

## Research Article

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# Carbon supported g-C<sub>3</sub>N<sub>4</sub> for electrochemical sensing of hydrazine

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**Abstract:** This study reports a synthesis of carbon supported graphitic carbon nitride (g-C<sub>3</sub>N<sub>4</sub>-KBC) obtained by pyrolysis of melamine with Ketjenblack 600JD carbon (KBC) at 550°C for 4 h in a N<sub>2</sub> atmosphere. g-C<sub>3</sub>N<sub>4</sub>-KBC oxidizes hydrazine at an onset potential 0.145 V vs. SCE close to the thermodynamic standard potential of hydrazine (0.23 V vs. SHE). In comparison to the controls, KBC and g-C<sub>3</sub>N<sub>4</sub>, g-C<sub>3</sub>N<sub>4</sub>-KBC oxidizes hydrazine at lower overpotential. Most research has tended to focus on transition metal-based catalysts and few are of carbon material such as graphene nanoflakes, graphene oxide, and carbon nanotubes. A comparison in terms of sensitivity, detection range and stability reveals g-C<sub>3</sub>N<sub>4</sub>-KBC electrode's superiority over other carbon material-based catalysts. To the best of our knowledge, the g-C<sub>3</sub>N<sub>4</sub>-KBC catalyst is not reported for sensing hydrazine in the literature.

**Keywords:** g-C<sub>3</sub>N<sub>4</sub>-KBC, hydrazine sensing, overpotential, electrochemical sensor

## 1 Introduction

Recently graphitic carbon nitride (g-C<sub>3</sub>N<sub>4</sub>) is in the spotlight owing to its applications in photo-degradation [1], photocatalytic hydrogen generation [2], oxygen reduction reaction [3], conversion of benzene to phenol [4], carbon dioxide sequestration [4] etc. g-C<sub>3</sub>N<sub>4</sub> is a semiconductor and most stable allotrope at ambient condition [1]. Moreover, as g-C<sub>3</sub>N<sub>4</sub> is made with strong covalent bonds between carbon and nitrogen, it is stable under light irradiation (for photocatalytic application), as well as in acidic and basic solution (for electrocatalysis applications such as ORR and CO<sub>2</sub> sequestration). This high stability coupled

with moderate band gap makes g-C<sub>3</sub>N<sub>4</sub> a suitable material for photocatalytic works. Many precursors, such as dicyandiamide, cyanamide, and melamine have been employed to synthesize g-C<sub>3</sub>N<sub>4</sub>. The former two precursors are expensive and hazardous in comparison to melamine. Several researchers synthesized g-C<sub>3</sub>N<sub>4</sub> by heat-treatment of melamine in low-vacuum systems [5, 6]. Reaction conditions decide the extent of condensation and hence the resultant properties.

World health organization (WHO) has identified hydrazine (N<sub>2</sub>H<sub>4</sub>) as a group B2 human carcinogen [7]. Hence, it is vital to develop cost effective and fast sensing sensors for N<sub>2</sub>H<sub>4</sub> detection. Hydrazine is a known neurotoxin, carcinogenic, mutagenic and hepatotoxic substance that harms the liver and brain glutathione. It is heavily employed in rocket fuels, weapons of mass destruction, missile and fuel cell systems [8, 9]. Further, in industries, hydrazine is used as a corrosion inhibitor, oxygen scavenger, emulsifier and antioxidant [10]. Myriad techniques are known for detecting N<sub>2</sub>H<sub>4</sub> including colorimetry [11], conductometry [12], fluorescence [13] and electrochemical [14]. Among these methods, the electrochemical method offers several benefits in terms of sensitivity, selectivity, low detection limit, wide linear range, and stability. Electrochemical oxidation of N<sub>2</sub>H<sub>4</sub> is limited by kinetically sluggish N<sub>2</sub>H<sub>4</sub> oxidation reaction and high overpotential involved in the reaction. A plethora of noble metal-based materials has been reported to reduce the overpotential of N<sub>2</sub>H<sub>4</sub> sensing [15–25]. But, only few metal-free catalysts are known for N<sub>2</sub>H<sub>4</sub> sensing, they are based on either carbon nanoflakes or graphene oxide or carbon nanotubes.

This paper proposes a new material (g-C<sub>3</sub>N<sub>4</sub>-KBC) for electrochemical sensing of N<sub>2</sub>H<sub>4</sub>. g-C<sub>3</sub>N<sub>4</sub>-KBC is obtained by pyrolysis of melamine with carbon at 550 °C. The vital function of carbon is to impart electrical conductivity in the g-C<sub>3</sub>N<sub>4</sub>-KBC catalyst as g-C<sub>3</sub>N<sub>4</sub> is semiconducting in nature.

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## 2 Experimental

### 2.1 Materials

Melamine and 5 wt.% Nafion 117 ionomer solution were procured from Alfa Aesar (Kolkata, India). Ketjenblack 600JD (KBC) was obtained from Akzo Nobel (Chicago, IL).  $\text{Na}_2\text{HPO}_4$  and  $\text{NaH}_2\text{PO}_4$  were procured from Thermo Fisher Scientific and Loba Chemie Pvt. Ltd. Mumbai, respectively. Hydrazine was procured from Qualigens Fine Chemicals, Mumbai, India. All the solutions were prepared using Milli Q water ( $18 \text{ M}\Omega \text{ cm}$  resistivity).

### 2.2 Preparation of carbon supported $\text{g-C}_3\text{N}_4$ ( $\text{g-C}_3\text{N}_4$ -KBC)

$\text{g-C}_3\text{N}_4$ -KBC was prepared by one step pyrolysis process. 200 mg of melamine was dispersed in 50 mL of isopropyl alcohol, followed by addition of 100 mg of KBC. The dispersion was stirred using magnetic stirrer overnight followed by heating at  $95^\circ\text{C}$  to obtain well-mixed melamine-carbon composite. Thus obtained melamine-carbon composite was pyrolyzed at  $550^\circ\text{C}$  for 4 h in the  $\text{N}_2$  atmosphere to obtain  $\text{g-C}_3\text{N}_4$ -KBC.  $\text{g-C}_3\text{N}_4$  obtained by pyrolysis of the neat melamine at  $550^\circ\text{C}$  for 4 h was used as a reference compound in this study.

