The preparation of lysine modified multi-walled carbon nanotubes and the study of its dispersion properties

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Abstract. The poor dispersion in aqueous solution limited the application of carbon nanotubes (CNTs) in biological field. Here we used DCC/DMAP as Catalysis to prepare lysine modified multi-walled carbon nanotubes (MWNTs). FT-IR and TGA demonstrated that lysine have been successfully grafted to MWNTs, EA showed that lysine graft rate up to 23.4%. The dispersion of lysine modified MWNTs was investigated by direct visual inspection and microscope observation, the result showed that lysine modified MWNTs can be dispersed in aqueous solution and keep stable for long time.

1. Introduction

CNTs had drawn wide spread attention as soon as it was discovered by Iijima in 1991 [1]. Numerous investigation about CNTs have been made. Researchers focus on the structure and properties of CNTs at the initial stage. The unique structure of CNTs endue excellent properties such as high mechanical strength, high electrical conductivity and chemical & thermal stability. CNTs have been widely used in hydrogen storage materials [2], field emission devices [3], supercapacitors [4], bio-medical materials [5] and other fields.

However, the poor dispersion in solvents and aqueous solution limited the application of CNTs in many fields. CNTs are easily aggregated in solvents for the strong π-π stacking interactions between tubes, covalent modifications and noncovalent modifications were taken to solve these problems [6]. Although the noncovalent modification could not disrupted the structure of CNTs, the noncovalent interaction between wrapping molecules and the CNTs is not as strong as the covalent bond caused by covalent modification. Covalent modified CNTs could be dispersed in solvent more stability than noncovalent method [7]. The water-solubility and biocompatibility of CNTs improved a lot after attached by amino acid and peptide, which lead to the high potential application of CNTs in biomaterials [8].

In this paper, we grafted lysine to the surface of MWNTs by chemical function. Dicyclohexylcarbodiimide (DCC)/ 4-dimethylaminopyridine (DMAP) were used as coupling agents to

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efficiently realize this reaction. Lysine modified MWNTs show excellent dispersion in water, in addition, the presence of amino improve reaction activity of CNTs. CNTs can be reacted with different functional groups to realized the applications in many fields.

2. Materials and method

2.1. Materials

The MWNTs (lengths 1.5 μm, diameters<10nm, purity 90%) were purchased from Shenzhen Nanotech Port Co., Ltd and used as received. Lysine, DCC, DMAP, N, N-dimethylformamide (DMF), Potassium permanganate ($KMnO_4$) were purchased from Sinopharm ChemicalReagent Co., Ltd. (China) and used as received. Sulfuric acid and hydrochloric acid were purchased from shanghai darui fine-chemical Co., Ltd. (China).

2.2. Characterization

Fourier transform infrared spectral (FT-IR) in the range of 400–4000 cm^{-1} were obtained by a Nicolet 8700 Fourier transform infrared spectrometer (Thermo Electron, American) with KBr pellets of MWNTs, and under the averaging of 32 scans at a resolution of 4 cm^{-1}. Thermogravimetric analyses (TGA) were performed by use of a TG 209 F1 Iris thermogravimetric analyzer (Netzsch-GeraetebauGmbH, Germany) under air flow. In each experiment, the MWNTs samples (5 mg) were heated from 30℃ to 900℃ at a rate of 20 K/min^{-1}. Elemental analyzes (EA) were got by a Vario EL III Elemental analyzer (Germany). Here we used as carrier gas, and the accuracy of result is (C, H, N) ≤ 0.1%. The dispersion of MWNTs were used a TK-C921EC metallurgical microscope (Japan, JVC) to take image at 40×10 shot.

2.3. Preparation of lysine modified MWNTs

MWNTs have been purified and carboxylation before we used [9]. 50 mg carboxylated MWNTs were added to a three-necked flask, 500 mg DCC and 10 mg DMAP followed, 40 ml DMF were used as solvent. The mixture were treated under a refluxed condenser for 5 h at 120℃. After filtration we got the Intermediates, DMF were used to wash it. Then we added 350 mg lysine and 40 ml DMF mixed with the Intermediates, treated under a refluxed condenser for 24 h at 120℃. Finally, we used ethanol and distilled H_2O rinsed the product and filtration for 3 times, and this lysine modified MWNTs were dried in a vacuum oven at 60℃ over night.

