Supporting Information

Morphology and Element Doping Effect：Phosphorus-Doped Hollow Polygonal g-C_3N_4 Rods for Visible Light-Driven CO_2 Reduction

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Quantitative analysis of product gases

After the reaction, partial gaseous products (1 mL) were taken from the tube using a syringe, and then analyzed by gas chromatography (GC, FuLi 9790II) with a TCD detector to determine the moles of CO. Afterwards, the total moles of CO obtained in the photocatalytic CO_2 reduction was calculated with the headspace volume of the Schlenk tube.

$$V_{co} = \left(S_{co}/S_{co(1mL)}\right)/\left(\frac{S_{H_2}}{S_{H_2(1mL)}} + \frac{S_{co_2}}{S_{Hco_2(1mL)}} + \frac{S_{co}}{S_{co(1mL)}}\right) \cdot V_{tube} \quad (1)$$

$$V_{H_2} = \left(S_{H_2}/S_{H_2(1mL)}\right)/\left(\frac{S_{H_2}}{S_{H_2(1mL)}} + \frac{S_{co_2}}{S_{Hco_2(1mL)}} + \frac{S_{co}}{S_{co(1mL)}}\right) \cdot V_{tube} \quad (2)$$

$$n_{co} = P \cdot V_{co}/RT \quad (3)$$

$$n_{H_2} = P \cdot V_{H_2}/RT \quad (4)$$

$$Selectivity(S) = \left[\frac{n_{co}}{\left(n_{co} + n_{H_2}\right)}\right] \cdot 100\% \quad (5)$$

where S_{H_2}, S_{CO}, S_{CO_2} represent the integral areas in the gas chromatography spectra (Shown as Fig. S3) of H_2, CO and CO_2 for 1 mL gaseous products respectively. $S_{H_2(1\,mL)}$, $S_{CO(1\,mL)}$, $S_{CO_2(1\,mL)}$ represent the integral areas for 1 mL pure H_2, 1 mL pure CO and 1 mL pure CO_2, respectively. In addition, $V_{tube}\,(mL)$, $V_{CO}\,(mL)$ and $V_{H_2}\,(mL)$ is the headspace volume of the Schlenk tube and the volume of CO and H_2 in the total gaseous products. And $n_{co}\,(\mu mol)$ and $n_{H_2}\,(\mu mol)$ represent the total moles of CO and H_2 in the headspace of the Schlenk tube.

Quantum efficiency calculation

Measurement of the Number of Moles of Photons: To a 25 mL flask, $Ru(bpy)_3Cl_2$ (0.1 mM), 1,9-diphenylanthracene (DPA, 0.1 mM) and 25 mL acetonitrile were added. After that, the absorbance at 372 nm was recorded as $A_{INITIAL}$. Then, the sample was irradiated under 500 W Xenon long-arc lamp ($\lambda \geq 400$ nm) for 10 min and a new UV-Vis spectra of sample at 372 nm was recorded, which was denoted as A_{FINAL}. The equation below was used to calculate the moles of consumed DPA.

$$\text{moles DPA consumed} = \left(\frac{A_{INITIAL} - A_{FINAL}}{\varepsilon_{372nm} l}\right) \times V$$

Where $A_{INITIAL}$ and A_{FINAL} are the absorbance of the solution at 372 nm before and after irradiation, respectively; ε_{372nm} is the extinction coefficient of DPA at 372 nm in acetonitrile (11000 $M^{-1}cm^{-1}$), l is the path length of the cuvette (1 cm), and V is the volume of sample for which the absorption was measured (3 mL). Since the quantum yield (Φ) for $Ru(bpy)_3Cl_2$ is known to be 0.019, the moles of photons absorbed by our sample per unit time $\frac{Nhv}{t}$ were determined using the consumed moles of DPA by following equation:

$$\frac{Nhv}{t} = \frac{moles\ of\ DPA\ consumed}{\Phi t}$$

Where Φ is quantum yield of DPA consumption and t is the irradiation time (seconds).

To determine the Φ_{CO} in our reaction, we applied the equation:

$$\Phi_{CO}(\%) = \frac{\frac{\#\ moles\ of\ CO}{t'} \times 2}{\frac{Nhv}{t}} \times 100\%$$

Where t' is the reaction time for photocatalytic CO_2 reduction and $\frac{Nhv}{t}$ is the number of photons absorbed by the sample per unit time.

