A self-assembled flavin protective coating enhances the oxidative thermal stability of multi-walled carbon nanotubes

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ABSTRACT

Multi-walled carbon nanotube (MWNT) has many commercial applications. However, its broad use is limited by the surface-bound oxygen lowering its thermal stability. Here, we developed a facile method to enhance the oxidative thermal resistance of MWNTs that involves molecular coating promoted surface passivation. In the approach, ball milling is employed to self assemble flavin mononucleotide (FMN) helically around MWNTs through non-covalent interactions with no increased defects in MWNT. Upon high temperature oxidation, the ribityl phosphate side chain of FMN in the nanoconstruct undergoes partial decomposition to generate a corresponding isoalloxazine derivative on the surface of the MWNTs. Transmission electron microscopy reveals that the oxidatively annealed material is comprised of a tight isoalloxazine coating stacked on the sidewalls of the MWNT. The results of thermal gravimetric analysis studies show that the coating further elevates long-term stability and the energy barrier for oxidation of the MWNT by 28 kJ/mol from 113 kJ/mol for the bare MWNT. The role of the isoalloxazine coating is proposed to be surface passivation from molecular oxygen. As a consequence of the passivation, the maximum oxidative temperature of the MWNT is raised to 938 K as compared to that of 843 K for bare MWNT.

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1. Introduction

Multi-walled carbon nanotubes (MWNTs), concentric cylindrical rolls of graphene sheets, have excellent electrical and thermal properties [1,2]. As compared to single-walled carbon nanotubes (SWNTs), MWNTs are amenable to economical (<$100 per kg) [3] large scale production. As a result, several applications exist for these materials including light-weighted battery electrodes [4,5], electromagnetic interference shielding [6], and high-performance polymer composites [7—9] and flame retardant additives [10] and hinge on high thermal stabilities in an air atmosphere.

Thermal stabilities of MWNTs, often given in terms of oxidation temperatures, are a direct consequence of the presence of aromatic rings within their structures. As a result, the thermal stabilities of these materials are influenced by the number and diameter of the walls [11,12], the length of the tube [13], and the presence of residual catalysts and/or defects. As compared to graphene, which is

stable up to 873 K [14—16], MWNT have inferior thermal stabilities in an air atmosphere owing to strain caused by the curvature of the π conjugated networks [11]. Generally, the maximum oxidation temperatures (T_p) of MWNTs, obtained using thermogravimetric analysis (TGA), varies from material-to-material in a range of 673—773 K [11,17,18]. It is known that oxidative degradation pathway of MWNTs involves reversible adsorption of gaseous O_2 on the basal graphene sidewalls to form mobile/static oxygenated carbons or direct reaction with edge carbon atoms leading to rapid CO_2 formation [19,20].

A facile approach to improve the oxidation stabilities of MWNTs is a necessary component of efforts to broaden applications of these materials. Our recent studies aimed at this goal focused on the use of flavin mononucleotide (FMN) as a carbon nanomaterial stabilizing agent. This substance (Fig. 1A), a phosphate monoester of riboflavin (RF) that serves as a redox cofactor in many enzymatic transformations [21], is known to disperse various nanomaterials as effective and selective manner [22—31]. In those study, it was shown that FMN wraps around SWNTs in a tight helical manner (Fig. 1C) as a consequence of π-π interactions between isoalloxazine rings of FMN and the graphene sidewalls. In addition,

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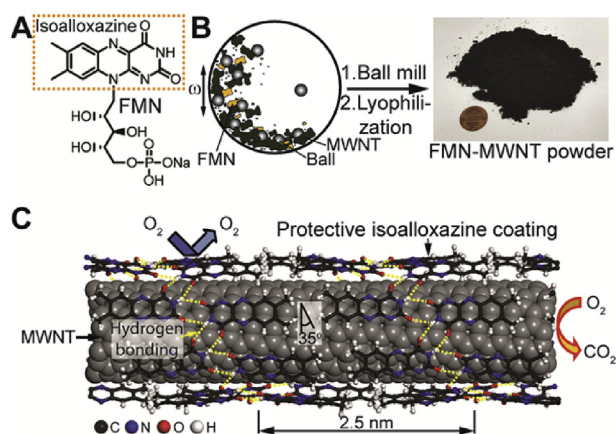
Fig. 1. Schematic of ball mill assisted FMN coating of MWNT. (A) Structure of FMN. (B) Ball mill assisted formation of non-covalent functionalized MWNT with FMN. Photograph: large scale preparation of FMN-MWNT powder. (C) Schematic representation of the enhanced thermal stability of MWNT helically wrapped by the isoalloxazine passivation layer, which prevents MWNT oxidation. The FMN tail is omitted for visual clarity. (A colour version of this figure can be viewed online.)

quadruple intermolecular hydrogen-bonding (yellow dotted line) exists in this complex between uracil components of the FMN structure. The tight FMN helix might protect the MWNT surface by protecting oxygen binding.

