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A Novel Electrochemical Sensor for Oxidative Stress and Cancer Biomarker (4-Nitroquinoline N-Oxide) Based on Iron Nitride Particles with Reduced Graphene Oxide Modified Electrode

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Abstract

Herein, a novel iron nitride nanoparticles (Fe_2N NPs) decorated reduced graphene oxide (rGOS) nanocomposite have been designed through a solvothermal method and followed by a nitridation process. After then, as-synthesized Fe_2N NPs@rGOS was characterized by HRTEM, FESEM, XPS, XRD, and EIS. Furthermore, the nanocomposite modified SPCE (screen-printed carbon electrode) shows excellent electrochemical sensing performance towards biomarker of 4-nitroquinoline N-oxide (4-NQO) with fast detection. 4-NQO is one of the important cancer biomarker. Moreover, the fabricated sensor showed a wide linear window for 4-NQO between 0.05–574.2 μM and nanomolar detection limit (9.24 nM). Further, the as-prepared Fe_2N NPs@rGOS/SPCE has been applied to the determination of 4-NQO in human blood and urine samples with recoveries close to 100%.

Scope of the work

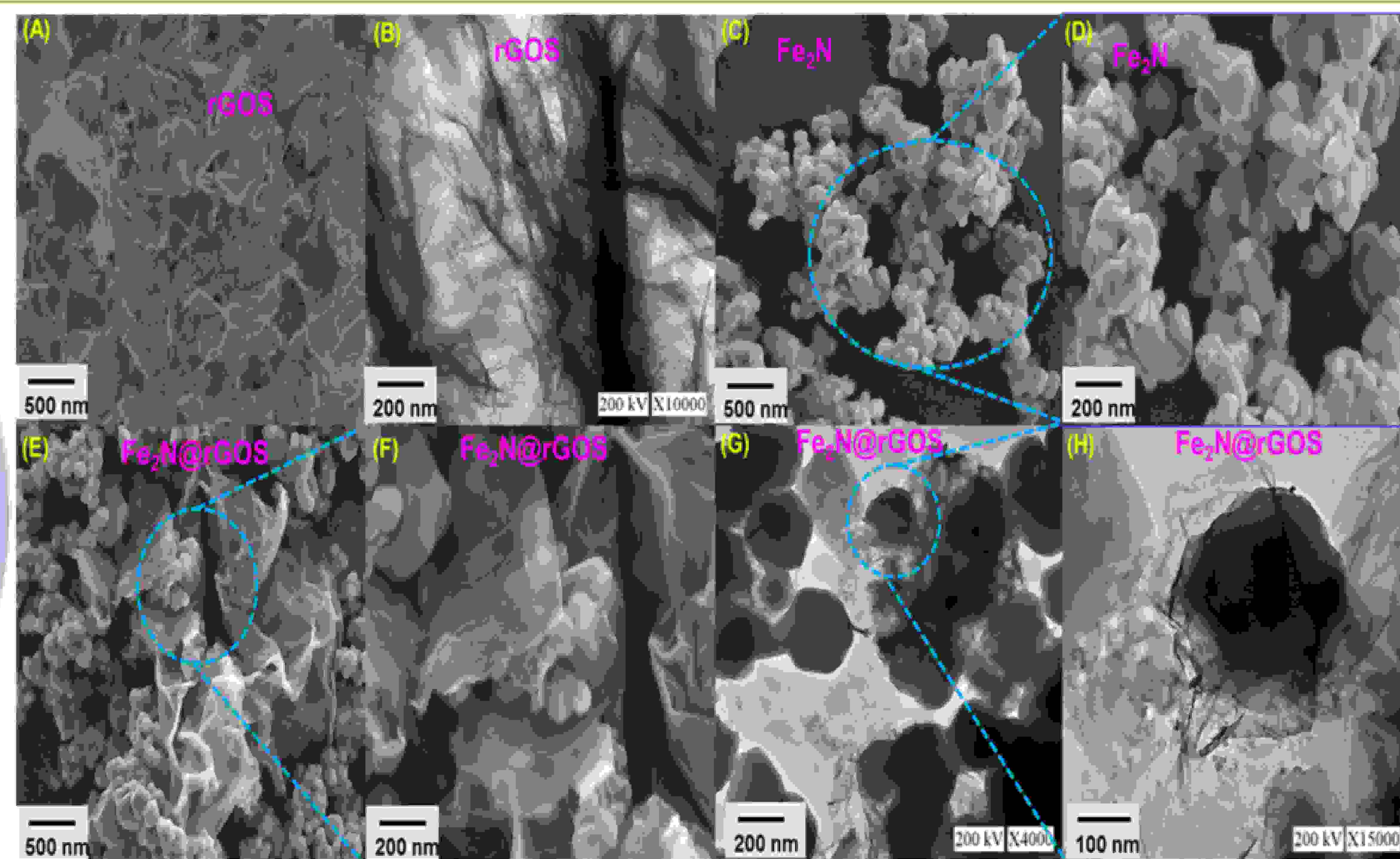
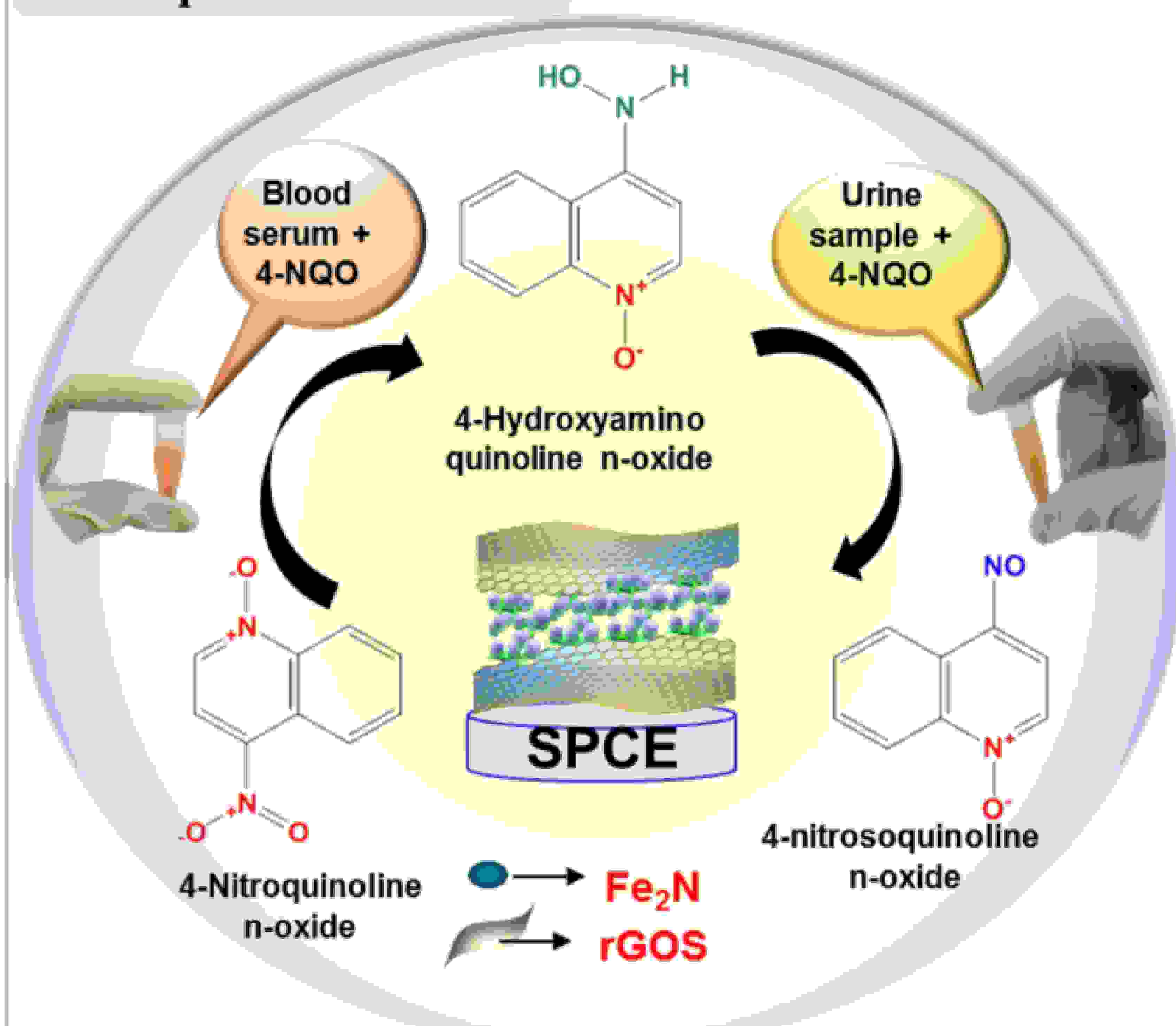


