

# Functionalization and dispersion of multiwalled carbon nanotubes modified with poly-L-lysine



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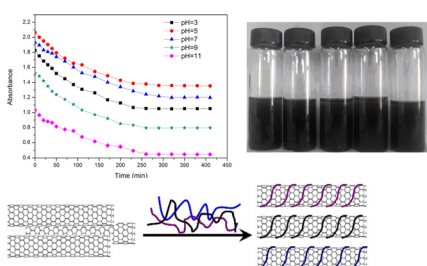
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## HIGHLIGHTS

- The multiwalled carbon nanotubes were functionalized with PLL.
- MWCNTs–PLL nanocomposite was characterized with FT-IR, TGA and UV–Vis.
- The dispersibilities of MWCNTs–PLL nanocomposite in water were evaluated.
- MWCNTs–PLL nanocomposite in water was pH-responsive.
- The method was a mild approach for MWCNTs modified with PLL.

## GRAPHICAL ABSTRACT



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## ABSTRACT

Poly-L-lysine (PLL) was synthesized using lysine as raw material by *N*-carboxyanhydride polymerization and characterized by Fourier transform infrared spectroscopy and <sup>1</sup>H NMR. Multiwalled carbon nanotubes (MWCNTs) were non-covalently functionalized using PLL in order to prepare MWCNTs–PLL composite. MWCNTs–PLL was characterized using Fourier transform infrared spectroscopy, thermogravimetric analysis and UV–Vis absorption spectroscopy. The dispersion of MWCNTs–PLL composite was investigated by UV–Vis absorption spectroscopy, dynamic light scattering analysis and digital photograph. The results showed that the dispersion of MWCNTs–PLL composite was obviously better than that of MWCNTs–SDS composite in water while it was also approximate with that of MWCNTs–SDBS. In addition, MWCNTs–PLL was pH-responsive in water so that it could be used as bio-nanomaterial in future.

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## 1. Introduction

Multiwalled carbon nanotubes (MWCNTs) which were reported by Iijima in 1991 [1], are a special hollow seamless cylinders with nanometer scale diameters and composed of multi-layer graphite sheets according to a certain spiral horn. The novel nanomaterial is an allotropic form of carbon which includes fullerenes, graphite and diamond. Due to their high mechanical strength, ultra-light weight,

excellent electronic properties, predominant chemical and thermal stability, carbon nanotubes (CNTs) have been attracting more and more research interests. CNTs are regarded as potential candidates in wide areas involving composite materials [2,3], energy storage media [4,5], field emitters [6], catalysts and catalyst supports [7], tips for scanning probe microscopy [8], bio-nanomaterials [9] and nanoelectronic devices [10] and so on. In the last few years, CNTs used as bio-nanomaterials both at molecular and cellular levels have attracted extensive attention [11–14]. However, the poor dispersion of CNTs in aqueous and organic solvents, due to strong van der Waals forces and  $\pi$ – $\pi$  stacking interactions between tube and tube, has prevented extensive application of CNTs in biological

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fields [15–17]. Therefore, strategic approaches toward the dispersion of CNTs are essential for their applications.

To overcome this problem, much effort has been made to develop approaches for modification of CNTs and reproducible dispersions of individual CNTs. There are two distinct approaches for dispersing CNTs: the mechanical methods and the methods that are designed to alter the surface energy of the solids, either physically (non-covalent functionalization) or chemically (covalent functionalization) [18]. The mechanical methods involve ultrasonication, grinding and rubbing, high impact mixing, high shear mixing and so on. The mechanical methods not only separate nanotubes from each other, but also break up the nanotubes and decrease their aspect ratio [19]. Both non-covalent and covalent functionalizations of CNTs are based on adsorption, wrapping, hydrophobic interaction or covalent bonding of different molecules and chemistries that make CNTs more hydrophilic [18,20–24]. Covalent functionalizations are used to improve their dispersion in the target medium (solvent or polymer), which enhance wetting or adhesion characteristics and make the aggregation of MWCNTs reduced. However, much aggressive covalent functionalizations, such as the use of concentrated sulfuric-nitric mixtures, introduce a significant number of defects and amorphous carbon that is undesirable. Moreover, a reduction in size makes short nanotubes unsuitable for many applications which are based on the nanotube length [25]. These structural defects introduced result in inferior properties for the tubes [24,26]. Compared with covalent functionalizations, non-covalent functionalizations are particularly attractive because they make polymers or surfactants adsorbed on CNTs without disturbing the  $\pi$  system of the graphene sheets [18]. CNTs which are modified with surfactants or polymers by non-covalent method can disperse steadily in both aqueous or organic solutions so that the high weight fraction of individual nanotubes can be obtained [11–13,27]. The studies of CNTs interfacing with biology were mainly focused on the interactions of CNTs and biological molecules, such as DNA [28], proteins [29] and peptides [30]. Poly-L-lysine (PLL) is a natural peptide that contains a high density of amine groups. When PLL was used as the modifier of CNTs, it has several advantages, such as plentiful amino groups, a flexible molecular backbone, good biocompatibility, enzymatic degradation and good solubility in water. At present, CNTs were found to be biocompatible in many articles so that they can be used as biomaterial [12,31]. CNTs play an important role as connectors to assemble these PLL chains when CNTs are modified with PLL. After some free amino groups of PLL cross-linked with the carboxyl groups of CNTs, the residual free amino groups of PLL could act as a linker between CNTs and bioactive molecules or drug. These modified CNTs are useful in cell adhesion [32], the multilayer assembly of polyelectrolytes [33], the electric potential of surfaces [34], and drug and gene delivery systems [35].

