

# Novel nickel (II) phthalocyanine/reduced graphene oxide: electrochemical sensing platform for analysis of hydroquinone and chloramphenicol in environmental samples

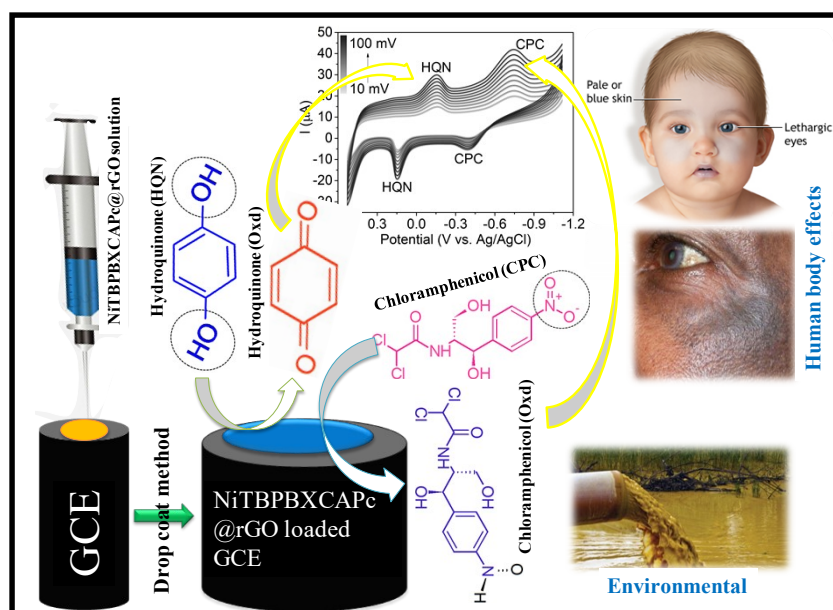
Mounesh <sup>a,\*</sup>, P. Manikanta<sup>a</sup>, Rohit Rangnath Nikam<sup>a</sup>, Girish Tigari<sup>b</sup>, Bhari Mallanna Nagaraja<sup>a,\*</sup>

<sup>a,\*</sup>Centre for Nano and Material Science (CNMS), Jain (Deemed-to-be University), Jain Global Campus, Kanakapura, Bangalore, Karnataka, India – 562112.

