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Microwave plasma treated carbon nanotubes and their electrochemical biosensing application

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Abstract

A convenient microwave plasma treatment method with ammonia precursor was proposed to enhance the solubility of carbon nanotubes (CNTs). The SEM, XRD and FTIR spectra clearly demonstrated that the carbon skeleton structure of the resultant ammonia plasma-treated CNTs (ammonia PT-CNTs) was not destroyed and amine groups of different forms were successfully coupled to CNTs in the MWP treatment process. The ammonia PT-CNTs have excellent solubility in water and are insoluble in nonpolar tetrahydrofuran, and the cyclic voltammograms suggest that the enhanced wetting properties clearly favor faster electron transfer kinetics on the ammonia PT-CNT electrodes. By choosing glucose oxidase as a model enzyme, the application of the ammonia PT-CNTs in construction of biosensors was further investigated. Due to the biocompatibility and electron transfer capability of the ammonia PT-CNTs, the resultant GOD biosensor displayed a good sensing performance. The biosensor has a fast response of less than 10 s, and the response current linearly increases with the glucose concentration in the range of 1.2×10^{-4} to 7.5×10^{-3} M with a detection limit of 1.0×10^{-5} M.

Keywords: Microwave plasma; Carbon nanotubes; Biosensor

1. Introduction

Electrochemical biosensors have gained increasing attention due to their potential application in the areas of food industry [1,2], clinical analysis [3,4], and environmental monitoring [5,6]. They are generally constructed by immobilizing biomaterials with recognizing and/or catalyzing abilities to sensing matrices and combining these with electrochemical sensing devices, which can convert analyte concentrations into electrical signals. For electrochemical biosensors, the electrochemical performance is directly related to the sensing matrix materials, and thus many efforts have still been directed to the development of new sensing materials with outstanding physicochemical properties.

Since Lijima [7] discovered carbon nanotubes (CNTs), they have led to many new technical developments and applications due to their high chemical stability, large surface area, unique electrochemical properties, and excellent mechanical strength [8]. In particular, their applications in electrochemical sensors and nanoscale electronic devices have attracted increasing attention [9–13]. It has been found that CNTs have a high electrocatalytic effect and a fast electron-transfer rate, and thus they have great potential to be applied to biosensors, especially amperometric biosensors, to enhance their sensing performances. However, one of major obstacles for developing the CNT-based devices is their insolubility nearly in all solvents [14,15], which is unfavorable to the immobilization of biomolecules in aqueous solutions and to the preservation of their bioactivities. At present, the challenge has somewhat been addressed through various chemical modifications. For instance, CNTs can be treated by refluxing in HNO_3 and/or H_2SO_4 to introduce −COOH and −OH groups and increase their aqueous solubility [15,16]. However, the treatment in such harsh conditions clearly deviates from principles of green chemistry, and it is also possible to damage their sidewalls [17], to decrease their stability [18], and even to cut them into short pieces [19].

Plasma treatment is an attractive technique as it is a rapid, versatile and contaminant-free procedure for the introduction of

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various functional groups. In a plasma treatment process, particle energies of plasmas are usually comparable with chemical bond energies, and the particle densities and energies can be controlled by the external plasma parameters (e.g. power, pressure, frequency, etc.). Accordingly, the plasma treatment technique enables various kinds of precursor monomers to be activated into reactive radicals, and thus the surface functionalization even of the most inert materials can also be conveniently tailored. Many reports have well demonstrated its applications in polymerization depositions, and the surface modifications of polymeric materials and fine powders [20–22]. Furthermore, plasma treatments to biosensor substrates have also been verified to be quite effective for the immobilization of enzymes [23,24], antibodies [25–27] or DNAs [28].

Recently, some efforts have been directed to the plasma modifications of CNTs [29,30]. Dai group [29] studied the acetaldehyde or ethylenediamine plasma activation of carbon nanotubes for chemical modification, and the resulting polysaccharide-grafted carbon nanotubes show good hydrophilicity. Khare et al. [30] successfully functionalized single-walled carbon nanotubes (SWCNTs) through a microwave discharge of ammonia. However, the effects of plasma modifications on the electrochemical properties and sensing applications of CNTs have not yet been addressed.

In this study, we used a microwave plasma (MWP) with an ammonia source to treat carbon nanotubes. This is primarily aimed at introducing hydrophilic groups on the surface of CNTs to enhance their aqueous dispersion. The electrochemical behavior of the modified CNTs was studied using glucose oxidase as a model enzyme for the construction and development of a working biosensor. Due to the good hydrophilicity and electrochemical performance of the modified CNTs, the CNT matrix can effectively entrap glucose oxidases and preserves their bioactivity giving excellent sensing response.

