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A facile approach to covalently functionalized carbon nanotubes with biocompatible polymer

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Abstract

Biocompatible poly(L-lactic acid) (PLA) was successfully covalently grafted onto the convex surfaces and tips of the multi-walled carbon nanotubes (MWNTs) by one step based on in situ polycondensation of the commercially available L-lactic acid monomers. The functional groups in the carboxylic multi-walled carbon nanotubes (MWNT-COOH) showed active enough for participating the polycondensation of L-lactic acid. The resulting PLA-*grafted*-MWNTs were characterized with Raman spectroscopy, Fourier-transform IR (FTIR), UV–vis, ^{1}H NMR, thermogravimetric analyses (TGA) and transmission electron microscopy (TEM). Raman, FTIR and ^{1}H NMR spectroscopies revealed that the PLA was covalently attached to the MWNT. TGA showed that the grafted PLA content could be controlled by the reaction time. The core/shell structures with MWNT as the "hard" core and the PLA polymer layer as the "soft" shell can be clearly seen through HRTEM.

Keywords: Carbon nanotube; Poly(lactic acid); Polycondensation

1. Introduction

Due to their unique topological structure and properties, carbon nanotubes (CNTs) have attracted the attention and imagination of many researchers worldwide since the discovery by Iijima in 1991 [1]. CNT, the quintessential nanomaterial as widely recognized, has compiled an impressive list of superlatives including the remarkable mechanical strength, the highest thermal conductivity, extraordinary optical properties and outstanding field emission properties which offer many opportunities for their applications such as reinforcement of fibers and nanocomposites, field-emission displays and nanosize probe tips for atomic force microscopy [2–6]. Another fast-moving and exciting application of the CNT is biological and biomedical systems and devices [7].

However, super amphiphobic property of the CNT is still the fundamental and technical barriers toward expanding many of the applications [8]. To improve the CNT solubility in various organic and aqueous solvents, as well as their miscibility with bulk polymer materials, the preparation of CNT derivatives through chemical modification has been the subject of intense recent interest [9]. The CNT functionalized with polymers has been identified to realize the above goals, allowing them to be homogeneously dispersed in bulk polymers without the danger of phase separation [10]. As one of the most important biocompatible and biodegradable materials, PLA incorporating with CNT will grant improvement of solubility and compatibility and may promise multipurpose applications in biomedical systems and bionanomaterials.

Chemical binding polymers to the CNT can be generally divided into "grafted to" [11] and "grafted from" approaches [12]. The "grafted to" approach means the CNT is bonded with the existing macromolecules whose terminal functional groups react with the anterior functional groups of the CNT. The "grafted from" approach means the monomers are in situ polymerized from the macroinitiators or catalysts of the CNT surface. As shown in Fig. 1(A), in many cases, more than two or three steps were usually taken to achieve the final product from CNT-COOH [4,10–18], which is inconvenient for the fascinating applications.

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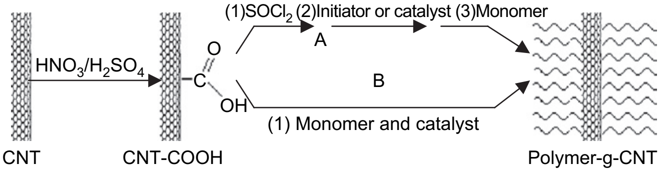

Fig. 1. Schematic illustration for the functionalization of CNTs by the traditional approach (A) and present route (B).

In this work, we present an in situ polycondensation approach, successfully directly functionalizing the MWNT-COOH with PLA by one step from commercially available polycondensation-type monomers, L-lactic acid, as shown in Fig. 1(B). In the usual route to the polymer-functionalized CNT, the CNT-COOH first react with thionyl chloride, and then with catalyst or macroinitiator to gain an active group on the CNT surface, and finally with the selected monomer or the existing macromolecule to give the final product. As a comparison in Fig. 1(B), a facile approach to the equivalent polymer-functionalized CNT is presented.

