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Synthesis and Characterization of Ester Bond-Containing Polyethyleneimine Functionalized Carbon Nanotubes

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Abstract. Carbon nanotubes (CNTs) are emerging transporters for delivery of gene and drug. The degradable polycation functionalized CNTs (CNTs-HDDAPEI) were fabricated by grafting ester bond-containing polyethyleneimine (HDDAPEI). Fourier transform infrared spectroscopy, Raman spectrum, transmission electron microscopy and thermogravimetric analysis were used to characterize the degradable polyethyleneimine decorated CNTs. Compared with pristine CNTs, the CNTs-HDDAPEI displayed better dispersability and stability in water.

1. Introduction

Carbon nanotubes (CNTs) are one-dimensional nanomaterials and have received much attention for applications in various fields due to their unique mechanical, electrical and chemical properties [1,2]. They are nanometer scale diameter, high aspect ratio and mechanical strength, which make them an ideal reinforcing agent for high performance polymer composites [3]. Their physical and chemical stability as well as high surface area makes them can be functionalized to achieve improved biological properties and functions [4, 5]. Therefore, CNTs have been widely used in biotechnology and medicine in recent years [6, 7].

For biological applications, pristine CNTs usually need to be functionalized to achieve improved dispersion and biological properties in an aqueous environment. Recently, CNTs were studied to carry nucleic acids and penetrate mammalian cell membranes into the cytoplasm [8]. However, the hydrophobic character and lack of functional groups limit their function to condense DNA. To meet the increasing demands for better performances, the properties of CNTs should be further tailored and improved by modification and functionalization [9]. The most popular way is incorporation of cationic polymer such as polyethyleneimine (PEI) [10], polyamidoamine (PAMAM) [11] and chitosan [12]. The polycation functionalized CNTs have improved dispersion and are able to securely immobilize negatively charged DNA onto the surface of CNTs. The transfection efficiencies of functionalized CNTs are similar to or even several times higher than that of cationic polymer alone. The PEI functionalized CNTs were reported as gene vector with high transfection efficiency. However, due to the undegradable and high positive charge of PEI, they always displayed high cytotoxicity. Some biodegradable PEI derivatives with low cytotoxicity were synthesized to reduce the cytotoxicity.

In this study, the ester bond linked PEI (HDDAPEI) was synthesized by Michael addition between 1, 6-hexanediol diacrylate and low molecular weight branched 1.8 k Da PEI. Then carboxyl CNTs were functionalized through grafting of HDDAPEI to obtain CNTs-HDDAPEI. The product was characterized using Fourier transform infrared spectroscopy, Raman spectrum, transmission electron microscopy. In addition, the thermal stability and water dispersibility were examined.



2. Materials and Methods

2.1. Materials

Carboxyl functionalized multi-wall carbon nanotubes (CNTs-COOH) with purity of 98 (wt%), containing 1.23 wt% carboxyl groups, having outer diameter of 20-30 nm, and length of 0.5-2 μm were obtained from Chinese Academy of Sciences Chengdu Organic Chemicals Co., LTD. BPEI (MW 1.8k, 25k) were purchased from Sigma-Aldrich. 1,6-hexanediol diacrylate, 1-Ethyl-3-(3-dimethylaminopropyl) carbodiimide hydrochloride (EDC), N-Hydroxysuccinimide (NHS), were purchased from Aladdin Co. (Shanghai, China). Acrylic acid, cyclohexane, thionyl chloride, triethylamine, dimethyl sulfoxide (DMSO), sodium bicarbonate and hydroquinone were purchased from Shanghai Chemical Reagent Company and used as received. Dialysis membrane (MWCO 3.5 kDa) was purchased from Biosharp.

2.2. Synthesis of 1,6-Hexanediol Diacrylate Linked PEI (HDDAPEI)

The 1, 6-hexanediol diacrylate PEI were synthesized according to the modification of literature [13]. 1.8 g of branched PEI 1.8 k Da was dissolved in a mixture solution of 6 mL distilled water and 6 mL DMSO. Then the solution was added to the three-necked flask equipped with a condenser. To obtain HDDAPEI, 0.27 g 1,6-hexanediol diacrylate (HDDA) was dissolved in 10 mL DMSO and added to the PEI solution by dropping slowly. The reaction mixture was stirred for 48 h at 45°C under nitrogen atmosphere. After the reaction, the product was dialyzed against distilled water (MWCO: 3500) for 48 h to remove the unreacted 1.8 k Da PEI. Lastly, the solution was lyophilized for 48 h.

