

# Catalytic Oxidation of Dopamine at a Copper Hexacyanoferrate Surface Modified GNP Graphite Wax Composite Electrode

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## Abstract

A chemically modified electrode was successfully fabricated by means of depositing a thin layer of Copper hexacyanoferrate (CuHCF) on an amine adsorbed gold nanoparticle graphite paraffin wax composite electrode using a new approach. The electrochemical characteristics of the modified electrode were studied using cyclic voltammetry and electrochemical impedance spectroscopy (EIS). The modified electrode was able to catalyze dopamine (DA) and moreover was able to eliminate the electrode fouling caused by the electrochemical oxidation of dopamine at the bare electrode.. However when the modified electrode was further covered with a Nafion membrane, the interference could be diminished. The catalytic current for oxidation of dopamine at the modified electrode increased linearly with a concentration range of  $3.5 \times 10^{-6}$  to  $1.4 \times 10^{-3}$  M. of dopamine with a correlation coefficient of 0.999. The limit of detection was found to be  $1.2 \times 10^{-7}$  M. Based on  $S/N=3$ . Flow injection analysis technique was used for the determination of dopamine and it was found that the electrode produced excellent reproducible results.

**Keywords-** GNP; Copper hexacyanoferrate; Dopamine

## I. INTRODUCTION

Noble metal gold nanoparticles have attracted much interest in the field of electro analysis due to their unusual of optical, chemical, photo electrochemical and electronic properties [1–3]. Nanoparticles play wide roles in electrochemical sensing based on their unique properties; the basic functions of the nanoparticles can be mainly classified as (a) for immobilization of redox mediators, polynuclear inorganic films and biomolecules; (b) catalysis of electrochemical reactions; (c) enhancement of electron transfer rate; (d) labeling of biomolecules and (e) acting as reactants. A gold nanoparticle not only provides a stable immobilization platform to redox mediators but also acts as electronic wires to enhance the electron transfer kinetics [4]. Modification of electrode surfaces with self-assembled monolayers (SAMs) of thiols provides a simple way to design tailored materials that can be further used as functionalized sites to immobilize gold nanoparticles and redox mediators [5]. Among various redox mediators used for the electrode modification, metal hexacyanoferrate have found many applications in different areas including electro analysis and site-selective electro catalysis [6–7] electro chromic devices [8], interfacial charge and electron transfer [9]. Ever since the pioneering work of Neff [10] and Itaya et al. [11] there has been great interest to electrochemist to develop modified electrodes with Prussian Blue (PB) and its analogues such as cobalt, copper, nickel, indium and hybrid metal hexacyanoferrate [12–16].

Dopamine (3,4-dihydroxyphenyl ethylamine) is an important neurotransmitter in the mammalian central nervous system (CNS), and it could be detected electrochemically because of its electro activity. The electrochemical oxidation of dopamine has been studied mostly on carbon base electrodes [15]. Parkinson's disease (PD) is a neurodegenerative disease which causes progressive disorders in extrapyramidal system that regulates the communication between the neurons in the brain and muscles in the human body. PD involves the breakdown of nerve cells that results in shortage of dopamine which in turn leads to interruption in the blood–brain barrier. Lack of dopamine supply will lose control over the basic movement patterns such as walking, writing, reaching for objects and other basic programs cannot operate properly [17].

Electrochemical methods finds a major applications in the current research for the fabrication of chemically modified electrodes (CMEs) with better sensitivity, selectively, stability and free from surface fouling properties compared to unmodified electrodes. Extensive reports have been published in literature for the electrochemical detection of L-dopa using CMEs such as electro polymerized p-Ni<sup>II</sup>TAPc glassy carbon electrode (GCE) [18], gold-screen printed disposable sensor [19], polycarbozole

electrode [20] and oxavandium salen thin film electrode [21]. However, several problems were associated with these modified electrodes like tedious procedure for electrode preparation, poor selection and poor detection limit.

