Supplementary information:

A Non-Enzymatic Highly Stable Electrochemical Sensing Platform Based on Allylamine Capped Copper Nanoparticles for the Detection of Soil Nitrate Content

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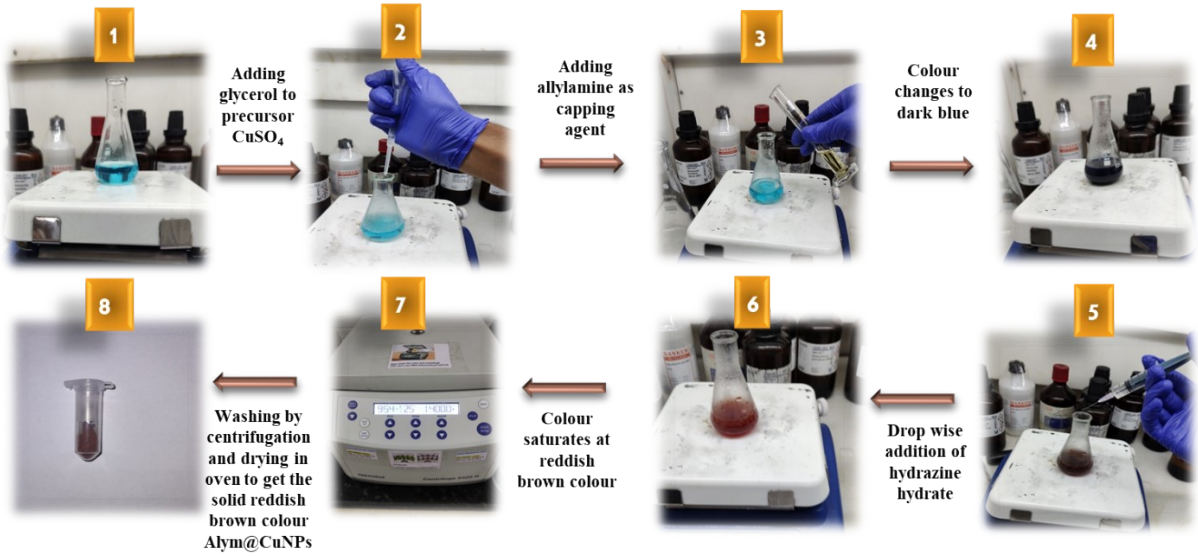
S1. Preparation of electrodeposited copper nanoparticles (eCuNPs) and uncapped copper nanoparticles (uCuNPs)

For electrodeposition of copper, 10 mM of $CuSO_4$ in 0.1 M H_2SO_4 medium was used as the electrolytic medium. The glassy carbon electrode (GCE) was used as the working electrode which was modified with 3 µL of Exf-CNT prior to its use for electrodeposition. Followed by 10 minutes of N_2 gas purging in the $CuSO_4$ medium, the 3 conventional electrode set up was dipped into the N_2 purged 10 mL of 10 mM $CuSO_4$ in 0.1 M H_2SO_4 solution for the electrodeposition process. The chronoamperometry technique was used for 400 s with -1.0 V of initial potential input. A uniform reddish-brown coloured copper nanoparticle was observed over the surface of the electrode.
For wet chemical synthesis of uncapped copper nanoparticles, $CuSO_4$ (2 g) was taken in a 50 ml conical flask and 20 ml of deionized water type 1 (DI type 1) was added to it at 600 rpm. Glycerine (2 ml) was added using an addition funnel and stirred for 3 minutes. Finally, hydrazine (4 ml) was added dropwise, keeping the temperature and stirring for 30 min more, then kept for 30 mins at room temperature to cool it down. After this treatment, the nanoparticles were recovered by centrifugation at 12,000 rpm and washed two times with ethanol and DI type 1 water. The supernatant was finally discarded and a residue nanoparticle was kept at hot air oven for 2 hours maintaining 60 degrees Celsius. The dried nanoparticles obtained as a black colour powder and labelled as uCuNPs.



Scheme S1. Pictorial representation of step-wise wet chemical synthesis of allylamine capped copper nanoparticles (Alym@CuNPs) and its purification steps.