2.3. Synthesis of CNTs-HDDAPEI

The HDDAPEI solution was prepared by dissolving certain HDDAPEI in 2 mL distilled water. CNTs-COOH (200 mg) was suspended in 20 mL distilled water and ultrasonic dispersed for 30 min at 50 °C. Then EDC (105 mg) and NHS (82.4 mg) were added to activate the carboxyl groups. Subsequently, the HDDAPEI solution was added and stirred for 24 h at room temperature. The weights of HDDAPEI used for functionalization process were 100 mg, 150 mg, and 200 mg. After the reaction, the product was centrifuged at $20,000 \times g$ for 15 min, then redispersed in distilled water and dialyzed (MWCO:12000) for 48 h to remove the unreacted HDDAPEI and activating agent. Lastly, the solution was lyophilized for 48 h to obtain CNTs-HDDAPEI in a black powdered form.

2.4. Characterization of CNTs-HDDAPEI

The Fourier transform infrared (FT-IR) spectra of CNTs-HDDAPEI was recorded on Nicolet Impact-420 Fourier transform infrared spectrometer in the range of 400 - 4000 cm^{-1} . Raman spectroscopy was conducted with a Kaiser optical system and a helium-neon laser of 532 nm wavelength. The morphology of CNTs-HDDAPEI was conducted by JEM-2100F field emission electron microscopy (TEM, JEOL, and Japan). Thermogravimetric analyzer (TGA) measurement of CNTs-HDDAPEI was performed by a TGA STA-409PC thermogravimetric analyzer under N_2 in the temperature range 30-600 °C with an increasing rate of 5 °C min^{-1} . The surface charge of CNTs-HDDAPEI was measured by a Nano-ZS ZEN3600 (Malvern Instruments).

2.5. Dispersibility Test

Each of 4 mg CNTs, CNTs-COOH and three kinds of CNTs-HDDAPEI was ultrasonic dispersed in 8 mL water sufficiently. The dispersions were recorded after 48 h to evaluate the water dispersibility and stability of CNTs, CNTs-COOH and CNTs-HDDAPEI.

3. Results and Discussion

3.1. The Preparation of CNTs-HDDAPEI

In this study, the ester bond-containing PEI (HDDAPEI) was synthesized by Michael addition between 1, 6-hexanediol diacrylate and low molecular weight branched 1.8 k Da PEI. The number

average molecular weight (M_n) of HDDAPEI is 8.15 kDa and polydispersity (M_w/M_n) is 1.36. Three CNTs-HDDAPEI were prepared by changing the weight ratio of carboxyl CNTs to HDDAPEI to study the influence of HDDAPEI content on the dispersion property of CNTs. The feed compositions of CNTs-HDDAPEI are listed in Table 1.

Table 1. Feed compositions of CNTs-HDDAPEI and grafting weight ratio of HDDAPEI to CNTs-COOH.

Sample ID	CNTs-COOH [mg]	HDDAPEI [mg]	Grafting weight ratio ^a	Zeta potential [mV]
CNTs-HDDAPEI ₁	200	100	25.76%	31.6
CNTs-HDDAPEI ₂	200	150	30.72%	36.7
CNTs-HDDAPEI ₃	200	200	36.17%	39.0

^a The grafting weight ratios of HDDAPEI to CNTs were calculated by thermogravimetric analysis.

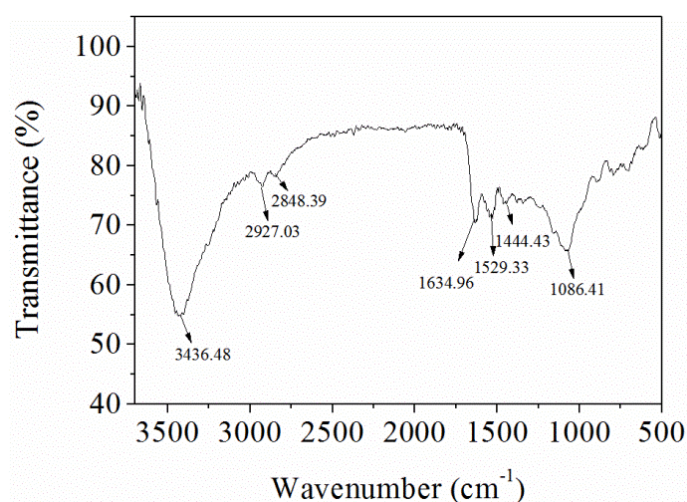


Figure 1. FTIR spectra of CNTs-HDDAPEI.

