

## Supporting Information for

# Cu-modified InVO<sub>4</sub> photocatalysts for enhanced N<sub>2</sub> fixation using chemical reagents and electroplating sludge as Cu source

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## Experimental section

### *Chemicals*

Indium (III) chloride tetrahydrate ( $\text{InCl}_3 \cdot 4\text{H}_2\text{O}$ ), sodium orthovanadate ( $\text{Na}_3\text{VO}_4$ ), copper nitrate hydrate ( $\text{Cu}(\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$ ), ethylene glycol and Nessler's reagent were purchased from Macklin (Shanghai, China). Nitric acid ( $\text{HNO}_3$ ) and sulfuric acid ( $\text{H}_2\text{SO}_4$ ) were purchased from Guangzhou Chemical Reagent Factory. All experiment used deionized (DI) water. All chemicals were of analytical grade and without further purification.

### *Preparation of photocatalysts*

$\text{InVO}_4$  nanosheets were synthesized by a simple hydrothermal method. 0.8 g  $\text{Na}_3\text{VO}_4$  were dispersed in 40 mL deionized water and stirred continuously for 30 min to form solution A. 0.586 g  $\text{InCl}_3 \cdot 4\text{H}_2\text{O}$  were dissolved in 20 mL deionized water to form solution B. Solution B was added dropwise into the above solution A under stirring condition to form a yellow solution. Then, the pH value of the above mixture solution was adjusted to 1-2 by adding nitric acid (1 mol/L). After vigorously stirred for 1 h, the solution was transferred to a Teflon-lined autoclave (100 mL) and heated at 180 °C for 18 h. After the autoclave was cooled naturally down to room temperature, the powders were washed several times with deionized water. Finally, the  $\text{InVO}_4$  nanosheets were obtained after drying at 60 °C for 24 h.

$\text{InVO}_4$  nanosheets loaded with copper ( $\text{Cu}/\text{InVO}_4$ ) powders were synthesized via a solvothermal treatment. 0.2 g  $\text{InVO}_4$  samples and a certain amount of  $\text{Cu}(\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$

(0.0059 g, 0.0118 g, 0.0295 g, 0.0590 g) were dispersed in reducing agent (i.e., ethylene glycol) and vigorously stirred for 1 h. Then, the mixture was transferred to a Teflon-lined autoclave (100 mL). After the treatment at 180°C for 10 h, InVO<sub>4</sub> photocatalysts containing different amounts of loading copper (marked as 1% Cu/InVO<sub>4</sub>, 2% Cu/InVO<sub>4</sub>, 5% Cu/InVO<sub>4</sub>, and 10% Cu/InVO<sub>4</sub> according to the mass ratio) were obtained. The following procedures were consistent with the preparation of InVO<sub>4</sub> photocatalysts.

In order to prepare Cu/InVO<sub>4</sub> from solid waste, the Cu(NO<sub>3</sub>)<sub>2</sub>·xH<sub>2</sub>O in the above step needs to be replaced with a copper-containing solution extracted from the solid waste. Here, the copper-rich electroplating sludge (Cu, 49.9 wt%, from Shenzhen Chongda Circuit Technology Co., Ltd.) was dried in an oven at 60 °C for 24 h, and then ground into powders. 8 g powders were soaked in 100 mL of dilute sulfuric acid (1 mol/L) and stirred continuously for 5 h. After centrifugation and filtration, a copper-rich supernatant was collected. The following procedures were consistent with the preparation of Cu/InVO<sub>4</sub> photocatalysts.

