

Supplementary Information

Performance of graphitic carbon nitride nanosheets derived from liquid and thermal exfoliations towards the electrochemical reduction of nitrobenzene

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Chemicals

Sodium dihydrogen phosphate dihydrate ($\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$), disodium hydrogen phosphate dihydrate ($\text{Na}_2\text{HPO}_4 \cdot 2\text{H}_2\text{O}$) and sodium hydroxide (NaOH) were purchased from Merck, India and were used as received. L-methionine (L-Me), ascorbic acid (AA), uric acid (UA) and melamine were purchased from Sigma-Aldrich. Phosphate buffer (PB) of different pH solutions were prepared by mixing $\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$ and $\text{Na}_2\text{HPO}_4 \cdot 2\text{H}_2\text{O}$. The pH of the PB solution in the acidic and basic range was adjusted with orthophosphoric acid and sodium hydroxide, respectively. All other chemicals are of analytical grade and were used as received without further purification. The solutions used for different studies were made by using double distilled (DD) water.

Instrumentation

The FT-IR measurements were carried out by using JASCO FT-IR 4500 equipped with ATR PRO with diamond crystal. HR-TEM images were taken from JEOL JEM 2100, operating at 200 kV. X-ray diffraction analysis was carried out with PANalytical XPERT 3 X-ray diffraction unit using Ni-filtered Cu K_α ($\lambda = 1.5406 \text{ \AA}$). Scanning electron microscopy (SEM) measurements were carried at VEGA3 TESCAN, Czech Republic. Brunauer–Emmett–Teller (BET) analysis was performed at Quantachrome Nova 2200e Surface Area and Pore Size Analyzer. The electrochemical measurements were carried out with CHI electrochemical workstation (Model 643B, Austin, TX).

Procedure for cleaning glassy carbon (GC) electrode

Before modification the GCE was carefully cleaned with 0.3 and $0.05 \mu\text{m}$ alumina slurry, respectively until a shiny mirror like surface was obtained and then sonicated in DD water for 5 min.

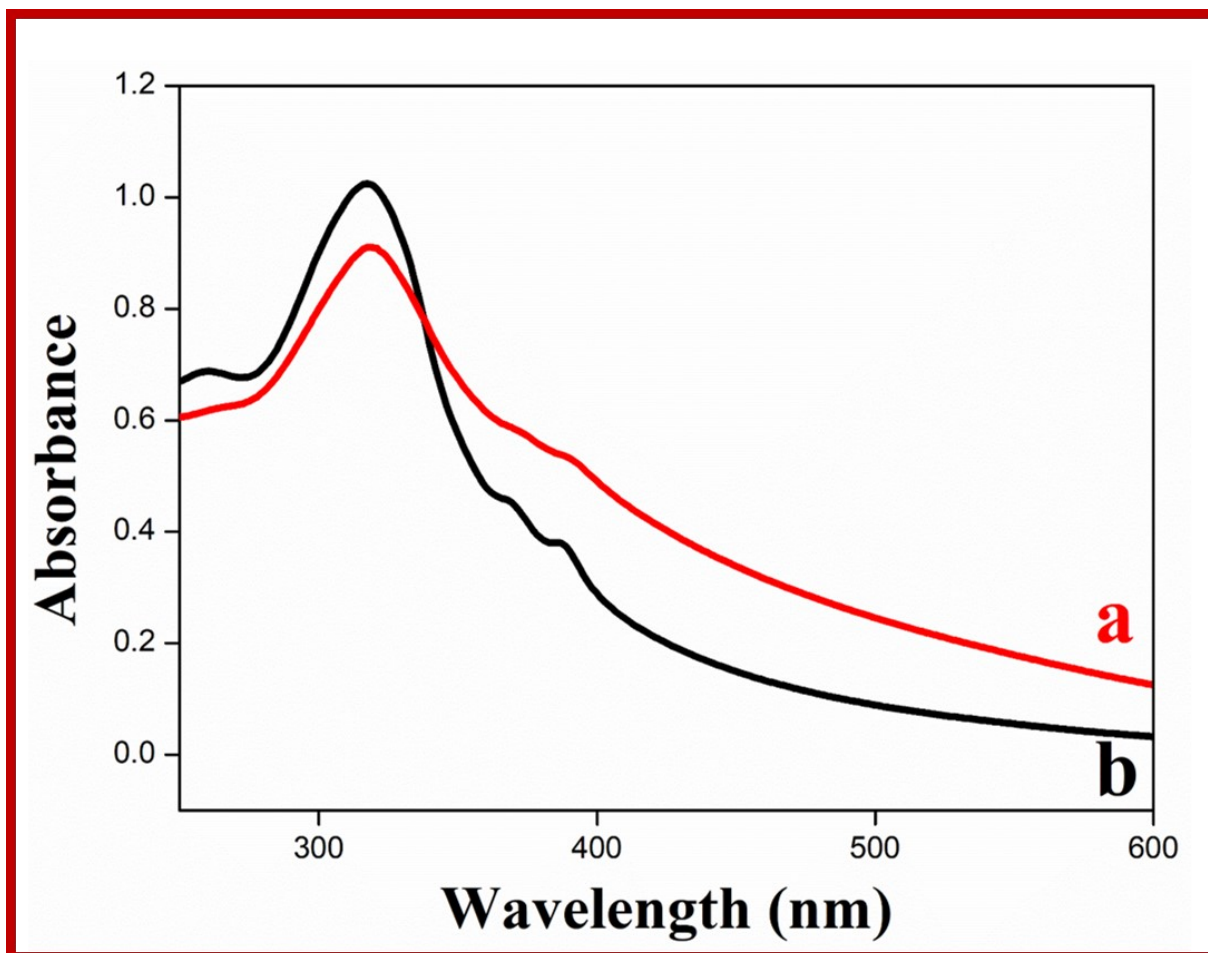


Fig.S1. Absorption spectra of (a) GNNS-S and (b) GNNS-T dispersed in water.

