Dual Performing Copper-Platinum Core-Shell Nanozyme for Environmental Electrochemistry-Electrocatalytic Oxidation and Electroanalysis of Ammonia

Bommireddy Naveen[a],Bommireddy Purusottam Reddy[b],Palathedath Suresh Kumar*[a]

Supporting Information

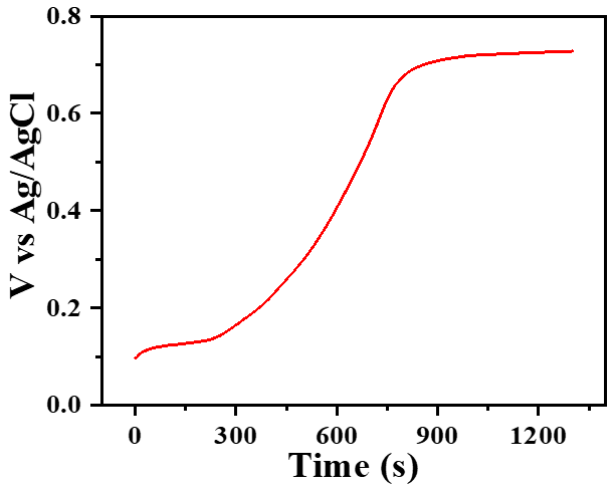

Figure S1: Galvanic replacement reaction of platinum over modified Cu/PGE monitored through open circuit potential technique

[0a] *Energy storage & Catalysis Laboratory, Department of Chemistry, School of Chemical & Biotechnology, SASTRA Deemed University, Thanjavur, India. E-mail: suresh@scbt.sastra.edu*
[b] *Department of Electronic Engineering, Yeungnam University, 280 Daehak-ro, Gyeongsan-si, Gyeongsanbuk-do, South Korea*

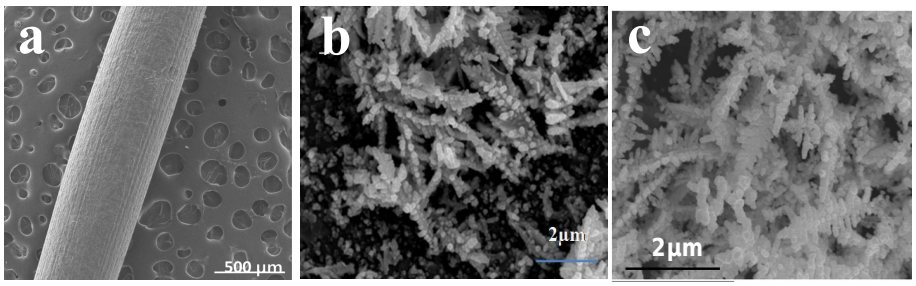

Figure S2: Scanning electron microscopic images of bare PGE (a) Cu/PGE (b), Cu@Pt/PGE (c).

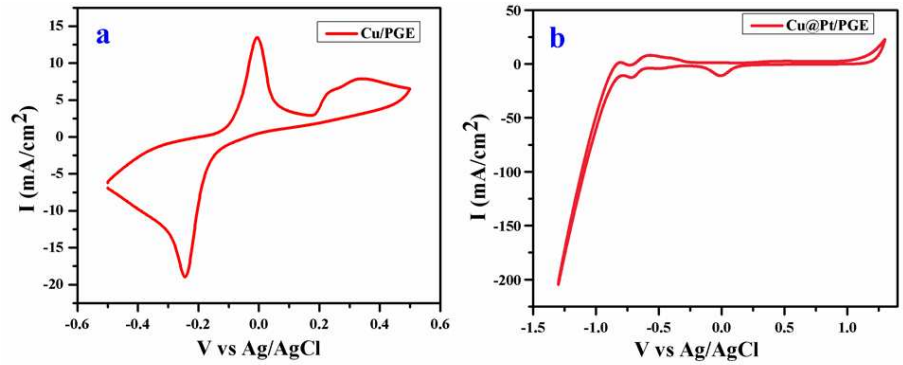

Figure S3: Cyclic voltammogram of Cu/PGE (a) and Cu@Pt/PGE (b) in 0.1 M phosphate buffer solution (PBS, 7.4 pH).

