

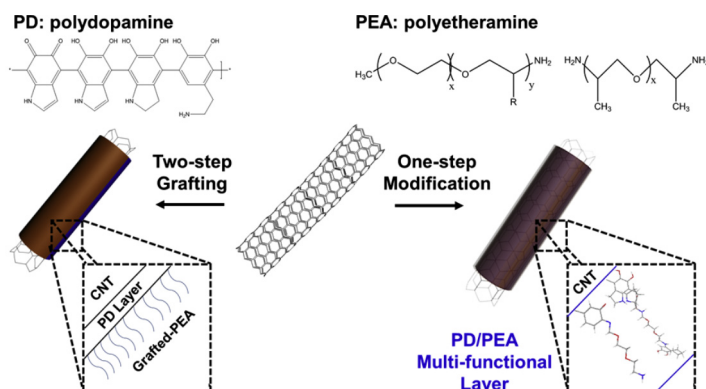
## Regular Article

## Defect-free surface modification methods for solubility-tunable carbon nanotubes

Hee Dae Lee<sup>1</sup>, Byung Min Yoo<sup>1</sup>, Tae Hoon Lee, Ho Bum Park<sup>\*</sup>

Department of Energy Engineering, Hanyang University, Seoul 04763, Republic of Korea

## GRAPHICAL ABSTRACT



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## ABSTRACT

Although carbon nanotubes (CNTs) have outstanding physical properties, there are still challenging issues such as poor dispersibility and miscibility between organic polymers and CNTs for polymer nanocomposites. Chemical modifications (e.g., strong acid based oxidation, carboxylation, etc.) can improve dispersion properties and compatibility, but such surface modification methods often lead to damage to the pristine CNT structure and also deteriorate the mechanical properties of CNTs. Here we demonstrate a simple, defect-free and scalable method for well-dispersed CNTs in common organic solvents, using dopamine and amine-terminated polyethylene glycol derivatives. This method makes it possible to prepare solubility-tunable CNTs without any severe structural deformation. As-modified CNTs were successfully characterized by thermal gravimetric analysis (TGA), Fourier-transformed infrared spectroscopy (FT-IR), X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM) and transmission electron microscope (TEM). The surface modified-CNTs were well-dispersed in polar and/or non-polar common solvents. The well-dispersed CNTs can be used in a nanofiller in commercial polymers such as thermoplastic polyurethane (TPU) polymer. The CNT/TPU composite showed improved tensile strength without sacrificing elongation at break relative to those of pristine TPU.

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## 1. Introduction

Carbon nanotubes (CNTs) have been extensively studied due to their unique electrical, magnetic, optical, and thermal properties [1]. Although the organic-inorganic nanocomposites can typically

<sup>\*</sup> Corresponding author.E-mail address: [badtzhb@hanyang.ac.kr](mailto:badtzhb@hanyang.ac.kr) (H.B. Park).<sup>1</sup> These authors contributed equally to this work.

include inorganic fillers with different particle dimensions [2–5], one-dimensional CNTs containing nanocomposites have a number of high-end applications. Due to their large surface area, high aspect ratio, and hydrophobic nature, however, CNTs tend to form bundles with each other, and thus do not disperse well in organic polymers or aqueous or polar solvents without any surface modifications [6]. Therefore, an adjustable surface modification strategy for CNTs with homogeneous dispersion in each mixture is required to change the nanocomposite morphology and subsequent properties.

In general, there are two common methods for surface modification of CNTs [7]. First, CNT surfaces can be covalently modified. Commonly, CNTs are pretreated by using strong acids (e.g., nitric acid) to generate acid functional groups on the sidewalls or tips of the CNTs [8]. Then, the acid groups (e.g., carboxylic acid) are subsequently reacted with polymeric precursors, such as reactive monomers, leading to surface-grafting polymerization [9,10] or in situ-polymerization [11]. However, the covalent functionalization of CNTs may cause structural defects in the wall structure of the CNT, decreasing the mechanical properties by disturbing the structural homogeneity of the CNTs [12]. Also, the reactive sites, generated by acid treatment, are limited for a variety of surface modifications. Second, to achieve surface functionalization, noncovalent means of surface modification are more popular. For noncovalent modification, polymer chains are wrapped around the CNT [13,14] or various surfactants can be preferentially adsorbed on the surface of the CNTs [15,16].  $\pi$ - $\pi$  stacking is a method of surface modification for CNTs [17,18]. These noncovalent CNT functionalization methods have several advantages compared to the covalent modification method, particularly in that they can keep the original properties of CNT intact.

