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Cysteine-anchored receptor on carbon nanoparticles for dopamine sensing

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ABSTRACT

Cysteine is covalently bound to carbon nanoparticle surfaces (Emperor 2000™, Cabot Corp., with sulfonate groups, ca. 9 to 18 nm diameter). Based on FTIR spectroscopic observations it seems the SH group is involved in the bonding to the CNP surface. The cysteine functionalized carbon nanoparticles are employed for the extraction and electrochemical determination of dopamine. The significant increase in voltammetric responses for pre-adsorbed dopamine compare with those for solution confirms high affinity of dopamine to carbon nanoparticles functionalized with cysteine (possibly due electrostatic interaction and hydrogen bonding between dopamine and cysteine at the surface carbon nanoparticles). To obtain the optimum of adsorption conditions, the effects of pH, agitation rate, and adsorption time are investigated. A Linear calibration curve is obtained for dopamine in the range of 1.0×10^{-8} to 1.0×10^{-5} mol L^{-1} and the limit of detection is estimated 3.6×10^{-9} mol L^{-1}. The effect of co-existing species such as ascorbic acid and uric acid on the determination of dopamine was investigated. Finally, the determination of dopamine in human serum is demonstrated.

1. Introduction

Recently, new types of carbon nano-materials such as nanotubes [1], graphenes [2], and nanofibers [3] have attracted considerable interests and have become a vast area of research owing to their unique physical and chemical properties which can provide an important and feasible platform for electroanalysis particularly in the design of modified electrodes for electrochemical sensing.

Like other carbon nano-materials, carbon nanoparticles (CNP) were also characteristic of excellent electrochemical activity. Applications of CNP in electroanalytical studies display extraordinary advantages over conventional electrodes including enhanced mass transport and catalysis, highly effective surface areas, high porosity, more absorption and reactive sites and control over the electrode macro-environment [4,5]. The CNPs modified electrode has been applied for the determination of triclosan [6], azathioprine [7] and dihydroxybenzene isomers [8] with high sensitivity.

Various methods for covalent surface attachment to carbon have been developed, for example, on diazonium chemistry [9], Kolbe attachment [10], photo-grafting of olefins [11] and silane attachment [12]. Recently, carbon nanoparticles with sulfonate surface functionality (Emperor 2000™ from Cabot Corp.) have been successfully used as modifier for chemically modified electrode [8,13–15]. It was formed surface sulfonamides with additional amine functionality at the surface of carbon nanoparticles [16]. In another research, the more permanent covalent "high density attachment" of anthraquinone to the amine functional groups is reported [17]. Coenzyme Q10 (or ubiquinone-10) redox processes are investigated on a substrate of dioctylamine sulphonamide functionalized carbon nanoparticles. Here, carbon nanoparticles are hydrophobised by introducing a dioctylamine-sulfonamide surface functionality [18].

Biochemically-modified surfaces are commonly employed in the electroanalytical sensing of various organic compounds. Cysteine, a small thiol-containing amino acid, has been particularly useful for electrode modifications. Since L-cysteine can be modified onto a silver electrode or gold electrode by covalent bonding through the sulfur to give stable and long-lived chemical electrodes, it has been widely applied to modify electrode for the electrochemical detection. L-cysteine modified gold electrode has been applied to the determination of ascorbic acid [19]. It has been reported L-cysteine modified silver has been used to determine hemoglobin [20]. L-cysteine has been applied to modified electrodes for determination of dopamine, recently [21,22].

Dopamine (DA), as one of the important neurotransmitters, plays a significant role in the function of human metabolism, cardiovascular, central nervous, renal, and hormonal systems. Its normal level in blood is very low (0.01–1 μmol L^{-1}) [23]. Significant fraction of the human population is affected by various neurological afflictions which can arise through abnormal DA concentration

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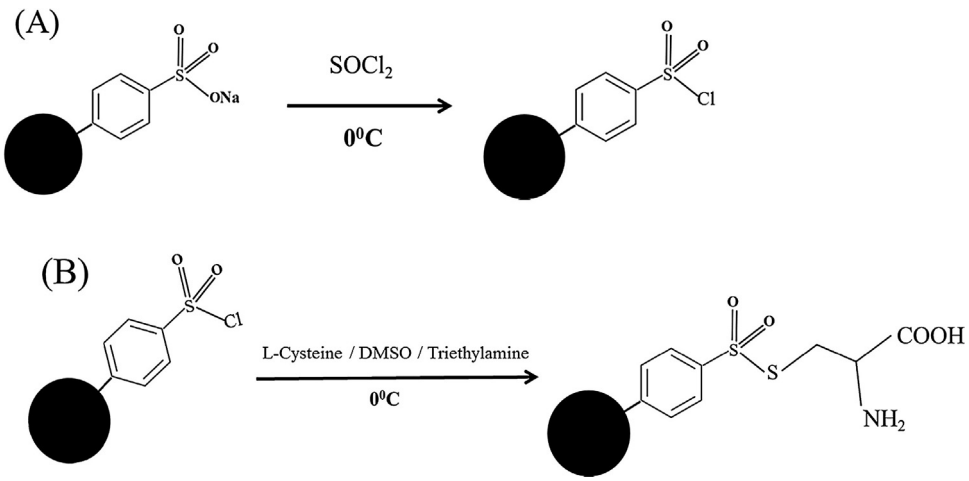