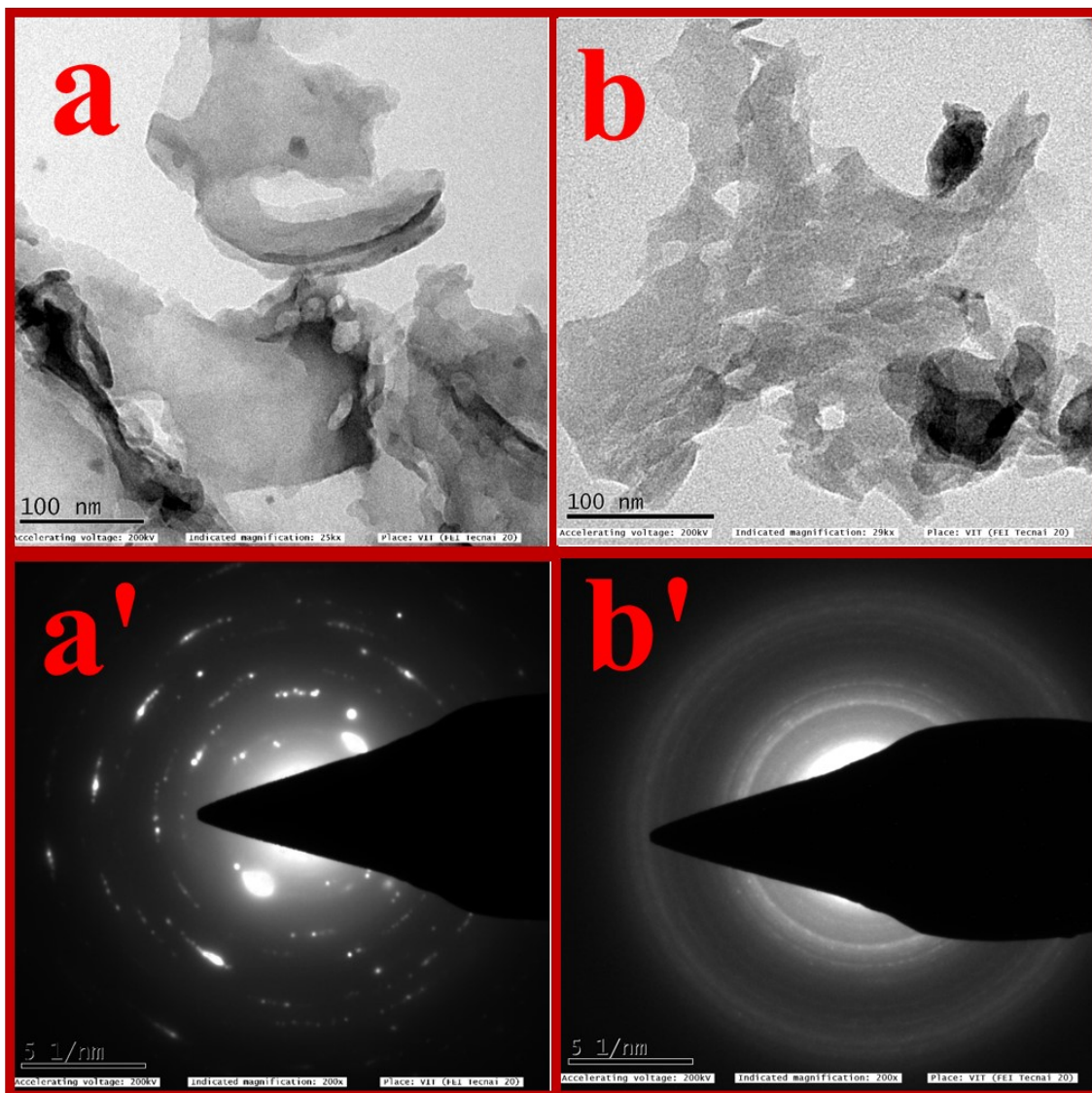


Fig.S2. (a and b) TEM images and (a' and b') SAED patterns obtained for GNNS-S and GNNS-T.