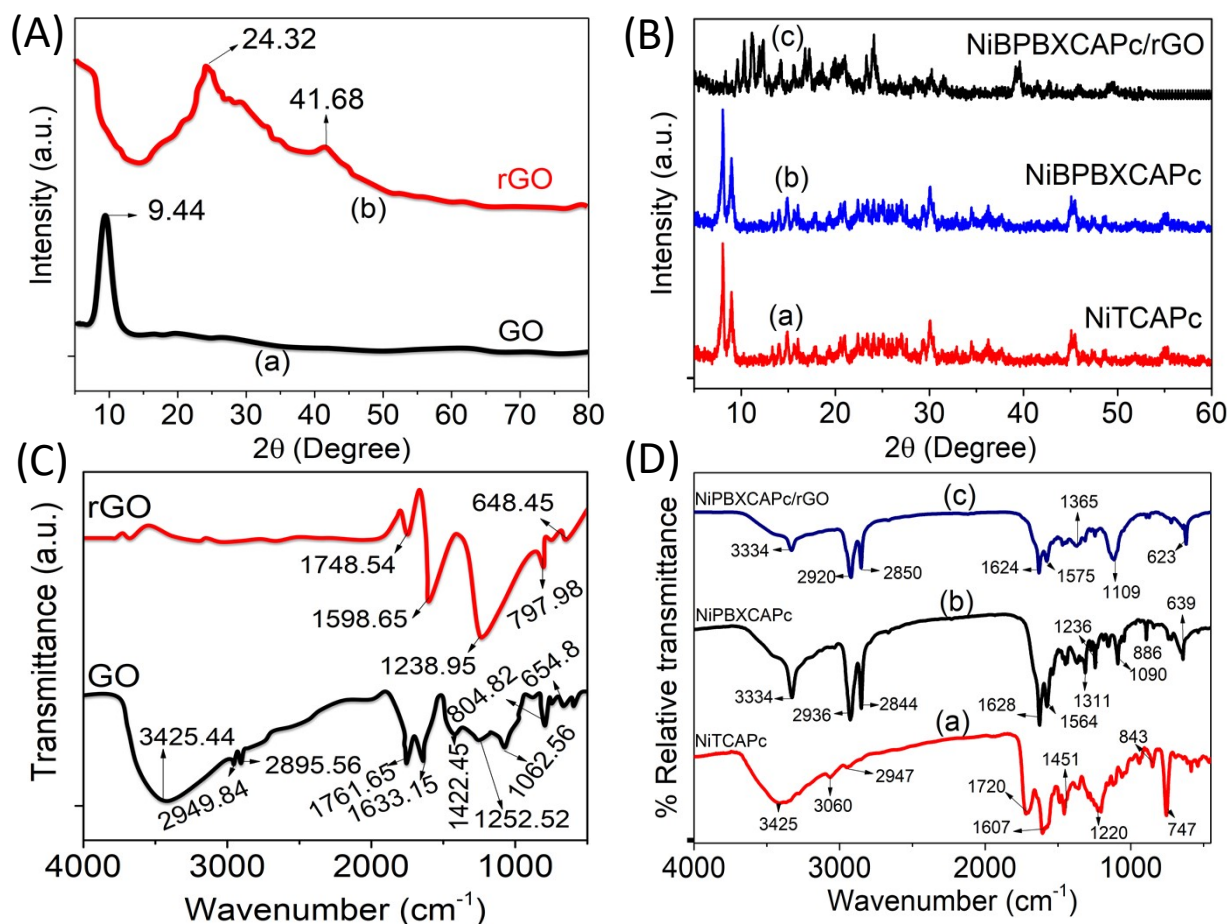
<sup>b</sup>Department of Chemistry, Nitte Meenakshi Institute of Technology, Yelahanka, Bangalore 560064, Karnataka, India

(\*Email: [mounesh.m.nayak@gmail.com](mailto:mounesh.m.nayak@gmail.com), Cell No: +91-8197546693)