Table S1. Real sample analysis and % recovery calculation by comparison with Ion chromatography technique

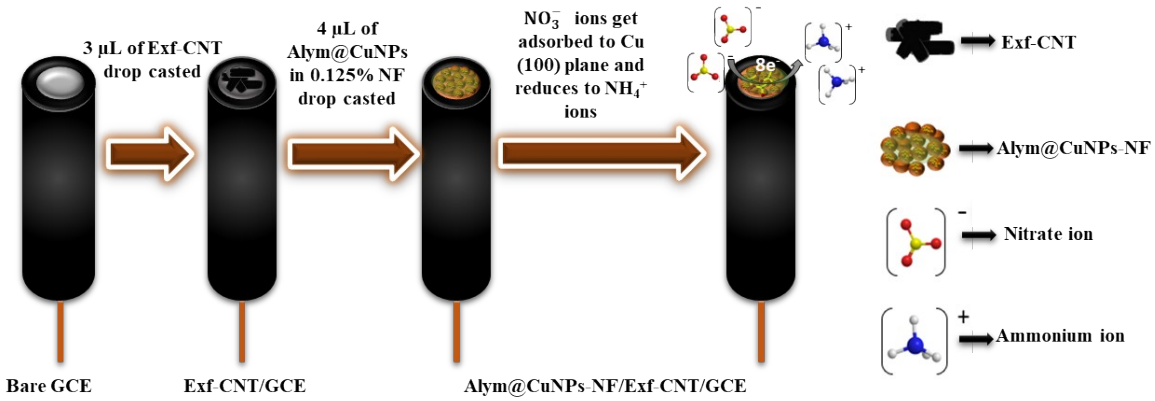
Soil sample name	NO_3^- ion content obtained from Ion chromatogrphy	NO_3^- ion content from Ion chromatography converted to mM (Soil helath: L/G/H/V)	NO_3^- ion content obtained from proposed sesnor data (Soil helath: L/G/H/V)	% Recovery
S-6	509.80 ppm	8.21 mM (H)	7.71 mM (H)	94.0%
S-7	21.54 ppm	1.73 mM (G)	1.54 mM (G)	92.0%

Detection Mechanism :-

Reduction: $NO_3^- + 10H^+ + 8e^- \longrightarrow NH_4^+ + 3H_2O$

Oxidation: $6H_2O \longrightarrow 2O_2 + 10H^+ + 8e^- + 2OH^-$

Overall: $NO_3^- + 3H_2O \longrightarrow NH_4^+ + 2O_2 + 2\ OH^-$



Scheme S2. Schematic diagram showing the fabrication of a non-enzymatic NO_3^- ion sensor using a Alym@CuNPs-NF/Exf-CNT/GCE arrangement and its detection mechanism in acidic environment (pH=2)