Such technique is considered to involve both "grafted to" and "grafted from" approaches. In the reaction system, the monomers can be initiated by functional groups from the surface of the CNT to form "grafted from" product. On the other hand, the formed free oligomers or polymers which can also react with the CNT functional groups to form "grafted to" product. It not only takes advantage of "grafted from" which is easier for controlling but also overcomes the limitation of "grafted to" in which the grafting density can't go high ascribed to the low reactivity and high steric hindrance of the macromolecules [18]. Compared to "grafted from" approach based on ring-opening polymerization of lactone, the strategy adopted in our experiment should be favored in industrialization for less step and much cheaper commercially available raw material.

2. Experimental section

2.1. Materials

The multi-walled carbon nanotubes (purity 95 wt%, diameter 20–30 nm, purchased from Chengdu Organic Chemistry Co. Ltd, Chinese Academy of Science) synthesized by chemical vapor deposition was annealed for 2 h in air at 400 °C to selectively etch amorphous carbon before use. L-Lactic acid (HPG90) kindly supplied by PURAC Co. Ltd. was used without any treatment. Stannous chloride dihydrate ($SnCl_2 \cdot 2H_2O$), xylene, chloroform, anhydrous calcium chloride, concentrated nitric acid (HNO_3, 70%) and concentrated sulfuric acid (H_2SO_4, 98%) were obtained from Shanghai Reagents Co. Ltd. and used as-received.

2.2. Instrumentation

Fourier-transform infrared (FTIR) spectra were recorded on a PE Paragon 1000 spectrometer. UV–vis spectra were collected with a Perkin–Elmer Lambda 20 spectrometer with 2 nm resolution. Hydrogen nuclear magnetic resonance (^{1}H NMR) spectra were measured with a Bruker 500 MHz spectrometer. Transmission electron microscopy (TEM) studies were performed on a JEOL JEM 2200FS electron microscope operating at 200 keV. Raman spectra were recorded on a LabRam-1B Raman spectroscope excited at 325 nm. Thermogravimetric analysis (TGA) was conducted on a PE TGA-7 instrument at a heating rate of 20 °C/min in a nitrogen flow (10 mL/min).

2.3. Purification of the CNTs

To remove the impurities, CNTs were treated with a mixture of concentrated sulfuric and nitric acids (volume 3:1). The mixture was ultrasonicated (power of 100 W and nominal frequency of 50 kHz at ambient temperature) for 2 h, and then magnetically stirred at 70 °C for 3 h. After the mixture was cooled to room temperature, it was diluted with deionized water and then vacuum-filtered through 0.22 μm millipore polypropylene membrane, and washed with distilled water until the pH value of the filtrate was ca. 7. The filtered solid was dried under vacuum for 24 h at 60 °C, giving the CNT-COOH.

2.4. Functionalization of the CNTs with PLA

The purified CNT-COOH, L-Lactic acid, catalyst stannous chloride and xylene were added to a four-neck flask. After ultrasonicated under the same condition as above for 30 min, the filled flask connected to a water knockout trap was immersed in an oil bath under nitrogen atmosphere with mechanical stirring. The temperature of the oil bath stayed at 120 °C for 2 h and then 140 °C for different times from 5 to 23 h. Each batch of the as-prepared product was dissolved in chloroform and vacuum-filtered through 0.22 μm millipore polytetrafluoroethylene membrane. The collected filter cake was re-dissolved in chloroform and precipitated by pouring the solution with an excess of ethanol. The precipitation was re-dissolved in chloroform and centrifuged, respectively, for more than four times until no PLA in the supernatant fluid could be detected. The precipitation was followed by drying in a vacuum oven at 60 °C to a constant weight to yield the final product, PLA-functionalized CNTs. PLA-functionalized CNTs were prepared with different polymerization times between 5 h, 9 h, 14 h, 18 h, and 23 h, which are represented as CNT-*g*-PLA5h, CNT-*g*-PLA9h, CNT-*g*-PLA14h, CNT-*g*-PLA18h and CNT-*g*-PLA23h, respectively.

2.5. Mixing of CNT-COOH with PLA and removal of PLA

To check if the un-grafted polymer can be efficiently removed from the CNT-*g*-PLA product by washing, filtering and centrifuging, the parallel experiment was done as follows [19]. Different batches of PLA were produced by the same condition as the PLA-functionalized CNTs were produced (just in the absence of the CNTs). Each batch of PLA

(100 mg) was added to the flask filled with CNT-COOH (10 mg) and chloroform (20 mL) pre-ultrasonicated for 30 min. The mixture was stirred for 24 h at room temperature. And then the mixture was just processed as PLA-functionalized CNTs treatment with filtration, redissolvation, centrifugation and drying to give the final solid product polymer absorbed MWNT. TGA measurements showed that the adsorbed polymer content is lower than 3 wt%.