Effect of P-doping level and morphology of g-C_3N_4 on the activity

In order to further confirm the effect of P doping and morphology change on the performance g-C_3N_4, the P-doped g-C_3N_4 with different P contents were prepared in the same way as P-HCNR by changing the amount of phosphoric acid used in the preparation process. Specifically, 4 mL and 2 mL phosphoric acid were added to the melamine aqueous solution and the pH values of the resulting solutions were 2.5 and 3.5 respectively with vigorous stirring for 1 h. And then, the mixture was transferred into a 500 mL Teflon-lined stainless-steel autoclave for subsequent hydrothermal reaction at 180 ^oC for 6 h. The obtained mixture was filtered, washed with a small amount of deionized water and dried in an oven at 80 ^oC for 6 h. Finally, the obtained solid was calcined at 550 ^oC for 4 h in the tube furnace under argon atmosphere, affording the final product denoted as P-HCNR2 and P-HCNR3.

Moreover, the common P-doped g-C_3N_4 denoted as P-CN was also prepared. In detail, 3 g melamine and 6 mL phosphoric acid (85%) were dissolved in 300 mL deionized water and stirred for 1 h. Subsequently, the mixture was filtered and dried in

an oven at 80 °C for 6 h. Finally, the final P-CN was obtained by calcining at 550 °C for 4 h in the tube furnace under argon atmosphere.

Subsequently, the activities of photocatalytic CO_2 reduction were tested and compared. The activities of all samples were displayed in Table S2.

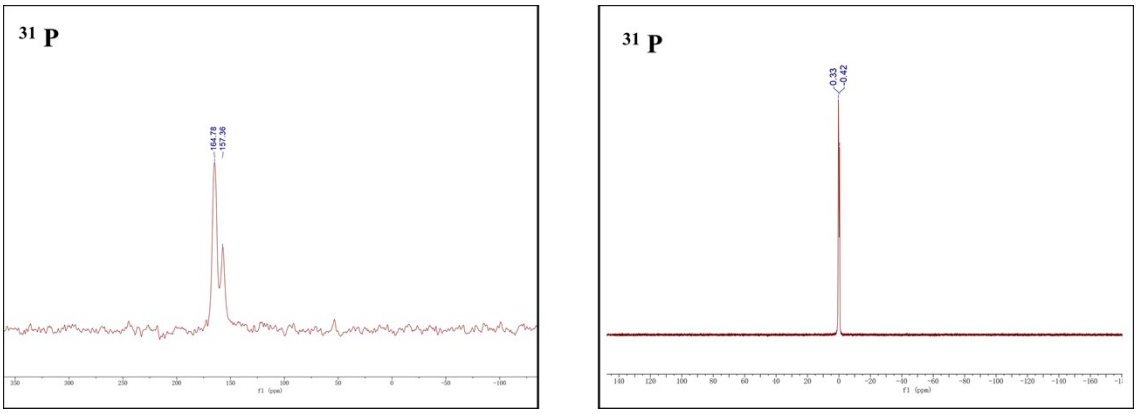

Fig. S1. ^{31}P MAS NMR spectra of P-HCNR and ^{31}P NMR of H_3PO_4 (162 MHz, CDCl3).

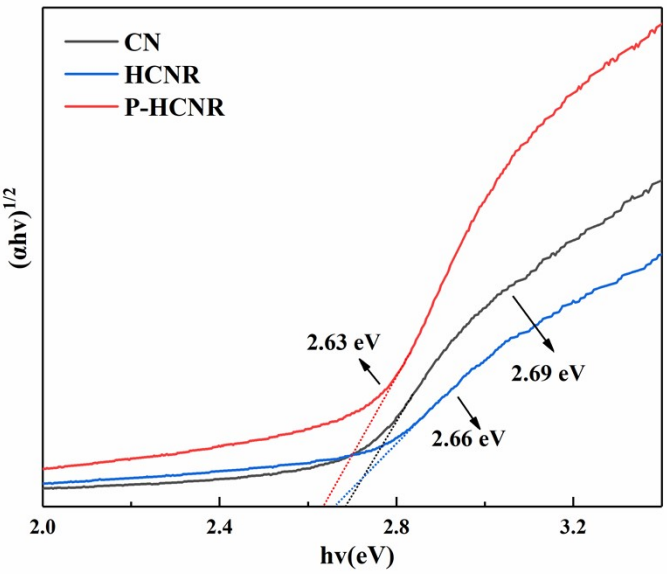

Fig. S2. Tauc plots of CN, HCNR and P-HCNR.