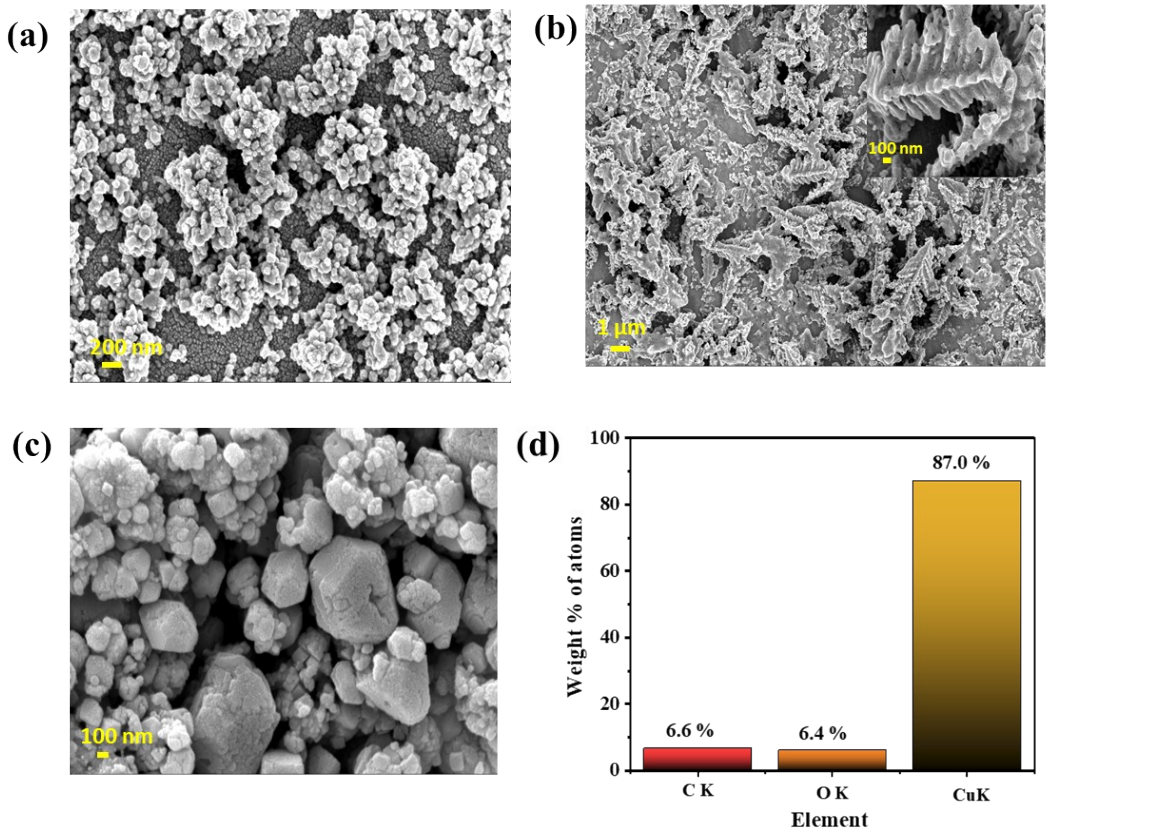


Fig. S1. SEM images of (a) eCuNPs/ITO (b) NF/eCuNPs/Exf-CNT/ITO (c) uCuNPs/ITO (d) Weight percentage of elements from EDAX analysis on ITO/eCuNPs

