



# Surface modification of carbon nanotubes via combination of mussel inspired chemistry and chain transfer free radical polymerization



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## ABSTRACT

In this work, a novel strategy for surface modification of carbon nanotubes (CNTs) was developed via combination of mussel inspired chemistry and chain transfer free radical polymerization. First, pristine CNTs were functionalized with polydopamine (PDA), which is formed via self-polymerization of dopamine in alkaline conditions. These PDA functionalized CNTs can be further reacted with amino-terminated polymers (named as PDMC), which was synthesized through chain transfer free radical polymerization using cysteamine hydrochloride as chain transfer agent and methacryloxyethyltrimethyl ammonium chloride as the monomer. PDMC perfectly conjugated with CNT-PDA was ascertained by a series of characterization techniques including transmission electron microscopy (TEM), Fourier transform infrared spectroscopy (FT-IR), thermal gravimetric analysis (TGA) and X-ray photoelectron spectroscopy (XPS). The dispersibility of obtained CNT nanocomposites (named as CNT-PDA-PDMC) was further examined. Results showed that the dispersibility of CNT-PDA-PDMC in aqueous and organic solutions was obviously enhanced. Apart from PDMC, many other amino-terminated polymers can also be used to functionalization of CNTs via similar strategy. Therefore, the method described in this work should be a general strategy for fabrication various polymer nanocomposites.

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## 1. Introduction

With the recent development of nanoscience and nanotechnology, a variety of nanomaterials with different size, shape and composition have emerged over the past few decades [1–7]. Carbon nanotubes (CNTs) should be one of the most studied carbon nanomaterials because of their unique one-dimensional structure and remarkable physicochemical properties [8–10]. Since their discovery in 1991, CNTs have been extensively explored for various applications, which include energy storage and conversion, environmental pollution control and biomedical applications [11]. For most of these applications, surface modification of CNTs is generally required to achieve better performance. It is well known that pristine CNTs can not be dispersed in both aqueous and organic solvents for their strong hydrophobic interaction between individual CNTs. In order to improve the solubility and dispersion of CNTs,

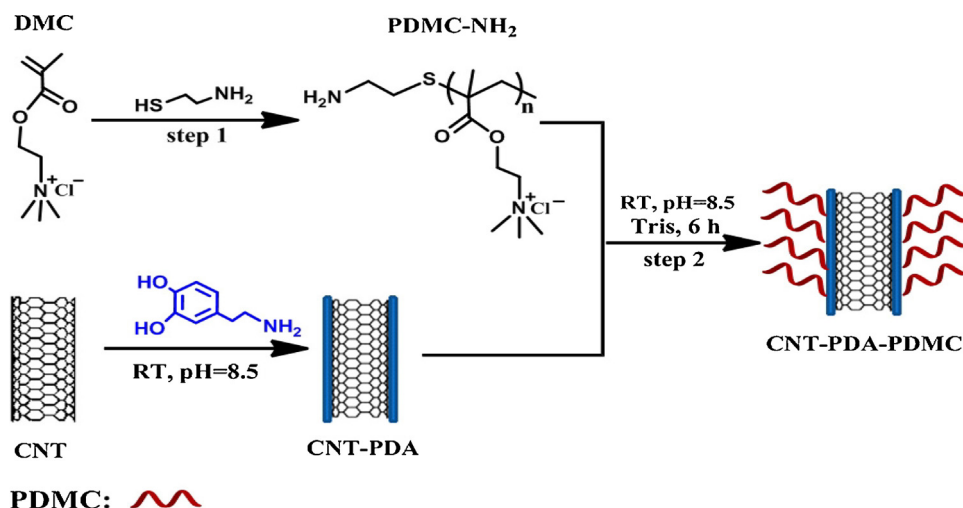
both covalent and non-covalent surface functionalization strategies have been developed previously [12–21]. It has demonstrated that the dispersibility of pristine CNTs in water could be significantly enhanced via non-covalent surface modification with surfactants. The underline mechanism of non-covalent method is that pristine CNTs are ready to interact with the hydrophobic segments of surfactants. On the other hand, the hydrophilic segments of surfactants were extended into the aqueous solution, resulting in enhanced dispersibility of CNTs in aqueous solution [22,23]. However, non-covalent modified CNTs are usually unstable when the solution properties were changed. Contrast with non-covalent methods, covalent strategies could provide robust surface modification of CNTs [24,25]. But the reactive conditions of covalent modification methods are rather harsh and complex. Furthermore, the structure and electronic properties of CNTs will be impacted during covalent modification procedure. It is therefore novel methods could overcome the drawbacks as described above is highly desirable.

