

Supporting Information

Microwave-Assisted N,S Co-Doped Reduced Graphene Oxide for Eco-Friendly Environmental Monitoring of Nitrobenzene

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S.1 Morphological Characterization

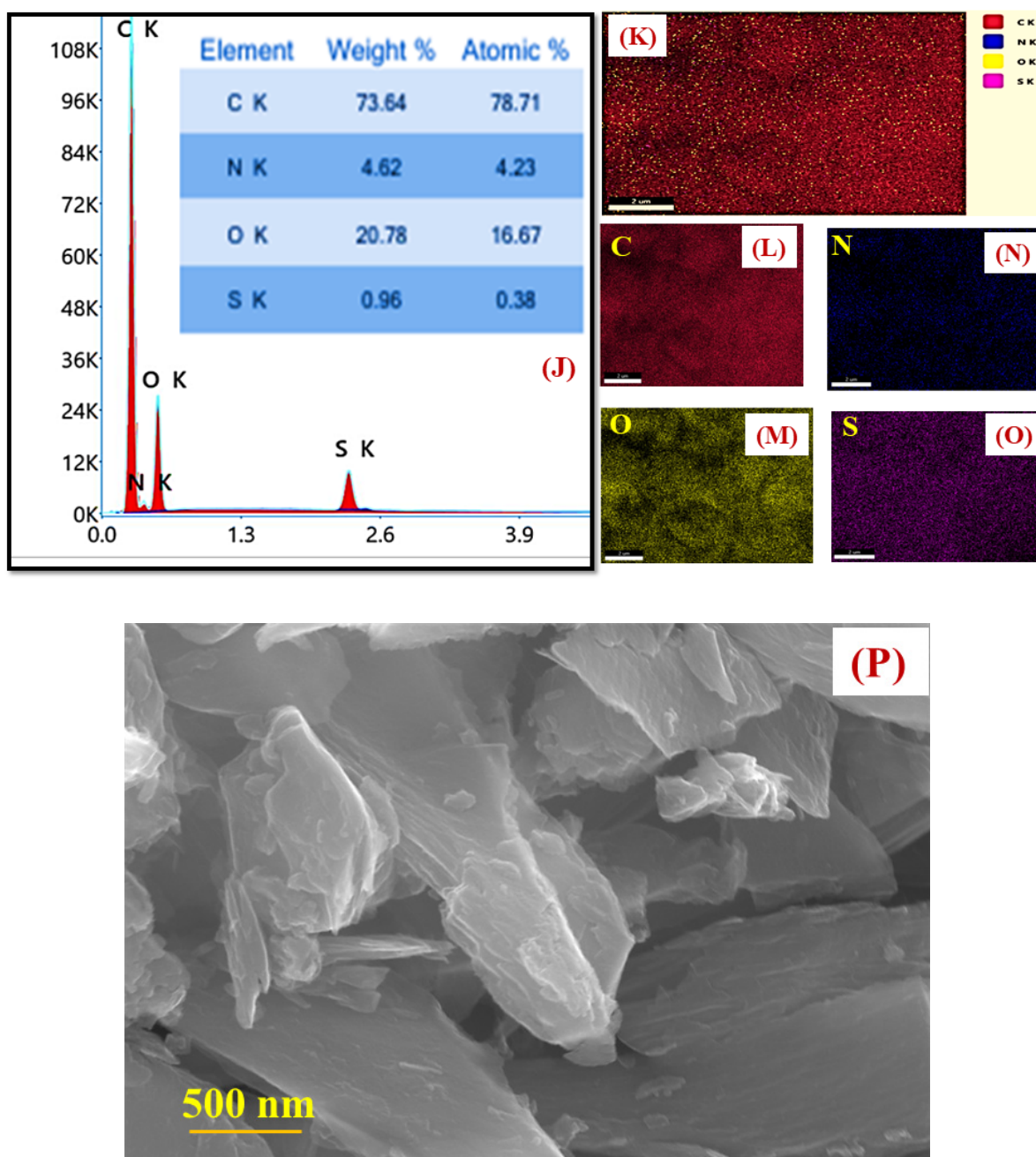


Figure 2. (J) EDX spectrum and (K-O) elemental mapping of N,S-RGO (P) SEM image after electrochemical sensing.

