



Carbon nanohorns/poly(glycine) modified glassy carbon electrode: Preparation, characterization and simultaneous electrochemical determination of uric acid, dopamine and ascorbic acid



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ABSTRACT

A novel carbon nanohorns/poly(glycine) based sensor was successfully fabricated by electropolymerization of glycine at carbon nanohorns modified glassy carbon electrode for simultaneous determination of uric acid (UA), dopamine (DA) and ascorbic acid (AA). Electrochemical responses of as-prepared electrodes were investigated by cyclic voltammetry, electrochemical impedance spectroscopy and differential pulse voltammetry. Owing to the synergistic effect of carbon nanohorns and poly(glycine), three well defined and separated oxidation peaks were observed. Peak separations between AA and DA, DA and UA at as-prepared electrode were 130 and 120 mV, respectively. The current of the oxidation peaks showed a linear dependent on the concentrations of UA, DA and AA in the range of 2–350 μM , 1–280 μM and 30–450 μM , respectively, and the detection limits were calculated as 0.18, 0.03 and 0.34 μM ($S/N = 3$), respectively. Based on the simple preparation and prominent electrochemical properties, the obtained carbon nanohorns/poly(glycine) modified electrode was applied for the simultaneous determination of UA, DA and AA in the urine samples.

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1. Introduction

Uric acid (UA), the primary product of purine metabolism, is an important biomolecule that presents in human urine and blood [1]. Abnormal concentration level of UA may cause a series of diseases, such as hyperuricaemia, gout and Lesch–Nyan disease [2,3]. Dopamine (DA) is a crucial neurotransmitter in mammalian central nervous system, which plays a critical role in the functioning of the central nervous, cardiovascular, renal and hormonal systems as well as in drug addiction and Parkinson's disease [4,5]. Ascorbic acid (AA), as a necessary vitamin for humans, plays a major role in the metabolic process of human body [6,7]. Its role in inhibition and treatment of common cold, mental illness, infertility and cancer has been investigated [8].

UA, DA and AA usually coexist in human body fluids, thus simultaneous determination of UA, DA and AA is extremely important not only for investigating their physiological functions but also for diagnosing diseases. In recent years, several methods have been developed to detect two or three components of UA, DA and AA simultaneously, such as capillary electrophoresis [9], high performance liquid chromatography [10], spectrophotometric method [11] and electrochemical

method [12]. Among these methods, electrochemical method for the detection of UA, DA and AA has attracted considerable attention because of its numerous advantages, such as simplicity, fast-response and low-cost [13].

It is noteworthy that the oxidation potentials of UA, DA and AA are too close to be separated at bare electrode for their overlapping signals. To overcome this problem, various materials have been utilized to modify electrodes over the past decades, such as metal nanoparticles, polymers, carbon nanomaterials [14–17]. Both theoretical and experimental studies have demonstrated that carbon nanomaterials have promising applications in sensor due to their unique and fascinating properties [18–22]. Significantly, carbon nanohorns (CNHs) synthesized by laser ablation of pure graphite have been studied directly for sensor applications [23]. As an active matrix, CNHs have horn-shaped sheaths composed of graphene sheets, which possess excellent electrical conductivity, high specific surface area and internal space [24].

As a modification method, electropolymerization has received enormous attention because of its simplicity, selectivity and sensitivity towards analytes, strong adherence of polymer film to electrode surface and ability to provide larger surface area by forming homogeneous membrane [25]. Chemically modified electrodes with poly(amino acid), poly(imidazole), poly(phenylene oxide), poly(pyrrole), polyaniline and poly(glycine) (PGLY) have been described in the literatures for the development of electrochemical sensors [26–31]. Moreover, the combined

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properties of PGLY and CNHs make them attractive for the electrochemical detection of UA, DA and AA.

In this work, by taking advantages of large surface area and perfect electronic conductivity of CNHs and excellent electrocatalytic activity of PGLY, we developed a highly sensitive sensor based on PGLY and CNHs towards simultaneous electrochemical determination of UA, DA and AA. The as-prepared electrode presented satisfactory sensitivity and selectivity, excellent reproducibility and long-time stability because of the synergistic effect of PGLY and CNHs. Separations of DA–AA and DA–UA oxidation peak potentials were 130 and 120 mV, which are large enough to realize the simultaneous electrochemical determination of UA, DA and AA.

2. Experimental

2.1. Reagents and materials

CNHs, glycine (GLY), N,N-dimethylformamide (DMF), potassium ferricyanide, UA, DA, AA, sodium chloride, potassium chloride (KCl), zinc sulfate, cupric nitrate, magnesium chloride, potassium nitrate, calcium chloride, citric acid, glucose, L-cysteine, folic acid, disodium hydrogen phosphate (Na_2HPO_4) and sodium dihydrogen phosphate (NaH_2PO_4) were of analytical grade and purchased from Chengdu Chemical Reagent Factory (Chengdu, China). Phosphate buffer solution (PBS) was prepared by mixing stock solutions of Na_2HPO_4 and NaH_2PO_4 (0.10 M). High purity nitrogen (99.999%) was used for deaeration. The stock solutions of UA, DA and AA were prepared daily and kept in an ice bath. Doubly distilled water was used throughout the whole experiments.

2.2. Preparation of CNHs/GCE, PGLY/GCE and CNHs/PGLY/GCE

Before modification, bare GCE was polished successively with 0.50 μm and 0.050 μm alumina powders and then washed by sonication in doubly distilled water repeatedly. 1.0 mg CNHs was dispersed in 1.0 mL DMF with ultrasonic agitation to obtain a black stable suspension. Subsequently, 5.0 μL as-prepared suspension was dropped onto GCE surface and dried in air to obtain CNHs/GCE.

