# Supplementary Information

# Interfacial Synergy of Pd Sites and Defective BiOBr for Promoting Solar-Driven Selective Oxidation of Toluene

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## 1. Supplementary experiments

### *1.1* ***Synthesis of BiOBr(no mannitol) and Pd/BiOBr(no mannitol) samples***

The BiOBr(no mannitol) sample was synthesized by the same solvothermal process as that for the synthesis of BiOBr nanostructures, except that no mannitol was added into the synthesis solution.

The Pd/BiOBr(no mannitol) sample was prepared by the same photodeposition process as that for the preparation of Pd/BiOBr photocatalyst, with using BiOBr(no mannitol) replacing BiOBr.

### *1.2* ***Synthesis of BiOBr(water) and Pd/ BiOBr(water) samples***

The BiOBr(water) sample was synthesized by a hydrothermal process in the absence of any organic additive. Typically, 1 mmol $Bi(NO_3)_3 \cdot 5H_2O$ and 1 mmol KBr were dissolved into 20 mL deionized water to form a suspension. After 20 min stirring, the suspension was transferred into a 50 mL autoclave which was sealed and kept at 160 ℃ for 8 h. After the reaction, the precipitate was collected by centrifugation, washed with deionized water and ethanol consecutively, and dried at 60 ℃.

The Pd/BiOBr(water) sample was prepared by the same photodeposition process as that for the preparation of Pd/BiOBr photocatalyst, with using the BiOBr(water) sample replacing BiOBr sample.

### *1.3* ***Synthesis of Au/BiOBr sample***

The Au/BiOBr sample with a theoretical Au content of 1.0 wt% was prepared by the same photodeposition process as that for the preparation of Pd/BiOBr photocatalyst, with using $HAuCl_4 \cdot 4H_2O$ replacing $(NH_4)_2PdCl_4$.

### *1.4 Recyclability test of Pd/BiOBr photocatalyst*

The recyclability test of Pd/BiOBr photocatalyst was performed by the photocatalytic selective oxidation of toluene under the irradiation of Xe lamp (PLS-SXE300, Beijing Perfectlight Technology Co. Ltd.). After each cycle of the photocatalytic reaction, the Pd/BiOBr photocatalyst was collected by centrifugation and washed three times with acetonitrile to remove the adsorbed impurities. After dried at 60 ℃, the Pd/BiOBr photocatalyst was reused in the next photocatalytic cycle under the same conditions. For each cycle, the conversion of toluene and the selectivity for producing benzaldehyde were determined by gas chromatograph.

### *1.5 Photocatalytic molecular oxygen activation*

Molecular oxygen activation was evaluated by the oxidation of 3,3’,5,5’-tetramethylbenzidine (TMB), based on monitoring the absorbance evolution at 370 nm of TMB solution along the irradiation time. Typically, 15 mg TMB was suspended in 8 mL deionized water, and 24 mL HAc/NaAc buffer solution (pH = 4.7) was then added in the suspension. 100 μL of the photocatalyst aqueous suspension (5 $g \cdot L^{-1}$) was injected into the above suspension. After ultrasonic dispersion, the mixture was stirred in the dark for 30 min to reach the equilibrium of adsorption resolution and then exposed to UV-visible irradiation. The reaction was probed by recording the absorbance at 370 nm on a UV–vis spectrophotometer.

In addition, to verify the generation of different reactive oxygen species, the controlled experiments in the presence of the corresponding scavenger were performed according to above experimental procedure. The added amounts of

scavengers were listed as follows: catalase (3500 unit/mL, 200 mL), superoxide dismutase (2000 unit/mL, 2 mL), mannite (10 mg), and carotene (5 mg).

