Covalent functionalization and characterization of Single-walled carbon nanotubes with Cu (II) complexes of meso-tetra(4-aminophenyl)porphyrin

Vyshnavi T Veetil*, G Prabhavathi* and R Yamuna**

Department of Sciences, Center of Excellence in Advanced Materials and Green Technologies (CoE-AMGT), Amrita School of Engineering, Coimbatore, Amrita Vishwa Vidyapeetham, India

r_yamuna@cb.amrita.edu.

Abstract. 5,10,15,20-tetra(4-aminophenyl)porphyrinatocopper(II) [CuTAP] was covalently linked via amide bond with SWCNTs. Notable changes in the FT-IR spectra reveal the covalent linking of the porphyrin chromophore with SWCNTs. Further, covalent functionalization was confirmed by the hypsochromic shift of this nano-hybrid in the UV-visible spectra as compared to that of pristine CuTAP. 38 % weight loss observed in the TGA due to the extent of Cu-TAP functionalization. Morphology study of this nano-hybrid reveals the tubular structure, which is retained even after covalent functionalization. SWCNT-CuTAP nano-hybrid shows the hypsochromic shift and hypochromic shift compared to reported TAP or Zn-TAP due to Cu metal ion substitution.

1. Introduction

Carbon nanotubes (CNTs) have been extremely employed as a heterogeneous metal catalysts support for the applications of fuel cell and organic synthesis [1,2]. CNTs enhance electron transfer reactions when employed as an electrode material in electrochemical devices [3]. CNTs are categorized as single-walled nanotubes (SWCNTs) and multi-walled nanotubes (MWCNTs). CNTs have many unique mechanical, optical, electrical, and thermal properties. Individual SWCNTs are therefore stronger than steel. Moreover, SWCNTs possess recognizable optical absorption and fluorescence responses. Thermal conductivity of SWCNTs may be comparable to that of diamond or graphite.

Such numerous unique properties of SWCNTs have accompanied many extensive ranges of applications. SWCNTs can be chemically modified to achieve anticipated properties for the wide-ranging of applications. Two chief methods for the chemical modification of SWCNTs are covalent and non-covalent functionalization. The covalent interactions are more stable and accordingly more favourable from an application point of view. Covalent modifications of CNTs introduce defects to the nanotubes with lower electrical conductivity as compared to non-covalent interactions. Therefore, the later can be best suited for a very high conductivity. Immobilization of metalloporphyrins onto CNTs (as solid support) can improve the stability and reactivity [4].SWCNT/porphyrins assemblies have been successfully used as photosensitizers [5]. Functionalized SWCNTs can display very limited toxicity than pristine SWCNTs and can penetrate through the cell membrane and are not immunogenic. Covalently functionalized SWCNT with an electron donor system such as porphyrins
or metallloporphyrins can improve their solubility and also provide greater optical properties [6]. Recently we have reported functionalization of MWCNTs with porphyrins (TAP) and metallloporphyrins (Zn-TAP and Cu-TAP) [7,8]. Varying electronic properties of these nano-hybrids were observed due to metal substitution. Therefore, we would like to study the linear absorption properties of covalently linked 5,10,15,20-mesotetra(4-aminophenyl)porphyrinatocopper(II) [CuTAP] with SWCNTs. Furthermore, porphyrins can also transform the magnetic behaviour of carbon nanotubes. Therefore, Cu-TAP has been employed due to its paramagnetic behavior. Covalently functionalized CuTAP with SWCNT (SWCNT-CuTAP, nanohybrid-A) has been characterized by Fourier transforminfra-red (FT-IR) and UV-visible spectroscopy. Thermal properties of nanohybrid-A has been studied using thermogravimetric analysis (TGA). Morphology of this compound was studied by high-resolution transmission electron microscope (HR-TEM).

2. Experimental Section

2.1. Materials and methods
Copper(II) acetate monohydrate and pyrrole were purchased from Merck. Pyrrole was purified by vacuum distillation. Dry tetrahydrofuran (THF),dimethylsulfoxide (DMSO) and triethylamine(Et3N) were purchased from Sigma Aldrich. The SWCNT–COOH was purchased from Nanoshel (Intelligent Materials Pvt. Ltd., India). Thin SWCNT–COOH with an average diameter of 1-2 nm, 5-15 µm length, and >95 wt% purity were used as received. Cu-TAP was synthesized according to the literature report [8].

2.2. Characterization and instrumentation
TGA was done in the SDT Q600 simultaneous DSC-TGA (heating rate: 5 °C/min, N2 purge: 100 mL/min). FT-IR spectrum was recorded on a Thermo Nicolet, iS10 spectrophotometer (KBr pellet method). Absorption studies were done using SHIMADZU, UV-1800 spectrophotometer. JEOL JEM 2100 HR-TEM instrument was utilized for recording the TEM images of nanohybrid-A.