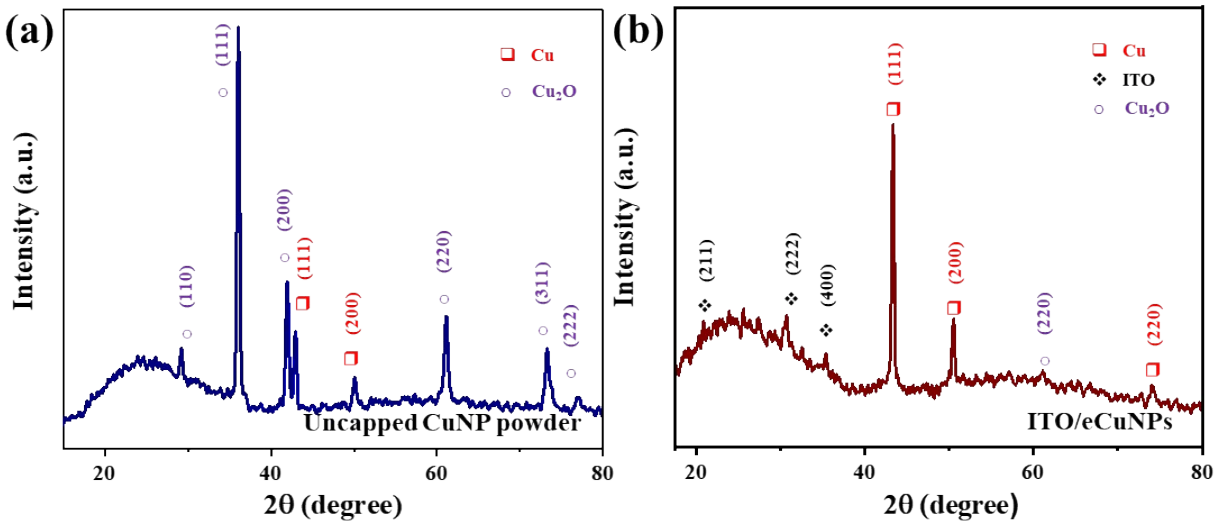


Fig. S2. XRD spectra of (a) uCuNPs (b) ITO/eCuNPs

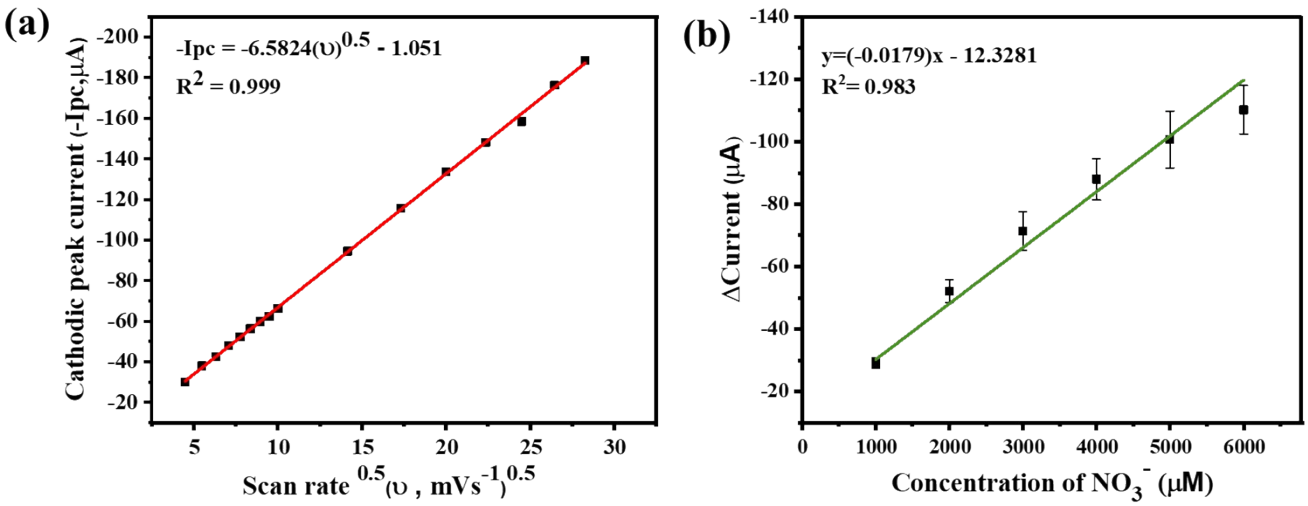


Fig. S3. (a) Cathodic peak current vs Scan rate$^{0.5}$ of 500 µM NO_3^- ion on Alym@CuNPs-NF/Exf-CNT/GCE in 0.1 M Na_2SO_4 (pH=2.0) (b) Calibration plot of change in cathodic peak current vs NO_3^- ion concentration in µM (linearity in high concentration range from 1000 µM to 6000 µM in 0.1M Na_2SO_4 (pH=2)

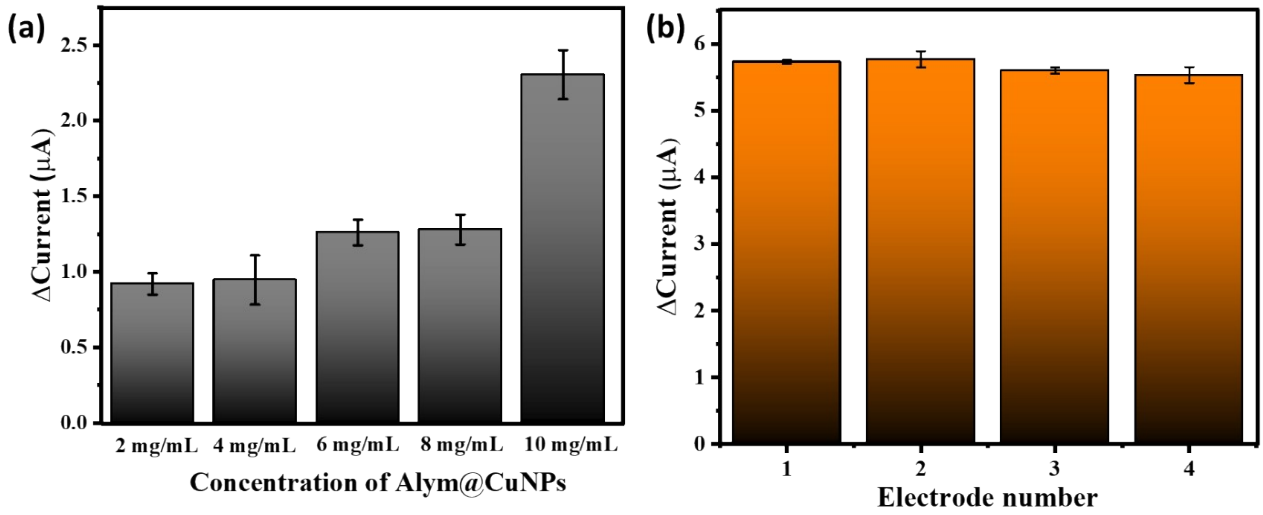
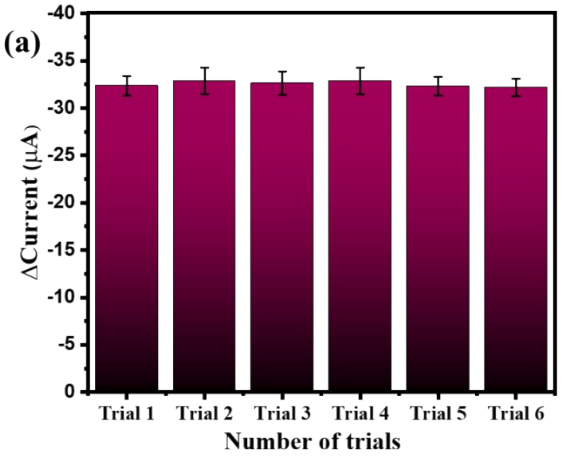


