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Simultaneous determination of hydroquinone and catechol using covalent layer-by-layer self-assembly of carboxylated-MWNTs

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ABSTRACT

A carboxylated multi-wall carbon nanotubes (CMWNTs) layer-by-layer (LBL) self-assembled film was prepared using ethylenediamine as an arm linker. Scanning electron microscopy (SEM) characterized the morphology of the LBL self-assembled film and Fourier transform infrared (FT-IR) spectroscopy confirmed the formation of covalent bond between CMWNTs and ethylenediamine. The electrochemical experiments indicated that the modified electrodes can simultaneously determinate hydroquinone (HQ) and catechol (CC). Differential pulse voltammetry (DPV) exhibited the oxidation peak current of HQ was linear to its concentration in the range of 10–120 μM with the detection limit of 2.3 μM in the presence of 0.1 mM CC, and at the same time the oxidation peak current of CC was linear to its concentration in the range of 5–80 μM with the detection limit of 1 μM in the presence of 0.1 mM HQ. Moreover, the CMWNTs modified electrode also showed excellent selectivity and stability.

1. Introduction

Hydroquinone (HQ) and catechol (CC) are two isomers of phenolic compounds, which usually coexist in environmental samples as environmental pollutants with high toxicity [1]. HQ may cause fatigue, headache, kidney damage, and CC may cause liver function decrease [2], [3]. The accurate determination of HQ and CC is needed urgently. Nevertheless, HQ and CC have similar structure and properties, which make it difficult to determinate them simultaneously. Accordingly, it is crucial to develop a selective and simple method for the simultaneous determination of HQ and CC. Recently, high-performance liquid chromatography [4], synchronous fluorescence [5], spectrophotometry [6], gas chromatography/mass spectrometry [7] and electrochemical methods [8–15] have been reported for simultaneous determination of HQ and CC. Among them, electrochemical methods have attracted more attention due to the advantages of fast response, low cost, high sensitivity and selectivity. However, similar chemical structure of HQ and CC could lead to the adjacent potential of redox peaks in their electrochemical signals at ordinary electrode. It is difficult to discriminate the overlapped redox peaks of HQ and CC, so the simultaneous determination of HQ and CC can hardly be achieved. Recently, new materials for simultaneous determination of HQ and CC were used to modify the electrodes, including carbon nanotubes [16,17], mesoporous Pt [18], mesoporous carbon [19], graphene [20–22] etc. However, it is still a challenge to explore novel electrode materials for the simultaneous determination of HQ and CC with wider linear range and higher stability.

Carbon nanotubes (CNTs) are formed by rolling graphite sheets, and they have quasi-one dimensional (1D) structure. Due to their good chemical stability, large aspect ratio, excellent electrical conductivity, and extremely high mechanical strength and stiffness, CNTs were widely used to the development of high-performance electrochemical sensors [23]. Recently, owing to the advantages of all kinds of assembled materials, layer by layer (LBL) self-assembly has become a very promising technique for fabricating multifunctional nanocomposites thin films. Regretfully, this strategy has poor stability and reproducibility when using it in electrochemistry detection because of the loose interactions like electrostatic adsorption or hydrophobic interaction [24,25]. And even if covalent bond was adopted in the LBL assembly, the substrates usually need to be modified with polymers firstly to obtain the function groups on the electrode surface [26,27]; this inevitably enhances the impedance between solution and electrode interface. Certainly the sensitivity and determination ability of modified electrode are seriously influenced. To solve these problems, it is very important to develop a method to assemble pure LBL films without any foreign materials. Up to now, using all CNTs as LBL assembled materials has been little reported [24,26,27].

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Herein, we fabricated a LBL covalently self-assembled carboxylated multi-wall carbon nanotubes (CMWNTs) film and modified it onto glassy carbon electrode (GCE) without any polymer, which can simultaneously determinate HQ and CC by cyclic voltammetric (CV) and differential pulse voltammetric (DPV) techniques. In the LBL process, ethylenediamine serviced as an arm linker [28] between CMWNTs. The multilayered nanostructure thin film was assembled using CMWNTs and ethylenediamine via carbodiimide procedure, which was evident from the scanning electron microscopy (SEM) images and the Fourier transform infrared (FT-IR) spectra. Furthermore, the obtained all CMWNTs films exhibits an excellent stability and selectivity.

2. Experimental

2.1. Reagents and apparatus

Multi-wall carbon nanotubes (MWNTs, 99%, diameter of 10–30 nm and length of 1–2 μm) were purchased from Shenzhen Nanotech Port Co., Ltd. (Shenzhen, China). N-hydroxysuccinimide (NHS), 1-ethyl-3-(3-dimethyllaminopropyl) carbodiimide hydrochloride (EDC), HQ and CC were purchased from Aladdin Reagent Co., Ltd. (Shanghai, China). Phosphate buffer solution (PBS) was prepared by mixing 0.1 M NaH_2PO_4–Na_2HPO_4. Other chemicals were analytical reagent grade and all solutions were prepared with redistilled deionized water.

