Effect of Graphite oxide and Exfoliated Graphite oxide for the electrochemical determination of dopamine: A Voltammetric study

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5.1. Introduction

In the present work, Graphite oxide (GO) was prepared by modified Hummer’s and Offemam method from graphite and exfolited by sonication to get Exfolited Graphite oxide (E-GO). The resulting nanomaterials were characterized using X-ray diffraction (XRD), scanning electron microscopy (SEM) and infrared absorption spectroscopy (IR). Then the electro catalytic behaviour of GO and E-GO nanoparticles modified carbon paste electrode towards dopamine (DA), uric acid (UA) and folic acid (FA) has been investigated by electrochemical techniques. Electrochemical results revealed that the oxidation peak currents obtained at the E-GO modified carbon paste electrode are much higher than those at the GO and bare carbon paste electrode electrodes, which might be ascribed to the good conductivity of E-GO. Electrochemical parameter, heterogeneous rate constant also calculated for GO and E-GO as different sweep rate. Due to large peak separation and good sensitivity of the electrode response it allows E-GO modified CPE electrode to analyze the DA individually and also simultaneously in presence of excess of UA and FA.

5.2. Chemistry and Biological Relevance of Dopamine and Uric acid

The chemistry and biological relevance of dopamine and ascorbic acid has been explained in details in chapter 2 (part A) section 2.2 and 2.4.

5.3. Review of Graphite oxide and ZnO

Graphite oxide (GO) is a two-dimensional plane prepared almost 150 years ago [1] and it is typically made by using strong oxidants [1-4]. During reaction, the graphite not only derivatized with oxygen-containing groups but also torn up into smaller pieces. But as a result of sonication, the graphite oxide was exfoliated this leads to the formation of multilayers to single layer graphene oxide, which may vary from synthesis to synthesis [5]. It has been suggested that, in GO each graphite layer of carbon is embedded with oxygen containing functional groups such as epoxy and keto groups across the basal plane, the phenolic and carboxyl group at the edges [6]. The unique properties of large surface area, excellent conductivity, good chemical stability and easy fabrication, it has been the ideal material in a variety of material sciences [7], electronic devices [8-9] sensors and electrocatalysis [10-12]. Due to their strong hydrophilicity and electrostatic repulsion effects, carboxylic acid groups attached to GO could ionize in water, resulting in minor GO sheets have carboxylic ions containing negative charges. Which make it exhibit uniform films also good electroanalytical
performance better than other carbon based nanomaterials [13]. Recently, Banks et al. reported that enhanced electron transfer of graphene occurs at its edge and the presence of oxygen-containing groups at its edges can influence the adsorption/desorption of molecules that takes place before and after an electrochemical reaction [14].

DA is an important neurotransmitter in the mammalian central nervous system. The quantitative determination of DA in human physiological fluids is very important in both biochemical and clinical diagnosis. Among the catecholamines, DA detection has attracted much interest because a change in DA levels in the body is a very effective route towards the understanding of brain functions, such as learning, memory formation, the physiological and pathological process of Parkinson’s disease [15]. Thus various commonly used analytical methods for DA and its analogs have been developed in the past. Methods for the detection of DA include Chemiluminescence [16], Fluorimetry [17] and Capillary Electrophoresis [18]. These methods are very sensitive. All of these techniques, however, require a compressing system, temperature controlling systems, separation systems, and other spectrophotometric or electric detection systems. Recently, there has been an increasing demand for more sensitive and simple analytical methods. Voltammetric techniques are very useful and popular for trace analysis, since these techniques are compact, efficient, and sensitive [19].

Uric acid (2,6,8–trihydroxypurine, UA), a major nitrogenous compound in urine, is a product of purine metabolism in human body and its higher levels leads to many clinical disorders like gout, kidney and cardiac problems [20]. Many epidemiological studies have suggested that elevated serum UA is also a risk factor for cardiovascular disease [21]. Hence, to explore a simple, accurate and reliable method for the determination of uric acid became an urgent need. Electrochemical methods were commonly accepted as the fastest analytical assay compared with traditional spectroscopic [22], Chemiluminescence [23-24], Chromatographic [25], Spectrofluorometric [26], Colorimetric [27-28], Electrophoretic [29-30] and Enzymatic approach [31] methods. They have been reported for the analysis of UA in the human body fluids, but these methods are often time consuming, inherently expensive or complicated.