### *Characterization*

Powder X-ray diffraction (XRD) patterns were measured using a Bruker D8-Advance X-ray diffractometer with Cu K $\alpha$  radiation ( $\lambda = 0.154$  nm) at 40 kV and 40 mA. Transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) images of the nanostructures were recorded on (FEI-TALOS-F200X) electron microscope operating at an accelerating voltage of 200 kV. The Raman spectra were collected by Renishaw micro confocal laser Raman

spectrometer (inVia, Renishaw plc). The composition and chemical states were analyzed using X-ray photoelectron spectroscopy (XPS, Thermo Fisher Scientific K-Alpha), equipped with an Al  $k\alpha$  (1486.8 eV) X-ray source. The binding energy corrections were made using carbon peak (284.6 eV) as a reference. Ultraviolet-visible (UV-Vis) absorbance spectra were measured using a UV-Vis spectrophotometer (Shimadzu, Cary 500). Photoluminescence (PL) spectra were collected by fluorescence spectrophotometer (PL, Edinburgh, FLS920) with a He-Cd Laser ( $\lambda_{ex} = 325$  nm) as an excitation source. Inductively coupled plasma spectrometer (ICP, Avio200) was used to measure the metal elements in the solution and analyze the composition of the metal-rich supernatant extracted from the electroplating sludge.

#### *Photocatalytic measurements*

Photocatalytic  $N_2$  reduction was conducted in a home-made quartz reactor. The reactor was equipped with a circulating water outer jacket to maintain a constant temperature of 25 °C. 20 mg  $InVO_4$  or  $Cu/InVO_4$  samples were dispersed in 100 mL pure DI water with continuously stirring in the dark. Then high-purity  $N_2$  was fed into the bottle at a flow rate of 60 mL/min for 60 min to obtain a  $N_2$ -saturated aqueous suspension. The reactor was then irradiated under the 300 W Xe lamp (CEL-HXF300) and bubbled high-purity  $N_2$  through the suspension at flow rate of 60 mL/min with continuous stirring. At regular intervals, 4 mL aliquots of the reaction solution were collected using a syringe, and then immediately filtrated to remove the photocatalysts. The concentration of  $NH_3$  in the aliquot (as  $NH_4^+$ ) was determined through a Nessler's reagent method.

### *Photoelectrochemical measurements*

Photoelectrochemical measurements were detected by a solartron 1470e electrochemical workstation using a standard three-electrode system in 0.5 M NaSO<sub>4</sub> solution. The counter electrode was a platinum foil and the reference electrode was a saturated Ag/AgCl electrode. The working electrode was a glass carbon electrode uniformly coated with photocatalyst. The light source for the photocurrent measurements was a Xe lamp. The electrochemical impedance spectroscopy (EIS) was recorded at open circuit potential.

### *Computational details*

All the density functional theory calculations were performed by using the Vienna ab initio Simulation Program (VASP)<sup>1, 2</sup>. The generalized gradient approximation (GGA) in the Perdew-Burke-Ernzerhof (PBE) form and a cutoff energy of 500 eV for plane-wave basis set were adopted<sup>3</sup>. A 3 × 3 × 1 Monkhorst-Pack grid was used for sampling the Brillouin zones at structure optimization<sup>4</sup>. The ion-electron interactions were described by the projector augmented wave (PAW) method<sup>5</sup>. The convergence criteria of structure optimization were chosen as the maximum force on each atom less than 0.02 eV/Å with an energy change less than 1 × 10<sup>-5</sup> eV. The DFT-D3 semiempirical correction was described via Grimme's scheme method<sup>6</sup>. The Gibbs free energy change ( $\Delta G$ ) for each elemental step is defined as<sup>7, 8</sup>:

$$\Delta G = \Delta E + \Delta ZPE - T\Delta S + \Delta G_U + \Delta G_{\text{pH}} \quad (1)$$

where  $\Delta E$  and  $\Delta ZPE$  are the adsorption energy based on density functional theory calculations and the zero-point energy correction, respectively.  $T$ ,  $\Delta S$ ,  $U$ , and  $\Delta G_{\text{pH}}$

represent the temperature, the entropy change, the applied electrode potential, and the free energy correction of the pH, respectively.

