



# Graphene oxide/copper terephthalate composite as a sensing platform for nitrite quantification and its application to environmental samples

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## Abstract

A robust electrochemical sensing platform based on graphene oxide-copper terephthalate (GO/Cu-tpa) composite has been fabricated. The prepared composite was characterized through FTIR, XRD, SEM, and EDS techniques. The electrochemical characterization of the composite was studied after immobilizing the composite material as a thin film on the glassy carbon electrode through voltammetry techniques. The fabricated electrode exhibited an excellent electrocatalytic activity in the oxidation of nitrite. The sensor showed a linear response in the concentration range 5 – 625  $\mu\text{M}$  with a detection limit of 0.3  $\mu\text{M}$  and sensitivity of  $0.86 \pm 0.06 \mu\text{A } \mu\text{M}^{-1} \text{ cm}^{-2}$ . The electrochemical sensor was validated by measuring the trace level nitrite from water samples, and the results are in good agreement with the standard protocol.

## Introduction

Metal organic frameworks (MOFs) are the new emerging class of highly porous crystalline materials fabricated using metal salt sources and organic linker molecules. These materials have the advantageous properties of high specific surface area, high porosity, and good stability [1, 2]. These properties have opened the new pathway for many applications

concerned with gas storage and separation, catalysis, energy storage and conversion, biological applications, and electrochemical sensors [3, 4].

Among various MOFs reported, very few have been utilized in the electroanalysis [5, 6]. The electrochemistry of MOFs is primarily based on the electroactive properties of metal ions in the framework and also the polyfunctional organic linker molecules [7]. However, the applications are still limited because of weaker properties of MOFs to suit in sensing mechanism. In order to overcome these limitations, MOFs based composite modified electrodes have been explored in studying the various electrochemical reactions at the interface [8, 9]. Among the various substrates used, carbon has been used as a versatile substrate material in the preparation of MOF composites with diversified applications. The facile charge transfer inside the framework can be accelerated by combining it with carbon substrates like carbon paste, CNTs, and graphene. This combination has the advantages of  $\pi$ - $\pi$  interaction and also hydrogen bonding between carbon substrate, metal ions, and organic linker molecules present in MOFs. This property facilitates the increased conductivity of the composite material to suit its utility as an electrocatalyst in various electrochemical applications [10].

Nitrite species being considered as a carcinogenic in nature are added as preservatives by food industries to store food products and to keep microbial growth at bay [11, 12]. These added nitrites can expend toxic effects on human health

## Highlights

- The graphene oxide/ copper terephthalate composite has been synthesized by a simple solvothermal route.
- The composite has been characterized by spectroscopic and electrochemical techniques.
- It has been used as a novel electrochemical sensing platform in the measurement of nitrite.
- The composite modified electrode showed a good linearity in the concentration range 5- 625  $\mu\text{M}$  with a detection limit of 0.3  $\mu\text{M}$ .
- The sensor has been successfully applied to real sample analysis and the results are in good agreement with the standard protocol results.

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[13]. Hence, it is quite essential to develop a simple strategy for its quantification from environment for monitoring purpose.

Existing conventional methods for nitrite determination, like spectrophotometric method, chromatographic method, flow-injection analysis, chemiluminescence, and electrophoretic methods are time consuming, require skilled personnel to operate the instrument as well as use of expensive reagents [14]. However the electrochemical methods have the advantages of rapid, simple, easy, and cost effective means over existing conventional methods [15]. In electrochemical analysis, the development of chemically modified electrodes is an important criterion to achieve selectivity and sensitivity in target analyte measurement [16]. A range of protocols have been published in recent years for nitrite measurement [17–28]. Various MOFs and its composites have been used as modifier molecules in fabricating chemically modified electrodes in the sensing of lead [29], ascorbic acid [30], hydrazine [31], nitrobenzene [32], acetaminophen, and dopamine [20].

Various MOF based composites [33–36], such as Au-ZnMOF [32], MOF-525/GNR [37], Au/CuMOF/CPE [38], Cu MOF/rGO [39], and Ag@MOF-5 [40] have been reported for nitrite measurement. Although very few reports are available for the Cu-MOF-based composite materials for nitrite detection [25], it is still necessary to explore new electrocatalyst based on MOFs because the above reported sensor materials require time consuming synthetic procedures, high temperatures, and expensive reagent-containing noble metals. To overcome these limitations, we have reported a simple protocol to prepare a Graphene oxide/Cu-terephthalate hybrid composite (GO/Cu-tpa) and its utility as an electrocatalyst in the quantification of nitrite at trace level.

## Experimental section

### Chemicals and reagents

Analar grade chemicals were used throughout the experiment without any further purification. Terephthalic acid was purchased from s.d. fine-chem limited, Mumbai, India. Cupric nitrate, dimethyl formamide (DMF), triethyl amine, and graphite power were procured from Sigma-Aldrich, India. Sodium nitrite, disodium hydrogen phosphate, sodium hydroxide, hydrochloric acid, chloroform, and ethyl alcohol were purchased from Merck specialties Pvt. Ltd., India. All the solutions were prepared using double distilled water.

