

## Supporting Information

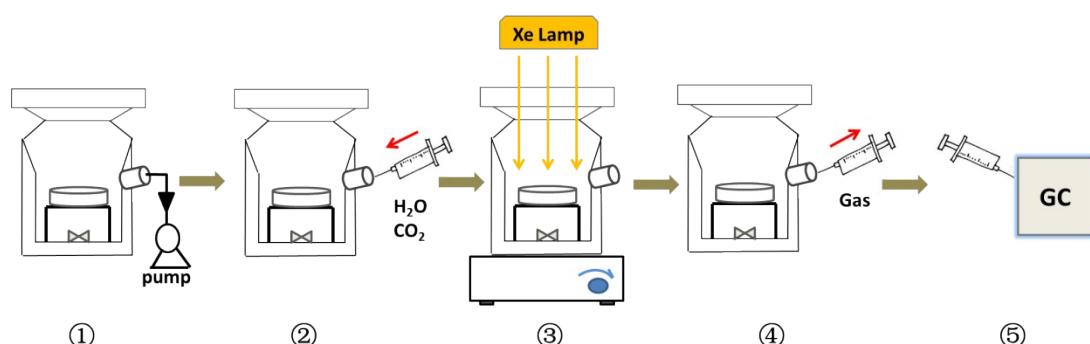
### Phosphorus-Doped Inverse Opal g-C<sub>3</sub>N<sub>4</sub> for Efficient and Selective CO Generation from Photocatalytic Reduction of CO<sub>2</sub>

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**Figure S1.** CO<sub>2</sub> photoreduction flowchart (1. Evacuate the reactor; 2. Inject 1 mL ultrapure water and 200 mL CO<sub>2</sub> into the reactor; 3. Irradiate the catalyst with Xe lamp for 4 h; 4. Extract 5 mL of reacted gas; 5. Inject gas into GC for analysis).

**The calculation of the evolution rate of CO is according to Eqs. S1:**

$$\text{CO evolution rate} = \frac{s}{S_0} * \frac{C_0 V_0}{22.4 m t} \quad (\text{S1})$$

*s*: Peak area of CO in the react gas in GC;

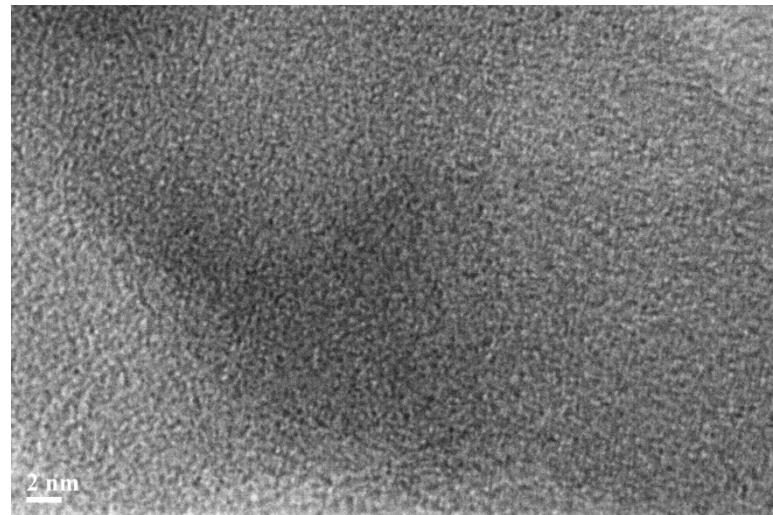
*S<sub>0</sub>*: Peak area of CO in standard gas in GC;

*C<sub>0</sub>*: Standard gas concentration (ppm);

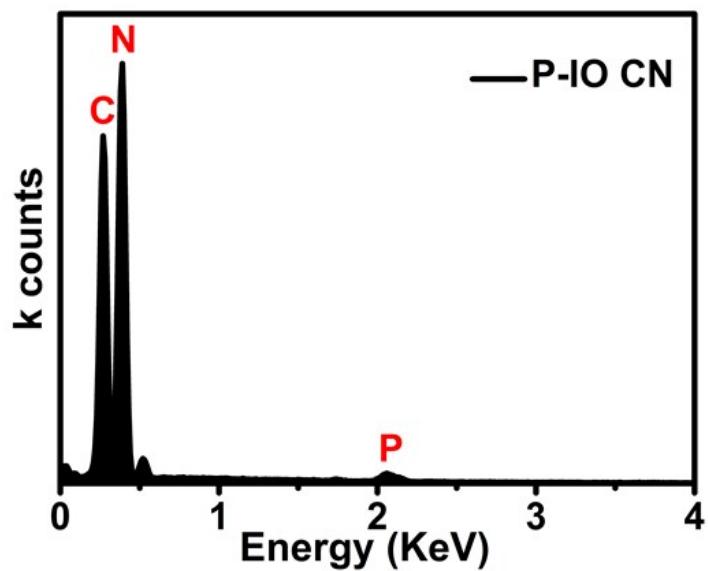
*V<sub>0</sub>*: The volume of the reactor (L);