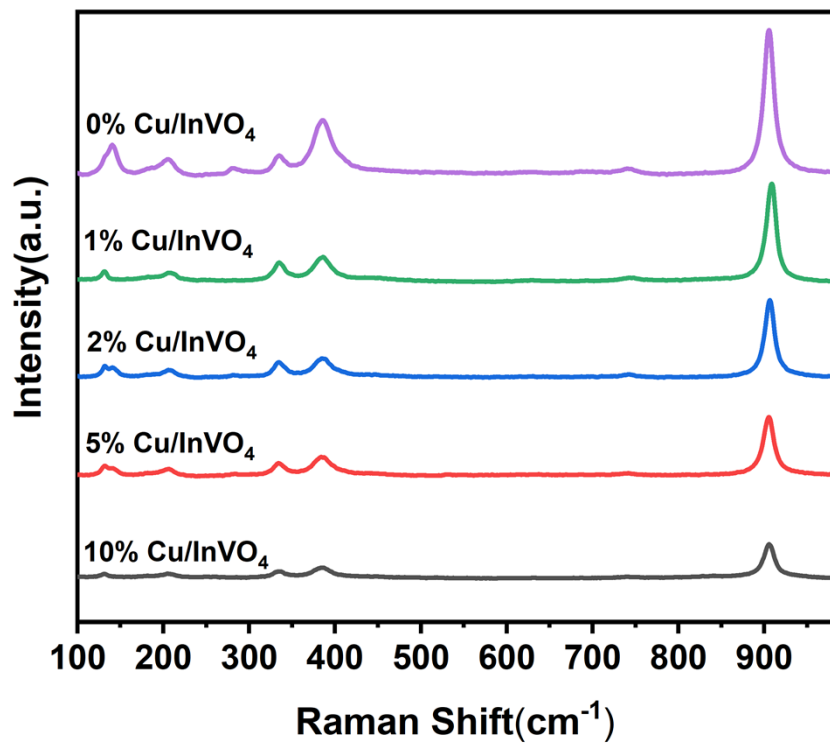


Figure S1. Raman spectra of Cu/InVO<sub>4</sub> with different Cu loading ratios.

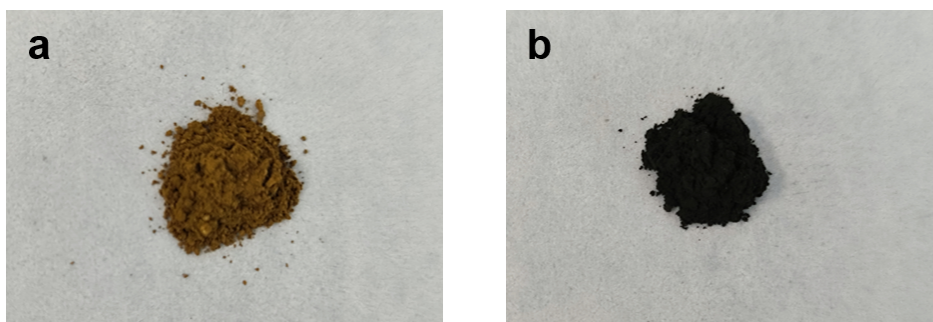


Figure S2. Digital image of (a)  $\text{InVO}_4$  and (b) 5%  $\text{Cu/InVO}_4$ .