In the investigation described below, we found for the first time that the oxidative thermal stability of MWNTs is enhanced by surface protection of small molecular organic flavin mononucleotide (FMN) wrapping. Vibrational ball mill method in the presence of FMN produces non-covalent, individualized, and shortened MWNT functionalization in effective and scalable manner. Atomic force microscopy (AFM) reveals that the organic coating consists of a tight helical self-assembly of FMN which is stacked on the MWNT sidewalls via π-π interaction. Especially, TGA along with liquid chromatography (LC)-mass spectroscopy (MS) show that, upon high temperature oxidation, the ribityl phosphate tail group of FMN partially decomposes, leaving the isoalloxazine sheath on MWNT surface. Such sheath passivates MWNT surface from oxidation by elevating oxidation activation energy (E_a) barrier by 28 kJ/mol, calculated by heating rate programmed TGA measurements. High resolution transmission electron microscopy (HRTEM) shows that the isoalloxazine on the MWNT remains intact as a coating. As a result, FMN-wrapped MWNT by π-π interaction displays enhanced thermal stability up to 933 K, departed from that (843 K) from MWNT only.

2. Experimental

2.1. Methods and materials

MWNT (diameter: ca. 11 nm, length: <40 μm, wall number: 10—11 layer) was kindly donated by LG Chemicals. FMN sodium salt (purity >93%) was purchased from TCI. Deionized (DI) water whose electrical resistance is greater than 18 MΩ was used throughout the experiment. HPLC-grade solvents are utilized for LC-MS measurements. Atomistic molecular structure of FMN-MWNT was generated and visualized by using Materials Studio according to the literature reported elsewhere [23]. Prior to scanning electron microscope (SEM) and Raman measurements, 285 nm thick SiO$_2$/Si substrates were piranha-cleaned, followed by washing with DI water, and final N$_2$ drying. SEM images were acquired by using a JSM-7001F (JEOL Ltd.) with a 15 kV acceleration. Length

distributions were obtained by analyzing 100 MWNTs. Raman spectra were acquired by using a custom-made setup [25,32] with 532 nm laser with 1 mW via a backscattering geometry. The Si peak (520.89 cm^{-1}) was used as an internal reference. UV—vis—NIR absorption spectra were obtained by using JASCO 770 with a cuvette having 10 mm beam path. For absorption measurements, 7.0 mL DI water was added to 0.1 g of the milled MWNT sample, and the supernatants were collected by decantation after settlement of large MWNT bundles. LC-MS spectra were acquired by using 3100 an LC-MS instrument (Waters). FMN and FMN-MWNT samples, following annealing at 543 and 723 K, respectively, under air for 1 h in a conventional quartz tubular reactor [32], were dissolved in *N,N*-dimethyl formamide (DMF). The mixtures were filtered using a 0.45 μm pore poly(tetrafluoroethylene) (PTFE) syringe to remove MWNT. After addition 0.1% trifluoroacetic acid, the solutions were subjected to LC using an acetonitrile and DMF gradient and a C18 reverse phase column. Electrospray ionization (ESI) MS spectra were acquired in a positive mode.

2.2. Non-covalent functionalization of MWNT with FMN

Vibrational ball milling was performed by using Pulverisette 23 (Fritsch, German) operated at ω = 50 Hz to functionalize MWNT with FMN. Briefly, a mixture of 0.10 g of MWNT and 0.08 g of FMN in 3.0 mL water was introduced into the milling setup with 2 %-v of zirconia balls (diameter = 5 mm). The milled samples were collected at time intervals of 5, 10, 30, 60, and 90 min. The samples were vacuum-filtered by using a Buchner funnel with a water-circulated aspirator (Eyela A-3S). The black MWNT paper was washed with water several times to remove free FMN. The sample was subject to lyophilization for 2 d to produce dry FMN-MWNT powder.

2.3. AFM measurements

AFM images were acquired by using the tapping mode with a Nanowizard I (JPK Instrument). Dried FMN-MWNT was dispersed in DI water, and 20 μL aliquot of the dispersion was dropcast onto freshly-cleaved mica substrate. Height and phase topographies were obtained by using an Al-coated silicon cantilever (force constant: 37 N/m, ACTA-20, App Nano) resonated at 361.96 kHz. The acquired 512 $\times$ 512 pixel images were flattened by using a polynomial routine.

2.4. TGA-differential scanning calorimetry (DSC) measurements

Thermal properties of the samples were obtained mainly by using a simultaneous TGA-DSC analyzer (STA80000, Perkin Elmer). For this purpose, *ca.* 10 mg of dried FMN-MWNT samples along with bare FMN and MWNT were loaded onto alumina pans. Bare FMN was initially annealed at 373 K for 1 h to eliminate adsorbed water. A typical scanning range was from 293 K to 1173 K with a ramping rate (β) of 5 K/min with a 100 standard cubic centimeter per min (sccm) flow of synthetic air composed of 21 v.% O$_2$ in N$_2$ unless otherwise noted. E_a measurements of MWNT derivatives were conducted using a narrower range (*i.e.*, 573—1023 K) by varying β (*i.e.*, 2, 5, 10, 20 K/min).

2.5. HRTEM and electron dispersive X-ray spectrometry (EDS) measurements

These measurements were made by using a spherical aberration-corrected scanning TEM (JEOL JEM-ARM 200F) with a 200 kV acceleration voltage. The 723 K annealed FMN-MWNT sample in water was briefly sonicated for 30 s, and the resulting