3. Results and discussion

This work attempted to control the functionalization of the CNTs with biocompatible PLA in a facile approach. The purified CNTs oxidized by the mixture of the strong acid without any further treatment or reaction, directly participate in the polycondensation of L-lactic acid. We focused on the characterization of this final product and the feasibility of such technique to produce the equivalent nanohybrid molecule.

Raman spectroscopy is a tool frequently used to characterize the functionalized CNTs. As shown in Fig. 2(a) (325 nm excitation), the D- and G-bands of CNTs at ca. 1404 cm^{-1} and 1582 cm^{-1} which were attributed to the defects and disorder-induced modes and in-plane E$_{2}$g zone-center mode were clearly observed for crude CNTs, the oxidized CNTs and the PLA-functionalized CNTs [4,20–22]. The D- to G-band intensity ratios (I_D/I_G) for the pristine CNTs and CNT-COOH are ca. 0.37 and 0.15, respectively. The D- to G-band peak intensity of the CNT-*g*-PLA were much weaker than that of the CNT-COOH, which means that the characteristic absorption peaks were strongly attenuated due to the combining PLA. Furthermore, Raman signals assigned to the neat PLA, which could be detected in the solution-blended MWNT-COOH/PLA composite, were not observed in the spectrum of the CNT-*g*-PLA, it is possible that the PLA grafted to the MWNT-COOH was completely different from the neat PLA in terms of the Raman characteristics [4].

Fig. 3 shows the FTIR spectra of the CNTs as well as the samples of CNT-*g*-PLA. The FTIR spectrum of the acid-treated CNTs (Fig. 3(A)) showed a relatively very weak C=O stretching at 1740 cm^{-1} corresponding to the carboxylic acid groups incorporated as a result of the acid treatment process. In Fig. 3(B)–(F), all samples showed relatively strong absorption peaks around 1730 cm^{-1} assigned to the C=O stretching, which clearly indicated that the PLA molecules were covalently bound to the MWNTs. The wave numbers shifted upward from 1720 (Fig. 3(B)) to 1740 cm^{-1} (Fig. 3(F)) by about 20 cm^{-1}, which indicated the wave number shift increases with the increase of polymerization time in the experiments. These blue shifts in the samples of CNT-*g*-PLA may be result from the sparsity of the hydrogen bond between the terminal carboxylic acid groups of the grafted PLA. It showed that more the blue shift, less the percent of the terminal carboxylic acid groups in the samples from CNT-*g*-PLA5h to CNT-*g*-PLA23h, which means the higher the molecular weight of the grafted PLA as the polymerization longer.

The PLA-functionalized CNTs' nanoparticles can be easily dispersed in chloroform to form a uniform suspension, which can be stably preserved for several weeks. However, the suspension made from the un-grafted CNTs' nanoparticles is completely precipitated from the solvent within a few minutes without stirring. The good dispersion of PLA-functionalized CNTs in chloroform makes it possible for ^{1}H NMR and UV–vis performance.

The measurement of ^{1}H NMR of CNT-*g*-PLA14h also confirmed that polymer was covalently bound on MWNT. The characteristic chemical shifts a and b ascribed to the CH and the CH$_3$ of the LA repeat units, respectively, were shown in Fig. 4.

