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Preparation and characterization of starch-grafted multiwall carbon nanotube composites

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ABSTRACT

A starch/carboxylated multiwall carbon nanotube (CCNT) composite (CCNT–starch) was prepared by covalently grafting a natural polymer starch onto the surfaces of CCNT. The obtained CCNT–starches were characterized by Fourier transform infrared spectroscopy (FTIR), thermogravimetric analysis (TGA), transmission electron microscopy (TEM), ultraviolet–visible spectroscopy (UV–vis) and electrochemical measurement. FTIR revealed that the covalent bonds between –OH groups of soluble starch and CCNT were formed in CCNT–starch. TEM and TG showed that CCNTs were covered with the grafted starch about 7.7 and 12.8 wt% in CCNT–starch, respectively. The grafted starch facilitated the dispersion of CCNT–starch in water and chitosan films because of the hydrophilic polysaccharide structure of starch components. CCNT–starch containing 12.8 wt% starch in water could form homogeneous solutions without obvious aggregation of CCNTs. The electrochemical properties of the CCNT–starch were characterized by casting CCNT–starch and chitosan solution on glassy carbon electrode. Compared to CCNT, CCNT–starch exhibited a couple of redox peaks in cyclic voltammograms testing.

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1. Introduction

Carbon nanotubes (CNTs) have received much attention since their discovery in 1991, however the wider application of CNTs in electronic, optical, sensor, and biomedical fields has been hampered by their limited solubility in solvents (Star et al., 2001) and by their bundling and aggregation due to van der Waals interactions (Lin et al., 2004). The dispersion of CNTs and the long-term stability of CNTs suspended in the solution have proved especially challenging for aqueous media (Alpatova et al., 2010).

Many efforts have been made to solublize CNTs through covalent modification and non-covalent functionalization (Jeykumari & Narayanan, 2008). Some biopolymers such as amylose (Lii, Stobinski, Tomasik, & liao, 2003), amylopectin (Stobinski et al., 2003), chitosan (Wu et al., 2007), and cellulose acetate (Ke, 2010) are known to effectively solubilize CNTs. Polymers have, however, a strong tendency to randomly wrap around CNT bundles, unless polymers have a specific binding interaction and an encapsulation process with CNTs (Kim et al., 2003). Starch is a hydrophilic polysaccharide that has received much attention in biological field. It is an attractive biocompatible, biodegradable, and non-toxic nature biopolymer. Amylose can form single helix in solutions, which may act as a host molecule to complex hydrophobic CNTs by hydrophobic interactions (Fu, Meng, Lu, Zhang, & Gao, 2007; Star, Steuerman, Heath, & Stoddart, 2002). However, large steric hindrance exists in the complex formation between single-walled carbon nanotubes (SWNTs) and amylose. Yang et al. (2008) synthesize amylose through vine-twining polymerization in the presence of SWNTs to obtain amylose–SWNTs supramolecular assembly. And starch/CNT composite films are also studied. Bonnet, Albertini, Bizot, Bernard, and Chauvet (2007) have prepared amylose/SWNT composites in aqueous solutions and deposited as films. Ma, Yu, and Wang (2008) fabricate glycerol plasticized-starch/multiwall carbon nanotube (MWCNT) composite films by casting. Although many successful functionalizations for CNT have been reported, as we know, most of them were obtained by non-covalent interactions. The covalent modification of CNT surface can form strong interaction between starch and CNTs, which will help to improve their dispersion stability and make the resulting composites more stable and controllable (Wu et al., 2007). However, there is few study about the starch covalently modified CNTs. The grafting of starch onto the surface of CNT may be desirable to improve the hydrophilicity of CNT, resulting in high dispersibility and long-term stability of CNT. In this study, soluble starch was grafted on carboxylated multiwall carbon nanotubes (CCNTs) to disperse well CNTs in water or the polysaccharide films. The obtained CCNT–starch will have wider application because they possessed both hydrophilicity of soluble