Characterization

The crystalline structure were employed using X-ray diffractometer (XRD, X'Pert-PRO, PANalytical B.V., The Netherlands) and adiffractometer with Cu K α radiation ($\lambda = 1.54 \text{ \AA}$) operating at 40 kV and 40 mA. The diffraction patterns were recorded over a 2θ range of $10 - 80^\circ$ with a scan step size of 0.02° and a counting time of 0.5-1 s per step. A Ni filter/monochromator was employed. Raman spectra were recorded using a Raman spectrometer (Waltham, MA, USA) equipped with a 532 nm excitation laser. The laser power applied to the sample was maintained at 1-5 mW to avoid thermal damage. The measurement were carried out with a spot size of $\sim 1\text{-}2 \text{ }\mu\text{M}$, and each spectrum was collected with 3 accumulations to improve the signal-to-noise ratio. The spectral resolution of the instrument was $\sim 1\text{-}2 \text{ cm}^{-1}$. Prior to analysis, the instrument was calibrated using a standard silicon wafer with a characteristic Raman peak at 520 cm^{-1} . The morphological features of the electrode surface were examined using FE-SEM (CARL ZEISS-SIGMA-300), operating at an accelerating voltage (range 0.3–30 kV) at 1 kV in high vacuum mode. Elemental mapping and energy-dispersive X-ray (EDX) analyses were carried out using a Bruker EDX system (energy resolution: 129 eV). Prior to SEM analysis, the powdered samples were ultrasonically dispersed in ethanol and drop-cast onto a clean silicon wafer/aluminium stub followed by drying at room temperature. HRTEM morphology of the synthesized material was studied by TEM with a FEI TECNAI G2 microscope operating at 200 kV. The sample suspension was sonicated for 1 min in a bath to ensure well-dispersed suspension. Then, a few drop was deposited onto a carbon-coated copper grid followed by drying under ambient conditions before analysis. The chemical and valence states of the composite were examined by X-ray photoelectron spectroscopy (XPS, Thermo ESCALAB 250) equipped with a monochromated Al K α X-ray source ($h\nu = 1486.6 \text{ eV}$). The X-ray source was operated at a power of 150 W under vacuum conditions. Survey spectra were recorded with a pass energy

of 100 eV, while high-resolution spectra were collected at a pass energy of 20 eV to obtain better energy resolution. The background subtraction was performed using the Shirley method, and peak fitting was carried out using mixed Gaussian-Lorentzian functions. The fit quality was evaluated based on the χ^2 value and residual line profile to ensure reliable deconvolution of the spectra. FT-IR spectra were studied using a Jasco FT-IR-6600 spectrometer (Shimadzu model).

The cyclic voltammetry CV and LSV measurements were carried out using a CHI 601E electrochemical workstation is supplied by CH instruments, Austin, Texas, USA. The instrument was procured through the financial support of Science and Engineering Research Board (SERB), New Delhi, India (File No. EEQ/2016/000427). The electrochemical measurements were carried out using a conventional three-electrode system containing the working electrode as the glassy carbon electrode (GCE), a saturated Ag/AgCl as the reference electrode and the platinum wire as the counter electrode. The impedance technique is performed in BioLogic SP-150 workstation, over a frequency range from 200 kHz to 100 mHz with an AC amplitude of 10 mV respectively.

Table -1

Average crystalline size comparison between Raman and XRD

Sample	Raman (La)	XRD (D) Average crystallite size
GO	23.4	3.5
RGO	23.13	3.01
N,S-RGO	22.58	2.73

The Randles-Sevcik equation was used to determine the EASA of N,S-RGO/GCE in this equation $I_{pa} = (2.69 \times 10^5) n^{3/2} A C D^{1/2} \nu^{1/2}$ Where I_p is the peak current, A is the active surface area of the electrode, C is the concentration of the ferricyanide solution, D is the diffusion coefficient of the electrolyte, n is the total number of electrons involved in the reaction, and ν is the scan rate. EASA was calculated from the obtained slope of the current vs square root of scan rate (mV s^{-1}) plot in Fig S3. The calculated EASA values were 0.003232, 0.003324 and 0.003445 cm^2 for the bare GCE, RGO and N,S-RGO/GCE is expected to provide benefits for the electrochemical reaction with NB.

