



Electrochemical Behaviour of Dopamine on A Glassy Carbon Electrode Modified by Graphene Chitosan Copper Composite

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ABSTRACT

Graphene is a hexagonal honeycombed network of carbon atoms arranged in a single layer which is the fundamental building block of all graphitic materials. The novel properties associated with graphene offer many advantages for electrochemical applications. The present work aims at preparing graphene copper chitosan composite for the voltametric determination of the most prominent catechol amine dopamine. Modified Hummers method was followed for Graphite oxide (GO) preparation. GO and $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ were brought into an aqueous solution, to this chitosan was added which was refluxed and subsequently reduced to obtain the required graphene –copper composite. The composite was characterized structurally and morphologically by XRD, SEM and it was used for modifying a glassy carbon electrode. The modified electrode was used for sensing dopamine by CV and DPV. The effect of scan rate and pH on the performance of modified glassy carbon electrode was evaluated. The fabricated electrode was also evaluated for the simultaneous determination of dopamine and uric acid. This electrochemical sensor was found to be most sensitive and reliable at the physiological pH 7.

Keywords: Graphene-Copper composite, electrochemical sensor, Dopamine

INTRODUCTION

Dopamine (DA) plays an important role in human body as a neurotransmitter in the central nervous system¹. The biochemistry of DA points to the facts that several diseases such as Schizophrenia, Parkinsonism and Huntington¹¹ are caused by abnormal levels of DA². Levels of

Uric acid (UA) which is the primary metabolic product of human body is in milli molar and micro molar levels in urine and serum respectively³. Monitoring the levels of these compounds is has been the target of many researchers. The studies on the electrochemistry of DA are helping us to understand its physiological functions and action mechanism in human body⁴. Different methods

like capillary electrophoresis, chromatography, fluorometry, chemiluminescence etc. are available for the detection of these molecules. But electro analytical techniques are more acceptable due to low cost, fast response, portable nature and easy fabrication of the sensor for the detection of these electro active species. The most challenging problem in the detection arises mainly due to overlapping of voltammetric signals at many of the solid electrodes and that can be addressed by modifying the working electrode for obtaining well resolved signals. Many modifiers such as polymers, metal oxides and metal complexes have been effectively used together with carbon based materials⁵⁻⁹. Graphene a single layer of hexagonal close packed honey comb crystal lattice is being extensively used in various fields such as electronics, optical, magnetic, biological, medicine, energy storage, catalysis etc. Graphene is being widely used in sensor applications due to its exceptional properties such as theoretical specific surface area, high values of Young's modulus, excellent thermal conductivity and amazing intrinsic mobility¹⁰. Chitosan (CHI) is an amino-polysaccharide. The novel CHI-metal based materials find many applications in the fields of environmental science and technology, catalysis, medicine and

engineering for the development of biosensors. For many years, Cu and Cu-based electrodes have been used extensively as anodes in electrooxidation of organic compounds¹¹⁻¹⁵. In the present work we aim at preparing Graphene Chitosan–Copper (GN-Cu) composite and using it for the voltammetric determination of dopamine (DA).

EXPERIMENTAL

MATERIALS AND METHODS

Analytical grade chemicals were used for the present study. Chemicals used for this work were graphite powder, potassium permanganate powder, conc. sulphuric acid, conc. phosphoric acid, 30% H_2O_2 , HCl, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, Acetic acid, Ascorbic acid, Sodium hydroxide, Hydrazine, Chitosan methanol, etc. All the prepared samples were analyzed by PXRD, SEM. Cyclic voltammetry (CV) and differential pulse voltammograms (DPVs) were recorded using CHI 604D electrochemical analyzer, in a conventional three-electrode cell. A platinum wire served as the counter electrode. The reference electrode was Ag/AgCl. The glassy carbon electrode (GCE) modified with the composite as working electrode. The study was conducted at room temperature.

Synthesis of graphene – copper composite

Modified Hummers method was followed for Graphite oxide (GO) preparation¹⁶. An aqueous solution of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ and graphite oxide (GO) was made by dissolving in double distilled water. This solution was added drop wise to a solution of chitosan. Reflux with stirring for 20 min. at 120 °C and added 0.05 M ascorbic acid. Then 0.6 M NaOH solution was added with stirring. Stir for another 30 minutes and then added N_2H_4 and continue stirring for 30 min. more for completion of the reaction and mixture is allowed to cool to room temperature. The solution was centrifuged and washed to obtain pure graphene (GN) Cu-NPs

Fabrication of working electrode

Alumina slurry was used to polish the bare GCE followed by ultrasonication. The dispersion of the composite in methanol was prepared and sonicated for two hours, and 6 μl of the composite suspension was drop casted on the surface of GCE and dried in air.

