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Short communication

High performance electrochemical sensor based on fullerene-functionalized carbon nanotubes/ionic liquid: Determination of some catecholamines

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ABSTRACT

The combination of fullerene (C_{60})-functionalized multiwalled carbon nanotubes (CNTs) and ionic liquid (IL) that yields a nanostructured modified electrode formed a novel kind of structurally uniform and electrocatalytic activity material. The modified electrode was characterized by different methods. It was found that the nanocomposite film of C_{60}-CNT/IL on glassy carbon electrode exhibits excellent electrocatalytic activity towards catecholamines, including norepinephrine (NE), isoprenaline (IP) and dopamine (DA) oxidation, resulting in a marked lowering in the peak potential and considerable improvement of the peak current as compared to the electrochemical activity at the bare glassy carbon electrode. The improvement of electrochemical response to catecholamine oxidation was found at modified electrode, revealing the synergetic effect of C_{60}-CNT and IL. Furthermore, the catecholamines were successfully used for the determination of catecholamines in real samples.

1. Introduction

In electrochemistry, particularly in the area of electroanalysis, electrocatalysis offers reductions in overpotential and increase in the magnitude of voltammetric peak heights, allowing low detection limits to be more achievable [1].

Since the first finding of C_{60}, the electrochemistry of fullerenes or their derivatives (including carbon nanotubes) has been one of the most intensely studied aspects of fullerene chemistry [2] and fullerene has previously been applied to electrocatalysis [3–6]. C_{60} appears to be attractive to researchers for modifying electrode surfaces because it is chemically stable, metallic impurity free and relatively simple to implement and gives rise to reproducible electrocatalytic responses [7,8]. The reports that C_{60} modified electrodes confer electrocatalysis have not been widely accepted [9]. However, recent work by Compton [10] has shown that the observed electrocatalysis in some cases was caused by either the small amount of graphite impurity in C_{60} sample, or the oxygenated species formed on the surface of glassy carbon electrodes by "electrode pretreatment", while electrocatalysis mediated by C_{60} is only likely "where C_{60} itself becomes oxidized or reduced" [10]. However the area remains contentious.

Carbon nanotubes (CNTs) have been deemed as excellent electrocatalysts for a large variety of compounds [11,12]. Strong promises were given, raising high expectations [13]. Due to rich electrochemistry of fullerene, electrochemistry of fullerene peapods (C_{60}@CNT and C_{70}@CNT) was investigated since synthesis of fullerene peapods was reported. Carbon nanotubes have also been applied to this purpose because of their remarkable electrocatalytic properties [14]. As an excellent electron acceptor, C_{60} could be dispersed in nanomaterials, such as carbon nanotubes, to facilitate electron transfer.

Recent investigations revealed that C_{60}-functionalized multiwalled carbon nanotube (MWCNT) films were more effective in facilitating the direct electron transfer of hemoglobin than MWCNT films [15]. Zhu et al. successfully constructed a C_{60}-functionalized MWCNT film to achieve a dopamine detection limit of 0.03 μM, compared to 0.15 μM at a MWCNT modified electrode [16]. Wael et al. developed a C_{60}-functionalized MWCNT film for the electrocatalytic determination of the vinclozolin [17].

To the best of our knowledge, no study has been published so far reporting the electroanalytical applications of C_{60}-functionalized CNT and ionic liquid composites (C_{60}-CNT/IL). Here in continuation to our studies concerning the preparation of modified electrodes [14,18–20], we developed a C_{60}-CNT and ionic liquid composite film as a new modifier for the electrocatalytic determination of catecholamines in human serum and urine samples. The results showed that the composite film of C_{60}-CNT/IL on a glassy carbon (GC) electrode is more sensitive for the detection of catecholamines compared to bare GC electrode and CNT/GC electrode. The improvement electrochemical response of catecholamines was found at C_{60}-CNT/IL/GC, revealing the synergetic effect of C_{60}-CNT and IL.

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2. Experimental

2.1. Apparatus and chemicals

Electrochemical measurements were performed by an Autolab potentiostat/galvanostat (PGSTAT-302 N, Eco Chemie, Netherlands). A three-electrode system was used, where a GC electrode or a modified GC electrode (2 mm diameter) served as the working electrode, a platinum wire as the counter electrode and an Ag/AgCl/KCl (3.0 M) electrode as the reference electrode. The morphology of nanomaterial was characterized using scanning electron microscopy (SEM, Hitachi S-4160) and transmission electron microscopy (TEM) (Philips EM208). For impedance measurements, a frequency range of 100 kHz to 0.1 Hz was employed. The AC voltage amplitude and DC voltage were 5 mV and 150 mV, respectively.

Norepinephrine, isoprenaline, dopamine, 1-butyl-3-methylimidazolium tetrafluoroborate and fullerene-C_{60} (99.5%) were reagent-grade from Sigma Aldrich. Phosphate salt, sodium hydroxide, solvents and reagents were of pro-analysis grade from Merck (Darmstadt, Germany). Multiwalled carbon nanotubes (purity more than 95%) were purchased from Plasma Chem (Germany).