Folic acid and derivatives that occur in nature, that are required in the single-carbon metabolism such as amino acid and nucleic acid biosynthesis [32] as well as in cell division and growth. This vitamin is essential for rapid cell growth like blood production, especially during pregnancy. The deficiency of FA is a common cause of anemia and is thought to increase the shells of heart attack and stroke. Many studies suggest that diminished folic acid
status is associated with enhanced carcinogenesis, as FA, along with vitamin B-12, participates in nucleotide synthesis, cell division, and gene expression [33]. Per conceptual supplementation of FA has been demonstrated to significantly reduce the incidence and reoccurrence of neural tube defects, such as spina bifida of women [34]. There are various methods available for the determination of FA, which include liquid chromatography, [35] high performance liquid chromatography [36], flow-injection Chemiluminometry [37] and Spectrophotometric method [38]. As FA is an electroactive component, some electrochemical methods have been reported for its determination [39]. Compared with other techniques, the electrochemical method is more desirable because of its convenience and low cost.

Carbon paste electrode has been widely used in determination of drugs, vitamins and other species because of its specific properties like easy preparation, wider potential window and 10 times lower residual currents than those of the glassy carbon electrodes [39]. To enhance the selectivity and sensitivity different modifiers have been incorporated in Carbon paste electrode [40-43]. In this study, carbon past electrode were modified by GO and exfoliate GO to obtain good selectivity and sensitivity towards the electrochemical detection of DA in physiological pH.

5.4. Experimental

5.4.1. Materials and Stock solution

Dopamine hydrochloride (DA), uric acid (UA), folic acid (FA), disodium hydrogen phosphate (Na$_2$HPO$_4$), sodium dihydrogen orthophosphate (NaH$_2$PO$_4$) and silicon oil were purchased from Himedia chemicals. Sodium hydroxide (NaOH), perchloric acid (HClO$_4$), potassium chloride (KCl) and graphite powder were purchased from Merck chemical. Stock solutions of DA were prepared in 0.1M perchloric acid, UA and FA in 0.1M NaOH respectively. All chemicals are of analytical grade quality and were used without further purification. Phosphate buffer (pH-7) was prepared as per the literature with 0.2 M NaH$_2$PO$_4$ and Na$_2$HPO$_4$ solution in double distilled water. The preparation of Graphite oxide (GO) was carried out using a harsh oxidation using the Hummers method as described in previous literature [2]. Then GO powder was dispersed in double distilled water and sonicated to exfoliate the Graphite oxide (E-GO). A feasible mechanism of synthesis of GO and E-GO shown in Scheme. 5.1.
5.4.2. Apparatus

X-ray diffraction (XRD) pattern of Graphite and GO sample are obtained using PHILIPS PW3710 diffractometer (Cu, $\text{K}_{\alpha}$ radiation) with a step scan at 0.2°. Fourier transformed infrared (FT-IR, Perkin-Elmer) spectra in KBr pellet were recorded to detect the functional group of GO and E-GO. Field emission scanning electron microscope (FE-SEM-supra 40VP, Carl Zees) were also obtained for the Graphite, GO and E-GO are used for knowing micro structure and energy dispersive X-ray (EDX) analysis are also measured for elemental composition of E-GO.

All electrochemical experiments were performed using CH instrument model 660c. A conventional three electrode system was used for all electrochemical experiments, which comprise a bare or modified CPE (GO/E-GO) as a working electrode. Potentials were measured using auxiliary electrode and saturated calomel as a reference electrode. All voltammetric curves were recorded at room temperature.

5.4.3. Preparation of bare CPE and modified CPE

The bare CPE was prepared by grinding 70:30 ratio of graphite powder and silicone oil in an agate mortar. The pestle was used to obtain a homogeneous paste. A portion of the resulting homogeneous paste was packed into the cavity of a Teflon tube and polished using smooth paper. Bare CPE was modified by adding (0, 2, 4, 6, 8 & 10) mg GO/E-GO to the above mentioned graphite powder and silicon oil mixture.