## 2. Supplementary Figures

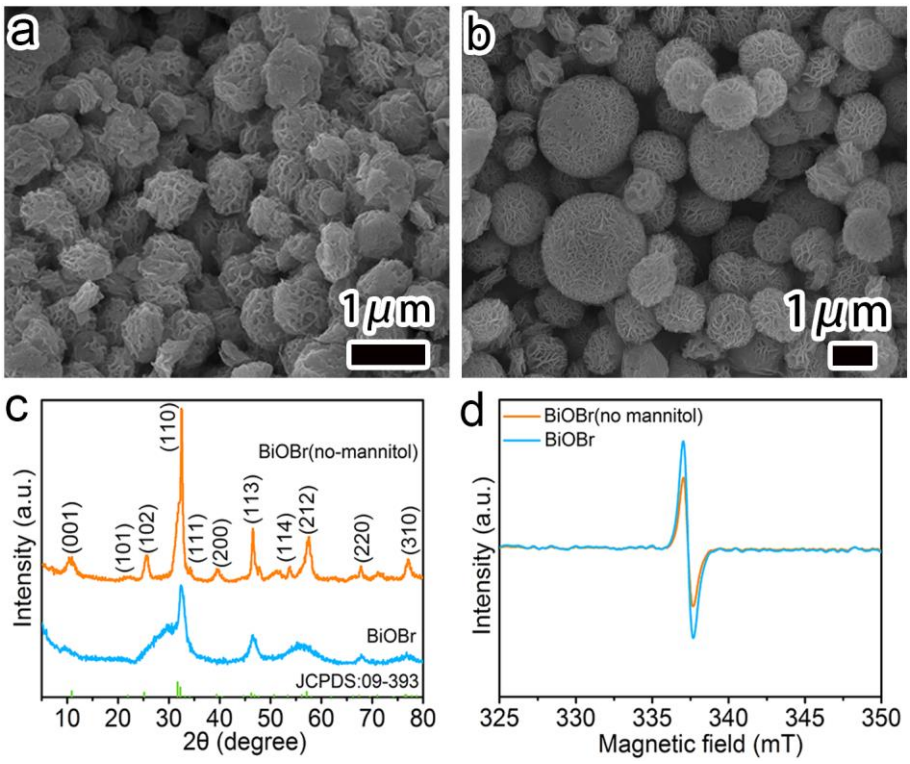


**Fig. S1** SEM images of (a) BiOBr and (b) BiOBr(no mannitol). (c) XRD patterns and (d) ESR spectra for $V_O$ signals of BiOBr and BiOBr(no mannitol).