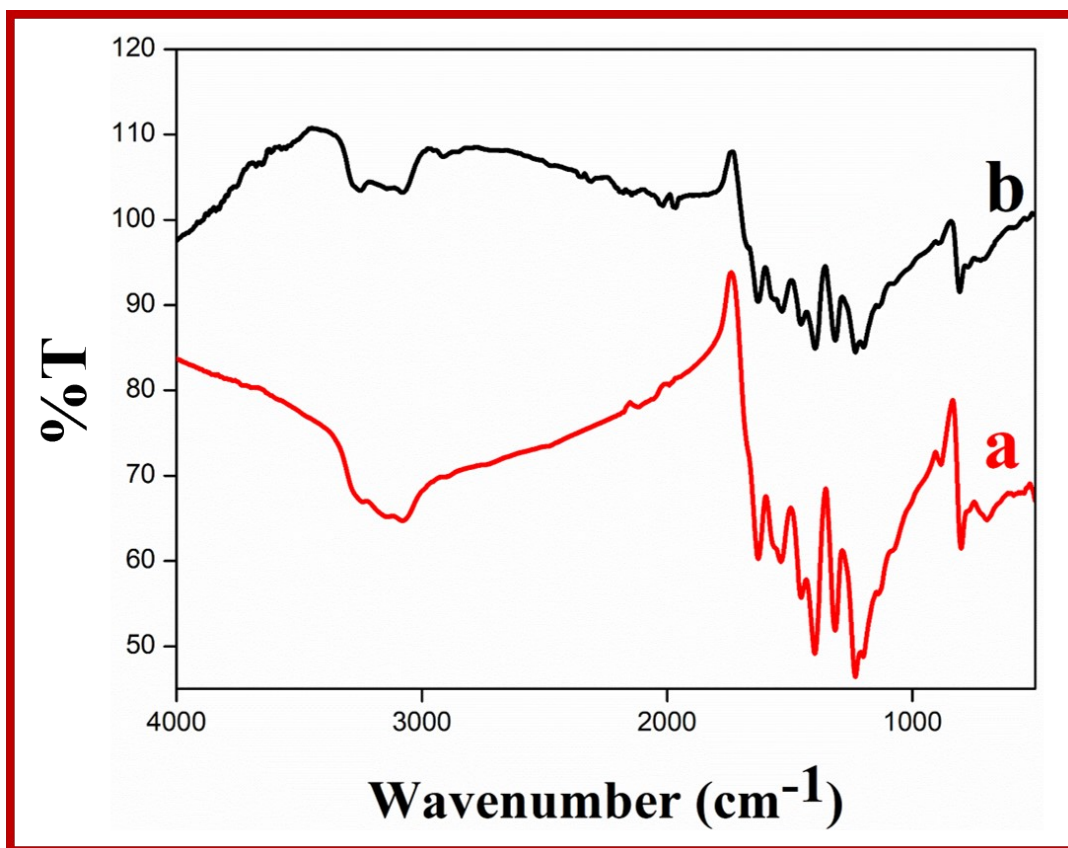


Fig.S3. ATR-FT-IR spectra of (a) GNNS-S and (b) GNNS-T coated GC plates.

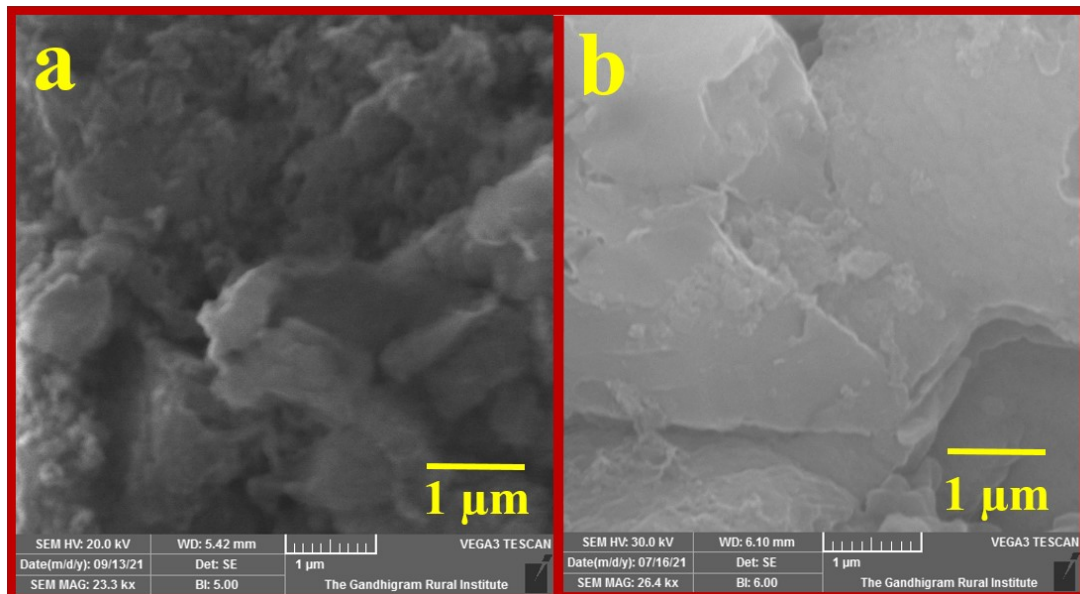


Fig.S4. SEM images of (a) B-GN and (b) B-GN coated on GC plate.

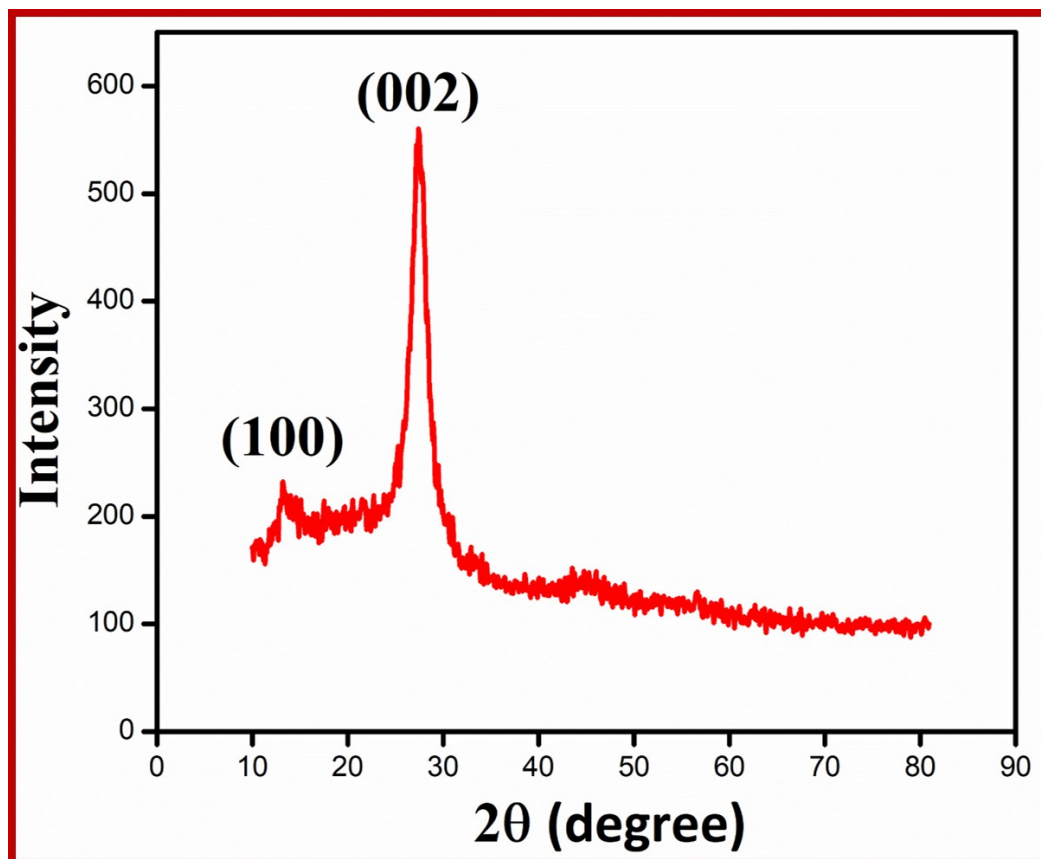


Fig.S5. XRD pattern obtained for GNNS-S coated on GC plate.

