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Electrochemical Reactivity of C_{60} Modified Carbon Paste Electrode by Physical Vapor Deposition Method

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The electrochemical performance of vapor deposited fullerene (C_{60}) on carbon paste electrode (CPE), by physical vapor deposition method (PVD) has been assessed. Fullerene deposited at different thickness and their voltammetric response to ferricyanide and dopamine are examined. Scanning electron microscopy was used to characterize surface morphology of C_{60}/CPE. The cyclic voltammetric studies reveal that the electrocatalytic activity depends on thickness of the fullerene film deposited. We found that catalytic activity slightly enhances when thickness of fullerene film maintained 3 angstrom onto CPE. These differences in the electrochemical reactivity are attributed to different surface chemistry of fullerene layers. Further the modified electrode was practically applied for the simultaneous determination of adenine (A) and guanine (G). Voltammetric studies shows that guanine and adenine produced well-defined oxidation peaks at about +0.67 and +0.99 V respectively in pH 7.2 phosphate buffer.

Keywords: Fullerene, Physical Vapor Deposition, Dopamine, Adenine, Guanine

1. INTRODUCTION

The discovery of fullerene [1], their production [2], fullerene electrochemistry [3] and electrochemical properties of fullerene [4] triggered rapt attention and application of fullerene in the filed of electrochemistry. Fullerene and carbon nanotube electrodes have great impact on catalytic and sensor applications [5-6]. Previous studies reveal that the preparation of C_{60} films by sublimation method [7-11] upholds the advantage over solvent evaporation method both by avoiding solvent entrapments and hopefully would be more continuous films, whereas in solvent evaporation method films were discontinuous and contained entrapped solvent. Deposition of fullerene films from C_{60} beams produced by sublimation of C_{60} powder in high vacuum using a home made effusive oven [12] was reported.

We know that C_{60} films constitute a new class of carbon electrodes with properties that differ from graphite and diamond electrodes. These films are quite stable to oxidative potentials, but show unusual electrochemical dependence on the method of preparation and the electrolyte medium. Adlayers prepared by sublimation in vacuum reveal good uniformity even when surface mobility is low and deposition (adsorption) is fast. This has been testified by scanning probe microscopy among other analytical methods [13]

Leiro *et. Al* [9] reported the sublimation of fullerene (C_{60}) films deposited on Si(111) surface. C_{60} films prepared by sublimation at 575 °C for 5 min on a pyrolytic carbon film electrode[11] reduction mechanism in which ion transport, the specific nature of the interaction between cation and fulleride is defined. Nanostructured fullerene films of controlled surface topography have been prepared by electrophoretic deposition [14].

Utilization of fullerene materials for the development of next generation nanodevices requires preparation of robust films on desired electrode surfaces with a well-controlled morphology. Since the properties of fullerene-containing films are profoundly controlled by the deposition conditions, substrate of adsorption, and influenced by impurities or disordered surface structures, the progress of such new fullerene-based materials strongly relies on the development of new versatile and broad preparative methodologies.

To our knowledge there is no literature regarding the physical vapor deposition of C_{60} onto carbon paste electrode. The goal of the present study is to report electrochemical reactivity and performance of carbon paste electrode modified with fullerene by physical vapor deposition (PVD) method. In the following sections we examined the influence of fullerene film onto carbon paste electrode on the electrocatalytic behavior and analytical performance of C_{60}-modified electrodes. Fullerene coating shown to influence the current response through their effect on the surface chemistry and morphology like, defect density or presence of impurities. Potassium ferricyanide and dopamine were selected as model analytes owing to their considerable importance in their accelerated electron transfer at fullerene modified electrodes. Dopamine is a neuromodulator in the brain, influencing a variety of motivated behaviors and involved in several neurologic diseases. Dopamine, which results as quasireversible system at GCE, Pt electrodes, here at C_{60}/CPE modified electrode, it acts as a reversible system, the difference in peak potential is 60 mV and current ratio is almost equal to unity was observed.

