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Electrochimica Acta 52 (2007) 6186–6191
ELECTROCHIMICA Acta
www.elsevier.com/locate/electacta

Nanoelectrode ensembles based on semi-interpenetrating network of carbon nanotubes

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Received 18 December 2006; received in revised form 27 March 2007; accepted 3 April 2007
Available online 7 April 2007

Abstract

A method for preparing nanoelectrode ensembles based on semi-interpenetrating network (SIN) of multi-walled carbon nanotubes (MWNTs) on gold electrode through phase-separation method is initially proposed. Individual nanoelectrode owns irregular three-dimensional MWNTs networks, which is denoted as SIN–MWNTs. On the as-prepared SIN–MWNTs nanoelectrode ensembles, the assembled MWNTs clusters in nanoscale serve as individual nanoelectrode and the electroinactive lipid networks located on the top of alkanethiol monolayer are used as a shielding layer. Cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS), tapping-mode atomic force microscopy (TM-AFM) and scanning electron microscopy (SEM) were used to characterize the as-prepared SIN–MWNT nanoelectrode ensembles. Experimental results indicate that the well-defined nanoelectrode ensembles were prepared through self-assembly technology. Meantime, sigmoid curves in a wide scanning range can be obtained in CV experiments. This study may pave the way for the construction of truly nanoscopic nanoelectrode arrays by bottom-up strategy.

Keywords: MWNT; Nanoelectrode; Lipid networks; TM-AFM; Phase-separation

1. Introduction

Ultramicroelectrode arrays (UMEAs) consisting of hundreds of individual metal microelectrode with several micrometers in diameter are attractive tools for undertaking a variety of electrochemical experiments [1–3]. The UMEAs have a great deal of advantages compared to the conventional electrodes such as high detection sensitivity, increased mass transport and a decreased influence of the solution resistance. Further size reduction of each individual electrode to nanometers and an increase in the total number of electrodes can significantly improve the detection limits and signal-to-noise ratio [4,5]. Currently, much attention has been paid to the fabrication of nanoelectrode arrays [6–10]. Several reports have dealt with the preparation of nanoelectrode ensembles, which are primarily confined in two ways: the "template synthesis" approach developed by Martin et al. [4,11,12] and the "microphase separation" approach to create molecule-sized defects on a gold surface developed by Crooks et al. [13–16]. In addition, colloidal chemical approach to microelectrode/nanoelectrode ensembles was well developed by several groups [17,18].

Carbon nanotubes (CNTs), a new form of element carbon, are composed of graphite sheets rolled into closed concentric cylinders with diameter of the order of nanometers and length of micrometers. Since their discovery in 1991 [19], extensive applications have been found in physical, chemical and material science fields [20,21]. CNTs electrodes could be of great significance in both fundamental and applied electrochemistry because of their unique properties such as a high aspect ratio and good electrical conductivity. Many research groups have already prepared nanoelectrode ensembles based on CNTs which have potential application in biosensors, DNA analysis and so on [22–29]. In this paper, the SIN–MWNTs for nanoelectrode ensembles were prepared on gold electrode surface. On the as-prepared nanoelectrode ensembles, the assembled MWNTs clusters serve as individual nanoelectrode and the electroinac-

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doi:10.1016/j.electacta.2007.04.018

tive lipid networks located on the top of alkanethiol monolayer are used as resisting layer in order to obtain good nanoelectrode behavior. The nanoelectrode ensembles prepared were characterized by cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS), tapping-mode atomic force microscopy (TM-AFM), and scanning electron microscopy (SEM).

2. Experimental

2.1. Materials

MWNTs (Shenzhen Nanotech Port Co. Ltd., China) were purified and functionalized through a well-established way with slight modification [30]. It is worth noting that the MWNTs thus prepared were functionalized with carboxyl groups and could be dispersed in both water and dimethylformamide (DMF). Fig. 1 shows SEM image of MWNTs dispersed in DMF solution on ITO substrate. The purity of MWNTs was in excess of 95% and the diameter of MWNTs was about 20–30 nm. Octadecanethiol (ODT), 4-aminothiophenol (4-ATP), *N*,*N*′-dicyclohexylcarbodiimide (DCC), potassium ferricyanide, potassium ferrocyanide, and dipalmitoleoyl-L-a-phosphatidylcholine (DPPC) were purchased from Sigma and used as received. KCl, absolute ethanol, HNO_3, H_2SO_4, NaH_2PO_4 and Na_2HPO_4 were from Beijing Chemical Factory (Beijing, China). All other chemicals were of analytical grade and aqueous solutions were prepared with doubly distilled water.