2. Experimental

2.1. Reagents

Glucose oxidase (GOD; EC 1.1.3.4. 196 U mg^{-1}) and vinylferrocene (VF, 98%) were supplied by Sigma. Nafion was purchased from Aldrich. β-D-glucose was obtained from ICN. The single-walled carbon nanotubes (SWCNTs) with a diameter of 1–2 nm and with a length of up to 0.5–1 μm were purchased from Organic Chemistry Engineering Technology Center (Chengdou, China) and were used without any further pretreatment. Glucose stock solution was allowed to mutarotate at room temperature overnight before use. All other chemicals were of analytical grade or higher commercially available purity and were used as received. Doubly distilled water was used throughout.

The supporting electrolyte was 0.067 M phosphate buffer (PB), which was prepared with KH_2PO_4 and Na_2HPO_4.

2.2. MWP treatment of CNTs

The plasma treatment of CNTs was completed in a stainless reactor with a MWP system (Guowei Limited Corporation, Hubei Province, China). Ammonia (30%) was used as a precursor, and pure hydrogen (99.99%) as a carrying gas. During the deposition process, the flowing rate of carrying gas was kept at 1.0 mL min^{-1}, the pressure of the reactor chamber at 266 Pa, and the MW power being 30 W. The resultant ammonia plasma-treated CNTs (ammonia PT-CNTs, 2 mg) was added into 0.5 mL water, and the mixture was then sonicated for 20 min in ultrasonic bath, a dispersed solution of carbon nanotubes was formed finally.

2.3. Fabrication of the GOD electrodes

A GOD solution of 10 mg mL^{-1} was prepared with 0.067 M PB at pH 6.9. Prior to use, the platinum disk (0.2 mm diameter) electrode was polished successively with 1, 0.3 and 0.05 μm of α-alumina powders in each experiment. After thoroughly rinsed in ultrasonic bath, the electrode was immersed in 50 μL of 0.15 M VF solution in methanol and air-dried. Subsequently, a mixture solution was prepared by mixing 3 μL of ammonia PT-CNTs solution, 2 μL of GOD solution, 5 μL of 1.0 mg mL^{-1} BSA (bovine serum albumen) and 2 μL of 2.5% GLU (glutaraldehyde), and 5 μL of the mixture solution was then pipetted onto the electrode surface and dried at 4 °C overnight. Finally, the electrode was rinsed with PB to remove the non-covalently bound enzymes, and the GOD electrode was then obtained. As a comparison, the GOD electrode without the ammonia PT-CNTs was prepared by the same procedure described above. When not in use, the electrodes were stored at 4 °C in a refrigerator.

2.4. Electrochemical measurements

Electrochemical measurements were performed using an electrochemical analyzer (Shanghai Chenhua Instrument Company, China). The three-electrode system consisted of a GOD electrode as working electrode, a saturated calomel reference electrode (SCE) and a platinum foil counter electrode. All electrochemical experiments were carried out in 10 mL phosphate buffer (pH 6.9) at room temperature (20 ± 2 °C) in an air-saturated condition unless otherwise stated. All potentials were measured versus a saturated calomel reference electrode under stirring conditions. Alternating current (ac) impedance experiments were performed in a laboratory-made measuring cell using a Model VMP2 Multichannel Potentiostat with Ec-Lab V6.70 and ZsimpWin Version 2.00 software (EG&G Princeton Applied Research, Princeton, NJ). Impedance spectra were recorded over a frequency range of 0.1–100,000 Hz at zero dc potential with the ac potential amplitude of ±20 mV.

3. Results and discussion

3.1. Characterization of ammonia PT-CNTs

Ammonia has been considered to be an effective precursor to introduce amine functionalities to the carbon nanotubes [30] and other materials [31,32], enhancing their hydrophilicity and biocompatibility. Fig. 1 shows the SEM images of the CNTs before and after the ammonia plasma treatment. It can