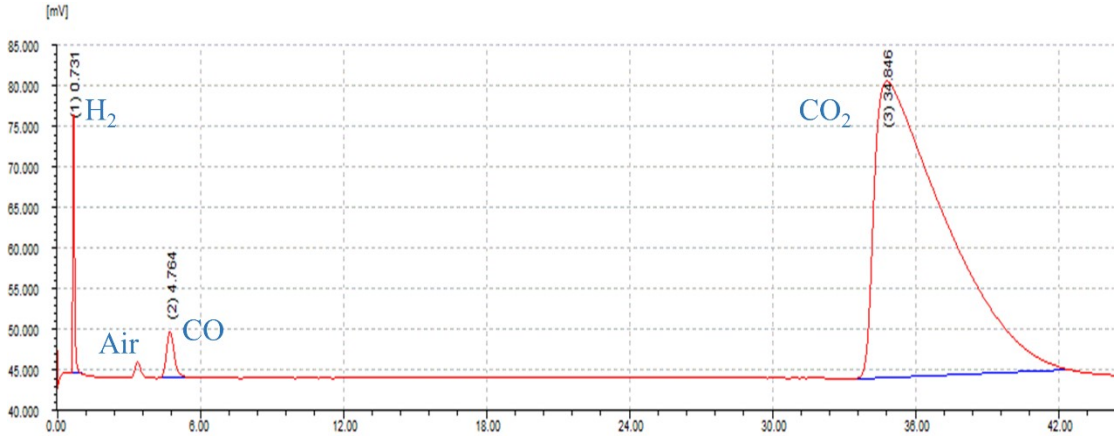

Fig. S3. Gas chromatography of product gases.

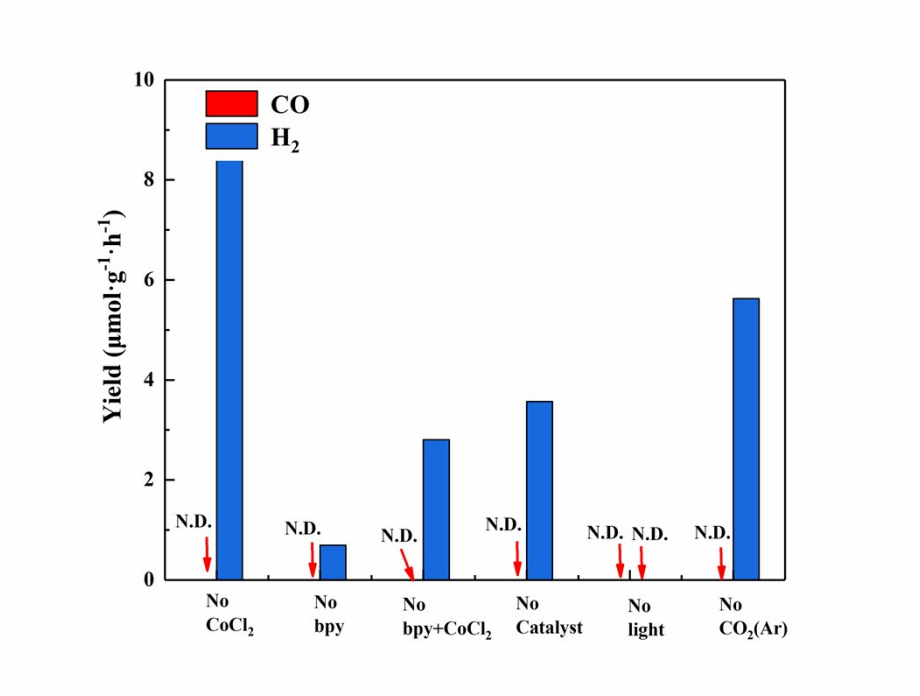

Figure. S4. Control experiments.