In the present work, we report a stable surface immobilization of copper hexacyanoferrate (CuHCF) film on gold nanoparticles (GNP) - graphite paraffin wax composite electrode. Thiol group (-SH) was covalently linked to GNP adsorbed on graphite electrode and the terminal amino group (-NH<sub>2</sub>) was utilized to anchor Cu<sup>2+</sup> for CuHCF film. The modified electrode fabricated using paraffin wax exhibited an excellent binding ability and robustness. We report electro catalytic oxidation of dopamine by metal hexacyanoferrate modified electrodes. Modified electrode was characterized by scanning electron microscopy (SEM). As compared to earlier reports, this proposed work for the electrode fabrication is very simple and effective. The CuHCF-GNP modified electrode showed an enhanced electro catalytic activity with high sensitivity towards the determination of dopamine in both standard samples and commercial tablets.

## II. EXPERIMENTAL

### A. Reagents and Chemicals

All reagents were of analytical grade; Graphite powder was from Aldrich (1-2 $\mu$ m), (Aldrich, Steinheim, Germany). Catechol from Alfa Aesar (Alfa Aesar chemicals, Kolkata, India). CuCl<sub>2</sub>, Potassium Ferro cyanides were obtained from Merck (Mumbai, India). Double distilled water was used for all electrochemical experiments. Studies on effect of pH were carried out using 0.1M HCl and 0.1M NaOH solutions. pH 7.0 was maintained using 0.1M KNO<sub>3</sub>, 0.1 M PBS), L-cysteine solution (20mM) was prepared using double distilled water and copper solution (0.01M) was prepared by dissolving the salt in ethanol. Potassium Ferro cyanide (0.02 M) in KNO<sub>3</sub> (0.1M) solution was used to derivatize the coordinated nickel ion. All measurements were done after carefully degassing the solutions with pure nitrogen for 10-15 min.

### B. Apparatus and Material

Electrochemical measurements were carried out using Electrochemical workstation CH Instruments 660B, Tx, USA controlled by an IBM personal computer with standard three-electrode configuration. The surface modified CuHCF graphite paraffin wax composite electrode was used as the working electrode, a platinum wire as the counter electrode and a standard calomel electrode as the reference.

### C. Chemicals and Reagents

Graphite powder ( $\approx$  1-2  $\mu$ m) was purchased from Aldrich Chemicals, Germany. Dopamine was obtained from Himedia Laboratories, India. HAuCl<sub>4</sub>.3H<sub>2</sub>O and all other reagents employed were of analytical grade and used as received. All the supporting electrolyte solutions (0.1 M) and potassium Ferro cyanide (0.02 M) solution were prepared in doubly distilled (DD) water. Dopamine (0.01 M) was prepared in DD water and pH of the supporting electrolyte was maintained using phosphate buffer (0.05 M). Sodium citrae solution (20 mM) and CuCl<sub>2</sub> solution (0.01 M) were prepared using dry ethanol. The present method was examined for the determination of dopamine.

### D. Synthesis of GNP

The citrate capped GNP was prepared as reported [22]. The maximum absorption peak for the synthesized GNP was observed at 550 nm which corresponds to a particle size ranging between 25 nm and 35 nm [23]. The electrochemical behavior of GNP showed a typical quasi-reversible redox response corresponding to the oxidation and reduction of GNP which is in accordance with earlier report [24].

### E. Fabrication of Modified Electrode

Graphite powder (1 g) was added to 125 ml of synthesized gold nanoparticles solution (0.6mM) and the mixture was stirred for two hours at 300 rpm in room temperature. The stirred mixture was centrifuged at 1450 rpm for 30 minutes and the residue was kept overnight for drying. A GNP graphite paraffin wax composite electrode was prepared as reported by mixing 900mg of gold nanoparticles adsorbed graphite powder with paraffin wax in the ratio of 4:1. Gold nanoparticles graphite wax mixture was tightly packed in a small glass tube of 3mm diameter. The electrode was removed gently from the tube after it turns hard. The electrode prepared in this ratio showed an excellent hardness and conductivity. This composite electrode was first dipped in 20 mM L- cysteine solution for 2 hours. Then, this L-cysteine modified GNP composite electrode was dipped in 0.01 M ethanolic solution of CuCl<sub>2</sub> for 2 minutes. The amino group of cysteine functionalized with gold nanoparticles has a greater affinity towards transition metal ion like Cu<sup>2+</sup>. The Cu<sup>2+</sup> ions coordinated to amine group was then derivatize using 0.02 M potassium Ferro cyanide solution dissolved in 0.1 M KNO<sub>3</sub> by cycling the potential in the range -0.2 V to 1.0 V at the scan rate of 50mVs<sup>-1</sup>.