Fig. S4. (a) Concentration optimisation of Alym@CuNPs obtained from DPV study on Alym@CuNPs-NF/Exf-CNT/GCE in the presence of 80 μM NO_3^- ion (b) Reproducibility study obtained from DPV for Alym@CuNPs-NF/Exf-CNT/GCE in presence of 200 μM NO_3^- ion



(b)

Soil sample	50 μM NO_3^- Spike % recovery	100 μM NO_3^- Spike % recovery
S-1	90.8%	87.5%
S-2	96.7%	86.3%
S-3	89.1%	88.7%
S-4	96.1%	88.4%
S-5	90.6%	86.8%

Fig. S5. (a) Repeatability study obtained from DPV for Alym@CuNPs-NF/Exf-CNT/GCE electrode in presence of 1 mM NO_3^- ion (b) Spiking studies with % recovery for 50 μM and 100 μM NO_3^- ion in 10 times diluted 1:5 extracted soil sample (overall 50 times dilution)

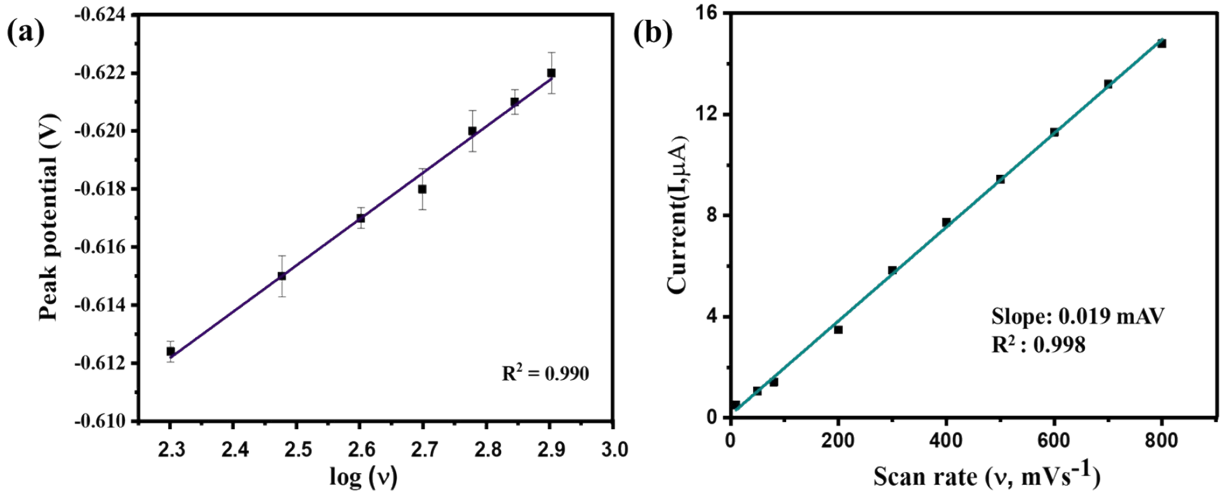
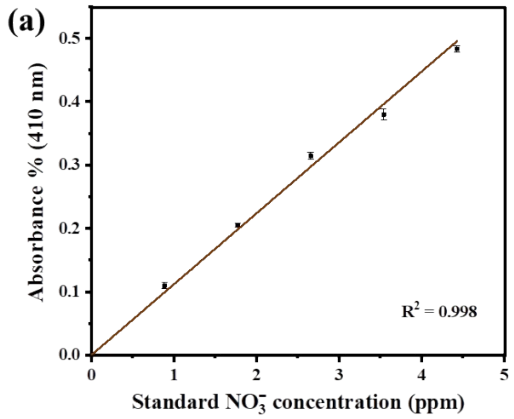


