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## Synthesis of MWCNT/nickel glycolate polymer core–shell nanostructures and their nonenzymatic electrocatalytic activity toward glucose

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## ABSTRACT

A series of multi-walled carbon nanotube (MWCNT)/nickel glycolate polymer core–shell nanostructures have been successfully synthesized in ethylene glycol medium using a solvothermal method, through which a conformal nickel glycolate polymer layer was deposited onto the MWCNTs. Furthermore, the thickness of the nickel glycolate polymer shell can be conveniently varied or controlled by the concentration of the metal salt ( $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ). Cyclic voltammetry study has revealed that these hybrid nanostructures possess significantly enhanced electrocatalytic activity toward the oxidation of glucose for the first time. There is an optimum  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  concentration at which the nanostructure obtained possesses the maximum electrocatalytic activity. Most importantly, these new MWCNT/nickel glycolate polymer core–shell nanostructures have shown potential applications as nonenzymatic glucose sensors.

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### 1. Introduction

Carbon nanotubes (CNTs), as one of the most promising candidates as building blocks in nanoscale electronic devices, have been extensively studied due to their high electrical conductivity, mechanical strength, and chemical stability [1–3]. To further optimize their performance, significant research interest has been generated in recent years concerning multifunctional composites of multi-walled carbon nanotubes (MWCNTs) with various inorganic and organic substances by physical and chemical approaches [4]. A variety of methods have recently been developed to prepare such MWCNT composites, including self-assembly [5,6], sol–gel coating [7,8], sonochemical processing [9], and liquid/vapor phase deposition [10,11]. Most of these methods are generally employed in aqueous reactive systems, where pristine hydrophobic MWCNTs need to be pre-oxidized in concentrated acids in order to hydrophilic –OH and –COOH surface functional groups. However, the oxidization usually causes excessive damage to the structure of MWCNTs, undesired surface defects and shortening of MWCNTs, which exerts adverse effects on the conductivity and mechanical properties of pristine MWCNTs. Therefore, it becomes important to develop new strategies for preparing uniform hybrids with pristine MWCNTs as starting supports [12].

Recently, there is an increasing interest of developing electrochemical glucose sensors due to its applications in biotechnology, clinical diagnostics and food industry. The glucose oxidase (GOD) based sensors have been widely studied, in which  $\text{O}_2$  is reduced by the enzyme to form  $\text{H}_2\text{O}_2$  while glucose is oxidized to form gluconolactone [13–15]. Thus, the detection of GOD-based sensor normally depends on the response from the oxidation of  $\text{H}_2\text{O}_2$  or the reduction of  $\text{O}_2$ . However, GOD-based biosensors suffer from a stability problem because of the intrinsic feature of enzymes. To overcome this obstacle, it is of great importance to prepare nonenzymatic sensors based on the direct oxidation of glucose for extended usage. Up to now, only several metals and metal oxides–MWCNTs composites, such as Au nanoparticles–MWCNTs [16], Cu–MWCNTs nanocomposites [17], and  $\text{Fe}_3\text{O}_4$ –MWCNTs [18], have been proposed to improve the performance of nonenzymatic glucose sensors. It is clear that new enabling materials are needed to develop effective enzyme-less glucose sensors.

Herein, we reported a facile route to synthesize MWCNTs/nickel glycolate polymer core–shell nanostructures, and it was used to modify an electrode which showed significantly enhanced electrocatalytic activity toward the oxidation of glucose for the first time. This new type of nanocomposites was prepared via a solvothermal method in a non-aqueous ethylene glycol (EG) medium. This method demonstrates the advantages of preparing the MWCNT/nickel glycolate polymer core–shell nanostructures without the need of using acid oxidized–MWCNTs. It is also a clean one-step process free from any catalysts, surfactants, complex metal ligands or fatty-acids to assist the conformal growth nickel

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glycolate polymer on MWCNT surfaces. The nanostructures prepared using this method are of high purity and particularly suitable for electrocatalytic materials because the reaction mixture only consists of MWCNT template,  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  and EG. Furthermore, the thickness and morphology of the nickel glycolate polymer shell can be conveniently varied or controlled by the concentration of the metal salt.

## 2. Experimental

All reagents were of analytical grade, purchased from the Shanghai Chemical Reagent Manufacturing Co., and used as received without further purification.