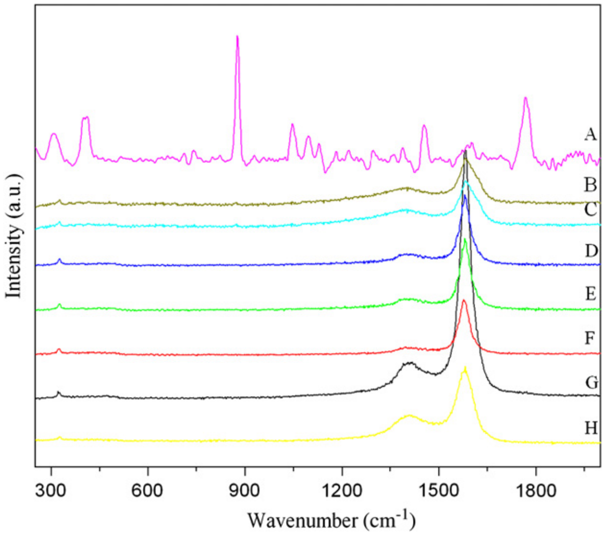

Fig. 2. (a) Raman spectra of PLA (A), CNT-*g*-PLA5h (B), CNT-*g*-PLA9h (C), CNT-*g*-PLA14h (D), CNT-*g*-PLA18h (E), CNT-*g*-PLA23h (F), oxidized CNT (G), the pristine CNT(H). (b) UV–vis spectra of MWNT-COOH (A) and CNT-*g*-PLA14h (B) in chloroform.

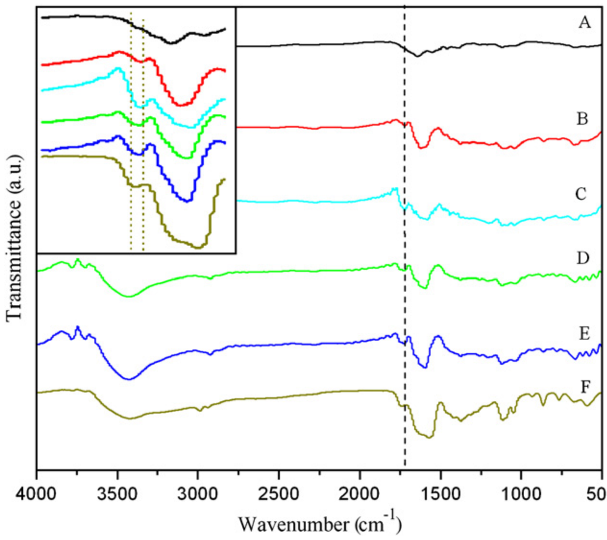

Fig. 3. FTIR spectra of oxidized CNT (A), CNT-*g*-PLA5h (B), CNT-*g*-PLA9h (C), CNT-*g*-PLA14h (D), CNT-*g*-PLA18h (E) and CNT-*g*-PLA23h (F).

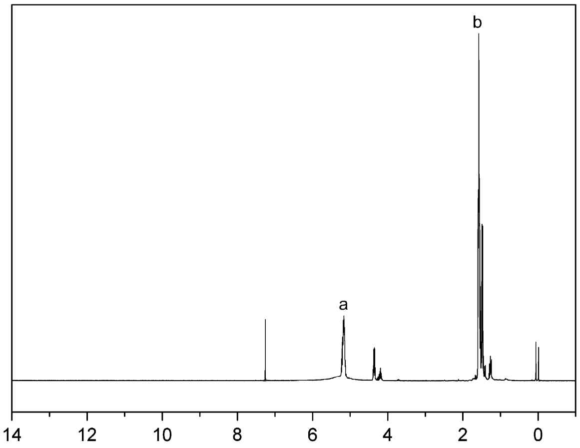

Fig. 4. The ^{1}H NMR spectra of CNT-*g*-PLA14h in $CDCl_3$.

UV–vis absorption spectra of CNT-*g*-PLA14h are shown in Fig. 5. The inset figure showed that the dependence of absorbance on solution concentration apparently obeys Beer's law, which indicated no effects that are associated with aggregation or absorption of any bi- and multi-molecular species [14]. That means the solutions of PLA-functionalized CNTs are homogeneous.

It was noteworthy that the adsorbed polymer can be effectively removed from the products by suitable treatment including washing, filtration and centrifuging as mentioned in Section 2. Furthermore, FTIR measurement for the supernatant fluid, collected by centrifuging of CNT-*g*-PLA, showed that no PLA signals appeared in the spectrum. This further confirmed that the adsorbed polymer quantity was negligible.

