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# Biomimetic PEGylation of carbon nanotubes through surface-initiated RAFT polymerization

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ABSTRACT

Carbon nanotubes (CNTs) are a type of one-dimensional carbon nanomaterials that possess excellent physicochemical properties and have been potentially utilized for a variety of applications. Surface modification of CNTs with polymers is a general route to expand and improve the performance of CNTs and has attracted great research interest over the past few decades. Although many methods have been developed previously, most of these methods still showed some disadvantages, such as low efficiency, complex experimental procedure and harsh reaction conditions etc. In this work, we reported a practical and novel way to fabricate CNTs based polymer composites via the combination of mussel inspired chemistry and reversible addition fragmentation chain transfer (RAFT) polymerization. First, the amino group was introduced onto the surface of CNTs via self-polymerization of dopamine. Then, chain transfer agent can be immobilized on the amino groups functionalized CNTs to obtain CNT-PDA-CTA, which can be utilized for surface-initiated RAFT polymerization. A water soluble and biocompatible monomer poly(ethylene glycol) monomethyl ether methacrylate (PEGMA) was adopted to fabricate pPEGMA functionalized CNTs through RAFT polymerization. The successful preparation of CNTs based polymer composites (CNT-pPEGMA) was confirmed by transmission electron microscopy, Fourier transform infrared spectroscopy, thermogravimetric analysis and X-ray photoelectron spectroscopy in details. The CNT-pPEGMA showed good dispersibility and desirable biocompatibility, making them highly potential for biomedical applications. More importantly, a large number of CNTs based polymer composites could also be fabricated through the same strategy when different monomers were used due to the good monomer adaptability of RAFT polymerization. Therefore, this strategy should be a general method for preparation of various multifunctional CNTs based polymer composites.



## 1. Introduction

Since they were officially recognized and named in 1991, carbon nanotubes (CNTs) have drawn much attention for their outstanding mechanical, thermal and electrical properties [1–3]. Therefore, they have been widely applied in structure materials, thermal conductor, environmental adsorption, energy storage and conversion, chem/biosensors and biomedical applications [4–16]. Even though CNTs own remarkable properties, it is wiser to make a combination with others, such as metal, inorganic substances, polymers and so on [17–20]. CNTs based polymer composites were considered as one of the significant parts, which were devisable and can maximize the potential of both polymers and CNTs [21]. So far, many studies have been done to fabricate CNTs based polymer composites and achieved certain success. For example, solution mixing, melt blending and in situ polymerization were developed from the point of practical application and theoretical research [22]. Compared with pure polymers or CNTs, these CNTs based polymer composites may overcome the defects such as poor designability, low conductivity and weak intensity [21,23]. In the process of preparation, dispersion and interfacial adhesion were two critical factors to create excellent composites. Because of the small size, high specific surface areas and aspect ratio, strong hydrophobic interaction was existed between CNTs, which lead to the serious aggregation of these pristine CNTs [24]. From the aspect of the micro, this behavior was resulted from electronic efficient and van der Waals attraction. Chemical functionalization, based on covalent linkages, was employed to exclude the electronic efficient and endow reactive sites on the surface of CNTs [25–28]. On the other hand, physical functionalization, based on non-covalent self-assembly, was also used to enhance interfacial adhesion. The later mainly depended on van der Waals attraction

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and π-π stacking between polymers and CNTs [29–31]. Nonetheless, the pretreatment of covalent linkages may cause irreparable damage to the structure of CNTs and negative impact on the thermal, mechanical or electrical properties. In addition, the strength of π-π stacking is relative unstable in some extent and only limited polymers can be choose for non-covalent strategies. The limitation of these conventional surface modification strategies will largely impede the further applications of CNTs. Therefore, it was still necessary to design and explore novel and efficient methods for fabrication of CNTs based polymer composites.

Mussel inspired chemistry is an emerged surface modification strategy, which has attracted increasing attention in the past few years [32, 33]. It has been demonstrated that dopamine (DA), a crucial component of mussel inspired chemistry, would be self-polymerized into PDA under alkaline environment. The resulting PDA films can not only strongly adhere onto almost any materials, but also provide a number of active sites for further reactions [34,35]. Because of these unique characteristics, mussel inspired chemistry have becoming the research focus for diverse applications [36–42, 44–48, 50]. For example, Lee et al. connected hydroxyapatite on the surface of CNTs by the aid of mussel inspired chemistry [49]. In the process, DA not only plays the role of adhesion but significantly weakened the toxicity of CNTs and enhanced the biocompatibility. On the other hand, we have demonstrated that amino groups functionalized CNTs can be facilely fabricated via the combination of mussel inspired chemistry and Michael addition reaction. These functionalized CNTs showed obviously enhanced adsorption capability toward $Cu^{2+}$ [50]. Furthermore, surface modification of graphene oxide with heparin and BSA was also demonstrated by Zhao and Cheng et al. [51] They confirmed that surface modification of graphene oxide with these biomacromolecules could effectively improve water dispersibility and biocompatibility of graphene oxide.

