

## Supporting Information

# Facilitating space charge directional separation for enhancing photocatalytic CO<sub>2</sub> reduction over tetragonal BiVO<sub>4</sub>

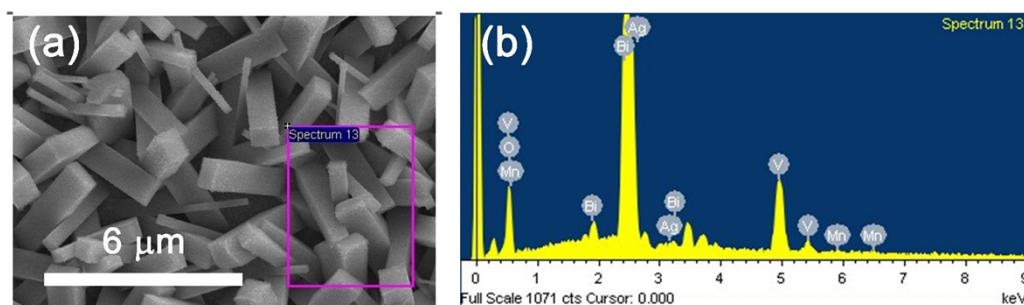
Dujuan Dai,<sup>a</sup> Yaqiang Wu,<sup>a</sup> Xiaolei Liu,<sup>a</sup> Yayang Xu,<sup>a</sup> Yuhao Guo,<sup>a</sup> Qianqian Zhang,<sup>a</sup> Zeyan Wang,<sup>a</sup> Zhaoke Zheng,<sup>a</sup> Yuanyuan Liu,<sup>a</sup> Hefeng Cheng,<sup>a</sup> Ying Dai,<sup>b</sup> Baibiao Huang<sup>a</sup> and Peng Wang\*<sup>a</sup>

<sup>a</sup> State Key Laboratory of Crystal Materials, Shandong University, Jinan 250100, China

<sup>b</sup> School of Physics, Shandong University, Jinan 250100, China

Corresponding author:

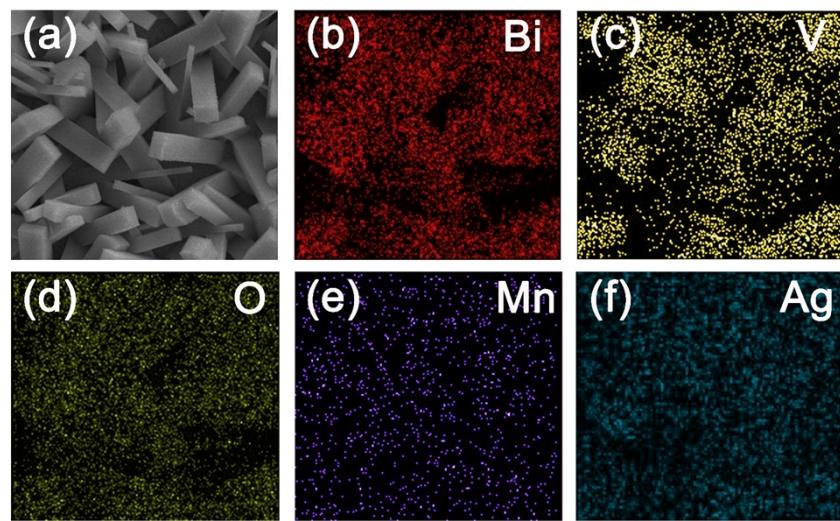
\*Email: [pengwangicm@sdu.edu.cn](mailto:pengwangicm@sdu.edu.cn)



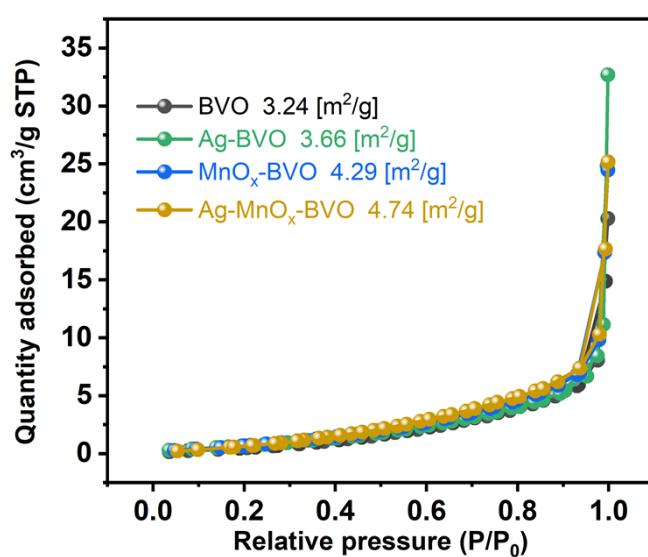
**Fig. S1** Energy Dispersive Spectrometer (EDS) spectra of Ag-MnO<sub>x</sub>-BVO sample.