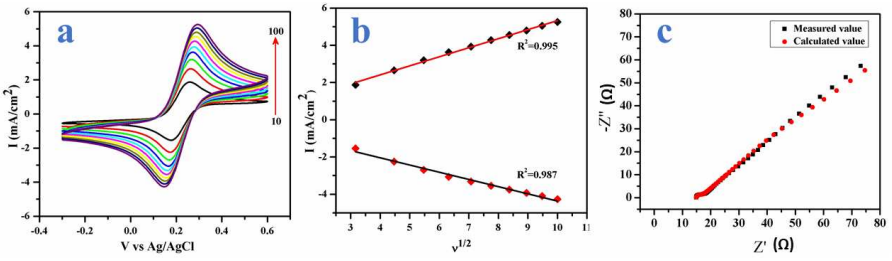

Figure S4: Cyclic voltammogram of Cu@Pt/PGE in 5 mM $[Fe(CN)_6]^{3-/4-}$ solution with 0.1 M KCl as supporting electrolyte at different scan rates (a) the corresponding peak current vs. square root of scan rate (i_p vs $\nu^{\frac{1}{2}}$) plot (b) and Nyquist plots obtained from electrochemical impedance measurements (c).

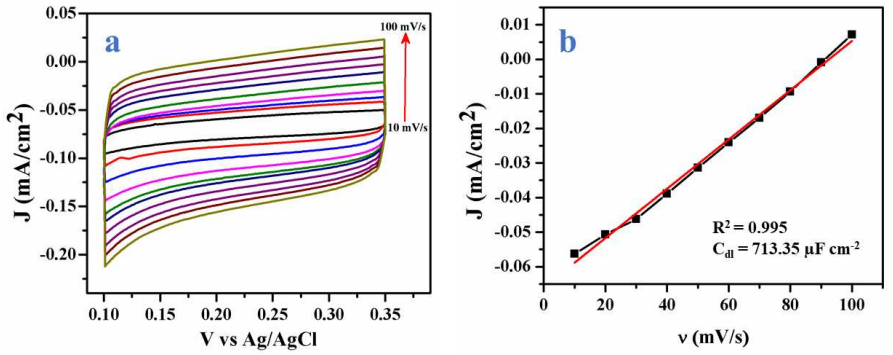

Figure S5: Cyclic voltammograms of Cu@Pt/PGE in 0.5 M H_2SO_4 at various scan rates in the double layer region (a) and dependece of capacitive current on scan rates (b)

