

Preparation and layer-by-layer self-assembly of positively charged multiwall carbon nanotubes

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Received 21 February 2005; received in revised form 28 May 2005; accepted 28 May 2005

Available online 14 July 2005

Abstract

The report described a method of more stably dispersing oxidized carbon nanotubes (CNTs) by forming complex with polycation and the layer-by-layer self-assembly behavior of the complex with polyanion was studied. The properties of the self-assembled multilayer film containing carbon nanotubes were studied. Cyclic voltammetry, UV–vis–NIR spectroscopy, electrochemical impedance spectroscopy and scanning electron microscopy were used for characterization of film assembly. UV–vis–NIR spectroscopy and cyclic voltammetry study indicated the uniform growth of the film. Electrochemical impedance spectroscopy results showed that incorporating of carbon nanotubes in the polyelectrolyte multilayers decreased in the electron-transfer resistance R_{ct} , indicating more favorable electrochemical reaction interface. The electrocatalytic property of the multilayer modified electrode to NADH was investigated mainly with different numbers of the bilayers and the results showed that along with the increase of the assembled bilayers the overpotential of NADH oxidation decreased. The detection limit could reach 6 μM at a detection potential of 0.4 V.

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Keywords: Carbon nanotubes; Complex; Layer-by-layer; Self-assembly; NADH

1. Introduction

Since the discovery of carbon nanotubes (CNTs), due to the unique electronic and chemical properties, CNTs have been widely used in electrochemical areas. For electrochemical applications, the immobilization of CNTs is an important step. Preliminary works mainly focused on simply drop-coating the suspension of CNTs to study the ability of the film formed after solvent evaporation in promoting the electrochemical behaviors of biologically or environmentally important substances [1–3]. But the films so-formed were not very stable and uniform actually. Later, in some studies polymer and CNTs composite films were used to immobilize CNTs and at the same time other reagents. The stability and uniformity of the film were greatly improved. For example, Nafion, chitosan and poly(ethylene vinylac-

etate) were mixed with CNTs forming robust conductive films [4,5,24]. Biomolecules were immobilized in the film creating CNTs based biosensors. Besides this, bulk CNTs paste electrodes were also made by using bromoform, epoxy, sol–gel or Teflon as a binder [6–9]. The bulk CNTs paste electrodes showed remarkable faster electron-transfer rate. CNTs in above-mentioned films or electrodes were in a random order. Arranging CNTs in an ordered manner is advantageous to develop nanoelectronic devices. CNTs arrays could form directly on substrates in the process of CNTs preparation [10,11]. Vertically aligned CNTs arrays on desired substrate could also be prepared by wet chemical self-assembling technique using cysteamine as linking molecule or using metal-assisted self-assembly [12,13]. CNTs with identical orientations favored efficient electron-transfer and proteins such as glucose oxidase, microperoxidase-11 and peroxidases covalently attached at the ends of vertically aligned CNTs showed direct electrochemistry and retained their bioactivity [13–15]. Multilayer films of CNTs were also fabricated on

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different substrates with the layer-by-layer method. Polymers such as poly(diallyldimethylammonium chloride) (PDDA), branched polyethyleneimine (PEI) and poly(4-vinylpyridine) (P4VP) were demonstrated to be able to stepwise assemble with CNTs via electrostatic force or donor–acceptor interactions [16–20]. Compared with the film made by drop-coating, the layer-by-layer method could control the amount of CNTs deposited and the uniformity so as to the properties of the film.

However, poor solubility of CNTs greatly limited their applications. Many studies focused on solving this problem and have gained good results. CNTs could be oxidized and cut when were treated in strong acid, resulting in the production of oxygen-containing groups (such as carboxylic acid groups) at the end or sidewall of CNTs [21]. Dispersion of the oxidized short CNTs in aqueous solution could keep stable for a few of days. Further covalent modification with soluble compounds such as glucoamine made CNTs soluble in water [22]. For the non-covalent modification, a series of polymers was demonstrated to solubilize CNTs. For example, helical amylose could solubilize single-wall CNTs (SWNTs) by supramolecular inclusion interaction [23]. Nafion, a perfluorated polymer, has been used to solubilize CNTs and the so-prepared film was robust in biosensor application [24]. Another non-covalent modification and solubilization technique by polymer wrapping could form single and well-dispersed pristine CNT in aqueous solution [25]. A variety of linear polymers such as polyvinyl pyrrolidone and polystyrene sulfonate (PSS) could be non-covalently attached.

