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Electrochemical activation of polyethyleneimine-wrapped carbon nanotubes/in situ formed gold nanoparticles functionalised nanocomposite sensor for high sensitive and selective determination of dopamine

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ABSTRACT

An electrochemical sensor based on polyethyleneimine (PEI)–multiwalled carbon nanotubes (MWNTs)–gold nanoparticles (AuNPs) nanocomposite was constructed for determination of dopamine (DA). MWNTs–PEI–AuNPs nanocomposite combined the advantages of PEI-well dispersed MWNTs and in situ formed AuNPs, thus endowed with high stability and some special properties to the enzyme-free sensor. The formation of the material was characterized by scanning electron microscope, transmission electron microscope and energy-dispersive X-ray. Electrochemical activation of the modified sensor at a positive potential remarkably enhanced the signal due to some introduced fragmentation in the side wall of MWNTs–PEI–AuNPs. Another important conclusion which was not recognized before is that CVD–CNT with open end caps of CNT also can be electrochemically activated after coating with polyelectrolytes (PEs). The prepared sensor showed good performance for the determination of DA in a linear range from 50 to 4000 nM with a limit of detection of 6.56 nM and a sensitivity of 5.2 μA μM^{-1}. It also exhibit high stability of at least 2 months and high selectivity of DA under the interferences of glucose, ascorbic acid, etc. due to the novel sensing materials and remarkable electrochemical activation. We also demonstrated the successful application of this sensor for the determination of dopamine in serum.

1. Introduction

Dopamine (DA), as a bioactive substance, plays an essential function in neurotransmission, metabolism, pressure regulation, emotional expression and mental activity [1]. Though DA is found in large quantities (50 μM) at the caudate nucleus, a region of the brain [2] but low concentration (<1 μM) in serum [3], brain measurement would be difficult and dangerous. Therefore, a rapid and reliable determination in the serum is strongly required due to the significance of DA. Some traditional methods, such as fluorescent spectrometry [4–6] and chromatographic [7], need expensive and large-scale instruments and complex pre-treatment, while the sensitivity or limit of detection (LOD) sometimes are far from satisfactory, thus it will cause some limitation of their application in on-line monitoring. Recently, rapid developments have been mainly focused on electrochemical determination of DA, because of the advantages such as high sensitivity and low LOD. Some examples concerning the determination of DA using enzyme-based sensors such as tyrosinase have been reported [8,9]. However, the activity of enzyme is greatly influenced by external factors such as conditions for immobilization or determination, and usually decreases rapidly with the elongation of working time. For this reason, enzyme-free sensors have been paid growing attention to. For example, Wang group [10,11] built an amperometric sensor based on carbon nanotubes/Nafion for the determination of DA and got linear behavior over 2–20 μM with a LOD of 70 nM. Later, they developed the sensor to an amperometric biochip for DA sensing by using polymer plate which contained the separation and injection channels for capillary electrophoresis. However, the concentration of DA in human body is less than approximately 1 μM [3], which is so low that enzyme-free sensors with higher sensitivity are strongly desirable.

To improve the performance of sensors, various materials like polyelectrolytes (PEs) and nanomaterials are used to modify the electrode. After the discovery of carbon nanotubes (CNTs) in 1991 by Iijima [12], CNTs, especially multiwalled-carbon nanotubes (MWNTs) have high aspect ratio, nanometer sized dimensions and good electrical conductivity compared with conventional carbon

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Abbreviations: PEI, polyethyleneimine; MWNTs, multiwalled carbon nanotubes; AuNPs, gold nanoparticles; SEM, scanning electron microscope; TEM, transmission electron microscope; EDX, energy-dispersive X-ray; LOD, limit of detection; DA, dopamine; PEs, polyelectrolytes; CNTs, carbon nanotubes; SDS, sodium dodecyl sulfate; Py, pyrrole; PSf, polysulfone; DPV, different pulse voltammetry; RSD, relative standard deviation; PBS, phosphate buffer solution.

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materials used in electrochemistry such as glassy carbon (GC), graphite, and carbon fiber [13]. The distinct structural and electronic properties make CNTs played an important role in the construction of biosensors [14–18]. For example, the MacPherson group [13,19] used CNTs modified sensors to detect DA with a creative method. However, the dispersion of MWNTs is not good enough to form an even film on the surface of the electrode [20]. Based on the electron donor and acceptor interaction between PEs and MWNTs, PEs are used to disperse MWNTs to overcome this shortage. Another interesting nanomaterial is Gold nanoparticles (AuNPs). Because the electrons can move freely, the electric field of the surface of AuNPs is largely enhanced, which caused the wide application of AuNPs. Basing on the respective advantages of MWNTs and AuNPs, the composites containing both PEs-dispersed MWNTs and AuNPs will bring some special properties and high potential of applications. Guo et al. [21] deposited AuNPs on the composite which was layer-by-layer assembled of MWNTs and chitosan. The obtained nanomaterial was then grown on the polystyrene templates to detect DA. Si et al. [22] prepared a positively charged AuNPs which were further immobilized on the negatively charged CNT/GC by electrostatic interaction. Importantly, when the AuNPs were in situ formed on the surface of MWNTs instead of simply mixing of these materials, the stability of the composites would be improved greatly, which made the performance of sensor more stable. However, as the best of our knowledge, there are few reports introducing the composites containing both PEs-dispersed MWNTs and in situ formed AuNPs into the enzyme-free sensors for the determination of DA. In addition to AuNPs, enzyme-free sensors to DA based on other materials and MWNTs were also very interesting [23,24].