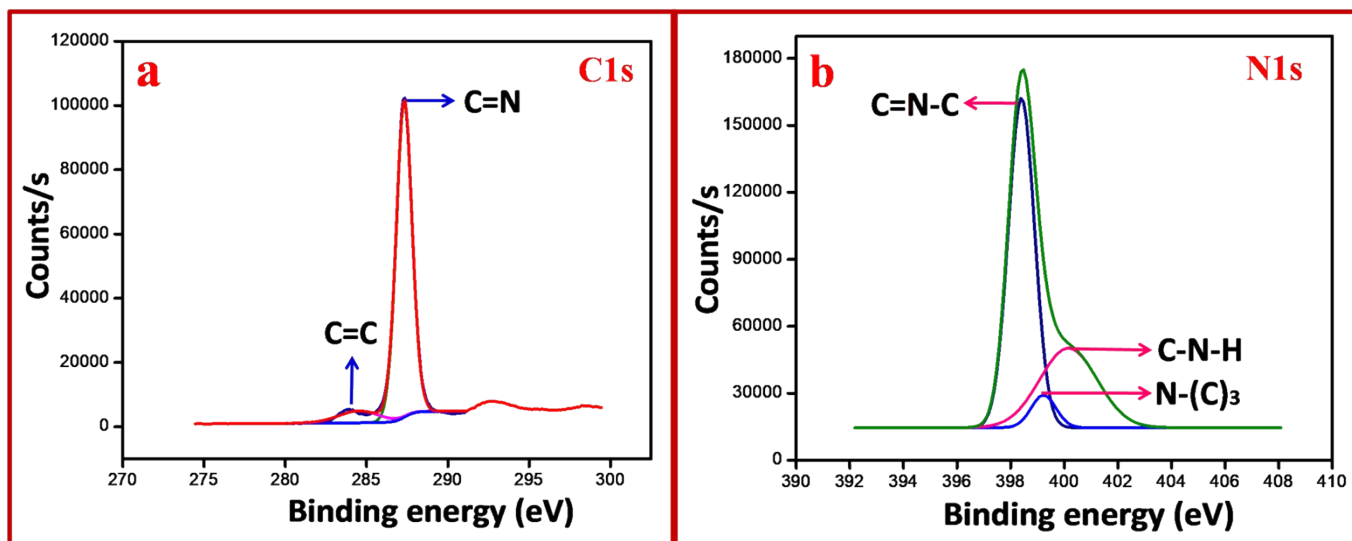


Fig.S6. Deconvoluted XPS of GNNS-T modified GC plate: (a) C1s and (b) N1s regions.

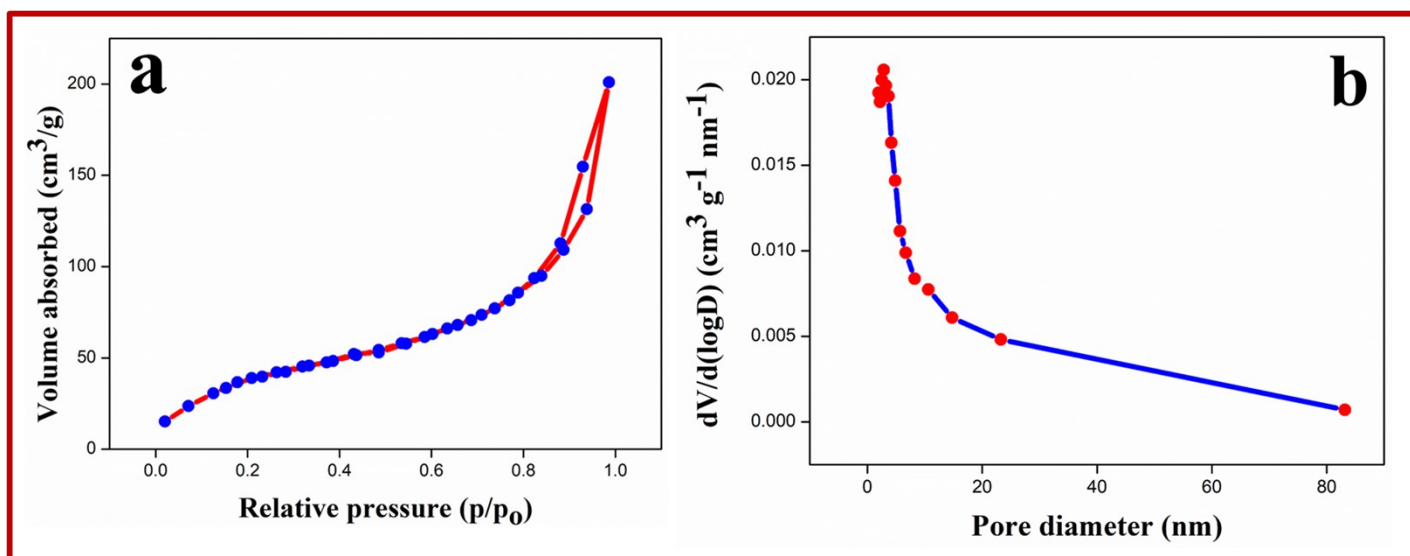


Fig.S7. (a) N₂-sorption isotherm and (b) the corresponding BJH pore-size distribution curve of GNNS-T.