In this report, by modifying CNTs with polycation PDDA, the charges of CNTs were converted to positive. The complex could form stable dispersion. The layer-by-layer self-assembly of the positively charged CNTs with polyanion PSS was investigated and the electrocatalysis of the film to NADH was studied.

2. Experimental

2.1. Reagents and measurement

Multiwall CNTs (MWNTs) were obtained from Shenzhen Nanotech Port Co. Ltd. (China). The purity was about 80%. MWNTs were purified through a well-established way with slight modification [21]. PDDA (M_w : 20,000) and sodium poly(styrenesulfonate) (PSS; M_w : 70,000) were purchased from Aldrich and used as received. NADH was purchased from Sino-American Biotechnology Co. (S_{ABC}). All other reagents were of analytical reagent grade and used without further purification. Doubly distilled water was used in all aqueous solution preparations and washings.

Electrochemical measurements were performed with a CH Instruments 832 voltammetric analyzer. A conventional three-electrode setup was used. The working electrode was

ITO electrode modified with the self-assembled films. An Ag/AgCl (saturated KCl) reference electrode was used for all measurements. A platinum coil was used as a counter electrode.

UV–vis–NIR spectra were recorded using a Cary 500 scan UV–vis–NIR spectrophotometer (Varian). The absorbance of MWNTs multilayer films assembled on quartz slide was measured. Before use, the quartz slide was soaked in freshly prepared “piranha” solution (a mixture of 7:3 volume ratio of 98% H₂SO₄ and 30% H₂O₂) at 90 °C for about 20 min and then washed in pure ethanol and water successively. *Caution! “Piranha” solution reacts violently with almost any organic materials and should be handled with extreme care!*

The AC impedance spectra of the self-assembled films were measured using Autolab with PGSTAT 30 (Eco Chemie B.V., Utrecht, The Netherlands) and with the help of frequency response analysis (FRA) system software under an oscillation potential of 5 mV over a frequency range of 100 kHz–0.1 Hz.

The morphology of the film was determined with a PHILIPS XL-30 ESEM. The accelerating voltage was 20 kV.

2.2. Preparation of the complex of PDDA and MWNTs and its multilayer film

Certain amounts of MWNTs were dispersed in doubly distilled water with sufficient ultrasonication for about 1 h. When they were dispersed thoroughly, PDDA aqueous solution was added. After a while, black sediment was observed. It was separated by centrifugation. Residual PDDA polymer was removed by high-speed centrifugation and the complex was rinsed with water for at least three times. The collected complex was redispersed in water with mild ultrasonication to produce a stable solution of the complex.

Tin doped indium oxide on glass (ITO; Shenzhen Hivac Vacuum Photo-electronics Co. Ltd., resistivity, <15 Ω) was used as substrate for multilayer film buildup and was cleaned by sonicating sequentially for 20 min each in acetone, 10% KOH in ethanol and distilled water. After the treatment, ITO electrodes were rich in negative charges. The cleaned pieces were kept in absolute methanol in plastic containers and were rinsed with water just before use.

The procedure for preparing multilayer films was as follows: ITO electrodes with original negative surface charges were treated with aqueous solution of PDDA for 20 min to form positive surfaces before LBL assembly. Multilayer films were grown by alternately dipping the modified ITO substrates into negatively charged PSS aqueous solution (10 mg/mL) and positively charged complex of MWNTs and PDDA (MWPD) aqueous solution (0.5 mg/mL) for 20 min, respectively. The films were carefully washed with water after each dipping step and then dried with N₂ gas. This sequence was repeated to obtain the desired numbers of layers designated as {PSS/MWPD}_n.