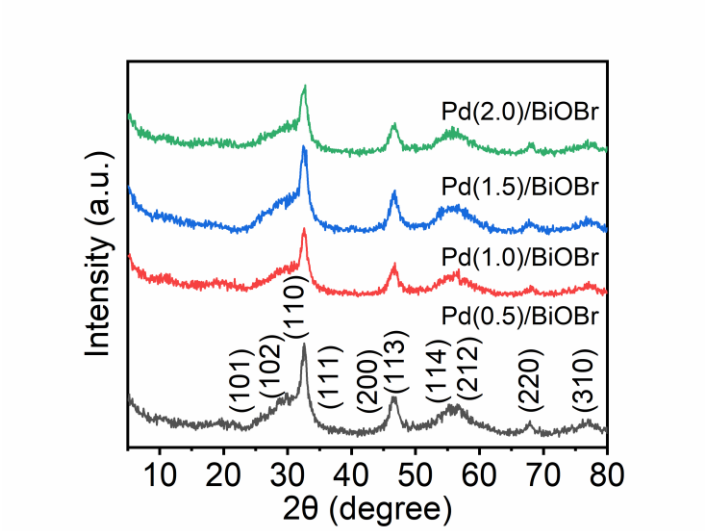


**Fig. S2** XRD patterns of Pd(*x*)/BiOBr samples with different theoretical Pd contents(*x*).

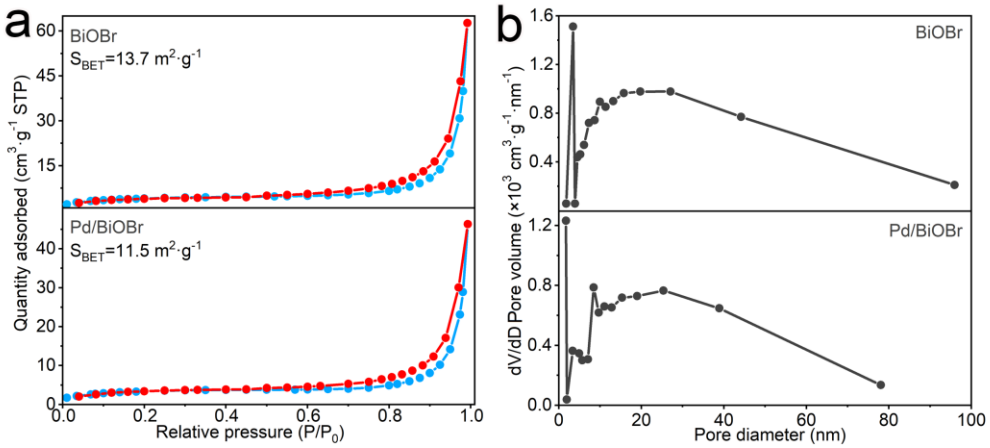


**Fig. S3** (a) $N_2$ adsorption-desorption isotherms and (b) pore size distribution of BiOBr and Pd/BiOBr samples, respectively.

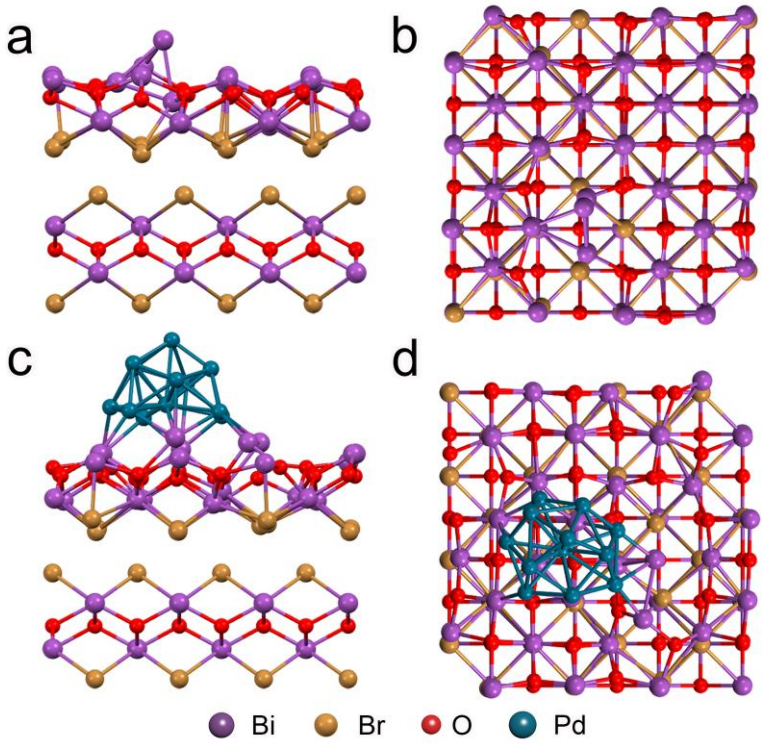


**Fig. S4.** The optimal configurations. (a) The side view and (b) top view of BiOBr-$V_O$ (001). (c) The side view and (d) top view of BiOBr-$V_O$ (001) with Pd cluster.