MWCNTs with 40–60 nm in diameter were synthesized following our previous method [19]. For a typical nanocomposites synthesis, 30 mg of as-prepared MWCNTs were dispersed in 50 ml of EG through ultrasonication for 40 min. After that, 0.164 g of sodium acetate (NaAc) and the pre-determined amount of  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  were added with constant ultrasonication for 20 min. The mixture was sealed in a Teflon-lined stainless steel autoclave and maintained at 200 °C for 12 h, and then cooled to ambient temperature. The black product was thoroughly rinsed with deionized water and ethanol for several times, and then dried at 80 °C for 4 h. To investigate the effect of metal salt concentration, different amount of  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  was used in the solvothermal process, while the other conditions remain unchanged. Products prepared with different concentrations of  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , i.e., 0, 0.015, 0.019, 0.025, 0.038 and 0.075 M, were assigned sample codes as Sa (pure MWCNTs), Sb, Sc, Sd, Se and Sf, respectively.

A mixture of graphite powder and paraffin were blended by hand mixing with a mortar and pestle for the preparation of carbon paste. The resulting carbon paste was mixed with MWCNT/nickel glycolate polymer nanocomposite at a ratio of 5:1 ( $\text{w w}^{-1}$ ). The mixture was then inserted at one end of a glass tube of 1 mm inner diameter. The electrical connection was implemented by a copper wire lead fitted through the top of the glass tube. A fresh electrode surface was generated rapidly by extruding a small plug of the paste out of the end of the glass tube and wiping it against on a flat sheet of clean paper until a smooth surface was obtained. Powder X-ray diffraction (XRD) measurements of the nanocomposites were performed with a Philips PW3040/60 X-ray diffractometer using  $\text{CuK}\alpha$  radiation at a scanning rate of  $0.06^\circ \text{ s}^{-1}$ . Scanning electron microscopy (SEM) was performed with a Hitachi S-4800 scanning electron microanalyzer with an accelerating voltage of 15 kV. Transmission electron microscopy (TEM) was conducted at 200 kV with a JEM-2100F field emission TEM. Cyclic voltammetry investigations were performed in 0.5 M NaOH and 0.5 mM glucose aqueous solution using an electrochemical workstation CHI842B and a three-electrode cell at room temperature. The carbon paste electrode (CPE) modified using a MWCNT/nickel glycolate polymer nanocomposite, a platinum electrode and a saturated calomel electrode (SCE) were used as working electrode, counter electrode and reference electrode, respectively.

## 3. Results and discussion

Fig. 1 shows the XRD pattern of the as-prepared MWCNT/nickel glycolate polymer nanocomposite. The peak at  $2\theta = 26.2^\circ$  can be well indexed as the characteristic (0 0 2) reflection of MWCNTs, and the strongest peak at  $2\theta = 10.3^\circ$  is assignable to the phase struc-