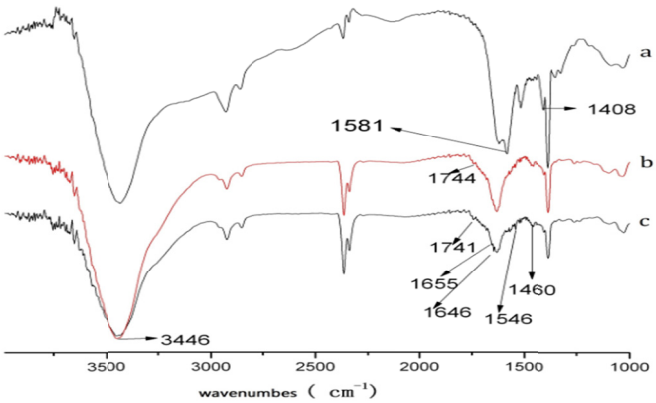


Figure 1. FT-IR spectra of (a) lysine, (b) carboxylated MWNTs and (c) lysine modified MWNTs.

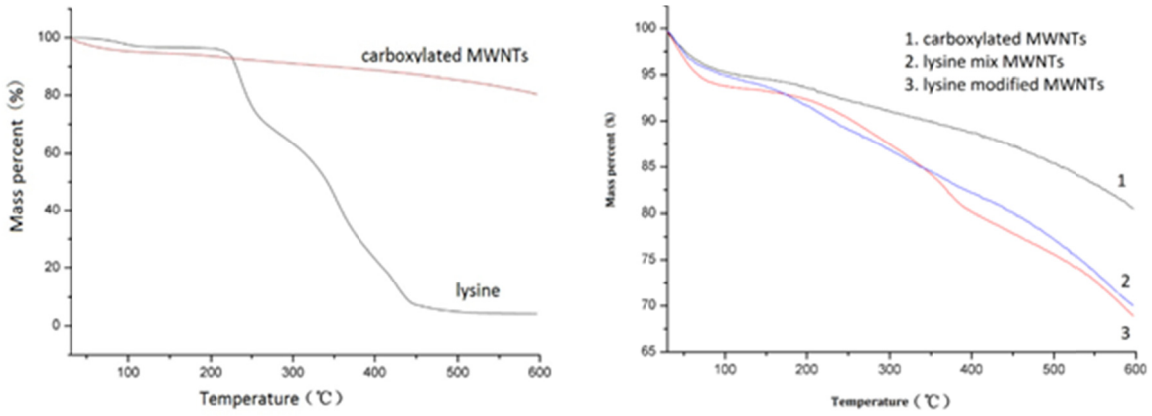
3. Results and discussion

3.1. FT-IR spectra of lysine, carboxylated MWNTs and lysine modified MWNTs

The FT-IR spectra (figure 1) were used to characterize the functional groups of MWNTs before and after modification. There are double stretching vibration of backbone C=C at 1655 cm^{-1} and 1460 cm^{-1} both in the spectrum of carboxylated MWNTs and lysine modified MWNTs, and also a stretching vibration for C=O at 1740 cm^{-1}. The weak peaks at 1646 cm^{-1} and 1546 cm^{-1} are the vibration of amide I and amide II in the spectrum of lysine modified MWNTs, but there is no same peak appeared in the spectrum of carboxylated MWNTs. It means that lysine has been successfully grafted to the surface of MWNTs.

3.2. TGA of carboxylated MWNTs and lysine modified MWNTs

TGA is a thermal analysis that can be used to distinguish the component of products for the different thermal stability. Figure 2 shows the TGA of different products, we can see that lysine have a significant mass loss at the temperature from 200℃ to 500℃ (figure 2a), and this temperature range is the decomposition temperature of lysine. Lysine mixed with MWNTs or grafted to MWNTs both have a mass loss at the temperature from 200℃ to 500℃ (figure 2b). It can be used to prove that lysine has been grafted to MWNTs, and the different of mass loss due to the method lysine attached to MWNTs.



a b

Figure 2. TGA curves of lysine, carboxylated MWNTs, lysine mixed MWNTs, lysine modified WNTs.