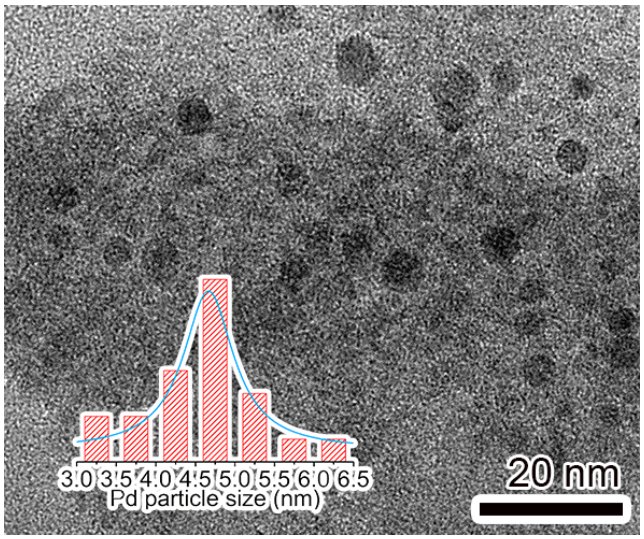


**Fig. S5** TEM image and size distribution of Pd NPs (inset) of Pd(2.0)/BiOBr sample.

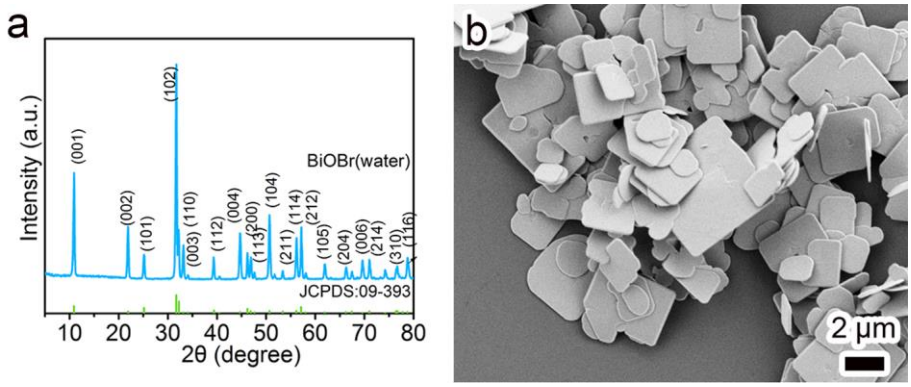


**Fig. S6** (a) XRD pattern, (b) SEM image of BiOBr(water) sample. The as-prepared BiOBr(water) nanosheets of tetragonal phase have a lateral width of 1.75–5.25 μm and thickness about 100 nm.