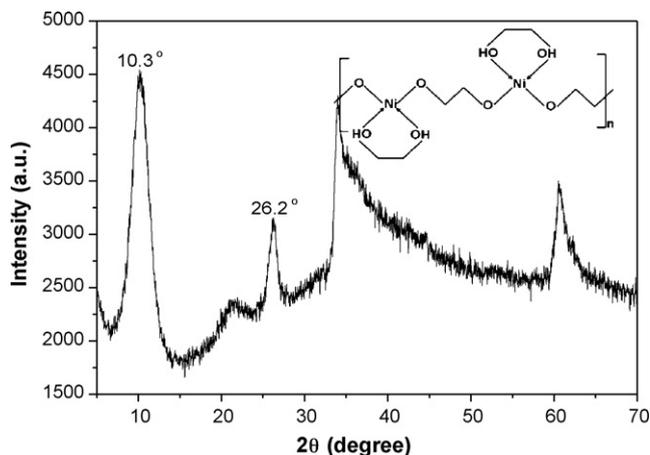


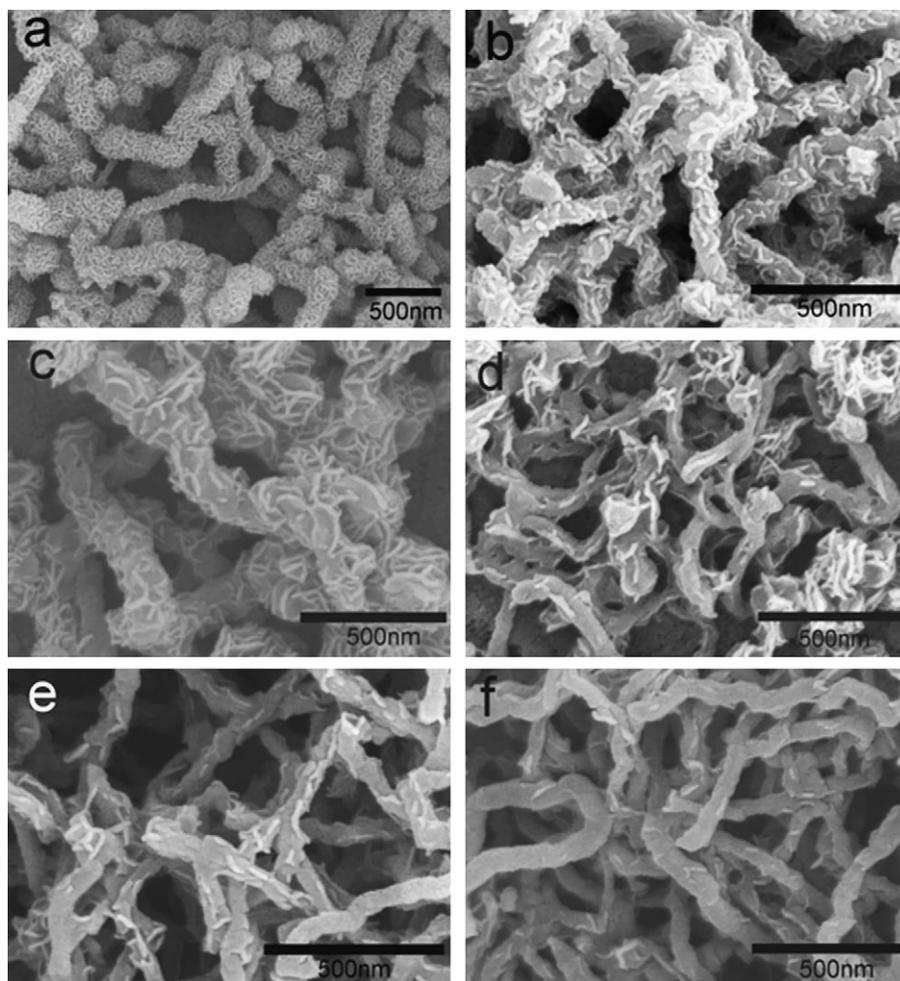
Fig. 1. XRD pattern of as-prepared MWCNT/nickel glycolate polymer core-shell nanostructures using 0.025 M of  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  at 200 °C for 12 h, and the presumed molecule structural scheme (inset).

ture of Ni-EG coordination polymer [20]. In addition, the proposed molecular structural scheme of nickel glycolate polymer is given as an inset in Fig. 1. SEM images of the as-prepared nanocomposites synthesized using different concentrations of  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  are shown in Fig. 2. From these images, distinct morphological changes can be observed. With increasing concentration of the metal salt, the surfaces of the MWCNTs (40–60 nm in diameter) became rougher and their diameter thicker, showing an increasing thickness of nickel glycolate polymer shell (50–100 nm in diameter). The TEM image further reveals that the surfaces of MWCNTs are covered uniformly by the nickel glycolate polymer. From the images of samples Sf (Fig. 3a) and Sd (Fig. 3b), we can observe that the surface of MWCNTs become thicker with increasing nickel salt concentration, and this result is also consistent with SEM.

A plausible mechanism may be proposed as following. First, upon dispersal of the as-prepared MWCNTs carbonaceous microspheres in nickel salt solutions, the functional groups on the CNT surfaces may bind nickel cations through coordination or electrostatic interactions, and then in situ coordinate with EG to form nickel glycolate during solvothermal treatment. Second, NaAc offers a slightly basic environment to catalyze the oligomerization of nickel glycolate, aiding the nickel glycolate polymer deposition on MWCNT. Meanwhile, the nonaqueous EG solution system could slow down the aggregation rate of the glycolate polymer because of fewer surface hydroxyls and greater viscosity than an aqueous solution. Thus, the conformal core-shell nanostructures can be obtained. Additionally, some organic media, such as benzyl alcohol, can as a surfactant enables  $\text{TiO}_2$  to interact with the hydrophobic surface of pristine MWCNTs without the need of covalent functionalisation [21]. Similarly, EG in this experiment do not only act as a reactant to form nickel glycolate polymer in following solvothermal process, but also may play a role of surfactant inducing nickel glycolate polymer deposited on the MWCNTs surfaces. EG absorbs at the MWCNTs' surface, while at the same time providing hydrophilic hydroxyl groups for the hydrolysis of the nickel precursor. Hence, pristine MWCNTs can indeed be used as a template without the need of covalent functionalisation. The dispersion of pristine MWCNTs could be significantly improved in the subsequent solvothermal process, thus also enabling the coating of individual MWCNTs with nickel glycolate polymer.