### III. RESULTS AND DISCUSSION

#### A. SEM Characterization of the Surface

Fig.1 shows the SEM images of bare graphite wax composite electrode (a), GNP adsorbed graphite wax composite electrode (b) which shows that GNPs are in the range from 6-9nm and CuHCF –GNP- graphite wax composite electrode(c). Figure (c) clearly suggests the formation of CuHCF particles on the electrode surface and that the particle size ranges from 100-120nm.

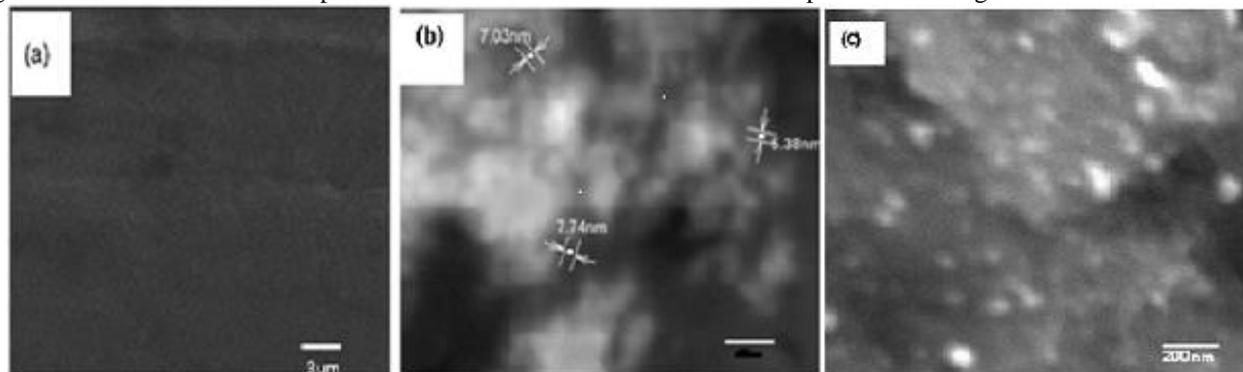


Fig. 1: SEM image of (a) Bare graphite electrode (b) GNP adsorbed composite electrode (c) CuHCF-GNP Modified electrode.

#### B. Cyclic Voltammetric Characterization of Modified Electrode

The GNP-L-Cys-CuHCF modified electrode showed a single redox peak with anodic and cathodic peak potentials at 0.58 V and 0.49 V respectively. Continuous cycling of the GNP-L-Cys-CuHCF electrode in 0.1M KNO<sub>3</sub> solution for more than hundred cycles showed no appreciable change either in the peak current or in peak potential indicating that the modified electrode is highly stable. Fig. 2 shows the current response of the GNP-L-Cys-CuHCF electrode at various scan rates. It is observed from the results (Inset A) that the current depends linearly with the square root of the scan rate in the range of 10 to 200 mV/s. A plot of log *i*<sub>pa</sub> versus log *v*, is shown (Inset B) where, *i*<sub>pa</sub> is the anodic peak current in A and *v* is the scan rate in V/s which has yielded the following results; slope = 0.53 ± 0.02, intercept = 2.1 ± 0.02 and correlation coefficient 0.999. These results indicate that the redox reaction involves a one electron diffusion-controlled process.

