

## **Cation vacancy activating surface neighboring sites for efficient CO<sub>2</sub> photoreduction on Bi<sub>4</sub>Ti<sub>3</sub>O<sub>12</sub> nanosheets**

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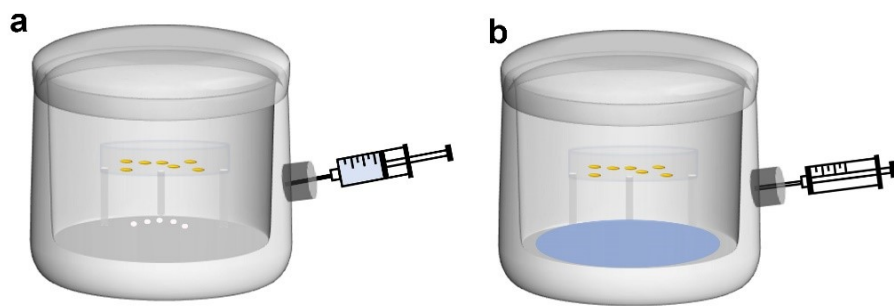
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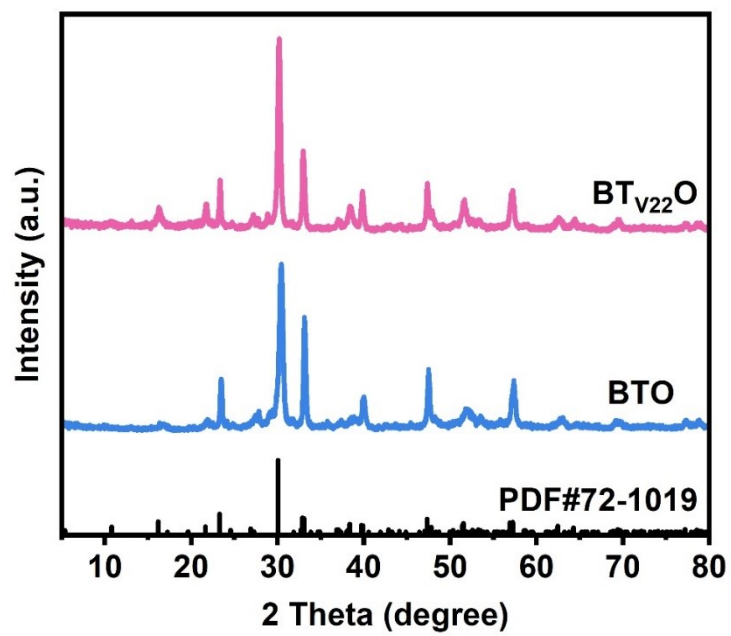
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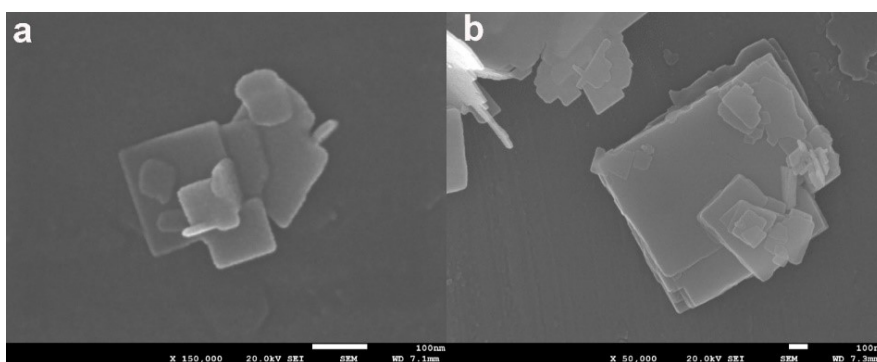
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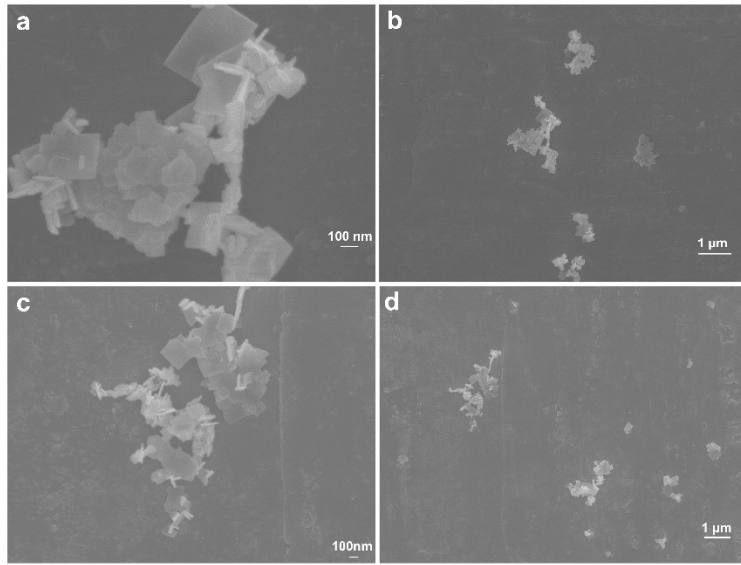
**Figure S1.** Schematic illustration of CO<sub>2</sub> photoreduction reactor.