### Instrumentation

All pH measurements were carried out using control dynamics pH meter (model: APX 175). Infrared spectroscopic

measurements were recorded using FTIR-8400S Shimadzu. X-Ray diffraction patterns were recorded using PXRD Bruker D8 advance diffractometer with Cu-K $\alpha$  radiation source. The energy dispersive spectroscopic (EDS) study for chemical composition and surface morphology through FESEM images were recorded using scanning electron microscope FEI ESEM QUANTA 200. All the electrochemical measurements were made by using CHI6194B series electrochemical analyzer (CH Instruments, Texas, USA) with a computer controlled potentiostat at room temperature ( $27 \pm 2$  °C). An electrochemical cell of 10 mL capacity with standard three electrode assembly was used throughout the experiment. The three electrode system consists of Ag/AgCl (3 M KCl) electrode as reference electrode, Platinum wire (99.9%) as counter electrode and composite modified glassy carbon electrode as working electrode throughout the experiment.

### Synthesis of GO

Graphitic powder was oxidized to graphene oxide by following Hummer's method with slight modification [41]. In brief, graphitic powder (1 g) was added to 23.5 mL of pre-cooled concentrated sulfuric acid.  $\text{KMnO}_4$  (3 g) was added slowly with constant stirring and cooling. The temperature was maintained less than 20 °C, and later the temperature was raised to 35 °C and maintained for 30 min followed by addition of 46 mL of distilled water and kept undisturbed for 15 min. The reaction was completed by adding 140 mL of distilled water and 10 mL of hydrogen peroxide. Finally the black residue obtained was centrifuged and washed repeatedly with 5% HCl followed by acetone. The prepared graphene oxide was dried overnight in an oven at 65 °C.

### Preparation of Cu-tpa and its composite

Cupric nitrate (180 mg) was dissolved in 50 mL of DMF solvent. Terephthalic acid (100 mg) was added as an organic ligand and stirred at room temperature into DMF solution. Triethyl amine was added drop wisely, and the system was sealed and stirred continuously for 4 h. The resulting precipitate was centrifuged and washed with DMF, chloroform, and ethanol. Finally, the obtained Cu-terephthalate crystals were dried overnight at 60 °C in a vacuum oven [42]. Similarly for the preparation of GO/Cu-tpa composite, along with metal precursor, previously prepared graphene oxide (100 mg) was added, and the same procedure was followed as mentioned above.

### Fabrication of GO/Cu-tpa composite modified electrode

Prior to the modification, the bare glassy carbon electrode was polished using alumina powder of decreasing sizes 1, 0.3, and

0.05  $\mu\text{m}$ . The polished electrodes were washed repeatedly with double distilled water and ultrasonicated in ethanol and water to remove adsorbed impurities. The composite modified electrode was fabricated by drop coating 10  $\mu\text{L}$  of GO/Cu-tpa dispersed solution on the surface of clean and polished bare glassy carbon electrode and dried at room temperature. This composite modified electrode was further used as a working electrode throughout the experiment.

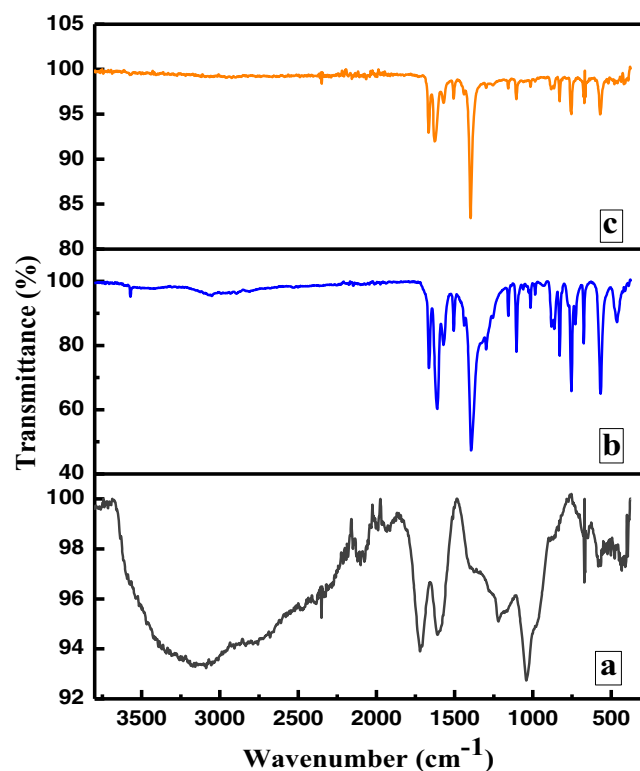
## Results and discussion

### Characterization of the composite

The prepared Cu-tpa crystals and GO/Cu-tpa composite were characterized using FTIR, XRD, SEM, and EDS techniques to ascertain the bond formation between Cu-tpa and graphene oxide, its morphology, and the elemental composition.

### FTIR study

The evidence for the nature of interaction between graphene oxide sheets and Cu-tpa in the composite was studied through FTIR study. The IR spectra of GO (Fig. 1a) showed a broad peak at  $3086\text{ cm}^{-1}$  is due to the characteristic of  $-\text{OH}$  stretching vibrations, and the IR spectrum of terephthalic acid is given in ESI 1. A