3. Results and discussion

3.1. Non-covalent modification of oxidized MWNTs

When two oppositely charged polymers were mixed in water, if the charges of one component were in access to charges of another component, interpolyelectrolyte complex was formed. It was based on spontaneous polymer complex formation [26]. This was often used in the assembly of small dye molecules and biomolecules. In the process of MWNTs purification, the end and sidewall of MWNTs were made negatively charged. So MWNTs could be regarded as a kind of polyelectrolyte. By mixing MWNTs with enough PDDA, complex of MWNTs and PDDA was formed. Resuspending the complex in aqueous solution, the charges of MWNTs were converted to positive. The dispersion could stay stable for 2 weeks. This phenomenon of CNTs was similar to that reported in the literature [27] where by ionic functionalization of the carboxylic acid groups present in the purified SWNTs with octadecylamine, SWNTs were rendered soluble in common organic solvents such as tetrahydrofuran and 1,2-dichlorobenzene. In the present study, it may be due to charges-riched PDDA wrapped along the MWNTs and PDDA had good water-solubility preventing MWNTs from conglomeration and sedimentation. Polymers or macromolecules with negative charges were possible to assemble with MWPD. In the following sections, we used PSS as a model polyanion to study the layer-by-layer assembly behavior of MWPD.

3.2. Characterization of the multilayer film

Cyclic voltammograms could be used as a characterization method for layer-by-layer assembly of electroactive species. According to the literature, CNTs showed a pair of redox wave, which was attributed to the redox of the oxygen-containing groups on the walls of MWNTs [1,2]. So the cyclic voltammetric behavior of the $\{\text{PSS/MWPD}\}_n$ multilayer film modified electrode was investigated. Fig. 1 shows typical cyclic voltammograms of the $\{\text{PSS/MWPD}\}_n$ multilayer films modified electrode in phosphate buffer solution (PBS, pH 7.5). From the formal potential and the increased current along with increasing assembly cycles, the redox peaks were attributed to MWNTs. It suggested that the electrochemical property of MWNTs was not changed in the complex. Along with film assembly, the peak current of the redox wave increased uniformly, indicating the uniform growth of MWNTs at the electrode.

The growth of multilayer film was also monitored by UV–vis–NIR spectroscopy. Fig. 2 shows the absorbance of the self-assembled $\{\text{PSS/MWPD}\}_n$ multilayers on the quartz slide. Clearly, there was an absorption peak at 263 nm in each bilayer. The strong absorbance was ascribed to MWNTs [19]. The absorbance increased linearly with the growth of layer number (inset in Fig. 2), which indicated the growth of the film assembly was uniform spectroscopically. When the

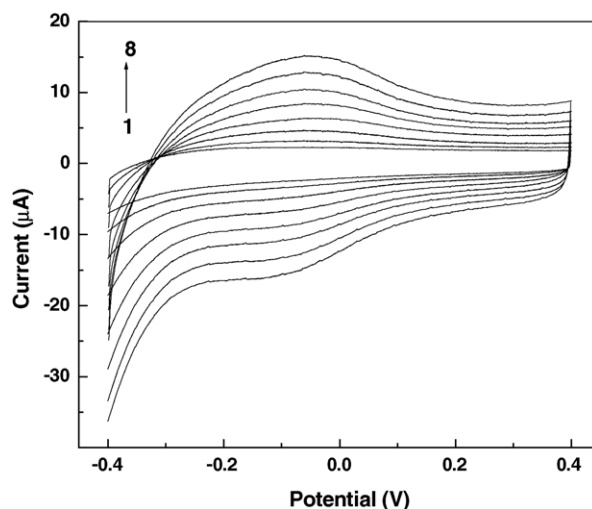


Fig. 1. The cyclic voltammograms corresponding to the $\{\text{PSS/MWPD}\}_n$ multilayer films assembled at ITO electrode in pH 7.5 PBS with $n = 1, 2, 3, \dots, 8$.

negatively charged PSS was replaced by positively charged PDDA, no growth of the film was observed. All this further demonstrated the formation of the complex and charge conversion of MWNTs.