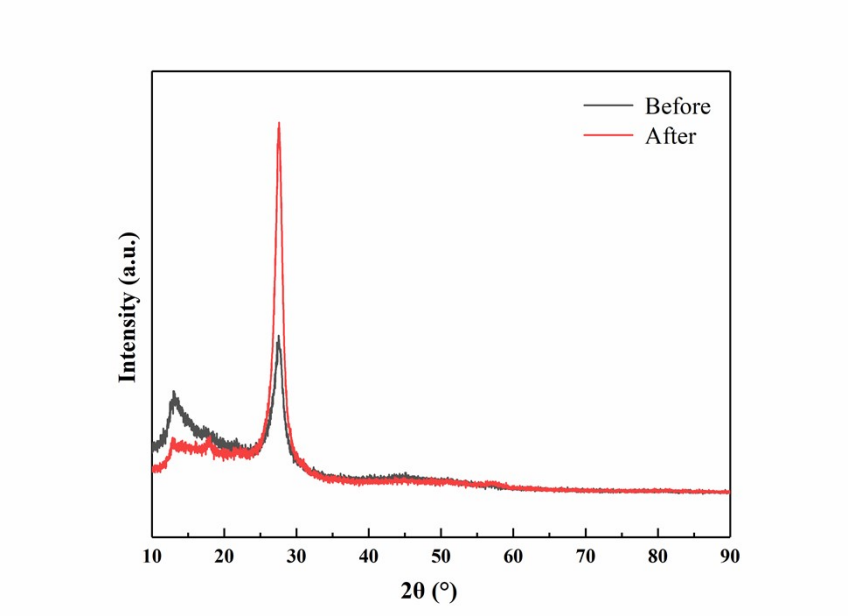

Figure. S5. XRD patterns of the P-HCNR before and after 10 hours' photocatalytic CO_2 reduction reaction.

Table S1 Effect of $CoCl_2$ amount on CO/H_2 evolution and selectivity to CO.

Entry	$CoCl_2$ (μmol)	CO(μmol/g·h)	H_2 (μmol/g·h)	Selectivity (%)
1	0	0	8.43	/
2	0.1	81.29	1.65	98
3	0.5	227.41	4.89	98
4	1	447.53	16.05	97
5	1.5	280.10	6.68	97
6	2	227.42	4.89	97
7	4	78.86	3.23	96

Table S2 CO/H_2 evolution and selectivity to CO for CN，HCNR, P-HCNR, P-HCNR2 and P-HCNR3.

Entry	Sample	CO(μmol/g·h)	H_2(μmol/g·h)	Selectivity (%)
1	CN	67.01	3.55	94
2	HCNR	256.40	24.17	91
3	P-HCNR	447.53	16.05	96
4	P-CN	121.34	2.43	98
5	P-HCNR2	120.54	3.34	97
6	P-HCNR3	83.02	1.93	97

Table S3 Control experiments.

Entry	Condition[a]	CO(μmol/g·h)	H_2(μmol/g·h)
1	no $CoCl_2$	0	8.44
2	no bpy	0	0.69
3	no bpy +$CoCl_2$	0	2.80
4	no catalyst	0	3.56
5	dark	0	0
6	Ar	0	5.62

[a]Deviation from standard method

Materials	Cocatalyst	Products and Activity	Sacrificial agent	References
P-HCNR	**$[Co(bpy)_3]Cl_2$**	**CO: 447.5 mol/g·h Selectivity = 96%**	**TEOA**	**This work**
C-doped BN nanosheet	$[Co(bpy)_3]Cl_2$	CO: 93 μmol/g·h Selectivity = 76%	TEOA	[1]
mtw-CNT	$[Co(bpy)_3]Cl_2$	CO: 253.3 μmol/g·h Selectivity = 96%	TEOA	[2]
Co^{2+} doped 0D/2D TiO_2/g-C_3N_4	$[Co(bpy)_3]Cl_2$	CO: 290 μmol/g·h /	TEOA	[3]
TiO-CN	$[Co(bpy)_3]Cl_2$	CO: 283.9 μmol/g·h Selectivity = 89%	TEOA	[4]
P-doped inverse opal g-C_3N_4	/	CO: 31.2 μmol/g·h Selectivity = 91%	H_2O (gas)	[5]
Ultra-thin porous g-C_3N_4 (THCN)	/	CO: ~1.8 μmol/g·h CH_4: ~2.1 μmol/g·h	TEOA	[6]
Co_1-C_3N_4/α-Fe_2O_3	/	CO: 14.9 μmol/g·h Selectivity > 99%	H_2O (gas)	[7]
WO_3/g-C_3N_4	/	CO: 41.47 μmol/g·h CH_4: 0.75 μmol/g·h	TEOA	[8]

Table S4 Comparison of photocatalytic CO_2 reduction performance with C_3N_4 based materials.

Reference:

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