Further, we try to utilize the C_{60}/CPE modified electrode for simultaneous determination of adenine and guanine, the analysis of these bases has great significance to bioscience and clinical diagnosis. To date, some electrochemical detection protocols have been developed, such as electrochemically pretreated glassy carbon electrode [15], nafion-ruthenium oxide pyrochlore chemically modified electrode [16], highly boron-doped diamond electrode [17], and cobalt (II) phthalocyanine modified carbon paste electrode [18], b-Cyclodextrin incorporated carbon nanotubes-modified electrodes [19] etc. Now C_{60}/CPE modified electrode applied for the successful simultaneous determination of adenine and guanine.

2. EXPERIMENTAL PART

2.1. Electrochemical Apparatus and Chemicals

High purity C_{60} (99.99%) was obtained from SES Research. Dopamine, adenine and guanine were obtained from Fluka and used without further purification. All other reagents used throughout the experiment were analytical grade. All solutions and subsequent dilutions were prepared daily, using doubly distilled water. Cyclic voltammetric measurements were conducted using a Electroanalyser model EA 201 from Chemilink Systems, Mumbai, India. The temperature of cell solution was maintained at 25.0 ± 0.1^{0}C. In all cases a standard three-electrode configuration was employed along with a typical cell. A fullerene modified or unmodified carbon paste electrode served as the working electrode with platinum wire as the counter electrode and an SCE reference electrode completing the cell assembly.

2.2. Scanning Electron Microscopy (SEM)

Micrographs of the electrode surfaces were obtained by scanning electron microscopy (SEM) using a Hitachi model S-3200N microscope.

2.3. Preparation of Carbon paste electrode

The carbon powder (particle size 50 mm, density 20-30g/100mL) was mixed with the binder, silicone oil, in an agate mortar and homogenized using the pestle. The electrode consisted of a teflon well, mounted at the end of a teflon tube. The prepared paste was filled into the teflon well. A copper wire fixed to a graphite rod and inserted into the Teflon tube served to establish electrical contact with the external circuit. The electrode surface of the working electrode was renewed mechanically by smoothing some paste off and then polishing on a piece of transparent paper before conducting each of the experiments. The experiments were performed in unstirred solutions.

2.4. Coating of the C_{60} onto CPE

Fullerene was coated on to the tip of the electrode by physical vapor deposition method using the vacuum coating unit, model 12a 4D; Hind high vacuum company Pvt. Ltd Bangalore, India.

3. RESULTS AND DISCUSSION

3.1. Physical vapor deposition of C_{60} Films

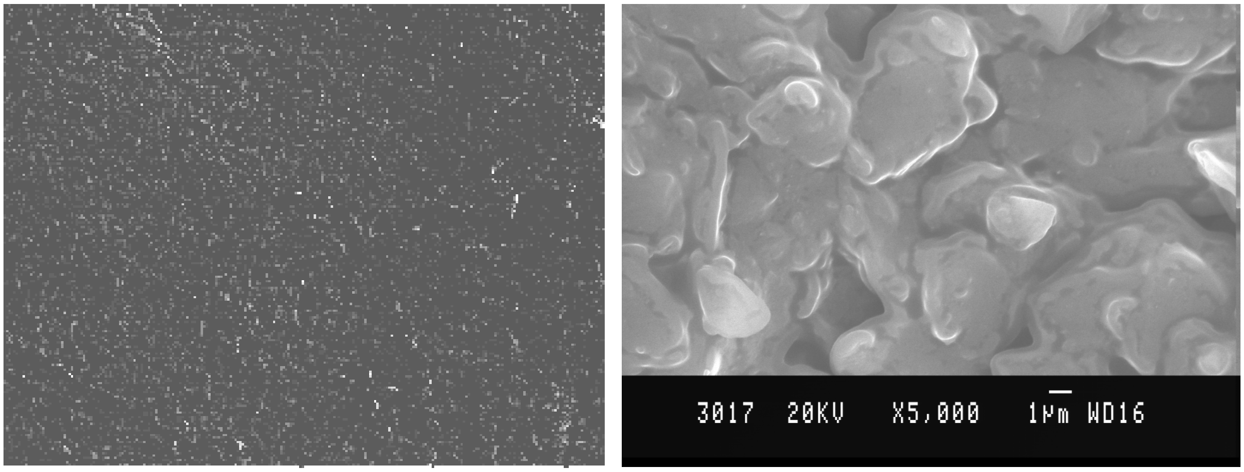
Fullerene was coated on to the tip of the electrode by physical vapor deposition method [7-11] using the vacuum coating. The electrode was mounted firmly on the substrate holder situated inside the vacuum chamber. The sample electrode was kept at a distance of 4.5 cm from the source to get the uniform coating. About 1 mg of the fullerene sample was taken in the molybdenum boat. A dimple was made to the molybdenum boat to keep the sample to act as a point source. The boat was connected to the electrode s for heating. The vacuum inside the chamber was made to 10^{-5} m bar (1 m bar = 0.76 Torr). When high current is applied to the molybdenum boat through the electrodes, the sample gets evaporated. The evaporation was made at the rate of 1 Å/ sec, which was controlled by applying the current. The C_{60} was coated to a desired thickness, which was monitored using a quartz crystal microbalance sensitive to mass changes of a thin metal electrode on a piezoelectric quartz crystal. Pure solid C_{60} forms a hexagonal lattice with a nearest neighbour distance close to 10 Å [20-21].

