Supplementary Information (SI) for ChemComm.

Supplementary Materials for

***In situ* construction of ZnP_2/CuP_2 heterojunction for efficient Nitrate-to-ammonia electroreduction**

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Experimental Section

Preparation of Zn-ZIF-8. 1.332 g of $Zn(NO_3)_2 \cdot 6H_2O$ was dissolved in 40 mL of deionized water to form solution A. In solution B, 8 g of 2-methylimidazole (MeIM) was added to 120 mL of deionized water. Solution B was then rapidly poured into solution A and vigorously stirred for 3 min. The mixture was allowed to set at room temperature for 2 h. After washing several times with deionized water and ethanol, the product was collected by suction filtration and dried under vacuum at 50 °C overnight. Subsequently, 200 mg of the obtained powder was dispersed in 30 mL of water and ultrasonicated at room temperature for 30 min. After forming a uniform dispersion, 2 mL of an aqueous tannic acid solution (5 mg mL^{-1}) was added and stirred at room temperature for 30 min. The resulting ZIF-8 nanocrystals were collected by centrifugation and dried under vacuum at 50 °C overnight.

Fabrication of the ZnP_2 catalyst. 0.4 g of the as-prepared Zn-ZIF-8 powder and 1.2 g of $NaH_2PO_2 \cdot 2H_2O$ were placed at downstream and upstream of an open alumina crucible, respectively. The mixture in the crucible was then heated in flowing N_2 atmosphere at a heating rate of 2 °C/min to 400 °C and held at this temperaturefor 2 h, followed by natural cooling to room temperature to obtain the ZnP_2 catalyst.

Fabrication of the CuP_2/ZnP_2 heterostructure. The CuP_2/ZnP_2 heterostructure was obtained *via* an ion exchange method based on the Kirkendall effect. Specifically, 190 mg of $CuCl_2 \cdot H_2O$ and 20 mg of ascorbic acid were dissolved in 60 mL of methanol solution. Then, 50 mg of the prepared ZnP_2 was dispersed in the above solution. After ultrasonication for 15 min, the resulting mixture was transferred into a 100 mL Teflon-lined autoclave and heated at 160 °C for different time (4, 8, and 15 h) to prepare heterostructures with different ZnP_2/CuP_2 ratios.

Physical characterization. We obtained X-ray diffraction (XRD) patterns through a Phillips X'pert Pro diffractometer with Co Kα radiation at 40 kV and 35 mA. The FESEM images were collected using a field emission scanning electron microscopy ZEISS Merli. The high resolution TEM images were performed on a ThermoFisher Talos F200X transmission electron microscope. The X-ray photoelectron spectroscopy (XPS) was recorded using a PHI 5000 Versa Probe equipped with a hemispherical electron analyzer and monochromatic Al Kα X-ray exciting source. The bonding energy (BE) calibration of the spectra was referred to the C 1s peak located at BE = 284.6 eV for the analysis. The Potential-dependent Raman spectra were determined by Confotec MR 520 using a 532 nm laser with an acquisition time of 5 s.

Electrochemical measurements. The eNO_3RR performance of ZnP_2/CuP_2 catalysts were recorded using a three-electrode system on an electrochemical workstation (CHI 660f). Pt mesh and Ag/AgCl electrode were used as counter electrode and reference electrode, respectively.

To prepare the working electrodes, synthesized ZnP_2/CuP_2 catalysts powder samples (5 mg) were dispersed in the mixed solution of 970 μL ethanol and 30 μL Nafion solution (10 wt %). Thereafter, the mixed solution was sonicated for 30 minutes to acquire a homogeneous catalyst suspension. Finally, 10 μL of catalyst suspension was cast onto the surface of the glassy carbon electrode with 5 mm diameter, and the working electrode was naturally dried at room temperature. The catalyst loading on the glassy carbon electrode was calculation as 0.255 mg cm^{-2}. Cyclic voltammetry (CV) was conducted at the potential of 0.355-1.635 V (*vs.* RHE) with a scan rate of 50 mV s^{-1} in 0.1 M Na_2SO_4 electrolyte. eNO_3RR polarization curves were collected in 0.1 M Na_2SO_4 and 0.1 M $NaNO_3$ mixed electrolyte with a scan rate of 10 mV s^{-1}. Chronoamperometry test was performed at -0.365 V *vs.* RHE.