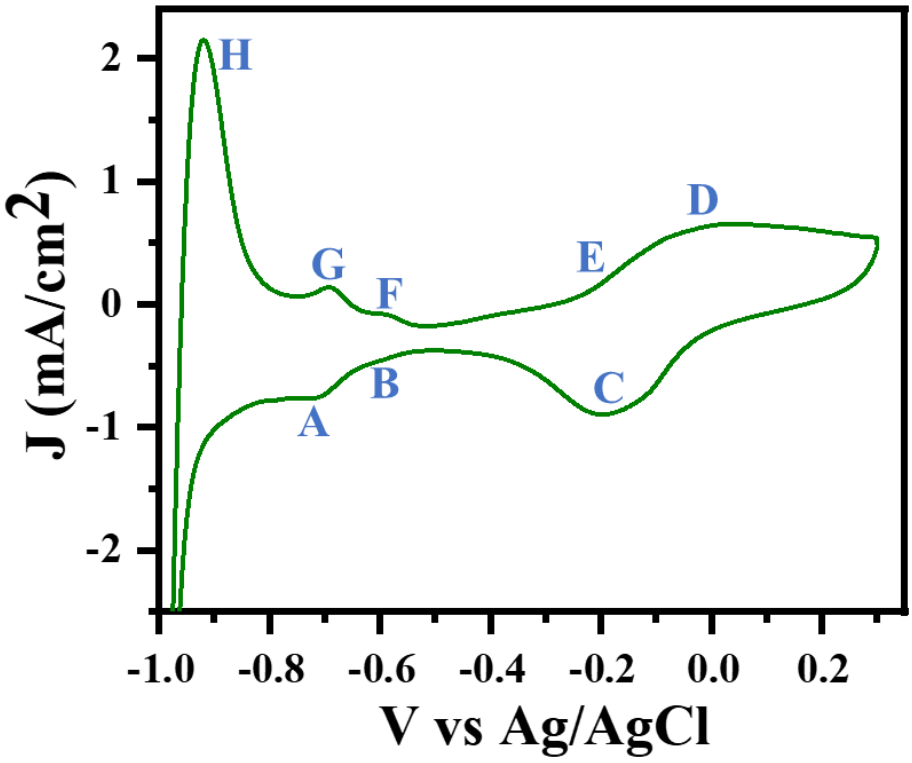

Figure S6: Cyclic voltammogram of Cu@Pt/PGE electrode in alkaline media (1 M KOH) with 50 mV s^{-1} (A) reversible peak of hydrogen under potential deposition (B) oxide desorption with hydrogen adsorption (C) irreversible oxide desorption peak (D) oxide growth - irreversible peak (E) oxygen adsorption (F and G) hydrogen desorption and (H) diffusional hydrogen desorption peak

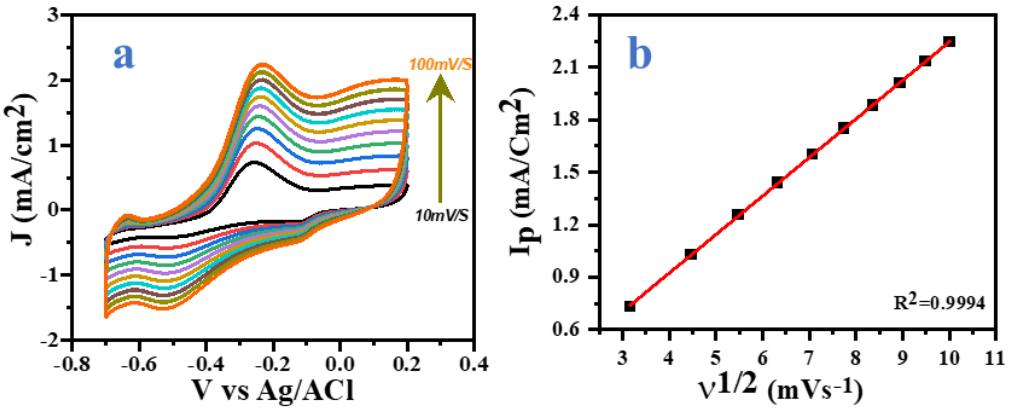

Figure S7: Typical voltammogram showing ammonia oxidation for 3 mM solution in 1 M KOH electrolyte at various scan rates using Cu-Pt/PGE electrode (a) and the corresponding linearity for $i_p/\nu^{\frac{1}{2}}$ against the scan rate (b)