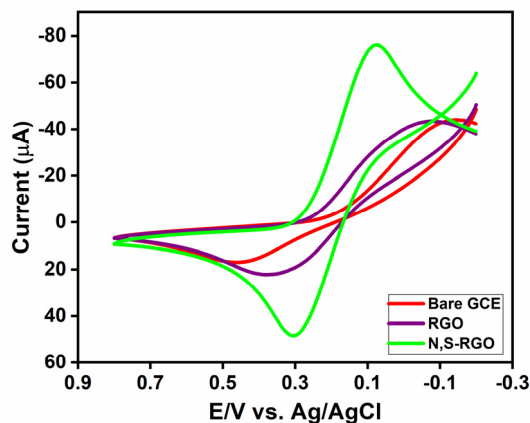


Fig S2. CV response of bare GCE, RGO/GCE and N,S-RGO/GCE at a scan rate 50 mVs^{-1} these experiments were carried out in $0.005 \text{ M } [\text{Fe}(\text{CN})_6]^{3-/4-}$ containing 0.1 M KCl solution.

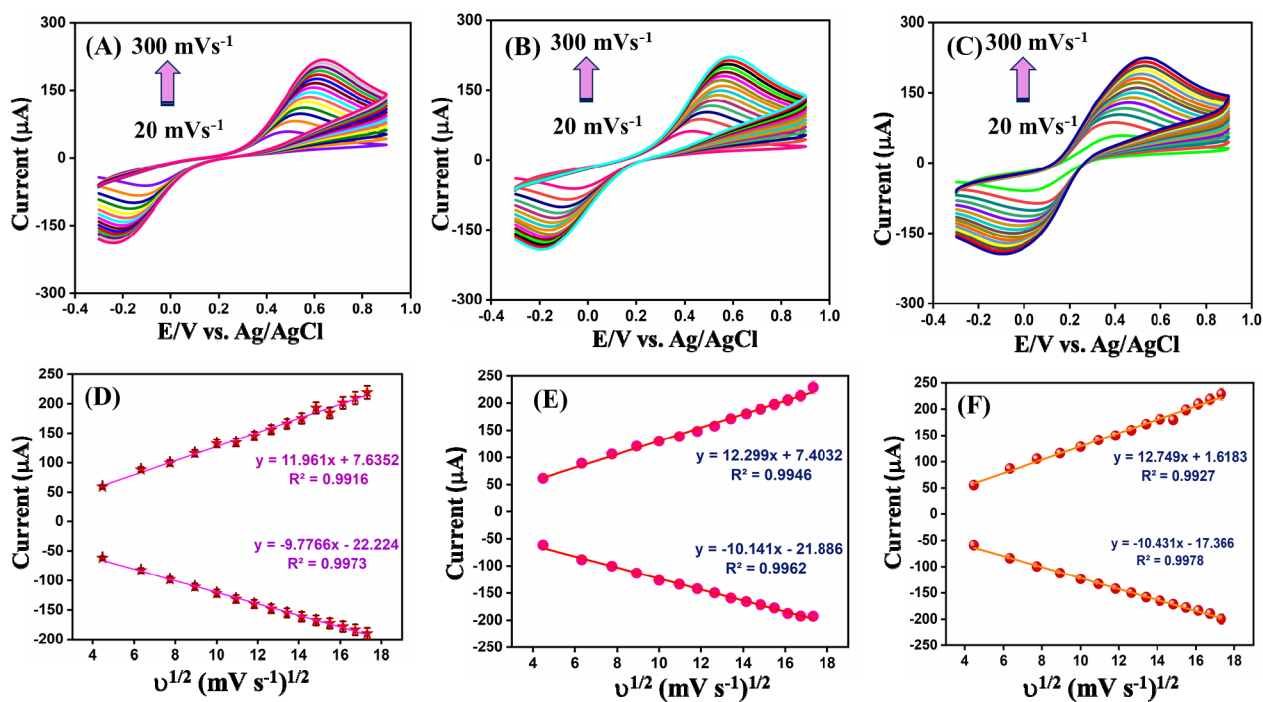


Fig S3. (A-C) CV response of bare/GCE, RGO/GCE and N,S-RGO/GCE at scan rate from 20 to 300 mVs⁻¹ all these experiments were carried out in 0.005 M [Fe(CN)₆]^{3-/4-} containing 0.1 M KCl solution and (D-F) calibration curves of current response versus square root of scan rates.

