## **Electronic Supplementary Information (ESI)**

## Self-assembled CoTiO<sub>3</sub> nanorods with controllable oxygen vacancy

## for efficient photochemical reduction of CO<sub>2</sub> to CO

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Fig. S1. Survey-scan XPS spectra of CoTiO<sub>3</sub> and OV-CoTiO<sub>3</sub>.



Fig. S2. XRD patterns of OV-CTO and pure CTO.



Fig. S3. Raman spectra of CTO and CTO-3 samples.



**Fig. S4.** <sup>1</sup>H NMR spectra of TEOA, photosensitizer, CH<sub>3</sub>CN and liquid phase substances after photoreduction.



**Fig. S5.** XRD pattern of OV-CTO (the dosage of NaBH<sub>4</sub> is 3 molar equivalent at 550 °C).



Fig. S6. CO<sub>2</sub>-TPD spectra.



Fig. S7.  $N_2$  adsorption-desorption isotherms and the corresponding pore size distribution (inset) of (a) CTO and (b) CTO-3.



Fig. S8. Recycling test of CTO-3 in photocatalytic CO<sub>2</sub> reduction.



Fig. S9. XRD pattern of recycling CTO-3.



Fig. S10. EPR spectrum of used CTO-3.

Entry	Catalyst/ CTO-3	Photosensitizer/ [Ru(bpy) <sub>3</sub> ]Cl <sub>2</sub> ·6H <sub>2</sub> O	CO <sub>2</sub>	TEOA	Light	Yield of CO (µmol)	Yield of H <sub>2</sub> (µmol)
1	×	$\checkmark$	$\checkmark$	$\checkmark$	$\checkmark$	0	1.1
2	$\checkmark$	×	$\checkmark$	$\checkmark$	$\checkmark$	0	0.4
3 <sup>b</sup>	$\checkmark$	$\checkmark$	×	$\checkmark$	$\checkmark$	0	14.3
4	$\checkmark$	$\checkmark$	$\checkmark$	×	$\checkmark$	0	0
5	$\checkmark$	$\checkmark$	$\checkmark$	$\checkmark$	×	0	0.1
6	$\checkmark$	$\checkmark$	$\checkmark$	$\checkmark$	$\checkmark$	31.8	18.3

Table S1. Control experiments of photocatalytic CO<sub>2</sub> reduction.<sup>a</sup>

<sup>a</sup>Conditions: CTO-3 (1 mg),  $[Ru(bpy)_3]Cl_2 \cdot 6H_2O$  (5 mg), acetonitrile :  $H_2O$  : TEOA = 4 mL : 1 mL : 1.5 mL in the quartz tube of 55 mL, CO<sub>2</sub> (1 atm), irradiation with white LED lamp at room temperature. <sup>b</sup>Degassed with argon.