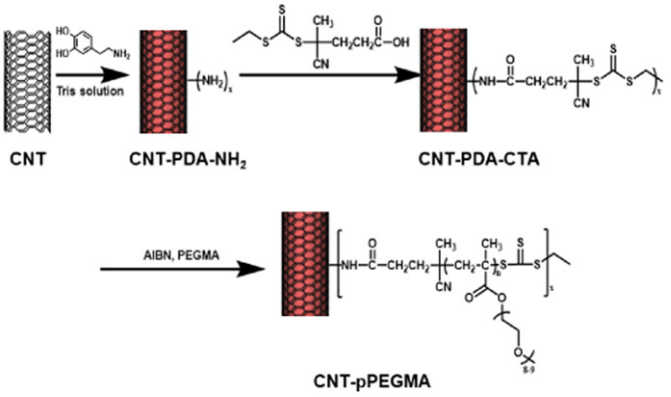
Surface modification of CNTs with synthetic polymers through in situ surface polymerization methods have demonstrated to be efficient routes to prepare CNTs based polymer composites [52–54]. Most of these strategies were mainly relied on the surface oxidation of CNTs. However, the procedure for surface oxidation of CNTs is rather complex and inefficient and will inevitably destroy the structure of CNTs. Therefore, some studies for surface modification of CNTs via the combination of mussel inspired chemistry and atom transfer radical polymerization (ATRP) and single-electron living radical polymerization (SET-LRP) have been demonstrated recently [55,56]. However, both ATRP and SET-LRP are required using copper ions as catalysts, which are toxic to living organisms and may influence the final properties of composites. Reversible addition fragmentation chain transfer (RAFT) polymerization is another controlled living polymerization method, which can be used for preparation of well controlled polymers in the absence of metal catalysts [57,58]. To the best of our knowledge, the preparation of CNTs based polymer composites through the combination of mussel inspired chemistry and surface-initiated RAFT polymerization has not reported thus far.

In this contribution, we describe a practical and efficient method to fabrication of CNTs based polymer composites, that combination of mussel inspired chemistry and RAFT polymerization. The pristine CNTs were first coated with PDA, which was used for surface immobilization of chain transfer agent (CTA) to initiate RAFT polymerization (Scheme 1). The successful preparation of CNTs based polymer composites (CNT-pPEGMA) were confirmed by a number of characterization techniques. Cell viability evaluation demonstrated that CNT-pPEGMA showed great cytocompatibility, indicating that these CNTs based polymer composites are potential for biomedical applications.

## 2. Experiment

### 2.1. Materials and characterization

All of the chemicals were directly used without further purification. CNTs were purchased from Sinonano (Beijing, China). Dopamine hydrochloride was purchased from Sangon Biotech. Co., Ltd. (Shanghai, China). *N*-(3-Dimethylaminopropy)-*N*-ethylcarbodiimide hydrochloride (EDC), *N*-Hydroxysuccinimide (NHS), Tris-(hydroxymethyl) aminomethane (Tris) and poly(ethylene glycol) methyl ether methacrylate (PEGMA, *M*w: 950 Da, 98%) and polyethylenimine (PEI, *M*w: 1800 Da) were obtained from Aladdin (Shanghai, China) without further purification. 2-Morpholinoethanesulfonic acid (MES) was supplied by Heowns (Tianjin, China). Chain transfer agent (CTA) was synthesized according to our previous report [29]. The other chemical agents were all of commercially available and analytical grade. The water involved in the experiment was deionized water (D.I. water).




**Scheme 1.** Schematic representation for the preparation of CNT-pPEGMA via the combination of mussel inspired chemistry and RAFT polymerization.

The Fourier transform infrared (FT-IR) spectra were gained in a transmission mode on a Nicolet 5700 spectrometer (Waltham, MA, USA). Thermal gravimetric analysis (TGA) was tested on a TA instrument Q50 with a heating rate of 20 °C $min^{-1}$ using crucibles of aluminum. The X-ray photoelectron spectra (XPS) were measured on a VGESCALAB 220-IXL spectrometer using an A1 Ka X-ray source (1486.6 eV). Transmission electron microscopy (TEM) images were recorded on a Hitachi 7650B microscope operated at 80 Kv. The TEM specimens were made by placing a drop nanoparticle ethanol suspension on a carbon-coated copper grid.

### 2.2. Preparation of CNT-PDA-$NH_2$

CNT-PDA-$NH_2$ was synthesized as described in the following procedure. 150 mg of pristine CNTs were added into 50 mL of Tris solution (10 mM $L^{-1}$, pH = 8.5) and sonicated for 10 min. Then, 150 mg of DA was also put into and the mixture was stirred at room temperature for 2 h. The mixture (CNT-PDA) was separated from the reaction solution through centrifugation. After that, 150 mg of PEI was added to react with CNT-PDA for further 2 h. The PEI can be immobilized on PDA coatings through Michael addition reaction between PDA and amino groups. On the other hand, the surplus amino groups that immobilized on the surface of CNTs can be further reacted with carboxyl group of CTA to facility the immobilization of CTA on CNTs. The CNT-PDA-$NH_2$ was got after centrifuging and washing at 8000 rpm for 10 min per time until suspension was clarified. Last, the product was dried under vacuum for further use.

### 2.3. Preparation of CNT-PDA-CTA

CNT-PDA-CTA was synthesized in MES buffer solution (25 mM, pH = 6). First, 10 mg of CTA was added into 10 mL of MES solution. And then, 4.5 mg of NHS and 7.5 mg of EDC were added in the CTA contained solution. After 10 min, 100 mg of CNT-PDA-$NH_2$ was added and further reacted overnight at room temperature. The resulting CNT-PDA-CTA was separated from MES solution by centrifugation at 8000 rpm for 10 min and vigorously washing with