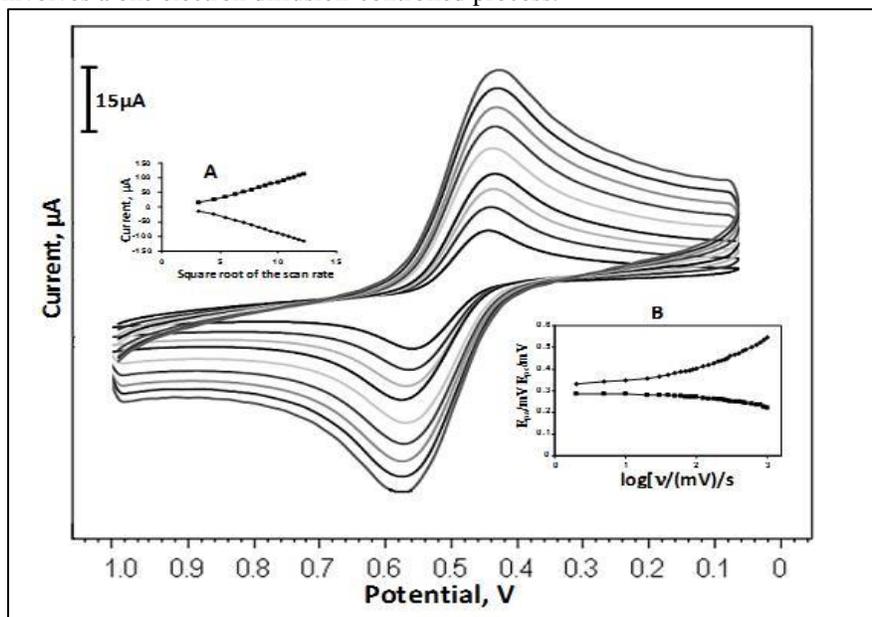


Fig. 2: Cyclic voltammogram of the CuHCF modified electrode at different scan rates in 0.1M KOH The scan rates from inside to outer are 10-150 mVs<sup>-1</sup> with increments of 10 from 10 mV<sup>-1</sup>; Inset A: Dependence of peak currents (*I*<sub>pa</sub> and *I*<sub>pc</sub>) on square root of scan rate(*v*); Inset B: variation of peak potential vs. logarithm of scan rates

#### C. Electrochemical Impedance Spectroscopy

Electrochemical Impedance Spectroscopy (EIS) was used to investigate the surface bound features of the CuHCF film modified electrode at the electrode-electrolyte interface. Fig.3. shows the Nyquist plots of the EIS for the bare electrode and CuHCF film modified electrode at varied potentials (0.54–0.62 V) in the frequency range of 0.1 Hz to 1.0 MHz. The complex plane spectrum was found to fit well with the Randels circuit. EIS parameters such as charge transfer resistance (*R*<sub>ct</sub>), double layer capacitance (*C*<sub>dl</sub>), solution resistance (*R*<sub>s</sub>) and Warburg impedance (*Z*<sub>w</sub>) for the electron transfer characteristics of the CuHCF film modified

electrode at the formal potential of 0.58 V was found to be  $31.32 \text{ k } \Omega \text{ cm}^{-2}$ ,  $15.20 \text{ nF cm}^{-2}$ ,  $298.6 \text{ k } \Omega \text{ cm}^{-2}$  and  $8.22 \times 10^{-4} \text{ } \Omega \text{ cm}^{-2} \text{ s}^{1/2}$  respectively and that of bare electrode are respectively  $22.56 \text{ k } \Omega \text{ cm}^{-2}$ ,  $43 \text{ nF cm}^{-2}$ ,  $382.5 \text{ k } \Omega \text{ cm}^{-2}$  and  $6.211 \times 10^{-4} \text{ } \Omega \text{ cm}^{-2} \text{ s}^{1/2}$ . The schematic representation of the modified Randle's equivalent circuit for this CuHCF film modified electrode is shown in the inset. The impedance data obtained for CuHCF film modified electrode at 0.58 V shows a lower resistance to the charge transfer kinetics which confirms that this modified electrode is a very attractive one for the electron transfer reactions.

