Supplementary Information (SI) for Nanoscale Horizons.

Ambient Microdroplet Synthesis of Pt and Pt–Cu Nanorods from Homogeneous Solutions for Electrocatalytic Nitrate Reduction

Kandampully Sahadevan Aswathi, Keerthana Unni, Sinchan Mukhopadhyay, Anirban Som, Soham Chowdhury, Sourav Kanti Jana, Depanjan Sarkar*, and Thalappil Pradeep*

DST Unit of Nanoscience (DST UNS) and Thematic Unit of Excellence (TUE), Department of Chemistry, Indian Institute of Technology Madras, Chennai – 600036, India.

Centre of Excellence on Molecular Materials and Functions, Department of Chemistry, Indian Institute of Technology Madras, Chennai – 600036, India.

Electrochemistry Experiments

Both Pt NRs and Pt-Cu NRs were fabricated into electrodes by scooping the film formed on the water surface using an activated carbon paper (0.4 cm × 0.4 cm), and Nafion™ was used as the binder to anchor the material to the substrate. Electrochemical measurements were performed using an SP-300 electrochemical workstation purchased from Biologic. The Ag/AgCl electrode served as the reference electrode, a Pt wire as the counter electrode, and the synthesized nanorods-fabricated electrode as the working electrode. The electrocatalytic activity of the prepared electrodes was evaluated in an H-type cell, where the cathodic compartment contained 0.1 M Potassium NO_3^- (KNO_3) dissolved in 20 mL of 1 M potassium hydroxide (KOH) as well as the working and reference electrodes, and the anodic compartment contained 20 mL of 1 M KOH solution along with the counter electrode. A Nafion™ membrane separated the two compartments. Chronoamperometry was conducted for 1 hour at different potentials to quantify the products of electrocatalytic NO_3^- reduction, and the electrolyte after electrolysis was analyzed using a UV-Vis spectrophotometer.

Quantification of NH_3

The concentration of NH_3 produced was determined using the indophenol blue method. After electrolysis, the electrolyte was diluted tenfold. To 2 mL of this diluted electrolyte, 2 mL of a solution containing 5 wt% salicylic acid and sodium citrate dissolved in 1M sodium hydroxide (NaOH) was added. Subsequently, 1 mL of 0.05 M sodium hypochlorite (NaOCl) was added, followed by the addition of 0.2 mL of 1 wt% sodium nitroferricyanide ($C_5FeN_6Na_2O$). The solution was then left to react for 2 hours, after which the UV-Visible absorption spectrum was measured. A concentration-absorbance calibration curve was obtained using NH_4Cl solutions with concentrations of 0, 0.2, 0.4, 1, 1.5, 2, 2.5, 5, and 10 ppm in 1 M KOH. The concentration of NH_3 in the standard solutions and samples was estimated from absorbance values at 650 nm.

Quantification of nitrite

To estimate the amount of nitrite (NO_2^-) produced during NO_3^- reduction, the electrolyte after electrolysis was analyzed using the Griess test. About 0.1 g N-(1-naphthyl) ethylenediamine dihydrochloride, 1.0 g sulfonamide and 2.94 mL H_3PO_4 were dissolved in 50 mL deionized water. The Griess reagent (1 mL) thus obtained was mixed with 1 mL of the electrolyte from the cathodic compartment, and kept for 10 min. The absorbance at 540 nm was measured. The calibration curves were obtained using NO_2^- solutions with concentrations of 0, 0.05, 0.1, 0.15, 0.2, 0.25, 0.5, 0.75, 1, 1.5, 2.0, 2.5, and 5 ppm in 1 M KOH.

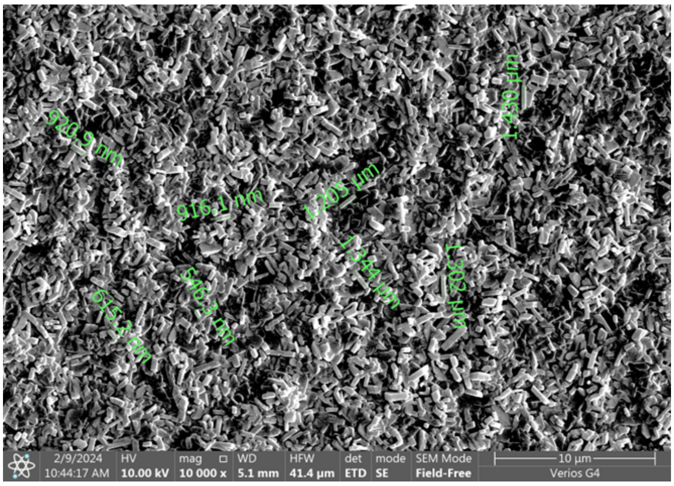


Fig S1. SEM image showing several nanorods with marked length measurements.

