

***Supporting Information***

**Constructing crystalline-amorphous hydrated niobium pentoxide homojunction for superior photocatalytic CO<sub>2</sub> reduction into CH<sub>4</sub> with high selectivity**

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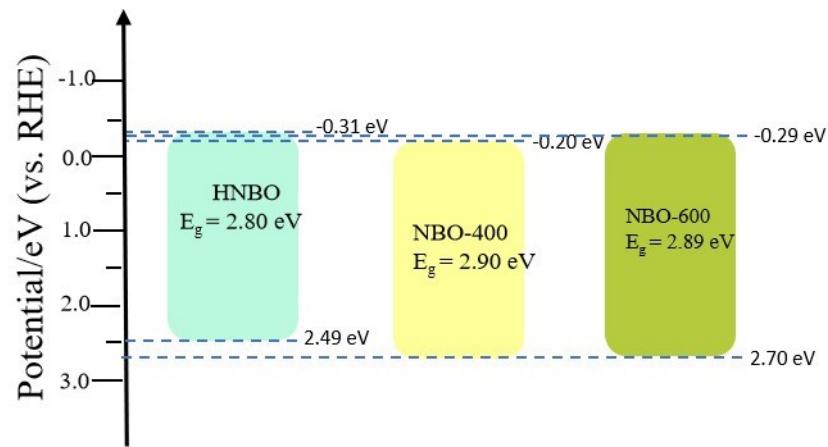
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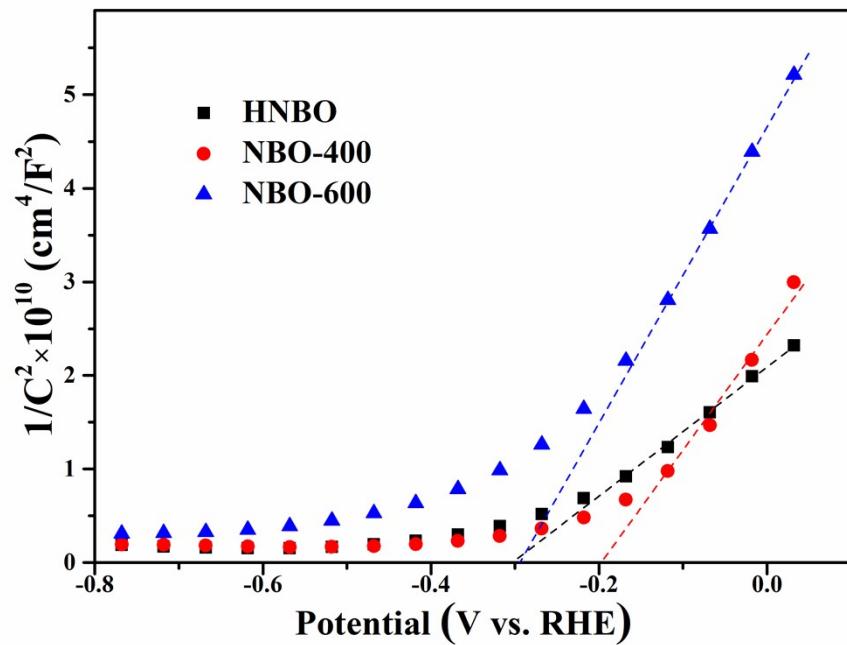
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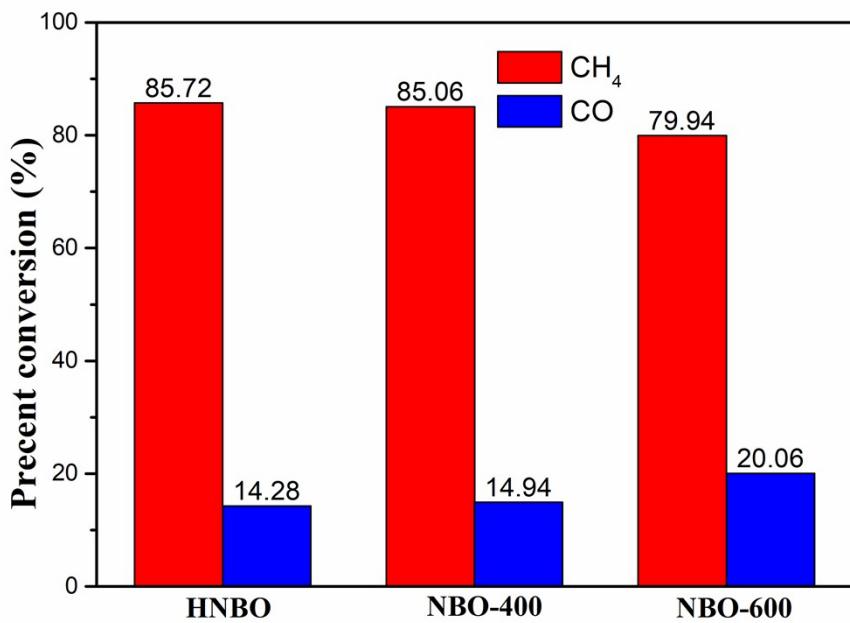
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**Fig. S1** Band structure of HNBO, NBO-400, and NBO-600.



