Noncovalent functionalization of single-walled carbon nanotubes with porphyrins

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ARTICLE INFO

ABSTRACT

The covalent and noncovalent interactions of porphyrins and related tetraazamacrocyclic compounds with single-walled carbon nanotubes (SWNTs) is a subject of increasing research effort, directed toward the design of novel hybrid nanomaterials combining unique electronic and optical properties of both molecular species. In this report, we used different experimental techniques as well as molecular mechanics (MM) calculations to analyze the adsorption of *meso*-tetraphenylporphine (or 5,10,15,20-tetraphenyl-21H,23H-porphine, H_2TPP) and its complexes with Ni(II) and Co(II) (NiTPP and CoTPP, respectively), as well as hemin (a natural porphyrin), onto the surface of SWNTs. Altogether, the results suggested that all four porphyrin species noncovalently interact with SWNTs, forming hybrid nanomaterials. Nevertheless, of all four porphyrin species, the strongest interaction with SWNTs occurs in the case of CoTPP, which is able to intercalate and considerably disperse SWNT bundles, and therefore absorb onto the surface of individual SWNTs. In contrast, NiTPP, CoTPP and hemin, due to a weaker interaction, are unable to do so and therefore are only capable to adsorb onto the surface of SWNT bundles. According to the scanning tunneling microscopy (STM) imaging and MM results, the adsorption of CoTPP onto SWNT sidewalls results in the formation of porphyrin arrays in the shape of long-period interacting helixes with variable periodicity, possibly due to different diameters and chiralities of SWNTs present in the samples. Since the remaining porphyrin species were found to adsorb onto the surface of SWNT bundles, the precise geometry of the corresponding porphyrin/SWNT complexes is difficult to characterize.

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1. Introduction

The covalent and noncovalent interactions of porphyrins and related tetraazamacrocyclic compounds with carbon nanomaterials is a subject of increasing research effort [1–17]. The studies involving carbon nanotubes (CNTs), including both single-walled (SWNTs) and multi-walled CNTs (MWNTs), are directed toward the design of novel hybrid nanomaterials combining unique electronic and optical properties of porphyrins and CNTs. The non-covalent functionalization of CNTs with porphyrins is based on π–π-interactions between the two components possessing highly delocalized π-electrons. Its evident advantage, as compared to the covalent functionalization techniques, is that the noncovalent

approach does not disrupt the intrinsic electronic structure of the nanotubes, keeping them totally intact, even though the covalent approach produces more thermodynamically stable structures. It was shown that the nanohybrids composed of CNTs and the easiest in preparation synthetic porphyrins, exemplified by *meso*-tetraphenylporphine (or 5,10,15,20-tetraphenyl-21H,23H-porphine, H_2TPP) and its metal(II) complexes, can be very readily obtained and exhibit charge transfer features persistent on the time scale of hundreds of nanoseconds [4]. Thus, CNTs noncovalently functionalized with simple porphyrins deserve more detailed and versatile characterization. In addition to photosensitized electron-transfer processes directly related to photovoltaic applications, the structural aspects of special interest are related to the amount of porphyrins adsorbed onto CNTs from solutions depending on the central metal ion, how porphyrin molecules are arranged on CNT surface, the possibility of their microscopic imaging on the nanotube sidewalls, spectroscopic characteristics of the nanohybrid materials obtained, etc.

In the present work, in continuation of our previous studies [18–20], we addressed the above characterization aspects by using different experimental techniques such as Fourier-transform infrared (FT-IR) and Raman spectroscopy, thermogravimetric analysis (TGA), scanning and transmission electron microscopy (SEM and TEM, respectively), and scanning tunneling microscopy (STM), as well as molecular mechanics (MM) calculations to assist interpretation of STM imaging results. The porphyrins studied were H_2TPP and its complexes with nickel(II) and cobalt(II) (NiTPP and CoTPP, respectively), as well as hemin (a natural porphyrin, the prosthetic group of hemoglobin), adsorbed on the sidewalls of SWNTs.

2. Materials and methods

We employed SWNTs obtained by arc-discharge process (95%+ purity, diameter of 1–1.2 nm and a few hundred nm long) from ILJIN Co., Inc., Korea. meso-Tetraphenylporphine (H_2TPP) and its complexes NiTPP and CoTPP were purchased from Strem Chemicals, Inc. Hemin was acquired from Fluka (98% HPLC pure).

The porphyrin/SWNT complexes were prepared as follows. Starting porphyrin solutions were prepared in dichloromethane for H_2TPP and CoTPP, chloroform for NiTPP, and acetone for hemin; at concentrations of approximately 244.01 μM, 223.33 μM, 223.41 μM and 230.08 μM, respectively. Additionally, the hemin solution was taken to its boiling point (approximately 57 °C) for enhancing solubility. All solutions were submitted to ultrasonic bath for 10 min. 5 mg of SWNTs were added to each of the above solutions, and submitted to ultrasonic bath for another 5 min. The resulting suspensions were left still to sediment for about 2 h. Finally, the supernatants were removed, and the precipitates were collected and kept dry in a vacuum desiccator until further utilization. For the high-resolution transmission electron microscopy (HR-TEM) and scanning tunneling microscopy, the powders were re-suspended in isopropanol and deposited by drop-casting onto corresponding supports (see below).

TGA analyses were performed on a simultaneous differential heat flow (DSC) and weight change (TGA) SDT-Q600 instrument (TA instruments) in heat flow mode, an air atmosphere at 100 ml min^{-1} and a lineal temperature ramp of 10 °C min^{-1}.