### 2.3 Preparation of $\text{g-C}_3\text{N}_4$ -KBC modified glassy carbon electrode ( $\text{g-C}_3\text{N}_4$ -KBC/GCE)

Glassy carbon electrode (GCE) was polished with alumina powder ( $0.05 \mu\text{m}$ ) followed by sonication in isopropyl alcohol and Milli Q water for 5 minutes. 5 mg of the  $\text{g-C}_3\text{N}_4$ -KBC was dispersed by sonication in  $1600 \mu\text{L}$  of water-isopropyl alcohol (5:1 V/V) solution to obtain an ink-like dispersion.  $12.5 \mu\text{L}$  of 5 wt.% Nafion ionomer solution was added to the ink to act as a binder. The required amount of this ink was drop-cast onto GCE and let dry in ambient conditions for 1 h to obtain a catalyst loading of  $200 \mu\text{g cm}^{-2}$ .

### 2.4 Electrochemical evaluation

All the electrochemical measurements were performed using a Biologic VSP-300 model potentiostat and a three electrode setup. Saturated calomel electrode (SCE), Pt-mesh and catalyst coated GC electrode were used as the reference, counter and working electrodes respectively. All

the electrochemical experiments were performed at  $25^\circ\text{C}$  in 0.1 M phosphate buffer solution (PBS, pH 7.0) electrolyte. Cyclic voltammetry (CV) was performed in the voltage range of  $-0.25$  to  $0.55 \text{ V}$  vs. SCE. 5 mM ferrocyanide/ferricyanide redox couple dissolved in 0.1 M  $\text{KNO}_3$  was used as the electrolyte. Amperometric experiments were carried out using catalyst coated glassy carbon rotating disc electrode (RDE, 5 mm glassy carbon, Pine instruments) rotating at 200 rpm and held at  $0.35 \text{ V}$  vs. SCE in PBS solution with a successive addition of hydrazine to the buffer solution. Electrochemical impedance spectroscopy (EIS) measurements of the electrodes were carried out in 5 mM ferrocyanide/ferricyanide dissolved in 0.1 M  $\text{KNO}_3$  solution. A voltage perturbation ( $\Delta V_{rms}$ ) of 10 mV was used for impedance measurement in the frequency range of 200 kHz to 100 mHz.

### 2.5 Characterization techniques

The catalyst samples were characterized using powder X-ray diffraction (XRD, Bruker 8 fitted with  $\text{Cu K}\alpha$  X-ray source) at a scan rate of  $1^\circ$  per minute. High-resolution transmission electron microscopy (HR-TEM) characterization was carried out using JEOL JEM 2100. Raman spectroscopy was carried out using Bruker FT-Multi Ram fitted with Nd: YAG laser source (1064 nm, 1000 mW intensity). Carbon-Hydrogen-Nitrogen (CHN) analysis was performed using Perkin-Elmer 2400 series equipment. FT-IR spectroscopy study was performed using JASCO-400 Type-A equipment. Laser desorption ionization Fourier-transform ion-cyclotron-resonance mass spectrometry (LDI-FT-ICR-MS obtained from MS Solarix-JA, Bruker Daltonics) is employed to study the low-molecular-weight species existing in  $\text{g-C}_3\text{N}_4$ -KBC. X-ray photoelectron spectroscopy (XPS) of the samples was recorded using Fisons Instruments (S-ProbeTM2803) fitted with  $\text{Al K}\alpha$  X-ray source. The analyzer was set at a pass energy of 20 eV to obtain N 1s and C 1s spectra. Shirley-type background correction was employed to the spectra and the peaks were deconvoluted to identify the chemical states of N and C in the samples. The measured binding energies were calibrated employing the C 1s peak at 284.8 eV as the reference.

### 3 Results and discussion

#### 3.1 XRD and CHN studies

XRD patterns of KBC, g-C<sub>3</sub>N<sub>4</sub>, and g-C<sub>3</sub>N<sub>4</sub>-KBC were recorded (Figure 1). KBC shows two broad peaks centered at around 26.5° (2θ) and 43.34°, that correspond to (002) and (101) planes of graphite. g-C<sub>3</sub>N<sub>4</sub> shows peaks at (2θ) 13.02° and 27.68° corresponding to (100) and (002) planes, respectively [26]. In the case of g-C<sub>3</sub>N<sub>4</sub>-KBC, since the (002) peak from KBC is merged with the (002) peak of g-C<sub>3</sub>N<sub>4</sub>, the peak position could not be ascertained clearly. However, the (100) peak at 13.5° confirms the presence of g-C<sub>3</sub>N<sub>4</sub>. CHN analysis of g-C<sub>3</sub>N<sub>4</sub> and g-C<sub>3</sub>N<sub>4</sub>-KBC indicates C:N ratio of 36:63 (remaining 1 % is from H) and 67:32, respectively. As the C:N ratio of g-C<sub>3</sub>N<sub>4</sub> is closer to the theoretical C:N ratio of 34:66, the formation of g-C<sub>3</sub>N<sub>4</sub> from pyrolysis of melamine is confirmed.

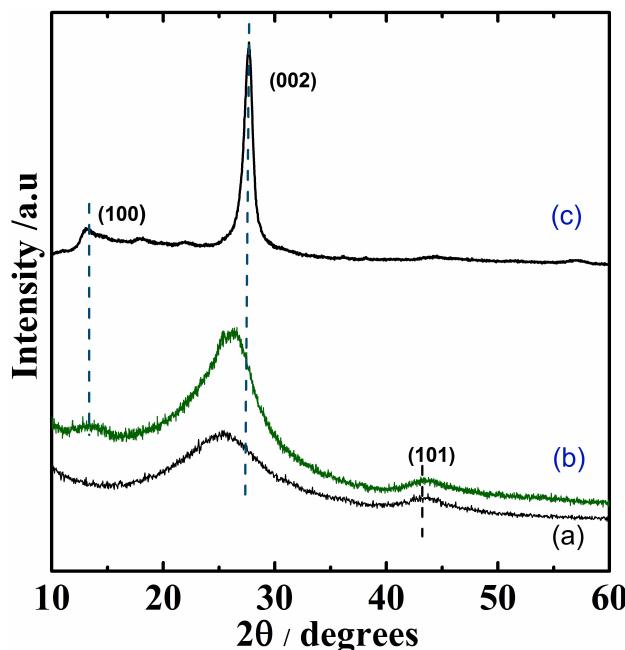


Figure 1: X-ray diffraction patterns of (a) KBC, (b) g-C<sub>3</sub>N<sub>4</sub>-KBC, and (c) g-C<sub>3</sub>N<sub>4</sub>.