3.3. EA of carboxylated MWNTs and lysine modified MWNTs

EA was used to analyze the element component of different kind MWNTs. There is no N in carboxylated MWNTs, but 4.5% N in Lysine modified MWCNTs (table 1), content of lysine which grafted to MWNTs was calculated to be 23.4% by calculating.

Table 1. C, H, N content of carboxylated MWNTs and lysine modified MWNTs.

	C (%)	H (%)	N (%)	Lysine (%)
carboxylated MWNTs	83.150	1.196	0.000	0.000
Lysine modified MWCNTs	75.520	3.077	4.515	23.381

3.4. Dispersion of Primitive MWNTs, carboxylated MWNTs and lysine modified MWNTs

Preparation solution of MWNTs, carboxylated MWNTs and lysine modified MWNTs at concentration of 0.1 mg/ml, ultrasonic 30 min, and settlement for 96 h.

Primitive MWNTs have fastest sedimentation rate, and lysine modified MWNTs keep good dispersion from the photo taken by digital camera (figure 3). All this due to that lysine have been grafted to MWNTs, it is a kind of water-soluble amino acid and contribute to improve the dispersion of MWNTs in water solution.

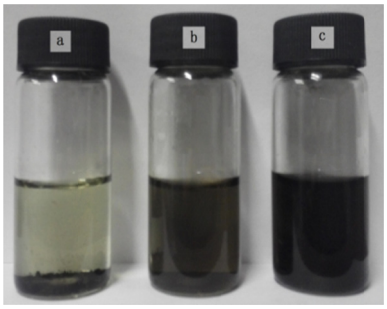


Figure 3. Digital photograph of different WWNTs solution taken by camera after settlement 96 h. MWNTs, (b) carboxylated MWNTs and (c) lysine modified MWNTs.

Image of microscope demonstrate the dispersion of MWNTs in the angle of microscopic (figure 4). After settlement 96 h, solutions of MWNTs have different degrees of aggregation and the size of aggregate reflect it. The image of different MWNTs solution taken by microscope at the same magnification (40×10) show that lysine modified MWNTs solution has the smallest size, followed by carboxylated MWNTs solution, then solution of MWNTs. The images taken by microscope in keeping with the photographs taken by camera, all this show that dispersion of MWNTs in aqueous solution improved after modified by lysine.

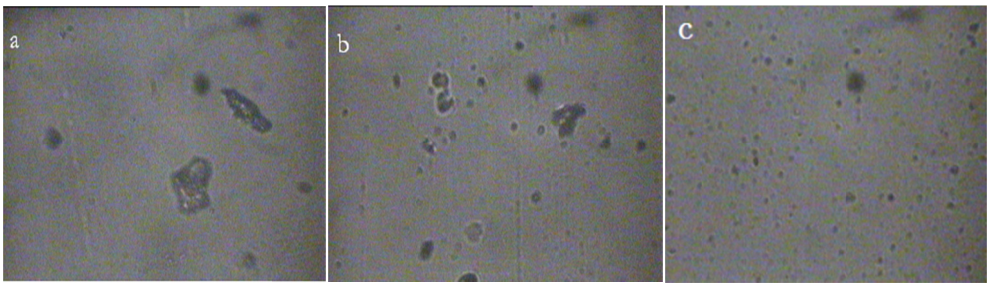


Figure 4. Image of different solution taken by microscope (40×10) after settlement 96 h. MWNTs, (b) carboxylated MWNTs and (c) lysine modified MWNTs.

4. Conclusions

DCC/DMAP Catalysis is an effective coupling agents to prepare lysine modified MWNTs, FT-IR and TGA demonstrated that lysine have been grafted to MWNTs, and the EA result Showed that lysine graft rate reach up to 23.4%. After modification MWNTs show excellent dispersion in water solution which made MWNTs have promising prospects in biological area.

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