3.2. Characterization of the fullerene film Layer

The fullerene film was characterized using different methodologies.

Physical Characterization**:** Sublimed fullerene films ranged in color from gold to dark brown, darkening with the sublimation time. Gold highlights on the film surface could be seen with the naked eye, indicating the film.

Scanning electron microscopy**:** The SEM images of the modified working electrode are shown in Fig.1, and compared the morphology of the immobilized layer of bare CPE and fullerene film surface on CPE. The growth process could be observed clearly by SEM.



(a) (b)

Figure 1. Scanning electron microscopic images of (a) bare carbon paste electrode (b) C_{60} deposited carbon paste electrode

The dispersion of fullerene film size became larger with the increasing amount of fullerene. It is seen from Fig. 1 that the carbon paste surface is covered by fullerene film. This morphology is very much different from that of original surface and the vapoured fullerene film is much smoother than the bare carbon paste surface.

3.3. Stability of the electrode

The modified electrode was found to be stable, even after 15 cyclic voltammetric scans. The fullerene film is quite stable, once prepared can be used for almost for about 15 days if preserved properly. We did not observe any damage to the fullerene film even it in the open air for about a week. Fullerene film display high stability and reproducibility during the electrochemical redox process.

3.4. Electrochemical studies

Cyclic voltammetric response to 1 mM potassium ferricyanide in 0.1 M KNO_3 studied at different scan rates. Current slightly enhances in the case of modified electrode compared to bare carbon paste electrode when the film thickness maintained at 3 angstrom units (figure 2), but decreases if the thickness increases to 6 angstrom units, because highly organized densely packed C_{60} films rarely find electrochemical applications because counterions can hardly enter the film during electrochemical oxidation and reduction, thus precluding efficient charge exchange with the electrode substrate [12].

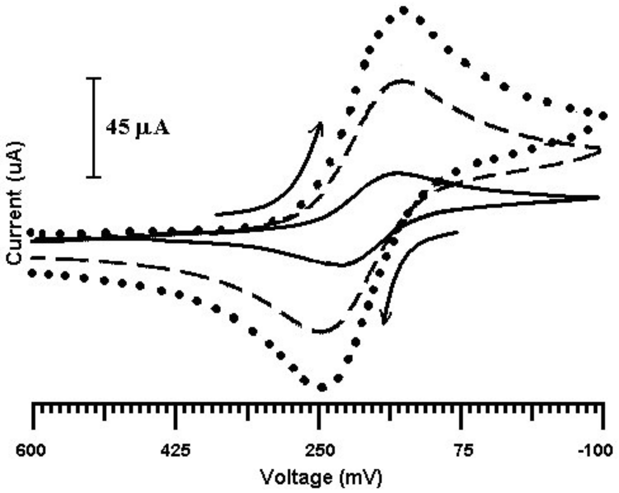


Figure 2. CVs of ferricyanide at bare CPE(solid line), at C60/CPE (dotted line) where coating of C60 = 3 Å and at C60/CPE (dashed line)where coating of C60 = 6 Å. Supp. electrolyte: KNO3, scan rate: 100 mV s-1

Here the thickness of the C_{60} coating onto carbon paste electrode important role, 3 angstrom coating onto CPE is very much felicitating rate of electron transfer.