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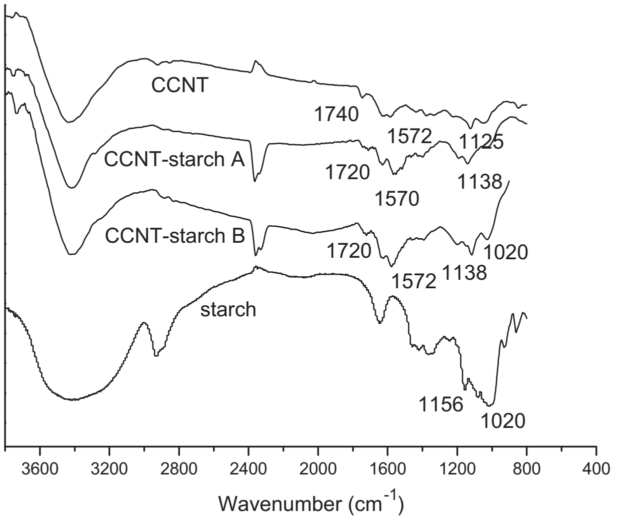

Fig. 1. FTIR of spectra of starch, CCNT and CCNT–starch.

starch and extraordinary (electrical, mechanical, and adsorption) properties of CNTs.

2. Experimental

2.1. Materials

Carboxylated MWCNTs (CCNTs) were purchased from Chengdu Institute of Organic Chemistry - Chinese Academy of Sciences, China. MWCNTs from the arc-discharge method were treated with acid oxidation to obtain the product. The content of carboxylic group was about 2 wt%. Soluble starch was obtained from Tianjin Fine Chemical Institute (Tianjin, China). Chitosan from shrimp shell was provided by Panan Chitosan Co., Ltd. (Zhejiang, China). The reagents, acetic acid, NaH_2PO_4, Na_2HPO_4, thionyl chloride, N,N-dimethylformamide (DMF), tetrahydrofuran, N,N-dimethylacetamide (DMAC), and LiCl were commercially available and of analytical grade. The activity unit (U) of glucose oxidase (GOD) is 300 U mg^{-1} (Hefei Bomei Biotechnology Co., Ltd.).

2.2. Preparation of CCNT–starch

CCNTs (0.7 g) were added in a solution of thionyl chloride and DMF (1 ml). The suspension was stirred for 6 h at 70 °C, and then it was filtrated and dried in vacuum. The obtained acyl chloride–CNTs and soluble starch (0.2 g) were added to the solution of DMF (30 ml) and pyridine (1 ml). The reaction was continued for a period at 110 °C. The sample was collected by filtration, washed with DMAC/LiCl (95/5) at room temperature to remove the soluble starch (Wang, Zhang, Liu, & Wang, 2009), washed with distilled water and then dried. The obtained samples were CCNT–starch A and CCNT–starch B, which were respectively synthesized for 6 and 24 h at 110 °C between acyl chloride–CNTs and soluble starch. And thionyl chloride was respectively 15 and 30 ml for the preparation of CCNT–starch A and CCNT–starch B.

2.3. Fourier transform infrared spectroscopy (FTIR)

FTIR spectra of soluble starch, CCNT and CCNT–starch were obtained on a BIO-RAD FTS3000 IR Spectrum Scanner.

2.4. Thermogravimetric analysis (TGA)

In order to estimate the starch contents of CCNT–starch, thermal properties of soluble starch and CCNT–starch powders were measured using a ZTY-ZP type thermal analyzer. Sample weights varied from 10 to 15 mg, which were heated from room temperature to 500 °C at a heating rate of 15 °C/min in a nitrogen atmosphere.

2.5. Transmission electron microscopy (TEM)

The aqueous suspensions of CCNT, CCNT–starch A and CCNT–starch B were dropped onto the copper grid and air dried. The samples were analyzed using a TEM JEM-1200EX.

2.6. The dispersion of CCNT–starch in distilled water

1 mg CCNT and CCNT–starch were respectively added in 20 ml distilled water and ultrasonically stirred for 30 min. The dispersions of them in distilled water were recorded after placing for 10 min.