5.5. Results and discussion

5.5.1. Characterization

Fig. 5.1(a) shows a typical XRD pattern for Graphite and Graphite oxide (inset). The interlayer distance changes after the oxidation of graphite and it was calculated based on 2θ position by using Bragg’s law. During oxidation process the functional groups such as carboxyl group and epoxy attached to the precursor graphite, these inter layer spacing of Graphite shift 1.3 Å to 11.2 Å (GO). The small inter layer spacing of graphite suggest a dense packing when compared to the GO, but the peak intensity for GO was reduced significantly. These results indicate that most of the GO layer exfoliated randomly while a small position of the sample still remained as layered structure. But sonication effect leads to exfoliates the more GO and this corroboration was shown in FESEM image, discussed below.
The FT-IR spectra of (a) GO and (b) E-GO was ground with KBr and pelletized. Oxidation involves several content of oxygen related functional groups shown in Fig. 5.1(b). A broad band at 3432 cm\(^{-1}\) is attributed to the stretching frequency of O–H bond and the band at 1730 cm\(^{-1}\) is due to stretching of the C=O bond of carbonyl or carboxyl group situated at the edges of GO sheets. The peak at 1623 cm\(^{-1}\) is due to aromatic C=C bond and peak at 1050 cm\(^{-1}\) is due to the epoxy (–O–) groups [44].

The morphological changes upon sonication and exclusive of sonication are analyzed by FESEM. The Fig. 5.2 (a) shows the image of graphite powder which clearly demonstrated the flat surface and stacked structure and the graphite oxide exhibits random wrinkled layer structure seen in Fig. 5.2 (b). This indicates the ordered layer structure in pristine graphite has been disrupted due to the oxidation. Upon sonication of graphite oxide for 2.5 hours the GO exfoliate and the interlayer distance increased tremendously can be clearly observed in 5.2(c). The EDX spectra shown in Fig. 5.2(d) C and O peaks and there are no other elemental impurities.

5.5.2. Optimization of modifiers at bare CPE

To investigate the effect of the amounts of modifiers (GO and E-GO) on the electrode response and to find the optimum amount some electrodes containing 0, 2, 4, 6, 8, 10 mg were prepared. The cyclic voltammograms were recorded for both the (GO/E-GO) modified electrode at sweep rate of 50 mVs\(^{-1}\) under identical conditions. The Fig. 5.3 (a) shows the plot of anodic peak current verses different amounts of modifier. With increasing the amounts of modifier anodic peak current increased and however, above 3 mg increasing the amount leads to undesirable properties, which correspondingly decreased the electron transfer rate. The Fig. 5.3 (b) shows the similar properties but the bare CPE enclose GO shows slight decrease in the anodic peak current due to less exfoliation of GO. Consequently, for both the modifiers the electrode comprising 4 mg (GO and E-GO) in the bare CPE is more active and it was chosen as optimum amount.

5.5.3. Electrochemical response of DA, UA and FA at bare CPE and modified CPE.

The Fig. 5.4 shows the cyclic voltammograms obtained for 0.02mM DA at the bare CPE (curve a), GO/modified CPE (curve b) and E-GO/modified CPE (curve c) in 0.2 M phosphate buffer solution at pH 7.0. The peak separation potential ΔE\(\text{p} = \text{E}\text{p}_a - \text{E}\text{p}_c\) for
curve a, b and c was found to be 49, 42 and 51 mV respectively this indicates the rate of reaction is fast and reversible electron transfer takes place. Under same condition the anodic peak current for curve a, b and c was increased significantly we can observe that for curve c there was increase in anodic peak current compare to curve b due to the high conductivity of E-GO. The DA which exists as cation in physiological pH gets fascinated towards the electrode surface and possibly because of the effect of this attraction, the amount of DA reaching onto the electrode surface is increased which may account for the increased peak currents at GO/modified CPE. Moreover, the DA molecules penetrate through the interlamellar space of negatively charged GO and E-GO [45]. The detailed oxidation mechanism of DA at modified electrodes was shown in scheme 5.2(a) [46].