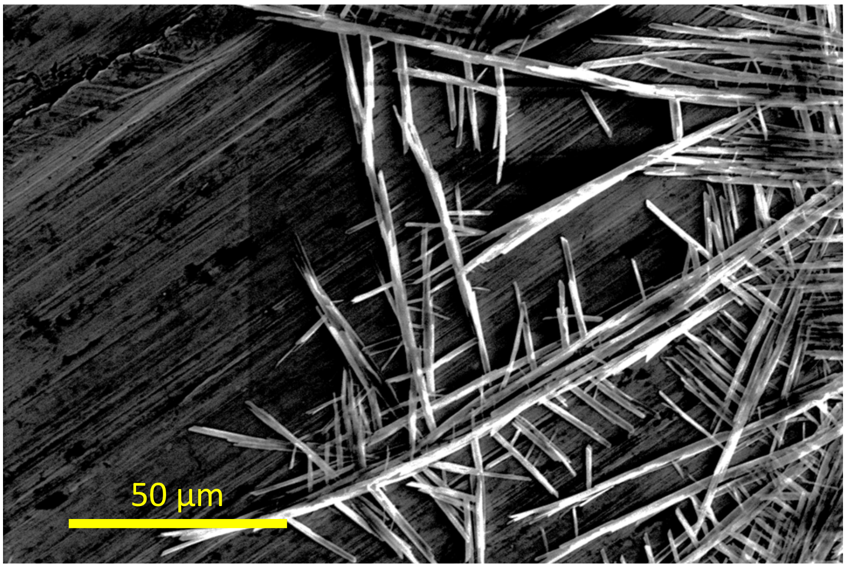


Fig S2. FESEM image of the $Pt(C_5H_7O_2)_2$ drop-casted on an aluminium sheet using a pipette tip.

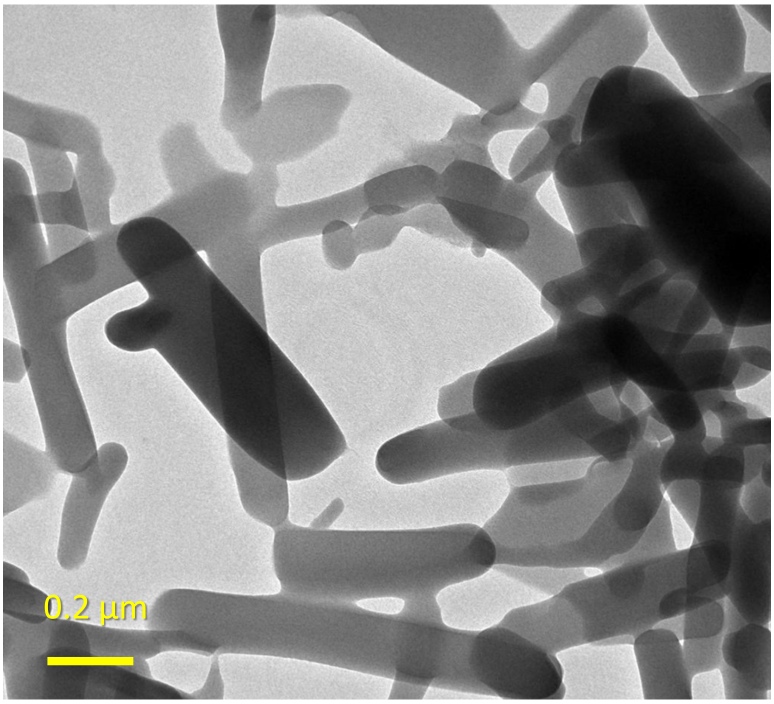


Fig S3. TEM image of Pt NRs synthesized by direct ESD of the precursor solution on a TEM grid.

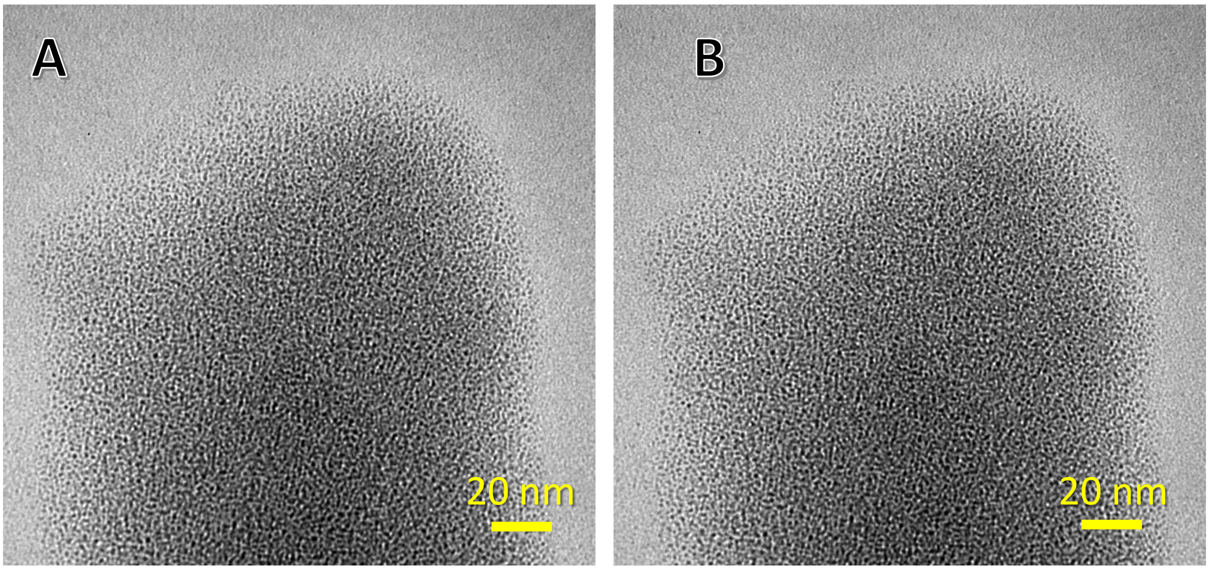


Fig S4. TEM image of a single Pt NR, A) before, and B) after electron beam exposure for 1 minute.