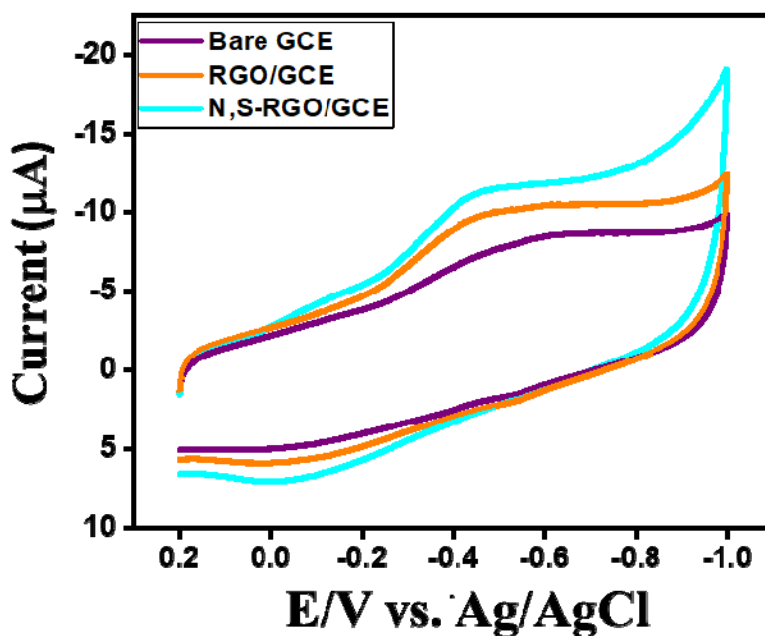


Fig S4. CV curves of the bare GCE and RGO/GCE in the absence of NB 0.1 M PBS

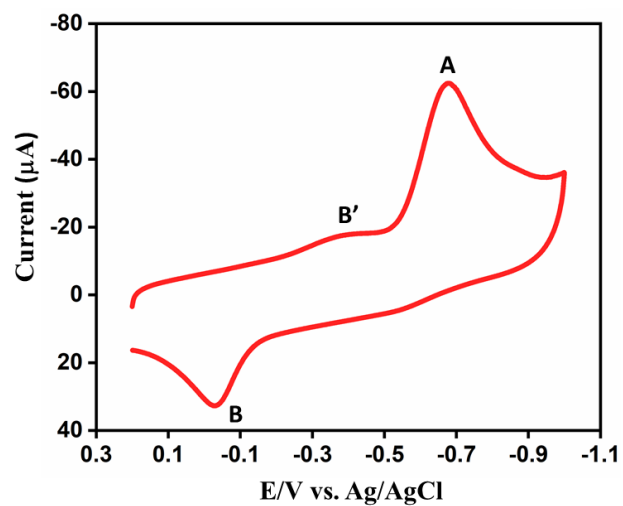


Fig S5. CV behavior of N,S-RGO/GCE recorded in 0.1 M PBS containing 100 μM NB at a scan rate of 50 mVs^{-1} .