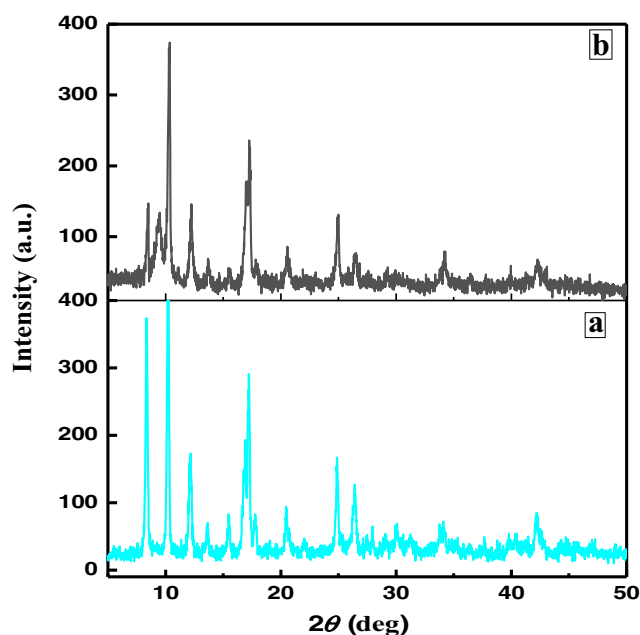


**Fig. 1** FTIR spectra of **a**) graphene oxide (GO) **b**) Cu-tpa and **c**) GO/Cu-tpa composite

strong band at  $1397\text{ cm}^{-1}$  is due to C-O stretching of terephthalic acid (Fig. 1b). The band at  $1570\text{ cm}^{-1}$  is due to asymmetric stretching of carboxylic group. The IR spectrum of the Cu-tpa shows less intense peak at  $1611\text{ cm}^{-1}$  and is shifted to  $1626\text{ cm}^{-1}$  and peak at  $1719\text{ cm}^{-1}$  due to  $-\text{C}=\text{O}$  stretching is shifted to  $1665\text{ cm}^{-1}$  after interaction. This shows that the bonding interactions have occurred between GO sheets and Cu-tpa crystals. The prominent peaks observed at  $1379\text{ cm}^{-1}$ ,  $1496\text{ cm}^{-1}$ ,  $1580\text{ cm}^{-1}$ , and  $1625\text{ cm}^{-1}$  for Cu-tpa, and the peaks obtained between  $1040$  and  $1650\text{ cm}^{-1}$  typical for GO are retained in the GO/Cu-tpa composite (Fig. 1c). Thus, FTIR study of the composite revealed that the necessary  $\pi$ - $\pi$  interaction and hydrogen bonding between graphene oxide sheets and Cu-tpa has resulted in increasing the surface defects in GO sheets. Hence, the facile electron transfer within the composite is enhanced, and these results are in good agreement with the reported literature [42].

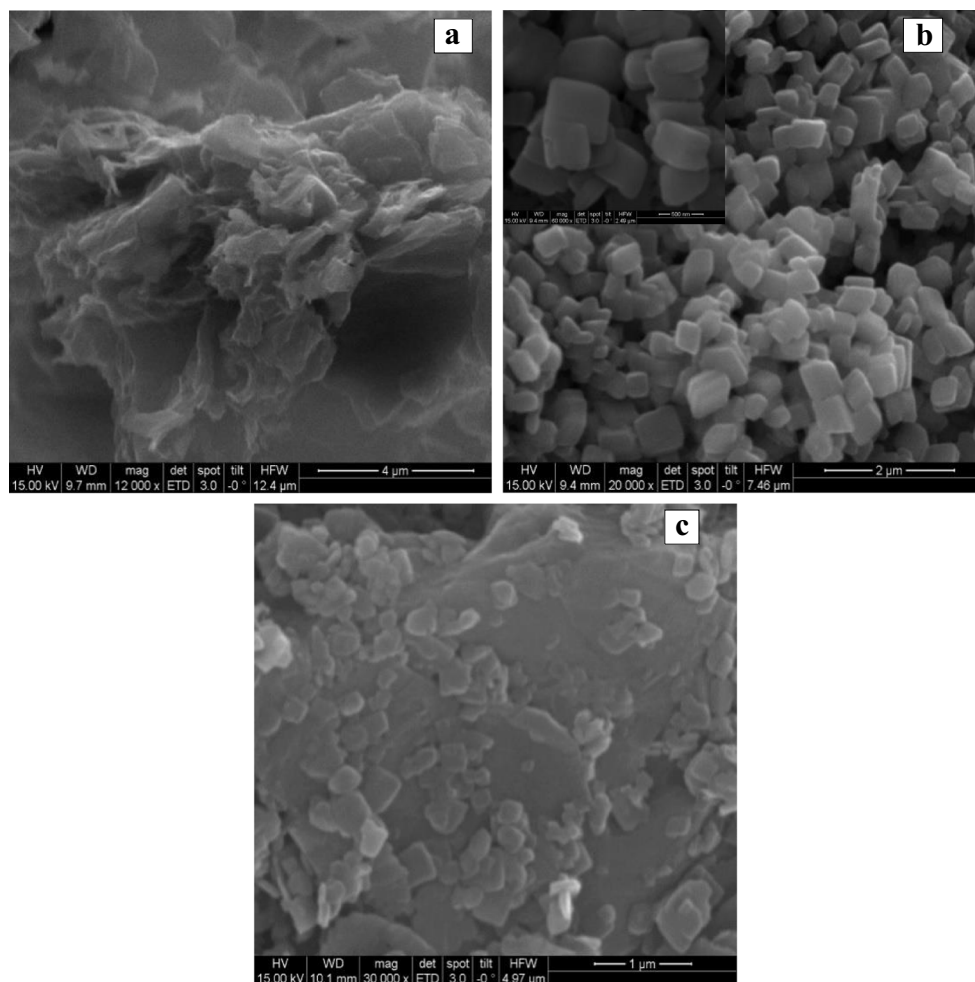
### X-ray diffraction study

The powder XRD pattern of GO/Cu-tpa composite (Fig. 2b) displayed the predominant diffraction peaks of Cu-tpa crystals (Fig. 2a) at  $2\theta$  degree values  $8.2^\circ$ ,  $10.2^\circ$ ,  $12^\circ$ ,  $13^\circ$ ,  $15^\circ$ ,  $17.2^\circ$ , and  $19.5^\circ$  and are present in the GO/Cu-tpa composite suggesting that the crystalline structure of Cu-tpa is well maintained even after its intercalation into the graphene oxide sheets [43].