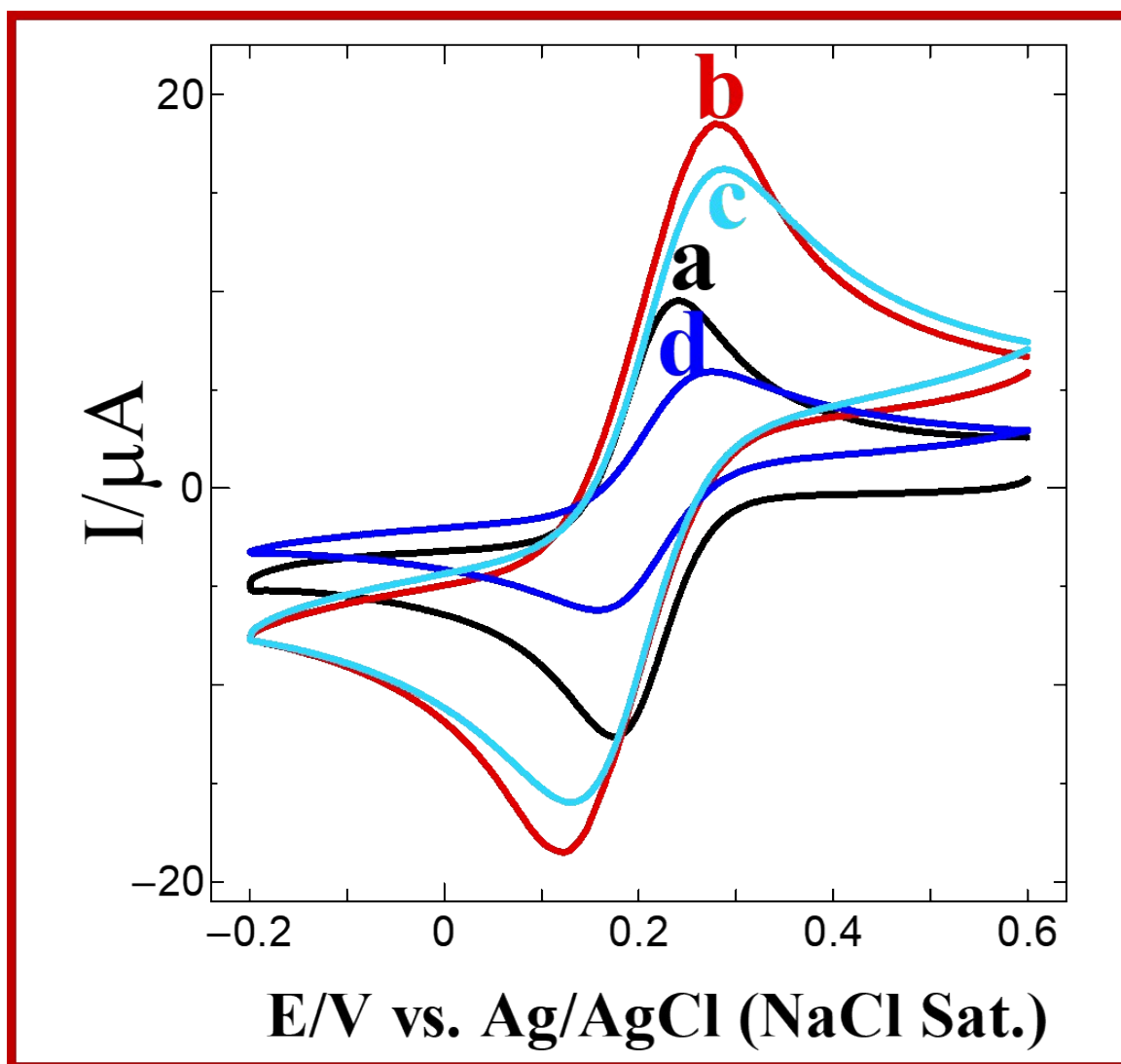


Fig.S8. CVs obtained for (a) bare GC, (b) GC/GNNS-S, (c) GC/GNNS-T and (d) GC/B-GN electrodes in 1 mM of each $\text{K}_3/\text{K}_4[\text{Fe}(\text{CN})_6]$ in 0.1 M KCl at a scan rate of 50 mV s^{-1} .