Detection of NH_3. The NH_3 concentration was determined by the ammonia photometric kit. An aliquot of the electrolytes after electrolysis was appropriately diluted with ammonia-free deionized water to fall within the linear range of the assay. 10 g of 5% salicylic acid and 11.395 g of 5% sodium citrate were added in 200 mL of 1 M NaOH solution to prepare Solution A. Then, 2 mL of Solution A and 1 mL of 0.05 M NaClO solution were mixed with 0.2 mL of 1% sodium nitroferricyanide solution thoroughly for colorimetry test. After incubating at room temperature for 120 min, the absorbance was recorded at a wavelength of 660 nm using a spectrophotometer. A standard curve was freshly prepared under identical conditions covering 0-2.0 ppm NH_4^+ and the ammonia concentration in the sample was calculated from the standard curve.

Detection of nitrite. The NO_2^- concentration was determined by the naphthalene ethylenediamine hydrochloride method. In acidic medium, nitrite was diazotized with sulfanilamide and then coupled with N-(1-naphthyl)ethylenediamine dihydrochloride, producing a rose-red azo dye whose color intensity was measured spectrophotometrically. To prepare the mixed color reagent, 0.2 g of N-(1-naphthyl)ethylenediamine dihydrochloride and 4.0 g of sulfanilamide were dissolved in 50 mL of deionized water, and 10 mL of phosphoric acid was added. For quantification, the electrolyte sample was collected and diluted to fall within the detection range, then 40 μL of the color reagent was added to 2.0 mL of the sample solution, mixed well, and allowed to stand at room temperature for 20 min. The UV-Vis absorbance was subsequently measured at 540 nm. A standard concentration-absorbance curve was constructed using KNO_2 standards prepared in 1.0 M KOH solution at concentrations of 0, 0.20, 0.50, 1.00, 1.50, and 2.00 ppm, and the NO_2^- product concentration was calculated by referring the sample absorbance to this calibration curve.

The faradaic efficiency and yields of NH_3 were measured using the hypochloricphenol method.

$$FE = \frac{8 \times F \times c_{NH3} \times V}{17 \times Q}$$

$$Yield = \frac{V \times c_{NH3}}{m \times t}$$

where the concentration of NH_3 (c_{NH3}) were determined using UV-vis spectrophotometer and standard $(NH_4)_2SO_4$ solution.

Supplementary Figures

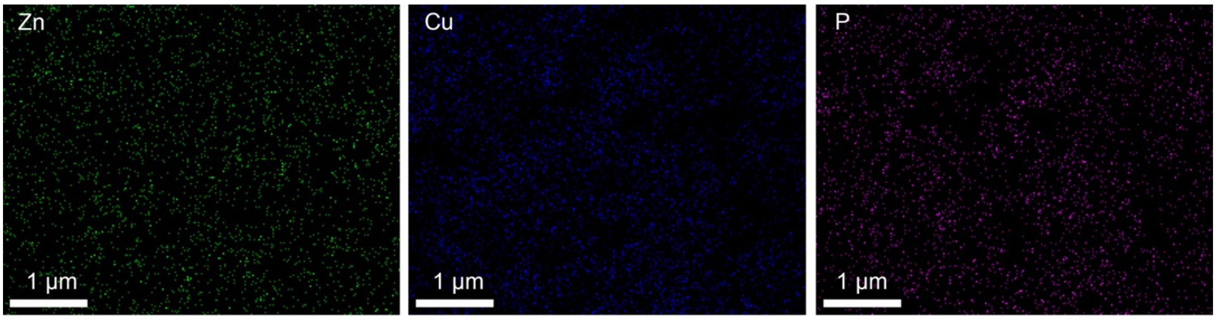

Fig. S1. SEM-EDS elemental mapping images of $Zn_{0.4}Cu_{0.6}P_2$.