Electrochemical activation of electrodes is a very interesting phenomenon, although its mechanism is still to some degree unclear. Several examples reported the electrochemical activation of CNTs or CNTs composites such as MWNTs/poly-sulfone (PSf), and SWNTs/poly-pyrrole (PPyox), and the determination performance of sensors was improved [25–30]. Pumera et al. [27] further investigated the reason why electrochemical activation of MWNTs/PSf composite could enhance the electron transfer rate, and they found the polymer wrapping of CNTs was partially removed during activation. Undoubtedly the potential of electrochemical activation for the improvement of sensors performance, especially some sensors with novel constructing materials or sensing devices, is still far from being revealed.

In this work, we prepared a novel composite containing polyethyleneimine (PEI)-dispersed MWNTs and in situ formed AuNPs and introduced it into an enzyme-free sensor for the high sensitive determination of DA. AuNPs were in situ formed on the surface of MWNTs–PEI using PEI catalyzed reduction of $HAuCl_4$ [31] and thus greatly improved the binding stability of AuNPs onto the MWNTs. The important electrochemical activation of the modified electrode further improved the determination sensitivity of the sensor, and the signal of the MWNTs–PEI–AuNPs modified electrode was six times higher than that without activation. SEM revealed the interesting morphology change of MWNTs–PEI–AuNPs modified electrode after electrochemical activation. Due to the reliable preparation procedure of novel electrode nanomaterials and the activation treatment of the sensor, the sensor exhibited good performance in the determination of DA and was applied in the serum sample.

2. Experimental

2.1. Chemicals and instruments

Multiwalled carbon nanotubes (MWNTs with a purity of 95%) were purchased from Shenzhen Nanotech Port. Co., Ltd., China. Chloroauric acid ($HAuCl_4$) was obtained from Sinopharm Chemical Reagent Co., Ltd. Polyethyleneimine (PEI, 10,000, 99%) was from Alfar Aesar. Dopamine Hydrochloride (from Sigma–Aldrich, Co.) was used in this study. A phosphate buffer solution (PBS) of pH 7.5 was prepared using 0.02 mol L^{-1} Na_2HPO_4 and NaH_2PO_4. All other chemicals used in this study were analytical reagent grade and without further purification. All solutions were prepared with double deionized water.

Electrochemical measurements were carried out with on a CHI 650 electrochemical analyzer (Shanghai CH Instrument Company, China). A conventional three-electrode system was used with a bare gold electrode or a modified gold electrode as the working electrode, a saturated calomel electrode as the reference electrode, and a platinum disk electrode as the auxiliary electrode. A scanning electron microscopy (SEM, FEI, USA) with an energy-dispersive X-ray spectroscopy (EDX) analyzer (LEO1530, Leo, Germany) was used to obtain scanning electron micrographs of the dopamine sensing film. A transmission electron microscope (TEM; JEM-1200EX) was used to obtain transmission electron micrographs of the dopamine sensing film.

2.2. The preparation of MWNTs/PEI/AuNPs composites

MWNTs were purified by refluxing in 3 M nitric acid for 12 h in the temperature of 150 °C. After subsiding, the sediments were washed with double deionized water. The suspension was suction filtered and subsequently been dried on the temperature of 60 °C. Followed by being washed and filtered until the filtrate was neutral, the resultant solid was sonicated in the mixed solution of HNO_3 and H_2SO_4 (1:3, v/v) for 3 h. Then the pH of the MWNTs was adjusted to 8.0 using NaOH (15%), and been centrifuged and dried subsequently. Then the expected anionoid carboxylated MWNTs were obtained.

The preparation of the composite was according to the literature [31]. Briefly, a total of 3.4 mg of carboxylated MWNT was distributed in 10 mL double deionized water. The mixture was sonicated for 10 min to form a uniform dispersion. Subsequently, 0.7 mL PEI aqueous solution (1 M) was added to it with a 5 min ultrasonic agitation. 2 mL $HAuCl_4$ (18 mM) was added to the dispersion and the mixture was taken a 70 °C water bath for 2 h to reduce $HAuCl_4$ to AuNPs. Next, the mixture was centrifuged at a rate of 14,500 rpm for 10 min twice to move away the redundant PEI and AuNPs. 1.5 mL double deionized water was added to the precipitation to obtain the sensing nanocomposite of MWNTs–PEI–AuNPs.

Cationic PEI was coated onto MWNTs by electrostatic force. More critically, amines on PEI possessed high affinity for physisorption along the MWNTs' surface which was similar to the polymer wrapping process [32,33]. The high density of imino-groups on PEI played an important role in the adsorption of anionic $AuCl_4^-$ followed by reducing of $AuCl_4^-$. Schematic illustration could be seen in Scheme 1.

2.3. Construction of MWNTs–PEI–AuNPs modified electrode

Before modification, the gold electrode (CHI, 2 mm in diameter) was polished with Al_2O_3 slurry (1.5 μm, 0.5 μm and 30 nm) and sonicated in double deionized water for 3 min. After being rinsed with double deionized water, it was immersed in freshly prepared and slightly cooled Piranha solution (3:1 mixture of concentrated H_2SO_4 and 30% H_2O_2, v/v) for 15 min followed by thoroughly ultrasonic rinsing. Subsequently, a further clean gold electrode was prepared after obtaining a stable cyclic voltammogram by using cyclic voltammetry between −0.2 and +1.5 V in 0.2 M H_2SO_4 solution.

The sensor was prepared by casting the nanocomposite on the surface of gold electrode. The nanocomposite could adhere on