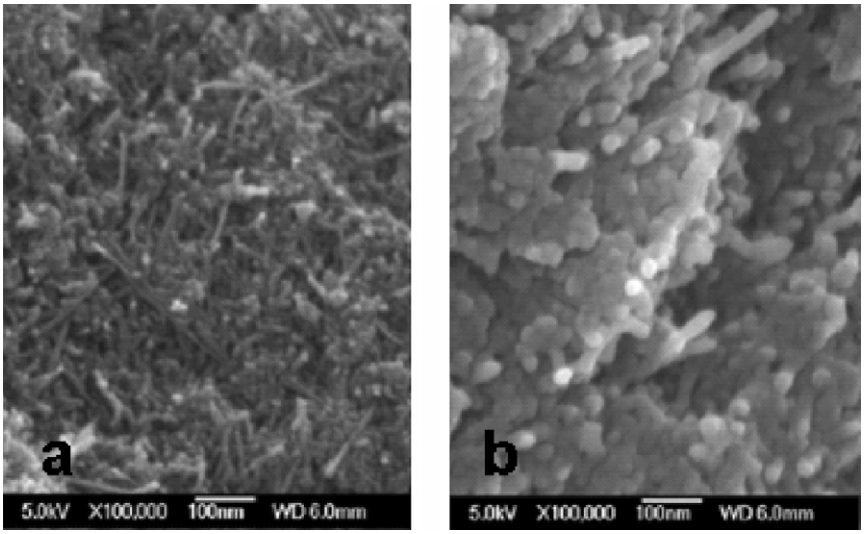

Fig. 1. SEM images of the CNTs (a) before and (b) after the ammonia plasma treatment.

be shown that after the ammonia plasma treatment, the tubular diameter of the ammonia PT-CNTs was about two times larger than that of the pristine CNTs, clearly indicating a homogeneous ammonia plasma deposition coating on the carbon nanotube sidewall. However, the MWP modification reactions are somewhat complex because the ammonia precursor can produce multiple reactive radicals, such as N, NH, NH_2, etc., under microwave radiation [33]. Fig. 2 shows the typical FTIR transmittance spectrum of the ammonia PT-CNTs. Compared to the absorption curve of the pristine CNTs (curve a), a peak at 3319 cm^{-1} can be observed from that of the ammonia PT-CNTs (curve b), indicating the presence of N–H stretching mode. And the absorption peaks at 1650–1458 cm^{-1} can be assigned to the deformation vibrations of N–H bonding. These absorption peaks clearly demonstrated that some hydrophilic amine groups were introduced in the ammonia PT-CNTs. Moreover, it can also be noticed that the peak at 3319 cm^{-1} is relatively wide and the peaks at 1650–1458 cm^{-1} are relatively complex. These phenomena seem to be related to the fact that amine groups of different forms and even some groups containing oxygen are coupled to CNTs in the MWP treatment process.

To investigate the effect of MWP treatment on the structure of CNTs, the XRD spectra of the CNTs before and after treated by MWP were compared (see Fig. 3). Fig. 3a displays the XRD spectrum of the pristine CNTs, and Fig. 3b displays the XRD spectrum of the ammonia PT-CNTs. It can be seen that the ammonia PT-CNTs have the same characteristic diffraction peaks at thetal 25.8 (assigned as a peak arising from the 002 lattice face) and thetal 43.4 (assigned as a peak arising from the 100 lattice face) as the pristine CNTs and the intensity of carbon peaks are not clearly changed, implying that the carbon skeleton structure of ammonia PT-CNTs is not destroyed in the MWP treatment process. On the other hand, we also notice that there are two small peaks in thetal 15 and thetal 35 in Fig. 3b, suggesting that CNTs is successfully modified and some new substances are formed in the MWP process. These results further demonstrate that the MWP treatment is a reliable and effective approach, which can conveniently endow CNTs with various new functional groups while maintaining their original physicochemical properties.

3.2. Solubility of the ammonia PT-CNTs

The photographs in Fig. 4 were used to describe the solubility of the ammonia PT-CNTs in different solvents. The

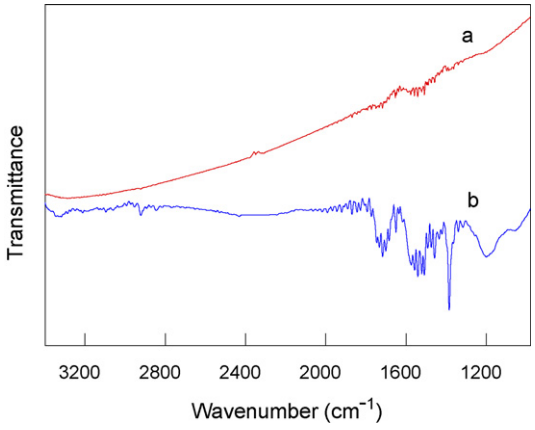

Fig. 2. FTIR spectra of the pristine CNTs (a) and the ammonia PT-CNTs (b).