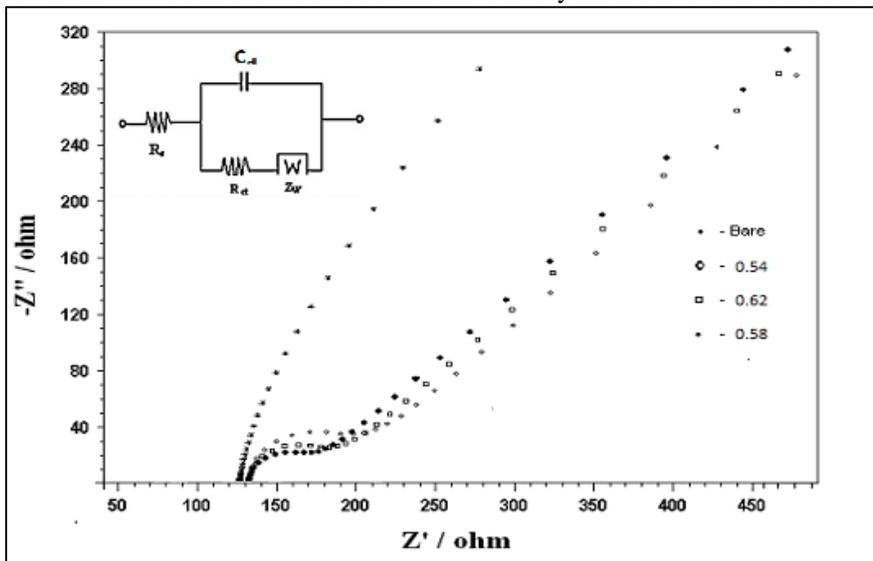


Fig. 3: Complex impedance plots of the CuHCF film modified electrode in 0.1 M KOH ,showing the Nyquist plot obtained for the electrode at the three different potentials (  $\circ$  -540mV), ( $\bullet$  -580mV), ( $\square$  -620mV) and bare composite electrode (bare-  $\bullet$ ) Inset: Randels equivalent circuit diagram.

#### D. Electrochemical Performances of the Modified Electrode as Dopamine Biosensors

The electrochemical oxidation of dopamine was investigated in 0.1M  $\text{KNO}_3$  using the CuHCF film electrode by cyclic voltammetry. For comparison the voltammetric response in the absence of dopamine was also recorded. The corresponding voltammograms are shown in Fig. 4. It is clear from the figure that there is a definite enhancement in the oxidation peak current in the presence of dopamine indicating that dopamine is oxidized by CuHCF via a cyclic mediation redox process.

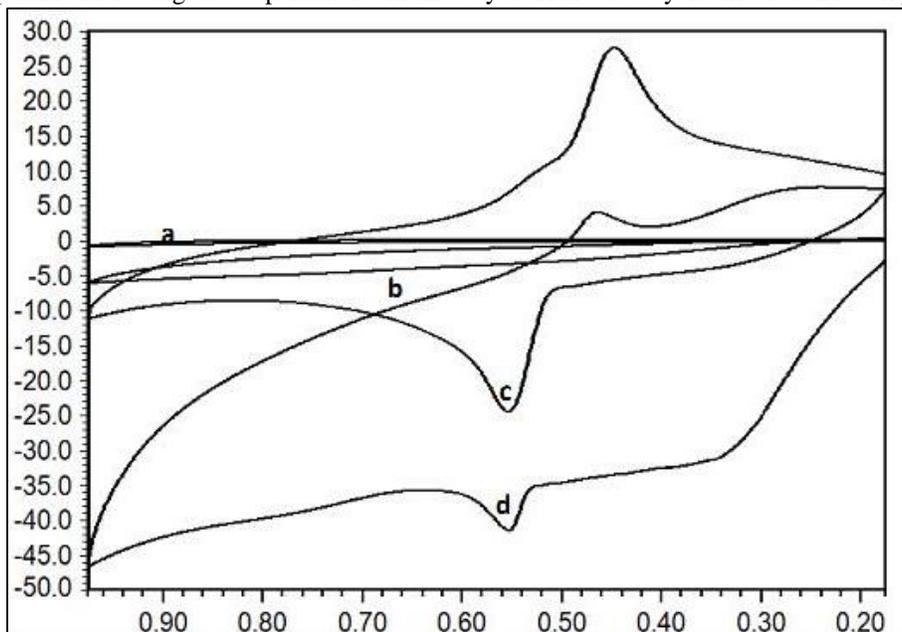


Fig. 4: (a) Bare electrode, (C) bare with  $4.0 \times 10^{-4} \text{ M}$  dopamine (b) CuHCF-GNP composite electrode and (d) modified electrode with  $4.0 \times 10^{-4} \text{ M}$ . scan rate at 20mV/s.

#### E. Electro Catalytic Oxidation of Dopamine by Differential Pulse Voltammetry (DPV)

To study the concentration range of dopamine that can be determined with the modified electrode, DPVs were recorded for different amounts of dopamine (Fig.5). The catalytic currents were then plotted against the amount of dopamine taken and the calibration graph is shown in the inset of Fig.5. A linear response for dopamine oxidation was observed in the concentration

range from  $3.5 \times 10^{-6}$  to  $1.4 \times 10^{-3}$  M with a correlation coefficient of 0.9996. To study the precision of the method, 15 successive measurements were carried out for  $7.2 \times 10^{-5}$  M dopamine and a relative standard deviation of 1.86% was found. A detection limit of  $1.2 \times 10^{-7}$  M dopamine was observed for the determination of dopamine.