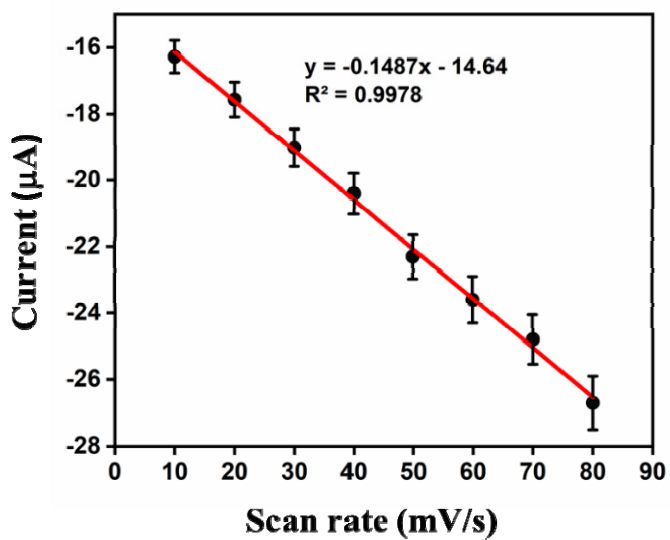


Fig S6. linear calibration plot of scan rate vs current

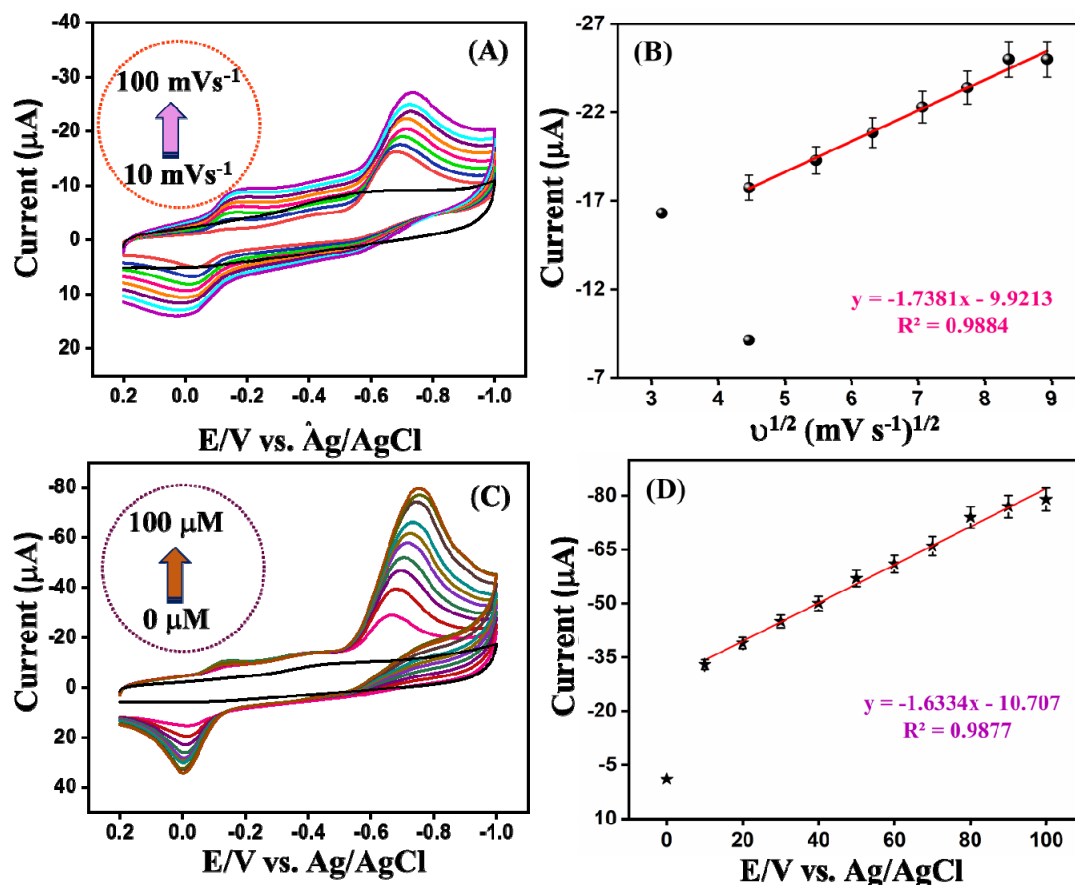


Figure S7. (A) CV curves of N,S-RGO/GCE recorded in 0.1M PBS (pH 7.0) containing 100 μM NB at various scan rates ranging from 10 to 100 mV s^{-1} along with bare without NB (black peak) (B) linear plot of cathodic peak current vs. square root of scan rate ($v^{1/2}$), (C) CV curves of N,S-RGO/GCE in 0.1M PBS (pH 7.0) with increasing concentrations of NB (0 -100 μM) at a scan rate of 50 mV s^{-1} and (D) linear plot of cathodic peak current vs. concentration