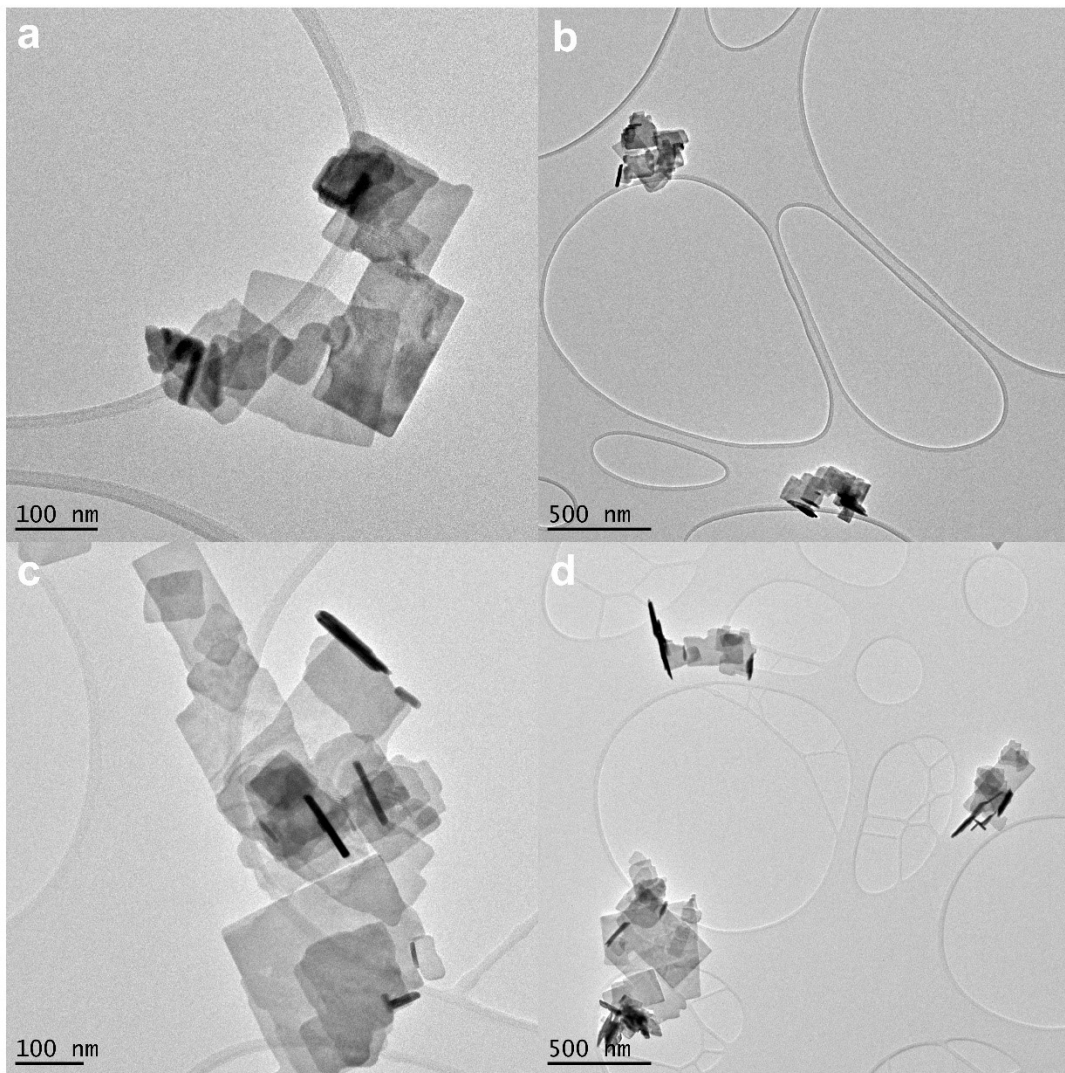
**Figure S2.** XRD patterns of BTO and  $BT_{V22}O$ .