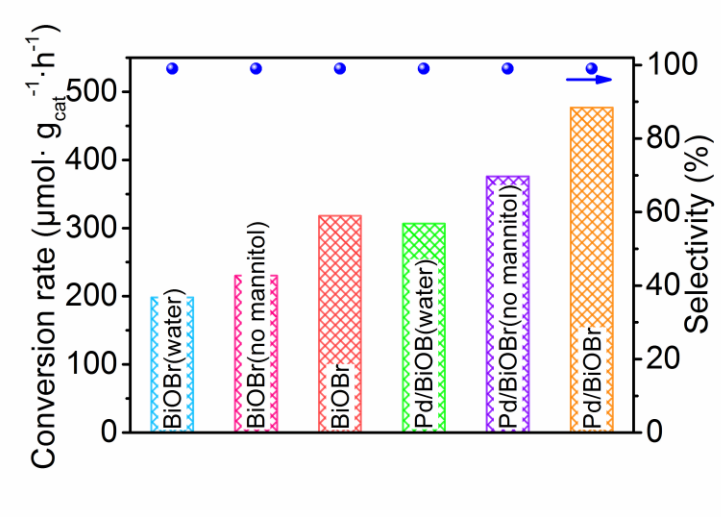


**Fig. S7** Photocatalytic selective oxidation of toluene to benzaldehyde over different photocatalysts.

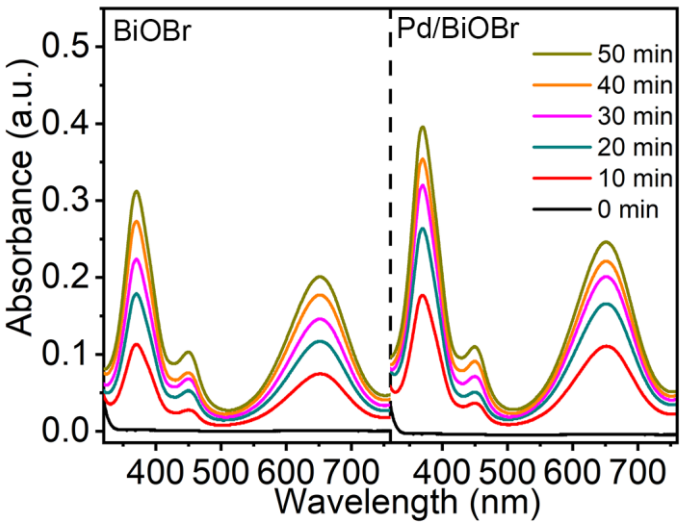


**Fig. S8** Time-dependent absorption spectra of TMB solution with BiOBr and Pd/BiOBr in $O_2$ atmosphere under UV-visible irradiation. Upon one-electron oxidation by the photoinduced reactive oxygen species, the colorless TMB ($\lambda_{max}$ = 285 nm) gradually turns into a blue charge transfer complex ($\lambda_{max}$ = 370, 650 nm) of the parent diamine and the diimine oxidation product. Herein, the absorbance evolution of 370 nm peak determines the oxidation process of TMB.