Fig. 1. Reaction scheme proposed for the formation of cysteine-modified carbon nanoparticles.

or transmission into the intercellular fluids like schizophrenia or Parkinson's disease [24]. The development of a simple and rapid method for the determination of DA with high selectivity and sensitivity is desirable for diagnostic applications. Many approaches, including capillary electrophoresis with laser-induced native fluorescence [25], high performance liquid chromatography–mass spectrometry [26] colorimetric detection based on silver nanoparticles [27], have been developed for DA detection. However, these protocols are complicated, expensive, time-consuming, and usually require specialized equipment. Electrochemical techniques have a series of advantages, such as rapid and sensitive response, ease of use, and low-cost small sized commercial detectors. Due to the electroactive nature of DA, its determination by electrochemical methods has been established during the past few decades [28–32].

In this paper, surface functionalization of carbon nanoparticle (Emperor 2000^{TM}) with L-cysteine is reported. The carbon nanoparticle functionalized with cysteine (CNP-Cys) was characterized by using various methods. The adsorption behavior of DA on the CNP-Cys surface has been studied by electrochemical studies that it was confirmed that DA was effectively adsorbed on CNP-Cys. The possible adsorption mechanism was also discussed. Due to the strong adsorption of DA on CNP-Cys modified glassy carbon electrode, a sensitive differential pulse voltammetry method was proposed for the determination of DA in human serum.

2. Experimental

2.1. Apparatus

Voltammetric experiments were performed using a Metrohm Computrace Voltammetric Analyzer model 797 VA. A conventional three-electrode system was used with a glassy carbon disk electrode (2 mm diameter GCE), a KCl- saturated calomel reference electrode (SCE), and a Pt wire as the counter electrode. A digital pH/mV/Ion meter (Metrohm) was applied for the preparing of the buffer solutions, which were used as the supporting electrolyte in voltammetric experiments. The surface morphology of the films was studied by a scanning electron microscope (SEM) images were obtained using LEO 1430VP.

2.2. Reagents

Carbon nanoparticles with surface sulfonate groups were obtained from Cabot (ca. 9 to 18 nm diameters, Emperor 2000^{TM}, Cabot Corporation). Uric acid was purchased from Alfa Aesar. All other chemicals (thionyl chloride, cysteine, dichloromethane, acetonitril, ascorbic acid and DMSO) were analytical reagent grade from Merck. All aqueous solutions were prepared with doubly distilled deionized water.

2.3. Procedure I. Covalently surface modification of carbon nanoparticles

Step (A) (see Fig. 1): typically 0.5 g of carbon nanoparticles (Emperor 2000) were sonicated in dry dichloromethane in a round bottom flask for 30 min. The flask was degassed with nitrogen at 0 °C and 5 mL of freshly distilled thionyl chloride was added dropwise under continuous stirring. The flask was then allowed to warm to room temperature whilst stirring for 2-3 h. Excess of thionyl chloride and solvent were removed in vacuum [16].

Step (B) (see Fig. 1): In a 100 mL round bottom flask containing 20 mL of DMSO and 0.8 mL of triethylamine L-cysteine (0.2 g, 0.016 mmol) was dissolved at 0 °C. The sulfonyl chloride functionalized carbon nanoparticles (step A) were added into the flask in small portions. The reaction mixture was allowed to warm to room temperature and stirred for 12 h. Excess of L-cysteine and DMSO was separated with centrifuge. Aqueous 1 M HCl was then added and the black solid (CNP-Cys) was collected by Buchner filtration.

2.4. Procedure II. Deposition of CNP-Cys onto glassy carbon electrodes

Pretreatment of GC electrode was done using 2500 emery (Germany) rinsed thoroughly with water. A stable suspension of CNP-Cys containing 1 mg/ml in acetonitril using 30 min ultrasonic agitation was prepared. 5 μL of this suspension was casted on the pretreated GC surface and dried in the air to evaporate solvent. The obtained modified GC was characterized by scanning electron microscopy (SEM), and cyclic voltammetry techniques (CV).

2.5. Procedure III. Extraction of DA from aqueous media onto GC/CNP-Cys

The adsorption of DA was performed onto modified electrode during 2 min in 25 mL solution with appropriate amount of DA. The volume of adsorption solution was constant in all experiments. The stirrer was switched on. Following the adsorption time, the stirrer was stopped. The electrode was taken out of the adsorption cell and was then transferred into voltammetric cell. Voltammograms were recorded by applying positive going potential from -0.25 to +0.7 V.