The electrochemical response of UA (0.06 mM) and FA (1 mM) were studied in 0.2 M phosphate buffer at pH 7.0. Both, UA and FA shows irreversible electron transfer at these electrodes. Fig. 5.5 shows the anodic peak potential of UA at bare CPE (curve a), GO/modified CPE (curve b) and E-GO/modified CPE (curve c) were observed at 302 mV, 287 mV and 290 mV respectively. At both modified CPE’s anodic peak potential shifted towards negative direction. The Fig. 5.6 shows the anodic peak potential of FA at bare CPE (curve a), GO/modified CPE (curve b) and E-GO/modified CPE (curve c) were observed at 671 mV, 665 mV and 685 mV respectively and showed the increase in electrocatalytic effect of the modified CPE is compared to bare CPE. The proposed oxidation mechanism of UA and FA at modified CPE was shown in scheme 5.2(b and c) [47-48].

5.5.4. Effect of sweep rate

The effect of sweep rate for DA in phosphate buffer solution at pH 7.0 was studied by CV at modified CPE prepared from GO and E-GO nanoparticles. Fig. 5.7(A) and (B) shows an increase in the redox peak currents at a sweep rate of 0.05–0.38 V s⁻¹ for modified CPE’s of GO and E-GO nanoparticles respectively. The graph obtained exhibited good linearity between the square root of the sweep rate and the redox peak currents for the modified CPE prepared with the GO and E-GO nanoparticles, with correlation coefficients of r² = 0.999 and 0.999. These results indicate that overall electrode process is controlled by diffusion process. According to an equation previously reported [49] for determining the value of heterogeneous rate constant (k⁰) from experimental peak potential difference (∆Ep) values, equation (1) was a valid approximation of such curves for ∆Ep greater than 10 mV.

\[ ∆Ep = 201.39 \log \left( \frac{v}{k^0} \right) - 301.78 \]  

………………..(1)
From the experimental $\Delta$Ep values as shown in Table 5.1 the values of the $k^0$ for the DA oxidation was determined for GO and E-GO modified CPE. The value of $k^0$ obtained at a sweep rate of 0.05 V s$^{-1}$ for both GO and E-GO modified CPE exhibits generously proportioned heterogeneous rate constant, all the parameters are tabulated in Table 5.1.

In the same way effect of sweep rate for UA and FA was studied by CV at E-GO modified CPE. The E-GO modified CPE showed with increase in sweep rate 0.05–0.38 V s$^{-1}$ the anodic peak current increases (Fig. 5.8 and 5.9). The graph obtained was good linearity between the sweep rate and anodic peak current and anodic peak current were proportional to the sweep rate for both UA and FA. The correlation coefficient for the UA was $r^2 = 0.991$ and 0.996 for FA with indicate the electrode reaction was adsorption controlled for the modified CPE prepared with E-GO.

### 5.5.5. Effect of concentration at E-GO Modified CPE

In order to obtain a much more sensitive peak current, Differential pulse voltammetry (DPV) shows better resolution than cyclic voltammetry, and it was employed in the trace level detection of DA, UA and FA. In the DPV mode background current is negligible leading to more accurate measurements. The Fig. 5.10 (a) shows, as the concentration of DA increases the peak current also increases, and the concentration of DA was varied from 0.5-20 µM in phosphate buffer solution at pH - 7.0. Fig. 5.10 (b) shows the graph of anodic peak current versus concentration of DA shows two linear relationship ranges of $0.5 \times 10^{-6}$M to $1.5 \times 10^{-6}$M and $2 \times 10^{-6}$M to $20 \times 10^{-6}$M with linear regression equation of $I_{pa} (\mu A) = 0.933 C(\mu M/L) + 1.49 \times 10^{-6}$ and $I_{pa} (\mu A) = 0.275 C(\mu M/L) + 2.17 \times 10^{-5}$, respectively. The correlation coefficient for the first linearity was 0.986, and that for the second was 0.996.

