## **Supplementary Information (SI)**

**Tab. S1.** The textural properties of different catalysts were calculated from  $N_2$  adsorption-desorption isotherms.

Catalyst	BET surface area (m² g⁻¹)	Pore diameter (nm)	Pore volume (cm <sup>2</sup> g <sup>-1</sup> )
RuP	1.82	5.33	0.02
Cu	29.71	21.80	0.16
4% RuP/Cu	19.83	13.59	0.07

Reaction conditions	CO productivity (mmol/g/h)		
H <sub>2</sub> atmosphere	1.65		
CO <sub>2</sub> atmosphere	Trace		
Ar atmosphere	Trace		
Quarta sand, without catalyst	Trace		

Tab. S2. The CO productivity of different reaction conditions of 4% RuP/Cu.

(Unless otherwise stated, the reaction condition was fixed: 20 mg catalyst, 300°C reaction temperature, 500 mW/cm<sup>2</sup> light intensity, 50 mL/min flow rate, the stoichiometric ratio of  $CO_2$ :H<sub>2</sub> is 4:1, and 1 h reaction period.)

	2				
Catalyst	Concentration of Ru	Concentration of Cu	Theoretical	Actual mass	
	(mg/L)	(mg/L)	mass ratio	ratio	
2%RuP/Cu	0.93	48.95	0.02	0.019	
4%RuP/Cu	1.77	47.84	0.04	0.037	
6%RuP/Cu	2.81	51.09	0.06	0.055	
8%RuP/Cu	3.96	53.50	0.08	0.074	

Tab. S3 the ICP-OES results of different catalysts.



Fig. S1 Schematic diagram of the photothermal device.



Fig. S2 XPS spectra of the Cu LMM of 4% RuP/Cu.



Fig. S3 (a) Transient photocurrent responses. (b) UV-Vis diffuse reflectance spectra.(c) Electrochemical impedance spectroscopy (EIS) analysis.



Fig. S4. TEM of 4%RuP/Cu after reaction (a-c), and XPS of 4% RuP/Cu after reaction (d) P 2p and (e)

Ru 3p.