**Figure S3.** SEM images of (a) BTO and (b) BT<sub>V22</sub>O.



**Figure S4.** SEM images with different magnifications of (a, b) BTO and (c, d) BT<sub>V22</sub>O.



**Figure S5.** TEM images with different magnifications of (a, b) BTO and (c, d)  $\text{BT}_{\text{V}22}\text{O}$ .

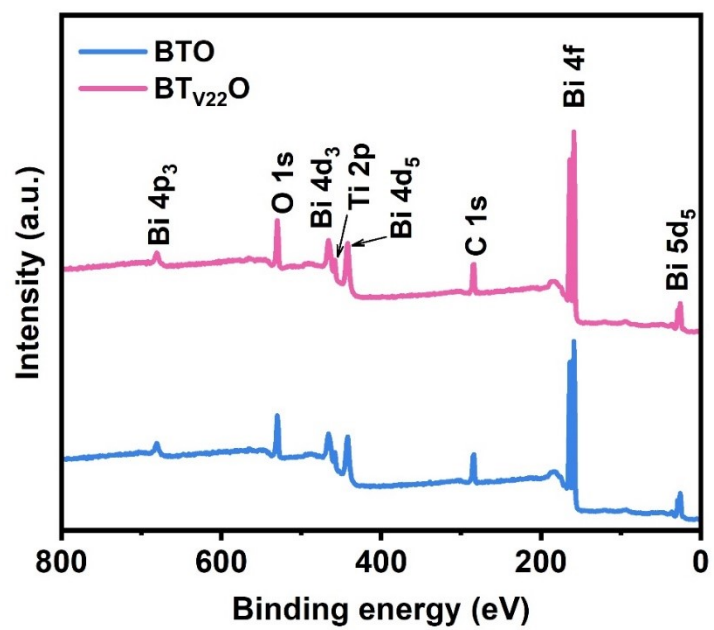
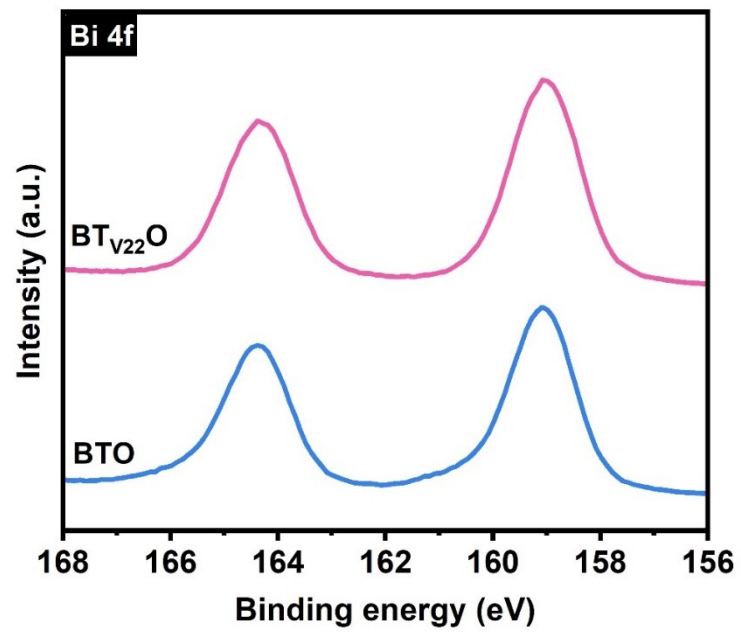
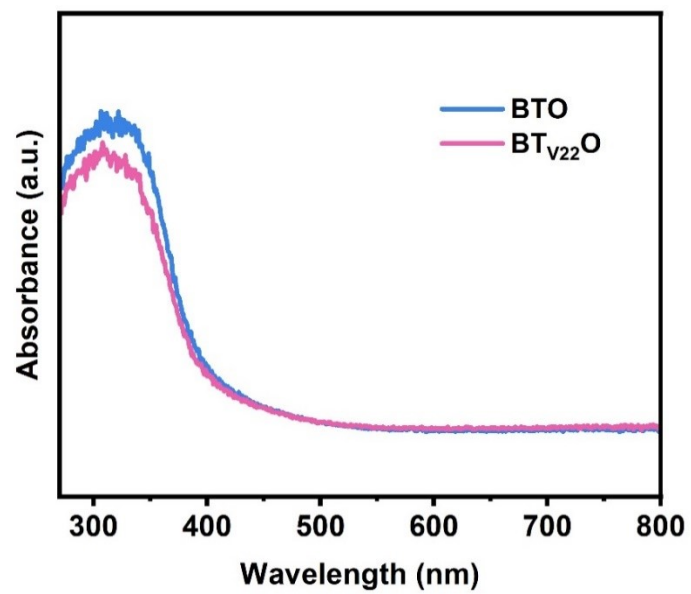


