Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Fe-CuP nanocubes for nitrate-to-ammonia conversion

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Supporting Information

Concentration determination of various ions

The initial step in this experimental procedure involved diluting the electrolytes to an appropriate concentration detection range for both the pre and post-tests. Subsequently, the diluted electrolytes were subjected to analysis using a UV-Vis spectrophotometer to observe and quantify the concentrations of various ions present. Such ions include NO_3^-, NO_2^-, and NH_3, which were specifically measured utilizing UV-vis spectrophotometry following established and recognized techniques that have been previously documented. The prescribed techniques used for this purpose are outlined in the subsequent sections.

Nitrite ions

A combination of N−(1−Naphthyl) ethylenediamine dihydrochloride (0.2 g), p−aminobenzene sulfonamide (4 g), 50 mL of pure water, and 10 mL of H_3PO_4 was utilized as a color reagent. A specific amount of electrolyte was extracted from the electrolytic cell and then diluted to 5 mL to fit within the UV-Vis detection range. Subsequently, 0.1 mL of the above-mentioned color reagent solution was added to the 5 mL solution and thoroughly mixed to ensure the solution was uniform. Following a 20-minute incubation period, the absorption intensity at a wavelength of 540 nm was measured. To calibrate the concentration–absorbance curve, a series of standard solutions of sodium nitrite were prepared, and the standard curve is presented in **Figure S1a**.

NH_3 ions

To determine the NH_3 -N amount, Nessler's reagent was utilized. A similar process of electrolyte dilution was carried out as mentioned for NO_2^-. Subsequently, 0.1 mL of potassium sodium tartrate solution was added to the aforementioned 5 mL of diluted electrolyte and thoroughly mixed. Then, 0.1 mL of Nessler's reagent was introduced to the solution. After thorough mixing and allowing it to sit for 20 minutes, the absorbance intensity at a wavelength of 420 nm was measured. To prepare for the calibration of the concentration-absorbance curve, the ammonium chloride crystal was dried at 105°C for 2 hours. A series of standard solutions of ammonium chloride were then created, and the calibration curve for NH_3 is represented in **Figure S1b.**