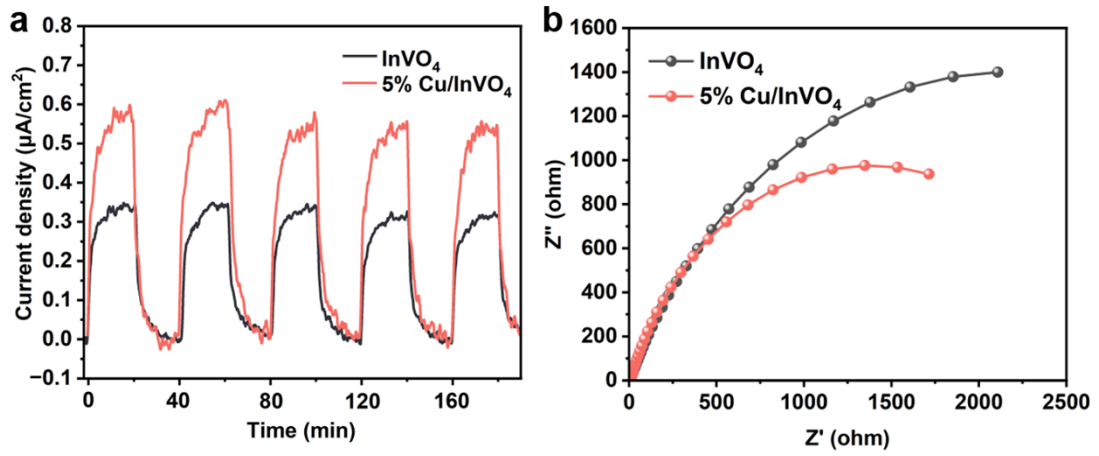


Figure S3. (a) Transient photocurrent responses and (b) EIS plots of  $\text{InVO}_4$  and 5%  $\text{Cu/InVO}_4$ .

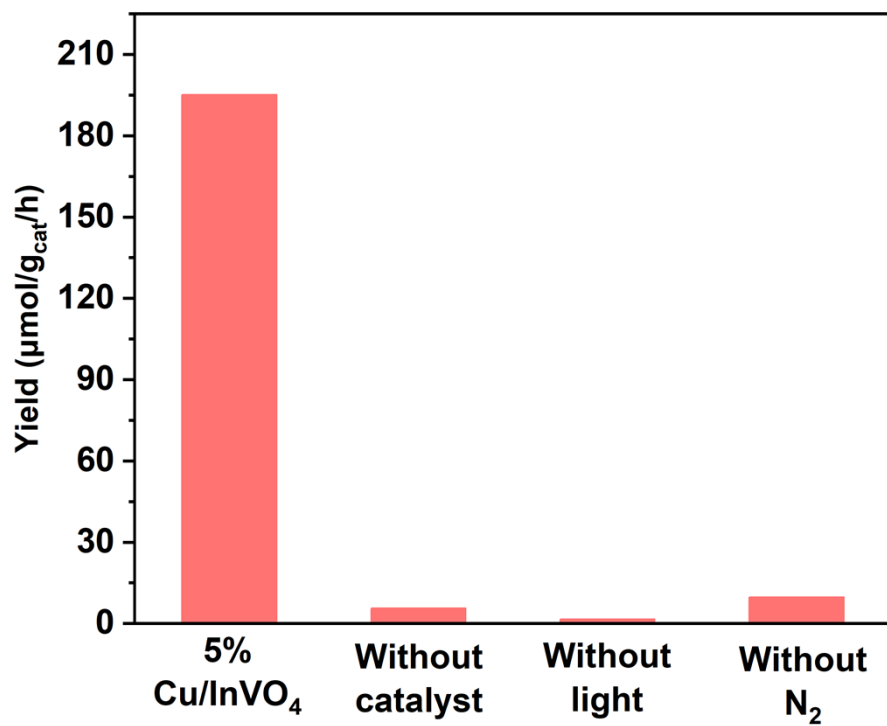


Figure S4. Control experiments under different conditions.