Figure S6. XPS spectra of BTO and  $\text{BT}_{\text{V}22}\text{O}$ .

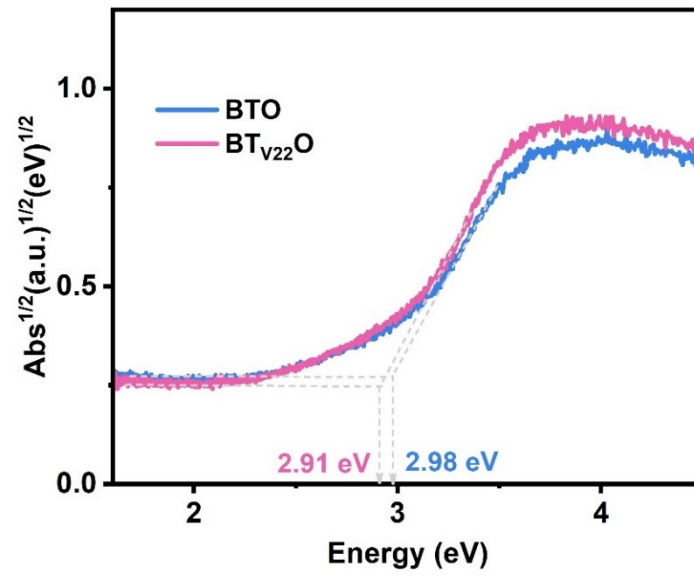


**Figure S7.** XPS spectra of Bi 4f of BTO and  $BT_{V22}O$ .

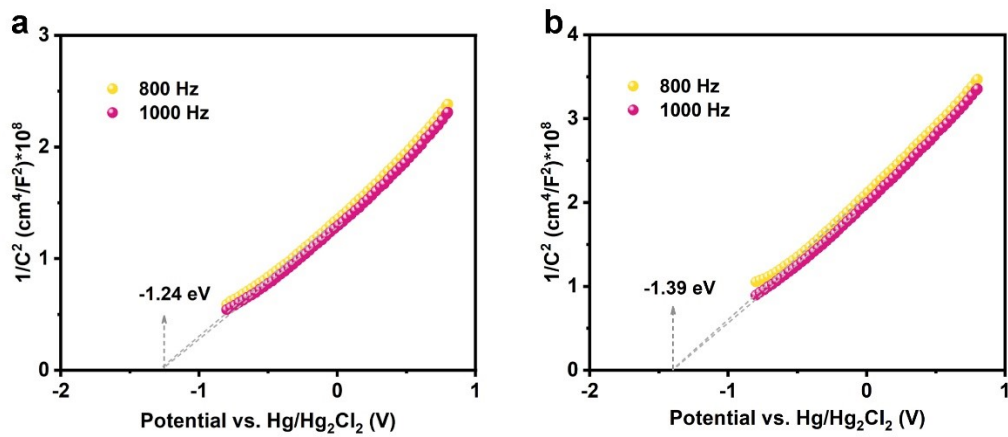