#### 3.2 Raman and FT-IR spectroscopy studies

Raman spectra of g-C<sub>3</sub>N<sub>4</sub>-KBC and KBC are shown in Figure 2.  $I_D/I_G$  ratio of KBC and g-C<sub>3</sub>N<sub>4</sub>-KBC are about 1.43 and 1.27, respectively. As the carbons of g-C<sub>3</sub>N<sub>4</sub> are sp<sup>2</sup> hybridized, the composite g-C<sub>3</sub>N<sub>4</sub>-KBC has more intensity for

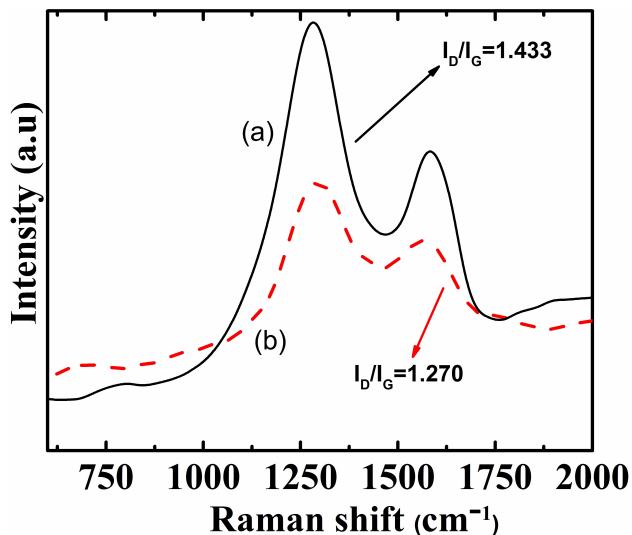


Figure 2: Raman spectra of (a) KBC and (b) g-C<sub>3</sub>N<sub>4</sub>-KBC.

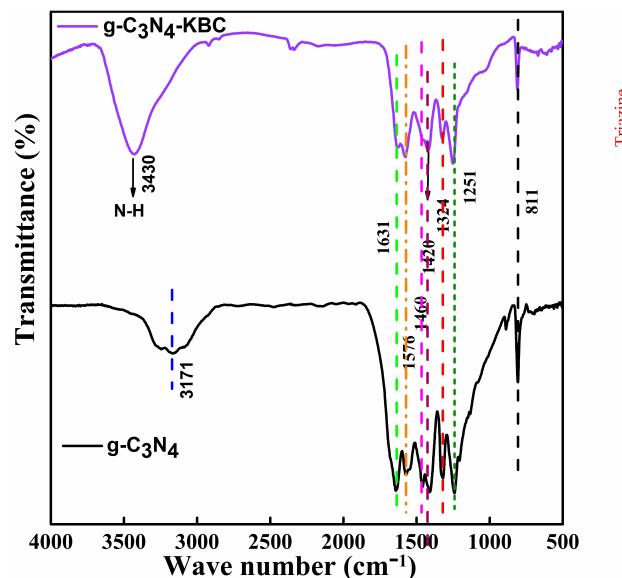


Figure 3: FT-IR-spectra of g-C<sub>3</sub>N<sub>4</sub> and g-C<sub>3</sub>N<sub>4</sub>-KBC.

G-band over D-band and hence the  $I_D/I_G$  ratio of g-C<sub>3</sub>N<sub>4</sub>-KBC is smaller than that of the KBC. FT-IR spectra (Figure 3) of both g-C<sub>3</sub>N<sub>4</sub> and g-C<sub>3</sub>N<sub>4</sub>-KBC feature peaks due to C=N (1631 cm<sup>-1</sup>), C-N (1251, 1324, 1420, 1460 and 1576 cm<sup>-1</sup>) stretching and out of plane breathing mode of triazine ring (811 cm<sup>-1</sup>). For g-C<sub>3</sub>N<sub>4</sub>-KBC, N-H stretching is observed [27] at around 3430 cm<sup>-1</sup>. In the case of g-C<sub>3</sub>N<sub>4</sub>, there was no peak at around 3430 cm<sup>-1</sup>, however, there was a broad peak at 3171 cm<sup>-1</sup> due to hydrogen-bonding interactions [28]. The absence of strong H-bonding interactions on g-C<sub>3</sub>N<sub>4</sub>-KBC probably due to the concentration of g-C<sub>3</sub>N<sub>4</sub> on KBC is lower than that of the neat g-C<sub>3</sub>N<sub>4</sub> limiting the H-bonding interactions among the -NH<sub>2</sub> func-