Electropolymerization of glycine at CNHs/GCE was carried out by cyclic voltammetry between -0.6 V– 1.4 V at a scan rate of 50 mV/s for 4 cycles in aqueous solution containing 0.040 M glycine and 0.20 M acetate buffer solution (pH 5.0) [29]. The electrode was thoroughly washed with distilled water after polymerization and used for electrochemical characterization. For comparison, preparation of PGLY/GCE was similar to that of CNHs/PGLY/GCE just using bare GCE instead of CNHs/GCE.

2.3. Characterization of CNHs and as-prepared electrodes

Scanning electron microscopy (SEM) was used to analyze the micro-morphology of CNHs (Ultra 55, Zeiss Corporation). Transmission electron microscopy (TEM) measurements were performed on a Zeiss Libra 200FE transmission electron microscope operated at an accelerating voltage of 200 kV.

Cyclic voltammogram (CV), electrochemical impedance spectroscopy (EIS) and differential pulse voltammogram (DPV) were recorded with a PARSTAT 2273 electrochemical workstation (Princeton Applied Research, USA) by introducing a three-electrode test system using a platinum electrode as counter electrode, bare or modified GCE as working electrode referred to saturated calomel electrode (SCE). The electrochemical parameters for DPV were as follows: increment potential of each point = 0.004 V, potential pulse amplitude = 0.05 V, potential pulse width = 0.05 s, data sampling width = 0.0167 s and potential pulse period = 0.2 s.

3. Results and discussion

3.1. Morphological characterization of CNHs

Shown in Fig. 1 were TEM images and SEM image of CNHs. It was revealed that a large number of CNHs restacked to form a clear spherical structure with a diameter of about 40–80 nm (Fig. 1A), which was further evidenced by TEM image (Fig. 1B), where many CNHs structural units restacked to formed dahlia-like assemblies with almost the same diameter of about 40–80 nm [32]. The individual CNH structural unit was shown clearly with diameter range from 2 to 5 nm (Fig. 1C). Lots of CNHs presented a good conductive network, which might provide favorable sites for electron transfer to molecules [33].

3.2. Electropolymerization of GLY

Electropolymerization is a convenient method to obtain PGLY with some desired properties such as low cost, increased sensitivity and selectivity, enhanced electrochemical response and increased electrode active surface area. Shown in Fig. 2 were CVs for electropolymerization of GLY at CNHs/GCE in 0.040 M GLY + 0.20 M acetate buffer solution (pH 5.0) at a scan rate of 50 mV/s. The decrease in peak currents on successive scanning from -0.6 to 1.4 V indicated the growth of conducting polymeric film at CNHs/GCE. The current was gradually stabilized after 4 cycles. After modification, a transparent layer of PGLY membrane was observed at the electrode surface.

The thickness and uniformity of the PGLY film could be facily controlled through regulating the scan cycles during electropolymerization process. To investigate the optimal film thickness, electropolymerization was carried out by cyclic voltammetry between -0.6 V– 1.4 V and the number of scan cycles were varied from 1 to 6. Usually, $[\text{Fe}(\text{CN})_6]^{3-/4-}$ was used as an electrochemical probe to test the electron transfer kinetic between electrode and species in solution [34].

Shown in Fig. 3 were CVs of 1.0×10^{-3} M $\text{K}_3\text{Fe}(\text{CN})_6$ + 0.10 M KCl solution at as-prepared electrodes with different scan cycles. It was indicated that current response decreased when the scan cycles were less than 4 cycles due to thin polymer film and less of effective sites. It was evident that the redox peak currents decreased after 4 cycles, suggesting that more cycles led to the formation of thicker film and the molecules of $[\text{Fe}(\text{CN})_6]^{3-/4-}$ could not arrive at the surface of electrode because of high mass transfer resistance. Therefore, electropolymerization of 4 CV cycles were used as optimum condition for the construction of the modified electrode.

3.3. Electrochemical characterization of as-prepared electrodes

Shown in Fig. 4 were CVs of 1.0×10^{-3} M $\text{K}_3\text{Fe}(\text{CN})_6$ in 0.10 M KCl solution at bare GCE and as-prepared electrodes. It was found that ΔE_p of 127 mV at PGLY/GCE was larger than that obtained at bare GCE (65 mV), suggesting that $[\text{Fe}(\text{CN})_6]^{3-/4-}$ redox couple had a slow electron transfer kinetics at PGLY/GCE, possibly due to the poor conductivity of PGLY (Fig. 4, curve a) [29]. In addition, ΔE_p of $[\text{Fe}(\text{CN})_6]^{3-/4-}$ probe at CNHs/GCE (Fig. 4, curve b) decreased to 84 mV and the peak currents on curve b were much larger than those on curve a, which was related to the fine electrical conductivity of CNHs and was beneficial to facilitate electron transfer between $[\text{Fe}(\text{CN})_6]^{3-/4-}$ ions and electrode [34]. More remarkably as shown in Fig. 4, curve c, the smallest ΔE_p of 79 mV was obtained for the $[\text{Fe}(\text{CN})_6]^{3-/4-}$ probe at CNHs/PGLY/GCE because of CNHs acting as effective electron conduction pathways. Additionally, after the combination of PGLY and CNHs, CNHs/PGLY/GCE showed the highest redox peak current among other electrodes, which might be the reason that the electron transfer process at the as-prepared electrode surface was promoted with improved ultrahigh surface area and good electronic conductivity. It was also demonstrated that the two materials in the composite had synergic effect for facilitating electron transfer between $[\text{Fe}(\text{CN})_6]^{3-/4-}$ ions and CNHs/PGLY/

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