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Controllable synthesis of multi-walled carbon nanotubes/poly(3,4-ethylenedioxythiophene) core-shell nanofibers with enhanced electrocatalytic activity

Kaixin Zhang[a,b,1], Jingkun Xu[a,1], Xuemin Duan[a,*], Limin Lu[b,*], Dufen Hu[a], Long Zhang[a], Tao Nie[b], Kenneth B. Brown[c]

[a] School of Pharmacy, Jiangxi Science & Technology Normal University, Nanchang, 330013, P R China
[b] College of Science, Jiangxi Agricultural University, Nanchang 330045, PR China
[c] Department of Chemistry, University of Virginia, Charlottesville, VA 22904, United States

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ABSTRACT

Core-shell structured poly(3,4-ethylenedioxythiophene)/multi-walled carbon nanotubes (PEDOT/MWCNTs) nanofibers were synthesized through an interfacial polymerization technique. The interfacial polymerization at a liquid-liquid interface allowed PEDOT to grow uniformly on the surface of MWCNTs due to the presence of π-π interactions between PEDOT and MWCNTs walls. The morphology, structure and composition of the as-prepared PEDOT/MWCNTs were characterized by transmission electron microscopy (TEM), X-ray diffraction (XRD), Raman spectroscopy and Fourier transform infrared spectroscopy (FT-IR). In addition, the electrocatalytic properties of PEDOT/MWCNTs toward redox reactions of magnolol, a widely used traditional Chinese medicine, were systematically investigated. The results showed that the PEDOT/MWCNTs nanofibers exhibited a distinctly higher activity for the detection of magnolol compared with those of pure MWCNTs and PEDOT. The remarkably enhanced activity for the nanofibers can be attributed to the unique configuration and synergistic contribution between PEDOT and MWCNTs. The presented method is a general, facile and green approach for the synthesis of polymer/CNTs nanofibers, which is significant for the development of high performance electrocatalysts for biosensing and fuel cell applications.

1. Introduction

In recent years, nanometer-scale conducting polymer materials have attracted great attention due to their unique electronic and optical properties derived from their small dimensions, high surface-to-volume ratio and enhanced current-carrying ability [1,2]. In particular, one-dimensional conducting polymer nanostructures, including nanowires, nanofibers and nanotubes, have received considerable attention because of their high electrical conductivity, large surface area, short path lengths for the transport of ions, and high electrochemical activity [3–5]. Among all known conducting polymers, poly (3,4-ethylenedioxythiophene) (PEDOT) has been recognized as one of the most promising conducting polymers for practical applications due to its low oxidation potential and band gap, remarkable conductivity, superior biocompatibility and stability over other conducting polymer families [6–9].

The hard template method is a universal and powerful controlled approach towards obtaining nanostructures. Carbon nanotubes (CNTs), consisting of graphitic sheets rolled up into a cylindrical shape, are often used as templates in such syntheses [10,11]. Up to now, several synthetic procedures have been reported for the synthesis of PEDOT/CNTs nanocomposites, such as the solid state mixing of both powder components, the mixture of dispersions of each component [12], the electrochemical polymerization of 3,4-ethylenedioxythiophene (EDOT) over a CNTs-based electrode [13] and in situ chemical polymerization of EDOT in CNTs suspensions [14]. However, these routes generally yielded insoluble powders and, moreover, these composites showed irregular

* Corresponding authors. Tel.: +86 791 83802632; fax: +86 791 83802393.
E-mail addresses: duanxuemin@126.com (X. Duan), lulimin816@hotmail.com (L. Lu).
[1] These authors contributed equally to this work and should be considered co-first.

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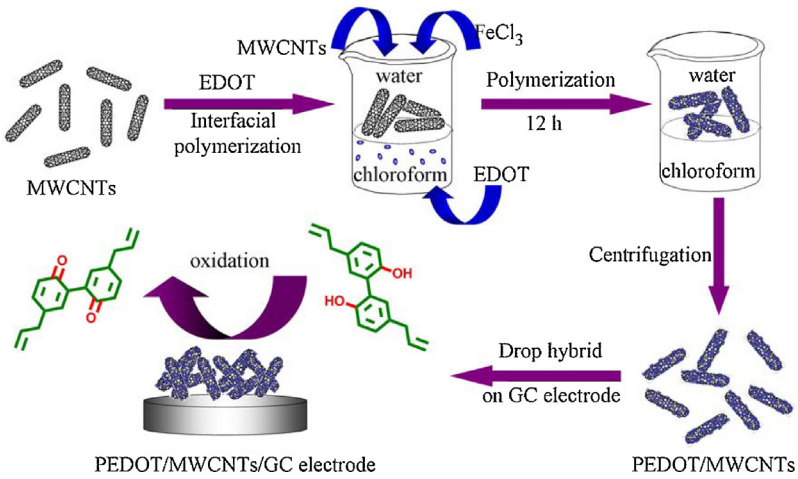

Scheme 1. The process of synthesis of PEDOT/MWCNTs nanofibers and the fabricating procedures of PEDOT/MWCNTs/GC electrode.

structures. Thus, it is necessary to develop a simple and effective method to prepare soluble and uniform nano-structured PEDOT/CNTs composites.