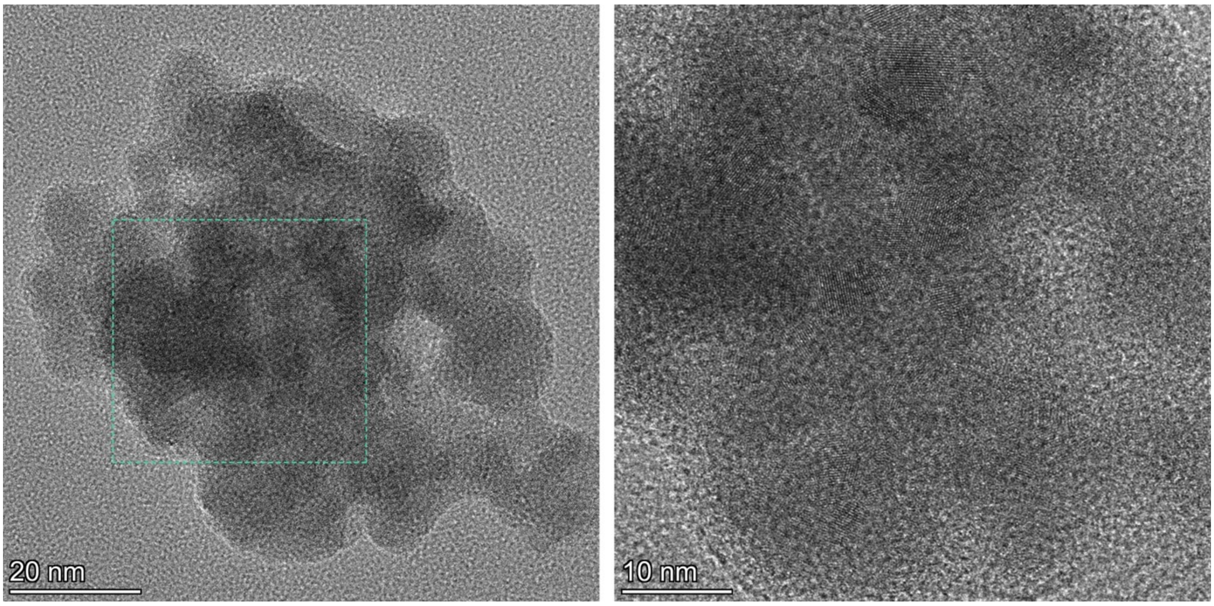

Fig. S2. TEM images of $Zn_{0.4}Cu_{0.6}P_2$.

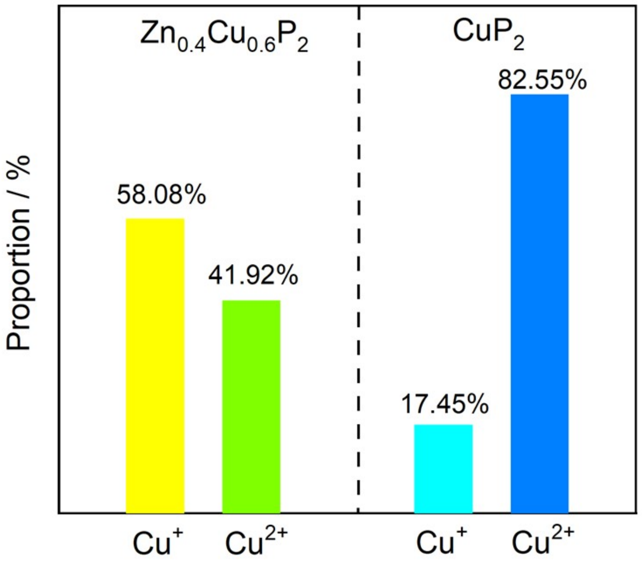

Fig. S3. Cu^+ and Cu^{2+} proportion of CuP_2 and $Zn_{0.4}Cu_{0.6}P_2$ heterostructure.

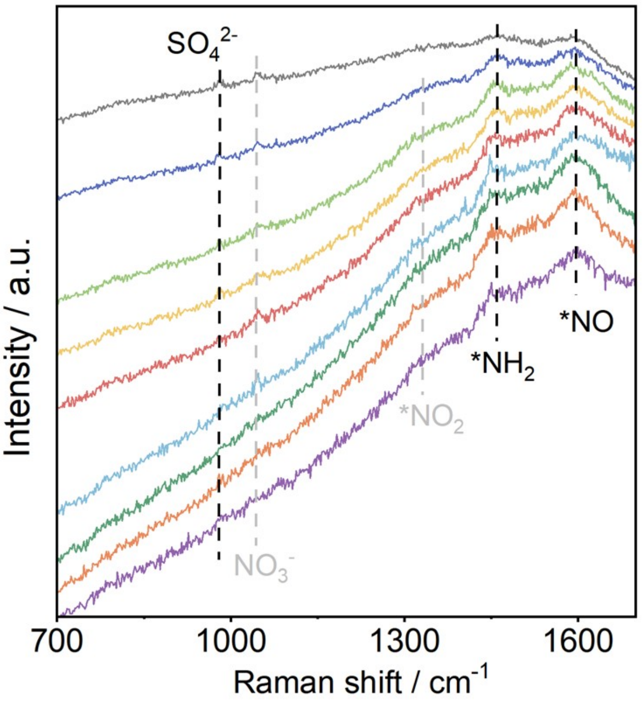

Fig. S4. The in situ Raman spectra of ZnP_2.

