300 W UV lamp ( $\lambda$ =365 nm) was vertically placed above the reactor. After the adsorption-desorption equilibrium was achieved, the lamp was turned on. The toluene gas was obtained from a compressed gas cylinder at the concentration of 500 ppm (in N<sub>2</sub>) with the flow rate of 100 mL/min. The initial concentration of toluene was diluted to 50 ppm by two separated air flows, respectively wet air at 500 mL/min and dry air at 400 mL/min. The toluene concentration was continuously detected by a gas chromatography (GC 7890 II, Techcomp Co. Ltd.). The toluene removal ratio ( $\eta$ ) was calculated as

$$\eta\% = (1 - C/C_0) \times 100\% \tag{4}$$

where C and  $C_0$  depict the toluene concentration in the outlet steam and the feeding stream, respectively.

*In situ* **DRIFTS investigation.** In situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) measurements were performed with a TENSOR II FT-IR spectrometer (Bruker) which was equipped with an *in situ* diffuse-reflectance cell (Harrick) and a reaction chamber (HVC), as shown in Scheme S2. The reaction chamber was equipped with three gas ports and two coolant ports. High-purity He, high-purity O<sub>2</sub>, and 100 ppm of toluene (in He) mixtures were fed into the reaction system, and a tri-way ball valve was used to switch between the target gas (toluene) and purge gas (He). The flow rate of total gas was set to 100 mL min<sup>-1</sup>, and the concentration of toluene was adjusted to 50 ppm by dilution with O<sub>2</sub>. The chamber was

enclosed with a dome having three windows, two for IR light entrance and detection, and one for illuminating the photocatalyst. The observation window was made of UV quartz and the IR windows were made of ZnSe. A Xe lamp (MVL-210, Japan) was used as the irradiation light source. Before measurements, prepared samples were pretreated 20 min at 110 °C to removal the adsorbed species on the catalyst surface. The observed absorption bands of the adsorbed species and their chemical assignments are listed in Table S2-S5. The pristine data of DRIFTS was further normalized to investigate the species evolution as time proceeded. For a specific species absorbed on the surface, the data of peak heights in both catalysts were extracted. Between the two data columns, the highest value was set to 1 and the lowest one was set to 0. The rest value were respectively calculated from 0 to 1. The normalized data were then described as a function of the DRIFTS time.

### Schemes:



Scheme S1. Schematic illustration for toluene purification experiment



Scheme S2. The designed reaction system for the *in situ* DRIFTS signal recording.

# **Figures:**



**Figure S1.** Constructed micro-structures of BOC-001 (a) and BOC-010 (b). Blue, yellow, red and pink spheres depict Bi, Cl, O and H atoms respectively.



**Figure S2.** Calculated reaction coordinates for benzyl oxidation on BOC-001 (a-c) and BOC-010 (d-f). Blue, yellow, red, pink and green spheres depict Bi, Cl, O H and C atoms respectively.



**Figure S3.** Calculated reaction coordinates for aromatic ring-opening on BOC-001 (a-d) and BOC-010 (e-h). The color coding of atoms is the same as in Figure S2.



**Figure S4.** Calculated reaction coordinates for carbon chain breakage on BOC-001 (a-d) and BOC-010 (e-h). The color coding of atoms is the same as in Figure S2.



Figure S5. TEM images with lower magnification of BOC-001 (a) and BOC-010 (b)



Figure S6. XPS survey spectra and atomic amount (inset) of BOC-001 and BOC-010.



**Figure S7.** Photocatalytic efficiency evaluation towards gaseous benzene (a) and dimethylbenzene (b) degradation under UV-light.



Figure S8. UV-vis DRS (a) and estimates band energies (b) of BOC-001 and BOC-010.



Figure S9. UPS results for BOC-001 and BOC-010.



Figure S10. Band structure for ROS generation on BiOCl.