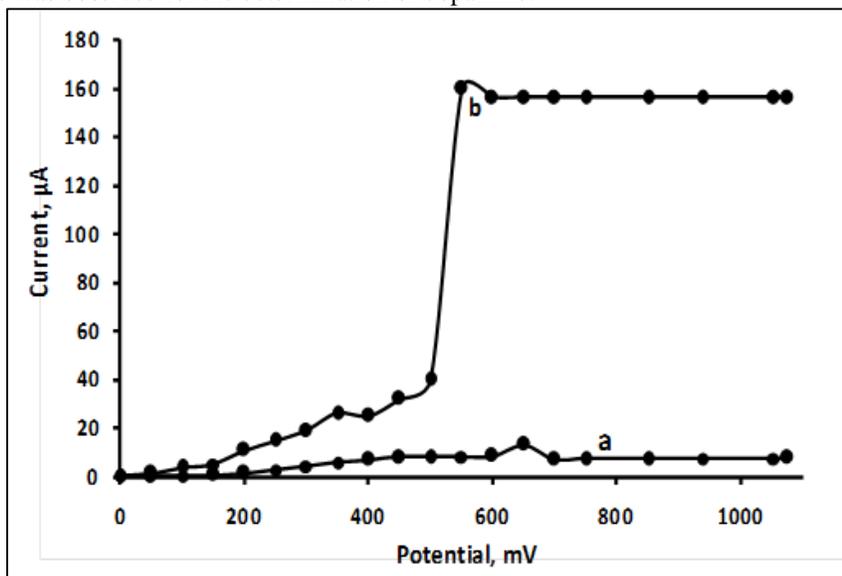


Fig. 5: Differential Pulse voltammograms successive additions of 0.3ml of 0.01M dopamine. Inset: shows the calibration plot of catalytic current versus concentration of dopamine

To study the applicability of the modified electrode as an amperometric sensor in flow systems, hydrodynamic voltammetric (HDV) experiments have been carried out for the electro catalytic oxidation of dopamine. The HDVs for dopamine at the bare electrode (curve a) and at the modified electrode (curve b) are shown in Fig.6. From the figure it is seen that the catalytic current for the oxidation of dopamine above 0.59 V is maximum and reaches a constant value. The potential can be fixed at any value in the constant current region and the determination of dopamine in flow systems can be conveniently carried out. As expected, the electro catalytic activity of the CuHCF permits convenient detection of dopamine at lower potential with high sensitivity. In contrast, the bare electrode offers detection of the dopamine only at higher potential with lesser sensitivity.

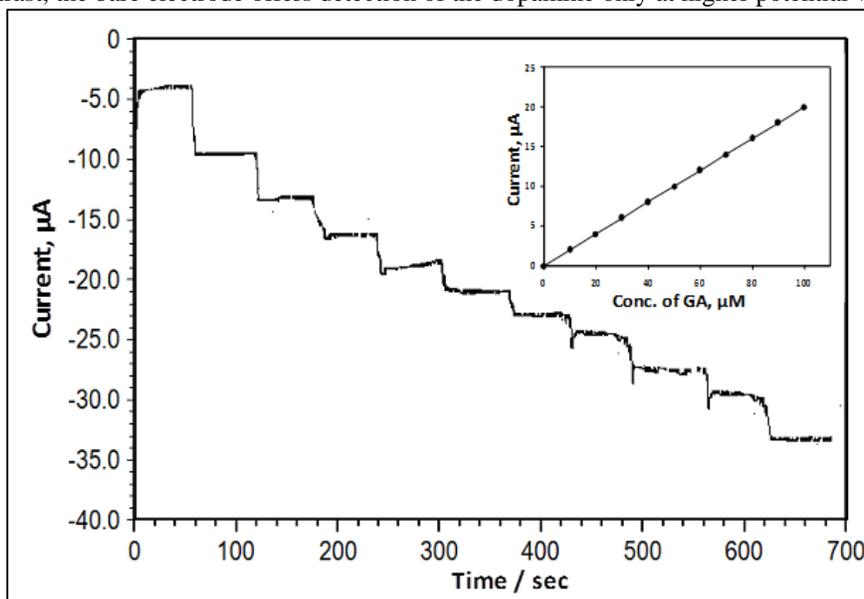


Fig. 6: Hydrodynamic voltammograms obtained in the presence of  $8.6 \times 10^{-5}$  M dopamine (a) bare composite electrode (b) modified electrode