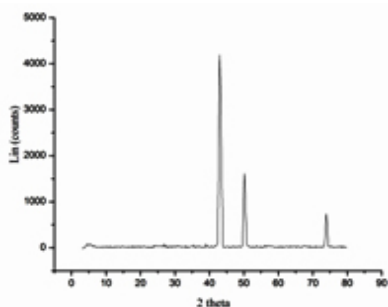


Fig. 1: (A). XRD of GO

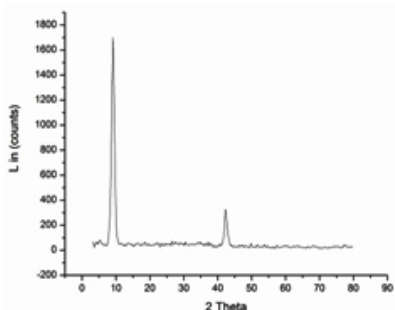


Fig.1: (B). XRD of GN-Cu composite

RESULTS AND DISCUSSION

Characterization

Fig 1A shows the XRD of GO, the 2θ peak at 11.7° corresponds to an interlayer distance of 7.6 Å. The XRD of (Fig 1B) GN-Cu nano composite does not have a peak around 10° indicating

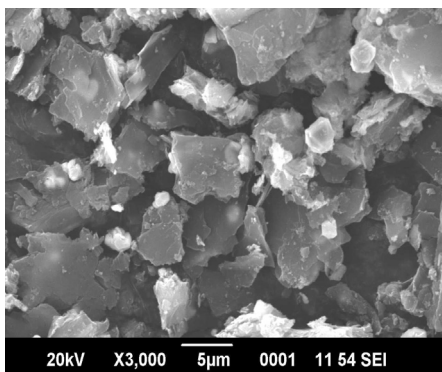


Fig. 2: SEM image of GN-Cu composite

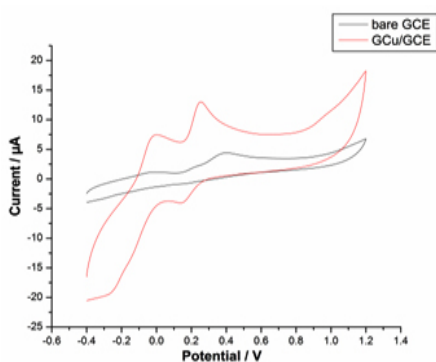


Fig. 3: CV recorded at bare GCE and GN-Cu modified GCE at pH 7 in 0.1M PBS containing DA

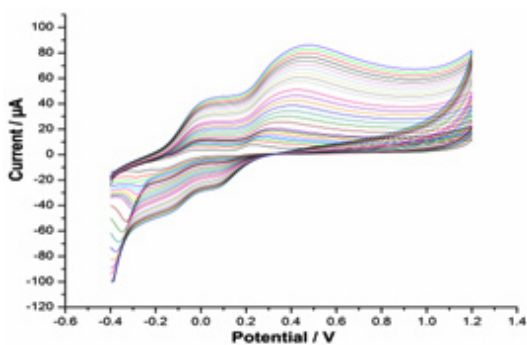


Fig. 5: CVs of 0.2mM DA in 0.1M PBS (pH7) at GN-Cu/GCE, recorded at different scan rates

successful reduction of GO¹⁶. Composite shows characteristic diffraction peaks at 43.01, 50.15 and 73.8 representing the (111), (200), and (220) crystalline planes of copper respectively¹⁷. XRD pattern showed that the composites prepared by chemical reduction method possess cubic face centered structure. Purity of the sample is evident

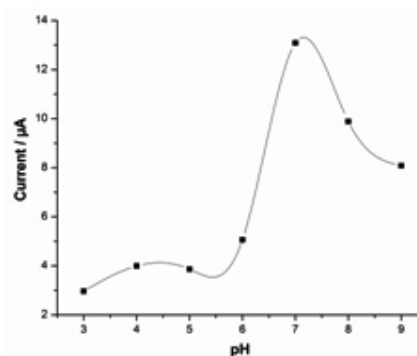


Fig.4 A. Effect of pH on oxidation peak current

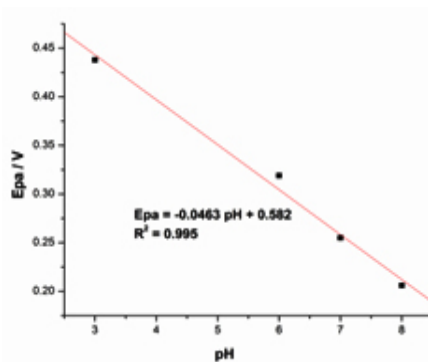


Fig. 4 B. Variation of anodic peak potential with pH

from the absence of other noticeable peaks in the pattern for CuO and Cu₂O. Particle size of as prepared composites by this method was found to be 23.4 nm

The SEM images (Fig 2) also reveals that the Cu particles are distributed on graphene sheets.