2.2. Instrumentation

All electrochemical experiments were carried out on an Autolab PGSTAT30 potentiostat (Eco Chemie B.V., the Netherlands) in a conventional one-compartment cell. Measurements used standard three-electrode systems. A saturated calomel electrode was used as the reference electrode, a Pt plate as the counter electrode and the modified gold plate electrode as the working electrode. The impedance spectra were measured in the frequency range from 10 mHz to 100 kHz with a voltage amplitude of 10 mV. TM-AFM was conducted with a SPI3800N microscope (Seiko Instruments, Inc.). Scanning electron microscopy images were determined with a Philips XL-30 ESEM. The accelerating voltage was 15 kV. For SEM and TM-AFM imaging, the SIN–MWNTs modified nanoelectrode ensembles was prepared on gold bead electrode and one of the Au (1 1 1) facets was employed as the substrate with diameter of about 2.5 mm.

2.3. The Preparation of SIN–MWNTs modified nanoelectrode ensembles

The gold bead electrode was prepared by melting the end of a gold wire (diameter 1.2 mm, purity 99.99%) in a hydrogen-oxygen flame [31–34]. The gold disk electrode was subjected to the following pretreatment procedure: the gold electrode was polished with 0.3 μm α-Al_2O_3 and washed ultrasonically with water. The preparation whole strategy of SIN–MWNTs nanoelectrode ensembles was shown in Scheme 1. First, the cleaned gold plate electrode was immersed in an ethanol solution of 1 mM 4-ATP and ODT (molar ratio 7:3) more than 24 h. After that, phase-separation mixed monolayers would be formed on electrode surface. Although 4-ATP molecules were dominated in the mixture at the beginning, they would gradually be replaced by ODT molecules with the increasing assembly time [35]. Ultimately, they would form the phase-separation mixed monolayers with few 4-ATP molecules as the active islands [35]. Second, the above electrode was dipped into a 0.2 mg/mL MWNTs of DMF solution containing DCC for 24 h. With the aid of DCC, MWNTs were covalently assembled on electrode by formation of the amide bond. Meanwhile, the remaining MWNTs were also adsorbed into covalently linked MWNTs on gold electrode surface due to the attractive interaction between the hydrophobic side-walls of carbon nanotubes [36]. Third, the above MWNTs modified electrode was dipped into 1 mg/ml DPPC colloid solution for more than 24 h. Surprisingly, lipid networks were spontaneously formed on the top of alkanethiol monolayer. In this experiment, the vesicles were prepared according to the literature [34].

In addition, we also prepared the SIN–MWNTs modified nanoelectrode ensembles on gold bead electrode. The assembly route was the same as that of gold plate electrode.

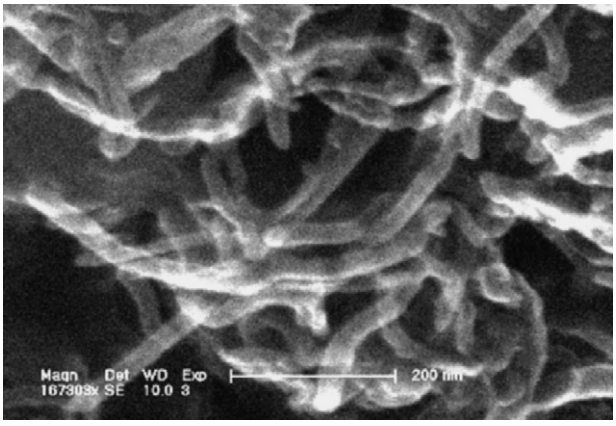
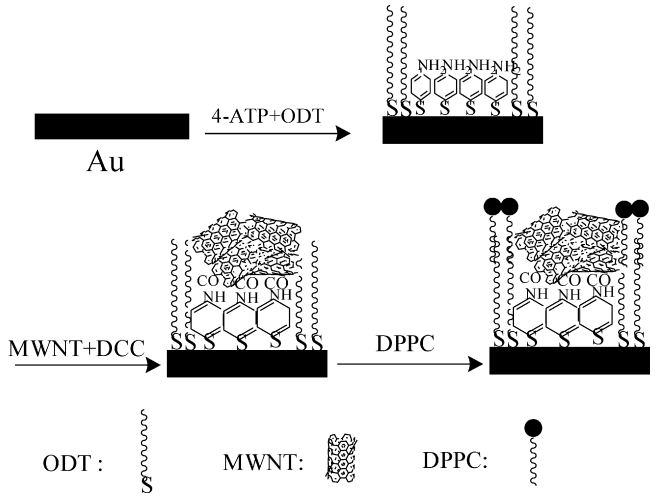


Fig. 1. SEM image of purified MWNTs on ITO substrate.



Scheme 1. Procedure to design the SIN–MWNTs nanoelectrode ensembles.