In order to evaluate the modified electrode as an amperometric sensor for the determination of dopamine, amperograms have been recorded with different amounts of dopamine and the amperogram obtained is shown in Fig.7. Similar amperograms were obtained for the lower concentration range as well. From the amperograms, a calibration plot was made with the catalytic current against the amount of dopamine taken and the results are shown in the inset of Fig.7. A linear relation between the catalytic current and the amount of dopamine in the range from  $3.5 \times 10^{-6}$  to  $1.4 \times 10^{-3}$  M is observed with a correlation coefficient

of 0.999. The detection limit was found to be  $1.2 \times 10^{-7} \text{M}$ . It can be concluded that the CuHCF composite electrode can be used as an amperometric sensor for the determination of dopamine with good sensitivity.

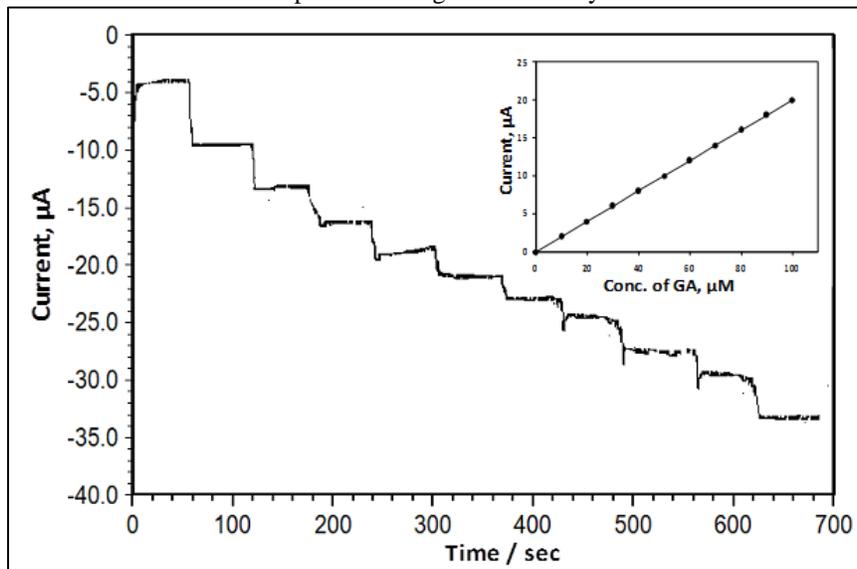


Fig. 7: Chronoamperometric response at CuHCF modified electrode for each addition of  $6.26 \times 10^{-5} \text{M}$  dopamine in  $0.1 \text{M KNO}_3$  stirring rate: 300 rpm; potential: 0.59 V. Fig.7b. Calibration graph for dopamine measurement.

#### F. Stability of the Modified Electrode

The stability of the GNP-L-CYS-CuHCF modified electrode was investigated both at time of operation and for long-term storage. The modified electrode exhibited a constant current response without much change in peak potential and peak current for 100 continuous cycles in  $0.1 \text{M KNO}_3$  at the scan rate of  $20 \text{mVs}^{-1}$ . The electro catalytic current response of the modified electrode towards dopamine was found to be unaffected for at least 8–10 hours under hydrodynamic conditions. To show the reproducibility, reliability and applicability of modified electrode, the CV studies were carried out for 100 cycles each day for the period of 45 days, the decrease in peak current was found to be very less.

### IV. CONCLUSION

An electro active thin film of CuHCF was immobilized on GNP-L-CYS-GWCE and the electrode achieved through this approach is highly stable. This CuHCF film exhibits excellent electro catalytic activity towards dopamine oxidation in aqueous phosphate buffer solution containing  $\text{K}^+$  ion, with a reduction in over potential of about 200 mV than the bare electrode. The process is pH dependent and a higher catalytic current is observed at (pH = 7.0). The reproducibility in the peak current indicates that the modified electrode is free from the surface fouling. The electrochemical studies of the GNP-L-CYS-CuHCF modified electrode obviously indicate the presence of GNP has offered a stable platform for the modification of CuHCF film through thiol cross-linker. The reproducibility and stability of the sensor is found to be very good and thus this modified electrode can be used as a reliable chemical sensor for the electrochemical determination of dopamine.

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