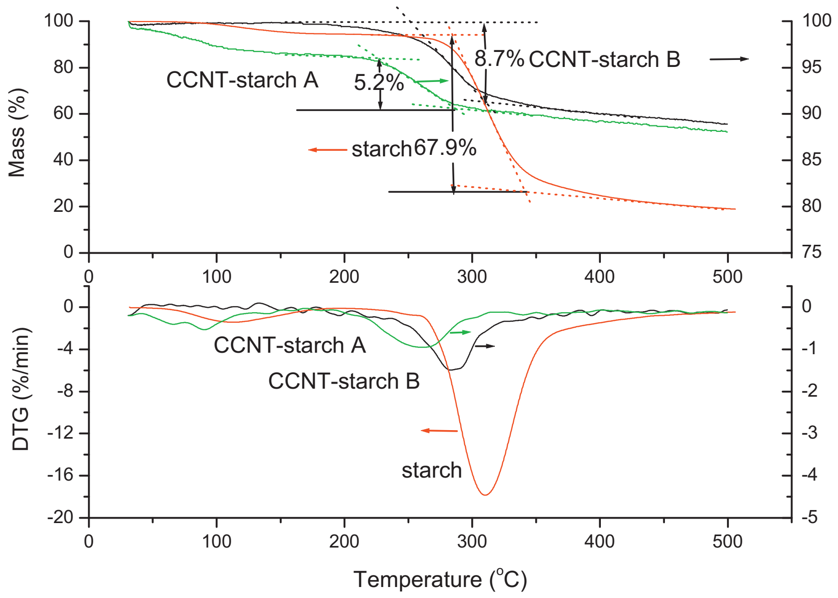

Fig. 2. The thermogravimetric (TG) and derivative thermogravimetric (DTG) curves of starch and CCNT–starch.

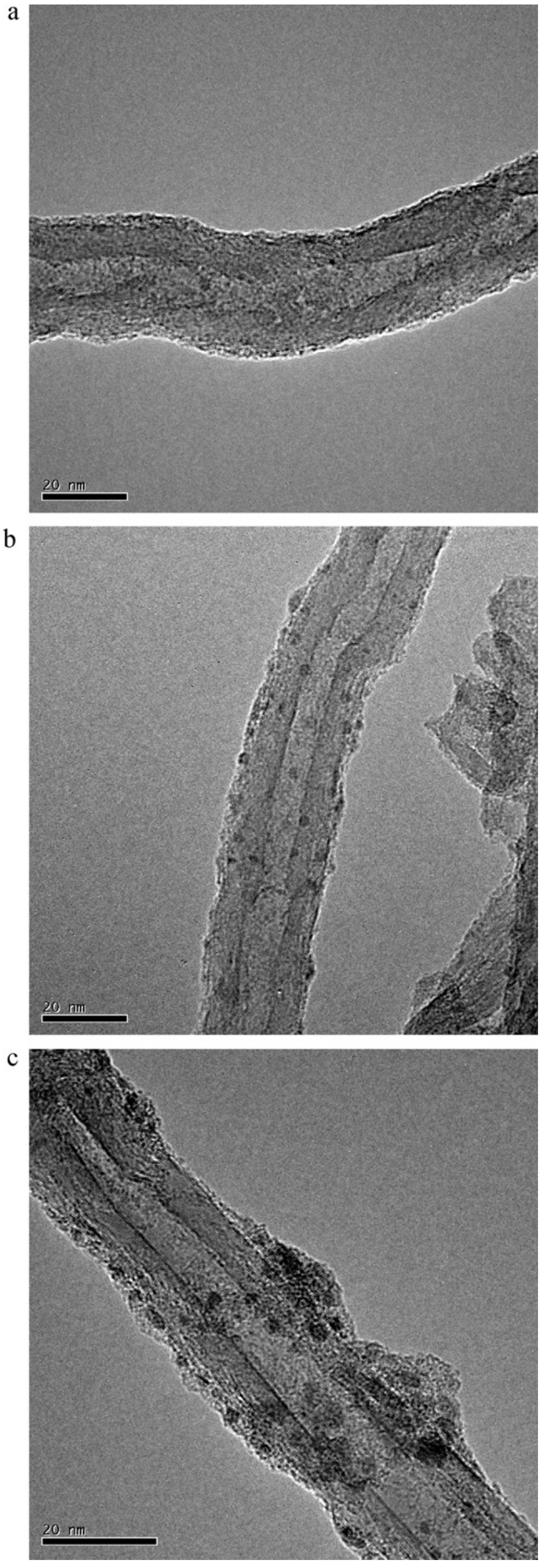

Fig. 3. TEM of CCNT (a), CCNT–starch A (b) and CCNT–starch B (c).