3.5. Determination of the surface area of the electrode

The surface area of the modified electrode was determined by using the 1 mM potassium ferricyanide system in 1 M KNO_3 using the equation

$$i_p = 2.65 \times 10^5\, n^{2/3}\, A\, D_0^{1/2}\, \nu^{1/2}\, C_0^*$$

where i_p is the peak current in amperes, A is the area of the electrode in cm^2, C_0^* is the concentration of electro active species in mM, D_0 is the diffusion coefficient in $cm^2.s^{-1}$ and ν is the sweep rate in Vs^{-1}. The surface area of the electrode was found to be 0.039 cm^2.

3.6. Voltammetry of dopamine at CPE and C_{60}/CPE.

Figure 3 shows the electrochemical studies of dopamine were carried out at both CPE and C_{60}/CPE electrode using pH 6.5 phosphate buffer aqueous solutions. Reversible behavior observed for dopamine system at C_{60}/CPE, the difference in peak potential is 60 mV and current ratio is almost equal to unity. The current increases for the dopamine system at C_{60}/CPE compared to bare carbon paste electrode due to the rate of electron transfer is quite good at C_{60}/CPE.

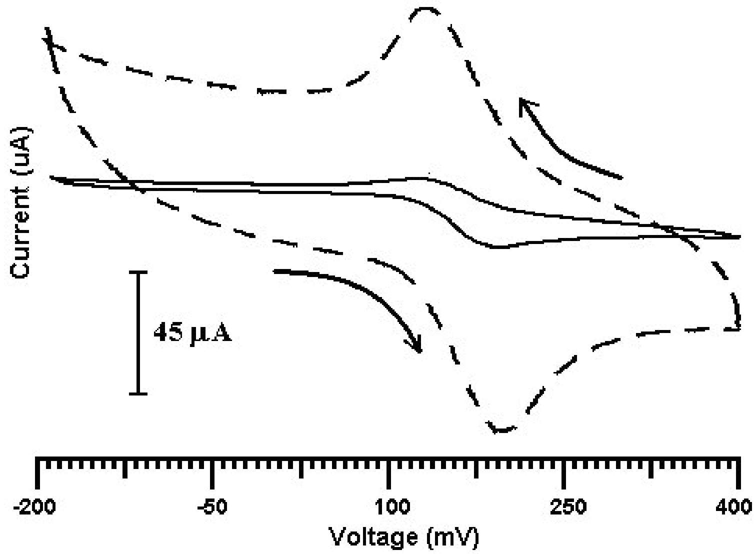


Figure 3. CVs of dopamine at bare CPE (solid line) and at C60/CPE (dashed line) Supp. electrolyte: 0.2 mol L -1 phosphate buffer (pH 6.5); scan rate: 100 mV s-1

3.7. Electrochemical behavior of guanine and adenine

Modified electrode was practically used in this present work on the electrochemical response of adenine and guanine individually in 0.2 mol L^{-1} phosphate buffer (pH 7.2) solution. Figure.4a shows voltammogram of 50 µmol L^{-1} guanine at C_{60}/CPE which has a sensitive oxidation peak at 0.77 V in phosphate buffer pH 7.2. Figure. 4b shows the voltammogram of 75 µmol L^{-1} adenine at C_{60}/CPE which has a sensitive oxidation peak at 0.98 V. We examine the enhanced electrochemical response of adenine and guanine at C_{60}/CPE when compared to conventional electrode.