**Fig. 2** PXRD pattern of **a**) Cu-tpa crystals **b**) GO/Cu-tpa composite

**Fig. 3** SEM images of **a**) graphene oxide **b**) Cu-terephthalate crystals [inset: enlarged view] **c**) GO/Cu-tpa composite

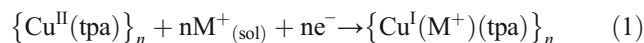


### Scanning electron microscopic study

The surface morphology of the synthesized Cu-tpa crystals and GO/Cu-tpa composite were studied by recording the scanning electron microscopy images (Fig. 3). Figure 3a shows the layered structure of graphene oxide sheets. Figure 3b clearly indicates the formation of Cu-tpa crystals (inset: enlarged view) in cubic shape. The morphology of the prepared composite clearly shows the immobilized cubic Cu-tpa crystals on layered GO sheets and is uniformly distributed without any agglomeration. This confirms that the Cu-tpa crystals are very well dispersed between graphene oxide sheets, and also, the crystalline nature is well maintained even after the addition of graphene oxide during the preparation of composite. The elemental composition analysis was carried out by recording the energy dispersive spectrum (Fig. 4) in conjunction with SEM. The EDS spectrum showed the presence of Cu, C, and O as major elements. The Cu content has been found to be 18.97% which is in close agreement with the theoretically calculated value of 17.97% in the prepared composite, and the atomic percentage of elements has been tabulated in Table 1, and the EDS spectrum of Cu-tpa is given in ESI 2.

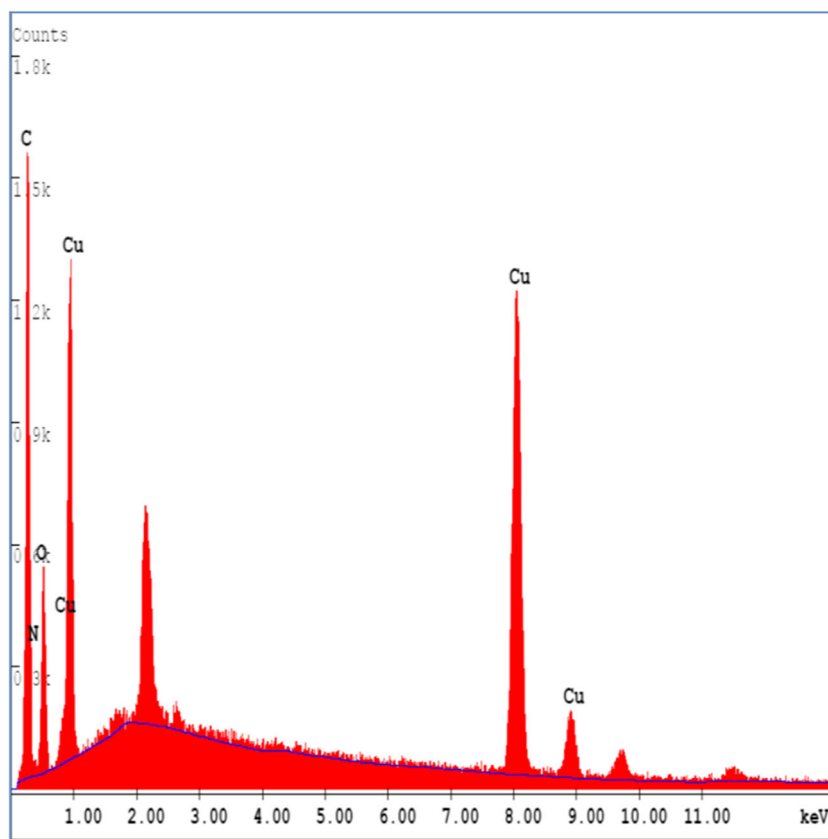
### Electrochemical characterization of modified electrode

The electrochemical behavior of GO/Cu-tpa modified glassy carbon electrode was studied by cyclic voltammetry. The voltammograms were recorded in the potential window  $-0.8$  to  $1.2$  V in a phosphate buffer solution of pH 7 at a scan rate of  $50 \text{ mV S}^{-1}$ . The resulting voltammograms showed significant redox peaks at  $-0.02$  V (a),  $-0.17$  V (b), and  $-0.25$  V (c) representing the oxidation of Cu to Cu (II) as well as topotactic reduction of Cu (II) to Cu (I) and Cu (I) to Cu metal respectively (Fig. 5 peaks a, b, c). This reduction process is electrolyte dependent which is coupled with the ingress of cations from the electrolyte into the GO/Cu-tpa coated on the electrode along with electron transfer.



Hence the modified electrode displayed a set of redox peaks of Cu metal centers, i.e., of copper, which are in good agreement with the reported literature [7].