**Table S1** The detailed information about the composition of Ag-MnO<sub>x</sub>-BVO sample.

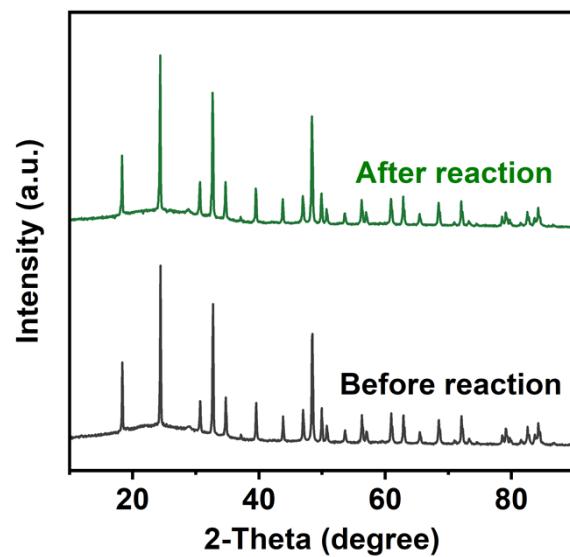
Element	Atomic%
O K	62.15
V K	17.02
Mn K	0.42
Ag L	0.55
Bi M	19.86
Totals	100



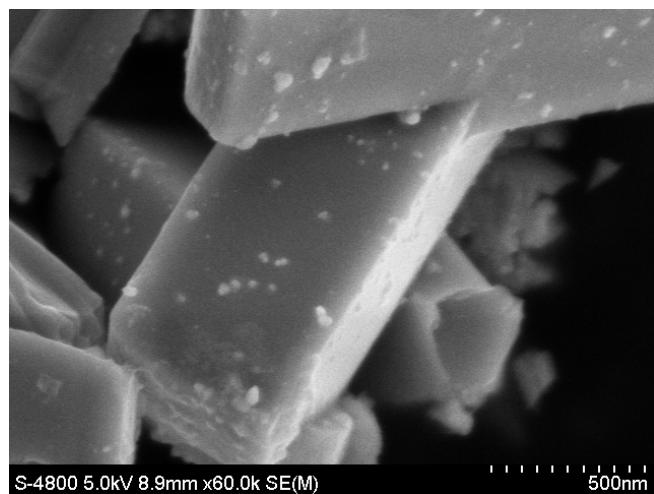
**Fig. S2** Mapping spectra of Ag-MnO<sub>x</sub>-BVO sample based on the selected region of Fig. S1a.



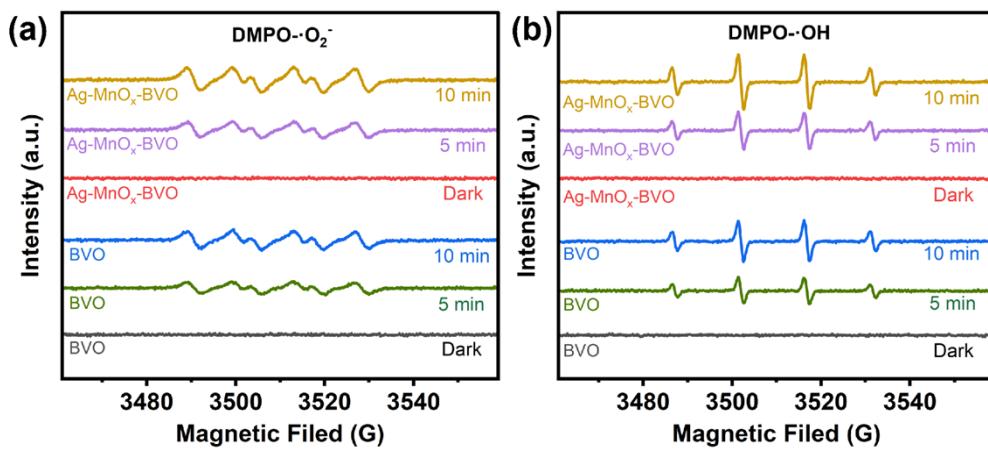
**Fig. S3** N<sub>2</sub> adsorption-desorption isotherms of BVO, Ag-BVO, MnO<sub>x</sub>-BVO and Ag-MnO<sub>x</sub>-BVO samples.



**Fig. S4** XRD patterns of Ag-MnO<sub>x</sub>-BVO sample before and after CO<sub>2</sub> reduction reaction.



**Fig. S5** SEM image of Ag-MnO<sub>x</sub>-BVO sample after CO<sub>2</sub> reduction reaction.



**Fig. S6** ESR signals of DMPO-•O<sub>2</sub><sup>-</sup> and DMPO-•OH over BVO and Ag-MnO<sub>x</sub>-BVO under dark and irradiation (full spectrum), respectively.

**Table S2.** The fitting parameters of time-resolved photoluminescence spectra via three-exponential decay fitting.

Sample	$\tau_1$ (ns)	$\tau_2$ (ns)	$\tau_3$ (ns)	$A_1$ (%)	$A_2$ (%)	$A_3$ (%)	$\tau_{\text{average}}$ (ns)
BVO	0.3115	1.5244	5.1691	57.93	23.89	18.17	1.48
MnO <sub>x</sub> -BVO	0.0159	1.3725	4.8224	39.61	53.91	6.48	1.06
Ag-BVO	0.0282	0.9728	4.1146	67.34	18.88	13.78	0.77
Ag-MnO <sub>x</sub> -BVO	0.0382	1.0362	4.3521	77.23	12.81	9.96	0.60

**Table S3.** The ICP-OES measurement of Ag and Mn on Ag-BVO,  $\text{MnO}_x$ -BVO and Ag- $\text{MnO}_x$ -BVO.

Catalyst sample	Ag loading (wt%)	Mn loading (wt%)
Ag-BVO	0.17	0
$\text{MnO}_x$ -BVO	0	0.05
Ag- $\text{MnO}_x$ -BVO	0.17	0.06