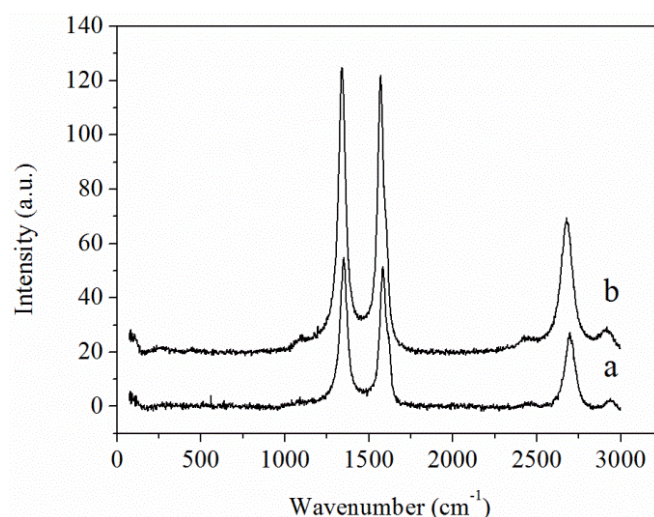


Figure 2. Raman spectra of carboxyl CNTs (a) and CNTs-HDDAPEI (b)

FTIR spectroscopy was employed to characterize the formation of CNTs-HDDAPEI. The typical FTIR spectrum of CNTs-HDDAPEI is shown in Figure 1. The broad and strong peak at 3436 cm^{-1} is attributed to -NH stretching vibrations which indicates the amine groups on the surfaced of CNTs-

HDDAPEI [14]. The characteristic bands of $-\text{CO}-\text{NH}-$ stretching are detected at 1634, 1529 and 1444 cm^{-1} , indicating the formation of CNTs-HDDAPEI [15]. The peak at 1634 cm^{-1} is associated with the stretching of $-\text{C}=\text{O}$. The peaks at 1529 cm^{-1} and 1444 cm^{-1} refer to $-\text{NH}_2$ and $-\text{C}-\text{N}$ stretching vibration, respectively. In addition, the peaks assigned to the H-C stretching vibrations at 2848 cm^{-1} and 2927 cm^{-1} are also detected. The peak at 1086 cm^{-1} could be the stretching vibration of C-O-C [16].

Raman spectrum was used to investigate the structure of CNTs-HDDAPEI. Three raman bands at 1580 cm^{-1} (G band), 1358 cm^{-1} (D band) and 2711 cm^{-1} (2D band) are observed for carboxylated CNTs and CNTs-HDDAPEI (Figure 2). The band at 1580 cm^{-1} is a first-order raman mode attributed to vibrations of sp^2 carbon atoms. The band at 1358 cm^{-1} is D band of a second-order scattering process, which related to the effect of defects or disordered structure in tubes. As we know that the ratio of D-band to G-band intensity (I_D/I_G) could be used to characterize the level of defect or disordered structure in CNTs. A higher value of I_D/I_G indicates the CNTs with a higher level of defect structure [17]. As presented in Table 2, there is no noticeable change of I_D/I_G values between the carboxyl CNTs and CNTs-HDDAPEI. This result shows that the functionalized process does not change the structure of carboxyl CNTs.

Table 2. I_D , I_G and I_D/I_G ratio of carboxyl CNTs and CNTs-HDDAPEI in Raman spectrum.

	I_D	I_G	I_D/I_G
CNTs-COOH	104.46	102.19	1.02
CNTs-HDDAPEI	54.53	50.43	1.08

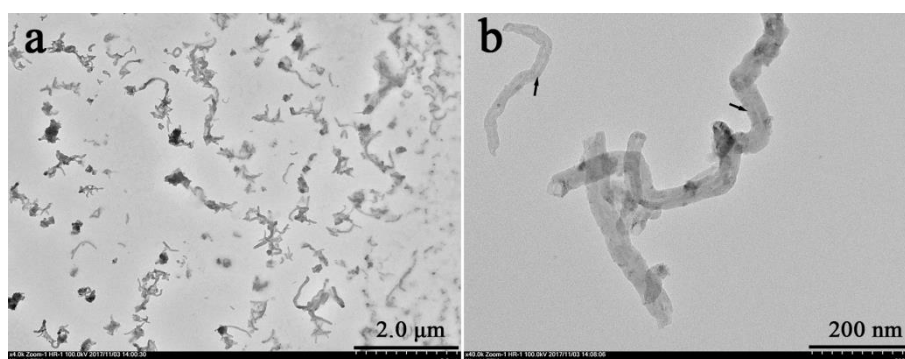


Figure 3. TEM images of CNTs-HDDAPEI.

The morphology and distribution of CNTs-HDDAPEI were explored by TEM. As shown in Figure 3a, the CNTs-HDDAPEI were dispersed into particles with the size of several hundreds nanometers. Figure 3b illustrates the morphology of single CNTs-HDDAPEI, which are the nanotubes with coating. The coating is attributed to the presence of HDDAPEI on the surface of CNTs. The length and dimensions are consistent with those given by the supplier.