Electrochemical response of DA at modified electrode

The detection of dopamine (DA) was performed using cyclic voltammetry and differential pulse voltammetric methods. The electro oxidation

of DA was first examined in bare and modified GCE by cyclic voltammetry in phosphate buffer at pH 7 (fig 3). At the bare GCE an irreversible oxidation peak appeared at 0.404 V. In the modified electrode the peak potential is reduced by 150mV by appearing a reversible peak at 0.254V and peak current is also enhanced compared with the bare electrode. This improvement can be attributed to the edge planes of graphene¹⁸. The peak at -0.018V is the oxidation peak of copper and it is assigned to Cu/Cu (II) transitions^{19,20}.

Optimization of parameters

Influence of pH

The influence of solution pH on the electrochemical response was investigated in phosphate buffer solution. The variation of peak current with respect solution pH in the range 3 to 9 was observed Fig.4A

Results show that solution pH varies linearly in the range of 3 to 9 with a linear equation of $E_p = 0.58 - 0.046 \text{ pH}$, $r = 0.995$, (Fig4B). This points to the fact that DA redox reaction is a

two electron two protons process as already reported^{21,22}. Oxidation peak current increases with pH and reaches a maximum at pH 7, then decreases as the pH continues to increase. Therefore the pH at this study is optimized as 7.

Effect of Scan rate

Cyclic voltammogram of DA at pH7 on GN-Cu/GCE was recorded at different scan rates (ν). The scan rate varied as 10-1000 mV/s are shown in fig.5. There is a linear relation between the oxidation peak currents and scan rate in low scan rate with correlation coefficient of 0.997 for DA (fig.6A), indicating adsorption controlled process. A similar linear relation was also observed between oxidation peak currents and scan rate in the high scan rate up to 1000mV/s (fig.6B) with correlations of 0.995 indicating it is also adsorption controlled mass transfer. Hence it is an adsorption controlled process both in low and high scan rate^{23,24}.

A linear correlation exists between peak potentials (E_p) and logarithm of scan rates. From the slope of the lines indicate, the number of electron (n)

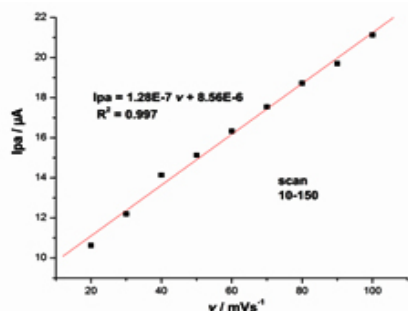


Fig.6A: Variation of oxidation peak current with scan rate (low)

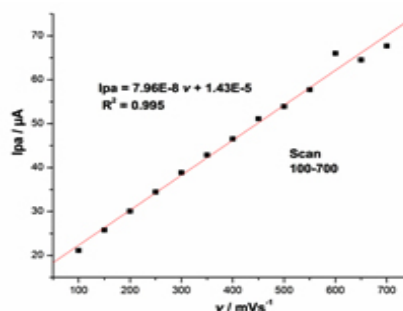


Fig.6B: Variation of oxidation peak current with scan rate (high)