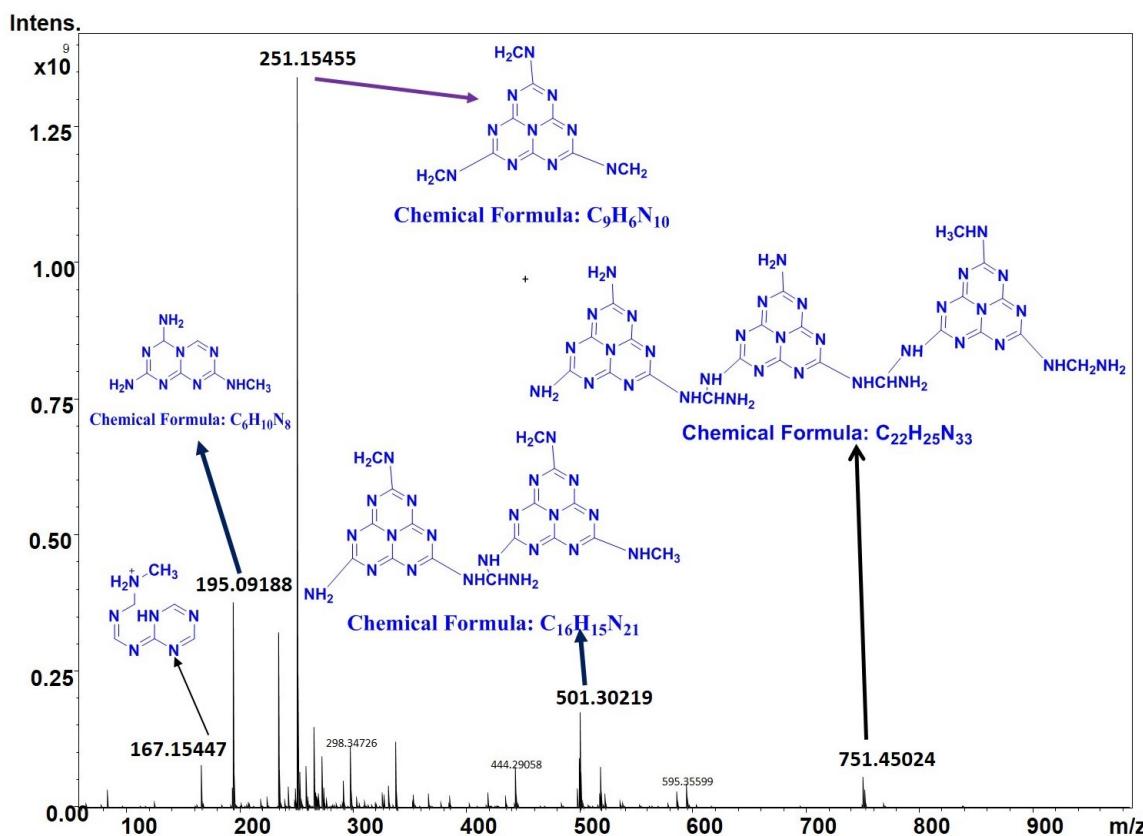


Figure 4: LDI-FT-ICR-MS spectrum of g-C<sub>3</sub>N<sub>4</sub>-KBC.

tional groups of g-C<sub>3</sub>N<sub>4</sub> particles. It is to be noted that CHN analysis indicated the presence of 1 wt.% of H in neat g-C<sub>3</sub>N<sub>4</sub>, whereas the H content was below detection limit in g-C<sub>3</sub>N<sub>4</sub>-KBC.

### 3.3 LDI-FT-ICR-MS

Figure 4 shows the LDI-FT-ICR-MS of g-C<sub>3</sub>N<sub>4</sub>-KBC with the structure of the possible species. The most intense peak at m/z 251.15 is the base peak. The peak at m/z of 751 is a molecular ion peak due to C<sub>22</sub>H<sub>25</sub>N<sub>33</sub>, which contains three heptazine ring moieties (2D-network of heptazine) [29]. The peaks below m/z of 751 are labeled with the possible decomposition products of C<sub>22</sub>H<sub>25</sub>N<sub>33</sub>.

### 3.4 XPS and TEM studies

XPS measurement was conducted to probe the elemental chemical spectra and the N/C atomic ratio in g-C<sub>3</sub>N<sub>4</sub>-KBC. The survey spectrum shows the presence of C, N, and O

(Figure 5(a)). Figure 5(b) shows the high-resolution C 1s spectrum, wherein presence of C=C (284.6 eV), C=O/C-N (285.6 eV), C=N (288 eV) and O-C=O (290.3 eV) functional groups were identified by deconvoluting the peaks [30]. The peak C-N originates from g-C<sub>3</sub>N<sub>4</sub>. Deconvolution of N 1s spectra (Figure 5(c)) indicates presence of C=N-C (398.7 eV), N-(C)<sub>3</sub> (399.6 eV) and pyridinic-oxide (404.7 eV) [30]. XPS measured N/C atomic ratio is 3.9, which is close to that of the theoretical N-C ratio of g-C<sub>3</sub>N<sub>4</sub> confirming the formation of g-C<sub>3</sub>N<sub>4</sub> on KBC surface during pyrolysis. HR-TEM image of the g-C<sub>3</sub>N<sub>4</sub>-KBC shows the presence of ordered region, which are possibly due to the layers of g-C<sub>3</sub>N<sub>4</sub> (Figure 6).

## 4 Electrochemical studies

### 4.1 Cyclic voltammetric studies

Electrokinetic parameters of the KBC and g-C<sub>3</sub>N<sub>4</sub>-KBC were analyzed using CV performed in potassium ferro/ferri

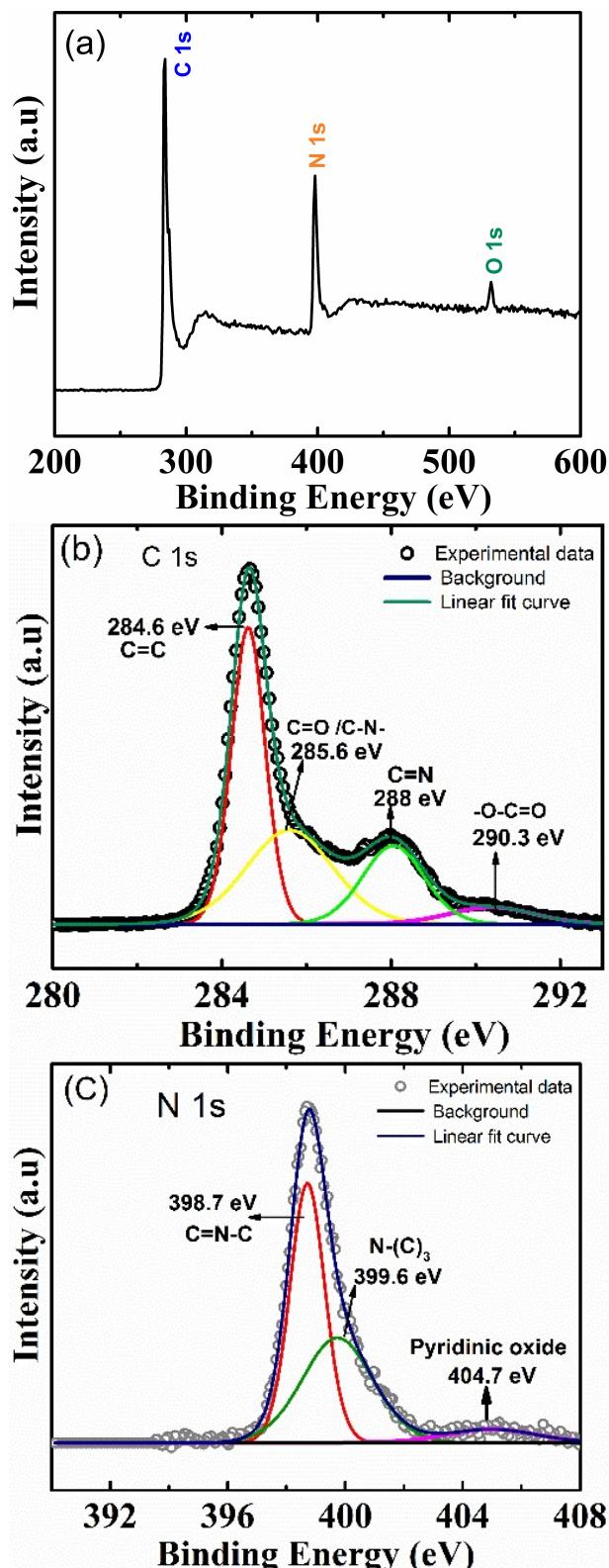


Figure 5: (a) Survey scan and high resolution, (b) C 1s, and (c) N 1s spectra of  $\text{g-C}_3\text{N}_4$ -KBC.