**Fig. S2** Mott-Schottky plots of HNBO, NBO-400, and NBO-600



**Fig. S2** CH<sub>4</sub> and CO selectivity comparison over HNBO, NBO-400, and NBO-600.

**Table S1** Comparison of CO<sub>2</sub> photoreduction activity and selectivity for CH<sub>4</sub> over HNBO with other representative works reported in the literature.

Photocatalytic Materials	Light Source	Reaction condition	Production rate of CH <sub>4</sub>	Selectivity of CH <sub>4</sub>	Ref.
HNBO	300 W Xe lamp	Gas-solid, H <sub>2</sub> O	31.39 μmol/g/h	85.7%	This work
Bi <sub>4</sub> O <sub>5</sub> Br <sub>2</sub> /AgBr	300 W Xe lamp	Gas-solid, H <sub>2</sub> O	1.8 μmol/g/h	21.9%	[1]
O-doped g-C <sub>3</sub> N <sub>4</sub> /N-doped Nb <sub>2</sub> O <sub>5</sub>	300 W Xe lamp	Gas-solid, H <sub>2</sub> O	68.11 μmol/g/h	21.1%	[2]
NiO <sub>x</sub> /Nb <sub>2</sub> O <sub>5</sub>	UV light	Gas-solid, H <sub>2</sub> O	138.9 μmol/g/h	40.9%	[3]
g-C <sub>3</sub> N <sub>4</sub> /Pt/(TiO <sub>2</sub> @carbon)	Simulated sunlight	Gas-solid, H <sub>2</sub> O	6.56 μmol/g/h	81.7%	[4]
MoO <sub>2</sub> /g-C <sub>3</sub> N <sub>4</sub>	300 W Xe lamp	Gas-solid, H <sub>2</sub> O	0.145 μmol/g/h	20.3%	[5]
CuO/Nb <sub>2</sub> O <sub>5</sub>	UV light	Liquid-solid, H <sub>2</sub> O	2 μmol/g/h	68.6%	[6]
Black Nb <sub>2</sub> O <sub>5-x</sub>	300 W Xe lamp	Liquid-solid, H <sub>2</sub> O	19.5 μmol/g/h	64.8%	[7]

[1] Jin, X.; Cao, J.; Wang, H.; Lv, C.; Xie, H.; Su, F.; Li, X.; Sun, R.; Shi, S.; Dang, M.; Ye, L. Realizing improved CO<sub>2</sub> photoreduction in Z-scheme Bi<sub>4</sub>O<sub>5</sub>Br<sub>2</sub>/AgBr heterostructure. Appl.

Surf. Sci. 2022, 598, 153758.

- [2] Qaraah, F. A.; Mahyoub, S. A.; Hezam, A.; Qaraah, A.; Xin, F.; Xiu, G. Synergistic effect of hierarchical structure and S-scheme heterojunction over O-doped g-C<sub>3</sub>N<sub>4</sub>/N-doped Nb<sub>2</sub>O<sub>5</sub> for highly efficient photocatalytic CO<sub>2</sub> reduction. Appl. Catal. B: Envir. 2022, 315, 121585.
- [3] Wang, Z.; Xiao, M.; Wang, X.; Wang, H.; Chen, X.; Dai, W.; Yu, Y.; Fu, X. Thermo-driven photocatalytic CO<sub>2</sub> hydrogenation over NiO<sub>x</sub>/Nb<sub>2</sub>O<sub>5</sub> via regulating the electron transfer behavior of reactant gas adsorption. Appl. Surf. Sci. 2022, 592, 153246.
- [4] Wang, C.; Liu, X.; He, W.; Zhao, Y.; Wei, Y.; Xiong, J.; L, J.; Li, J.; Song, W.; Zhang, X.; Zhao, Z. All-solid-state Z-scheme photocatalysts of g-C<sub>3</sub>N<sub>4</sub>/Pt/macroporous-(TiO<sub>2</sub>@ carbon) for selective boosting visible-light-driven conversion of CO<sub>2</sub> to CH<sub>4</sub>. J Catal. 2020, 389, 440-449.
- [5] Li, H. J. W.; Zhou, H.; Chen, K.; Liu, K.; Li, S.; Jiang, K.; Zhang, W.; Xie, Y.; Cao, Z.; Li, H.; Liu, H.; Xu, X.; Pan, H.; Hu, J.; Tang, D.; Qiu, X.; Fu, J.; Liu, M. Metallic MoO<sub>2</sub>-modified graphitic carbon nitride boosting photocatalytic CO<sub>2</sub> reduction via Schottky junction. Solar Rrl. 2020, 4(8), 1900416.
- [6] Nogueira, A. E.; Silva, G. T.; Oliveira, J. A.; Lopes, O. F.; Torres, J. A.; Carmo, M.; Ribeiro, C. CuO decoration controls Nb<sub>2</sub>O<sub>5</sub> photocatalyst selectivity in CO<sub>2</sub> reduction. ACS Appl. Energy Mater. 2020, 3(8), 7629-7636.
- [7] Lin, X.; Xia, S.; Zhang, L.; Zhang, Y.; Sun, S.; Chen, Y.; Chen, S.; Ding, B.; Yu, J.; Yan, J. Fabrication of Flexible Mesoporous Black Nb<sub>2</sub>O<sub>5</sub> Nanofiber Films for Visible - Light - Driven Photocatalytic CO<sub>2</sub> Reduction into CH<sub>4</sub>. Adv. Mater. 2022, 34(16), 2200756.