Recently, a universal coating method using an aqueous dopamine solution has been extensively used for hydrophilic surface modification of almost all materials, including metals, metal-oxides, inorganics, and polymers [19]. The deposited coating (termed “polydopamine” and PD from herein) was found to be hydrophilic and has extraordinarily strong adhesion to a number of materials, even in the liquid state. The coating layer can be tuned

at the nanoscale. Using this method, PD-coated CNTs have been reported [20,21], showing much improved dispersion properties in aqueous solution due to the increasing hydrophilicity of the modified CNT. This method is a powerful noncovalent surface modification method for CNTs because the PD layer can be used as a versatile immobilization platform to covalently anchor any polymer chains to the PD surfaces [22,23].

In this study, we prepared two kinds of surface-modified CNTs using a PD and amine terminated polyetheramines (PEA-NH<sub>2</sub>) coating method: (1) PD/PEA-NH<sub>2</sub> CNT (PD/PEA CNT) and (2) PEA-NH<sub>2</sub> grafted PD CNT (PD-g-PEA CNT). PD/PEA CNT prepared by the one-step coating process has a randomly mixed coating layer whereas PD-g-PEA CNT produced by two-step wrapping and grafting processes consist of two phases. Unlike covalent bonding based modification reaction, these coating methods do not require carboxylic acid and/or epoxy functional group of CNTs. Thus, these simple methods can make surface-modified CNTs without any structural defects. Especially, PD/PEA coating layer can be simply coated on CNTs surface by one-step process. Moreover, this method can tune and enhance the solubility parameter and dispersion properties of CNT by changing PEA species (e.g., chain length and/or functional group). Fig. 1 showed a schematic illustration of the overall modification process with the proposed structure.

## 2. Experimental section

### 2.1. Materials

Multi-walled CNTs (MWCNT, outer diameter: 6–9 nm, inner diameter: 2–4 nm) were purchased from Sigma Aldrich (St. Louis, MO). Dopamine hydrochloride (Sigma Aldrich, St. Louis, MO) and tris hydrochloride buffer (Sigma Aldrich, St. Louis, MO) solution were used for dopamine-based hydrophilic nano-layered coating on a MWCNT surface. Anodisc membranes (AAO, pore sizes of 0.1 and 0.2  $\mu$ m) were purchased from WHATMAN (Maidstone, England, UK) for filtration. Amine-terminated PEA (Jeffamine M-1000) and diamine-terminated PEA (Jeffamine D-230) were kindly supplied by Huntsman Corp. (Salt Lake, Utah). Hydrochloric acid

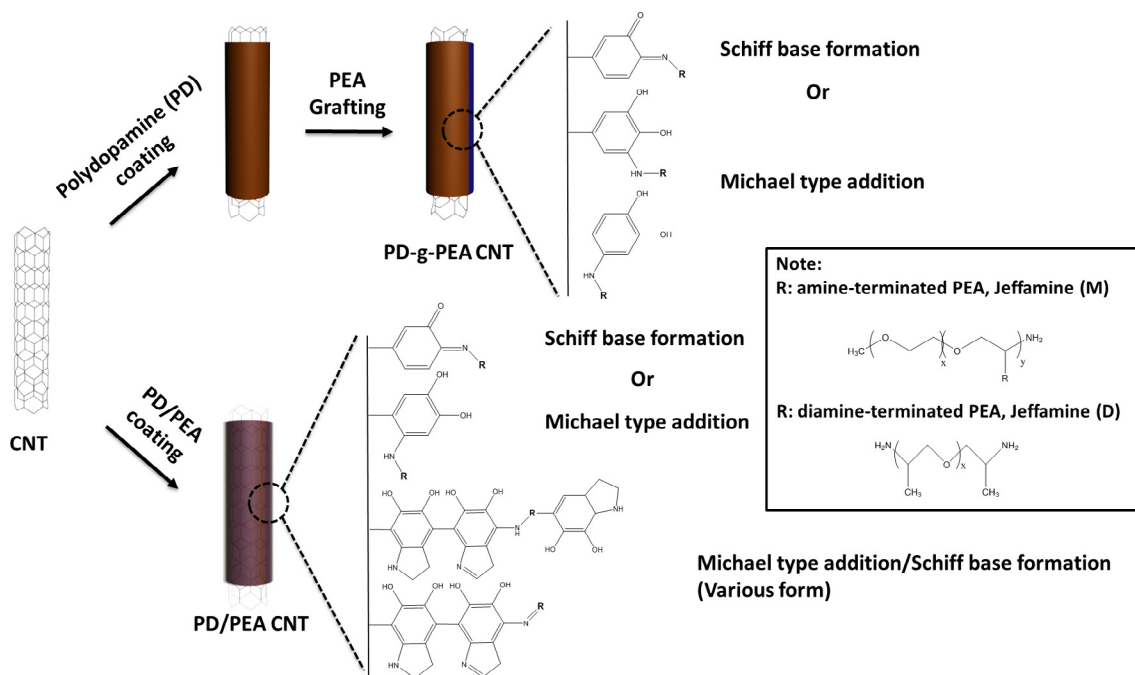


Fig. 1. Schematic illustration of the proposed structure of a surface modified CNT.

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