Fig. 1 FESEM (A) and HRTEM (B) image of rGOS. FESEM image of Fe_2N nanoparticles (C–D). FESEM (E–F) and HRTEM (G–H) images of Lower and higher magnification view of the Fe_2N NPs@rGOS NC.

Scheme 1. Real time detection of oxidative stress biomarker in human blood and urine based on Fe_2N NPs@rGOS NC/SPCE.

XRD and XPS analysis

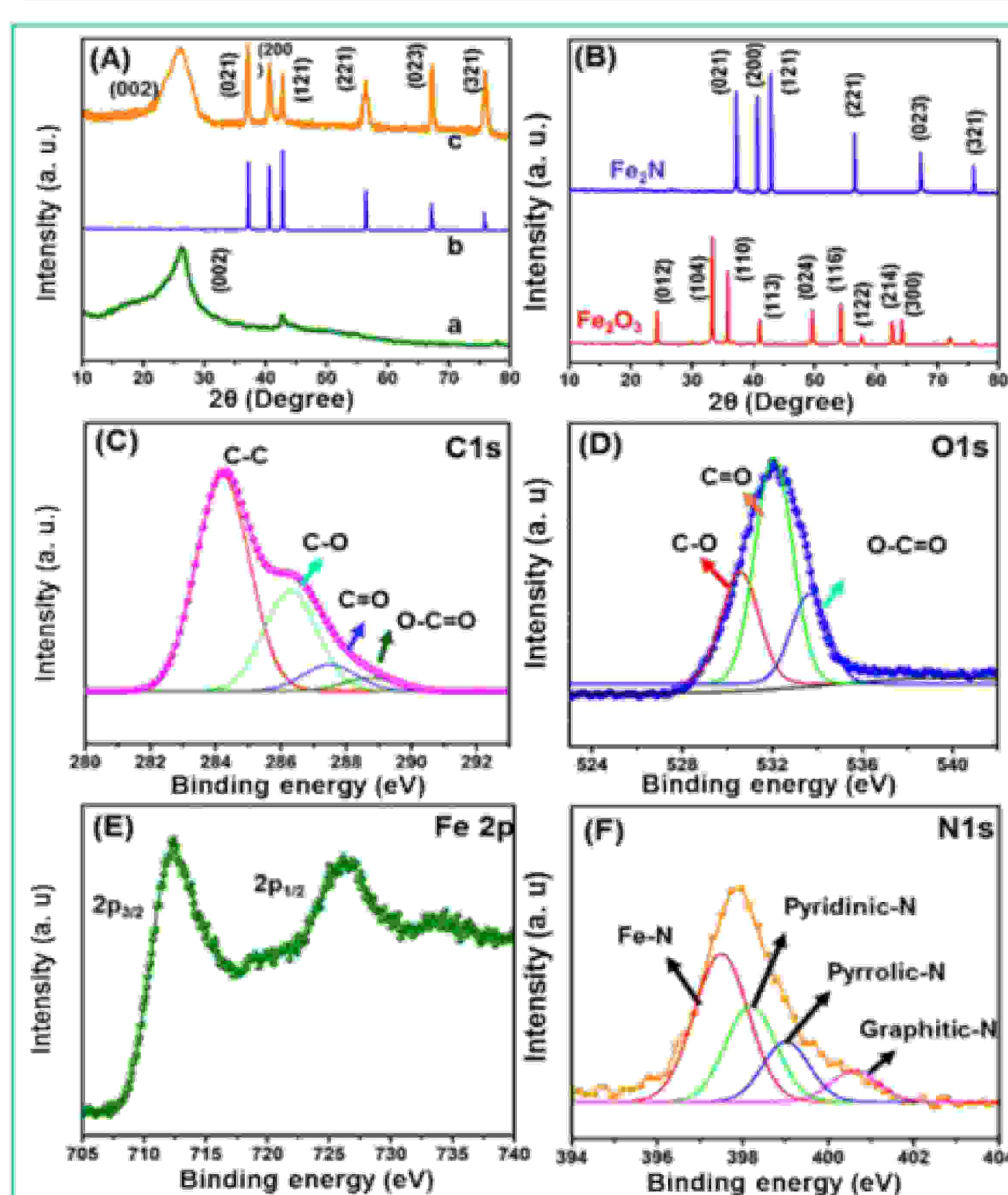


Fig. 2. (A) XRD analysis of rGOS (a), Fe_2N (b), Fe_2N NPs@rGOS (c). (B) XRD analysis of Fe_2O_3 and Fe_2N . XPS spectrum of C 1s (C), O 1s (D), Fe 2p (E) and N 1s (F).