The dispersions of CCNT and CCNT–starch were recorded by the digital camera.

2.7. Ultraviolet–visible (UV–vis) spectroscopy

The UV–visible spectra of different concentrations CCNT and CCNT–starch in distilled water were recorded using a UV-vis spectrophotometer model U-1800, Hitachi Company.

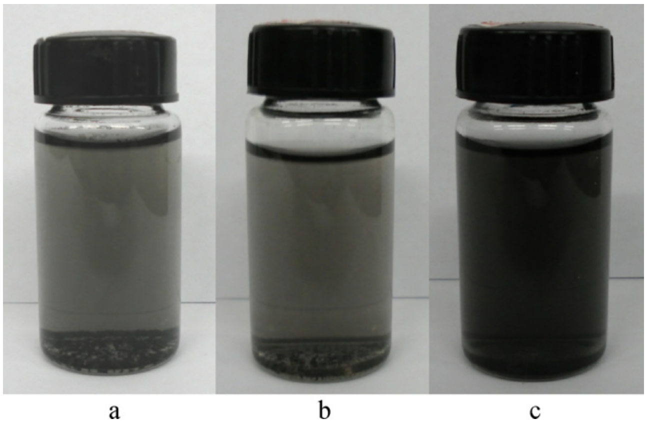

Fig. 4. The dispersion of CCNT (a), CCNT–starch A (b) and CCNT–starch B (c) in water.

2.8. The preapartion of modified glassy carbon electrode (GCE) and electrochemical measurements

Before each experiment, GCE was first polished with 0.3 and 0.05 μm alumina slurry, rinsed with doubly distilled water, sonicated with ethanol and doubly distilled water for 10 min each to remove the excess of the physical absorption.

CNTs (including CCNT, CCNT–starch A and B) were respectively dispersed in 10 ml of 0.5 wt% chitosan solution (2% acetic acid) and 1 mg GOD, and sonicated for 20 min. The ratios of CCNT and chitosan were 0. 625%, 1.25% and 5%, respectively. GCE was modified by a drop of above obtained solution. After being dried in air, the electrode was immersed in phosphate-buffered saline (PBS, 0.1 mol/L NaH_2PO_4 + 0.1 mol/L Na_2HPO_4, pH 7.0) containing 0.01 mmol/L glucose. Electrochemical measurements were performed with a ZAHNER electrochemical system at room temperature. A three-electrode system arranged with a modified GCE (round 5 mm diameter) was used as working electrode, a Pt wire as counter electrode and a saturated calomel electrode as reference.

3. Results and discussion

3.1. FTIR

In Fig. 1, the spectrum for the CCNT showed absorbances at 1740 cm^{-1} and 1125 cm^{-1}, which were ascribed, respectively, to the C=O and C–O stretching of carboxylic acids. And the peak 1572 cm^{-1} could be related to the C=C stretching of CCNT (Hamon, Hui, Bhowmik, Itkis, & Haddon, 2002). In the fingerprint region of the soluble starch spectrum, there are three peaks that are characteristic of –C–O– stretching. The peak at 1156 cm^{-1} was ascribed to C–O bond stretching of the C–O–H group, and the two peaks at 1080 and 1020 cm^{-1} were attributed to C–O bond stretching of the C–O–C group in the anhydroglucose ring (Ma, Chang, Yang, & Yu, 2009). A weak absorbance at 1375 cm^{-1} was the characteristic absorbance spectrum of O–C–H, C–C–H and C–O–H groups on the starch chains (Iizuka & Aishima, 1999). In the FTIR spectrum of CCNT–starch, the peak at 1138 cm^{-1} may be the overlapped –C–O– stretching of the starch and CCNT. The absorptions at 1020 and about 1570 cm^{-1} were indicative of starch and CCNT component, respectively. And the new absorbance at 1720 cm^{-1} is characteristic of an ester (C=O stretching mode). These absorbances indicate the formation of covalent bonds between –OH groups of soluble starch and CCNT.