**Fig. 4** EDS spectrum of GO/Cu-tpa composite



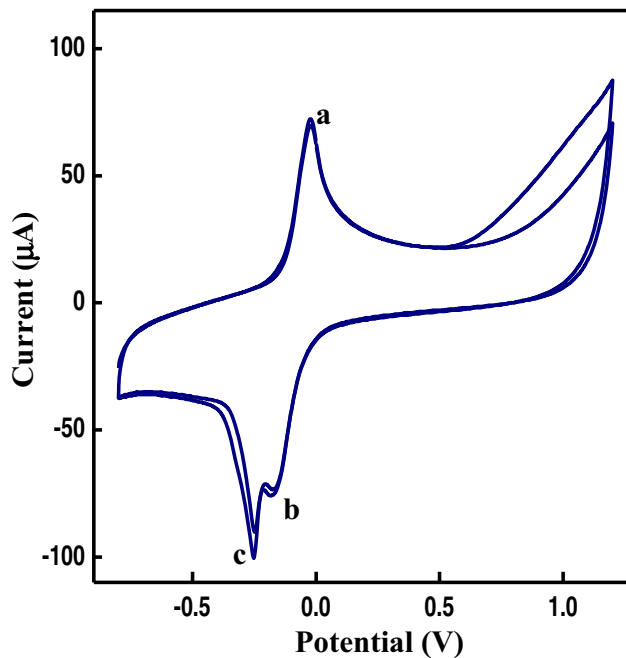
**Electrocatalytic oxidation of nitrite at GO/Cu-tpa modified electrode**

The initial cyclic voltammetric study revealed the redox nature of the composite. Hence the electrocatalytic behavior of the composite modified electrode in the electro oxidation of nitrite has been thoroughly examined through the electrochemical behavior of bare, Cu-tpa and GO/Cu-tpa modified electrodes. The Cu-tpa modified electrode in presence of nitrite did not show any considerable analytical signal. The current response for bare electrode showed a sluggish behavior. Whereas, the GO/Cu-tpa composite modified electrode showed a significant enhancement in the peak current response (fourfold rise) for the electro oxidation of nitrite at 0.9 V compared with Cu-tpa modified and bare glassy carbon electrodes (Fig. 6). Generally, EC mechanism occurs when an anodic peak current increases and cathodic peak current decreases during analyte addition to the supporting electrolyte solution. In the present investigation, GO/Cu-tpa modified

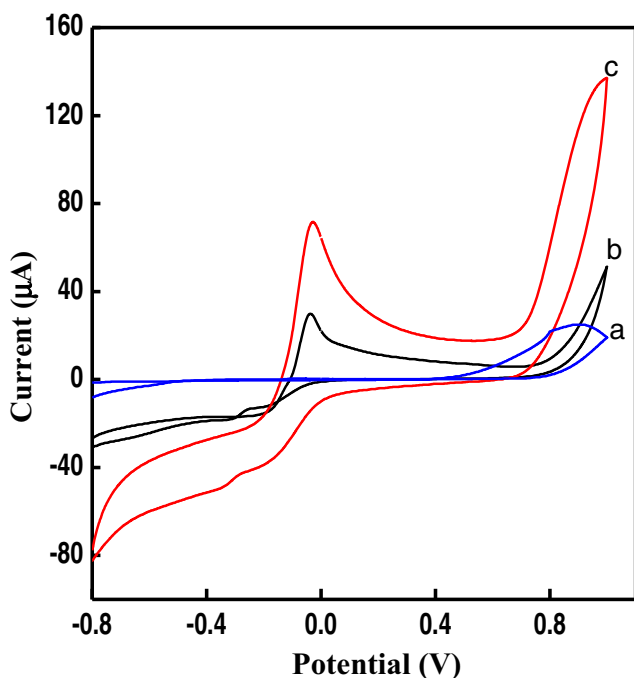
electrode showed a single anodic peak at  $-0.023$  V in absence of nitrite and two cathodic peaks at  $-0.171$  and  $-0.25$  V which could be assigned to the reduction of Cu (II) to Cu (I) and Cu (I) to Cu-metal. The composite showed a significant

**Table 1** Elemental composition of Cu-tpa and GO/Cu-tpa composite in atomic percent

Sample	C (%)	N (%)	O (%)	Cu (%)
Cu-tpa	65.44	1.36	5.48	27.72
GO/Cu-tpa	70.72	1.68	6.48	18.97

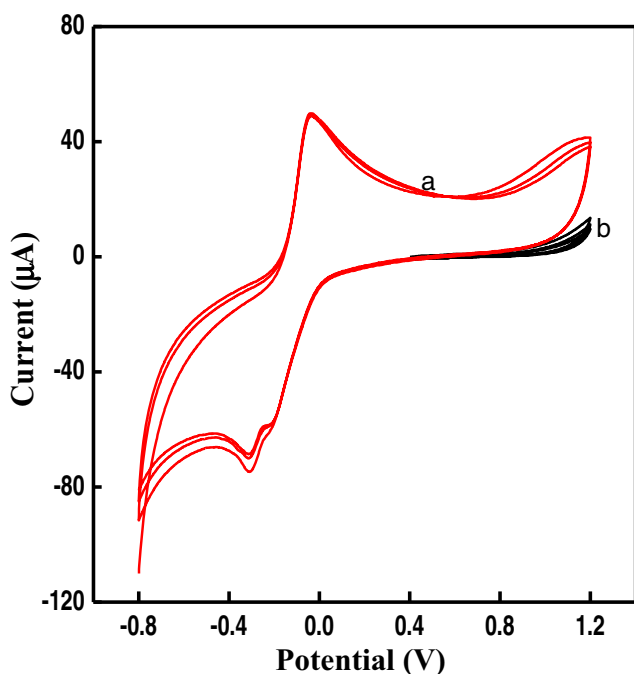


**Fig. 5** Cyclic voltammograms of GO/Cu-tpa composite modified electrode in phosphate buffer solution of pH 7 at scan rate  $50 \text{ mV S}^{-1}$



**Fig. 6** Overlaid cyclic voltammograms of glassy carbon electrode at a) bare b) Cu-tpa modified c) GO/Cu-tpa composite modified electrode in presence of 5 mM nitrite and phosphate buffer solution of pH 7 at scan rate  $50 \text{ mV S}^{-1}$

