

## Electronic Supplementary Information

# Superior NO<sub>x</sub> photocatalytic removal over hybrid hierarchical Bi/BiOI with high Non-NO<sub>2</sub> selectivity: synergistic effect of oxygen vacancies and bismuth nanoparticles

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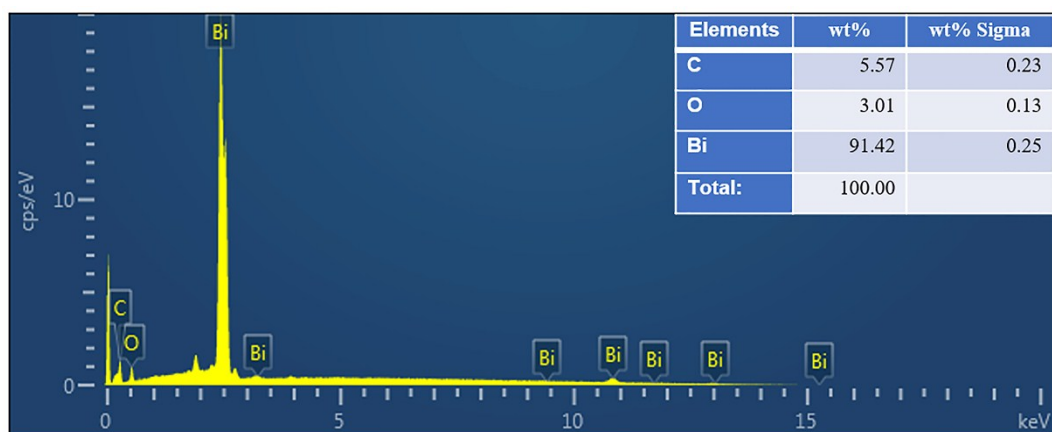
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**Table S1.** Surface area, average pore size and average desorption pore volume of BiOI and *x*-Bi/BiOI.

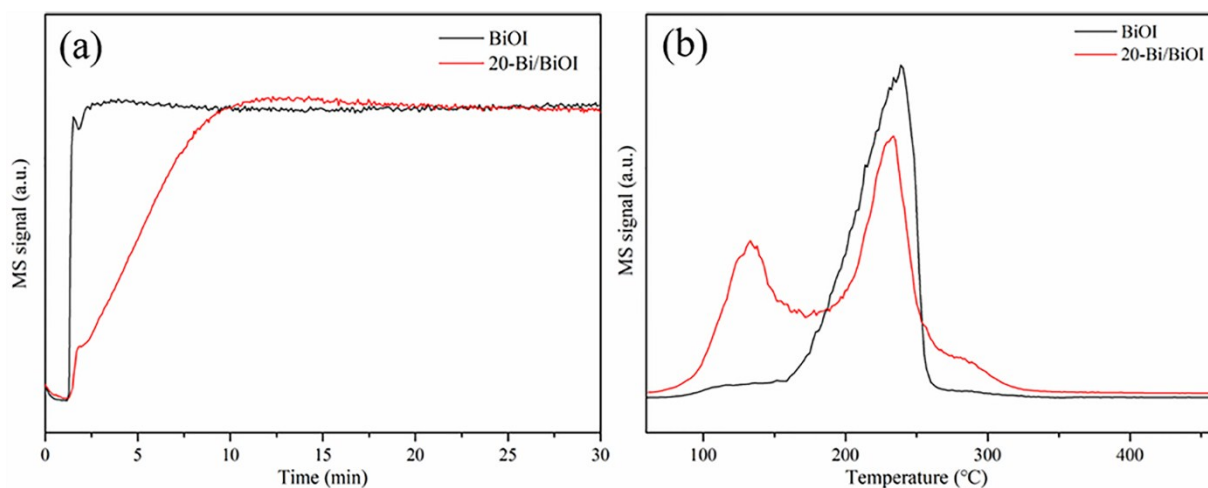
| Sample     | Surface area<br>(m <sup>2</sup> /g) | Average<br>pore size(nm) | Average desorption<br>pore volume (m <sup>3</sup> ) |
|------------|-------------------------------------|--------------------------|---|
| BiOI       | 65.61                               | 14.19                    | 0.266   |
| 5-Bi/BiOI  | 51.68                               | 14.63                    | 0.215   |
| 10-Bi/BiOI | 47.98                               | 15.18                    | 0.221   |
| 20-Bi/BiOI | 46.82                               | 16.62                    | 0.224   |
| 40-Bi/BiOI | 18.27                               | 18.10                    | 0.100   |

**Table. S2.** NO<sub>2</sub><sup>-</sup> and NO<sub>3</sub><sup>-</sup> accumulated on the surface of BiOI and x-Bi/BiOI after 2 h NO photocatalytic reactions.