Fig. S6. (a) Peak potential (V) vs log (scan rate) obtained from CVs of scan rates ranging from 200 mVs^{-1} to 800 mVs^{-1} for 500 µM NO_3^- on Alym@CuNPs-NF/Exf-CNT/GCE (b) Current vs scan rate plot obtained from CVs of non Faradic region between -0.1 V to -0.25V on Alym@CuNPs-NF/Exf-CNT/GCE



(b)

Soil sample name	NO_3^- ion content obtained in 5 times diluted soil sample	NO_3^- ion content actually present in soil samples
S-1	15.34 ppm	76.72 ppm
S-2	10.13 ppm	50.67 ppm
S-3	13.98 ppm	69.90 ppm
S-4	21.62 ppm	108.09 ppm
S-5	16.94 ppm	84.70 ppm

Fig. S7. (a) Calibration plot obtained from UV-VIS data of range of standard concentration of NO_3^- ion (b) Table representing NO_3^- ion concentration in ppm obtained from UV-VIS data for different soil samples

S2. Electrocatalytic performance of eCuNPs and uCuNPs modified electrodes towards reduction of NO_3^- ion

S2.1 For NF/eCuNPs/Exf-CNT/GCE

Concentration studies were done on NF/eCuNPs/Exf-CNT/GCE (Fig. S8a) ; 10 µM to 1000 µM of NO_3^- ion was added gradually in the 0.1 M Na_2SO_4 (pH=2) electrolytic medium and a delta current (µA) versus concentration of NO_3^- (µM) graph was plotted to obtain the calibration curve. The calibration curve was found to be linear within the range of concentrations of 10 µM to 1000 µM, with a R^2 value of 0.989, as depicted in Fig. S8b. The limit of detection (LOD) was calculated to be 13.2

µM which was obtained from 3.3 (SD_B / S), where SD_B is the standard deviation of current value of three blank data (absence of NO_3^- ion) and S is the slope of the calibration curve.

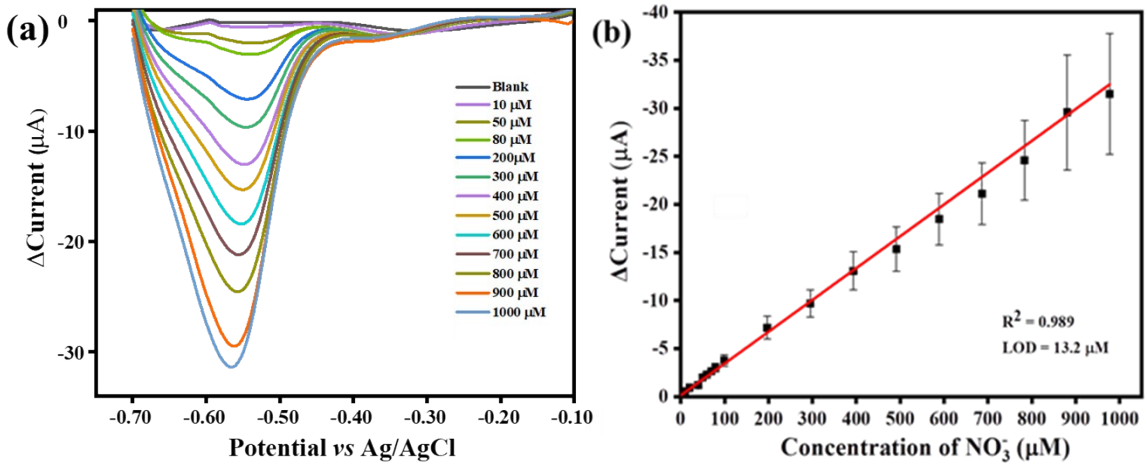


Fig. S8. (a) DPV study of NO_3^- ion concentration studies from 10 µM to 1000 µM on NF/eCuNPs/Exf-CNT/GCE in 0.1 M Na_2SO_4 (pH=2) (b) Calibration plot of change in cathodic peak current vs NO_3^- ion concentration in µM on NF/eCuNPS/Exf-CNT/GCE in 0.1 M Na_2SO_4 (pH=2)

S2.2 For uCuNPs-NF/Exf-CNT/GCE

NO_3^- ion concentration studies were also done on uCuNPs-NF/Exf-CNT/GCE, for a range of 50 µM to 1000 µM concentration. But generation of multiple peaks were observed between -0.35 V and -0.6 V due to which it becomes quite complex to interpret the correct peak position, so further calibration studies were not done for uCuNPs modified electrode.