2.2. Preparation of the electrode

Modified electrodes were prepared by a simple casting method. Prior to the surface coating, the GC electrode was polished on a polishing cloth with 0.05 μm alumina powder. Purified MWCNTs and C_{60} (MWCNTs/C_{60} = 2:1, mass ratio) with a total amount of about 1 mg were dispersed in 10 mL toluene in an ultrasound bath for 30 min to give a 0.1 mg mL^{-1} suspension. A volume of 10 μL of the suspension was applied directly on a GC electrode surface and the solvent was allowed to evaporate at room temperature (10 min). This C_{60}-MWCNT film electrode was subjected to potential scanning in acetonitrile containing 0.1 M tetrabutylammonium hexafluorophosphate between 0.0 and −2.0 V (vs Ag/AgCl) until reversible multistep electron-transfer reaction was obtained [21]. The resulting C_{60}-CNT film electrode was then washed with acetonitrile several times to remove the electrolytes and dried at room temperature. Then, 50 μL of IL was dispersed in 0.3 mL 1% chitosan solution in 1 M of acetic acid. After the mixture was sonicated for 30 min, 3.0 μL was applied to the surface using a microsyringe and this was allowed to dry in a stream of hot air (15 min).

3. Results and discussion

3.1. Characterization of the C_{60}-CNT/IL composites

In order to understand the performance of the C_{60}-CNT/IL composites, we investigated modified electrodes by TEM, SEM, electrochemical impedance spectroscopy (EIS) and cyclic voltammetry (CV), respectively.

The response of a modified electrode is related to its physical morphology. Fig. 1A and B shows the TEM and SEM micrographs of C_{60}-CNTs/GC electrode and C_{60}-CNTs/IL/GC electrode, respectively. Fig. 1A clearly shows nanoclusters of C_{60} and CNTs that resulted from the

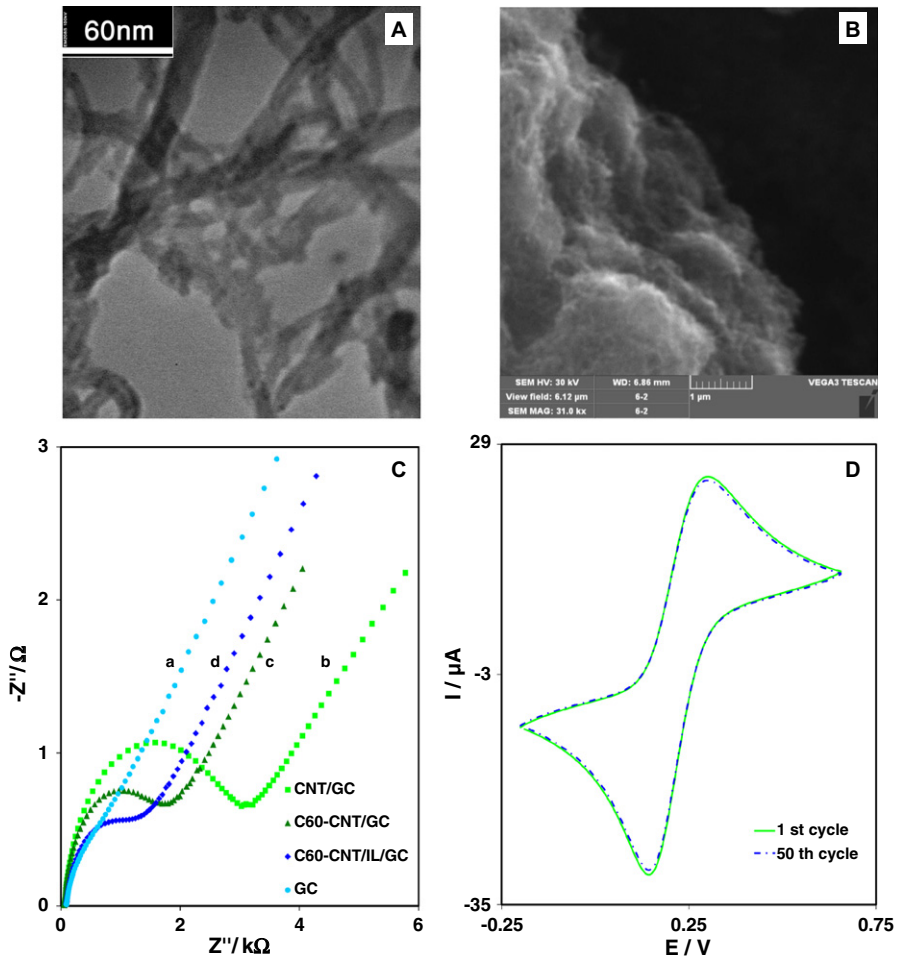

Fig. 1. (A) TEM image of C_{60}-CNT, (B) SEM image of C_{60}-CNT/IL nanocomposite, (C) Nyquist plots of bare GC electrode (a), CNT/GC (b), C_{60}-CNT/GC (c), C_{60}-CNT/IL/GC, (D) 1st cycle and 50th cycle of C_{60}-CNT/IL/GC in 1 mM $Fe(CN)^{3+/4+}$ containing 0.1 M KCl.