The cyclic voltammograms of the different samples (Sa–f) modified CPEs toward the oxidation of glucose are shown in Fig. 4a. As seen from Fig. 4a, MWCNTs modified CPEs (Sa) does not give obvious redox peaks and its electrochemical response to glucose is low. However, pair of well-defined redox peaks with current response is observed using MWCNT/nickel glycolate polymer nanocomposites modified CPEs. We believe this is due to the redox reaction of the Ni(III)/Ni(II) couple on MWCNT. It can be seen that when the concentration of  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  was less than 0.025 M, the electrocatalytic activity was enhanced steadily with increasing concentration of the metal salt. The improved electrocatalytic performance could be ascribed to the synergistic effect of conducting MWCNTs and catalytic nickel glycolate polymer. However, further increase in concentration of  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  during solvothermal treatment results in decreasing electrocatalytic activity. This indicates that a thick nickel glycolate polymer layer is undesirable as it may reduce the ability of electron transfer. The potential differences ( $\Delta E$ ) and current differences ( $\Delta I$ ) of the redox peaks in these modified electrodes are also plotted in Fig. 4b, which clearly indicate that the best electrocatalytic activity toward glucose oxidation is attained in sample Sd when concentration of  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  is  $0.025 \text{ mol L}^{-1}$ .

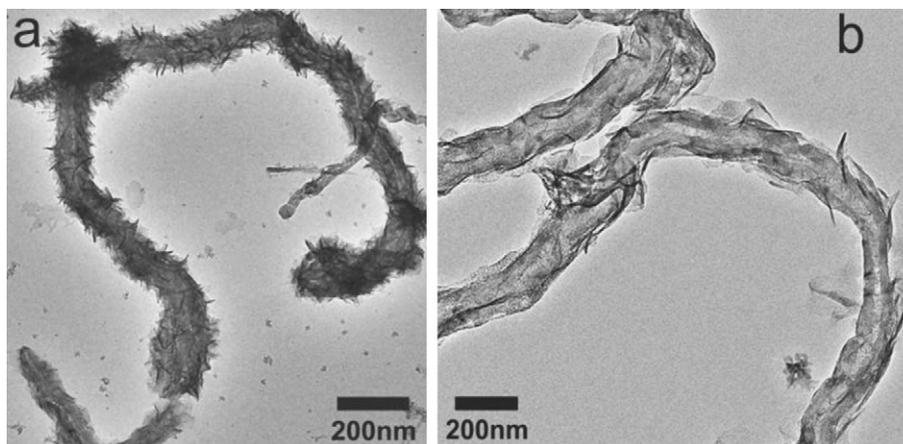
The amperometric response of the sample Sc modified electrode with the successive addition of glucose to 0.1 M NaOH at



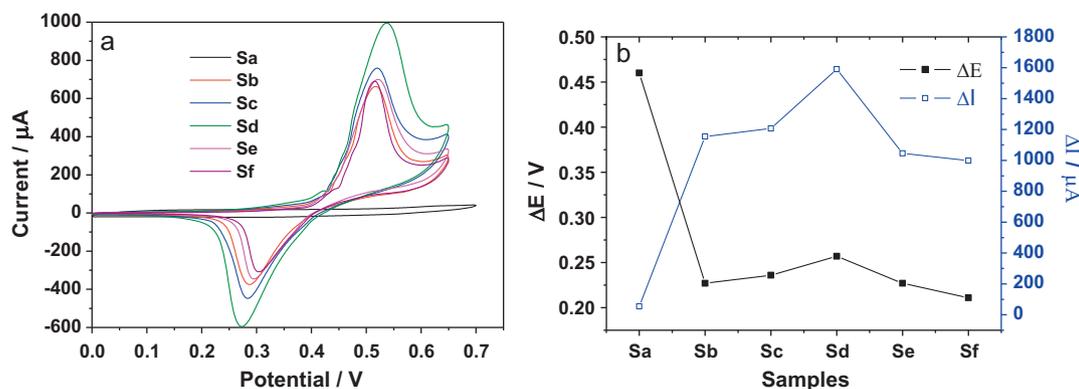
**Fig. 2.** SEM images of as-prepared MWCNT/nickel glycolate polymer nanocomposites using different concentration of  $\text{Ni}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ : (a) 0.075 M, (b) 0.038 M, (c) 0.025 M, (d) 0.019 M and (e) 0.015 M.