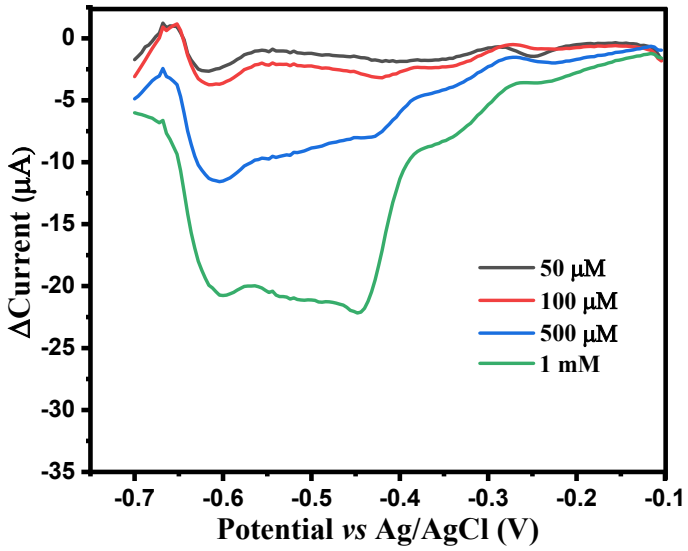


Fig. S9. DPV study of NO_3^- ion concentration studies from 50 µM to 1000 µM on uCuNPs-NF/Exf-CNT/GCE in 0.1 M Na_2SO_4 (pH=2)

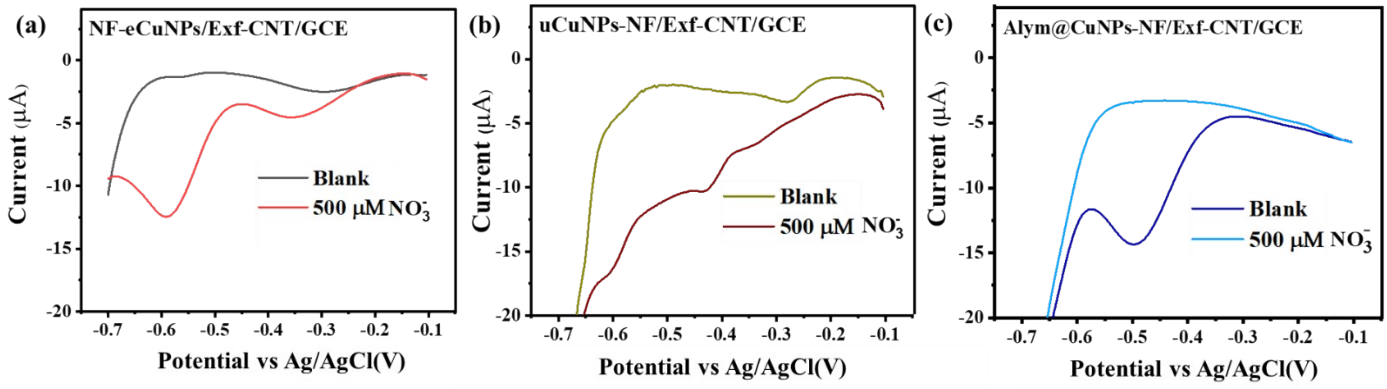


Fig. S10. DPV comparison study of 500 µM NO_3^- ion on three different sets of modified electrodes in 0.1 M Na_2SO_4 (pH=2) ; (a) NF-eCuNPs/Exf-CNT/GCE, (b) uCuNPs-NF/Exf-CNT/GCE, (c) Alym@CuNPs-NF/Exf-CNT/GCE

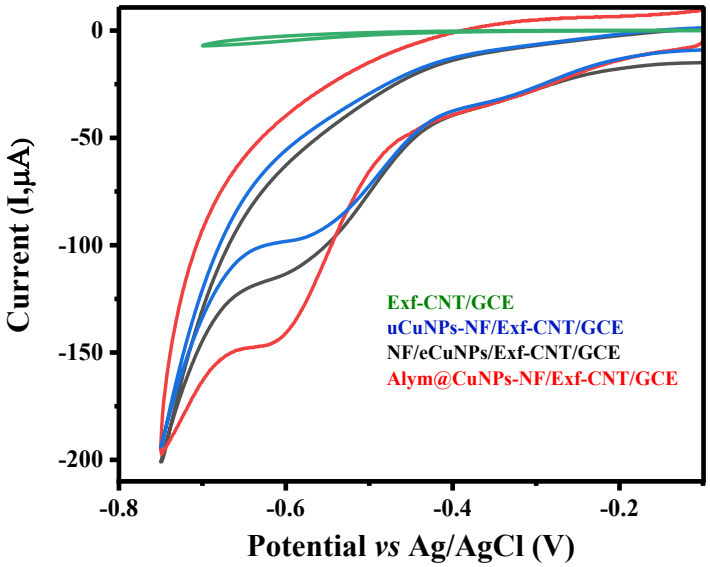


Fig. S11. CV comparison study of 500 µM NO_3^- ion concentration on different modified electrodes in 0.1 M Na_2SO_4 (pH=2)