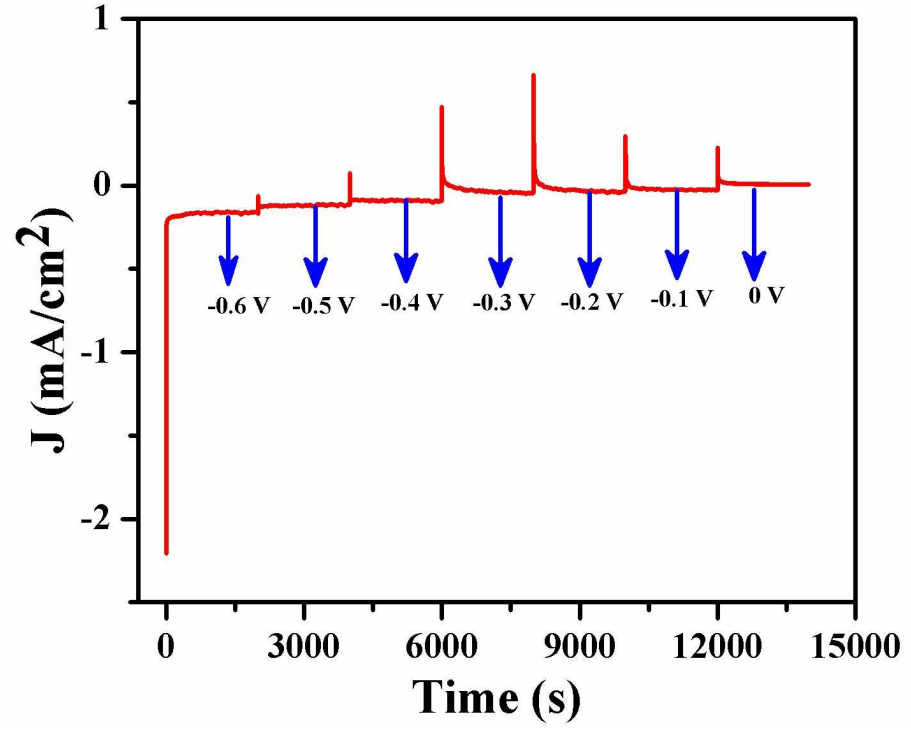

Figure S8: Current response towards potential scan on Cu@Pt/PGE for a duration of 2000 seconds

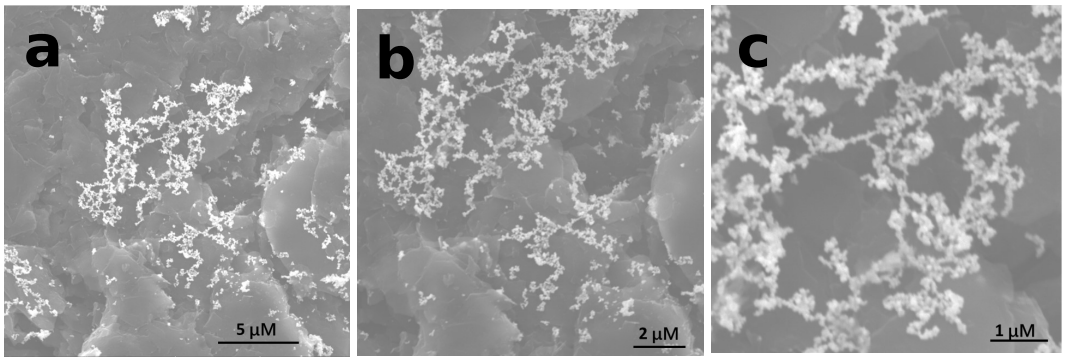

Figure S9: Scanning electron microscopic images of Cu@Pt/PGE at different magnifications after electrocatalysis of ammonia