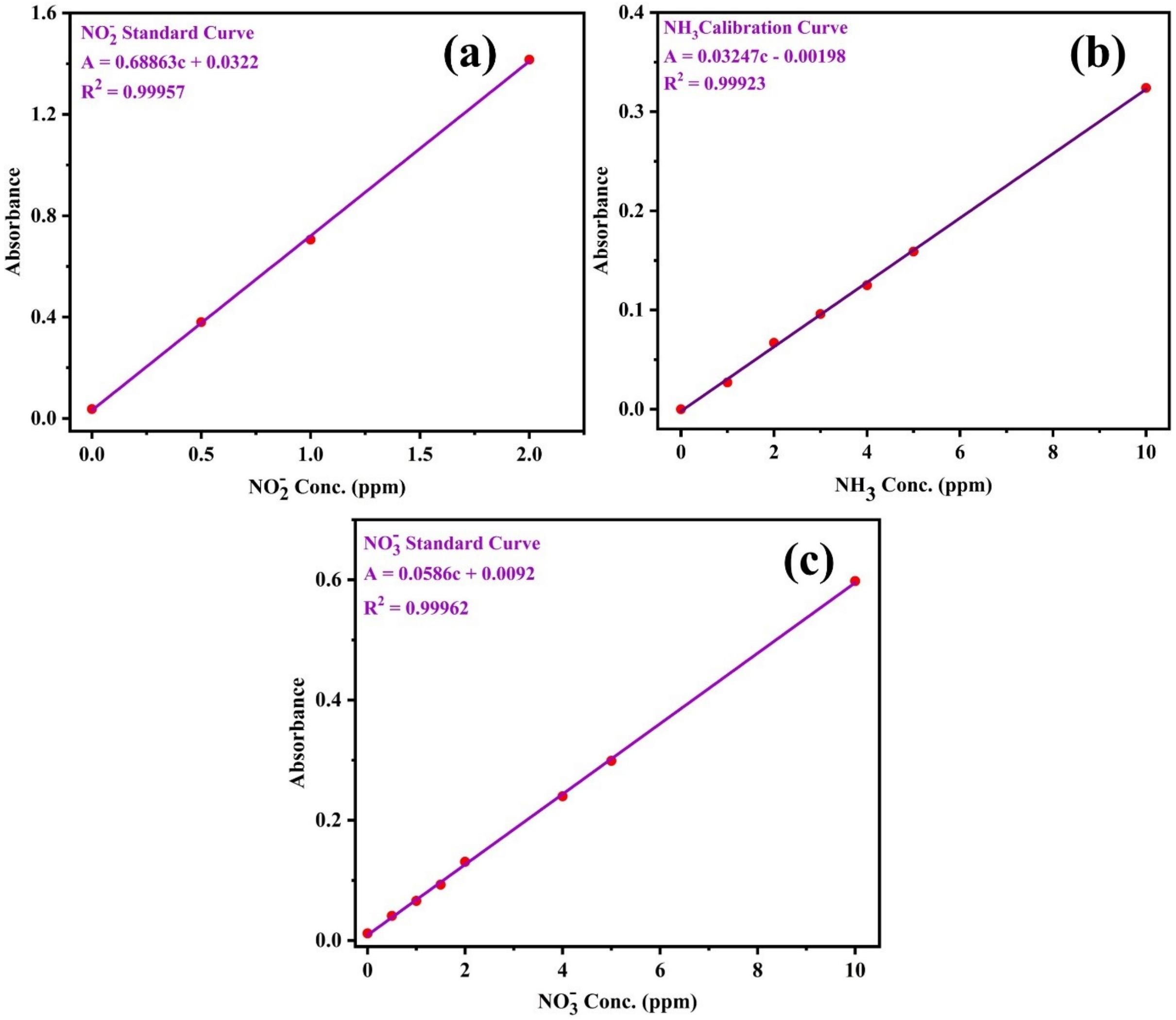

Figure S1: Calibration curves with 0.1 M K_2SO_4 solution in ultrapure water as background solution, **(a)** NO_2^- **(b)** NH_3 **(c)** NO_3^-

NO_3^- ions

A specific amount of electrolyte was extracted from the cathode compartment of the electrolytic cell and was subsequently diluted with water within the UV-vis detection range. Following this, 0.1 mL of 1 M HCl and 0.01 mL of a 0.8 wt% solution of sulfamic acid were put into the aforementioned 5 mL solution. The absorption spectrum was then tested using a UV-Vis spectrophotometer, and the absorption intensities at wavelengths of 220 nm and 275 nm were recorded. The final absorbance value was calculated using the equation $A = A_{220nm} - A_{275nm}$. To establish the standard concentration-absorbance calibration curve, a range of standard solutions of KNO_3 were utilized, and the standard curve is shown in **Figure S1c**.

Ammonia yield rate and Faradaic efficiency Calculations

The ammonia yield rate in this experimental study was determined using Equation 1.

$$\text{NH}_3 \text{ Yield Rate} = (C_{NH3} \times V) / (M_{NH3} \times t \times S) \quad (1)$$

This equation calculates the NH_3 Yield Rate by considering the concentration of NH_3 (CNH_3), the volume of electrolyte (V), the molar mass of NH_3 (MNH_3), the electrolysis time (t), and the surface area of the catalyst (S).

Similarly, the Faradaic efficiency (FE) was computed using Equation 2

$$FE = (8F \times C^{NO_3^-} \times V) / (M^{NO_3^-} \times Q) \times 100\% \quad (2)$$

This equation takes into account the Faradaic constant (F), the concentration of NO_3^- (C NO_3^-), the volume of electrolyte (V), the molar mass of NO_3^- (M NO_3^-), and the total charge passing the electrode (Q).

