***Supporting information for***

# Photothermal catalytic $CO_2$ oxidation dehydrogenation of propane to propylene over BiOX (X = Cl, Br, I) nanocatalysts

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**Table S1** Photothermal catalytic $CO_2$-ODHP over different photocatalysts

| Entry | Catalyst | Conv. (%) | Activity (μmol·$g_{cat}^{-1}$·$h^{-1}$) | | | | | $C_3H_6$ Sele.[c] (%) |
|---|---|---|---|---|---|---|---|---|
| | | | $CH_4$ | $C_2$[a] | $C_3H_6$ | $C_4$[b] | CO | |
| 1 | None | <0.1 | 0.4 | 0.4 | 5.6 | 2.4 | 0.2 | 60.9 |
| 2 | $TiO_2$[d] | 0.1 | 0.4 | 0.7 | 26.4 | 14.6 | 202.4 | 56.8 |
| 3 | BN | 0.1 | 0.3 | 0.7 | 20.8 | 12.8 | 19.8 | 54.2 |
| 4 | g-$C_3N_4$ | 0.1 | 0.7 | 0.3 | 9.4 | 13.9 | 32.2 | 33.1 |
| 5 | $Co_7Cu_1Mn_1$[e] | 0.1 | 4.6 | 2.2 | 22.2 | 11.5 | 16.6 | 54.6 |
| 6 | GaN | 0.1 | 3.6 | 0.2 | 9.6 | 13.3 | 18.3 | 33.4 |
| 7 | Bi | 0.2 | 0.6 | 2.8 | 80.8 | 8.0 | 24.9 | 86.4 |
| 8 | $Bi_2O_3$ | 0.1 | 0.5 | 0.2 | 47.9 | 9.3 | 52.6 | 79.0 |
| 9 | BiOCl nanosheets | 0.1 | 1.2 | 0.7 | 25.0 | 8.5 | 10.0 | 67.2 |
| 10 | BiOBr nanosheets | 0.1 | 1.6 | 1.6 | 38.9 | 8.8 | 13.9 | 74.5 |
| 11 | BiOI nanosheets | 0.7 | 3.6 | 11.6 | 282.6 | 20.4 | 525.2 | 89.0 |
| 12 | BiOI nanoflowers | 0.2 | 1.8 | 2.6 | 75.6 | 13.1 | 31.9 | 79.2 |
| 13 | $BiI_3$ | <0.1 | 0.3 | 0.1 | 1.3 | 7.4 | 20.3 | 11.5 |
| 14 | $Bi_2S_3$ | 0.1 | 6.9 | 0.2 | 21.1 | 8.2 | 76.5 | 61.2 |
| 15 | $Bi_2Fe_4O_9$ | <0.1 | 1.0 | 0.4 | 10.3 | 6.7 | 7.6 | 51.9 |
| 16 | $Bi_2WO_6$ | <0.1 | 2.2 | 0.5 | 2.0 | 9.5 | 57.8 | 12.5 |
| 17 | $BiVO_4$ | 0.1 | 1.0 | 1.1 | 32.4 | 12.4 | 80.9 | 64.9 |
| 18 | $Bi_2MoO_6$ | <0.1 | 1.2 | 0.2 | 2.9 | 13.8 | 24.1 | 13.4 |
| 19 | $Bi_{12}TiO_{20}$ | 0.2 | 0.8 | 3.9 | 65.2 | 11.3 | 45.2 | 78.5 |
| 20 | BiOI nanosheets[f] | - | - | - | - | - | 121.7 | - |
| 21 | BiOI nanosheets[g] | - | - | - | - | - | 11.4 | - |
| 22 | KI | <0.1 | 0.6 | 0.4 | 6.3 | 1.3 | 0.3 | 74.1 |
| 23 | KI+$H_2O$[h] | <0.1 | 0.9 | - | 5.9 | - | 0.8 | 95.1 |
| 24 | $I_2$ | 0.5 | 1.8 | 28.3 | 196.3 | 7.7 | 105.5 | 86.9 |

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| 25 | BiOI nanosheets (UV, 300 - 420 nm)[i] | 0.4 | 2.1 | 8.9 | 167.4 | 10.2 | 361.7 | 89.2 |
| 26 | BiOI nanosheets (420-1100 nm)[j] | 0.2 | 0.9 | 14.8 | 69.2 | 9.5 | 130.1 | 75.2 |

[a]Mainly ethane and ethylene. [b]Including *n*-butane, isobutane, *n*-butene, and isobutylene. [c]The selectivity of $C_3H_6$ in the total hydrocarbon products. [d]Prepared according to ref. 1. [e]Prepared according to ref. 2. Conditions: catalyst 30 mg, $C_3H_8/CO_2$ molar ratio 1/5, total volume 180 mL, 270 °C, 1 h, and full irradiation under 300 W Xe lamp, 621 $mW \cdot cm^{-2}$. [f]The reaction gases were 15 ml $H_2$, 15 ml $CO_2$, and 150 ml Ar. [g]The reaction gases were 15 ml $CO_2$ and 165 ml Ar. [h]2 mL of water were added. [i]The light intensity was 412 $mW \cdot cm^{-2}$. [j]The light intensity was 264 $mW \cdot cm^{-2}$.