Electrochemical behavior of 4-NQO

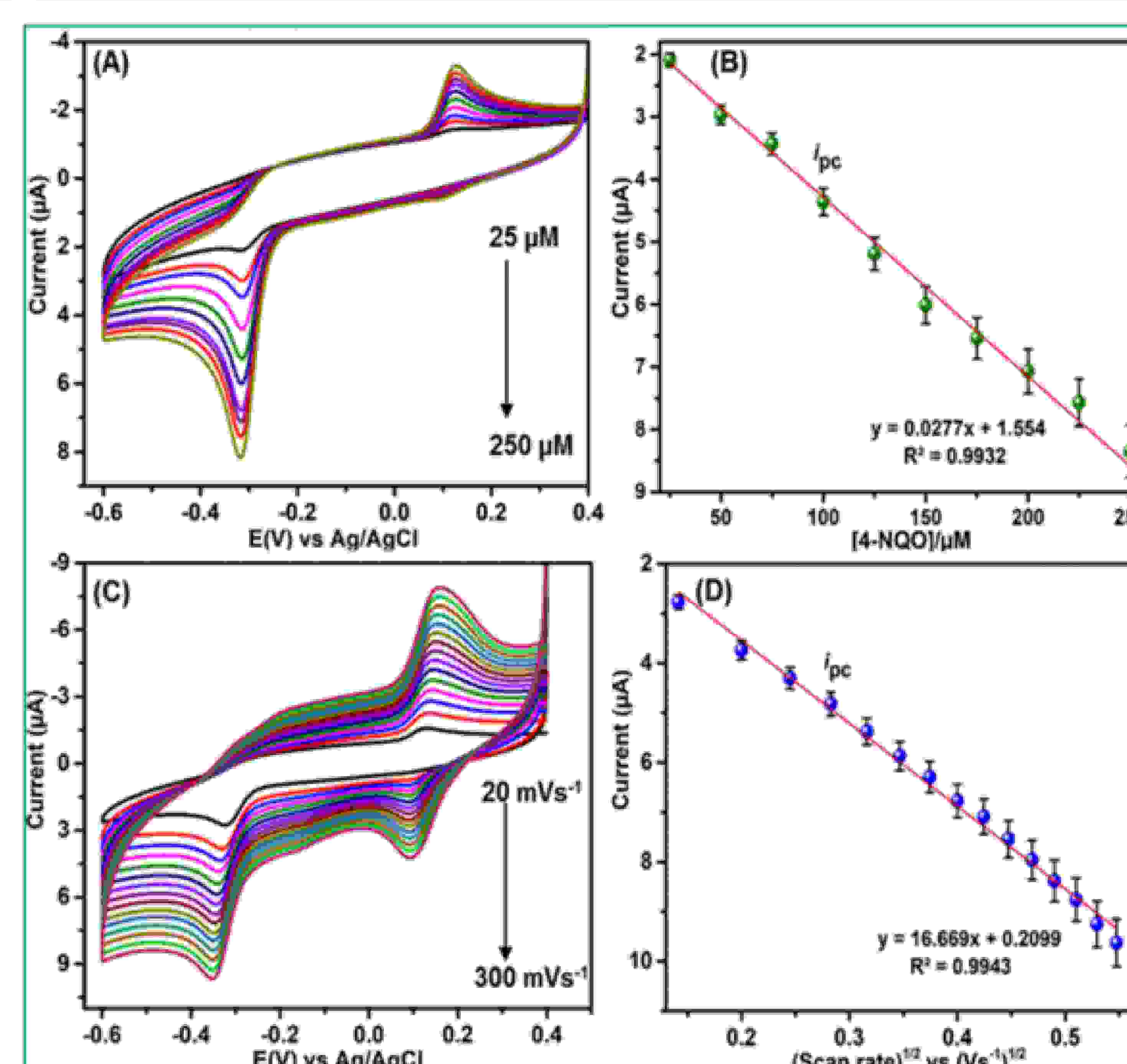


Fig. 3. (A) Different concentrations of 4-NQO (25–250 μM) in 0.05 M PB (N_2 saturated) at Fe_2N NPs@rGOS NC/SPCE. (B) Plot between $[\text{4-NQO}]/\mu\text{M}$ versus cathodic peak current. (C) CVs of different scan rates from 20 to 300 mV/s on Fe_2N NPs@rGOS NC/SPCE for the reduction of 100 μM 4-NQO in 0.05 M PB (N_2 saturated). (D) The calibration plot between the cathodic peak current versus the square root of the scan rates.