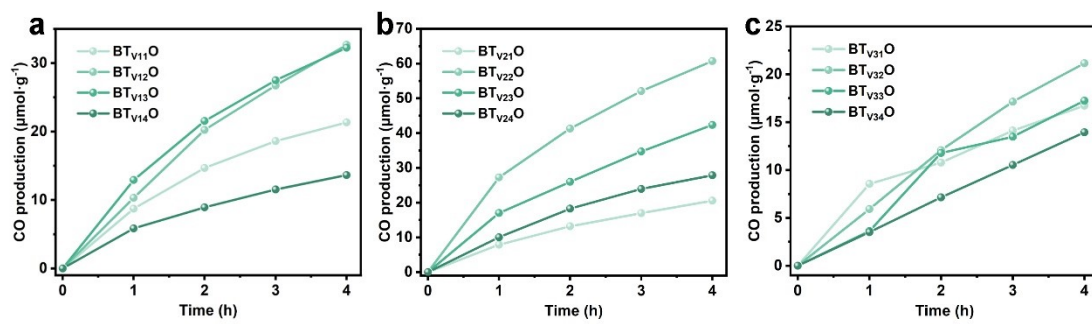
**Figure S8.** DRS spectra of BTO and  $BT_{V22}O$ .



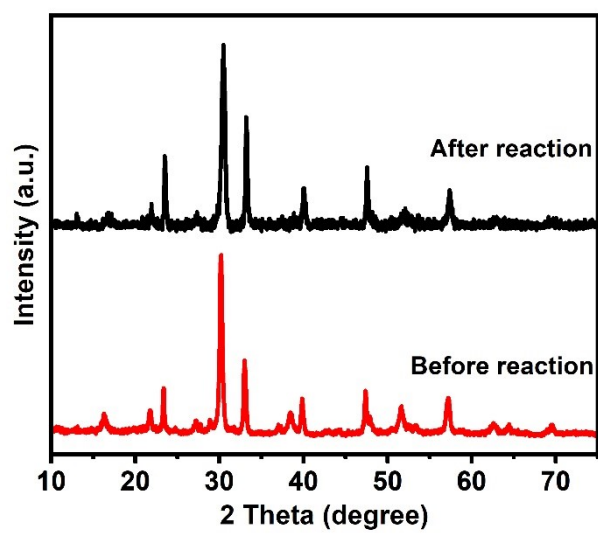
**Figure S9.** Bandgap of BTO and  $\text{BT}_{\text{V}22}\text{O}$ .