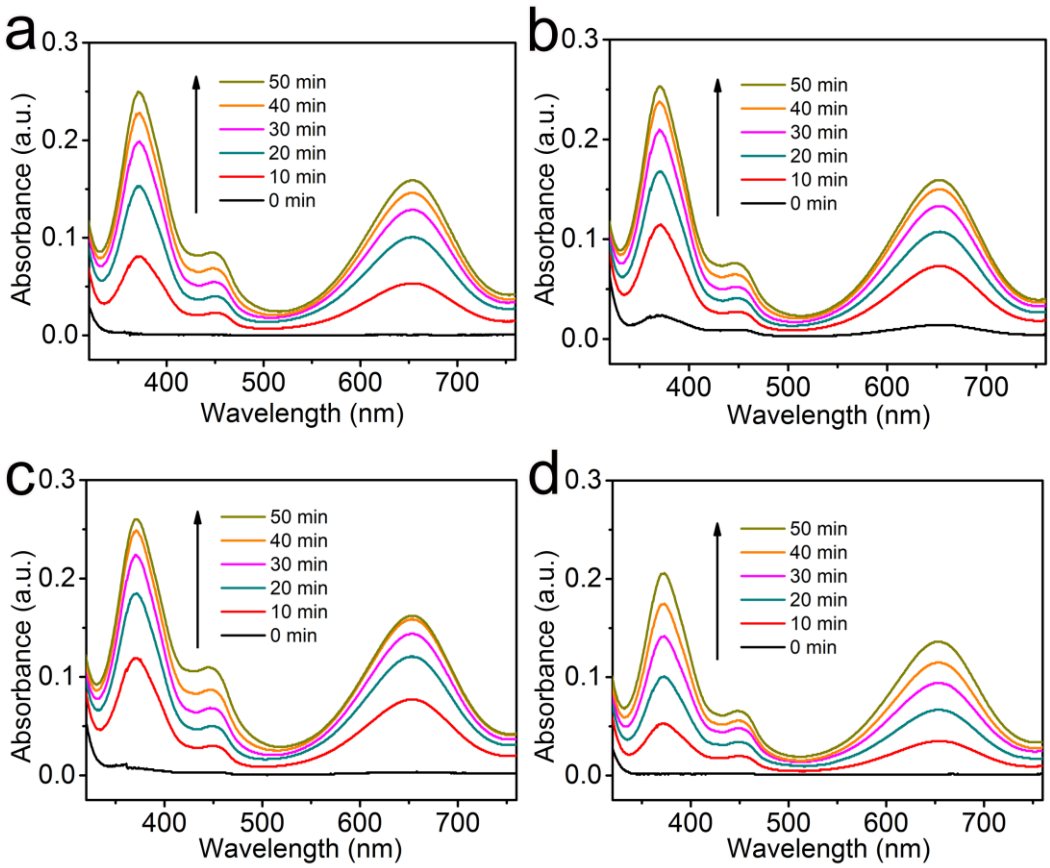


**Fig. S9** Time-dependent absorption spectra of TMB solution with **BiOBr photocatalyst and various scavengers** in $O_2$ atmosphere under UV-visible irradiation. (a) Catalase (3500 unit/mL, 200 μL), (b) superoxide dismutase (2000 unit/mL, 2 mL), (c) mannite (10 mg), and (d) carotene (5 mg).

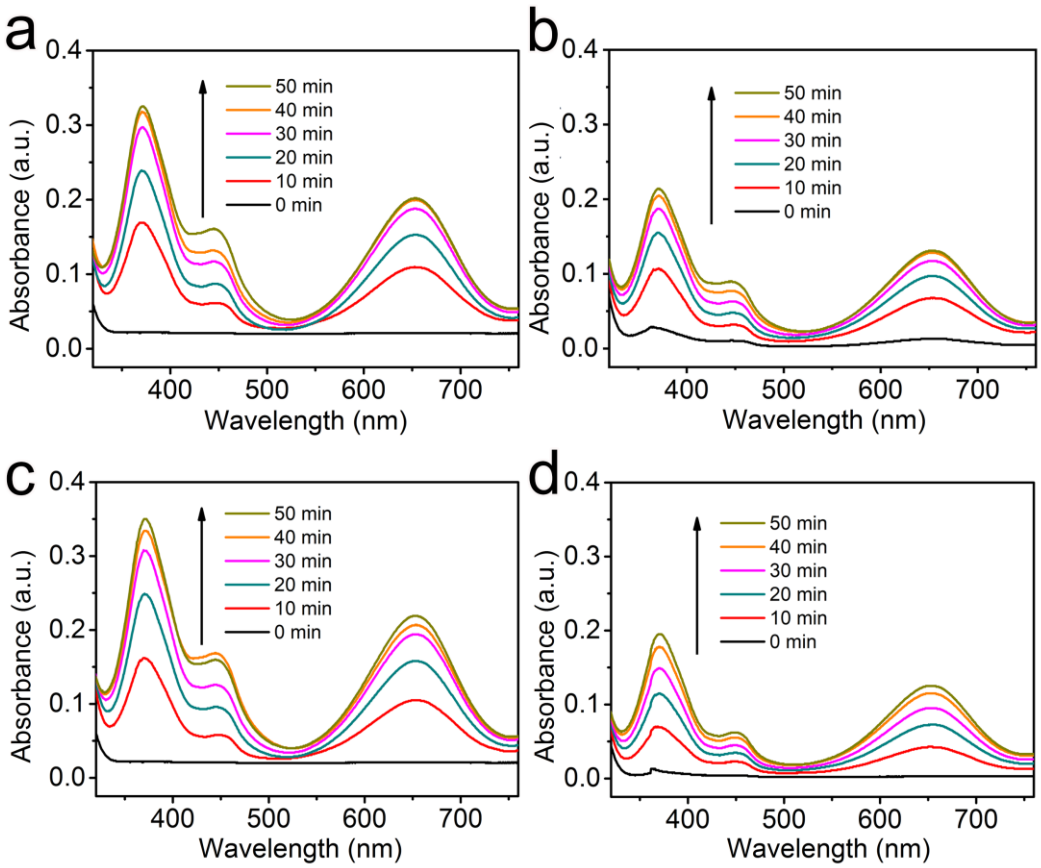


**Fig. S10** Time-dependent absorption spectra of TMB solution with **Pd/BiOBr photocatalyst and various scavengers** in $O_2$ atmosphere under UV-visible irradiation. (a) Catalase (3500 unit/mL, 200 μL), (b) superoxide dismutase (2000 unit/mL, 2 mL), (c) mannite (10 mg), (d) carotene (5 mg).