3.3. AC impedance spectroscopy study of the MWNTs-containing film

AC impedance spectroscopy was widely employed to investigate the interface properties of surface-modified electrode and used to characterize the layer-by-layer assembly process [28–30]. Compared with polymer electrolyte, MWNTs had good conductivity. Fig. 3A shows the AC impedance spectroscopy of the modified ITO electrode after assembling PDDA (1), PDDA/PSS (2) and PDDA/PSS/MWPD (3) layer in 0.067 M PBS containing

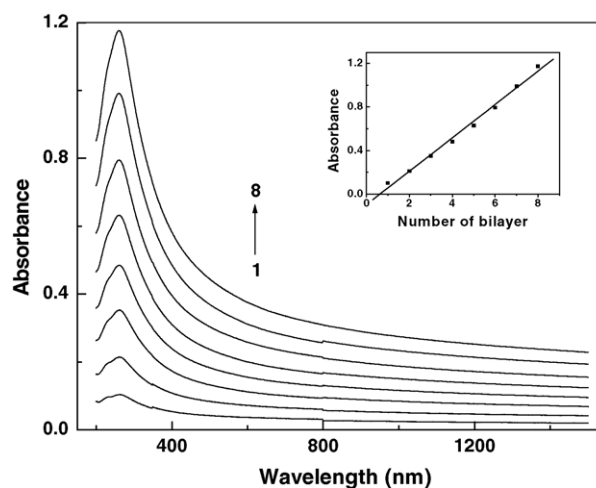
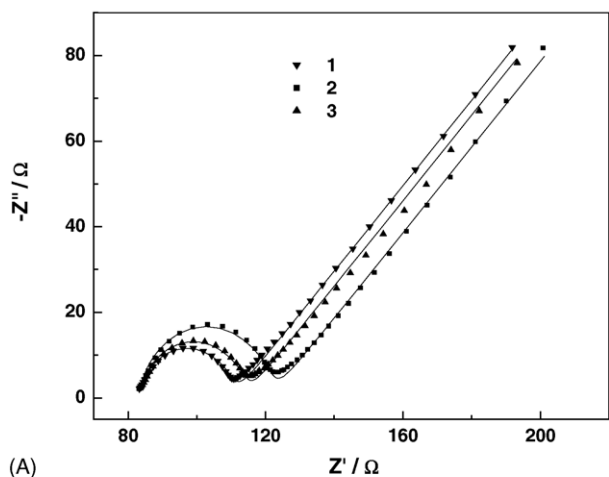
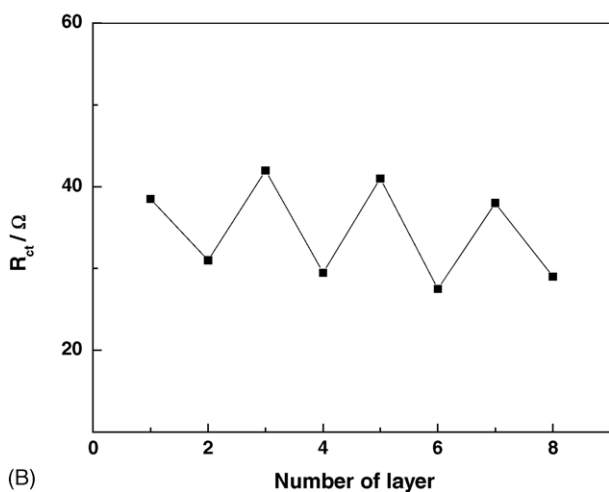


Fig. 2. UV–vis–NIR absorption spectra of $\{\text{PSS/MWPD}\}_n$ multilayer films with $n = 1, 2, 3, \dots, 8$. Inset: the relationship between the number of layers and the absorption peak values at 263 nm.



(A)



(B)

Fig. 3. (A) Nyquist plots (Z''_{im} vs. Z'_{re}) of $\{PSS/MWPD\}_n$ multilayer films in 5 mM $K_4Fe(CN)_6 + K_3Fe(CN)_6 + 0.067$ M pH 7.0 PBS. (1) ITO electrode modified with PDDA monolayer. (2) PSS layer was assembled on PDDA layer. (3) MWPD layer was assembled on PSS layer. (B) Relationship between the electron-transfer resistance R_{ct} and the number of assembled monolayer.