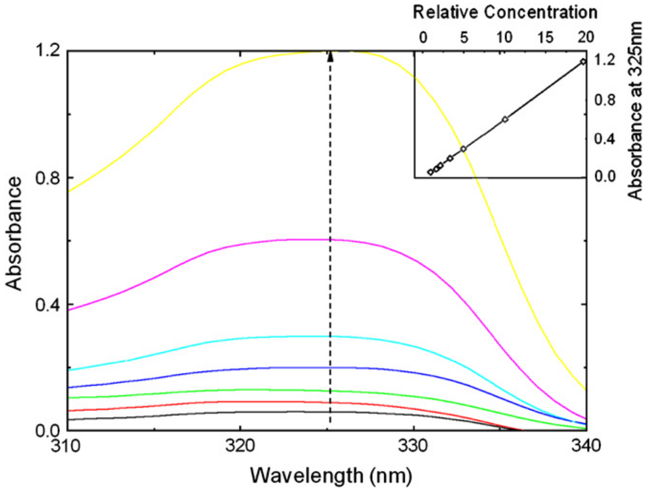

Fig. 5. Absorption spectra of CNT-*g*-PLA14h in chloroform at different concentrations (the direction of the arrow indicating the increasing concentration).

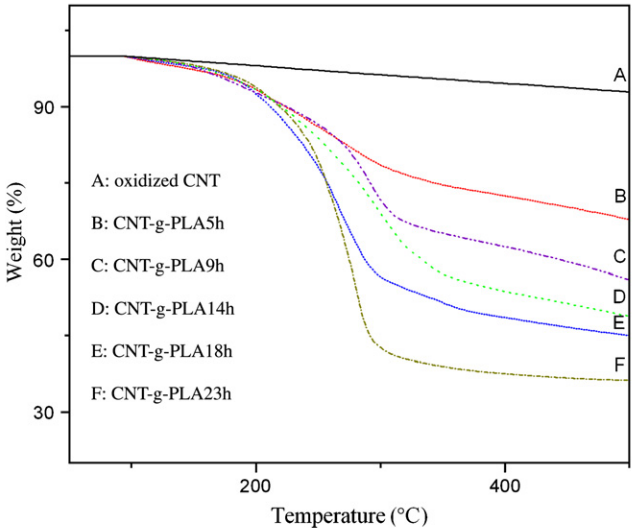

Fig. 6. TGA weight loss curves of the oxidized CNTs and the samples of PLA-g-CNTs.

The grafted polymer content in CNT-*g*-PLA was determined by TGA. As shown in Fig. 6(A), there was a continuous weight lose of the oxidized CNT, and the amount of the weight lose is less than 5% typical for acid-functionalized MWNT [17,23–27]. From the TGA weight loss curves in Fig. 6(B)–(F), the major weight loss was happened in the temperature range from 200 to 350 °C due to the degradation of the PLA grafted to the MWNT. The content of the PLA grafted to the MWNT increased from 21 to 62 wt% as the polymerization time increased from 5 to 23 h.

The increase of the grafted polymer content may be originates from two factors: (1) the increase of the grafting efficiency; (2) the increase of the molecular weight of the grafted polymer.

Generally in the polycondensation of L-lactic acid, the PLA molecular weight depends mainly on the efficient removal of condensation water as the reaction goes on. In the initial grafting reaction, the L-lactic acid monomer reacted with carboxyl acid group in the surface of the CNT, which was attributed to "grafted from" approach, at the same time the formed free dimer or tripolymer couples with the carboxylic supported by the outmost wall of CNT, attributed to "grafted to" approach. As the polymerization went on, the surface of CNT was almost coated with a layer of grafted PLA, which makes it much more difficult for the free oligomer to hit the surface of CNT due to the high steric hindrance than the terminal groups of the grafted PLA. Therefore, during this period the number of graft sites on CNT was almost constant. As regard to the five samples (Fig. 6), the increment of the grafted polymer content came from increasing the molecular weight of the grafted polymer theoretically. As can be seen from the TGA curves, the decomposition temperature of the grafted PLA increased with the grafted polymer content (from Fig. 6), which was the result of the higher molecular weight of the grafted PLA. This result was in agreement with the theoretical analysis and the observation gained from the FTIR spectrum.

It can be concluded that it was feasible for us to control the molecular weight of the grafted PLA or the grafted polymer content by altering the reaction time with the technique to produce the polymer-functionalized CNTs based on in situ polycondensation from the commercially available monomers and CNT-COOH by one step.

Compare with "grafted to" approach, the final product in our experiment may gain the higher grafting density and the lower number-average molecular weight of the grafted polymer, as the grafted content equals.