## 3. Supplementary tables

**Table S1.** Specific surface areas and pore volumes of BiOBr and Pd/BiOBr samples, determined by $N_2$ adsorption-desorption measurements.

| Sample | BET Surface area ($m^2/g$) | Average pore width (nm) |
|---|---|---|
| BiOBr | 13.7 | 29.9 |
| Pd/BiOBr | 11.5 | 28.3 |

**Table S2.** Lifetimes ($\tau_1$, $\tau_2$ and $\tau_{average}$[a]) and the relative intensities ($A_i$) for fitting the TRPL decay curves of BiOBr and Pd/BiOBr samples by a bi-exponential decay function $I_{(t)} = A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2)$ .

| Sample | $\tau_1$ (ns) | $\tau_2$ (ns) | $A_1$ | $A_2$ | $\tau_{average}$ (ns) |
|---|---|---|---|---|---|
| BiOBr | 0.87 | 4.73 | 62.2 | 37.7 | 0.84 |
| Pd/BiOBr | 0.59 | 2.97 | 30.1 | 69.9 | 0.58 |

[a] Average lifetime: $\tau_{average} = \frac{A_1 \cdot \tau_1^{\,2} + A_2 \cdot \tau_2^{\,2}}{A_1 \cdot \tau_1 + A_2 \cdot \tau_2}$

**Table S3.** Photocatalytic selective oxidation of toluene in the presence of different photocatalysts. Reaction conditions: 5 mg catalyst, 0.05 mmol toluene, 2 mL acetonitrile, Xe lamp (200 mW $cm^{-2}$), 5 h, $O_2$ atmosphere and room temperature.

| **Entry** | **Catalyst** | **Conversion (%)** | **Conversion rate ($\mu mol \cdot g_{cat}^{-1} \cdot h^{-1}$)** | **Selectivity (%)** |
|---|---|---|---|---|
| 1 | BiOBr | 15.9 | 317.8 | ＞99 |
| 2 | Pd(0.5)/BiOBr | 21.3 | 426.9 | ＞99 |
| 3 | Pd(1.0)/BiOBr | 23.8 | 476.8 | ＞99 |
| 4 | Pd(1.5)/BiOBr | 20.2 | 404.4 | ＞99 |
| 5 | Pd(2.0)/BiOBr | 16.1 | 320.9 | ＞99 |
| **6** | BiOBr(no mannitol) | 11.5 | 230.1 | ＞99 |
| **7** | Pd/BiOBr(no mannitol) | 18.8 | 375.8 | ＞99 |
| **8** | BiOBr(water) | 10.1 | 198.2 | ＞99 |
| **9** | Pd/BiOBr(water) | 15.3 | 306.4 | ＞99 |
| **10** | Au(1.0)/BiOBr | 16.6 | 331.9 | ＞99 |
| 11 | BiOBr-calcined | 0.7 | 12.9 | ＞99 |
| 12 | Pd(1.0)/BiOBr-calcined | 2.0 | 39.3 | ＞99 |
| **13**[a] | Pd(1.0)/BiOBr | 0 | 0 | / |
| **14**[b] | Pd(1.0)/BiOBr | 1.08 | 21.68 | ＞99 |

[a] The reaction was performed at 45 ℃ in dark.

[b] The photocatalytic reaction performed under $N_2$ atmosphere.