The morphology of the produced materials was analyzed via SEM on the LEO 1530 SEM instrument (German). FT-IR spectra were recorded on a Bruker IFS66V FT-IR spectrometer. Electrochemical experiments were performed with a CHI 660C electrochemical workstation (Shanghai Chenhua Instrument Co., Ltd.) with a conventional three-electrode cell. A bare or modified GCE with LBL covalent self-assembly of CMWNTs was used as working electrode, Ag/AgCl (3.0 M KCl) and platinum wire was used as reference electrode and auxiliary electrode, respectively.

2.2. Pretreatment of MWNTs

CMWNTs were fabricated as reported in the literature [24] with little modification. Briefly, the MWNTs were refluxed 2 h in the concentrated HNO_3 (70%) at 140 °C, and then washed with redistilled deionized water several times until the filtrate pH value reached *ca.* 7.

2.3. Fabrication of CMWNTs LBL self-assembly

The LBL self-assembly of CMWNTs was fabricated via the procedure reported in our previous work [29]. A GCE used as the substrate was sequentially polished with 1.0, 0.3 and 0.05 μm alumina powders before being ultrasonically cleaned with distilled water and ethanol for 1 min each. The CMWNTs were activated by the solutions containing 5.0 mg mL^{-1} EDC and 9.0 mg mL^{-1} NHS for 30 min to convert the carboxyl groups into active carbodiimide esters. The CMWNTs film assembling process can be described as: (i) the cleaned GCE was first oxidized in 20 mM $KMnO_4$ solution containing 2 M H_2SO_4 for 30 min; (ii) then immersed it in mix solutions containing 5 mg mL^{-1} EDC and 9 mg mL^{-1} NHS for 1 h; (iii) kept in ethylenediamine for 1 h for the carbodiimide procedure; (iv) and 5 μL 1 mg mL^{-1} activated CMWNTs were dropped on the pretreated GCE surface and dried in air. Recycling the step of (ii), (iii) and (iv) can obtain the $(CMWNTs\text{-}NHCH_2CH_2NH)_n$/GCE. From our previous work [29], a six-layered film of CMWNTs was confirmed to have the best electrocatalytic activity. So in this case, we directly chose six-layered CMWNTs films. The scheme for the LBL assembling process had been shown in Ref. [29].

3. Results and discussion

3.1. Characterization of the six-layered self-assembled CMWNTs film

A typical SEM image of the $(CMWNTs\text{-}NHCH_2CH_2NH)_6$ film is present in Fig. 1A. It can be observed that randomly oriented CMWNT assemblies covered the entire electrode surface. CMWNTs could align with their long axis parallel to each other into the assemblies with flat-cable structure having width of 30–40 nm and length of up to 200 nm or with small-bundle structure further aligned by the flat cables in smaller sizes. These small bundles and flat cables can be readily used as electrochemical sensing units because they are fully and easily accessible to substrates. Another point worth noting is that the LBL self-assembled CMWNTs film exhibited an interlinking of the surface-confined nanocables to form an integrated free-standing three-dimensional network structure with well-developed nanoscale pores. Such homogeneous films are expected to be very attractive for various electrochemical applications [25,27,30], because they can not only maximize the available sensing surface area with their 3D-structures, but their porous networks can also work as conducting channels for the rapid transport of electrons and ions, which helps to facilitate an efficient electron transfer between the substrate and the electrode and yield a higher signal-to-noise ratio.

The covalent binding between CMWNTs and ethylenediamine can be confirmed by the FT-IR spectroscopy, as shown in Fig. 1B. The CMWNTs clearly exhibited the bands at 1720 and 1637 cm^{-1} (curve a), which are typically attributed to the C═O stretching of the carboxylic acid and its acyl derivatives, respectively. The $(CMWNTs\text{-}NHCH_2CH_2NH)_6$ film showed three characteristic bands at 1648, 1276 and 1068 cm^{-1} (curve b), corresponding to the C═O stretching (amide I), C—N stretching/N—H in-plane bending (amide III), and NH_3^+ rocking, respectively [27,31–33], which suggests that amide bonds between CMWNTs and ethylenediamine were formed.

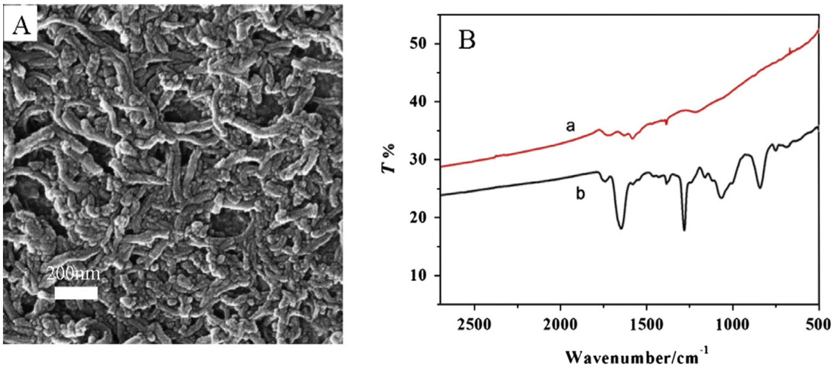

Fig. 1. (A) SEM image of $(CMWNTs\text{-}NHCH_2CH_2NH)_6$/GCE and (B) FT-IR spectra of the CMWNTs (a) and the LBL self-assembled CMWNTs film (b).