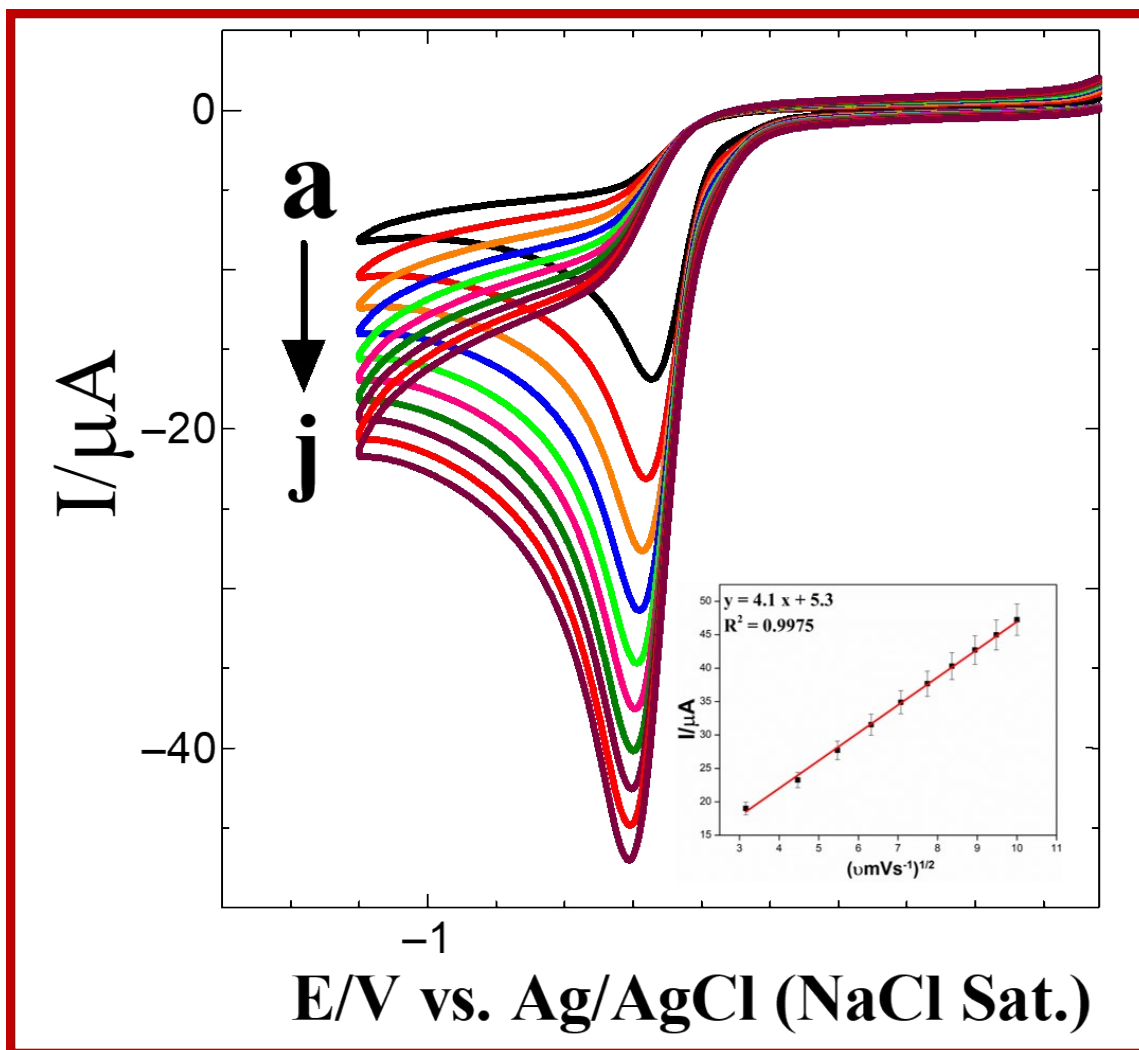


Fig.S9. CVs obtained for the reduction of 0.5 mM Nb at GC/GNNS-S electrode at different scan rates from 10-100 mV s^{-1} in 0.2 M PB solution (pH 7). Inset: Plot of reduction current of Nb vs. square root of scan rate.

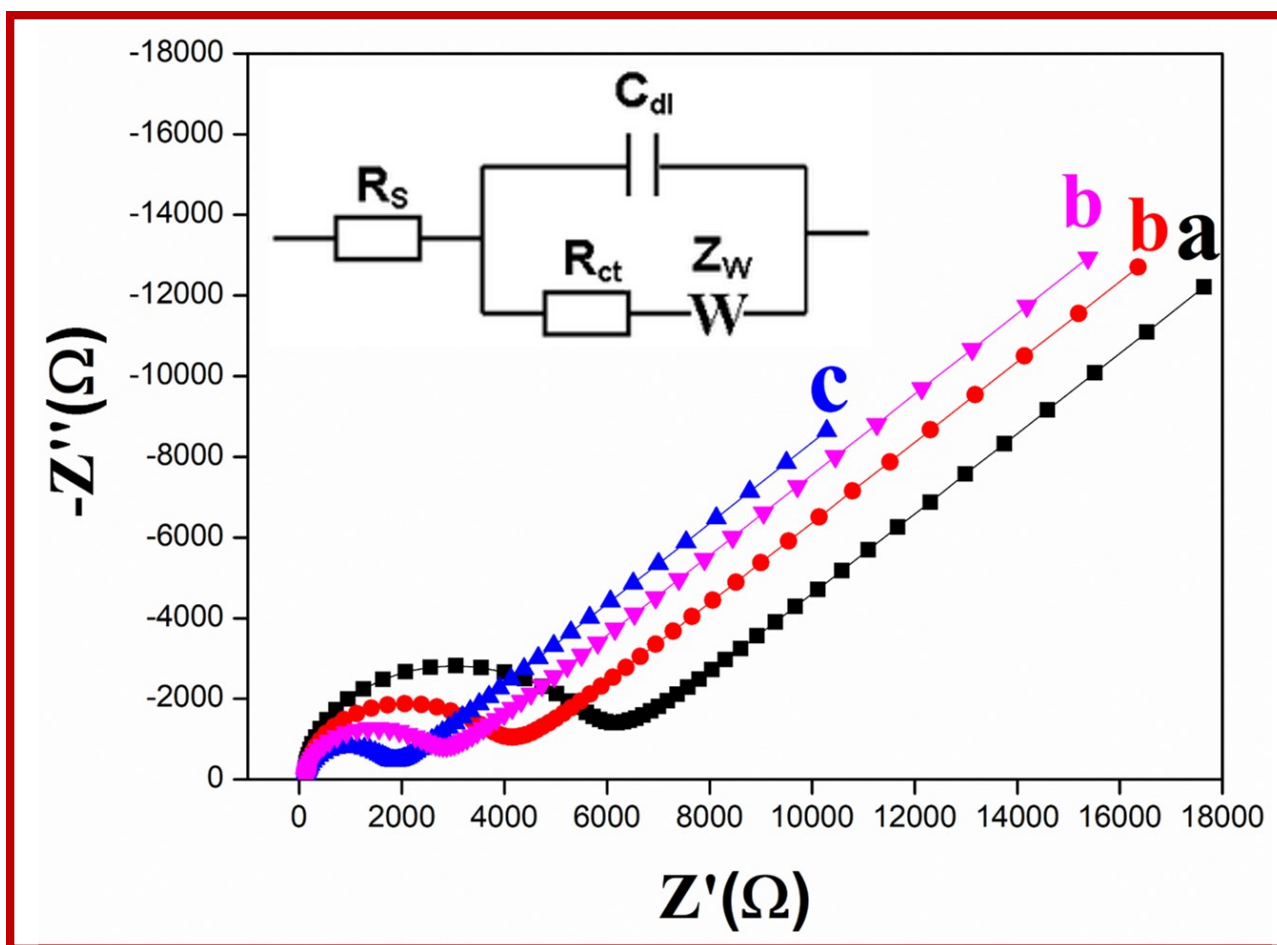


Fig.S10. Nyquist plots obtained for various loading levels of GNNS-S on GC electrode in 1 mM each $K_3/K_4[Fe(CN)_6]$ containing 0.1 M KCl at a scanning frequencies from 0.01 to 100 000 Hz: (a) 0.5 (b) 0.75 (c) 1 and (d) 1.25 $mg mL^{-1}$ (Inset: simple Randles circuit).