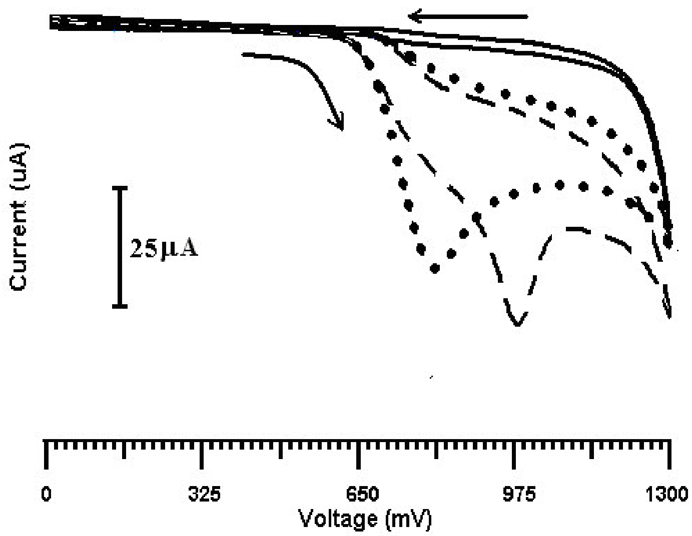


Figure 4. CVs of blank shown by solid line, dotted line represents 50 μmol L^{-1} G and dashed line for 75 μmol L^{-1} A at C_{60}/CPE Supp. electrolyte: 0.2 mol L^{-1} phosphate buffer (pH 7.2); scan rate: 100 mV s^{-1}

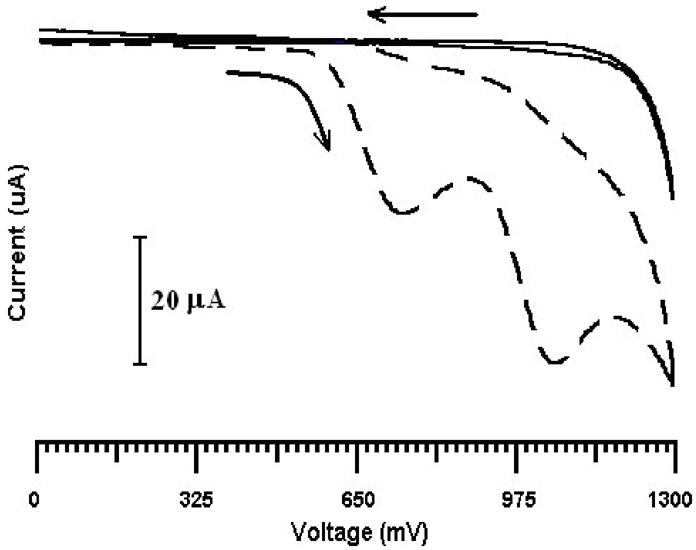


Figure 5. CVs of blank(solid line) and 50μmol L^{-1} G and 75 μmol L^{-1} A (dashed line) at C_{60}/CPE Supp. electrolyte: 0.2 mol L^{-1} phosphate buffer (pH 7.2); scan rate: 100 mV s^{-1}.

3.8. Simultaneous determination of adenine and guanine

Figure 5 illustrated the CV response of 50 μmol L^{-1} G and 75 μmol L^{-1} A in 0.2 mol L^{-1} phosphate buffer (pH 7.2) solution on C_{60}/CPE and bare graphite electrode. It can be seen that, in the case of bare graphite electrode, the voltammograms of adenine and guanine exhibit just a small hump peak with the overlapping potential. Compared to the electrochemical response on bare electrode, in the case of C_{60}/CPE, the peak current signals of adenine and guanine enhance significantly with their oxidative potential moving negatively, especially the oxidative potential of guanine moves negatively for about 300 mV which leads to the effective separation of the peak potentials of adenine and guanine. No cathodic peaks were observed on the reverse scan within the investigated potential range which indicated that adenine and guanine oxidation is an electrochemically irreversible process. The oxidation of guanine at solid electrode is expected to follow a two-step mechanism involving the total loss of four electrons and adenine occurs in three steps with total six electrons loss. In both cases, the first two-electron oxidation is rate-determining [15, 22 – 25].