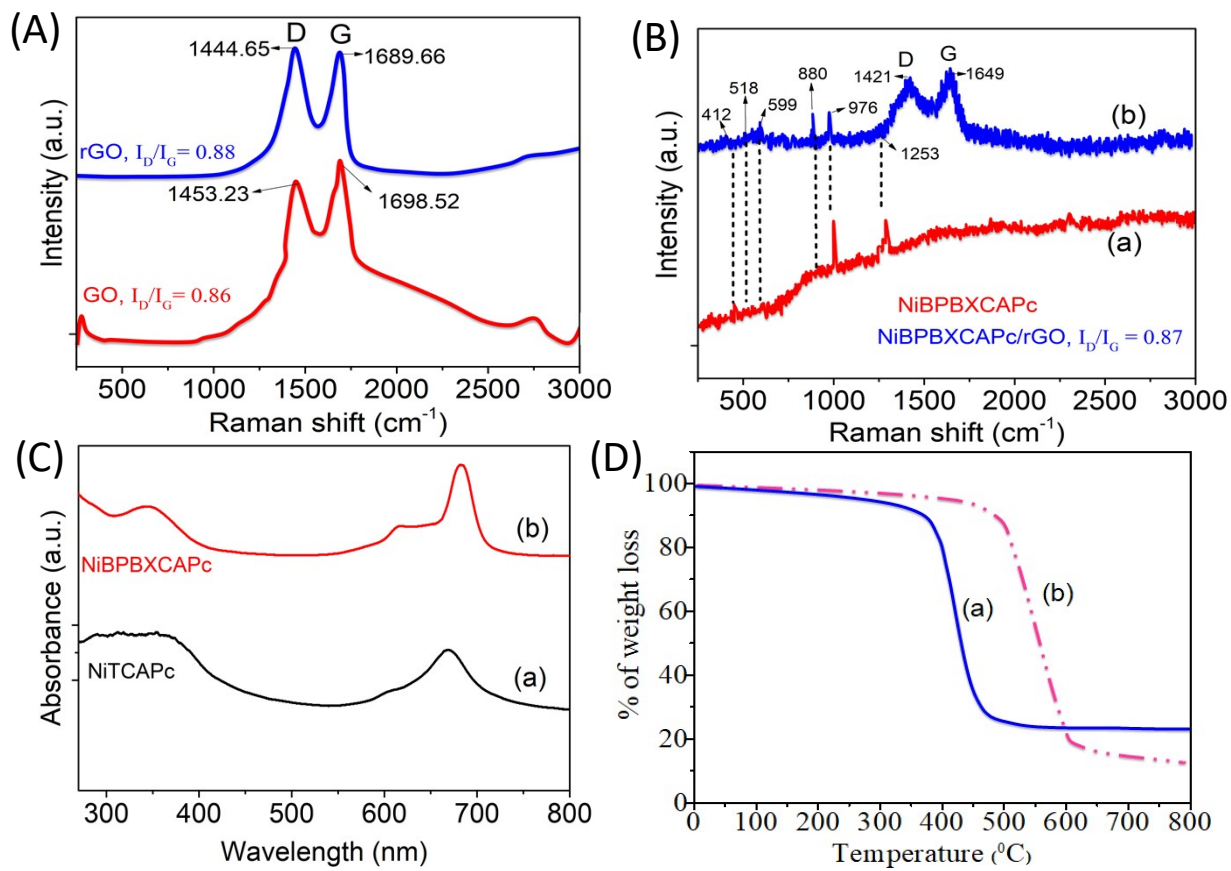
(\*Email: [bm.nagaraja@jainuniversity.ac.in](mailto:bm.nagaraja@jainuniversity.ac.in), Cell No: +91-8105523666)



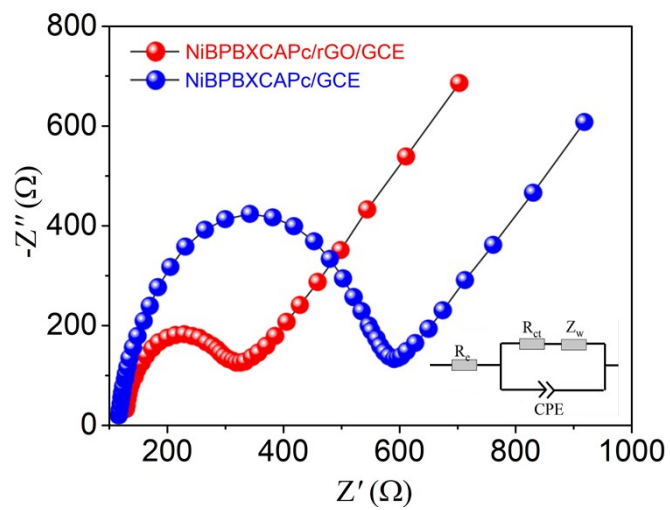
The novel tetra-2-(biphenyl-4-yl)-1,3-benzoxazol-carboxamide nickel (II) phthalocyanine (NiTBPBXCAPc) and rGO were confirmed by physico-chemical and electro-chemical characterization. The NiTBPBXCAPc and rGO nanocomposite has been developed for sensitive and selective detection of hydroquinone and chloramphenicol.