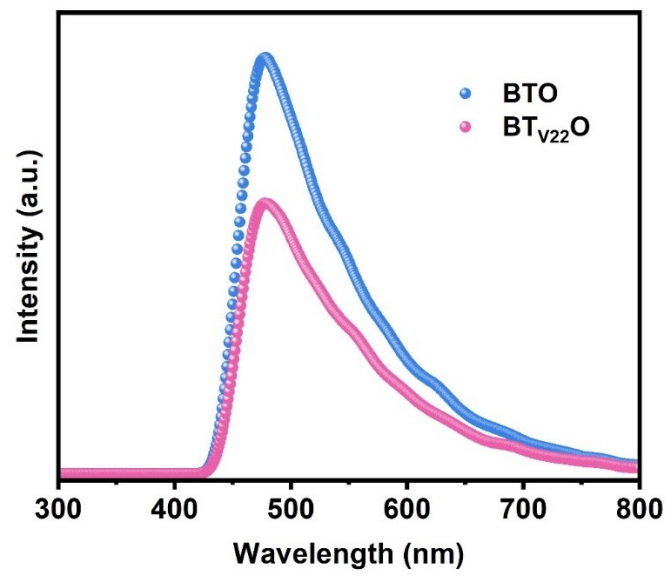
**Figure S10.** Mott-Schottky plots of (a) BTO and (b) BT<sub>V22</sub>O.



**Figure S11.** (a-c) Time-dependence CO production of BT<sub>VXY</sub>O (X=1, 2, 3; Y=1, 2, 3, 4).



**Figure S12.** XRD patterns of  $\text{BT}_{V22}\text{O}$  before and after photoreduction reaction.



**Figure S13.** PL spectra of BTO and  $\text{BT}_{V22}\text{O}$ .

**Table S1.** The concentrations (wt%) of Ti vacancy. (0.1, 0.5 and 1 M corresponding to the NaOH concentrations; 15, 30, 60 and 90 min corresponding to the treating time)

Treating time	0.1 M	0.5 M	1.0 M
15 min	1.08	1.82	3.47
30 min	4.38	7.20	10.01
60 min	4.63	9.84	10.34
90 min	10.01	15.55	15.88

**Table S2.** Comparison of the CO<sub>2</sub> photoreduction activity of BTO with the some selected Bi-based catalysts reported in the references.

<b>Photocatalyst</b>	<b>Light sources</b>	<b>Photoactivity</b>	<b>Ref.</b>
BT <sub>V22</sub> O	300W Xe lamp	CO: 15.17 μmol g <sup>-1</sup> h <sup>-1</sup>	This work
Bi <sub>4</sub> Ti <sub>3</sub> O <sub>12</sub> hollow-spheres	300W Xe lamp	CO: 13.1 μmol g <sup>-1</sup> h <sup>-1</sup>	[1]
Bi <sub>2</sub> O <sub>2</sub> (OH)(NO <sub>3</sub> ) with Br grafting	300W Xe lamp	CO: 8.12 μmol g <sup>-1</sup> h <sup>-1</sup>	[2]
BiVO <sub>4</sub> /Bi <sub>4</sub> Ti <sub>3</sub> O <sub>12</sub> heterojunction	300W Xe lamp	CO: 13.29 μmol g <sup>-1</sup> h <sup>-1</sup>	[3]
Hollow-hierarchical Bi <sub>2</sub> WO <sub>6</sub> nanosheets	300 W Xe lamp	CH <sub>4</sub> : 2.6 μmol g <sup>-1</sup> h <sup>-1</sup>	[4]
Bi <sub>2</sub> MoO <sub>6</sub>	300W Xe lamp	CO: 14.38 μmol g <sup>-1</sup> h <sup>-1</sup>	[5]
BiOI flowerlike hierarchical structures	300W Xe lamp	CH <sub>4</sub> : 0.40 μmol g <sup>-1</sup> h <sup>-1</sup>	[6]
g-C <sub>3</sub> N <sub>4</sub> /BiOCl heterostructures with OVs	300W Xe lamp	CO: 4.73 μmol g <sup>-1</sup> h <sup>-1</sup>	[7]



## References

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