**Table S4.** Photocatalytic selective oxidation of toluene under different UV-visible irradiation intensity. Reaction conditions: 5 mg Pd/BiOBr catalyst, 0.05 mmol toluene, 2 mL acetonitrile, Xe lamp, 5 h, $O_2$ atmosphere and room temperature.

| Catalyst | Irradiation intensity (mW $cm^{-2}$) | Conversion (%) | Conversion rate ($\mu mol \cdot g_{cat}^{-1} h^{-1}$) | Selectivity (%) |
|---|---|---|---|---|
| Pd/BiOBr | 100 | 16.7 | 333.8 | ＞99 |
| | 200 | 23.8 | 476.8 | ＞99 |
| | 300 | 17.8 | 355.3 | ＞99 |
| | 400 | 18.8 | 376.2 | ＞99 |

**Table S5.** Photocatalytic selective oxidation of toluene with different toluene dosages. Reaction conditions: 5 mg catalyst, different toluene dosages, 2 mL acetonitrile, Xe lamp (200 mW $cm^{-2}$), 5 h, $O_2$ atmosphere and room temperature.

| Entry | Catalyst | $n_{toluene}$ (mmol) | Conversion (%) | Conversion rate ($\mu mol \cdot g_{cat}^{-1} h^{-1}$) | Selectivity (%) |
|---|---|---|---|---|---|
| 1 | BiOBr | 0.05 | 15.9 | 317.8 | ＞99 |
| 2 | Pd/BiOBr | 0.05 | 23.8 | 476.8 | ＞99 |
| 3 | Pd/BiOBr | 0.2 | 13.9 | 1108.8 | ＞99 |
| 4 | Pd/BiOBr | 1.0 | 6.1 | 2440.2 | ＞99 |
| 5 | Pd/BiOBr | 5.0 | 2.2 | 4387.7 | ＞99 |
| 6 | Pd/BiOBr | 9.4 | 1.6 | 6022.5 | ＞99 |

**Table S6.** Photocatalytic selective oxidation of para-substituted derivatives of toluene over Pd/BiOBr. Reaction conditions: 5 mg catalyst, 0.05 mmol substrate, 2 mL acetonitrile, Xe lamp (200 mW $cm^{-2}$), 5 h, $O_2$ atmosphere and room temperature.

| Substrate | Conversion (%) | Conversion rate ($\mu mol \cdot g_{cat}^{-1} h^{-1}$) | Selectivity (%) |
|---|---|---|---|
| p-H | 23.8 | 476.8 | ＞99 |
| p-F | 16.0 | 320.6 | ＞99 |
| p-Cl | 21.7 | 434.5 | ＞99 |
| p-$CH_3$ | 27.5 | 549.5 | ＞99 |
| p-$OCH_3$ | 24.0 | 479..4 | ＞99 |

**Table S7**. Recycling tests of Pd/BiOBr for photocatalytic selective oxidation of toluene. Reaction conditions: 5 mg catalyst, 0.05 mmol toluene, 2 mL acetonitrile, Xe lamp (200 mW $cm^{-2}$), $O_2$ atmosphere and room temperature, 5 h for each cycle.

| Cycle number | Conversion (%) | Conversion rate ($\mu mol \cdot g_{cat}^{-1} h^{-1}$) | Selectivity (%) |
|---|---|---|---|
| 1 | 23.8 | 476.8 | ＞99 |
| 2 | 22.6 | 451.8 | ＞99 |
| 3 | 22.1 | 442.0 | ＞99 |
| 4 | 21.6 | 431.2 | ＞99 |
| 5 | 20.6 | 410.9 | ＞99 |

**Table S8.** The adsorption energy of $O_2$ and $C_6H_5CH_3$ on different sites of BiOBr-$V_O$ (001) without and with Pd, respectively.

| **Adsorption sites** | **$\Delta E(O_2)$ (eV)** | **$\Delta E(C_6H_5CH_3)$ (eV)** |
|---|---|---|
| BiOBr-$V_O$ (001) | -1.58 | -0.96 |
| BiOBr-$V_O$ (001) with Pd | -2.72 | -4.72 |