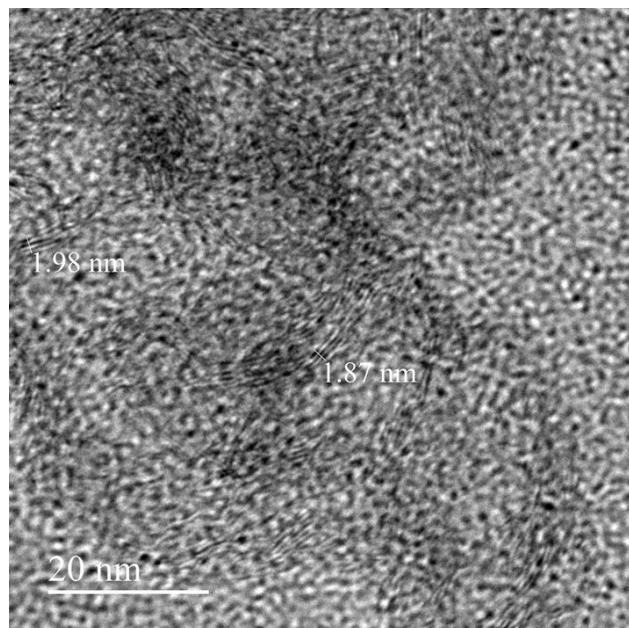


Figure 6: TEM micrograph of  $\text{g-C}_3\text{N}_4$ -KBC.

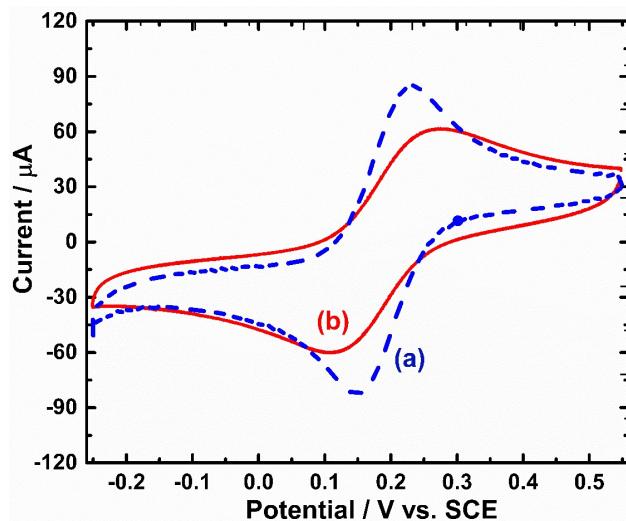
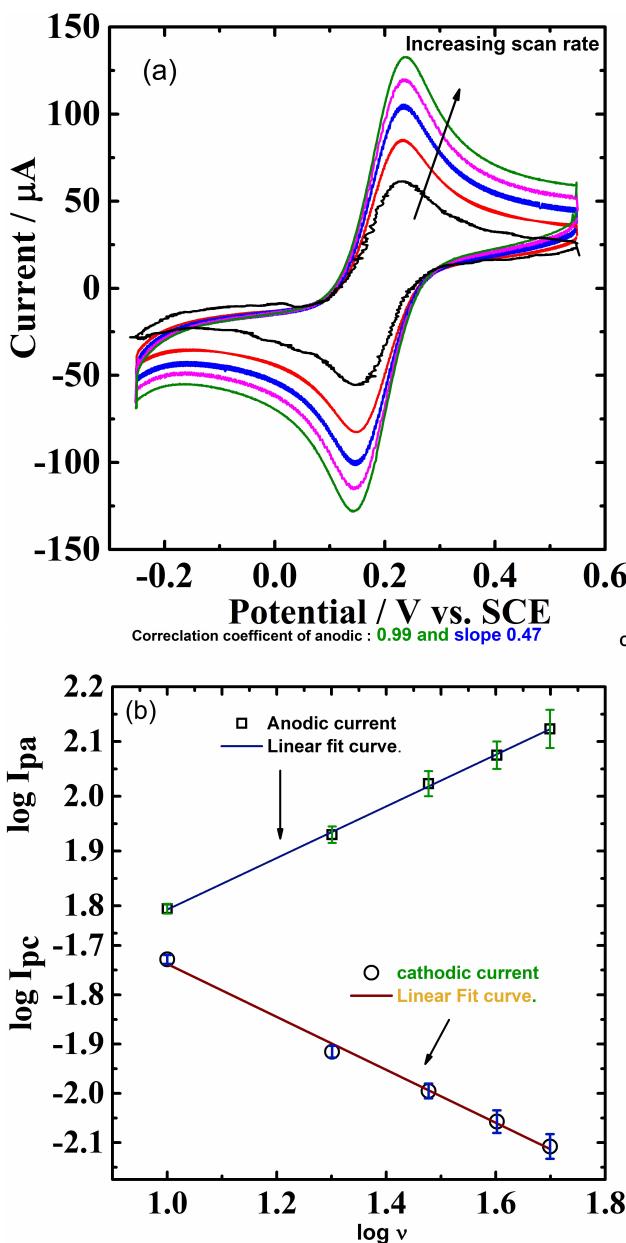


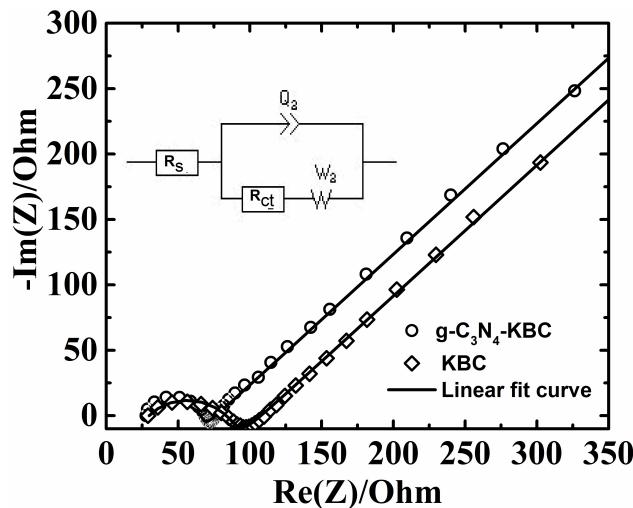
Figure 7: Cyclic voltammogram of (a)  $\text{g-C}_3\text{N}_4$ -KBC and (b) KBC electrodes recorded at 20 mV  $\text{s}^{-1}$  scan rate at 25°C in a solution containing 5 mM of each potassium ferricyanide and potassium ferrocyanide in 0.1M potassium nitrate solution.