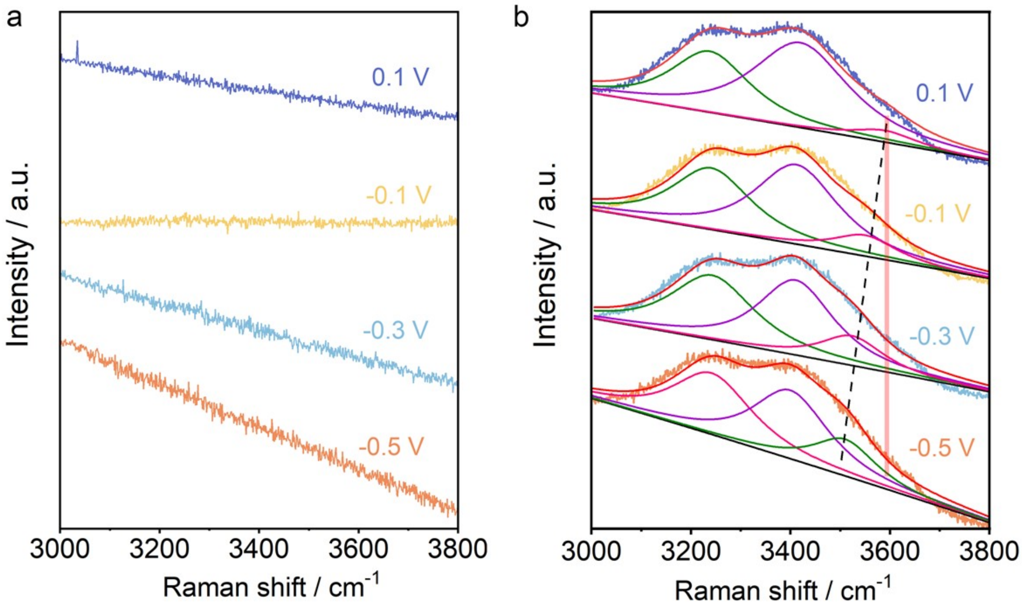

Fig. S5. The in situ Raman spectra of (a) CuP_2 and (b) ZnP_2.

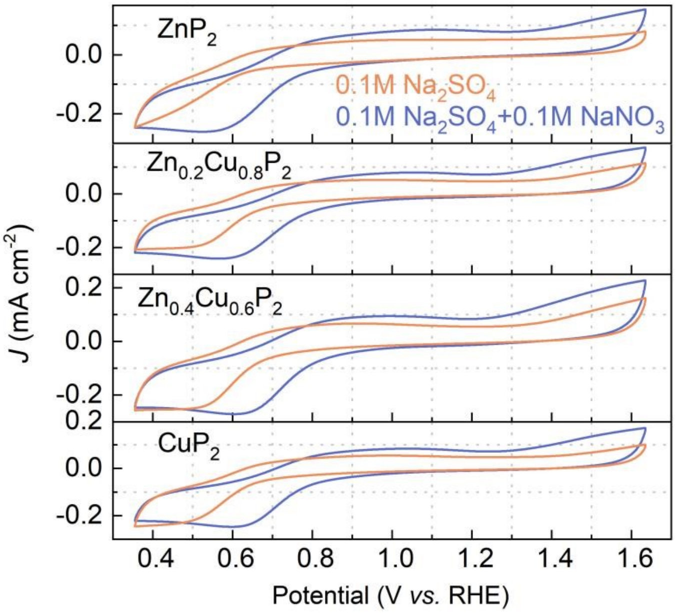

Fig. S6. CV curves of ZnP_2, CuP_2 and CuP_2/ZnP_2 heterostructures.