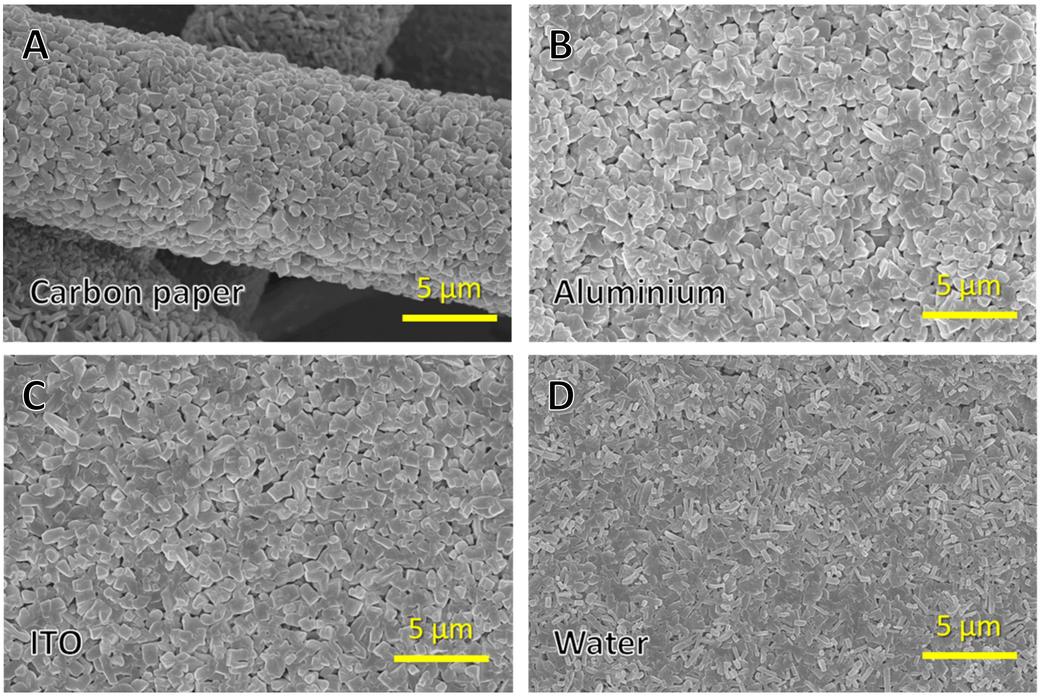


Fig S5. FESEM images of Pt NRs synthesized using ESD of charged microdroplets on various deposition substrates such as A) activated carbon paper, B) aluminium sheet, C) ITO-coated glass slide, and D) water.

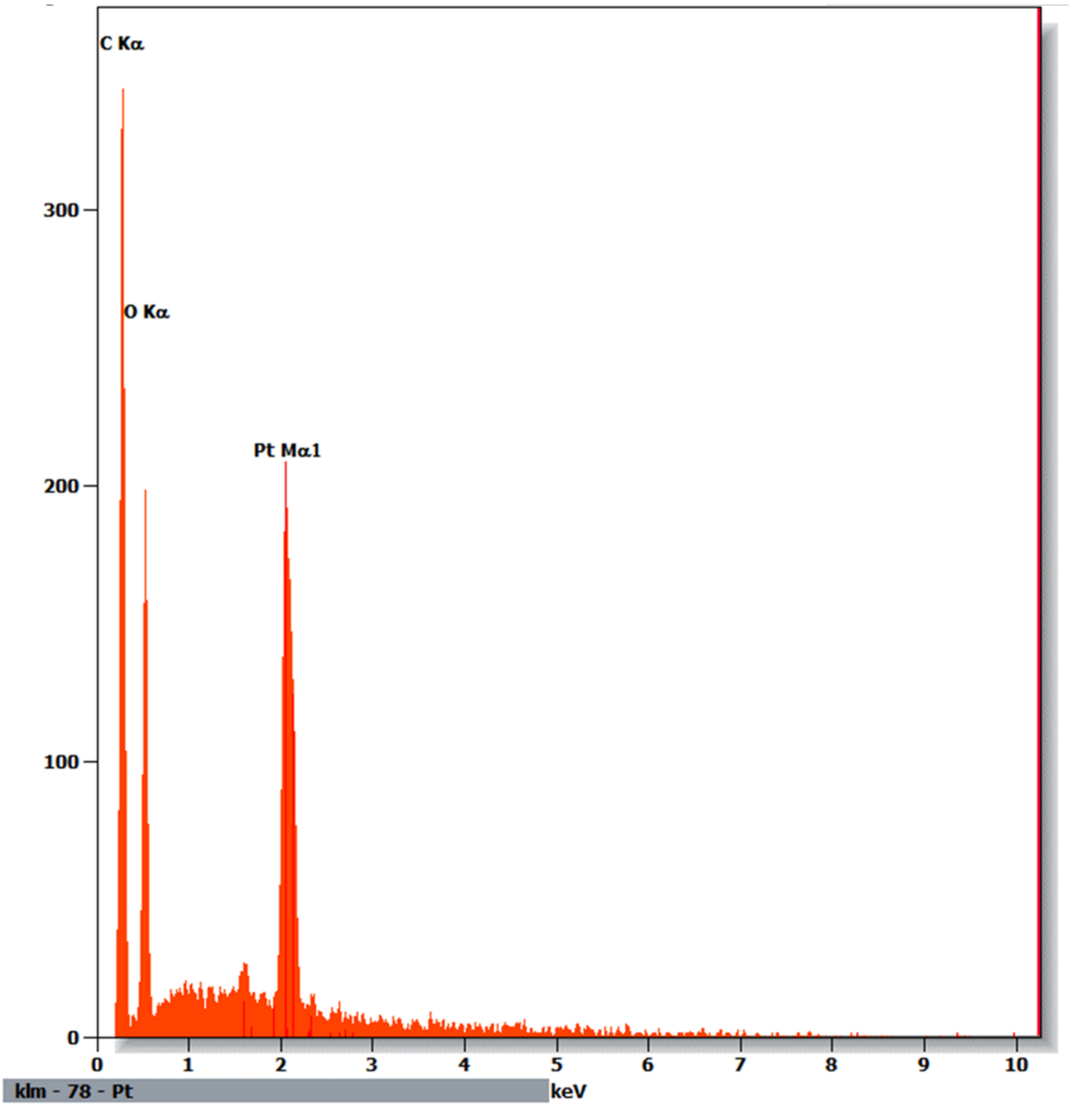


Fig S6. EDS spectrum collected from Pt NRs synthesized using ambient microdroplets.