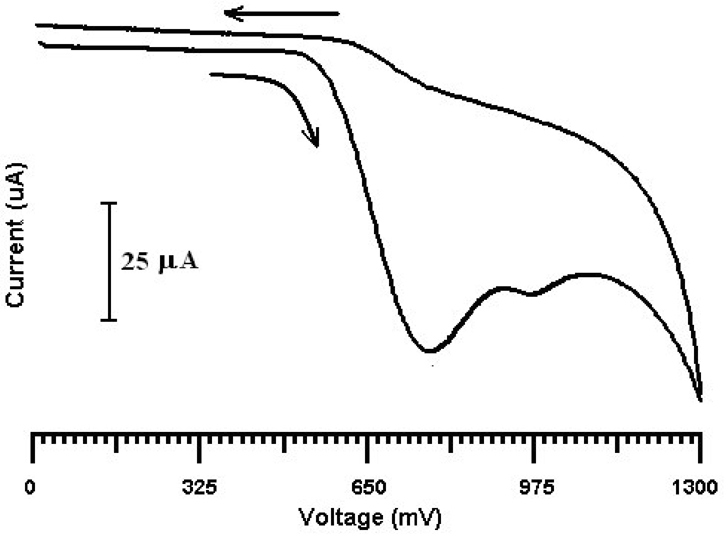


Figure 6. CV of 75 μmol L^{-1} G and 50 μmol L^{-1} A at C_{60}/CPE Supp. electrolyte: 0.2 mol L^{-1} phosphate buffer (pH 7.2); scan rate: 100 mV s^{-1}.

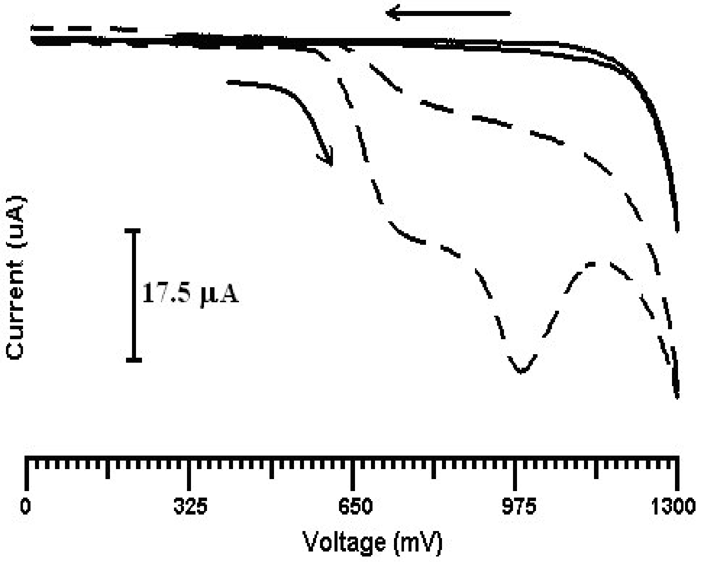


Figure 7. CVs of blank (solid line) and 40 μmol L^{-1} G and 75 μmol L^{-1} A (dashed line) at C_{60}/CPE Supp. electrolyte: 0.2 mol L^{-1} phosphate buffer (pH 7.2); scan rate: 100 mV s^{-1}.

We studied the reaction process at C_{60}/CPE, by effect of scan rate to guanine electrochemical response. The CV of C_{60}/CPE in the presence of 75 μmol L^{-1} guanine in phosphate buffer is directly proportional to the scan rate over the range of 10–200 mV s^{-1} further confirms that the guanine is absorbed on the surface of electrode. With increasing scan rate, the oxidation peak potential (Ep) shifts to more positive values and there is a linear correlation between the peak potential and the logarithm of scan rate, log (v). These results indicate that the electrode process was controlled simultaneously by diffusion and adsorption. Figure 6 shows CV of 75 μmol L^{-1} of guanine and 50 μmol L^{-1} adenine at C_{60}/CPE. Figure 7 shows CV of 75 μmol L^{-1} of guanine and 50 μmol L^{-1} adenine at C_{60}/CPE A in 0.2 mol L^{-1} phosphate buffer (pH 7.2),

4. CONCLUSIONS

The present paper, demonstrates the electrochemical behavior of unmodified carbon paste surface and carbon paste modified by fullerene film. Fullerene film could be fabricated directly on the carbon paste surface by a simple physical vapor deposition process. Fullerene-modified CPE showed a high catalytic activity towards dopamine and potassium ferricyanide. Dopamine shows reversibility on C_{60}/CPE. Various thickness of fullerene film can be fabricated on the CPE surface using the same protocol. Fullerene film display high stability during the electrochemical redox process. Adlayers prepared by sublimation in vacuum reveal better uniformity and fewer defects than original surface. This achievement has been demonstrated by scanning electron microscopy. The C_{60}/CPE modified electrode can be successfully used to determine simultaneously adenine and guanine. Future efforts will aim at understanding better the structural-electrochemical reactivity of fullerene-modified electrodes and the factors that govern the electron-transfer kinetics of these attractive devices.

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