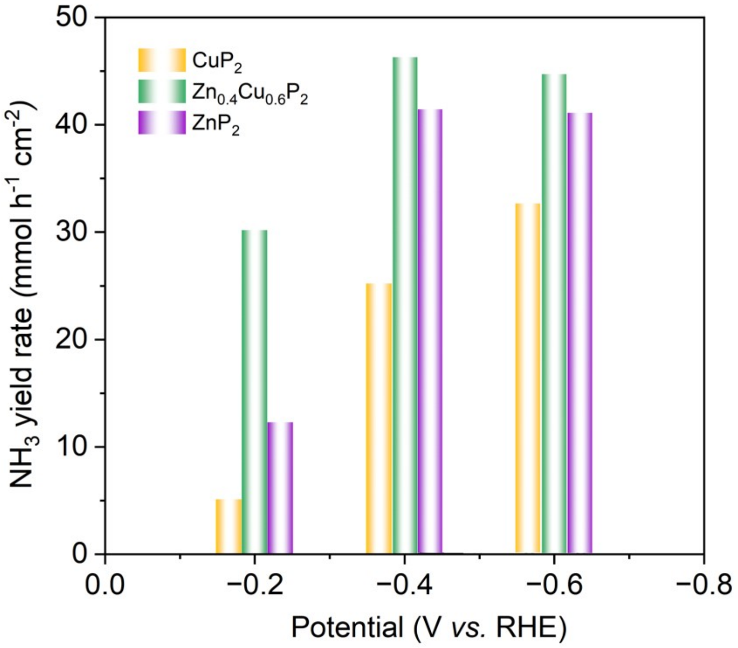

Fig. S7. NH_3 yields of eNO_3RR for the samples at different potentials.

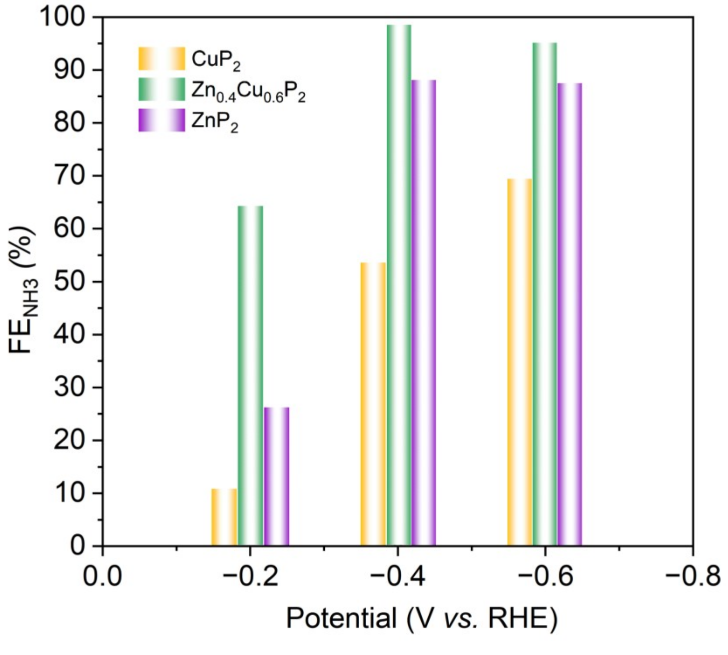

Fig. S8. Faradaic efficiencies of eNO_3RR for the samples at different potentials.

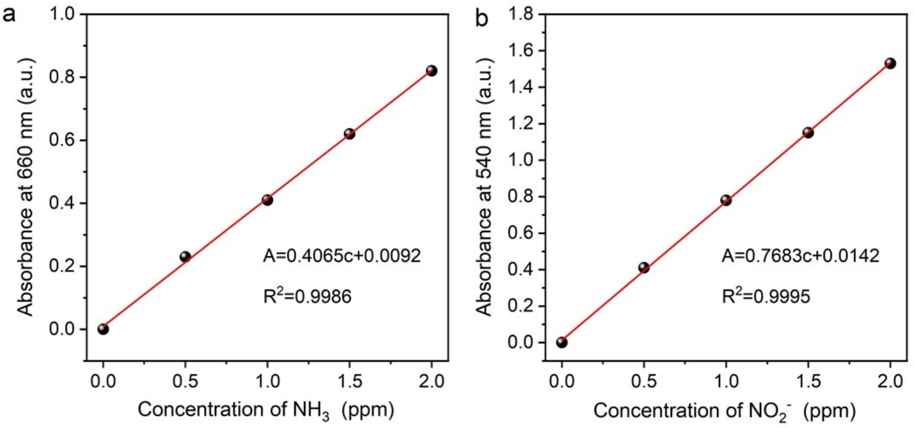

Fig. S9. The concentration-absorbance calibration curves for (a) NH_3, and (b) NO_2^-.

Table S1. ICP-OES results.

Sample	Element	Element concentration / mg/L	Element content / %
$Zn_{0.2}Cu_{0.8}P_2$	Zn	1.98	5.50%
$Zn_{0.2}Cu_{0.8}P_2$	Cu	7.05	19.59%
$Zn_{0.4}Cu_{0.6}P_2$	Zn	3.27	9.10%
$Zn_{0.4}Cu_{0.6}P_2$	Cu	5.69	15.82%
ZnP_2	Zn	9.09	25.27%
CuP_2	Cu	8.69	24.15%