3.2. Dispersion Study

The dispersion states of carbon nanotubes, carboxyl CNTs, and three HDDAPEI functionalized CNTs were observed after sonication in water and maintained for 48 h. All the samples could be dispersed in water after sonication. However, as shown in Figure 4, pure carbon nanotubes were settled after 48 h. It is well known that CNTs usually agglomerate due to Van der Waals interactions and are difficult to disperse in water. Therefore, in order to improve dispersibility of CNTs, some water-soluble polymers were granted to CNTs [18, 19]. In this study, CNTs were decorated by HDDAPEI to increase the water dispersibility. As shown in the Figure 4b-e, the carboxylated CNTs and three HDDAPEI grafted CNTs did not settle and maintained homogeneous solution after 48 h. This enhanced dispersibility and stabilization in water is attributed to the hydrophilic groups of carboxyl on the carboxyl CNTs and amino on the CNTs-HDDAPEI.

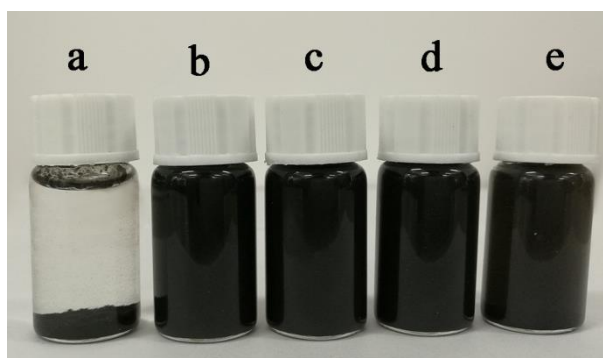


Figure 4. The dispersibility of CNTs(a), carboxyl CNTs(b), CNTs-HDDAPEI₁ (c), CNTs-HDDAPEI₂ (d) and CNTs-HDDAPEI₃ (e) in water after ultrasounding and incubated for 48 h.

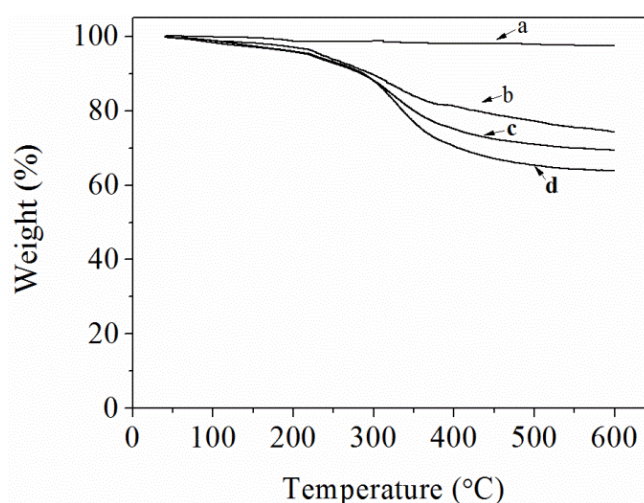


Figure 5. TGA profiles of carboxyl CNTs (a), CNTs-HDDAPEI₁ (b), CNTs-HDDAPEI₂(c) and CNTs-HDDAPEI₃ (d)

3.3. Thermogravimetric Analysis

TGA was used to assay the HDDAPEI content in the CNTs-HDDAPEI. As shown in Figure 5, all the samples show small mass loss below 200 °C; this is due to the evaporation of moisture. Above 200 °C, carboxyl CNTs do not occur significant weight loss up to 600 °C because of their good thermal stability. However, the HDDAPEI grafted CNTs samples show a sharp weight decrease from 200 °C to 400 °C, which is mainly due to the thermal decomposition of HDDAPEI. There is no significant weight loss around 600 °C, indicating the functional groups of HDDAPEI are completely decomposed and the final residues are carbon nanotubes. The weight residues at 600 °C on TGA plots show the average weight residue of 74.24%, 69.38% and 63.83% for CNTs-HDDAPEI₁, CNTs-HDDAPEI₂ and CNTs-HDDAPEI₃, respectively. Therefore, the grafting weight ratios of CNT-HDDAPEI were calculated and listed in Table 1. It has to be pointed out, compared with the feed ratios during synthesis, the grafted ratios are small. This is maybe because of the small amount carboxyl groups on the surface of CNTs (1.23 wt%). With the increasing of feed ratio of HDDAPEI to CNTs-COOH, the HDDAPEI is excess. The zeta potential of CNTs-HDDAPEI is also listed in Table 1. The positive charge of surface demonstrated HDDAPEI was grafted to carbon nanotubes.

4. Conclusions

A novel ester bond-containing PEI decorated CNTs was prepared. The FTIR, Raman spectrum, TEM and TGA studies demonstrated that HDDAPEI was functionalized to CNTs successfully. The CNTs-HDDAPEI exhibited good dispersability and stability in water. These results indicated that CNTs-HDDAPEI would have promising potential applications in nanobiotechnology and nanomedicine.

Acknowledgments

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