*m*: The quality of the catalyst (g);

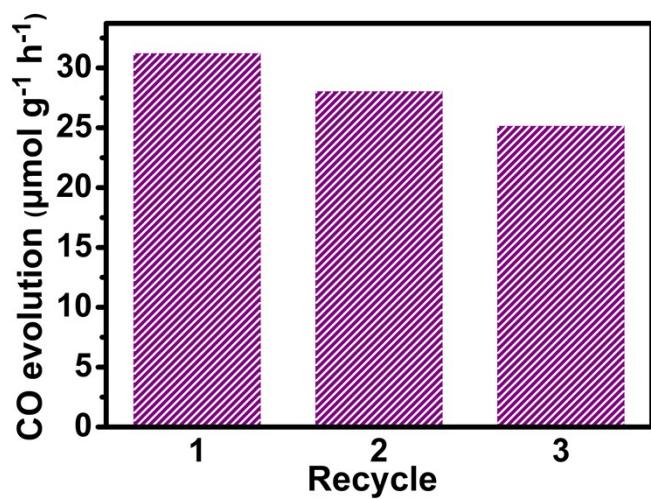
*t*: The time of irradiation (h).



**Figure S2.** HRTEM images of P-IOCN



**Figure S3.** EDS analysis of P-IOCN



**Figure S4.** Cycling tests of photocatalytic CO<sub>2</sub> reduction into CO over P-IOCN

**Table S1.** Specific surface area and pore volume of the photocatalysts

Catalyst	Surface Area(m <sup>2</sup> /g)	Pore Volume(cm <sup>3</sup> /g)
Bulk CN	3.89	0.034556
IO CN	34.19	0.145081
P-IO CN	19.88	0.123472

**Table S2.** Elemental analysis and ICP-AES of P-IOCN

Catalyst	N (wt%)	C (wt%)	P (wt%)	C/N (wt%)
IO CN	52.14	32.73	0	0.6277
P-IO CN	52.12	32.09	0.68	0.6156

**Table S3.** Comparison of CO<sub>2</sub> photoreduction activity of the P-IO CN with other reported photocatalysts.

Catalyst	Catalyst amount (mg); Reaction solution	Light source	Evolution rate (μmol g <sup>-1</sup> h <sup>-1</sup> )	Reference
P-IO CN	30 mg H <sub>2</sub> O (1 mL)	300 W Xe lamp	CO: 31.22	This work
α-Fe <sub>2</sub> O <sub>3</sub> /g-C <sub>3</sub> N <sub>4</sub>	25 mg H <sub>2</sub> SO <sub>4</sub> (5 mL, 4 M)	300 W Xe lamp	CO: 27.2	<sup>1</sup>
Ti <sub>3</sub> C <sub>2</sub> MXene/ g-C <sub>3</sub> N <sub>4</sub>	20 mg NaHCO <sub>3</sub> (1.26 g) H <sub>2</sub> SO <sub>4</sub> (4 mL, 2 M)	300 W Xe lamp with 420 nm filter	CO: 5.2	<sup>2</sup>
Flower-like g-C <sub>3</sub> N <sub>4</sub>	30 mg H <sub>2</sub> O (0.5 mL)	300 W Xe lamp	CO: 18.8	<sup>3</sup>
ZnO/g-C <sub>3</sub> N <sub>4</sub>	100 mg NaHCO <sub>3</sub> (0.12 g) HCl (0.25 mL, 4 M)	500 W Xe lamp with 420 nm filter	CO: 29	<sup>4</sup>
CoZnAl- LDH/RGO/g-C <sub>3</sub> N <sub>4</sub>	50 mg H <sub>2</sub> O (0.4 mL)	300W Xe lamp	CO: 10.1	<sup>5</sup>
CQDs/g-C <sub>3</sub> N <sub>4</sub>	20 mg water vapor	300W Xe lamp with 400 nm filter	CO: 23.4	<sup>6</sup>
WO <sub>3</sub> /g-C <sub>3</sub> N <sub>4</sub>	30 mg H <sub>2</sub> O (95 mL) TEOA (5 mL)	300W Xe lamp with 420 nm filter	CO: 14.6	<sup>7</sup>

## Notes and references

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