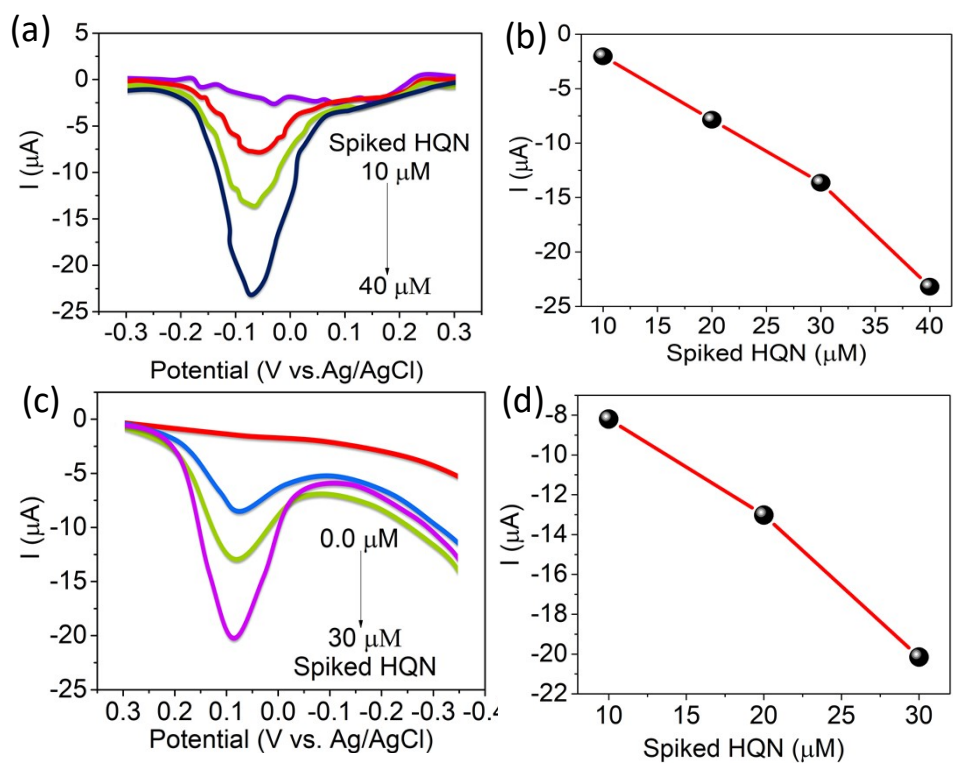
**Fig.S1:** PXRD analysis of GO, rGO, NiTCAPc and NiBPBXCAPc@rGO nanocomposite. (A) PXRD spectra of GO and rGO. (B) PXRD spectra of NiTCAPc and NiBPBXCAPc@rGO nanocomposite. (C) FT-IR spectra of GO and rGO. (D) FT-IR spectra of NiTCAPc, NiBPBXCAPc and NiBPBXCAPc@rGO nanocomposite.



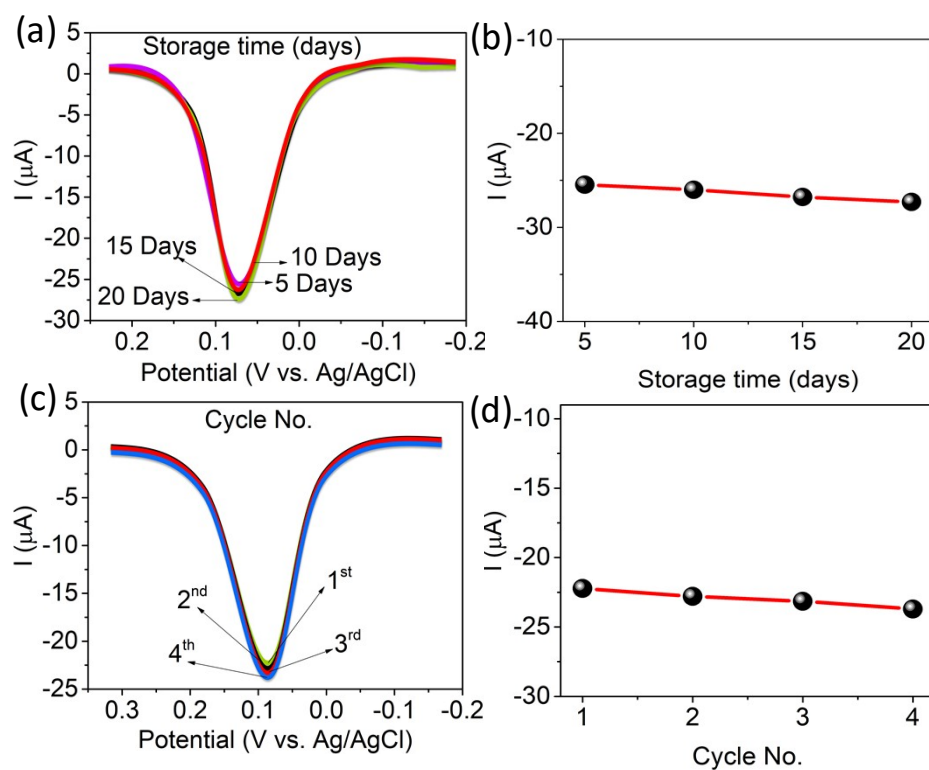
**Fig.S2:** Raman, UV-Vis and TG analysis of GO, rGO, NiTCAPc and NiTBPBXCAPc@rGO nanocomposite. (A) Raman spectra of GO and rGO. (B) Raman spectra of NiTCAPc and NiTBPBXCAPc@rGO nanocomposite. (C) UV-Vis spectrum of NiTCAPc and NiTBPBXCAPc and (D) Thermogravimetric Analysis of NiTCAPc and NiTBPBXCAPc.