cyanide containing electrolyte. In the CV,  $\text{g-C}_3\text{N}_4$ -KBC shows higher redox current values and lower peak-to-peak potential separation ( $\Delta E_p$ ) in comparison to that of the KBC.  $\Delta E_p$  value of  $\text{g-C}_3\text{N}_4$ -KBC is 79 mV, which indicates the close to Nernstian behavior (~59 mV) of the ferro/ferricyanide redox couple on the  $\text{g-C}_3\text{N}_4$ -KBC electrode surface.  $\Delta E_p$  of KBC is around 137 mV indicating quasi-redox behavior of ferro/ferri cyanide. Further, heterogeneous electron transfer rate constant ( $k_s$ ) values



**Figure 8:** (a) Cyclic voltammograms of g-C<sub>3</sub>N<sub>4</sub>-KBC recorded at different scan rates (10-50 mV s<sup>-1</sup>) at 25°C in a solution containing 5 mM of each potassium ferricyanide and potassium ferrocyanide in 0.1 M potassium nitrate solution and (b) log I<sub>p</sub> Vs. log v plot derived from the CVs recorded at different scan rates.

were calculated for g-C<sub>3</sub>N<sub>4</sub>-KBC and KBC using Laviron equation (eq. 1).  $k_s$  value of g-C<sub>3</sub>N<sub>4</sub>-KBC and KBC are 0.3 s<sup>-1</sup> and 0.24 s<sup>-1</sup>, respectively. Muthyal *et al.* [31] have reported a  $k_s$  value of 0.4 s<sup>-1</sup> for graphene nanoflakes. Potassium ferro/ferricyanide redox reaction is an outer-sphere electron transfer reaction. Hence, high  $k_s$  value indicates good electrical conductivity of the electrode surface. As g-C<sub>3</sub>N<sub>4</sub> is a semiconductor, if it is not uniformly supported by KBC, a low  $k_s$  value is expected. Since the  $k_s$  value of g-



**Figure 9:** Electrochemical impedance spectroscopy (EIS) responses of KBC and g-C<sub>3</sub>N<sub>4</sub>-KBC solution containing 5 mM of potassium ferricyanide and potassium ferrocyanide in 0.1 M KNO<sub>3</sub> solution.

C<sub>3</sub>N<sub>4</sub>-KBC is close to that of KBC, we surmise that g-C<sub>3</sub>N<sub>4</sub>-KBC to remain as conducting as KBC.

$$\log k_s = \alpha \log(1 - \alpha) + (1 - \alpha) \log \alpha \quad (1)$$

$$- \log \frac{RT}{nFv} - \frac{\alpha(1 - \alpha)nF\Delta E_p}{2.303 RT}$$

Where  $n$  is the number of electrons involved in electrochemical reaction,  $F$  is the Faraday constant (96486 C mol<sup>-1</sup>);  $k_s$  is the heterogeneous electron transfer rate constant (s<sup>-1</sup>);  $R$  is the gas constant (8.314 J K<sup>-1</sup> mol<sup>-1</sup>);  $v$  is the scan rate (V s<sup>-1</sup>);  $T$  is the absolute temperature and  $\alpha$  is the transfer coefficient (0.5).

Figure 8(a) shows the CVs of g-C<sub>3</sub>N<sub>4</sub>-KBC recorded at different scan rates from 10 mV s<sup>-1</sup> to 50 mV s<sup>-1</sup>. The anodic and cathodic peak currents of g-C<sub>3</sub>N<sub>4</sub>-KBC electrode increase with increase in scan rate ( $v$ ) i.e. follow the Randles-Sevcik equation. In both cases, the obtained correlation coefficient is 0.99, which indicates that g-C<sub>3</sub>N<sub>4</sub>-KBC has unique electronic structure with fast electrode kinetics [32]. A plot of log  $i$  vs. log  $v$  (Figure 8(b)) displays a linear behavior and portrays a gradient of 0.47, which confirms that electroactive behavior of ferro/ferri cyanide at g-C<sub>3</sub>N<sub>4</sub>-KBC electrode is a diffusion controlled process [33].

## 4.2 Electrochemical impedance spectroscopy

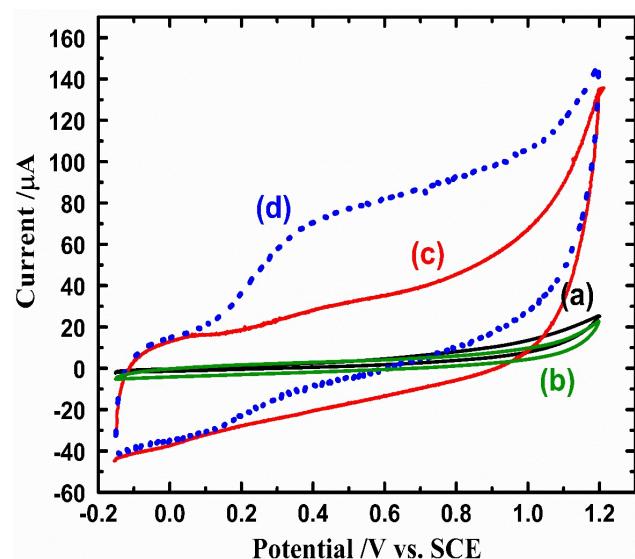
Further, the electron transfer characteristics of g-C<sub>3</sub>N<sub>4</sub>-KBC modified GC electrode and KBC were characterized by EIS at open circuit potential in ferro/ferricyanide containing electrolyte. Figure 9 shows the Nyquist plot, where

a semicircle followed by a linear portion is observed. The semicircle corresponds to charge transfer process, and the linear portion at lower frequencies corresponds to diffusion process. The equivalent circuit used for fitting the experimental EIS data is shown as inset in Figure 9. The charge transfer resistance ( $R_{ct}$ ) of the ferro/ferricyanide redox couple at the electrode surface is quantified from the diameter of the semicircle.  $R_{ct}$  values of  $44\ \Omega$  and  $68\ \Omega$  are observed for  $g\text{-C}_3\text{N}_4$ -KBC and KBC electrodes, respectively. The lower  $R_{ct}$  value of  $g\text{-C}_3\text{N}_4$ -KBC indicates its higher electrocatalytic activity towards ferro/ferricyanide in comparison to that of KBC. Table 1 lists the EIS parameters  $Q$ ,  $R_{ct}$  and  $n^*$ .