Chemical interfacial polymerization is an interesting approach for the synthesis of polymers/CNTs nano-structures, which makes it possible to prepare very stable dispersions [15]. It is a general chemical route based on a polymerization reaction performed in an immiscible aqueous/organic biphasic system, with the monomer of polymers dissolved in the organic phase and the oxidant and CNTs dissolved in the aqueous phase. The polymerization reaction starts at the interface, and subsequently, the resulting polymer migrates to the aqueous phase. The interfacial polymerization avoids the successive steps of heterogeneous nucleation, yielding small nano-film on the surface of CNTs that result in very stable water dispersions.

Magnolol is an effective component of Magnoliae Cortex, a useful drug prescribed in many Chinese traditional medicines. It can alleviate gastric and abdominal distension, and reduce the symptom of cough and asthma. Recently, pharmacological investigations have also shown that magnolol has a broad range of physiological activities such as anti-tumor [16], anti-inflammatory [17], anti-bacteria [18], anti-oxidant [19], anti-platelet [20], anti-arrhythmia [21], etc. Therefore, it is important to develop a simple, rapid and low-cost method for the detection and quantification of magnolol in physiological media for academic research and clinic applications. Since magnolol is an electroactive compound, interests have been focused on the development of chemically modified electrodes for magnolol detection.

Herein, for the first time, uniform PEDOT/MWCNTs nanofibers were successfully prepared by using a liquid-liquid interfacial polymerization approach, which is described in Scheme 1. The liquid-liquid interfacial system was established by using MWCNTs and $FeCl_3$ as the top aqueous phase while MWCNTs as the template and $FeCl_3$ as the oxidizing agent, and using EDOT and $CHCl_3$ as the bottom organic phase, which effectively suppresses second growth of PEDOT and obtains uniform PEDOT/MWCNTs composites. The obtained nanocomposites were characterized by TEM, XRD, Raman spectroscopy and FT-IR spectroscopy. The results suggested that PEDOT was attached onto the wall of MWCNTs to form a uniform PEDOT/MWCNTs structure. The core-shell structural nanomaterials could thus serve as the electrode's active material for magnolol detection due to its enhanced catalytic properties and stability. Electrochemical measurements revealed that the PEDOT/MWCNTs modified electrode displayed high electrocatalytic activity to magnolol with high sensitivity, wide linear range and low detection limit. Moreover, this modified electrode was further applied to determine magnolol in real samples with satisfactory results.

2. Experimental

2.1. Chemicals

Magnolol was obtained from Aladdin. Magnolol stock solution (5×10^{-3} M) was prepared with absolute ethanol and stored at 4-8 °C. MWCNTs were purchased from Chengdu Institute of Organic Chemistry, Chinese Academy of Sciences. Lithium perchlorate trihydrate ($LiClO_4$), ferric chloride ($FeCl_3$) and chloroform ($CHCl_3$) were purchased from Shanghai Chemical Co. Ltd. (Shanghai, China), Phosphate buffer solutions (PBS) were prepared from stock solution of 0.1 M NaH_2PO_4 and 0.1 M Na_2HPO_4. All these were used as received without further purification and doubly distilled water was used throughout the experiments.

2.2. Appratus

TEM images were obtained at a JEM-3010 transmission electron microscope (JEOL Co., Ltd., Japan). XRD patterns were recorded on a Rigaku powder diffractometer equipped with Cu Kα 1 radiation (λ = 1.5406 Å). Raman spectra (Bruker Raman RM2000) was used to analyze the samples using a 785 nm laser. Infrared spectra were recorded using Bruker Vertex 70 Fourier spectrometer with samples in KBr pellets. The cyclic voltammetric measurements were carried out on a CHI660D electrochemical workstation (Shanghai, China). A three-electrode cell (5 mL) was used with the modified glassy carbon (GC) electrode as the working electrode, a saturated calomel electrode (SCE) as the reference electrode and a platinum foil electrode as the counter electrode.

2.3. Preparation of the PEDOT/MWCNTs nanocomposites.

The MWCNTs were first purified as reported previously [22]. In brief, 0.5 g MWCNTs were oxidized using a strong acid mixture of 30 ml HNO_3/H_2SO_4 (1/3, v/v) at 60 °C for 6 h. The resultant suspension was subsequently centrifuged and washed with doubly distilled water until the pH value was close to 7, and then the black solid powder was collected and dried in a vacuum at 60 °C.

In a typical procedure (shown in Scheme 1) for the synthesis of PEDOT/MWCNTs composites: 1 ml of $FeCl_3$ (1 M) was added into 1 ml of MWCNTs dispersion aqueous (0.5 mg mL^{-1}), followed by sonication for 10 min. Then the above solution was slowly added into 2 mL of EDOT solution in $CHCl_3$ (25 mg ml^{-1}) and an interface was generated between two layers. The above mixture was heated at 50 °C under static conditions. After the reaction proceed for 12 h, the upper layer mixture was centrifuged, and the