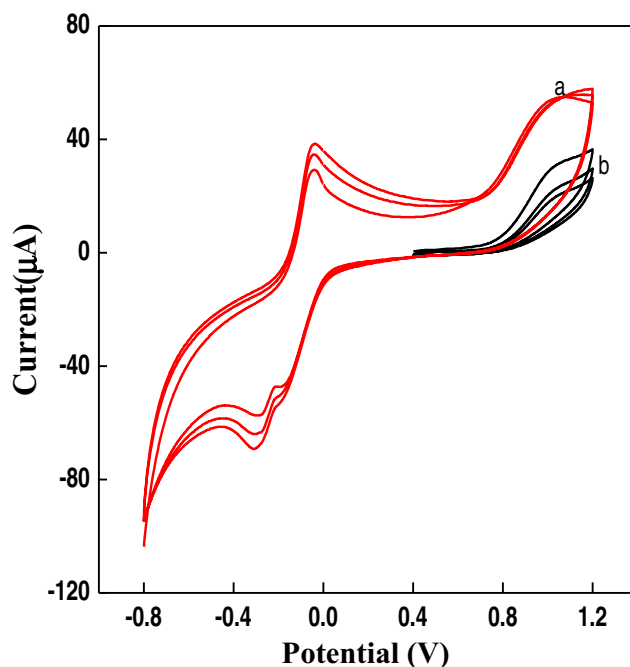
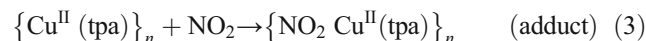
enhancement in the current response in presence of nitrite species along with a shift in Cu oxidative peak potential at  $-0.028 \text{ V}$  and reductive peak potentials at  $-0.17 \text{ V}$  and  $-$



**Fig. 7** Overlaid cyclic voltammograms at GO/Cu-tpa composite modified electrode surface for successive scans in absence of nitrite at different starting potentials a)  $-0.8 \text{ V}$  b)  $0.4 \text{ V}$  in phosphate buffer solution of pH 7 at scan rate  $50 \text{ mV S}^{-1}$

$0.34 \text{ V}$ . This behavior might be due to the interaction of GO/Cu-tpa with nitrite in forming an adduct which is also favored by the accessibility of the MOF framework to charge transfer. Hence the reduction potential of Cu (II) centers becomes significantly shifted from  $-0.25$  to  $-0.35 \text{ V}$  due to its interaction. The electrocatalytic process is also modulated by electrolyte counter ions. The catalytic effect is associated with Cu (II) to Cu (I) and Cu metal conversions. In the presence of size allowed cations, the electrochemical pathway changes significantly and reduction occurs in two steps. Here the charge conservation involves the entry of electrolyte cations coupled with electron transfer by means of series of faradaic reactions which involves electron mobility between adjacent immobilized redox centers, and redox conductivity can be easily achieved between GO/Cu-tpa/GCE and electrolyte interface. The GO/Cu-MOF composite accelerated the electron transfer rate in the oxidation of nitrite. Hence the enhanced current response has been attributed to the increased electron conductivity of GO/Cu-tpa composite with the mediation of Cu redox centers on the glassy carbon electrode surface [44].

The catalytic activity of Cu-tpa might be attributed to their immediate reduction to Cu(I) and Cu metallic species. The plausible mechanism in the oxidation of nitrite at the modified interface might be shown as given below.

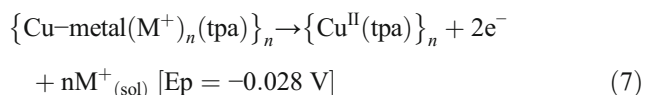
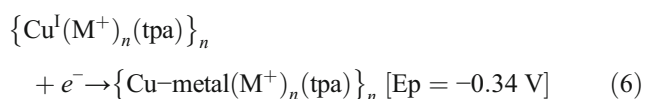
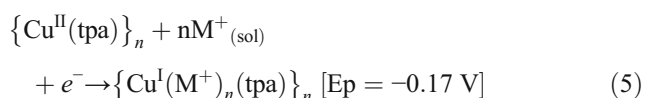
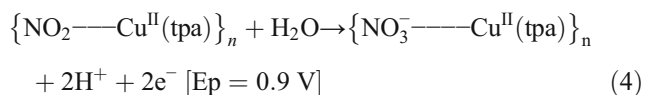


**Fig. 8** Overlaid cyclic voltammograms at GO/Cu-tpa composite modified electrode surface for successive scans in presence of 1.5 mM nitrite at different starting potential a)  $-0.8 \text{ V}$  b)  $0.4 \text{ V}$  in phosphate buffer solution of pH 7 at scan rate  $50 \text{ mV S}^{-1}$

**Table. 2** Comparison of proposed nitrite sensor with reported methods

Electrode	Linear range (μM)	Limit of detection (μM)	Sensitivity (μA μM <sup>-1</sup> cm <sup>-2</sup> )	Ref.
MOF-525/GNR	100–2500	0.75	0.093	[49]
Au/Cu-MOF/CPE	0.05–717	0.030	Not reported	[37]
Cu-MOF/rGO	3–40,000	0.033	43.73	[38]
N-doped rGO	0.5–5000	0.2	0.228	[50]
MOF-525	20–800	2.1	0.095	[51]
CuS/MWCNTs	1.0–8100	0.33	0.131	[52]
rGO/Pani/AsM	25–7500	0.803	10.71	[53]
AgNPs/CS/GSPE	30–1140	1.84	0.59	[54]
GO/Cu-tpa	5–625	0.3	0.86 ± 0.06	This work