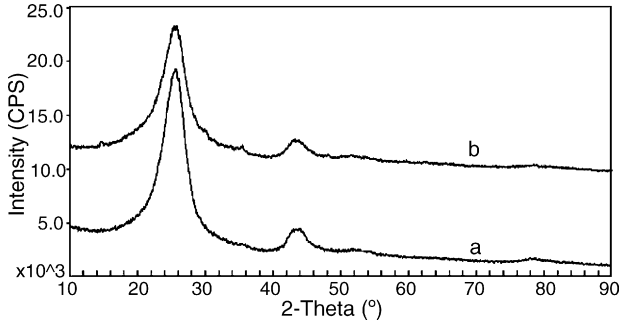

Fig. 3. XRD spectra of the pristine CNTs (a) and the ammonia PT-CNTs (b).

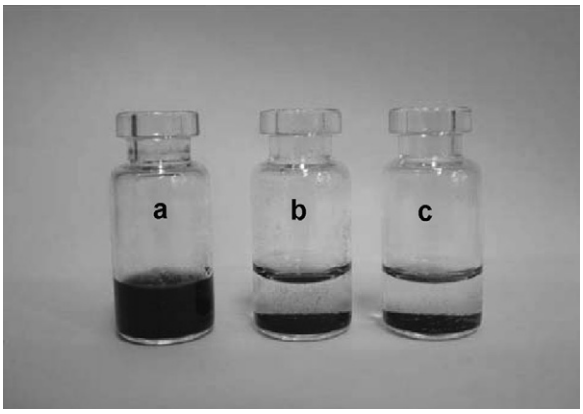

Fig. 4. Photographs of the ammonia PT-CNTs in water (a) and in THF (b) and the pristine CNTs in water (c).

ammonia PT-CNTs were uniformly dispersed in water even after 10 days (Fig. 4a), whereas the untreated pristine CNTs rapidly settled in water in about 1 h (Fig. 4c). Moreover, the solubility of the ammonia PT-CNTs in tetrahydrofuran (THF) was also investigated (Fig. 4b), and the result showed that the ammonia PT-CNTs also settled in a nonpolar solvent in about 1 h. These phenomena suggest that the introduction of polar amino groups in the MWP treatment process greatly increase the hydrophilicity of CNTs, and consequently the ammonia PT-CNTs are soluble in water and insoluble in nonpolar solvent. The improvement in hydrophilicity of CNTs will not only benefit their biocompatibility to a certain degree but also make the applications of CNTs in biomolecular immobilizations and biosensor constructions more convenient. For instance, the couple between biomolecules and CNTs can be completed at an aqueous environment, and thus the activity of biomolecules can be better maintained.

3.3. Electrochemical performance of the ammonia PT-CNTs

It has been recognized that the electron transfer capacity of electrodes in electrochemical processes is directly associated to the surface conditions of electrode materials. The plasma treatment of electrodes has also been demonstrated to be an effective approach to drive the electron transfer faster [34]. For the ammonia PT-CNTs, the introduction of the hydrophilic groups greatly enhances the wetting properties of CNTs interface, as well as improving the electron transfer properties of CNTs. In this study, the oxidation of potassium ferrocyanide served as a benchmark to compare the electrochemical properties of the ammonia PT-CNTs and the pristine CNTs. In view of the bad dispersibility of the pristine CNTs in water, both the CNTs were dispersed in 0.5% Nafion solution in an ultrasonic bath for 2 h. The two kinds of CNTs (10 μL of 3 mg mL^{-1} solutions) were then coated onto the rinsed electrodes, respectively, to form the CNT-modified electrodes. Fig. 5 shows the current-normalised cyclic voltammograms of 5 mM potassium ferrocyanide at the two electrodes. It can be seen that for the ammonia PT-CNTs modified electrode, the peak potential separation (ΔE_p) of the cyclic voltammetric