## 2. GC spectra

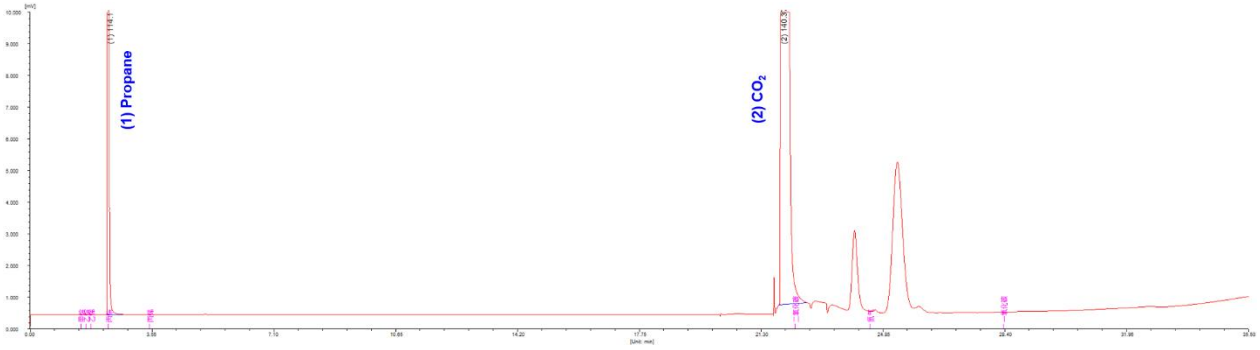


**Fig. S1** The GC spectrum of the reaction gas.

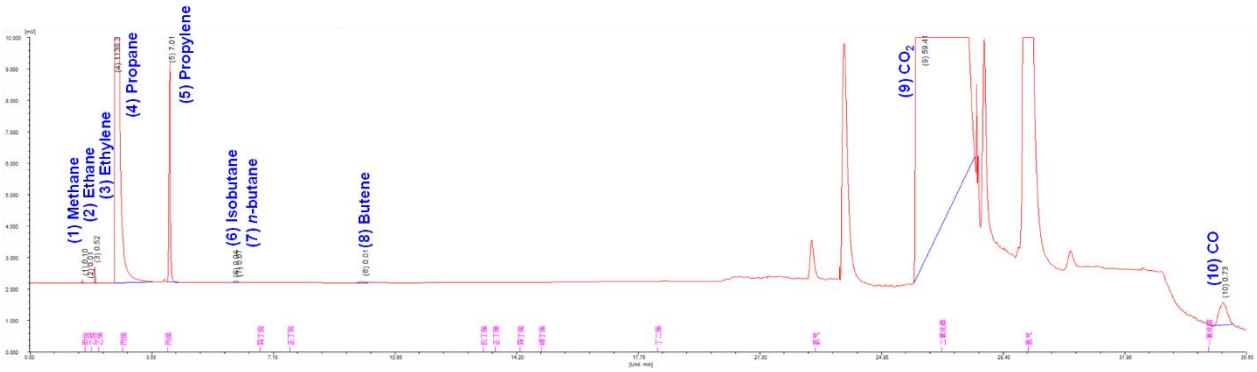


**Fig. S2** The GC spectrum of photothermal catalytic $CO_2$-ODHP reaction over the BiOI nanosheets catalyst.

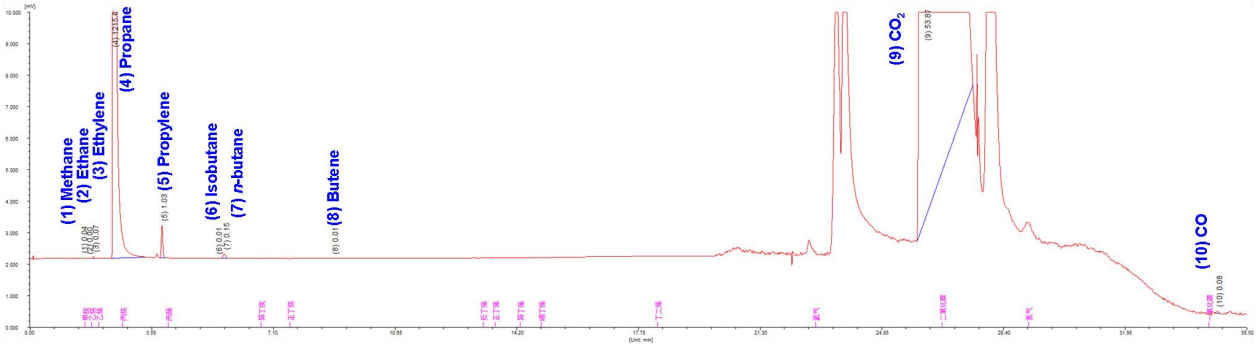


**Fig. S3** The GC spectrum of the photothermal catalytic $CO_2$-ODHP reaction over the BiOI nanoflowers catalyst.

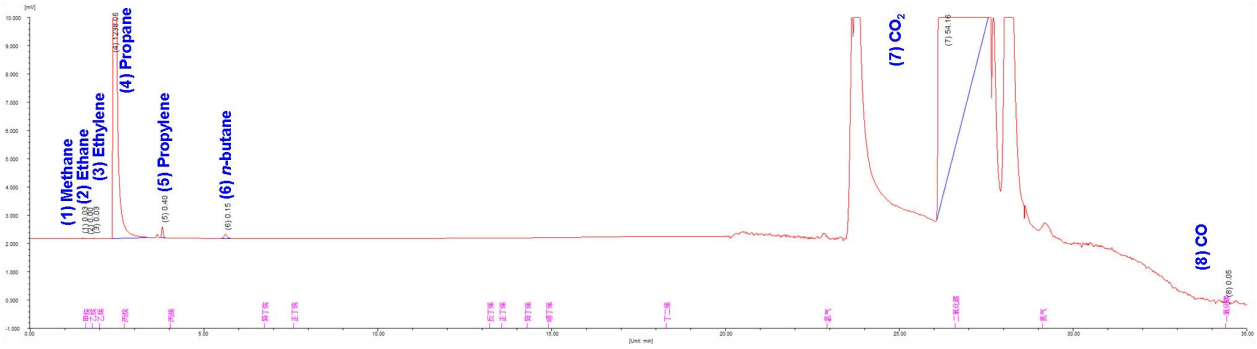


**Fig. S4** The GC spectrum of photothermal catalytic $CO_2$-ODHP reaction over the BiOBr nanosheets catalyst.

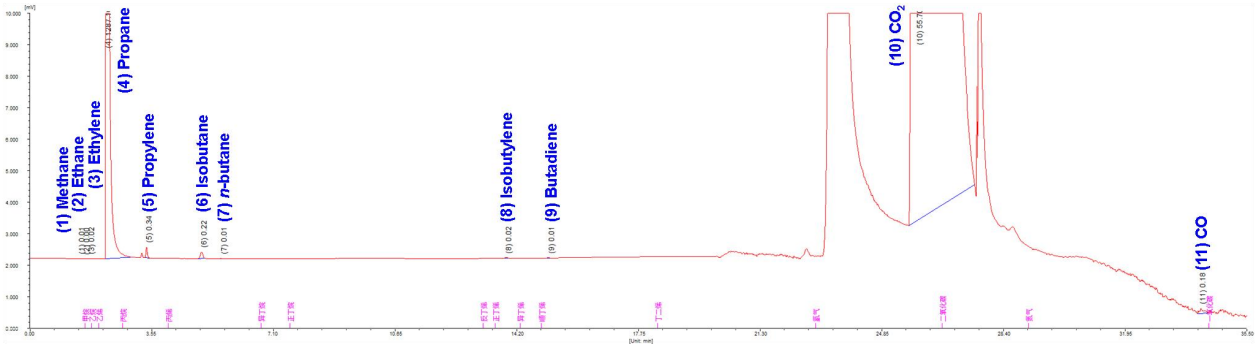