MOF Metal organic frameworks, rGO reduced graphene oxide, GNR graphene nano ribbons, CPE carbon paste electrode, N nitrogen, Pani polyaniline, AsM arsenomolybdate, AgNPs silver nanoparticles, CS chitosan, GSPE graphitic screen printed electrode, MWCNTs multi walled carbon nanotubes

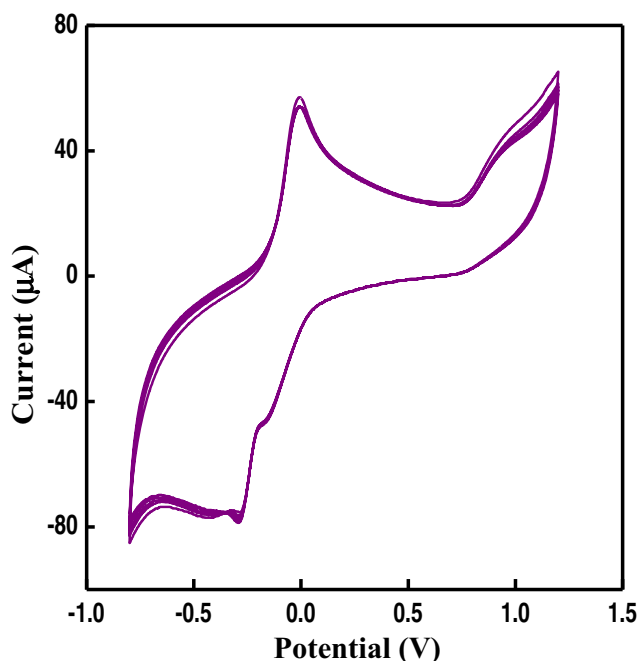


The Cu-tpa MOF with large surface area suffers from low conductivity and limits their application in electrochemical studies. The introduction of conductive bridges like graphene oxide sheets boosts up the electron transfer rate within the composite causes the enhancement of analytical response. In the present study, the anodic peak current response for the oxidation of nitrite in comparison with other modified electrodes demonstrates the positive synergism between Cu-tpa crystals and conductive GO sheets leading to the improved charge transfer ability to the composite. These results are in good agreement with the reported literature [32].

In order to study the species responsible for electrocatalysis in the present study, cyclic voltammetric scans initiated at different starting potentials, i.e., -0.8 V and 0.4 V were recorded. From these experimental results, we have observed that the peak currents are absolutely different at different potential window ranges. In absence of nitrite (Fig. 7), the scan initiated at -0.8 V, the modified interface showed higher current compared with the scan initiated at 0.4 V. This is due to the pronounced charge transfer ability within the GO/Cu-tpa composite between graphene oxide and Cu redox centers of Cu-tpa. Similarly in presence of nitrite (Fig. 8), higher oxidative current intensities were observed for nitrite oxidation for the scans initiated at -0.8 V and lower peak current responses

for the scans initiated at 0.4 V. Therefore we can conclude that at more negative potentials, the formation of metallic copper with the ingress of charge balancing electrolyte cations and the oxidative redissolution of electrochemically generated metal within the MOF matrix might be taking place. The above electrocatalytic phenomenon is operating at the electrode interface which is mainly responsible for the electrolyte dependent nitrite oxidation process.

Further, the enhanced current response is also attributed to the increased conductivity of the composite which is confirmed through electrochemical impedance measurements. From the Nyquist plot (ESI 3), it has been found that the charge transfer resistance (*R<sub>ct</sub>*) value for the bare glassy carbon electrode is 3.40 × 10<sup>7</sup> Ω whereas the GO/Cu-tpa composite



**Fig. 9** Cyclic voltammograms at GO/Cu-tpa composite modified electrode for continuous 5 cycles in presence of 1.5 mM nitrite in phosphate buffer solution of pH 7 at scan rate of 50 mV S<sup>-1</sup>

modified electrode showed the  $R_{ct}$  value of  $1.40 \times 10^5 \Omega$ . This indicates that the composite modified electrode has lower impedance value which greatly improves the conductivity and hence increases the electron transfer rate at the modified interface. The influence of scan rate on the electrochemical behavior of modified electrode was studied. The overlaid cyclic voltammograms of GO/Cu-tpa modified electrode measured at different scan rates in presence of nitrite are shown in ESI 4. It was observed that the anodic peak current increased linearly with the scan rate towards more positive values with  $R^2 = 0.98$ . This indicates that the electrocatalytic oxidation of nitrite at GO/Cu-tpa modified electrode surface is adsorption controlled process [45].

### Optimization study

Square wave voltammetry (SWV) as a sensitive technique was further utilized in the trace level measurement of nitrite [45]. The experimental conditions responsible in the quantitative measurement of nitrite with increased selectivity were optimized by varying the conditions like pH, pulse frequency, pulse amplitude (Figs. ESI 5–7), and analyte concentration. The optimized conditions are used in the nitrite measurement. Medium pH 4, pulse frequency—10 Hz and pulse amplitude—70 mV [46–48].