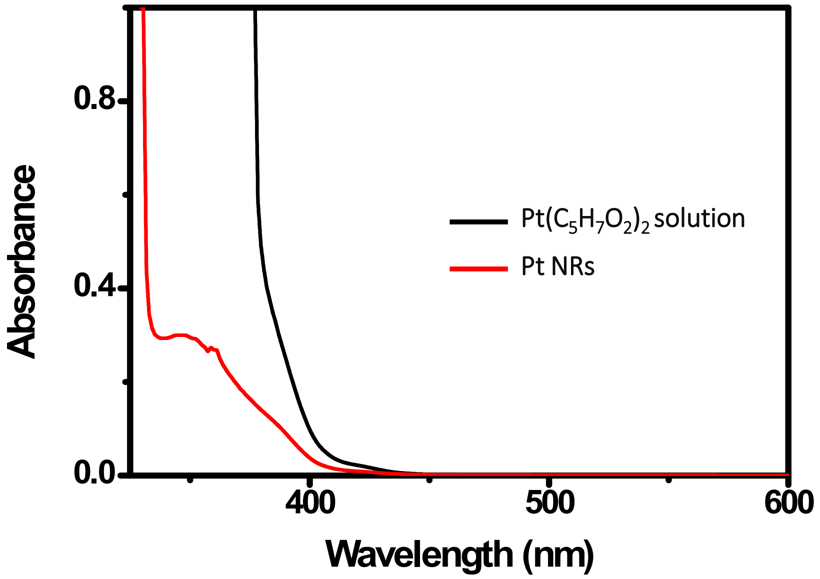


Fig S7. UV-Vis spectra of the precursor ($Pt(C_5H_7O_2)_2$) solution (black trace) and the synthesized Pt NRs (red trace).

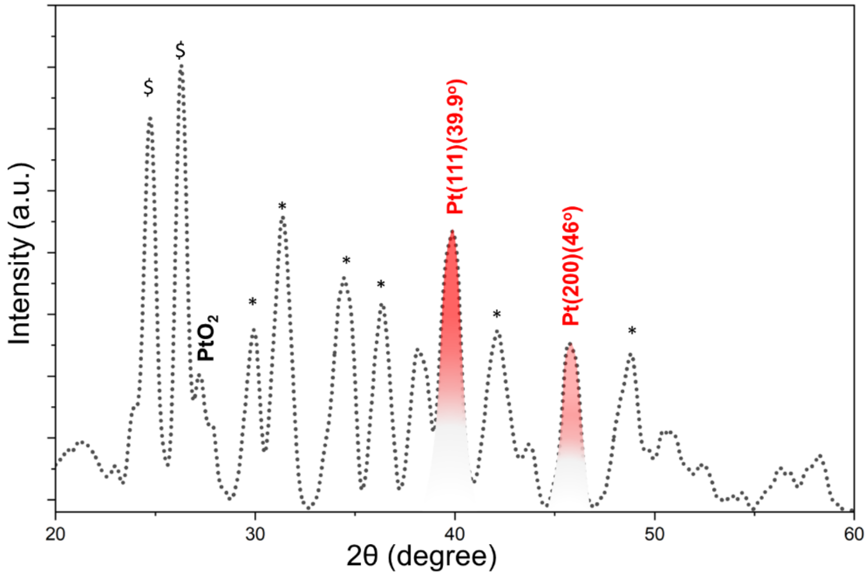


Fig. S8. XRD spectrum collected from Pt NRs synthesized using charged microdroplets by electrospray deposition at a high flow rate to enable XRD measurements. The substrate was an ITO-coated glass slide. Peaks due to the precursors are marked with $, and ITO-coated glass slide peaks. are marked with *.

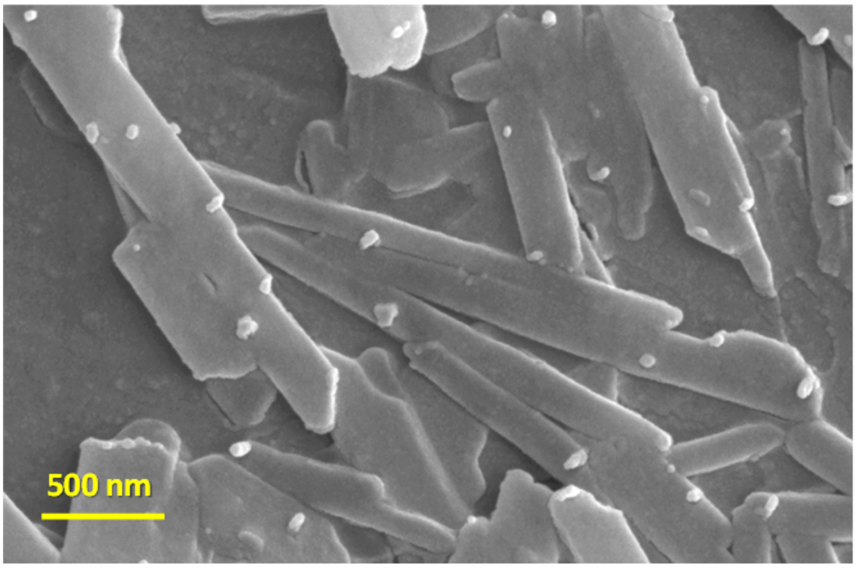


Fig S9. FE SEM image of the Pt NRs after 2 minutes of ESD. The small bead-like structures seen in the image indicate that the Pt NPs are formed at first, then these NPs stack by layers to form the rods.