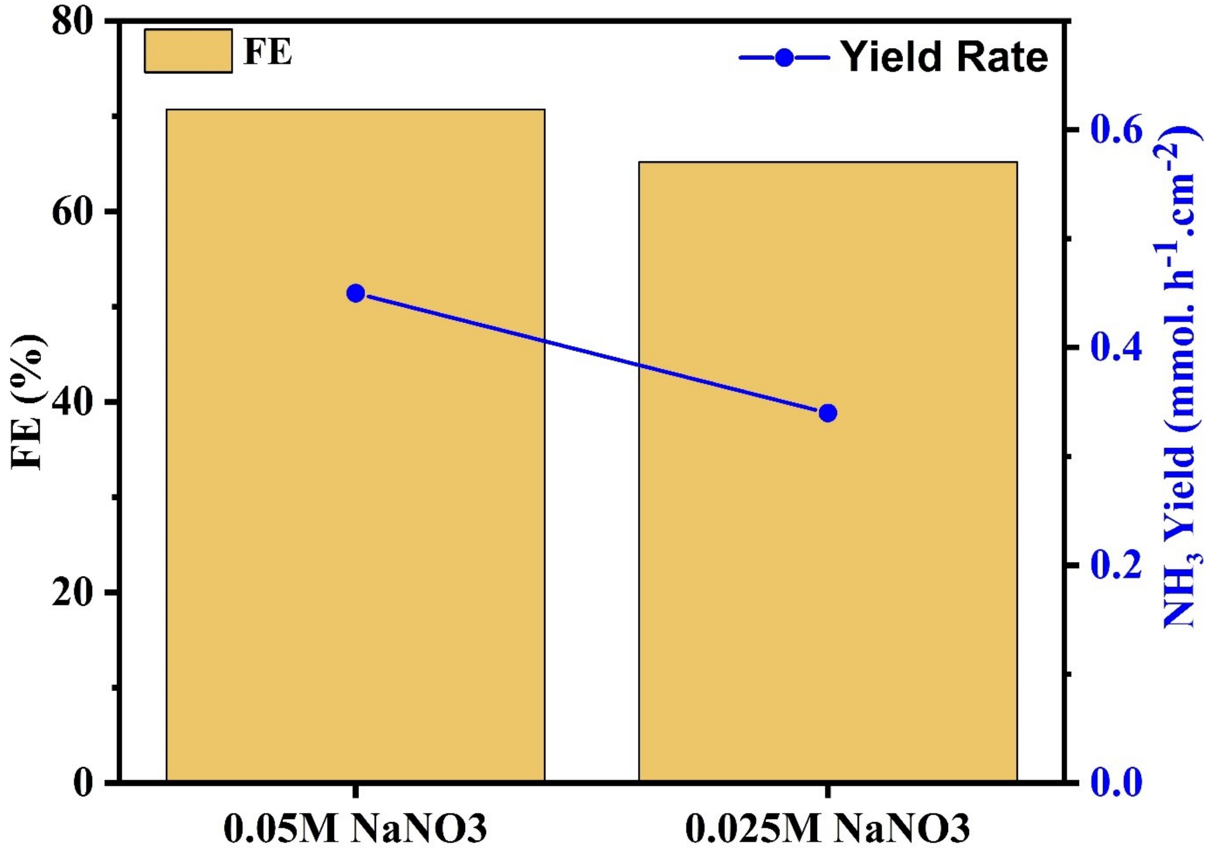

Figure S2: The NH_3 yield rate and Faradaic efficiency of S2-based Fe-CuP electrocatalyst at lower $NaNO_3$ concentration.