In the same way the concentration of UA varied from $3 \times 10^{-6}$M to $1 \times 10^{-5}$ M shown in Fig. 5.11 (a). The corresponding graph of anodic peak current versus concentration of UA shows two linear relationships (Fig. 5.11 (b) ranges of $3 \times 10^{-6}$M to $4 \times 10^{-6}$M and $5 \times 10^{-6}$M to $1 \times 10^{-5}$M with linear regression equation of $I_{pa} (\mu A) = 0.465 C(\mu M/L) + 1.926 \times 10^{-6}$ and $I_{pa} (\mu A) = 0.312 C(\mu M/L) + 2.055 \times 10^{-5}$, respectively. The correlation coefficient for the first linearity was 0.997, and that for the second was 0.981.

The concentration of FA varied from $1 \times 10^{-6}$M to $9 \times 10^{-6}$M shown in Fig. 5.12 (a). Above 9 µM increasing the folic acid concentration induces further reduction in the peak (that is anodic peak will disappear). This phenomenon was due to the presence of amine group on one ring in the folic acid structure that could be adsorbed onto the E-GO modified CPE. These
findings indicate E-GO modified CPE is a suitable for the detection of folic acid at trace levels in the range of $1 \times 10^{-6}$M to $5 \times 10^{-6}$M. The corresponding graph of anodic peak current versus concentration of FA shows two linear relationships (Fig. 5.12(b) ranges of $1 \times 10^{-6}$M to $5 \times 10^{-6}$M and $6 \times 10^{-6}$M to $9 \times 10^{-6}$M with linear regression equation of $I_{pa}$ (µA) = $0.094 C$(mM/L) + $1.401 \times 10^{-5}$ and $I_{pa}$ (µA) = $0.032 C$(mM/L) + $2.136 \times 10^{-5}$, respectively. The correlation coefficient for the first linearity was 0.997 and that for the second was 0.981. The detection limit for DA, UA and FA in the lower concentration linear range region was found to be 0.031µM, 0.21µM, and 0.57 µM for E-GO modified CPE and was calculated [50]. The resultant LOD of this study are comparable to the values reported previously, with their comparison tabulated in Table 5.2.

5.5.6. Simultaneous measurements of DA, UA and FA

The Fig. 5.13 shows the cyclic voltammograms obtained for the electrochemical response of DA (0.02 mM), UA (0.06 mM) and FA (1mM) at bare CPE (curve a) and E-GO/modified CPE (curve b) in 0.2 M phosphate buffer solution of pH 7.0. The utilization of the modifier (E-GO) showed the 3 well-distinguished anodic peaks at potentials of 162, 323, and 674 mV for DA, UA and FA with enhancement in the peak currents. The electrochemical peak to peak separation of between DA and UA is 161 mV and for UA and FA is 351. This results were large sufficient to identify DA in the presence of UA and FA at E-GO/modified CPE.
5.6. Conclusion

- The carbon paste electrode was modified with GO and E-GO for the electrooxidation of DA, UA and FA and their mixtures by electrochemical methods.

- The results show that the oxidation of DA, UA and FA was catalyzed at physiological pH and the peak potential of these analytes is shifted to a less positive potential at the surface of the GO and E-GO modified CPE’s.

- The value of heterogeneous rate constant obtained at 0.05 V s\(^{-1}\) for the E-GO modified CPE exhibits a larger heterogeneous rate constant compared with other sweep rate variation.

- The prepared modified CPE shows low detection limit compared with the previous literatures and these results indicate that these GO and E-GO nanoparticles is scientifically interesting. This method has good potential for use in sensors and other electrochemical applications.
Fig. 5.1(a). Powder XRD pattern of Graphite and Graphite oxide (inset).

Fig. 5.1(b). FT-IR spectra of (a) GO and (b) E-GO.
Fig. 5.2. SEM image of the powdered (a) Graphite, (b) GO and (c) E-GO sample and the EDX spectra.