Raman spectra were recorded on a Thermo-Nicolet Almega Dispersive Raman instrument (λ = 532 nm). Fourier-transform infrared (FT-IR) spectra were measured on a Nicolet Nexus 670 FT-IR spectrometer (λ = 532 nm) in KBr pellets.

Scanning electron microscopy was carried out on a JEOL JSM-5900LV SEM instrument operating at 20 kV. Energy-dispersive X-ray spectra (EDS) were recorded with an Oxford spectrometer coupled with the SEM equipment. HR-TEM observations of the samples were performed on a JEOL JEM-2010 microscope at 200 kV, employing formvar/carbon-coated copper grids from Ted Pella, Inc. STM imaging was carried out in constant current mode under open-air conditions and a temperature of 17 °C on a JEOL JSPM-5200 instrument using freshly cleaved HOPG supports (ZYB grade, mosaic spread 0.8 ± 0.2°) of ca. 5 mm × 5 mm size from Nanoscience Instruments, and Pt/Ir wire probes of 0.25-mm diameter from Nanosurf AG. The STM images were analyzed employing the Nanotec Electronica WSxM© Scanning Probe Microscopy software [21].

The porphyrin adsorption onto SWNT surface was also modeled theoretically by means of molecular mechanics (MM) using HyperChem version 7.01 software (from Hypercube, Inc.), employing the MM+ force field with Polak-Ribiere gradient algorithm and a root mean square (RMS) gradient of 0.001 kcal Å^{-1} mol^{-1}. We used a closed-end zigzag (15,0) SWNT model, of 8.21 nm × 1.16 nm dimensions after geometry optimization. The porphyrins used in the simulation were hemin and H_2TPP (as a model for all

meso-tetraphenylporphines, or TPPs). The simulations were carried out as described in our previous reports [19,20].

3. Results and discussion

A series of experimental techniques together with MM simulations were applied to analyze the adsorption of four porphyrin species, namely H_2TPP, NiTPP, CoTPP and hemin, onto the surface of SWNTs. The porphyrin/SWNT complexes (or hybrids) were prepared as described above, and characterized by means of TGA, Raman and FT-IR spectroscopies, as well as SEM, HR-TEM and STM imaging.

According to the TGA results (Fig. 1), the decomposition of the crystalline porphyrins initiates at about 355 °C, 418 °C, 354 °C and 252 °C for H_2TPP, NiTPP, CoTPP and hemin, respectively. Pristine SWNTs start to decompose at about 600 °C. In the porphyrin/SWNT complexes, the differences between the weight percentages (Δ values on the graphs in Fig. 1) corresponding to temperatures at which the decomposition of porphyrins and that of SWNTs begins give the following values: 17% for H_2TPP/SWNT (Fig. 1a), 12% for NiTPP/SWNT (Fig. 1b), 57% for CoTPP/SWNT (Fig. 1c), and 13% for hemin/SWNT (Fig. 1d). These values demonstrate that in the H_2TPP/SWNT, NiTPP/SWNT and hemin/SWNT complexes, the porphyrin content is rather low compared to that of SWNTs (with approximate proportions of 1:5, 1:7 and 1:7, respectively). In contrast, in the CoTPP/SWNT complex, such proportion is of roughly 1:1, suggesting a full coverage of the surface of SWNTs with CoTPP molecules. An important observation is that in the TGA graph corresponding to the CoTPP/SWNT complex (red line in Fig. 1c), the decomposition of SWNTs begins at about 530 °C, whereas in the remaining porphyrin/SWNT complexes it starts at about 600 °C. This may be attributed to the fact that the thermal decomposition of CoTPP molecules adsorbed onto the sidewalls of SWNTs causes an enhanced production (due to the high porphyrin concentration) of free radicals which covalently attach to the surface of the SWNTs modifying their structure and making them less stable, consequently causing them to decompose at lower temperatures. On the other hand, in the CoTPP/SWNT complex (red line in Fig. 1c), it is evident that the CoTPP decomposition is faster (manifested in a slightly more pronounced slope) compared to that of the crystalline porphyrin (blue line in Fig. 1c). This may be explained by the fact that CoTPP molecules become more exposed to the effect of the elevated temperature when adsorbed onto the sidewalls of SWNTs, and therefore decompose at a faster rate. Altogether, the TGA results suggest that all four porphyrin species analyzed adsorb onto the surface of SWNTs, resulting in the formation of hybrid nanomaterials. Nevertheless, the highest porphyrin content was found in the CoTPP/SWNT complex, suggesting that due to a strong interaction the CoTPP molecules are capable of intercalating and dispersing the bundles of SWNTs and therefore covering the surface of individual nanotubes. The remaining three porphyrin species were found to be in significantly lower amounts in the corresponding porphyrin/SWNT complexes, suggesting that due to a weaker interaction they are unable to disperse the SWNTs and therefore adsorb onto the surface of SWNT bundles. In other words, the bundles provide a reduced surface area for the adsorption of porphyrins, which might account for the low porphyrin content in the H_2TPP/SWNT, NiTPP/SWNT and hemin/SWNT complexes.

Raman spectral characterization of pristine SWNTs and their complexes with H_2TPP, NiTPP and CoTPP is illustrated in Fig. 2. The full spectrum (Fig. 2a) shows two intense characteristic peaks at 1594 and 2666 cm^{-1}, confirming the presence of SWNTs in all samples. The absence of the D-band (which would normally occur at about 1300 cm^{-1}) indicates that the SWNTs are free of impurities such as amorphous carbon, as well as that the sidewalls were not