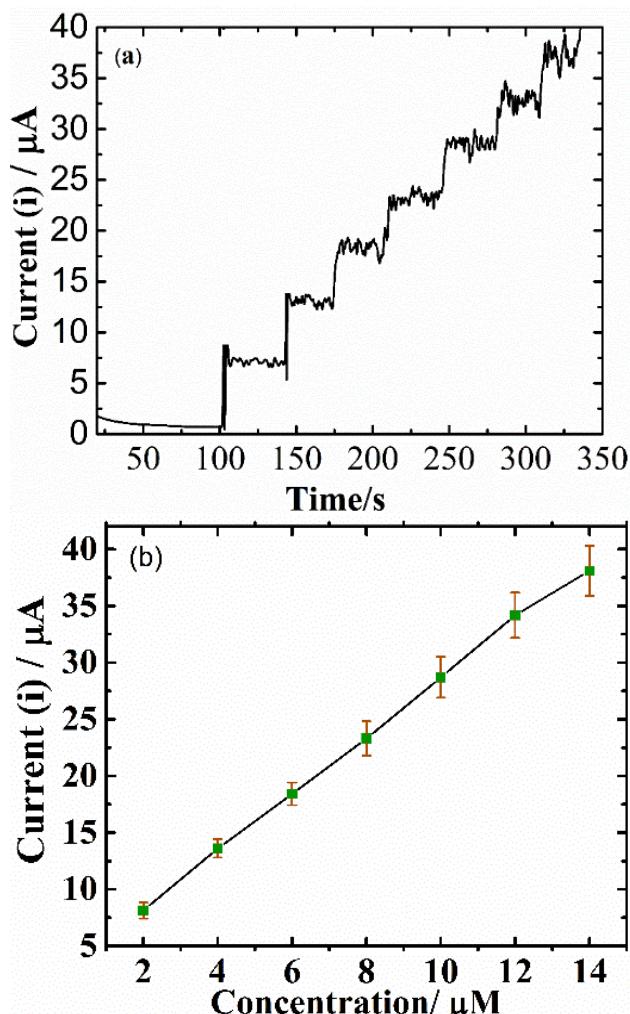
**Table 1:** List of the EIS parameters of KBC and  $g\text{-C}_3\text{N}_4$ -KBC electrodes measured at open circuit potentials.

Electrode name	Charge transfer resistance ( $R_{ct}$ ) / Ohm	Constant-phase-element ( $Q$ ) / $\text{F}\cdot\text{s}^{(n-1)}$	$n^*$
KBC	$68 \pm 2.2$	$0.264 (8) \times 10^{-6}$	0.6
$g\text{-C}_3\text{N}_4$ -KBC	$44 \pm 0.7$	$0.141 (2) \times 10^{-6}$	0.5

Where  $n^*$  = Constant phase element ideality factor associated with the distortion of the capacitance due to electrode surface roughness



**Figure 10:** Cyclic voltammograms of (a) GCE, (b)  $g\text{-C}_3\text{N}_4$ , (c) KBC, and (d)  $g\text{-C}_3\text{N}_4$ -KBC electrodes in  $1\text{ mM N}_2\text{H}_4$  containing PBS ( $\text{pH}=7.0$ ) measured at scan rate  $0.05\text{ V s}^{-1}$  scan rate.



**Figure 11:** (a) Amperometric response of  $g\text{-C}_3\text{N}_4$ -KBC electrode in PBS ( $\text{pH } 7.0$ ) for successive addition of  $2\ \mu\text{M}$  of hydrazine and (b) the corresponding calibration plot of Figure 11(a) obtained using three freshly prepared  $g\text{-C}_3\text{N}_4$ -KBC electrodes.

#### 4.3 Electrochemical oxidation of $\text{N}_2\text{H}_4$

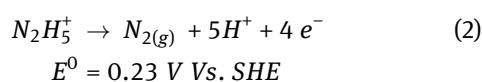
A hydrazine electrochemical sensor was set up using  $g\text{-C}_3\text{N}_4$ -KBC as electrode material. Figure 10 compares the CV profiles of  $g\text{-C}_3\text{N}_4$ -KBC, KBC,  $g\text{-C}_3\text{N}_4$ , and GCE in  $1\text{ mM}$  hydrazine containing PBS solution.  $g\text{-C}_3\text{N}_4$ -KBC showed very low onset potential of about  $0.145\text{ V}$  vs. SCE in comparison to that of the KBC, GCE, and  $g\text{-C}_3\text{N}_4$ . Due to low surface area of the GCE, the double layer current observed in the potential region  $-0.2$  to  $1.2\text{ V}$  is lowest for GCE. Similarly, due to the semiconducting nature of  $g\text{-C}_3\text{N}_4$ , the double layer current is very low for  $g\text{-C}_3\text{N}_4$ /GCE as well.  $g\text{-C}_3\text{N}_4$ -KBC has both electrical conductivity and catalytic activity towards  $\text{N}_2\text{H}_4$ , hence showed lower overpotential towards  $\text{N}_2\text{H}_4$  oxidation and higher double layer current,

**Table 2:** Comparison of  $E_{onset}$ , sensitivity, linear range, and detection limit of different electrode materials towards  $\text{N}_2\text{H}_4$  sensing at pH 7

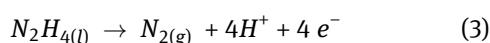
Electrode	$E_{onset}$ / V vs. SHE	Sensitivity / $\mu\text{A}/\text{mM}$	Linear Range / $\mu\text{M}$	Limit of detection (LOD) / $\mu\text{M}$	Reference
MSS-Co(salen)/GCE	0.360	-	10-210	-	[34]
CuS/rGO/GCE	0.326	7.96	1-1000	0.3	[35]
MSS-	0.090	-	10-50	-	[34]
Co(salophen)/GCE					
NPC-2 / GCE	0.200	45.2	1-330	0.47	[22]
WO <sub>3</sub> NPs/Au modified electrode	0.222	0.005	100-1000	144.73	[36]
GCE / Au-MSM	0.206	1.62	500-18000	0.11	[37]
(PANI/Au <sub>0</sub> ) <sub>5</sub> /GCE	0.177	-	10-6000	1	[38]
AuNP-GPE	0.197	-	0.05-25	3.07	[39]
PdHCF-Al	0.872	-	390-10,000	4.6	[40]
GNF/GCE	0.347	0.028	0.5-7.5	0.3	[31]
NiFe <sub>2</sub> O <sub>4</sub> /MWCNTs/GC	0.431	-	5-2500	1.5	[41]
RMWCNT/GCE	0.160	0.065	2-190	0.61	[42]
BiHCF/CC	0.130	-	7-1010	3	[43]
Mn(II)-complex/MWNTs/GCE	0.225	0.038	1-1050	0.5	[44]
Manganese hexacyanoferrate	0.210	0.047	33-8, 180,000	6.65	[45]
Catechin GCE	0.110	0.008	2-58	0.16	[46]
Pd-GG-g-PAM-silica/GCE	0.151	33.26	600-180,000	4.1	[47]
HMWCNT/GCE	0.125	0.020	2-122	0.68	[48]
Graphene/GCE	0.206	-	3-300	1.0	[49]
RGO/GCE	0.550	-	-	-	[50]
PDA-RGO/GCE	0.430	-	0.03-100	0.01	[50]
g-C <sub>3</sub> N <sub>4</sub> -KBC	0.386	2.5	2-14	0.7	This work