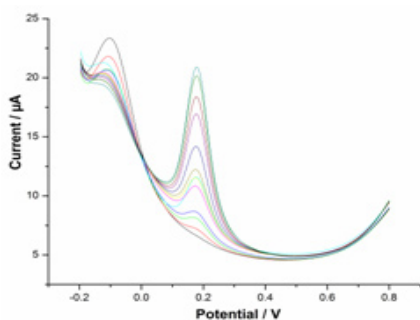


Fig.7: DPVs of different concentration of DA in 0.1M PBS (pH 7) at GN-Cu/GCE

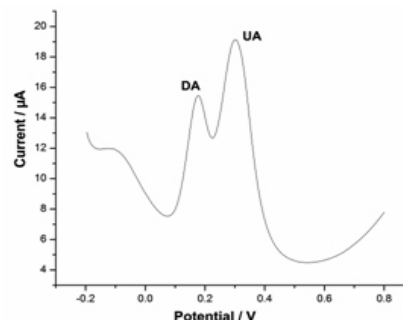


Fig.8: DPV of mixture of 0.1mM DA and 0.1mM UA at pH 7 in 0.1M PBS at GN-Cu/GCE

involved in the reaction which is estimated to be two assuming the value of α to be 0.5²⁵. Therefore the electro oxidation of DA giving electroactive Dopamine quinone²⁶ is a two electron two proton process at GN-Cu/GCE. There is appreciable increase in the adsorption and rate of electron transfer at the modified electrode compared to bare GCE²⁷. At pH 7, protonation of the amine group occurs and DA forms

an acid conjugate which gets strongly adsorbed on the electrode surface. The phenyl structure of DA and two dimensional planar hexagonal carbon structure of graphene enter into pi-pi interaction making electron transfer highly feasible²⁸. The electro oxidation was also accelerated by the copper oxide nanoparticles. Fig.7. represents the DPVs of different concentrations of DA from 0.5 μ M to 0.1mM in 0.1 M PBS (pH 7), at GN-Cu/GCE. A linear voltammetric response was observed and the detection limits as low as 200 nM. The results obtained promise the use of the GN-CuO as an excellent sensor for dopamine.

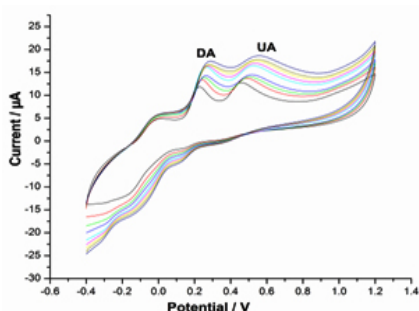


Fig.9: CVs of mixture of 0.1mM DA and UA at pH 7 at GN-Cu/GCE recorded at various scan rate.

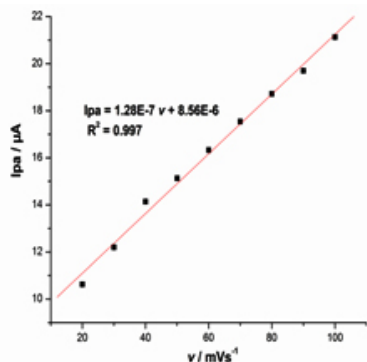


Fig.10A: oxidation peak current Vs scan rate for DA

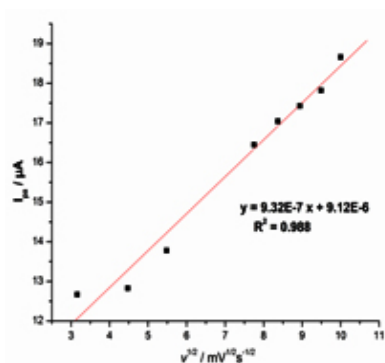


Fig.10B: Variation of oxidation with square root of scan rate for UA

Simultaneous determination of DA and UA

Uric acid (UA) is an important interferent as the metabolic end product in the human body^{29,30}. Simultaneous determination of DA and UA at GN-Cu modified GCE was investigated using DPV (fig.8). The modified electrode is successful in resolving separate anodic peaks for DA and UA. The GN-Cu/GCE resolve the voltammetric response of DA and UA into well defined peaks at 0.176 and 0.300V respectively indicating that their voltammetric response is independent of each other.

Role of scan rate on simultaneous determination of DA and UA

The CVs of mixture of 0.1mM DA and UA in 0.1M PBS (pH 7) at GN-Cu/GCE was recorded at different scan rate range from 10 to 100 mV/s (fig.9). Peak currents exhibited linearly with scan rate indicating oxidation process is surface controlled. Appreciable peak current and separation were obtained at a scan rate of 50mV/s and it was optimized for this study. There existed a linear relation between oxidation peak current and scan rate. A correlation of 0.997 (fig.10A) points to adsorption controlled process occurring at the electrode³¹. But for UA a diffusion controlled process is taking place as oxidation peak current varies with square root of scan rate (fig.10B)³².

CONCLUSION

Glassy carbon electrode modified by graphene copper chitosan composite served as an effective sensor for dopamine at physiological pH 7. Evaluation of the influence of scan rate revealed that it was an adsorption controlled process.

The redox reaction confirms to a two electron two proton transfer process. The voltametric response was found to be linear for an appreciable range

of concentration and reaching a detection limit of 200 nM.

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