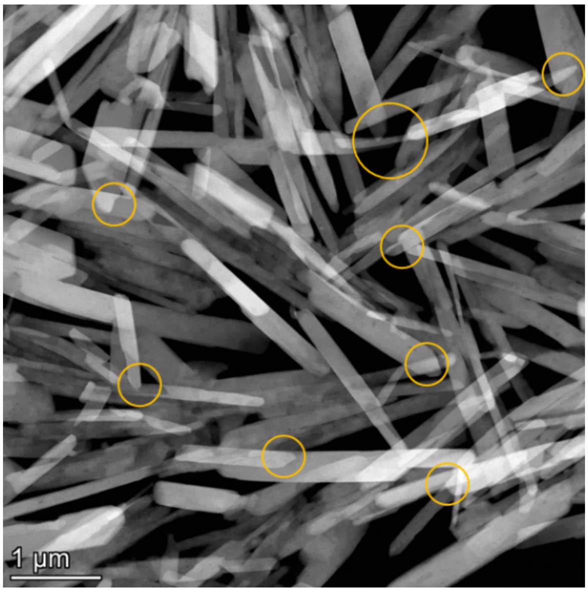
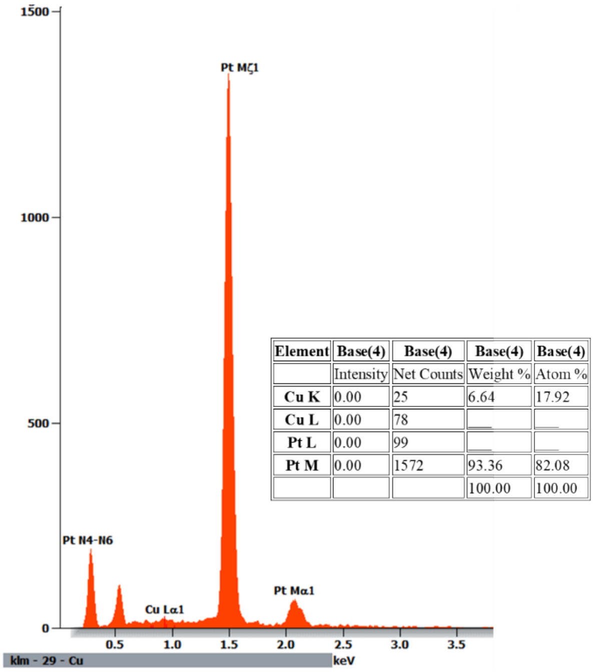


Fig. S10. Large-area STEM image showing multiple Pt Cu NRs exhibiting the characteristic sharpened, dagger-like structure.



Element	Base(4)	Base(4)	Base(4)	Base(4)
	Intensity	Net Counts	Weight %	Atom %
Cu K	0.00	25	6.64	17.92
Cu L	0.00	78	___	___
Pt L	0.00	99	___	___
Pt M	0.00	1572	93.36	82.08
			100.00	100.00

Fig S11. EDS spectrum collected from Pt-Cu NRs.