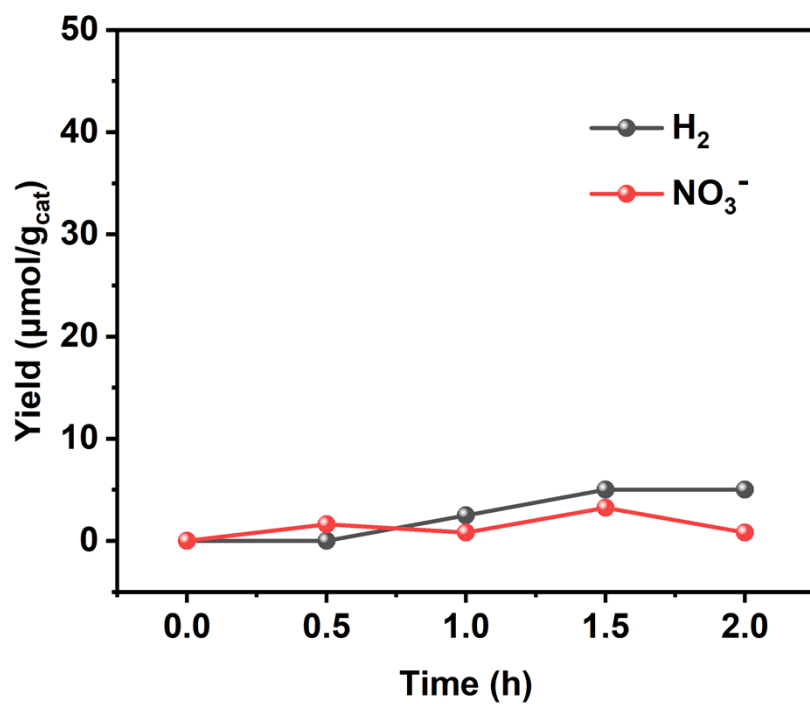


Figure S5. Yields of H<sub>2</sub> and NO<sub>3</sub><sup>-</sup> of 5% Cu/InVO<sub>4</sub> photocatalysts.

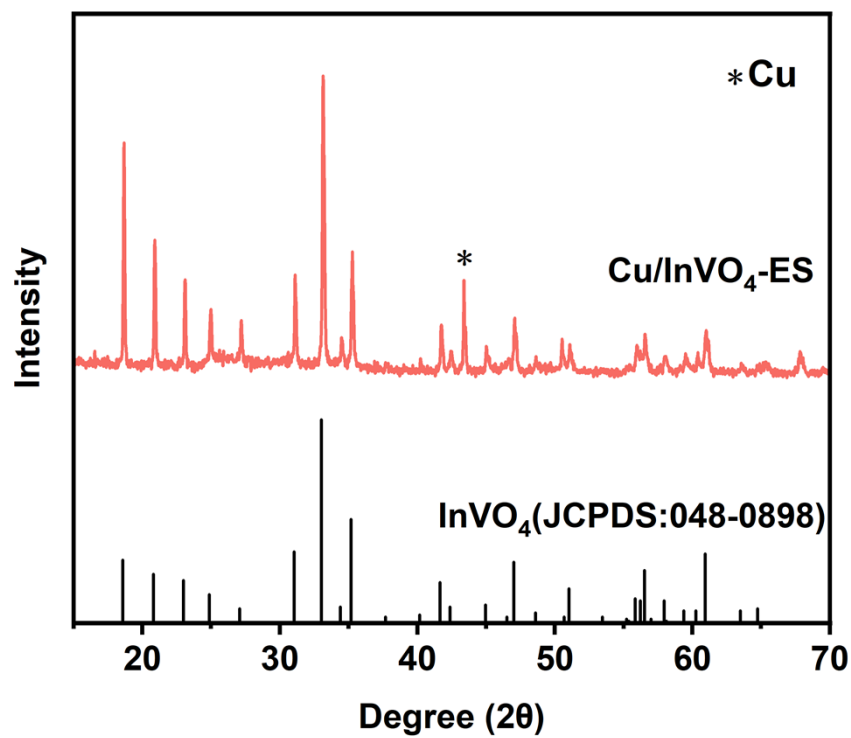


Figure S6. XRD pattern of Cu/InVO<sub>4</sub> synthesized using Cu source from electroplating sludge.