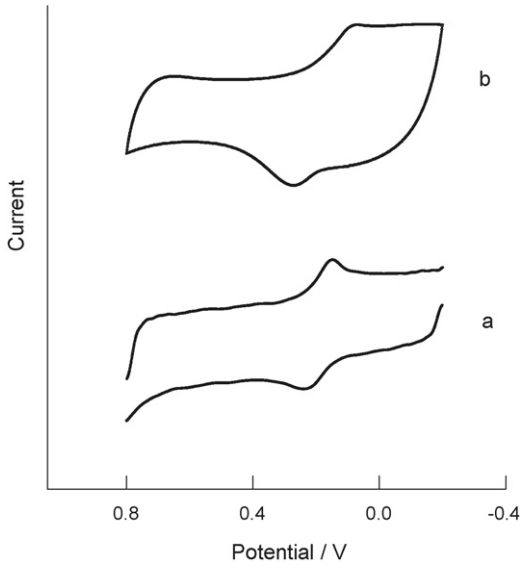

Fig. 5. Cyclic voltammograms of 5 mM potassium ferrocyanide at the two Nafion membrane electrodes consisting of the ammonia PT-CNTs (a) or the pristine CNTs (b).

curve (curve a) at a sweep rate of 150 mV s^{-1} is 80 mV, while the ΔE_p value for the pristine CNTs modified electrode is 200 mV. The clear decrease in the ΔE_p value indicates that the ammonia PT-CNTs has a faster electron transfer capability than the pristine CNTs, and the electron transfer rate constant (k_0) values of potassium ferrocyanide at the two electrodes were estimated to be 0.5 and 0.06 cm s^{-1}, respectively [35]. These results demonstrate that the enhanced wetting properties can favour faster ET kinetics on the ammonia PT-CNTs electrodes as well as this convenient MW plasma treatment has little effect on the carbon skeleton structure of CNTs, retaining conducting properties of the ammonia PT-CNTs.

3.4. Performance of the ammonia PT-CNTs in biosensor construction

To further study the electrochemical properties and biosensing applications, we applied the ammonia PT-CNTs to construct an electrochemical GOD biosensor and investigated the influences of the ammonia PT-CNTs on the electrochemical behaviors and sensing characteristics of the biosensor in detail. Fig. 6 is the Faradaic impedance spectra corresponding to the GOD electrodes with the ammonia PT-CNTs or without the ammonia PT-CNTs. It can be seen that the Faradaic resistance of the electrode only with a VF layer is 400 Ω (curve a), whereas a linear Faradaic impedance curve is observed and the Faradaic resistance almost reaches zero when 5 μL of ammonia PT-CNTs (1.0 mg mL^{-1}) is added on the electrode (curve b). Moreover, curve c and d reveal that the Faradaic resistances of the GOD electrode consisting of VF, GOD, GLU, and BSA with or without the ammonia PT-CNTs are 450 and 4000 Ω, respectively. It is thus obvious that the presence of the ammonia PT-CNTs can clearly increase the Faradaic resistance of enzyme membrane and enhance the electron transfer kinetics of GOD biosensor.

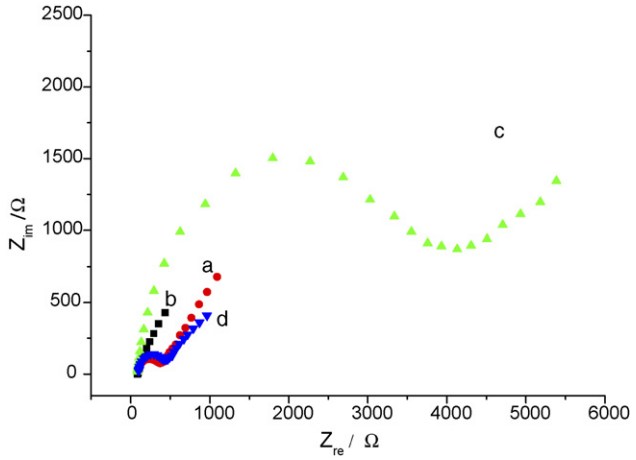

Fig. 6. Nyquist plots (Z_{im} vs. Z_{re}) corresponding to the Faradaic impedance analyses of the electrodes. (a) With only a VF layer; (b) with a mixture layer of the ammonia PT-CNTs and VF; (c) with a mixture layer of GOD, GLU and BSA on the VF layer; (d) with a mixture layer of GOD, GLU, BSA and ammonia PT-CNTs on the VF layer. All impedance spectra are recorded in 0.1 M phosphate buffer in the presence of 5 mM $[Fe(CN)_6]^{3-/4-}$.