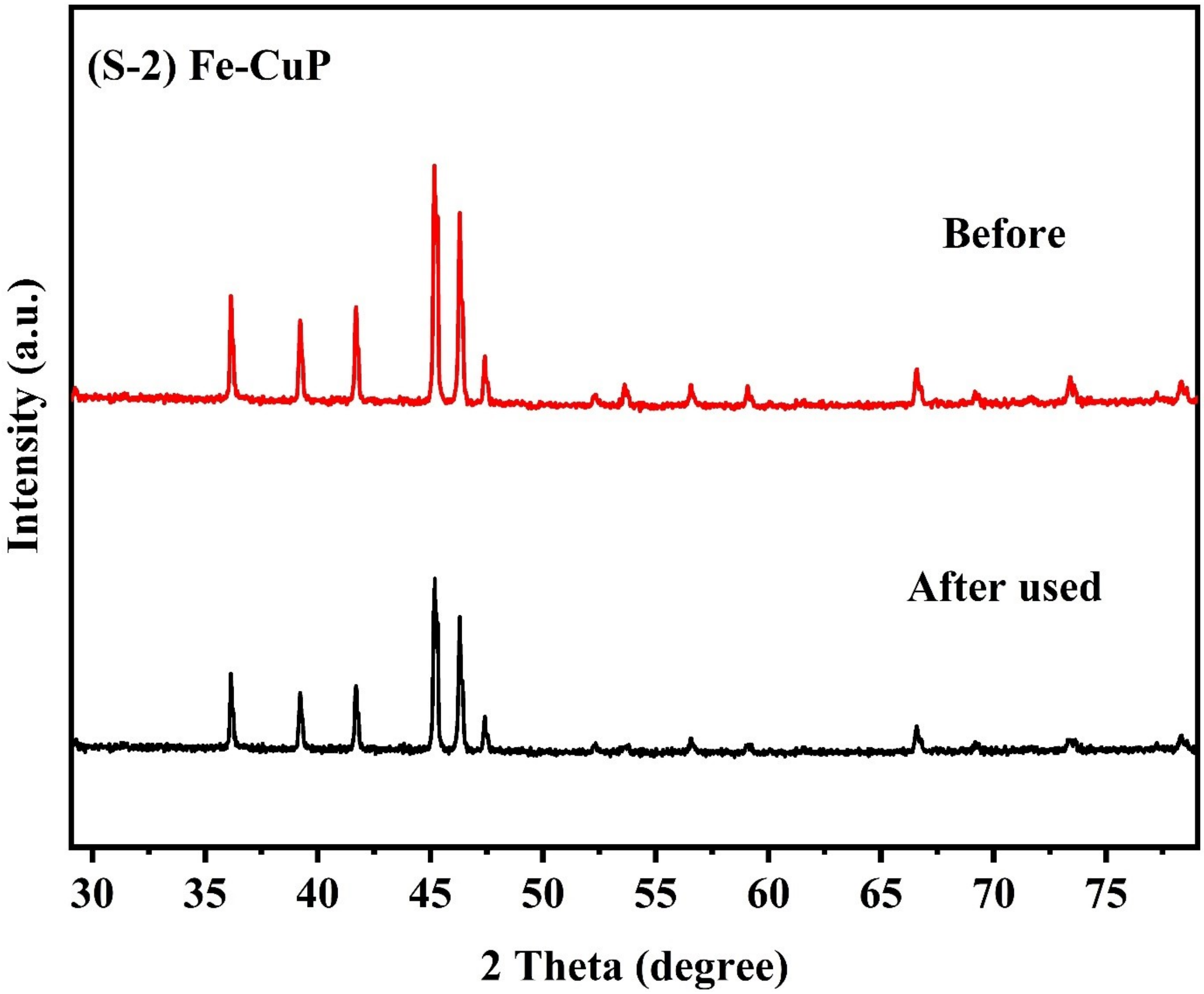

Figure S3: XRD patterns of the S2- based Fe-CuP catalyst before and after after the stability test**.**

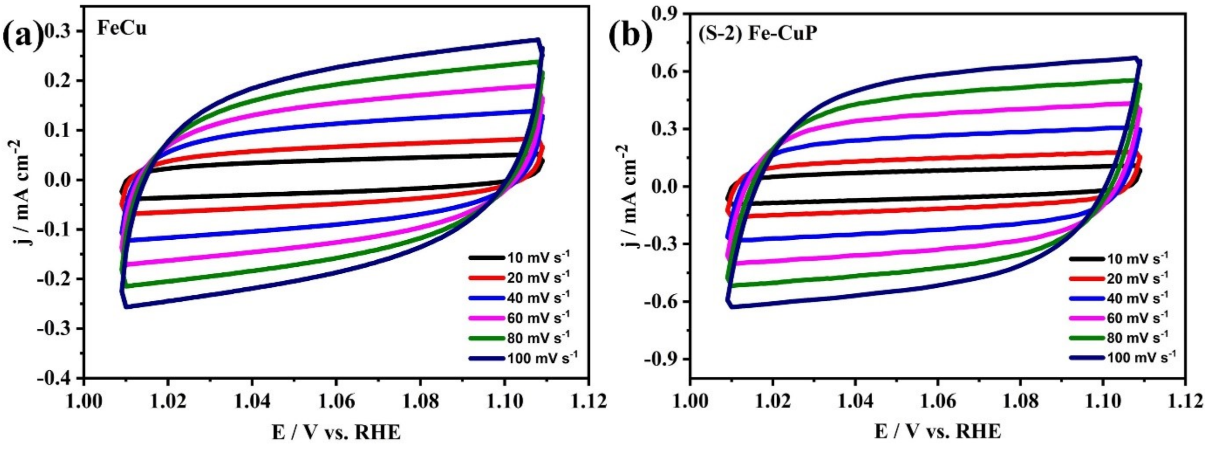

Figure S4: CV curves of the different catalysts at 10, 20, 40, 60, 80, and 100 mV s^{-1} **(a)** FeCu **(b)** S2- based Fe-CuP.

Table S1. EIS parameters of the investigated catalysts

Sample	$R_s(\Omega)$	$R_{ct}\ (\Omega)$	C_{dl}	W1-R	W1-T	W1-P
FeCu	102.1	**3572**	1.2315E-5	8356	323.4	0.14631
(S2) Fe-CuP	103.7	**2262**	1.148E-5	1756	35.32	0.31712