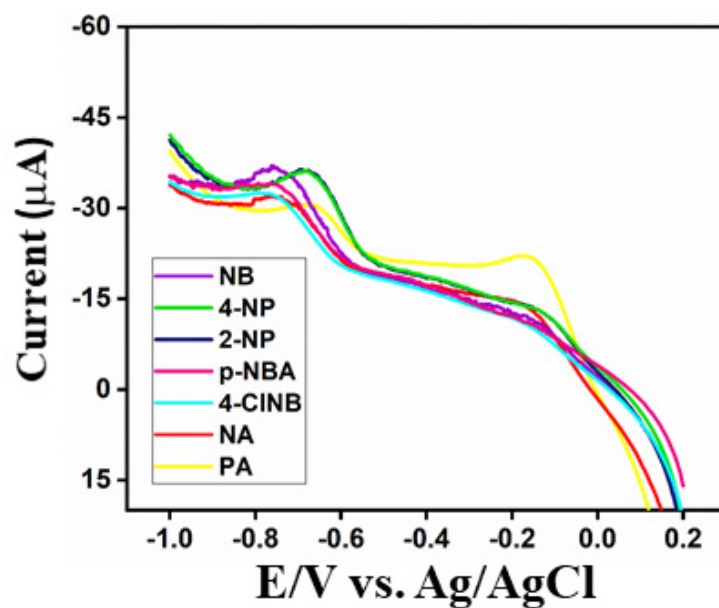


Fig S8. LSV records of 100 μM NB with various interferents (4-nitrophenol, 2-nitrophenol, p-nitrobenzaldehyde, 4-chloro nitrobenzene, nitroaniline, picric acid)

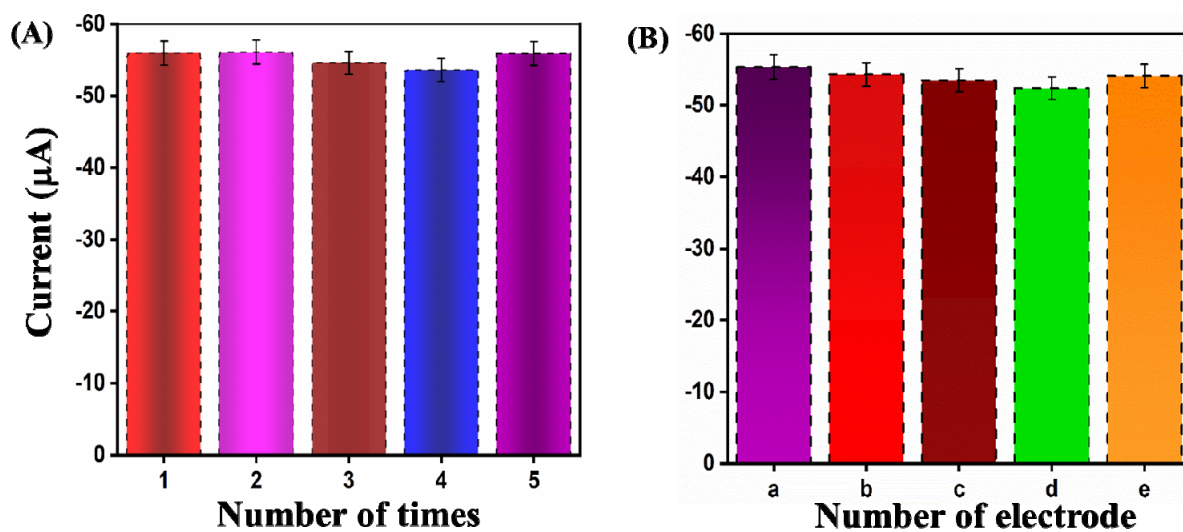


Fig S9. (A) CV responses of N,S-RGO/GCE for the five repeating experiments its bar graph (B) CV responses of five independent N,S-RGO/GCEs its bar graph.

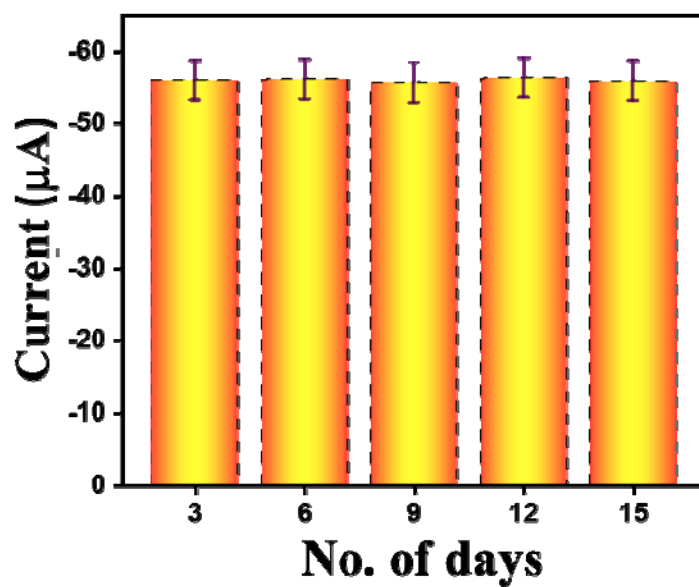


Fig S10. The bar diagram for stability of N,S-RGO/GCE over 15 days.