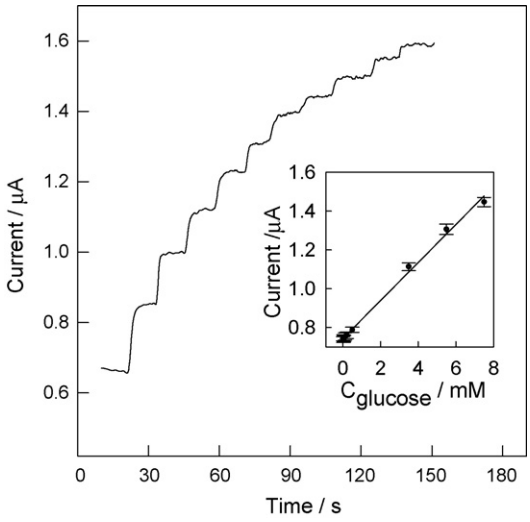

Fig. 7. Dynamic response of the GOD electrode to successive addition of 0.3 mM glucose in 0.067 M phosphate buffer (pH 6.9) at the applied potential of +400 mV vs. SCE. The insert figure shows the calibration curve.

To investigate the influence of the ammonia PT-CNTs on the sensing performance of GOD electrodes, we compared the current responses of the GOD electrodes with and without the ammonia PT-CNTs to glucose at the applied potential of +400 mV versus SCE. The result showed that the response current values of the GOD electrode with the ammonia PT-CNTs in glucose solutions of different concentrations were much larger than those obtained from the GOD electrode without the ammonia PT-CNTs. For example, the response current of the GOD electrode with the ammonia PT-CNTs in 12 mM glucose solution is 1.48 μA while that of the GOD electrode without the ammonia PT-CNTs is only 0.32 μA. The result suggests that the ammonia PT-CNTs can play a similar role as the common CNTs in enhancing the electron transfer of enzymatic electrodes as well as making the immobilization of biomolecules and the construction of biosensors more convenient. On the other hand, the amount of the ammonia PT-CNTs in the GOD matrix membrane also affects the sensing characteristics of the biosensor. The ammonia PT-CNTs of different concentrations is used for the construction of the GOD electrodes. The experiment result shows that the addition of the ammonia PT-CNTs distinctly increases the response current. When the concentrations of the ammonia PT-CNTs are 0.5, 1, 2 and 4 mg mL^{-1}, the response currents of the prepared GOD electrodes in 6 mM glucose solution were 0.46, 0.90, 1.65 and 2.23 μA, respectively. However, the increasing ammonia PT-CNTs make the stability of the GOD matrix membrane somewhat deteriorated. In this experiment, 1 mg mL^{-1} CNTs is preferably used for the remainder of experiments.

3.5. Response characteristics of the GOD electrodes

The applied experimental potential could affect the amperometric determination of glucose, and thus we investigated the electrode responses at different potentials. With the increasing potential from 400 mV to 700 mV, the response current of the GOD electrode reached a plateau. To avoid interference at higher applied potential, a potential of 400 mV (versus SCE) was selected as the applied potential for amperometric measurements. Fig. 7 displayed typical amperometric i–t curve of the GOD electrode for successive additions of the same amounts of glucose (0.3 mM) under the optimized experimental conditions. The GOD electrode exhibited a rapid and sensitive response to glucose solution, and the response time was less than 10 s. As shown in the inset figure in Fig. 7. The response current linearly increased with the glucose concentration in the range of 1.2×10^{-4}–7.5×10^{-3} M, and the detection limit was 1.0×10^{-5} M (S/N > 3).

The repeatability of response current of the GOD electrodes was studied at a glucose concentration of 0.12 mM. The variation coefficient (VC) was 2.5% for five successive assays. Three GOD electrodes prepared independently in the same batch showed an acceptable reproducibility with a VC of 4.76% ($n = 4$) for the current determinations in 0.3 mM glucose solution.

Moreover, the GOD electrodes also displayed good storage stability. We measured the sensing response of the GOD electrode to 0.1 mM glucose. The response current of the GOD electrode decreased to 97.3% after storing for 10 days, and it maintained about 85.7 and 70.4% of its original response after 20 and 30 days, respectively.

4. Conclusion

A microwave plasma treatment method has been developed to enhance the solubility of carbon nanotubes. By using ammonia as precursor monomer, the resultant ammonia PT-CNTs maintained the carbon skeleton structure, while grafting new functional groups. The introduction of polar functional groups in the MWP treatment process greatly increased the hydrophilicity of CNTs, making the applications of CNTs in immobilizations of biomolecules and construction of biosensors more convenient.

Moreover, the ammonia PT-CNTs had a faster electron transfer capability than the pristine CNTs. It is thus evident that this microwave plasma treatment is a quite effective and reliable method for the functionalization of CNTs.

Acknowledgements

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