In this paper, PLL was synthesized using lysine as raw material by *N*-carboxyanhydride (NCA) polymerization, and MWCNTs-PLL composites were prepared by non-covalent functionalization using MWCNTs and the resulting PLL. A simple, facile, green and general approach to disperse MWCNTs functionalized with PLL in aqueous solutions was reported. This dispersion approach presented here is expected to be a useful strategy for the preparation of MWCNTs-polymer nanocomposites. These nanocomposites have a great potential in the biological fields.

## 2. Materials and method

### 2.1. Materials

The MWCNTs (Nanocyl™ NC7000, average diameters 9.5 nm, lengths 1.5  $\mu\text{m}$ , carbon purity 90% by TGA) were purchased from

Sambreville Nanocyl S.A. (Belgium) and used as received. Molecular sieve (4 Å), L-lysine, copper sulphate penta hydrate, sodium hydrogen carbonate, sodium hydroxide, ethyl acetate, ether, acetone, sodium carbonate, sodium sulfide nonahydrate, hydrogen chloride, tetrahydrofuran (THF), cyclohexane, *N,N*-dimethylformamide (DMF), sodium dodecyl sulphate (SDS) and sodium dodecyl benzenesulfonate (SDBS) were purchased from Sinopharm Chemical Reagent Co., Ltd. (China). Benzoyloxycarbonyl chloride (CBZ-Cl), triphosgene, trifluoroacetic acid (TFA) and hydrobromic acid in acetic acid (wt%, 33–35%) were purchased from Shanghai Darui Fine-chemical Co., Ltd. (China). All solvents were used as received except THF and DMF which were dried on molecular sieve before use. All reagents were used as received.

### 2.2. Characterization

Fourier transform infrared spectroscopy (FT-IR) measurements were performed using a Nicolet 8700 Fourier transform infrared spectrometer (Thermo Electron, American) with KBr pellets of MWCNTs. Spectra in the range of 400–4000  $\text{cm}^{-1}$  were obtained by the averaging of 32 scans at a resolution of 4  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR spectra were recorded on a Bruker Avance DPX 400 (400 MHz) spectrometer (Bruker Biospin AG, Switzerland). All chemical shifts were reported in parts per million (ppm) downfield of tetramethylsilane. Mass spectra (ESI-MS) were recorded on a 310-MS TQ Liquid chromatography-mass spectrometer (Varian Inc., American). Thermogravimetric analyses (TGA) were performed using a TG 209 F1 Iris thermogravimetric analyzer (Netzsch-Geraetebau GmbH, Germany) under air flow. In each experiment, the MWCNTs samples ( $\sim 5$  mg) were heated from 30 °C to 900 °C at a rate of 20  $\text{K}/\text{min}^{-1}$ . UV-Vis absorption spectra were recorded with a TU-1901 spectrometer (Purkinje General Instrument Co., Ltd., China) between 190 nm and 450 nm at 1-nm intervals. Samples were diluted regularly with distilled water (7 equiv) in order that certain MWCNTs contents were suitable for UV-Vis measurements. The blank used was distilled water. The solutions of four MWCNTs samples were subjected to dynamic light scattering (DLS) spectroscopy (Nano ZS Nano 85, Malvern Instruments Ltd, UK) at a fixed scattering angle of 90 at 25 °C. Particle size distribution and zeta potential of the MWCNTs solutions were measured. The elemental analyses (EA) were performed using Leeman Prodigy inductively coupled plasma atomic emission instrument (Prodigy, Teledyne Leeman Labs, American).

### 2.3. Synthesis and characterization of PLL

According to the route shown in Scheme 1, PLL was prepared using lysine as raw material by chelation of metal ion, protection, demetalization, cyclization, polymerization and deprotection. The synthesis and characterization of all compounds were summarized in supplementary materials.

### 2.4. Preparation of colloid solutions of MWCNTs

The as-received MWCNTs (0.5 g) and 6 mol/L HCl solution (200 g) were added to a round-bottom flask. The mixture was subjected to sonicate in a powerful bath-type ultrasonicator (KUDOS, SK1200H, 50 W, 53 kHz) for 1 h and then treated under a refluxed condenser for 20 h at 95 °C in order to remove iron catalysts. The suspension of MWCNTs and HCl was filtered. The precipitate was washed with deionized water to neutral pH and dried in vacuum drying oven at 80 °C for 24 h. MWCNTs (1 mg) were added to 20 mL aqueous solutions of SDS, SDBS and PLL (1 mmol/L), respectively. Three MWCNTs solutions were sonicated for 1 h at 50 W. Three above solutions were centrifuged at  $1.0 \times 10^4$  rpm for 5 min using centrifuge (TG1650-WS, Shanghai Lu Xiangyi Centrifuge

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