In order to estimate the grafting sites or the grafting density and the number-average molecular weight of the grafted polymer, 1,4-butylene glycol was added to the reaction system instead of L-lactic acid. The obtained glycol functionalized MWNT was treated with repeated filtration, washing, and vacuum drying. The as-prepared product contained 0.64 mmol glycol per gram of carbon calculated from the TGA data (ca. 7% weight loss). According to the mole percent of PLA terminal groups and the weight loss data in each CNT-*g*-PLA sample, the number-average molecular weight of the grafted polymer was estimated. The results were shown in Table 1.

The fine nanostructures of the as-prepared CNT-*g*-PLA nanohybrid as well as the purified CNT were investigated by HRTEM. In Fig. 7(A) the outmost layer of the purified CNT was not very smooth, which was attributed to the strong acid

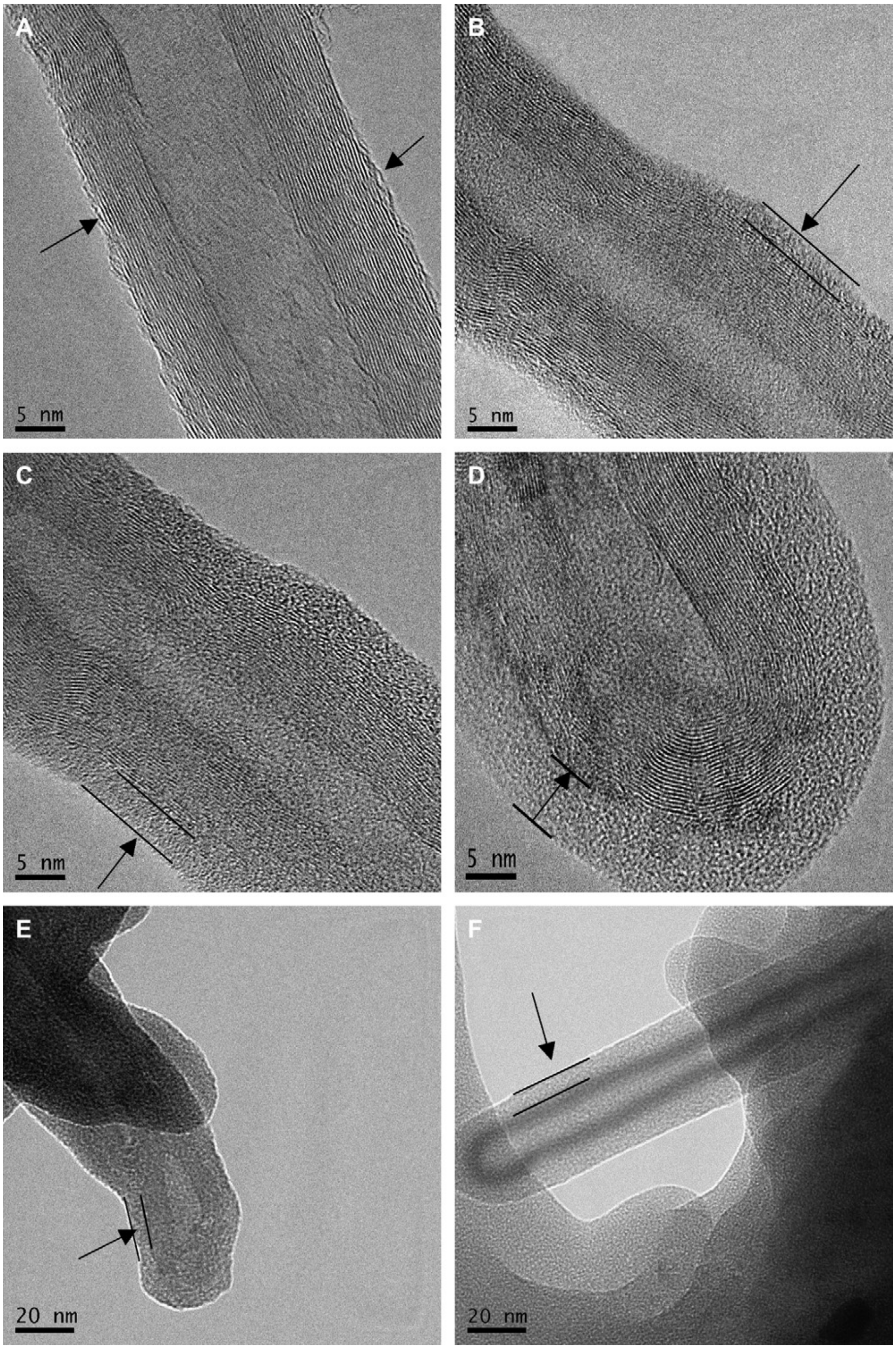

Fig. 7. HRTEM images of oxidized CNT (A), CNT-*g*-PLA5h (B), CNT-*g*-PLA9h (C), CNT-*g*-PLA14h (D), CNT-*g*-PLA18h (E) and CNT-*g*-PLA23h (F).

Table 1
The analysis of the grafted polymer

Sample	Thickness of the grafted polymer (nm)	Weight of the grafted polymer (%)	Number-average molecular weight of the grafted polymer
CNT-*g*-PLA5h	2–3	21	410
CNT-*g*-PLA9h	3–4	32	730
CNT-*g*-PLA14h	6–7	41	1100
CNT-*g*-PLA18h	7–9	48	1400
CNT-*g*-PLA23h	8–12	62	2500

oxidization, and its morphology was sharp different from that of the polymer-functionalized CNTs as shown in Fig. 7(B)–(F). A core/shell structure with CNT at the center can be clearly observed for the PLA-*g*-CNT nanohybrid, which indicated that the CNT core was evenly covered with a layer of PLA chains acted as the soft shell. In the Fig. 7(D) and (E), it can be concluded that the grafting reaction took place not only on