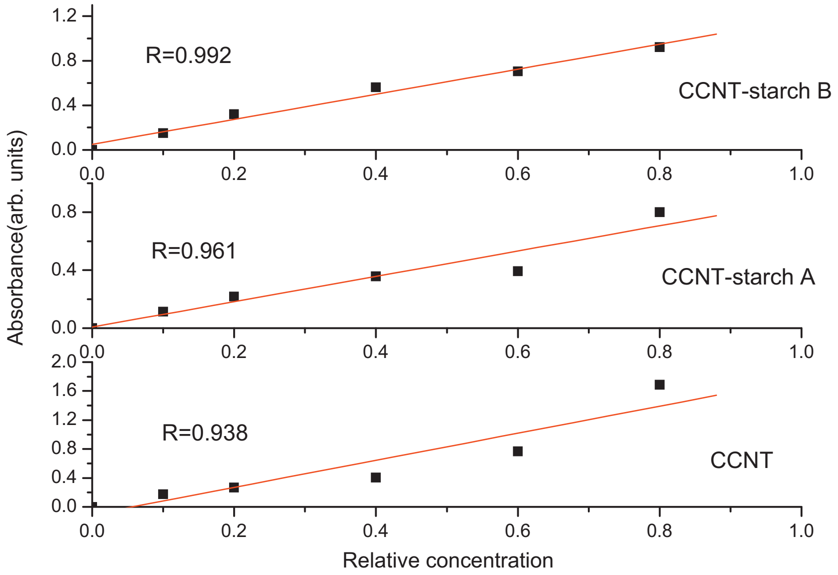

Fig. 5. The ultraviolet–visible absorbance of CCNT and CCNT–starch in water.

3.2. *TG*

The thermogravimetric (TG) and derivative thermogravimetric (DTG) curves of soluble starch and CCNT–starch are shown in Fig. 2. As TG curve exhibited the rapid mass loss, the thermal decomposition of starch covered a range of the temperature, where the peak located at 310.1 °C in DTG curve. Because the decomposed peak temperature of soluble starch was higher than those of starch in CCNT–starch, soluble starch had better thermal stability than starch in CCNT–starch. It could be ascribed to starch degradation during the synthesis of the CCNT–starch. The CCNT–starch A and B respectively showed a weight loss of about 5.8 and 8.7 wt% at the range of starch decomposed temperature. It was assumed that the contents of mass loss of starch were constant at the decomposed temperature range when starch grafted on CNT. The quantity of starch was calculated by matching mass loss of CCNT–starch to weight loss of soluble starch at the range of decomposed temperature (about 67.9 wt%). The starch contents of CCNT–starch A and B respectively were estimated to be about 7.7 and 12.8 wt%.

3.3. *TEM*

The morphology of CCNT and CCNT–starch was observed by TEM. As shown in Fig. 3, the surface of CNT was smooth, while CCNT–starch became rough. In Fig. 3b and c, CCNT was covered with the grafted starch. No gap between starch and CCNT exhibited that the good interaction was formed between them. It was obvious that more amount of starch was graft onto CCNT in CCNT–starch B (Fig. 3c) than CCNT–starch A (Fig. 3 b). It was consistent with TG result.

3.4. *The dispersion of CCNT–starch in water*

The dispersions of CCNT and CCNT–starch in distilled water are displayed in Fig. 4. A great amount of CCNT was precipitated (Fig. 4a), and CCNT–starch B precipitation (Fig. 4b) was less than CCNT. Since water was a good solution for soluble starch, CCNT–starch B could be dispersed well in the solution (Fig. 4c), and no obvious precipitation was found. The more the grafted starch was, the better the dispersion of CCNT was in distilled water. It was dependent on the interaction between starch and the surface of CCNTs.

Fig. 5 shows the absorbance at 265 nm of CCNT and CCNT–starch with different concentrations in distilled water. The straight line passing through the origin described the relationship of the observed absorbance and CCNT (or CCNT–starch) concentrations. The linear correlation was only 0.938 for CCNT (Fig. 5a). This optical behavior was typical aggregation of any multi-molecular species. With the increasing of starch components, the linear correlation became better. A small amount of starch in CCNT–starch A was still not enough to homogeneously disperse CCNT (Fig. 5b). The absorbance of CCNT–starch B was dependent on the solution concentrations in a linear fashion ($R = 0.992$) (Fig. 5c), following Lambert–Beer's law (Lin, Rao, Sadanadan, Kenik, & Sun, 2002). It indicated that CCNT–starch B formed homogeneous solutions without aggregation of any multi-molecular species (Sun et al., 2001). In addition, the independence of the absorbance at 265 nm on sonication time (30, 45 and 60 min) revealed that the interaction between CCNT and starch was covalent grafting rather than physical absorption (Wu et al., 2007).