which is nearly similar to that of KBC in the potential region  $-0.2$  to  $0$  V.

In comparison to GCE, the current due to hydrazine oxidation observed on KBC was higher due to high surface area of KBC ( $\sim 1400$   $\text{m}^2/\text{g}$ ). The thermodynamic standard potential of hydrazine oxidation is  $0.23$  V.



g-C<sub>3</sub>N<sub>4</sub>-KBC oxidizes  $\text{N}_2\text{H}_4$  at an onset potential close to that of  $E^0$  of  $\text{N}_2\text{H}_4$ . Similar onset potential is reported for hydrazine oxidation on graphene nanoflakes [17]. Eq. 3 shows the overall mechanism involved in  $\text{N}_2\text{H}_4$  oxidation

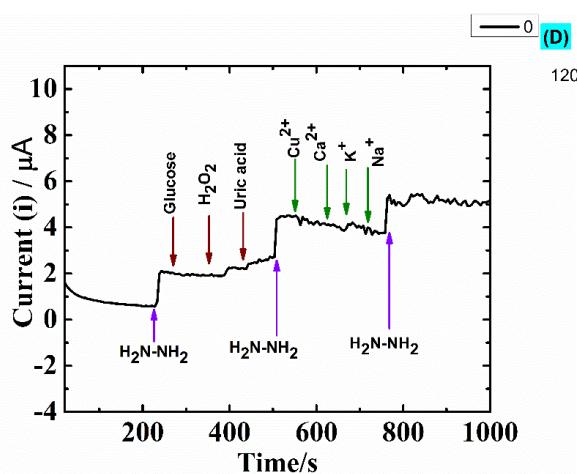


The g-C<sub>3</sub>N<sub>4</sub>-KBC sensor is further characterized using chronoamperometry, to understand its detection limit, sensitivity and signal-to-noise ratio.

Figure 11 (a) portrays the steady-state response obtained for hydrazine oxidation at  $0.35$  V vs. SCE on g-C<sub>3</sub>N<sub>4</sub>-KBC electrode with successive addition of  $2 \mu\text{M}$  hydrazine in PBS. A calibration plot was made (Figure 11(b)) plotting the steady-state current against the concentration of the  $\text{N}_2\text{H}_4$ . This plot shows a good linear fit in the concentration range of  $2 \mu\text{M}$  to  $14 \mu\text{M}$  with a correlation coefficient of  $0.99$ . The sensitivity and limit of detection were  $2.5 \mu\text{A}/\mu\text{M}$  and  $0.7 \mu\text{M}$  respectively, with a signal-to-noise (S/N) ratio of  $3$ . In the literature, most of the hydrazine sensors reported are based on transition metal-based catalysts. There are few reports using carbon materials such

as graphene nanoflakes, graphene oxide, and carbon nanotubes. Table 2 compares the sensitivity, linear range, and limit of detection of various materials reported in the literature.

Selectivity plays a vital role in sensor characterization. Real samples contain many species along with  $\text{N}_2\text{H}_4$  which could probably respond in the same potential region as  $\text{N}_2\text{H}_4$ . Most common interferences are  $\text{H}_2\text{O}_2$ , uric acid, glucose,  $\text{Cu}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{K}^+$ , and  $\text{Na}^+$ . Although  $\text{Cu}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{K}^+$ , and  $\text{Na}^+$  cannot be oxidized further, they may interfere in the kinetics of the hydrazine oxidation on  $\text{g-C}_3\text{N}_4$ -KBC (Figure 12). 20  $\mu\text{M}$  hydrazine was used in this study and 3-times more of glucose, uric acid and  $\text{H}_2\text{O}_2$  were injected and found not to interfere with  $\text{N}_2\text{H}_4$  sensing. Similarly,  $\text{Cu}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{K}^+$ , and  $\text{Na}^+$  are injected at 60  $\mu\text{M}$  concentration and found not to interfere with  $\text{N}_2\text{H}_4$  sensing. This experiment demonstrated the high selectivity towards  $\text{N}_2\text{H}_4$  sensing on  $\text{g-C}_3\text{N}_4$ -KBC.



**Figure 12:** Amperometric response of  $\text{g-C}_3\text{N}_4$ -KBC in a PBS solution containing 20  $\mu\text{M}$   $\text{N}_2\text{H}_4$  and three-fold concentration of different interfering species hydrogen peroxide, uric acid,  $\text{Na}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{K}^+$ , and glucose.

## 5 Conclusions

Pyrolysis of melamine leads to formation of  $\text{g-C}_3\text{N}_4$ . Formation of  $\text{g-C}_3\text{N}_4$  was confirmed using XRD, FT-IR, CHN, XPS, LDI-FT-ICR-MS and TEM studies. This work demonstrates the  $\text{N}_2\text{H}_4$  sensing property of  $\text{g-C}_3\text{N}_4$ -KBC. It oxidizes  $\text{N}_2\text{H}_4$  at an onset potential closer to that of the thermodynamic oxidation potential of  $\text{N}_2\text{H}_4$ . Using chronoamperometry, the detection limit, linear range, sensitivity,

and signal-to-noise ratio were measured.  $\text{g-C}_3\text{N}_4$ -KBC exhibited a detection limit of 0.7  $\mu\text{M}$  with a sensitivity of 2.5  $\mu\text{A}/\mu\text{M}$ . In this study, the amperometric response of the interfering electroactive species such as  $\text{Ca}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{K}^+$ ,  $\text{Na}^+$ , glucose, uric acid, and  $\text{H}_2\text{O}_2$  were examined and found not to interfere with  $\text{N}_2\text{H}_4$  sensing.

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