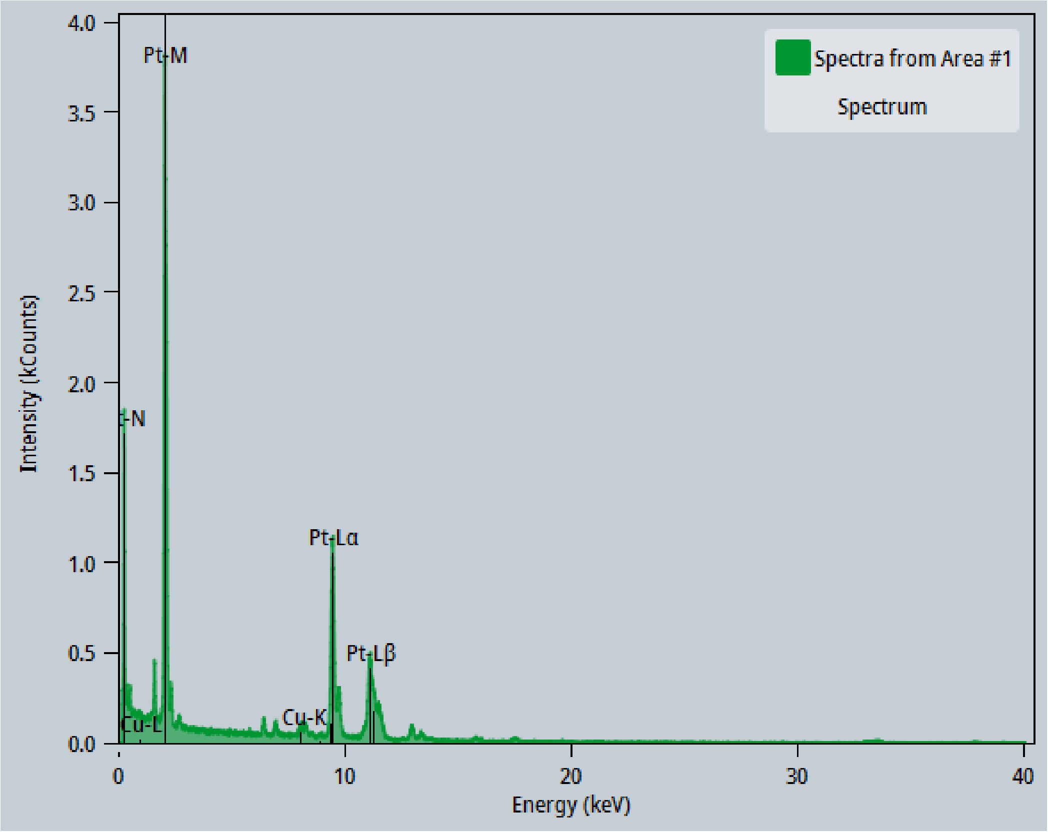


Fig. S12. EDS spectrum collected from a single Pt-Cu NR.

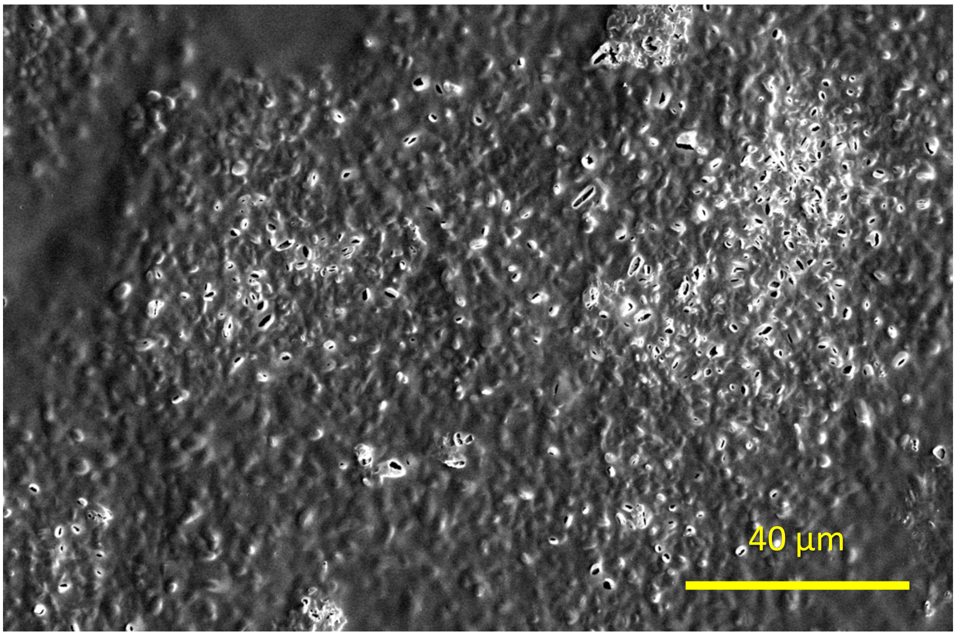


Fig. S13. FE SEM image of Nafion-coated Pt NR electrode after dipping the electrode underwater for 1h.

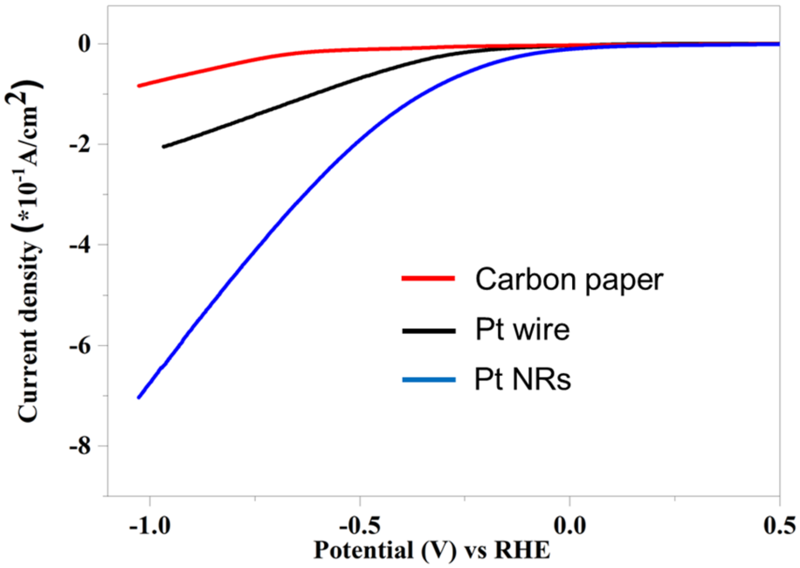


Fig S14. LSV measurements for NO_3^- reduction using different catalytic surfaces.