**Fig.S3:** EIS analysis of NiBPBXCAPc and NiBPBXCAPc@rGO/GCE. Nyquist plots for NiBPBXCAPc loaded GCE and NiBPBXCAPc@rGO/GCE.



**Fig.S4:** DPV current responses of real samples analysis. (a) DPV response for IWS-1 real sample with HQN spiking. (b) The dependence of oxidation currents over spiked HQN. (c) DPV response for TWS-2 real sample with HQN spiking. (d) The dependence of oxidation currents over spiked HQN.



**Fig.S5:** DPV current responses of stability and reproducibility analysis. (a) DPV response of NiTBPBXCAPc@rGO/GC electrode with HQN for 20 days, inset shows the dependence of oxidation over time. (c) DPV NiTBPBXCAPc@rGO/GC electrode in presence of HQN for four repetitive cycles and inset shows the dependence of oxidation current over each cycle. (b,d) linear dependence current versus storage time (days) and cycle number.

**Table S1.** Comparison of the HQN and CPC detection effects between NiTBPBXCAPc@rGO/GC electrode and reported electrode materials.

| Material                                             | Method          | Analyte | LOD                                                                | Linear Range                                                                                                                              | Ref.      |
|------------------------------------------------------|-----------------|---------|--------------------------------------------------------------------|-------------------------------------------------------------------------------------------------------------------------------------------|-----------|
| Gr/CuPc/GCE                                          | DPV             | CPC     | $0.27 \times 10^{-7}$                                              | $0.1 \times 10^{-6}$ - $20 \times 10^{-6}$                                                                                                | [1]       |
| MWCNT-CTAB-poly (diphenylamine)/GCE                  | DPV             | CPC     | $2.0 \times 10^{-9}$                                               | $1.0 \times 10^{-8}$ to $1.0 \times 10^{-5}$                                                                                              | [2]       |
| Boron-doped diamond thin-film (BDD) electrode        | CA              | CPC     | $3.0 \times 10^{-8}$                                               | $1.0 \times 10^{-7}$ to $5.0 \times 10^{-5}$                                                                                              | [3]       |
| Molecularly imprinted polymer carbon paste electrode | DPV             | CPC     | $2.0 \times 10^{-9}$                                               | $8.0 \times 10^{-9}$ to $1.0 \times 10^{-6}$                                                                                              | [4]       |
| SWCNT-AuNPs-ionic liquid composite film              | LSV             | CPC     | $5.0 \times 10^{-9}$                                               | $1.0 \times 10^{-8}$ to $6.0 \times 10^{-6}$                                                                                              | [5]       |
| Fe <sub>3</sub> O <sub>4</sub> /GCE                  | SWV             | CPC     | $0.09 \times 10^{-6}$                                              | $0.09 \times 10^{-6}$ to $47 \times 10^{-6}$                                                                                              | [6]       |
| rGO/PdNPs/GCE                                        | DPV             | CPC     | $0.05 \times 10^{-6}$                                              | $0.05 \times 10^{-6}$ to $1 \times 10^{-6}$                                                                                               | [7]       |
| 3DCNTs@Cu NPs/GCE                                    | CV              | CPC     | $10 \times 10^{-6}$                                                | $10 \times 10^{-6}$ to $500 \times 10^{-6}$                                                                                               | [8]       |