the convex sidewalls but also at the tips of the oxidized CNTs, and moreover the soft polymer shells both on the walls and tips of the CNTs were all uniform. The images of the various CNT-*g*-PLA indicated that the thickness of the soft polymer shell of the CNTs increases from ca. 2–3 nm to 8–12 nm with the polymerization time from 5 to 23 h. The polymer shell became thicker as polycondensation longer. The results were in agreement with those obtained from FTIR and TGA characterizations as shown in the table. The relatively low resolution TEM image of CNT-*g*-PLA14h as shown in Fig. 8 indicated the CNTs in the polymer-functionalized CNTs were exfoliated well, which is in accordance with Fig. 8.

4. Conclusion

The oxidized purified CNTs, without any further modification, were directly covalently functionalized with biocompatible PLA by one step based on in situ polycondensation of the commercially available L-lactic acid monomer. The TEM images of core/shell nanostructures clearly indicated that the coating soft shell of the grafted polymer was uniform both on the convex sidewall surface and at the tips of the CNT; moreover, the molecular weight and content of the grafted polymer can be well controlled by altering polycondensation time. As one of the most important biocompatible and biodegradable materials, PLA incorporating with CNT will grant improvement of solubility and compatibility and may promise multipurpose in biomedical systems and bionanomaterials. The route to the final product CNT–PLA should be favoured in industrialization for less step and cheaper commercially available raw material.

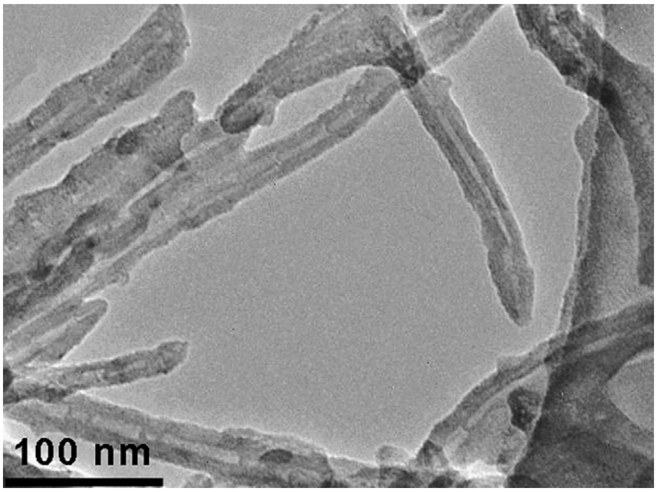

Fig. 8. The relative low magnification TEM images of CNT-*g*-PLA14h.

Acknowledgment

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