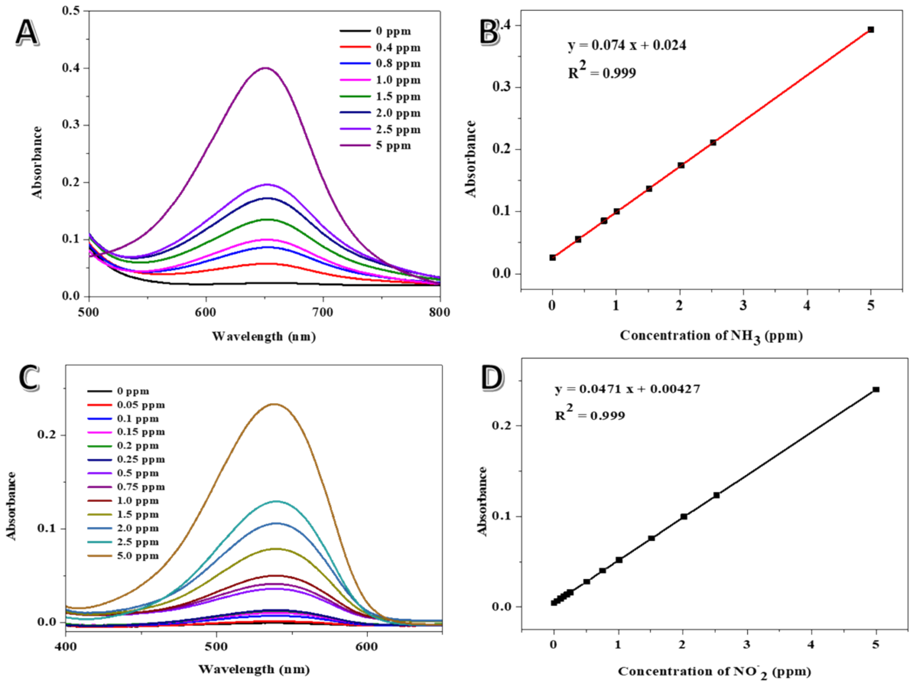


Fig S15. A) UV-Vis spectra, and B) corresponding concentration-absorbance calibration curve for quantitation of NH_3 using indophenol method. C) UV-Vis spectra, and D) corresponding concentration-absorbance calibration curve for quantitation of NO_2^- using Greiss test.

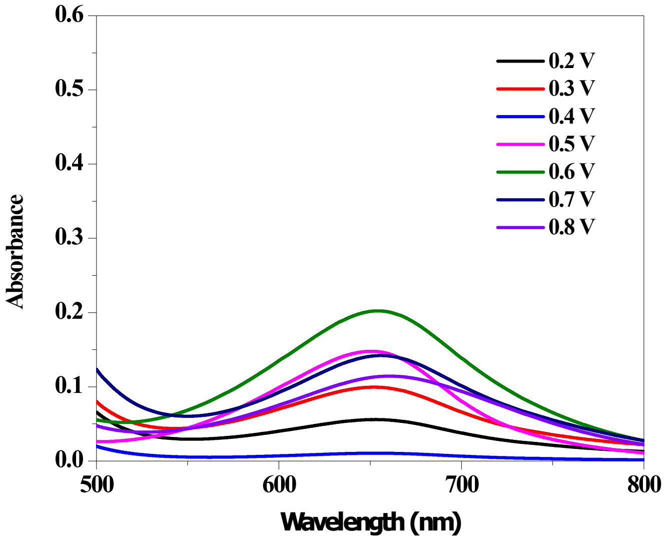


Fig S16. UV-visible spectra of the peak corresponding to NH_3, collected after chronoamperometric measurement of NO_3^- to NH_3 reduction process at different voltages using the Pt NRs as a catalyst. The indophenol method was used for quantitative measurements.

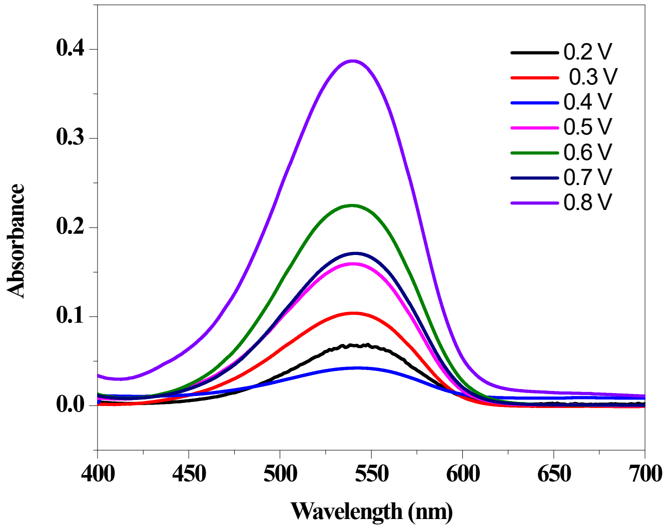


Fig S17. UV-visible spectra of the peak corresponding to NO_2^-, collected after chronoamperometric measurement of NO_3^- to NH_3 reduction process at different voltages using the Pt NRs as a catalyst. The Greiss test was used for quantitative measurements.

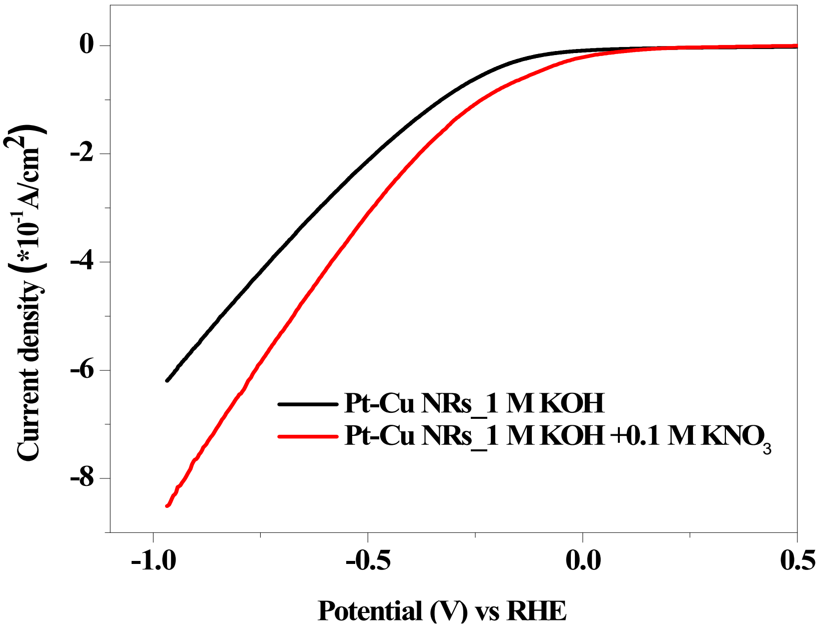


Fig S18. LSV curves with and without the presence of KNO_3 using Pt-Cu NRs electrodes.