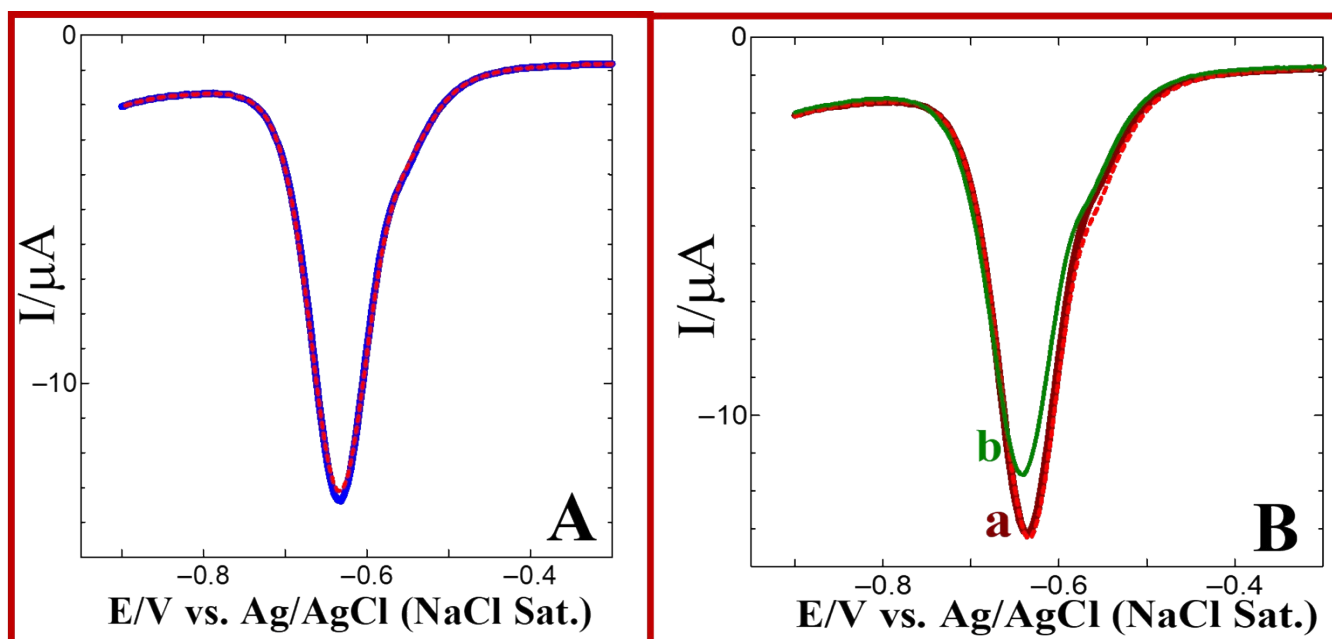


Fig.S11. DPV obtained for the determination of 200 μM Nb at GC/GNNS-S electrode. (A) in the presence 5000 μM of each Na^+ , K^+ , Mg^{2+} , Ca^{2+} , Cu^{2+} , Al^{3+} , Cl^- , F^- , NO_3^- , $\text{C}_2\text{O}_4^{2-}$ ions. (B) in presence of (a) 0 (solid line) and 200 μM (dotted line) and (b) 300 μM of major interferences like aniline, p-nitrophenol, p-cresol, benzonitrile, 4-nitrotoluene and Phenol in 0.2 M PB solution (pH 7).