3.5. *Electrochemical performances of CCNT–starch modified electrodes*

Since starch and chitosan are natural polysaccharides, CCNT and CCNT–starch were blended with chitosan to form modified electrodes to evaluate the effect of the grafted starch on the conductivity and the dispersion of CCNT–starch in polysaccharide films. GOD can catalyze the oxidation of glucose, and modified CNTs are used as the electron transfer mediator between GOD and the electrode (Lin, He, & Zhao, 2009). If CCNT s can be dispersed well in the films, the low loading of CCNTs will form the nanotube network for the electron transfer between GOD and the electrode. Fig. 6 shows cyclic voltammograms of CCNT and CCNT–starch modified electrode with different contents of CCNT and CCNT–starch in chitosan films. In Fig. 6a, with the increasing of CCNT contents from 0.625 to 5 wt%, the sensitivity was not expectedly increased. The aggregations of CCNT could counteract the higher loading in films. When starch was covalently grafted on CCNTs, as shown in Fig. 6b, a couple of redox peaks were detectable at −48 and 28 mV at the content of 5 wt% CCNT–starch A. The grafted starch facilitated the dispersion of CCNT–starch A in chitosan films, because of the similar polysaccharide structure between starch and chitosan. As shown in Fig. 6c, CCNT–starch B with higher starch content in chi-

