Synthesis and characterization of carbon nanoparticles and their modified carbon paste electrode for the determination of dopamine

T.V. Sathisha [a], B.E. Kumara Swamy [a,*], Mark Schell [b], B. Eswarappa [c]

[a] Dept. of P.G. Studies and Research in Industrial Chemistry, Kuvempu University, Shankaraghatta, 577 451 Shimoga, Karnataka, India
[b] Dept. of Chemistry, Southern Methodist University, Dallas, TX, USA
[c] Dept. of P.G. Studies in Chemistry, Sir M.V. Govt Science College, Bhadravathi, Shimoga, Karnataka, India

ARTICLE INFO

ABSTRACT

In this paper, a green and facile approach is presented for the synthesis of carbon nanoparticles (CNPs) by a soot based method using the natural precursor castor oil. The synthesized carbon nanoparticles were used in the detection and electrochemistry of dopamine (DA), ascorbic acid (AA) and uric acid (UA). The synthesized product is characterized by Powdered X-ray diffraction (PXRD), UV–visible absorption spectroscopy, Scanning electron microscopy (SEM), Energy dispersive X-ray spectrum (EDS) and Infrared spectroscopy (IR). CNPs modified carbon paste electrodes provided a detection limit for DA 1.2×10^{-7} M. The cyclic voltammetric response of DA at a carbon nanoparticles modified carbon paste electrode was excellent when compared to a bare carbon paste electrode. The effect of scan rate, concentration, and pH effects on the voltammogram of DA were studied as well as the effects of the surfactants sodium dodecyl sulfate (SDS), cetyltrimethylammonium bromide (CTAB) and Triton X-100 (TX-100).

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

In the emerging field of nanomaterials, carbon nanostructures have potential significance. The various categories of carbon nanostructures include fullerenes, carbon nanotubes (CNTs), graphitic nanofibres (GNFs), graphene, etc. Carbon nanotubes (CNTs) have outstanding electrical, thermal and mechanical properties which make them interesting material for applications in nanoelectronics and sensors. Two-dimensional graphene nanosheets (GNS) and graphene based materials have received significant attention in recent years due to their unique electronic, mechanical, and thermal properties. This unique nanostructure holds great promise for potential applications in many technological fields such as nanoelectronics, sensors, capacitors and nanocomposites [1–9]. Furthermore, their large surface areas and ability to be functionalized allow them to undergo high-capacity binding to various biomolecules. Considering their wide spectrum of applications, the economical synthesis of carbon nanoparticles (CNPs) remains an attractive challenge. Soot-based syntheses of CNPs have attracted increasing attention recently. For example, it has allowed the simple preparation of luminescent nanocarbons. Raw candle soot mixed with nafion exhibits good electrochemical activity. In addition, carbon materials obtained from oil seeds and fibrous plant materials can be used for the storage of hydrogen [10–12].

Dopamine (DA) is a well-known biogenic amine acting as a neurotransmitter in the brain. It has received considerable attention because of its suspected role in a variety of neuropsychiatric disorders such as Parkinson's disease and Schizophrenia [13–16]. It has been found that the DA possesses very strong electrochemical activity by giving dopamine-o-quinone as the oxidation product. The selective detection of DA remains a challenge because of the presence of large excesses of ascorbic acid (AA) and uric acid (UA). UA is the primary end product of purine metabolism. Abnormal levels of UA result in several diseases, such as gout, hyperuricemia, and Lesch Nyan disease [17,18]. Similarly, AA is the agent which prevents scurvy and is known to take part in several biological reactions. It is generally believed that direct redox reactions of these three species at bare electrode are irreversible and therefore require high over potential [19]. Moreover the direct redox reactions of these species at bare carbon paste electrodes take place at common potentials and often suffer from a fouling effect, which results in rather poor selectivity and reproducibility. The ability to determine DA, UA and AA selectively has been a major goal of electroanalytical research [20]. Development of both sensitivity and selectivity are of equal importance in voltammetric procedures [21,22].

* Corresponding author. Tel.: +91 8282 256225; fax: +91 8282 256255.
E-mail address: kumaraswamy21@yahoo.com (B.E. Kumara Swamy).

Surfactants, amphiphilic molecules with a hydrophilic head on one side and a long hydrophobic tail on the other, have been widely applied in electrochemistry to improve the property of the electrode/solution interface. Zheng and Zhau [23] reported that sodium dodecyl sulfate (SDS) formed a mono-layer on a carbon paste electrode surface with a high density of the negative charged end directed outside the electrode. Wen et al. [24] have investigated the micellar effect on the electrochemistry of DA and found that the anodic peak current of DA is enhanced in SDS micelle, but the interference coming from AA cannot be eliminated [23]. At the physiological pH, DA and AA exist in different ion forms. AA is in the anionic form (pK_a = 4.10) while DA in the cationic form (pK_a = 8.87). Taking advantage of the opposite micelle effect of DA and AA, these two bioactive compounds can be simultaneously determined in the ionic micelles or by using surfactant-modified electrodes. On the other hand, surfactants have proven effective in the electroanalysis of biological compounds and drugs. For example, it was recently shown that surfactants are highly effective in stabilizing the voltammetric response of serotonin by protecting the electrode surface from fouling [25–29]. In addition, the presence of ascorbic acid in SDS micelles greatly enhances the electrochemical response of DA via a catalytic electrochemical process that can be used for a sensitive determination of DA [30]. When using carbon paste electrodes (CPEs), the incorporation of the surfactant to the carbon paste material has proved to be very useful for voltammetric determination, improving the sensitivity and selectivity of the measurements [31,32].