**Fig. S5** The GC spectrum of photothermal catalytic $CO_2$-ODHP reaction over the BiOCl nanosheets catalyst.

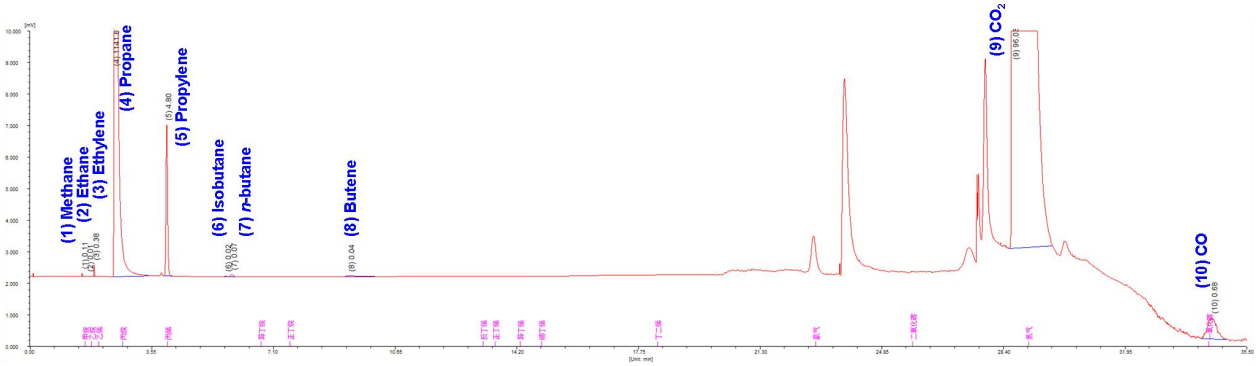


**Fig. S6.** The GC spectrum of photothermal catalytic DHP reaction over the BiOI nanosheets catalyst.

### 3. Pictures of the fresh BiOI nanosheets catalysts


**Fig. S7.** Pictures of the fresh BiOI nanosheets catalyst (a), the used BiOI nanosheets catalyst (b), and the catalyst after calcination at 400 °C(c), respectively.

## 4. XRD and XPS characterizations of the BiOI nanosheets catalyst after 13 runs

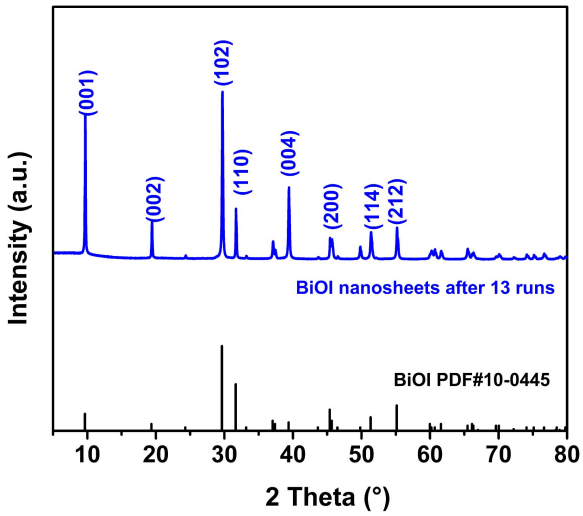


**Fig. S8** XRD of the catalyst after 13 runs.

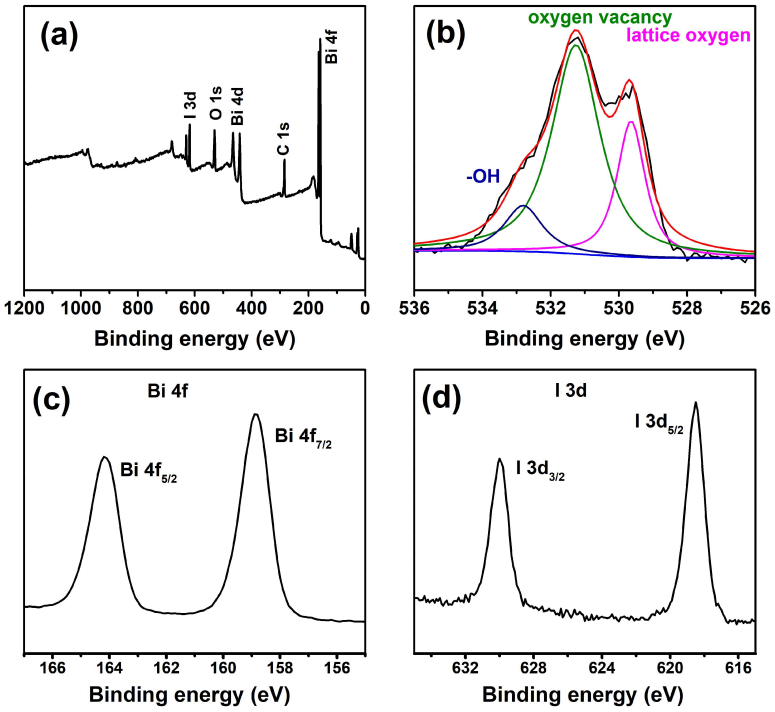


**Fig. S9** XPS spectra of the catalyst after 13 runs.

## References

[1] J. Wang, K. Wang, Z.-H. He, S.-S. Li, R.-R. Zhang, P. Guo, W. Wang, Y. Yang, Z.-T. Liu, Solvent-induced synthesis of hierarchical $TiO_2$ nanoflowers with tunable morphology by monolayer self-assembly for probing the photocatalytic performance, J. Nanostructure Chem., 2021, https://doi.org/10.1007/s40097-021-00445-2.

[2] Z.-H. He, Z.-H. Li, Z.-Y. Wang, K. Wang, Y.-C. Sun, S.-W. Wang, W.-T. Wang, Y. Yang, Z.-T. Liu, Photothermal $CO_2$ hydrogenation to hydrocarbons over trimetallic Co-Cu-Mn catalysts, Green Chem., 2021, 23, 5775-5785.