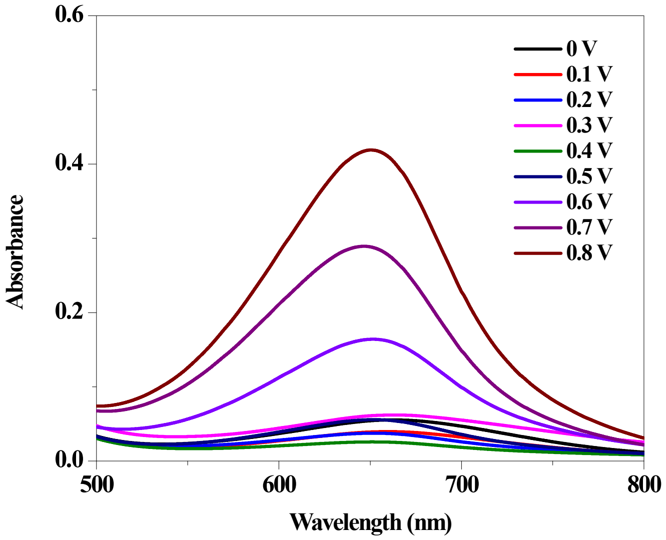


Fig S19. UV-visible spectra of the peak corresponding to NH_3, collected after chronoamperometric measurement of NO_3^- to NH_3 reduction process at different voltages using the Pt-Cu NRs as a catalyst. The indophenol method was used for quantitative measurements.

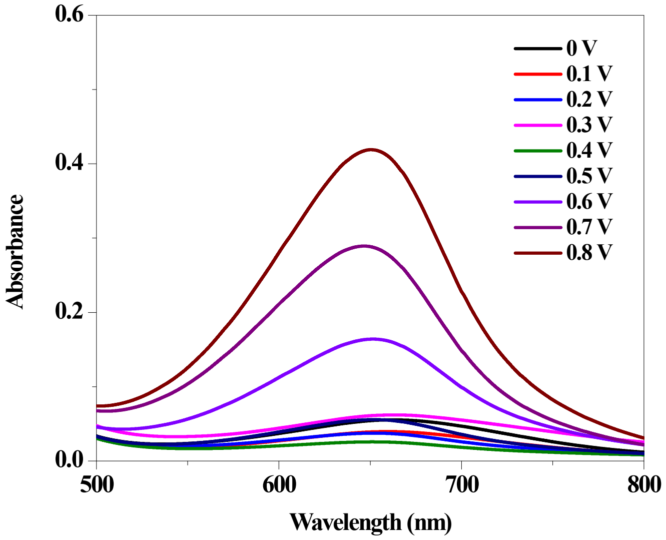


Fig S20. UV-visible spectra of the peak corresponding to NO_2^-, collected after chronoamperometric measurement of NO_3^- to NH_3 reduction process at different voltages using the Pt-Cu NRs as a catalyst. The Greiss test was used for quantitative measurements.

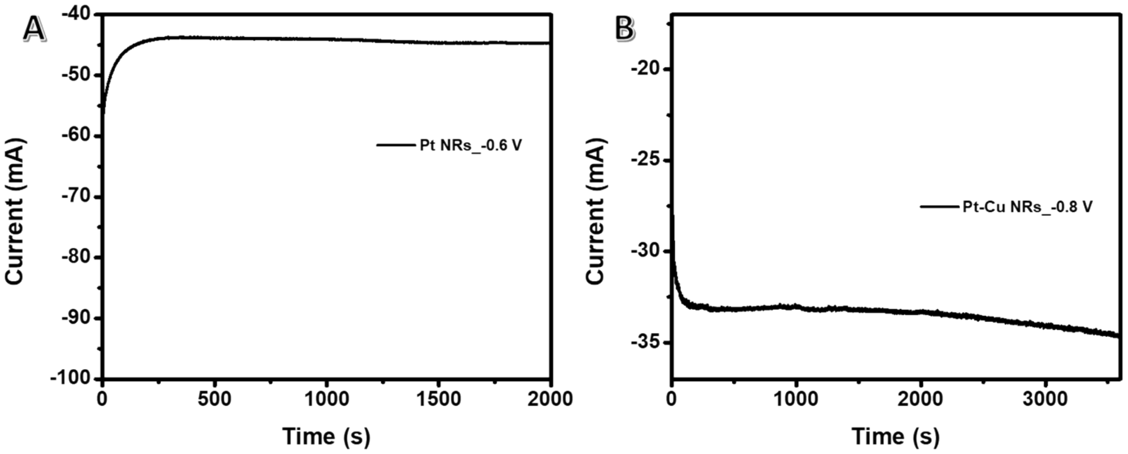


Fig S21. Plot for chronoamperometric measurements for the fabricated electrodes at their respective optimal potentials, i.e., Pt NRs at 0.6 V and Pt-Cu electrodes at 0.8 V, to assess their stability during the process.