### Electrochemical measurement of nitrite

The quantification of nitrite was performed using square wave voltammetric technique under optimized conditions at GO/Cu-tpa composite modified electrode. The resulting overlaid voltammograms showed a substantial increment in the anodic peak current responses at composite modified electrode with successive additions of known concentrations of nitrite. Hence the calibration plot was constructed by considering the anodic peak current against nitrite concentration and is given in ESI 8 under supplementary information. The current response was proportional to the increasing nitrite concentration over the range from 5 to 625  $\mu\text{M}$  with a correlation coefficient of 0.985. Further, the limit of detection (LOD) was found to be 0.3  $\mu\text{M}$ . The sensitivity of the modified electrode

was found to be  $0.86 \pm 0.06 \mu\text{A } \mu\text{M}^{-1} \text{cm}^{-2}$ . Conversely, the peak potentials were found to shift towards negative values showing the EC mechanism in electrocatalytic oxidation of nitrite. This might be accounted to the synergistic effect of Cu-tpa and GO sheets, which facilitates the conducting pathway through the transfer of electrons.

For completeness, the comparison of analytical sensing parameters such as type of modified electrode, linear range, LOD, and sensitivity of the existing nitrite sensors along with the proposed nitrite sensor has been summarized in Table 2. Although the sensitivity of GO/Cu-tpa composite modified electrode is not so superior than some of the existing nitrite sensors, but still, it is higher than few mentioned in the comparison table. Hence these results depicts that the composite can be used as an alternate electrode material for the measurement of nitrite at low level concentration.

### Selectivity of the composite modified electrode towards nitrite

The presence of common interfering ions may seriously influence the overall performance of the modified electrode. Hence the effect of some cations such as  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Cu}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{NH}_4^+$ , and anions like  $\text{NO}_3^-$ ,  $\text{ClO}_4^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{SO}_3^{2-}$ ,  $\text{CO}_3^{2-}$ ,  $\text{CH}_3\text{COO}^-$ , ascorbic acid, acetaminophen, dopamine, and citric acid on the analytical response at GO/Cu-tpa modified electrode towards electro oxidation of 250  $\mu\text{M}$  nitrite has been studied. The variations in the current response in presence of 100 mM concentration of the interfering species have been studied. No significant change in the peak current response was observed in presence of these anions and cations. However the current responses were found to be varied slightly at 5 fold increase in the concentration of interfering species. The graphical representation of interference study has been shown in ESI 9 under supplementary information.

### Stability and reproducibility

The stability of the modified electrode is an important aspect in assessing the superiority of the developed sensor. Hence the composite modified electrode surface was checked by

**Table 3** Application study

Sl No	Sample	Nitrite ( $\mu\text{M}$ )		Total nitrite ( $\mu\text{M}$ )[ $n = 3$ ]			
		Originally found	spiked	Proposed method	Recovery $\pm$ RSD (%)	Standard method	Recovery $\pm$ RSD (%)
1	Tap water <sup>a</sup>	ND	280	289	103.2 $\pm$ 0.2	297	101.3 $\pm$ 1.4
2	Bore well water <sup>b</sup>	64	250	310	98.7 $\pm$ 0.7	319	101.5 $\pm$ 0.7
3	Sewage water <sup>c</sup>	157	50	202	97.5 $\pm$ 1.0	212	102.4 $\pm$ 1.5

$n$  Number of measurements, <sup>a</sup> Collected from local water supply, <sup>b</sup> collected from east region of Bengaluru, <sup>c</sup>-collected from local open sewage line in city outskirts. ND- not detected



measuring the voltammograms up to 5 continuous repeated cycles in presence of 1.5 mM of nitrite. A decrease of 7% in current response was observed after the second cycle (Fig. 9). As the cycling continues, the peak intensity for Cu oxidation/reduction was also found to increase. This might be due to the slow and partial disintegration of Cu-MOF lattice upon consecutive cyclic scans which may block the active sites present in the substrate [7]. However considerable analytical signal was obtained for the electro oxidation of nitrite even after 5 cycles showing the greater stability of the modified electrode interface. These results demonstrate that the modified interface is stable towards nitrite detection which can be used for prolonged study.

Additionally, the reproducibility of the proposed sensor has been checked at different time intervals from the day of experiment to 15 days and 30 days. The modified interface displayed a significant response within  $\pm 5\%$  variation of the anodic peak current in the oxidation of nitrite after 30 days (ESI 10).

### Application study

The utility of the GO/Cu-tpa prepared composite modified electrode as a sensor was evaluated by the measurement of nitrite in real water samples such as tap, bore well, and sewage water samples. The tap and bore well water samples were used as it is whereas the sewage water was treated with activated charcoal and filtered to remove the suspended particulate matter and odor. Each 5 mL of sample was taken in an electrochemical cell containing 4 mL of buffer solution. The pH of the samples was pre-adjusted to pH 7. The nitrite concentration was measured in both original and spiked samples. The results obtained were found to be in good agreement with the standard Griess–Ilosvay method [55]. The recovery studies were carried out for three successive measurements ( $n = 3$ ) and were found to be satisfactory with RSD between 97.5 and 103.2% (Table 3). These results demonstrated that the GO/Cu-tpa composite modified electrode serves as a suitable electrochemical platform in the trace level measurement of nitrite for routine analysis.

### Conclusions

A simple and sensitive electrochemical sensing platform comprising GO/Cu-tpa composite has been fabricated. The composite has been characterized using FTIR, XRD, SEM, and electrochemical techniques. The fabricated electrode showed an excellent electrocatalytic activity towards the electro oxidation of nitrite with wide linearity in the concentration range 5–625  $\mu\text{M}$  with a very low detection limit of 0.3  $\mu\text{M}$ . The proposed method has been successfully applied to measure trace level nitrite from various water samples. The results

showed a quantitative recovery of spiked samples in comparison with the standard protocol. Hence GO/Cu-tpa composite can be used as a novel sensing material in the electrochemical nitrite quantification study.

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