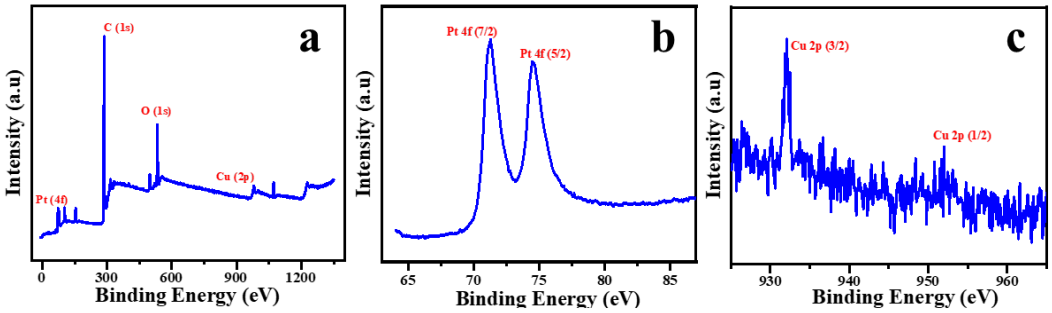

Figure S10: XPS analysis of Cu@Pt/PGE after 500 potential cycling towards AOR

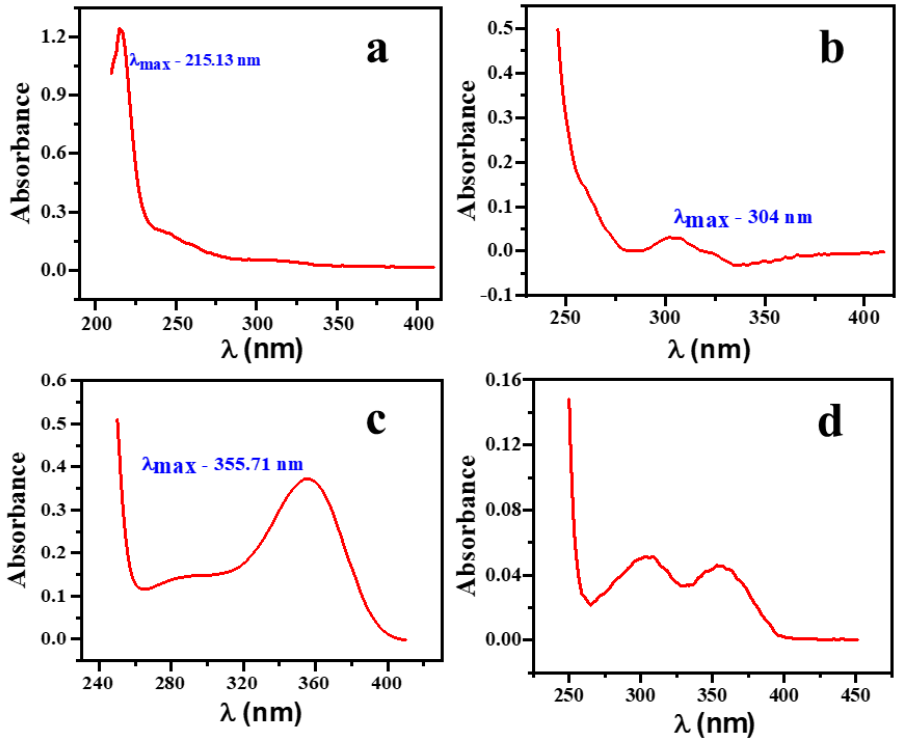

Figure S11: UV-Vis adsorption spectra of ammonium sulphate (a) sodium nitrate (b) sodium nitrite (c) hydroxylamine (d) and solution after electrocatalysis of AOR

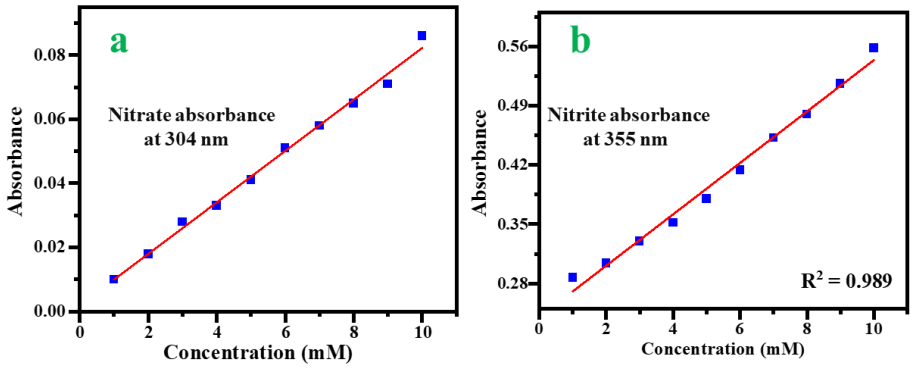

Figure S12: Calibration graph of measured absorbance for different concentrations of sodium nitrate (a) and sodium nirite (b)