5 mM $Fe(CN)_6^{3-}/Fe(CN)_6^{4-}$ (1:1). The Randles circuit was chosen to fit the obtained impedance data. Seen from it, when PSS was assembled onto the PDDA modified electrode, R_{ct} increased from 28 to 39 Ω , it could be attributed to the decrease of permeability of the film, which led to a reduction in the active area of the electrode. And when the film was terminated with negatively charged PSS layer, it was less permeable to negatively charged ion probe $Fe(CN)_6^{3-}/Fe(CN)_6^{4-}$ due to electrostatic repulsion. However, when the film was assembled with the complex MWPD, the R_{ct} decreased by 8 Ω . It suggested that the assembly of MWPD was beneficial to the access of the redox probe. The result indicated that MWNTs played important role similar to a conductive wire or electron-conducting tunnel and made the electron-transfer easier. It may be due to the good electrical conductivity and large surface area of MWNTs. It also agreed with the previous studies [31]. Proceeding with the assembly of the multilayers,

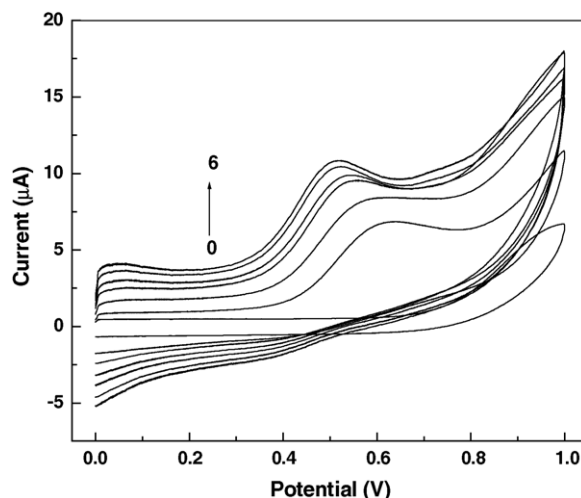


Fig. 4. The cyclic voltammograms corresponding to the $\{PSS/MWPD\}_n$ multilayer films assembled at ITO electrode in pH 7.5 PBS containing 0.1 mM NADH. For $n=0$, it referred to blank ITO electrode.

R_{ct} changed regularly with increasing when PSS assembled and decreasing when MWPD assembled. So the growth of the film was obvious seen from the Fig. 3B.

3.4. Electrocatalytic behavior of the multilayer film toward NADH

Many papers have demonstrated that CNTs had good catalytic ability towards the oxidation of NADH due to CNTs' unique electronic structure in spite of different preparation methods of the CNTs modified electrode. The assembled MWPD modified electrode was also used to study the electrocatalytic oxidation activity to NADH. As shown in Fig. 4, at blank ITO electrode ($n=0$), NADH had a high oxidation overpotential with oxidation peak at above 0.9 V. When the first layer of MWPD ($n=1$) was assembled at the electrode, the oxidation potential greatly decreased to 0.6 V. It showed that the MWNTs in the interpolyelectrolyte complex still remained their electrochemical properties and they had good electrocatalytic activity to NADH with a decrease of overpotential up to 0.3 V. And interestingly, increasing with the number of bilayers, the overpotential decreased gradually. For the sixth bilayer, the oxidation peak potential moved to 0.5 V ($n=6$). This could be explained by the morphology of the film given by scanning electron microscopy. As shown in Fig. 5, the first layer of MWPD had certain amount of MWNTs revealing that MWNTs were successfully deposited on the PSS underlayer. But the electrode surface was not fully covered by MWNTs, it was the same as self-assembled polyelectrolyte multilayers [30]. For the second bilayer, the coverage of MWNTs was far greater than the first layer therefore the relatively separated MWNTs were interlinked partially. So the morphology of the electrode was changed and electrode surface area greatly increased with the assembly of bilayers, which were favorable for the oxidation of NADH.