The aim of this work is to fabricate novel electrode material with low cytotoxicity, high stability, good catalytic activity and an excellent conductivity to achieve the challenge of determining DA in the presence of excess amounts of AA and UA in physiological pH. Carbon paste electrodes were modified by CNPs/SDS to obtain good selectivity and sensitivity towards the electrochemical detection of DA.

2. Experimental

2.1. Reagents

Castor oil was purchased from a local market. Dopamine hydrochloride, AA, UA, CTAB, TX-100 and SDS were obtained from Himedia Chemicals. Sodium hydroxide, perchloric acid, sodium dihydrogen orthophosphate dihydrate, and di-sodium hydrogen phosphate anhydrous were obtained from Merck. Graphite powder was acquired from Lobo Chemie and all chemicals were analytical grade quality. 25×10^{-4} M DA, 25×10^{-3} M AA, and 25×10^{-4} M UA stock solutions were prepared by dissolving in 0.1 M perchloric acid solution, double distilled water, and 0.1 M NaOH respectively. All the other reagents solutions were prepared in double distilled water.

2.2. Apparatus

Electrochemical measurements were carried out with a CHI model 660c Electrochemical Workstation connected to a personal computer for control and data storage. All electrochemical experiments were performed in a standard three-electrode cell. The bare carbon paste electrode, or the carbon paste electrode modified with carbon nanoparticles (CNPs/CPE), or the latter electrode modified with the surfactant SDS (CNPs/SDS/CPE) were used as a working electrode. The counter electrode was platinum wire and the reference electrode was a saturated calomel electrode (SCE). All potentials reported are with respect to the SCE.

Powder X-ray diffraction (PXRD) measurements were performed on a PAN analytical Xpert Pro X-ray Diffractometer using Cu Kα radiation (λ = 0.154 nm) at 40 kV, at a scanning rate of 2 °min^{-1}. UV–visible spectra were performed by using UV–visible Spectro Photometer–Shimadzu (1650), using sonicated carbon nanoparticles in double distilled water. Samples were loaded in a quartz cell and the measurement was taken in the wavelength range 200–800 nm. The structural analysis and composition of the carbon nanoparticles was studied using a JEOL JSM-848 scanning electron microscope (SEM), with energy-dispersive spectroscopy (EDS). The infrared (IR) spectra of samples were collected using a Nicolet IR200 FT-IR spectrometer using KBr pellets, in the range 4000–400 cm^{-1} with 4 cm^{-1} resolution.

2.3. Preparation of CNPs

The CNPs were prepared according to the method reported in the literature [10] with a slight modification. Castor oil is placed in a 50 ml glass beaker containing a cotton wick 1 cm residue in length above the oil surface. Castor oil soot was collected by placing a stainless steel plate on top of the smoldering castor oil. The formation of soot particles was assembled (from the stainless steel plate). The black soot particles are carbon nanoparticles (CNPs).

2.4. Preparation of bare carbon paste electrode

The bare carbon paste electrode was prepared by mixing graphite powder and silicon oil at a ratio of 70:30 (w/w) in an agate mortar until a homogenous paste was obtained. The prepared carbon paste was tightly packed into a PVC homemade cavity (3 mm in diameter) and then smoothed on a weighing paper. The electrical contact was provided by a copper wire connected to the paste in the end of the tube.

2.5. Preparation of CNPs/SDS film modified carbon paste electrode

The CNPs/SDS/CPE was prepared by adding 6 mg CNPs to the 70% graphite powder and 30% silicon oil mixed in an agate mortar to produce a homogenous carbon paste. The paste was packed into the homemade cavity (3 mm in diameter) and then smoothed on a weighing paper. A 0.1 mm SDS solution was immobilized on the CNPs/CPE surface (A 5 μL solution of 0.1 mM SDS solution was added onto the CNPs/CPE by using micro pipette and was incubated for 2 min). The electrical contact was provided by a copper wire connected to the paste in the end of the tube.

3. Results and discussion

3.1. Characterization of prepared CNPs

The PXRD pattern of the obtained CNPs is shown in Fig. 1, and reveals a high intensity diffraction peak at 2θ is 24.9° and an additional peak at 44.3°. They are recognized as diffraction for graphitic carbon [33]. The average particle size was calculated using Debye Scherer's formula and was found to be 14 nm. The UV–visible absorption spectra of the CNP dispersed in double distilled water with double distilled water as a reference is shown in Fig. 2, which features a peak in the 250–275 nm region. These peaks represent the typical absorption of an aromatic π-system, which is similar to that of polycyclic aromatic hydrocarbons [34,35]. The FT-IR spectra for the CNPs in Fig. 3 exhibits peaks at 3440 and 1385 cm^{-1}, which are recognized as O—H stretching vibrations. The small peaks at 2922 cm^{-1}, and 1611 cm^{-1} correspond to the stretching of C—H and C=C bonds, respectively [1,36]. The SEM data reveals that spherical shaped structures were grown with a diameter of ∼100 nm with some irregular shaped particles smaller than ∼300 nm as shown in the Fig. 4. The EDS of CNP shows the