an applied potential of 0.55 V is shown in Fig. 5a. The response time is less than 3 s, revealing a rapid and sensitive response to glucose, which is ascribed to the good electrocatalytic property of the modified electrodes. Moreover, the current density at 0.55 V presents a better linearity with glucose concentration ranging from 1 to 12 mM with a correlation coefficient of 0.9952. In addition,

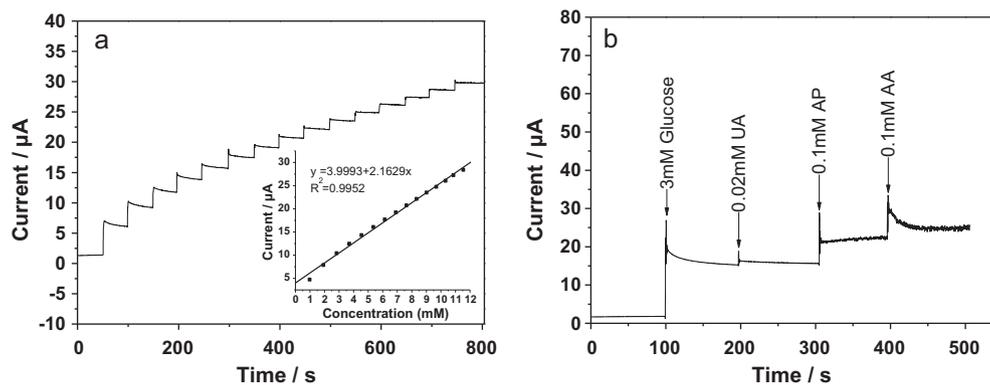
it is well known that uric acid (UA), ascorbic acid (AA) and p-acetamidophenol (AP) in the biological samples could be easily oxidized at positive potential and often interfere the detection of glucose [22]. Fig. 5b shows the response of the modified electrode to UA (0.02 mM), AA (0.1 mM), AP (0.1 mM) and glucose (3 mM) on the physiological level at 0.55 V. It is observed the interfering



**Fig. 3.** TEM images of as-prepared MWCNT/nickel glycolate polymer nanocomposites using different concentration of  $\text{Ni}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ : (a) 0.075 M and (b) 0.025 M.



**Fig. 4.** (a) Cyclic voltammograms of different samples modified electrode in 0.5 M NaOH solution in the presence of glucose. (b) The peak potential differences ( $\Delta E$ ) and peak current differences ( $\Delta I$ ) of redox system using different samples modified electrode. Scan rate:  $0.1 \text{ V s}^{-1}$ .



**Fig. 5.** The amperometric response of the sample Sc modified electrode to successive addition of glucose from 1 to 12 mM into 0.1 M NaOH with stirring; the working potential was 0.55 V, and the linear relationship between the catalytic current and glucose concentration (inset). (b) Successive injection of 3 mM glucose and interfering species 0.02 mM UA, 0.1 mM AP and 0.1 mM AA at 100 s intervals into 0.1 M NaOH, with working potential was 0.55 V.

species of UA, AA and AP is weak, and the response of glucose still had relatively large current value. Thus, the MWCNT/nickel glycolate polymer core-shell composites based sensor displays a faster response, wider linear range and higher sensitivity, which indicate its potential application in nonenzymatic glucose sensing.

#### 4. Conclusion

A new type of MWCNT/nickel glycolate polymer core-shell nanostructures has been prepared via a facile and mild solvothermal method. The thickness of nickel glycolate polymer shell could be varied or controlled by the concentration of metal salt. The electrochemical performance of the nanocomposite was investigated by cyclic voltammetry in alkaline media, and the results indicated that these nanostructures possess potential as a candidate for application in enzyme-less glucose sensing.

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