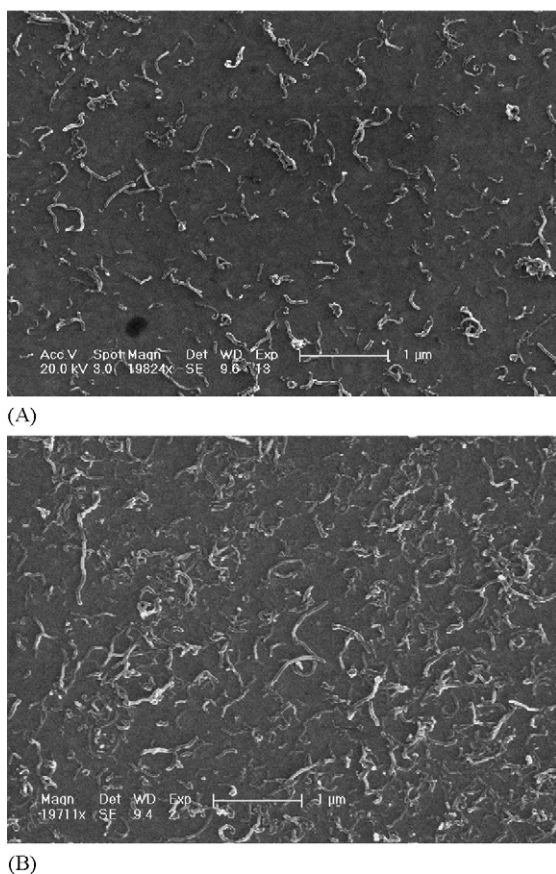


Fig. 5. ESEM images of ITO electrode modified with one (A) and two (B) bilayers of PSS/MWPD.

The electrocatalytic behavior of the $\{\text{PSS/MWPD}\}_6$ multilayer modified electrode to NADH was studied further with the change of scan rate. As shown in Fig. 6, increasing with scan rate from 0.01 to 0.13 V/s, the peak current of NADH

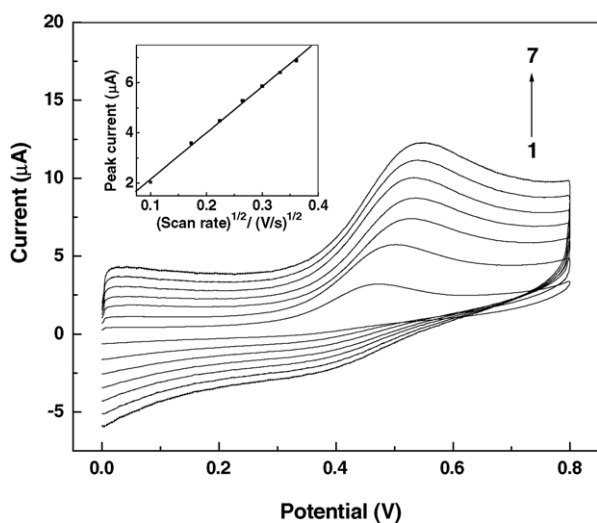


Fig. 6. The cyclic voltammograms of $\{\text{PSS/MWPD}\}_6$ multilayer films modified ITO electrode in pH 7.5 PBS containing 0.1 mM NADH at different scan rates. From curves 1 to 7: 0.01, 0.03, 0.05, 0.07, 0.09, 0.11, 0.13 V/s. Inset: the relationship between the peak currents and scan rates.

oxidation increased, while the peak potential moved positively slightly. The peak current increased linearly with the square root of scan rate in the range of 0.01 to 0.13 V/s indicating it was a diffusion-controlled process. The steady-state response of the modified electrode with five bilayers was recorded at a potential of 0.4 V. The detection limit could reach 6 μM . So the modified electrode had good electrocatalytic activity toward NADH.

4. Conclusion

By modifying MWNTs with positively charged polyelectrolyte PDDA, a complex was formed. The complex suspension could stay stable for 2 weeks due to abundant positive charges on the walls of MWNTs. The complex was demonstrated to be able to assemble with negatively charged PSS. AC impedance spectroscopy study showed that the incorporation of MWNTs in the film decreased in the electron-transfer resistance R_{ct} . The modified electrode remained the electrocatalytic ability towards NADH and along with the increase of the assembly layers, the overpotential decreased.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (No. 20275036, 20211130506) and special funds for major state basic research of China (2002CB713803).

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