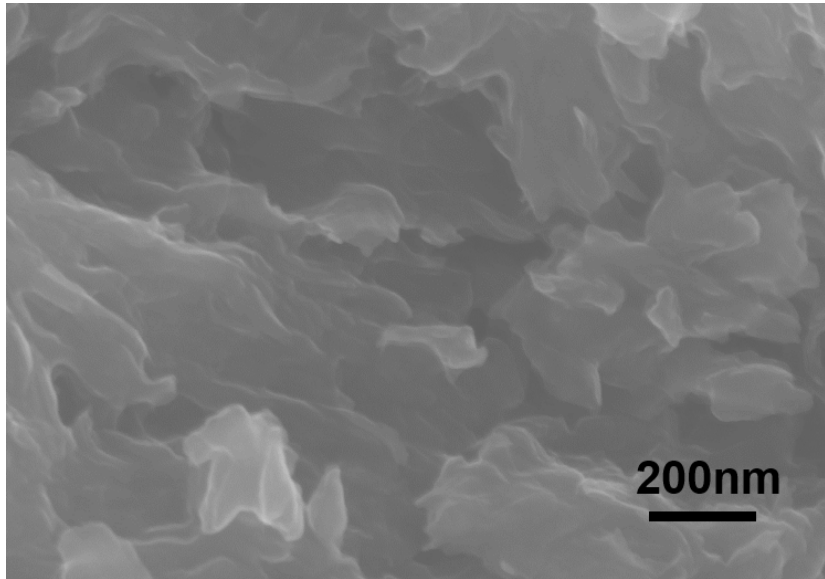


Figure S7. SEM image of Cu/InVO<sub>4</sub>-ES nanosheets.

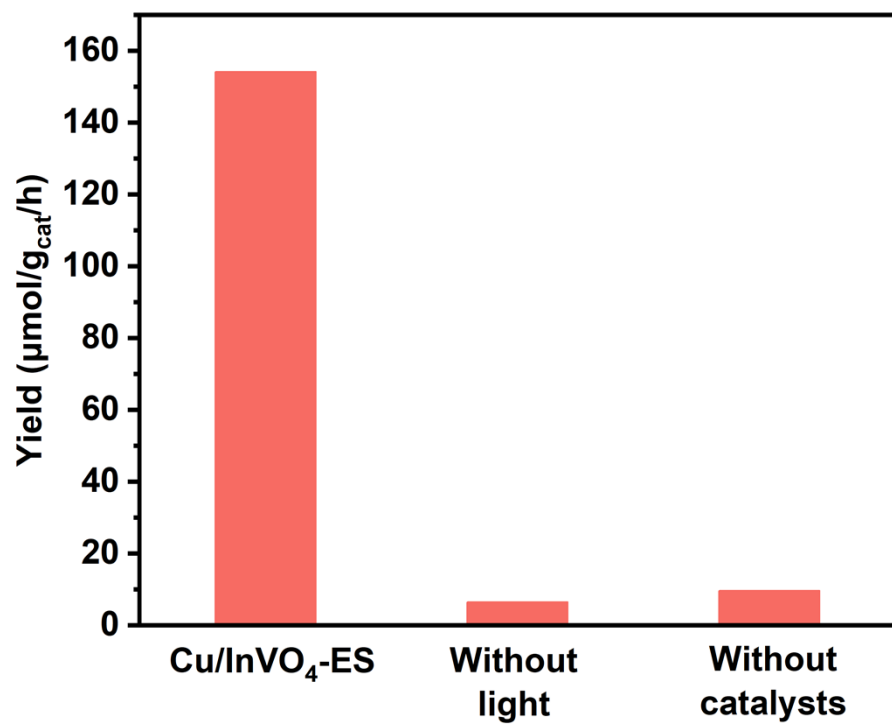


Figure S8. NH<sub>3</sub> yield and control experiment of Cu/InVO<sub>4</sub> synthesized using Cu source from electroplating sludge.



Scheme S1. Schematic diagram of the process of extracting copper from electroplating sludge to prepare Cu/InVO<sub>4</sub>.

**Table S1.** The concentration of various metals in the supernatant extracted from electroplating sludge.

Concentration (mg/L, diluted 2000 times)							
Mg	Ca	Al	Ni	Fe	Mn	Cr	Cu
0.1714	0.4504	0.1371	0.1419	1.5399	0.2584	0.0212	7.1278



## Notes and references

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