Fig. 5.3. Graph of Ipa vs. quantity of (a) GO and (b) E-GO in carbon paste electrode.
Fig. 5.4. Cyclic voltammograms of 0.02 mM DA at the bare CPE (curve a), GO (curve b) and E-GO (curve c) in 0.2 M phosphate buffer solution at pH 7.0 with sweep rate 0.05 V s⁻¹.

Fig. 5.5. Cyclic voltammograms of 0.06 mM UA at the bare CPE (curve a), GO (curve b) and E-GO (curve c) in 0.2 M phosphate buffer solution at pH 7.0 with sweep rate 0.05 V s⁻¹.
**Fig. 5.6.** Cyclic voltammograms of 1 mM FA at the bare CPE (curve a), GO (curve b) and E-GO (curve c) in 0.2 M phosphate buffer solution at pH 7.0 with sweep rate 0.05 V s\(^{-1}\).

**Fig. 5.7.** Cyclic voltammograms of 0.02 mM DA at (A) GO modified CPE (B) E-GO modified CPE in 0.2 M phosphate buffer solution at pH 7.0 with sweep rate variation (0.05 – 0.38 V s\(^{-1}\)).
Fig. 5.8. Cyclic voltammograms of 0.06 mM UA at E-GO modified CPE in 0.2 M phosphate buffer solution at pH 7.0 with sweep rate variation (0.05 – 0.38 Vs\(^{-1}\)).

Fig. 5.9. Cyclic voltammograms of 1 mM FA at E-GO modified CPE in 0.2 M phosphate buffer solution at pH 7.0 with sweep rate variation (0.05 – 0.38 Vs\(^{-1}\)).
Fig. 5.10. (a). Differential pulse voltammograms for different concentrations of DA (a-r; ) at E-GO modified CPE 0.2 M phosphate buffer solution. (b) Graph of anodic peak current vs. concentration of DA.

Fig. 5.11. (a). Differential pulse voltammograms for different concentrations of UA (a-o; ) at E-GO modified CPE 0.2 M phosphate buffer solution. (b) Graph of anodic peak current vs. concentration of UA.
**Fig. 5.12.** (a). Differential pulse voltammograms for different concentrations of FA (a-i:) at E-GO modified CPE 0.2 M phosphate buffer solution. (b) Graph of anodic peak current vs. concentration of FA.

**Fig. 5.13.** Cyclic voltammograms for mixture of DA (0.02 mM), UA (0.06 mM) and FA (1mM) at bare CPE (curve a) and E-GO/modified CPE (curve b) in 0.2 M phosphate buffer solution of pH 7.0.
Scheme. 5.1. A feasible mechanism of synthesis of GO and E-GO.

Scheme. 5.2. A feasible schematic illustration of the catalysis of (a) DA, (b) UA, (c) FA.
Table. 5.1. Variation of some of the parameters derived from Fig. 5.7, heterogeneous rate constant ($k^0$) as a function of potential sweep rate.

<table>
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<tr>
<th>$v$ (mVs$^{-1}$)</th>
<th>$\Delta Ep$ (mV) for GO and E-GO</th>
<th>$k^0$ (s$^{-1}$) for GO and E-GO</th>
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<td>E-GO</td>
<td>GO</td>
</tr>
<tr>
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<td>63</td>
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Table. 5.2. Comparison of detection limits of DA, UA, and FA of E-GO Modified CPE with other working electrode.

<table>
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<th>Analyte</th>
<th>Electrode</th>
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<th>Detection limit (M)</th>
<th>References</th>
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<td>DA</td>
<td>SWCNT/GCE</td>
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<td>MC/GCE</td>
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<td>[52]</td>
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<td>F-MWCNT/GCE</td>
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<td>[53]</td>
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<td>CNT-TN/CPE</td>
<td>$1.0\times10^{-7}$ to $8.0\times10^{-5}$</td>
<td>$3.0\times10^{-8}$</td>
<td>[54]</td>
</tr>
<tr>
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<td>E-GO/MCPE</td>
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<td>Present Work</td>
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<tr>
<td>UA</td>
<td>Helical CNT/GCE</td>
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<td>Graphene/GCE</td>
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5.7. References