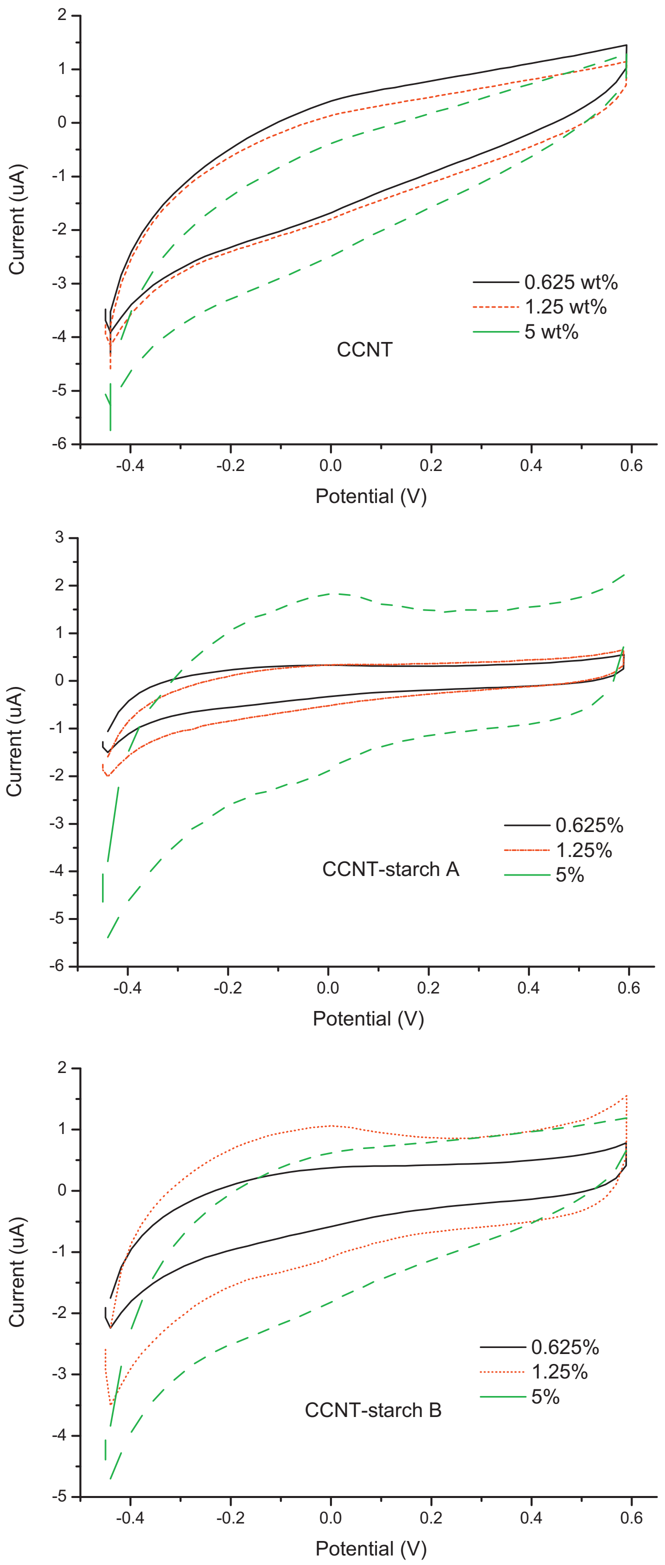

Fig. 6. Cyclic voltammograms of the CCNT and CCNT–starch modified electrode in phosphate buffer (pH 7.0) with 0.01 mM glucose at a scan of 50 mV/s.

tosan film exhibited a couple of redox peaks at the lower content of 1.25 wt%. Due to the creation of the interconnecting conductive channels at 1.25 wt%, higher loading CCNT–starch B (i.e. 5 wt%) had little effect on the improvement of the sensitivity. As revealed by Fig. 7, the CCNT–starch B (1.25 wt%) modified electrode displayed a linear response to glucose in the concentration range from 0.01 to 10 mM with a correlation coefficient of 0.9964. And the linear regression equation was I (μA) = 0.0185[glucose] + 1.0934.

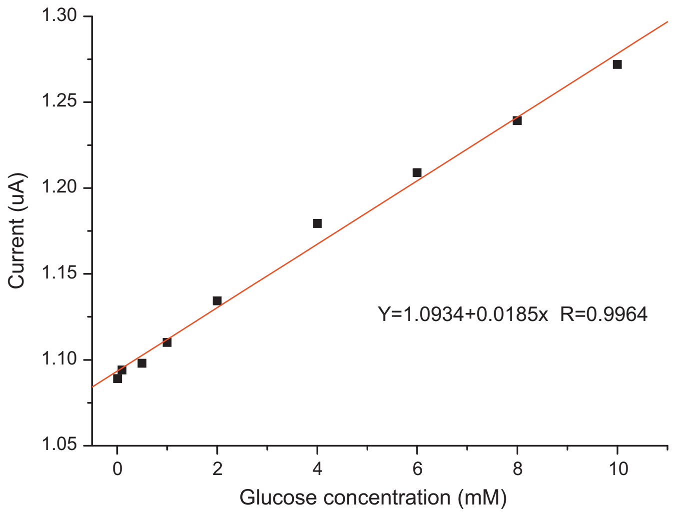

Fig. 7. Current response of CCNT–starch B (1.25 wt%) modified electrode various concentrations of glucose in phosphate buffer (pH 7.0).

4. Conclusions

In the present study, a novel method was used to prepare starch-grafted multiwall carbon nanotube composites. FTIR, TG and TEM proved that about 7.7 and 12.8 wt% starch were respectively grafted on CCNTs to obtain CCNT–starch A and B. The grafted starch could improve the hydrophilicity of CCNTs, which facilitated the dispersion of CCNT–starch in both water and the polysaccharide based films. The more the grafted starch was, the better the dispersion of CCNT–starch was in water. The UV absorbance of CCNT–starch B was linearly dependent on the concentrations in water, following Lambert–Beer's law. And the CCNT–starch B (1.25 wt%) modified electrode displayed a linear relation to glucose concentration range from 0.01 to 10 mM.

The CCNT–starch composites were composed of starch and CNT, so they possessed the features of starch and CNT. Starch provided the biocompatibility and hydrophilicity, while CNT had extraordinary electrical, mechanical, and adsorption properties. Therefore, CCNT–starch will have the potential applications in biosensor, medical, agriculture, drug release and the filler for the matrix of other natural polysaccharides (agar, alginate and chitin).

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