Differential pulse voltammetric responses of 4-NQO

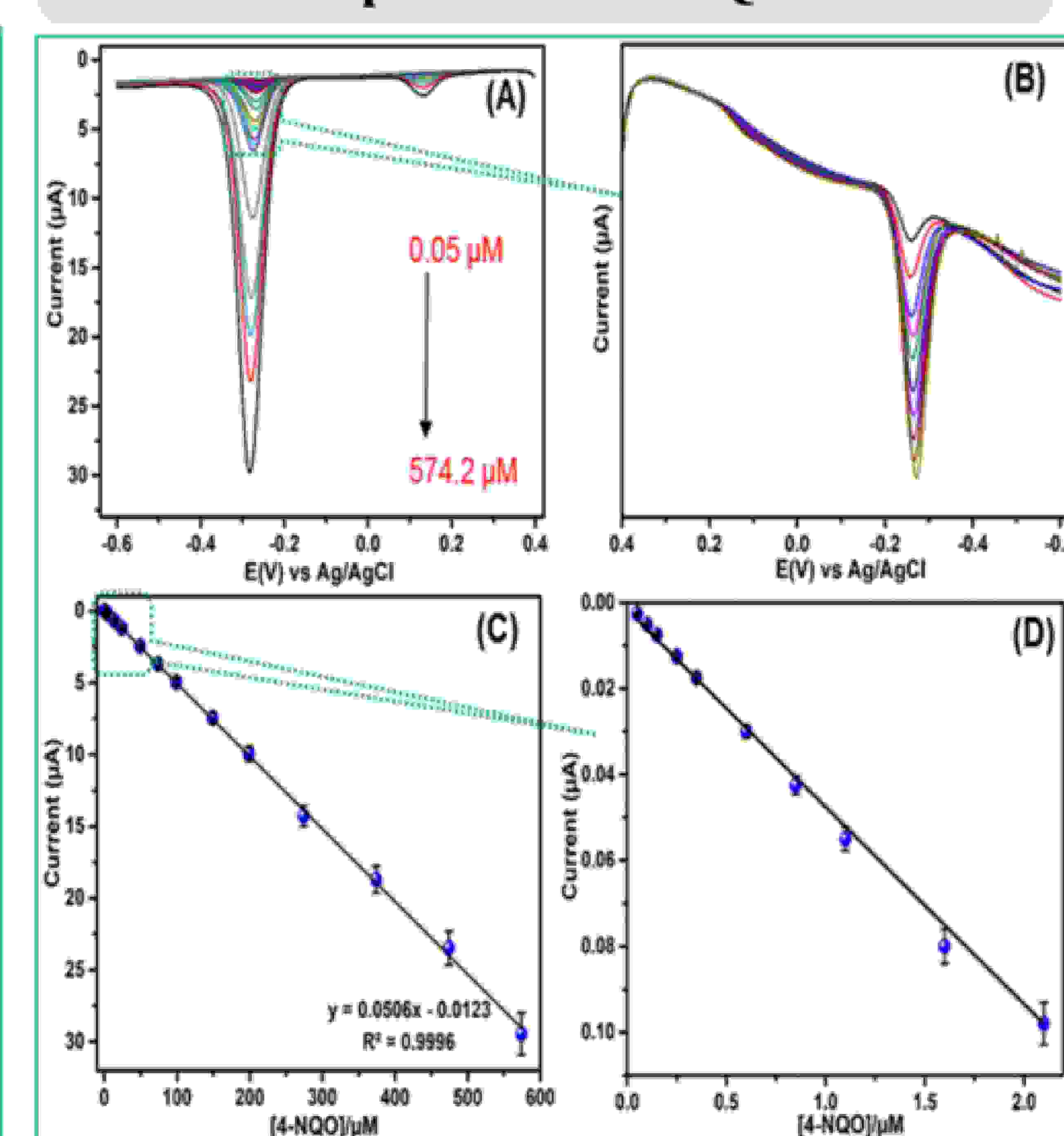


Fig. 4. (A and B) DPV responses for the low and high concentrations of 4-NQO in (N_2 saturated) 0.05 M PB (pH 7.0) at Fe_2N NPs@rGOS NC/SPCE. (C and D) The linear plot of $[\text{4-NQO}]/\mu\text{M}$ versus cathodic peak currents.

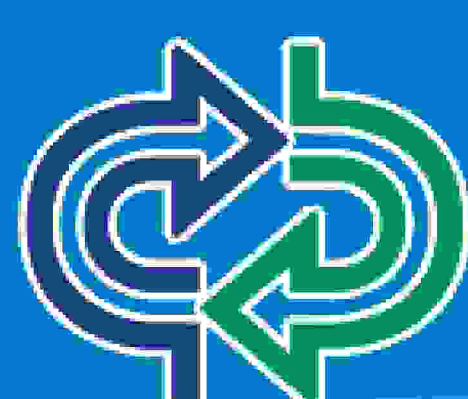
Real sample analysis

Real Samples	Added/nM	Found/nM	Recovery/%	RSD/%
Serum samples	100	97.36	97.36	2.79
	200	189.78	94.89	3.55
	500	481.45	96.29	3.16
Urine	100	96.21	96.21	3.29
	200	190.34	95.17	2.14
	500	486.52	97.3	2.98

a-Related standard deviation (RSD) of n = 3 independent experiment

Conclusion

- In summary, Fe_2N NPs decorated reduced graphene oxide sheets have been successfully prepared by an in-situ synthesis strategy.
- Mainly, the DPV analysis reveals the wide linear range 0.05–574.2 μM with LOD is 0.0092 μM towards 4-NQO.
- A novel electrocatalytic based biosensor was successfully constructed for 4-NQO detection with high selectivity and high stability.
- Our work has provided a promising sensing route for biomarker detection of 4-NQO and also demonstrated great potential for the real-time sensing of the biomarker.



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