The energy position of the valance band  $(E_{VB})$  and conduction band  $(E_{CB})$  of BiOCl are calculated with the following equations:

$$E_{\rm VB} = X - E^{\rm e} + 0.5E_{\rm g} \tag{S1}$$

$$E_{\rm CB} = E_{\rm VB} - E_{\rm g} \tag{S2}$$

where X and  $E^{e}$  refer to the electronegativity and the energy of free electrons in hydrogen atoms (ca. 4.5 eV) respectively.  $E_{g}$  stands for the gap energy of BiOCl, which can be calculated with the UV-vis results.

Reaction pathways for the generation and transfer of ROS on BiOCl based on the band structure:

$$H_2O \to H^+ + OH^- \tag{S3}$$

$$OH^- + h^+ \rightarrow \bullet OH$$
 (S4)

$$2^{\bullet}\mathrm{OH} \to \mathrm{H}_{2}\mathrm{O}_{2} \tag{S5}$$

$$\mathrm{H}_{2}\mathrm{O}_{2} + \mathrm{h}^{+} \rightarrow 2\mathrm{H}^{+} + {}^{\bullet}\mathrm{O}_{2}^{-} \tag{S6}$$

$$\bullet O_2^- + h^+ \to {}^1O_2 \tag{S7}$$



**Figure S11.** Calculated H<sub>2</sub>O molecules adsorption on BOC-001 (a-d) and BOC-010 (e-h). The color coding of atoms is the same as in Figure S1.



**Figure S12.** Calculated reactants and intermediates adsorption on BOC-001 (a-d) and BOC-010 (e-h). The color coding of atoms is the same as in Figure S2.



**Figure S13.** Calculated projected density of states (PDOS) for C 2p in benzene series adsorbed on BOC-001 and BOC-010.

# Tables:

	BOO	C-001	BOC	C-010
Reaction pathways	$E_{\mathrm{a}}$	$E_{\rm r}$	$E_{\mathrm{a}}$	$E_{ m r}$
1	/	-0.30	/	-0.38
2	/	-1.38	/	-1.41
3	/	-0.07	/	-0.50
4	1.91	1.32	1.55	0.38
5	2.31	0.63	1.66	0.30
6	1.71	0.45	1.46	0.17
7	1.45	0.22	1.24	0.12
8	/	-0.74	/	-0.93
9	/	-0.48	/	-0.62
10	/	-0.54	/	-0.87
11	/	-1.14	/	-0.85

Table S1. Summary of activation energy  $(E_a)$  and reaction energy  $(E_r)$  for toluene degradation

These pathways included benzyl oxidation (path 1-3), aromatic ring-opening (path 4-7) and cabon chain breakage (path 8-11). All the energies are given in eV.

Table S2. Assigned DRIFT bands for toluene adsorption in dark on BOC-001

Wavenumber, cm <sup>-1</sup>	Assignment	References
3469	benzyl alcohol	3, 5
3049	aromatic ring	4, 6
2924	toluene	4
1699	benzaldehyde	2, 3, 4, 5
1509	benzoic acid	2, 3, 4

Wavenumber, cm <sup>-1</sup>	Assignment	References
3470	benzyl alcohol	3, 5
3032	aromatic ring	4, 6
2926	toluene	4
1496	benzoic acid	2, 3, 4

Table S3. Assigned DRIFT bands for toluene adsorption in dark on BOC-010

Table S4. Assigned DRIFT bands for toluene degradation under light irradiation on BOC-001

Wavenumber, cm <sup>-1</sup>	Assignment	References
3463 (negative)	benzyl alcohol	3, 5
3045	aromatic ring	4, 6
2923 (negative)	toluene	4
1705	benzaldehyde	2, 3, 4, 5
1519	benzoic acid	2, 3, 4
1383	C-H bending vibration	3, 6, 7, 8

Table S5. Assigned DRIFT bands for toluene degradation under light irradiation on BOC-010

Wavenumber, cm <sup>-1</sup>	Assignment	References
3458 (negative)	benzyl alcohol	3, 5
3059	aromatic ring	4, 6
2933 (negative)	toluene	4
1688	benzaldehyde	2, 3, 4, 5
1525	benzoic acid	2, 3, 4
1384	C-H bending vibration	3, 6, 7, 8

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