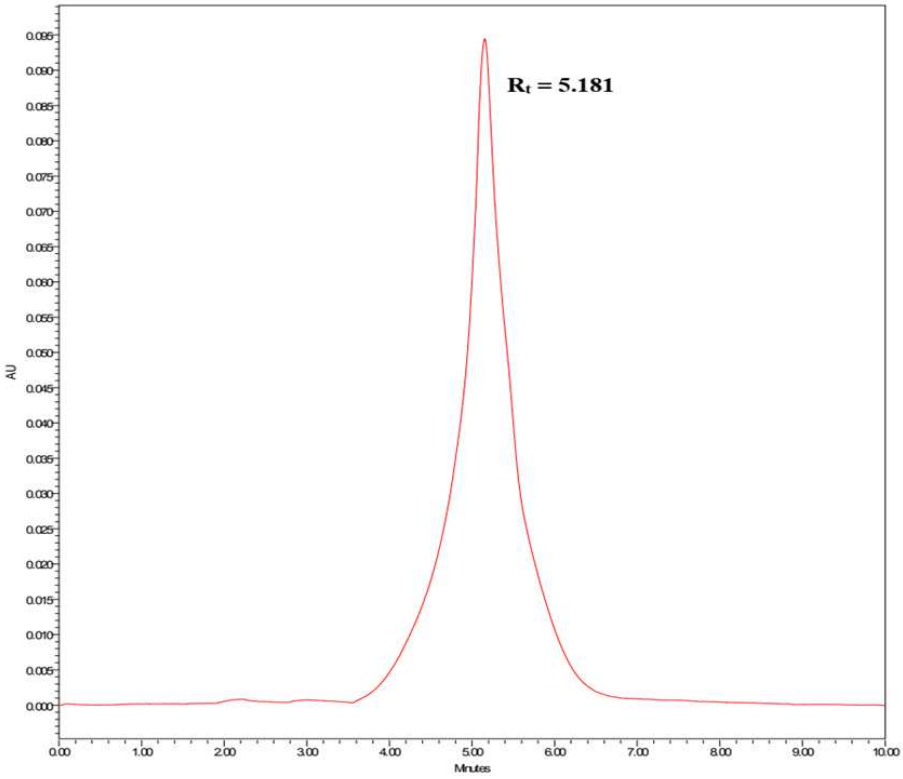

Figure S13: HPLC chromatogram of 1 mM sodium nitrate

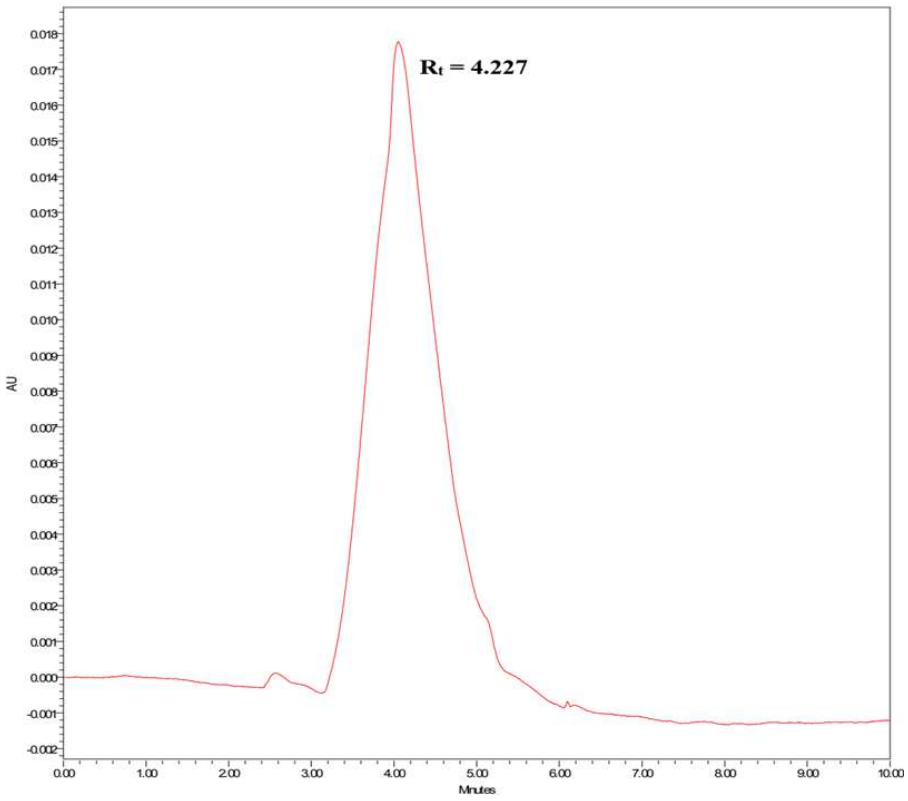

Figure S14: HPLC chromatogram of 1 mM sodium nitrite

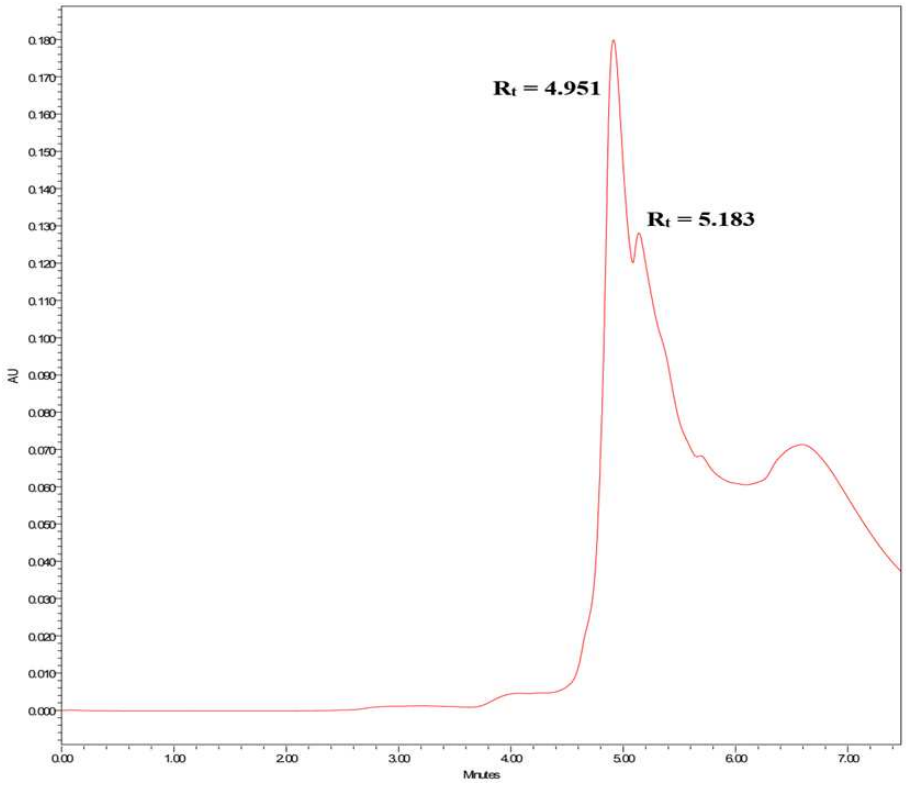

Figure S15: HPLC chromatogram of the solution after electrochemical oxidation of ammonia over Cu@Pt/PGE

Table 1: Parameters of fitting for the electrochemcial impedance analysis using the LR(CR(QR)) equivalent circuit for Cu@Pt/PGE in 20 mM ammonia

Potential (V) vs Ag/AgCl	Inductance (L) (μH)	R_u (Ω)	C_{dl} (μF)	R_{ct} (Ω)	CPE(Q) ($S.s^n$)	n	R_3 (Ω)
-0.7	1.661	3.61	0.21	1024	0.0017	0.93	7.17
-0.6	1.669	3.60	0.19	987	0.0005	0.84	9.87
-0.5	1.702	3.56	0.15	787	0.0008	0.75	2.82
-0.4	1.751	3.53	0.82	686	0.0008	0.81	0.02
-0.3	1.726	3.56	0.15	397	0.0005	0.74	1.74
-0.2	1.742	3.55	0.81	1105	0.0004	0.87	0.94
-0.1	1.738	3.56	0.80	1437	0.0003	0.86	0.15

Table 2: Standard electrode potentials for various nitrogen intermediates

Compound	Product	V vs Ag/AgCl (sat.KCl)
NH_3	N_2	-0.46
NH_3	NO_X	-0.22
N_2H_4	N_2	-1.3
NH_2OH	NO_X	-0.23
N_2O	N_2	+0.70
NO	N_2	+0.65
NO_2^-	N_2	+0.49
NO_3^-	N_2	+0.24