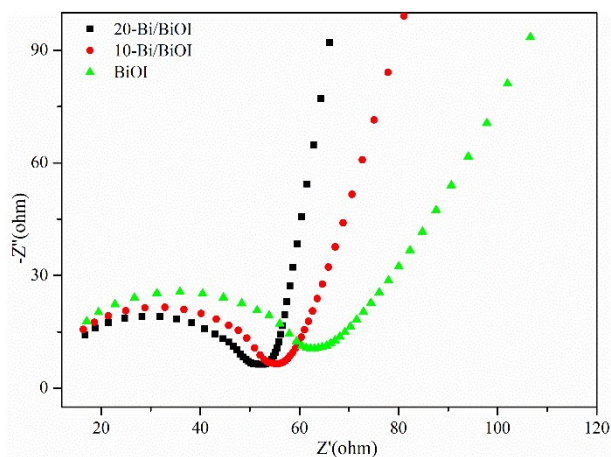
| Samples    | NO <sub>2</sub> <sup>-</sup> (μmol) | NO <sub>3</sub> <sup>-</sup> (μmol) | Total (μmol) |
|------------|-------------------------------------|-------------------------------------|--------------|
| BiOI       | 0.035                               | 1.690                               | 1.725        |
| 5-Bi/BiOI  | 0.049                               | 1.660                               | 1.709        |
| 10-Bi/BiOI | 0.583                               | 1.578                               | 2.161        |
| 20-Bi/BiOI | 1.185                               | 1.967                               | 3.152        |
| 40-Bi/BiOI | 1.975                               | 0.776                               | 2.751        |



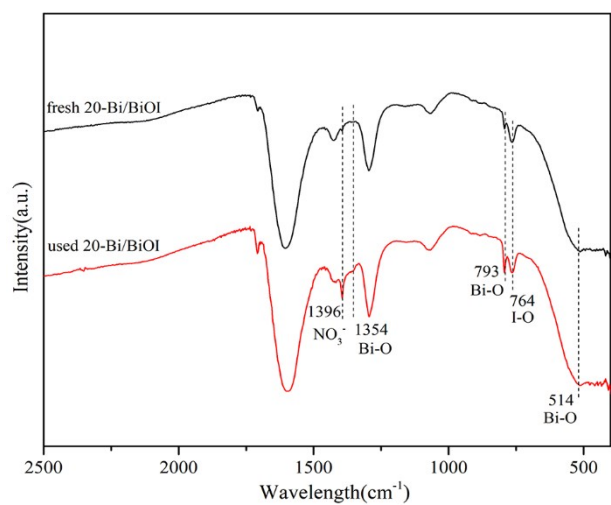
**Fig. S1.** SEM mapping EDS of as-prepared Bi metal.



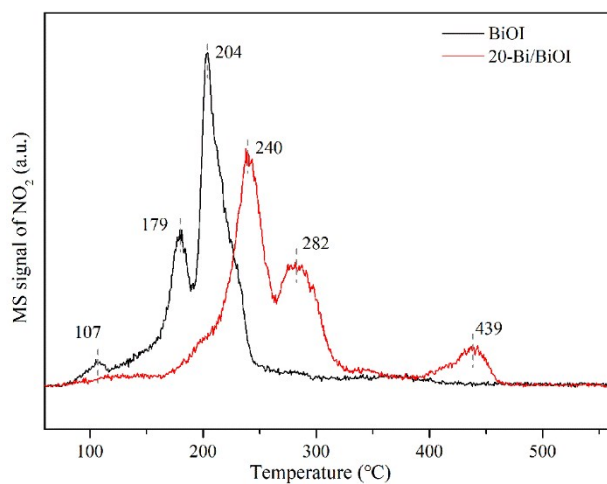
**Fig. S2.** NO adsorption spectra (a) and NO-TPD results (b) of BiOI and 20-Bi/BiOI.



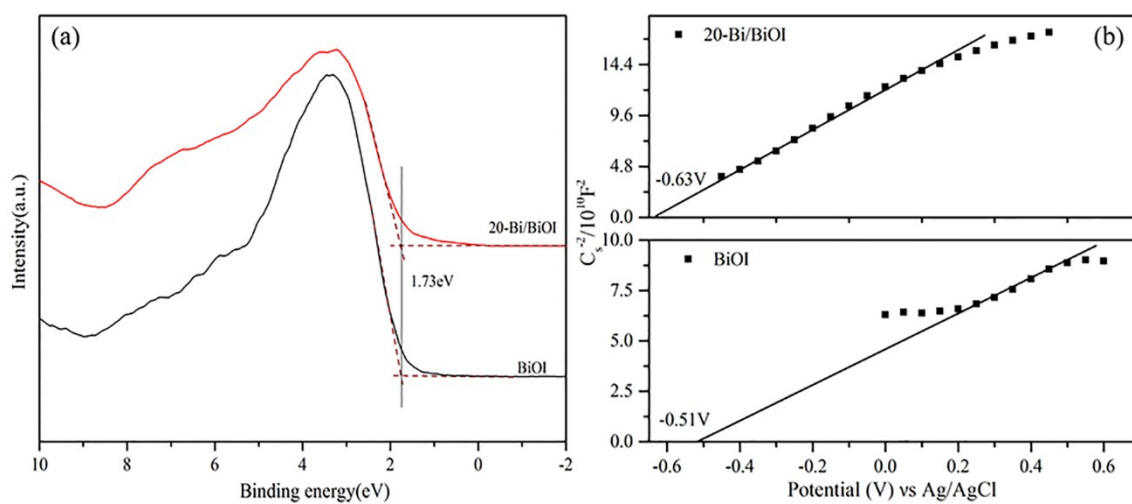
**Fig. S3.** EIS Nyquist plots of BiOI, 10-Bi/BiOI, and 20-Bi/BiOI in the dark.



**Fig. S4.** Comparison of the FTIR spectra of fresh and used 20-Bi/BiOI.



**Fig. S5.** NO<sub>2</sub>-TPD results of BiOI and 20-Bi/BiOI.



**Fig. S6.** XPS VB spectra (a) and flat-band potentials (b) of BiOI and 20-Bi/BiOI.