Marine mussels are known for their superior ability for adhering to various surface [26–34]. The strong adhesive force between the mussels and surface of materials can be attributed to mussel adhesive proteins (MAPs). The major ingredients of MAPs are unusual amino acid 3,4-Dihydroxyphenyl-L-alanine, which

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**Scheme 1.** Schematic representation for the synthesis of CNT-PDA-PDMC nanocomposites via combination of mussel inspired chemistry and chain transfer free radical living polymerization. Step 1: PDMC-NH<sub>2</sub> was synthesized via chain transfer free radical polymerization under rather mild reaction conditions using cysteamine hydrochloride as the chain transfer agent and DMC as the monomer. Step 2: the PDMC was further conjugated onto surface of PDA functionalized CNTs (CNT-PDA) in Tris buffer solution for 6 h at room temperature (pH value is about 8.5).

participate in the intermolecular cross-linking reaction. Inspired by this, a novel surface modification strategy has been developed by Lee et al. in 2007 [35]. They demonstrated that dopamine could mimic the function of MAPs, which could self-polymerize under alkaline solution and form a polydopamine (PDA) coating. The PDA coating could further react with amino and thiol functional groups through Michael addition reaction [36–40]. Because of its simplicity, universality and effectiveness, mussel inspired chemistry has emerged as a very useful surface functionalization strategy, which has been extensively explored for different applications recently [41–52].

In this work, a novel method was developed for surface modification of CNTs via combination of mussel inspired chemistry and chain transfer free radical living polymerization. As shown in Scheme 1, poly(methacryloxyethyltrimethyl ammonium chloride) (PDMC) terminated with amino-group was synthesized via chain transfer free radical polymerization using cysteamine hydrochloride as the chain transfer agent and methacryloxyethyltrimethyl ammonium chloride (DMC) as monomer. And then the amino-terminated PDMC was conjugated with surface of functional CNTs with PDA coating through Michael addition reaction.

## 2. Materials and methods

### 2.1. Reagents and instruments

All chemical agents were of analytical grade and were used as received without any further purification. All aqueous solution was prepared with doubly distilled water. DMC (MW: 207.7, 98%), ammonium persulphate (MW: 228.2, 98.5%) and cysteamine hydrochloride (MW: 113.61, 98%) were purchased from Aladdin (Shanghai, China). And CNTs (>95%, diameter of 30–50 nm) were purchased from Sino Nanotech Ltd. (Beijing, China), Tris (hydroxymethyl) aminomethane (Tris) is obtained from Sinopharm Chemical Reagent Co., Ltd. Dopamine hydrochloride was purchased from Sangon Biotech. Co. (Shanghai, China).

<sup>1</sup>H NMR spectra were recorded on Bruker Avance-400 spectrometer with D<sub>2</sub>O as the solvent. Transmission electron microscopy (TEM) images were recorded on a Hitachi 7650B microscope operated at 80 kV; the TEM samples were made by placing a drop of nanoparticle ethanol suspension on a carbon-coated copper grid. The Fourier transform infrared (FT-IR) spectra were obtained

by using a Nicolet 380 Fourier transform spectrometer with a resolution of 2 cm<sup>-1</sup>. The samples were pressed with KBr into a pellet before measuring the infrared absorption spectra. TGA was conducted on a TA instrument Q50 with a heating rate of 20 °C min<sup>-1</sup>. Samples weight between 10 and 20 mg were heated from 25 to 800 °C in N<sub>2</sub> flow. The X-ray photoelectron spectra (XPS) were performed on a VGESCALAB 220-IXL spectrometer using an Al Kα X-ray source (1486.6 eV). The energy scale was internally calibrated by referencing to the binding energy of the C1s peak of a carbon contaminant at 284.6 eV.

### 2.2. Synthesis of amino-terminated polymer (PDMC-NH<sub>2</sub>)

The PDMC-NH<sub>2</sub> was synthesized by free radical polymerization using cysteamine hydrochloride as the chain transfer agent and DMC as the monomer. And ammonium persulphate is an oxidizing agent that was used as catalyst for the polymerization. All reagents are provided by the depicted above. In a typical experiment, DMC (30 mM, 6.23 g), cysteamine hydrochloride (0.1 mM, 0.13 g) and ammonium persulphate (3 mM, 0.8 g) were dissolved in distilled water (30 mL) and introduced in a polymerization bottle with a magnetic stir bar and purged by nitrogen flow at 80 °C for 48 h. The final reaction mixture was purified by dialysis treatment for 3 days with distilled water. Then soak in methanol about 6 h, taken out the product, and dried for further characterization and experiments.

### 2.3. Preparation of CNT-PDA

CNT-PDA was prepared according to our previous method [53,54]. The pure CNTs (100 mg) were added to the Tris buffer solution (30 mL, 10 mM, pH 8.5) and ultrasonic treatment for 10 min. In the next moment, the dopamine (100 mg) was put into Tris solution contained CNTs and stirred at room temperature for 4 h. The CNTs coated with PDA and Tris buffer solution were separated by centrifugation at 8000 rpm for 10 min (Shuke Centrifuge TG-16, Sichuan shuke instrument Co., Ltd., China). Precipitation was washed with distilled water and ethanol three times and dried at 40 °C for 12 h.

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