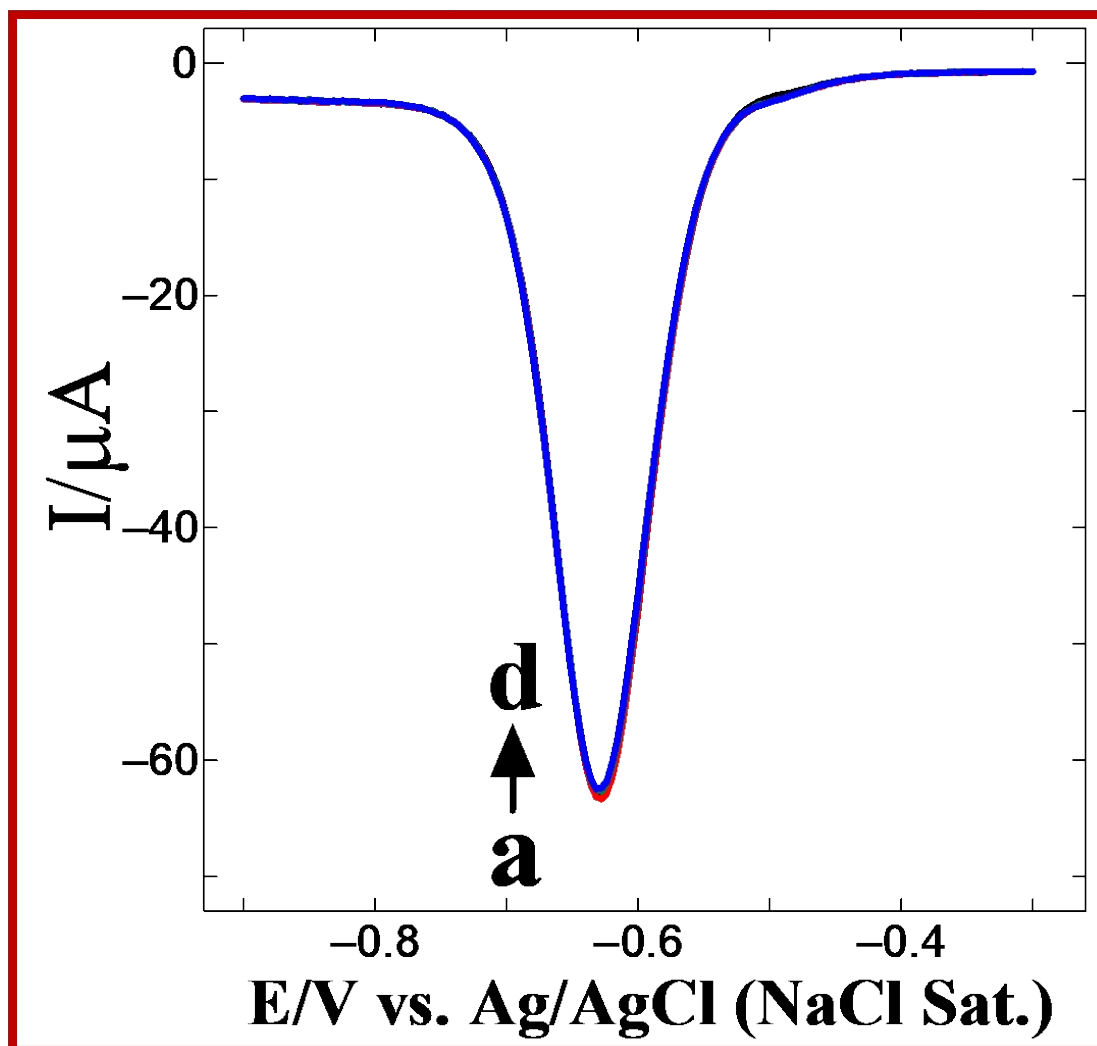


Fig.S12. DPVs recorded for every 25 cycles for the reduction of 1 mM Nb at GC/GNNS-S electrode: (a) 25, (b) 50, (c) 75 and (d) 100 cycles.

| Band positions (cm ⁻¹) | | Peak assignments |
|------------------------------------|----------------|-----------------------------------|
| GC/GNNS-S | GC/GNNS-T | |
| 3156 | 3211 | N-H stretching |
| 1629, 1530 | 1627,1536 | C=N |
| 1448, 1316, 1234 | 1452,1318,1238 | C-N |
| 806 | 808 | Breathing mode of triazine moiety |

Table S1. ATR-FT-IR peaks obtained for GNNS-S and GNNS-T coated on GC plate and their assignments.

| GCN loading level (mg ml⁻¹) | R_{CT} (kΩ) | k_{et} (cm² s⁻¹) |
|---|----------------------------|---|
| 0.50 | 4.94 | 7.68 × 10 ⁻⁴ |
| 0.75 | 3.82 | 9.93 × 10 ⁻⁴ |
| 1.00 | 2.11 | 1.80 × 10 ⁻³ |
| 1.25 | 2.76 | 1.37 × 10 ⁻³ |

Table S2. The impedance fitting results for GC/GNNS-S electrode with different loading levels of GNNS-S.

| Electrode | pH | Linear range (μM) | LOD (μM) | Reference |
|---|----------|---------------------------------|-----------------------|------------------|
| GC/SSG-AuAg | 7 | 1 - 80 | | 25 |
| GRGO/NiTPP | 7 | 5 - 878 | 0.14 | 26 |
| CMF/RGO | | 0.2 – 927.7 | 0.088 | 27 |
| GC/GO | 7 | 0.1-1 | 0.146 | 28 |
| NHCPs-750/GCE | | 5 - 2610 | 2.29 | 29 |
| Ni-MOF-PVP/GCE | 7.2 | 0.2 - 1000 | 0.097 | 30 |
| GMPP@AMP/GCE | 7 | 34 - 246 | 0.243 | 31 |
| ZSO-GCN/GCE | 7.2 | 30 - 900 | 2.2 | 32 |
| Ni/Fe(SDS)-LDH | | 1 – 10 10 – 100 100 - 350 | 0.093 | 33 |
| GC/EDAS/g-C ₃ N ₄ - Ag(2 mM) _{NC} | 7.4 | 5 - 50 | 2 | 34 |
| GC/MMPCMs | 6 | 0.2-40 | 0.008 | 35 |
| GC/AuNPs | 7 | 0.1-600 | 0.016 | 36 |
| GC/Nafion/PNMPC | 7 | 1-200 | 0.05 | 37 |
| GC/GCN-Tu | 7.2 | 1-1000 | 1.3 | 19 |
| GC/GNNS-S | 7 | 0.5-2000 | 0.0073 | This work |

Table S3. Comparison of the performance of the present GNNS-S modified electrode towards the determination of Nb with the latest reported papers.

Silicate sol-gel matrix- AuAg, green reduced graphene oxide/nickel tetraphenyl porphyrin, reduced graphene oxide supported cellulose microfiber, graphene oxide, N-doped hollow carbon nanospheres, nickel organic framework capped with polyvinylpyrrolidone, graphene oxide@ polymerized-manganese-porphyrin composite, zinc stannate-graphitic carbon nitride, Ni/Fe layered double hydroxides functionalized with sodium dodecyl sulphate, graphitic carbon nitride-thiourea, silver nanoparticles-decorated N-[3-(trimethoxysilyl) propyl]ethylenediamine - modified graphitic carbon nitride nanocomposites, macro-/mesoporous carbon materials, Pt nanoparticles ensemble on macroporous carbon hybrid nanocomposites.

| ^a Tap water | Spiked (μM) | Found (μM) | Recovery (%) |
|------------------------|--------------------------|-------------------------|--------------|
| Sample 1 | 0 | 0 | 0 |
| | 10 | 9.97 | 99.7 |
| | 15 | 24.9 | 99.6 |
| | 15 | 39.8 | 99.5 |

^a Three replicate measurements were made on the sample

Table S4. Determination of Nb in tap water sample using GC/GNSS-S electrode.