| NiTBPBXCAPc@rGO/GC electrode                         | CV<br>DPV<br>CA | CPC     | $3.5 \times 10^{-9}$<br>$2.5 \times 10^{-9}$<br>$4 \times 10^{-9}$ | $10 \times 10^{-6}$ to $100 \times 10^{-6}$<br>$10 \times 10^{-6}$ to $110 \times 10^{-6}$<br>$10 \times 10^{-6}$ to $100 \times 10^{-6}$ | This Work |
| MIL-101(Cr)-rGO-CPE                                  | DPV             | HQN     | $0.66 \times 10^{-6}$                                              | $4 \times 10^{-6}$ to $1000 \times 10^{-6}$                                                                                               | [9]       |
| Fe <sub>2</sub> O <sub>3</sub> /CNTs/FTO             | CV              | HQN     | $0.5 \times 10^{-6}$                                               | $1 \times 10^{-6}$ to $260 \times 10^{-6}$                                                                                                | [10]      |
| cathode-polarized/GCE                                | CV              | HQN     | $3.57 \times 10^{-6}$                                              | $10 \times 10^{-6}$ to $300 \times 10^{-6}$                                                                                               | [11]      |
| Mesoporous Pt                                        | UV-vis          | HQN     | $1.36 \times 10^{-6}$                                              | $3.37 \times 10^{-6}$ to $360 \times 10^{-6}$                                                                                             | [12]      |
| Au NPs/Fe <sub>3</sub> O <sub>4</sub> -PTESGO/GCE    | CA              | HQN     | $1.1 \times 10^{-6}$                                               | $3 \times 10^{-6}$ to $137 \times 10^{-6}$                                                                                                | [13]      |
| polynuclear red                                      | DPV             | HQN     | $4.97 \times 10^{-6}$                                              | $20 \times 10^{-6}$ to $120 \times 10^{-6}$                                                                                               | [14]      |
| rGO/SPCE                                             | DPV             | HQN     | $0.27 \times 10^{-6}$                                              | $1 \times 10^{-6}$ to $312 \times 10^{-6}$                                                                                                | [15]      |
| NiTBPBXCAPc@rGO/GC electrode                         | CV<br>DPV<br>CA | HQN     | $4.5 \times 10^{-9}$<br>$1.5 \times 10^{-9}$<br>$5 \times 10^{-9}$ | $10 \times 10^{-6}$ to $80 \times 10^{-6}$<br>$10 \times 10^{-6}$ to $150 \times 10^{-6}$<br>$10 \times 10^{-6}$ to $100 \times 10^{-6}$  | This Work |

CV = Cyclic voltammetry, DPV = Differential pulse voltammetry, CA = Chrono-amperometry, UV-vis = UV-vis spectrum.

**Table S2.** Real sample analysis for the validation of NiBPBXCAPc/rGO loaded GCE sensor.

| Sample | HQN         |            |               |                |               |
|--------|-------------|------------|---------------|----------------|---------------|
|        | Spiked (μM) | Found (μM) | Detected (μM) | Recoveries (%) | RSD (%) (n=3) |
| IWS-1  | 10          | 0          | 9.9           | 99             | 103.18        |
|        | 20          |            | 20.1          | 100.5          | 102.53        |
|        | 30          |            | 30.2          | 100.6          | 104.58        |
| TWS-2  | 10          | 0          | 9.7           | 97             | 103.29        |
|        | 20          |            | 19.5          | 97.5           | 102.67        |
|        | 30          |            | 29.5          | 98.4           | 104.28        |

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