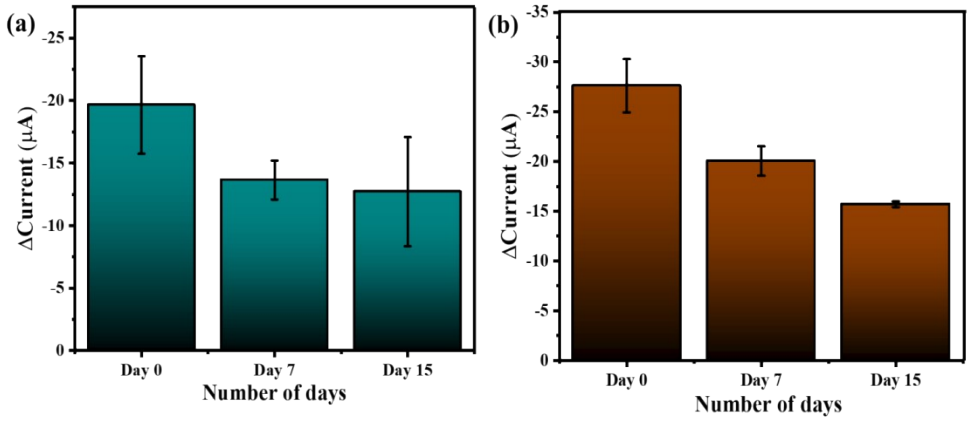


Fig. S12. Storage stability obtained from DPV study for **(a)** uCuNPs-NF/Exf-CNT/GCE **(b)** NF/eCuNPs/Exf-CNT/GCE in the presence of 1 mM NO_3^- ion in 0.1 M Na_2SO_4 (pH=2)

S3. Delta current response for peak current measurement of NO_3^- ion reduction

Delta current response means difference in peak current of the NO_3^- ion at a concentration and blank current (absence of NO_3^- ion) at the same potential. In the absence of NO_3^- ion, the background current attributed to the blank signal can vary a bit due to the hierarchical non-uniform porous structure of Alym@CuNPs which is evident from the FESEM image in Fig.2a. In the presence of NO_3^- ion, the catalytic activity of Alym@CuNPs facilitates consistent electron transfer efficiency, resulting in a comparable increment in current response for a fixed concentration of NO_3^- ion in different modified electrodes. For further clarification, it has been shown here in Fig.S13 that two different Alym@CuNPs-NF/Exf-CNT/GCE electrodes 1 and 2 give almost same delta current response, 23.8 µA (1) and 24.1 µA (2) respectively for 1 mM NO_3^- ion concentration

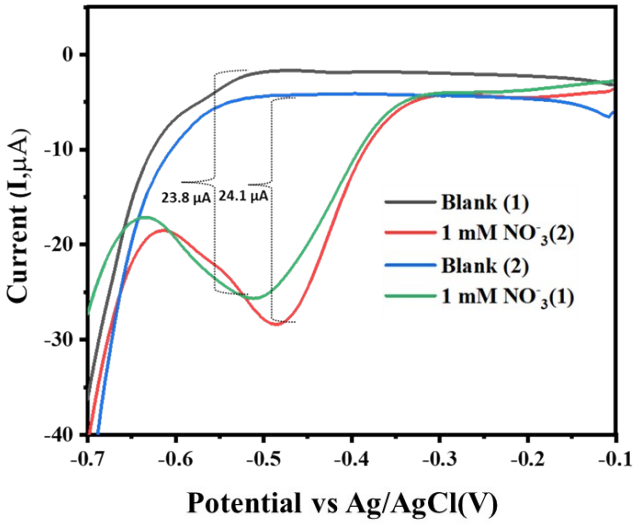


Fig. S13. DPV study for comparison of blank current respone and 1 mM NO_3^- ion current response for two electrodes (1 and 2) in 0.1 M Na_2SO_4 (pH=2)