2.3. Synthesis of SWCNT-CuTAP nano hybrid
100 mg of carboxyl functionalized SWCNTs were refluxed with SOCl2 (50 mL) for 24 h at 70 °C under inert atmosphere with 1 mL of DMF to form SWCNT-COCl. Surplus SOCl2 were removed by using rota-evaporator and the residue was washed with dry THF. Equal amount of SWCNT-COCl (100 mg) and CuTAP (100 mg) were dissolved in DMF (30 mL) and this was heated at 130 °C for 72 h under inert atmosphere in the presence of 2 mL triethylamine (Et3N). This reaction mixture was cooled to room temperature. Rota-evaporator was used to remove excess DMF. In order to precipitate the product 100 mL ether was added into the reaction mixture. Ultracentrifugation was used to separate nanohybrid-A and further filtered through a nylon filter membrane. Purification of the precipitate was done by washing with dry THF (3 mL) and further five times washing with CHCl3. Excess Cu-TAP and other impurities were removed from the residue. Thin layer chromatography (TLC) was utilized to ensure the removal of excess Cu-TAP in the final washing. Removal of Et3N.HCl from the nano-hybrid was done by washing the product with water. Finally, the nano-hybrid was dried under vacuum.

3. Result and discussion

3.1. Synthesis of nanohybrid-A
The synthesis of CuTAP has been done by refluxing TAP with acetate salt of copper in DMSO as reported in the literature [8]. A covalent linkage between CuTAP and SWCNT via an amide bond was achieved by heating CuTAP and SWCNT-COCl in DMF at 130 °C for 72 h under inert atmosphere as shown in scheme 1.

Scheme 1. Covalent functionalization of CuTAP with SWCNTs

Figure 1 represents the FT-IR spectrum of nanohybrid A. FT-IR spectra of SWCNT–COOH and Cu-TAP are also included in the Figure 1 for the comparison. SWCNT–COOH shows characteristic band due to O–H and carbonyl (C=O) stretching frequencies at 3411 cm⁻¹ and 1714 cm⁻¹, respectively. The presence of amide linkage (CO-NH) is confirmed by the disappearance of carbonyl stretching frequency at 1714 cm⁻¹ and appearance of new absorption band at 1633 cm⁻¹. In CuTAP, a single peak appeared at ~ 3386 cm⁻¹ which is due to the N-H stretching of free –NH₂ group. This band was replaced by a broad peak at 3425 cm⁻¹ in nanohybrid-A which is owing to the combined stretching frequency of -NH₂ group and amide bond. A strong band is appeared at 1000 cm⁻¹ in CuTAP and nanohybrid-A that is attributed to the Cu substituted TAP skeletal ring vibration [9]. These prominent changes in the FT-IR, reveal the formation of covalent linking of nanohybrid A.

Figure 1. FT-IR spectra of a) SWCNT-COOH  b) CuTAP and c) nanohybrid-A
The thermal stability of the nanohybrid-A was carried out by TGA as depicted in the Figure 2. TGA plot of SWCNT-COOH and CuTAP are also included in the Figure 2 for comparison. TGA plot of SWCNT-COOH shows 16 % weight loss in the temperature range 40–800 °C which is due to the decarboxylation of the oxidized species [10]. SWCNT-COOH and CuTAP reveal more thermal stability and these compounds display below 20 % weight loss between the temperatures 100-800 °C. Whereas nanohybrid-A reveals ~ 38 % weight loss around the temperature 150-800 °C. This is owing to the loss of CuTAP from the nanohybrid-A that were covalently linked to the SWCNTs [8].

Figure 2. TGA plot of a) CuTAP b) SWCNT-COOH and c) nanohybrid-A

Morphology of SWCNT-CuTAP has been analysed by using HR-TEM. TEM image of SWCNT-CuTAP nano-hybrid has been shown in the Figure 3. As shown in Figure 3, tubular morphology was retained even after Cu-TAP functionalization. Dark spots were seen on the surfaces of the SWCNTs due to the functionalization of Cu-TAP on SWCNTs.

Figure 3. TEM image of nanohybrid-A
Figure 4 represents UV-vis spectra of nanohybrid-A in DMF solvent. CuTAP and SWCNT-COOH spectrum are also included in the figure 4 for comparison. CuTAP reveal fewer Q bands (two peaks, at 500 – 700 nm) compared to TAP (4 bands) due to Cu substitution [8]. Soret peak of CuTAP (425 nm) and nanohybrid-A (422 nm) shows hypochromic shift (blue shift) and further the intensity of this peak is reduced (hypochromic shift) as compared to TAP and Zn-TAP. This is owing to the paramagnetic nature of Cu ion substitution [8]. This shift in the peak specify that difference in the electronic energy level arises which is owing to the various metal ion substitution. The covalent functionalization of CuTAP with SWCNT was confirmed due to the hypochromic shift of nanohybrid-A as compared to CuTAP [8]. The solubility of CuTAP is less compared to TAP and ZnTAP. Moreover, no fluorescent emission peak was obtained for CuTAP and nanohybrid-A which is owing to the paramagnetic nature of copper.

![UV-visible spectra](image)

Figure 4. UV-visible spectra of CuTAP (3.39 X 10^-5 M), nanohybrid-A (4.5 mg/100 mL) and SWCNT-COOH (1 mg/100 mL).

4. Conclusion
CuTAP was successfully connected covalently with SWCNTs via an amide bond. Notable changes in the FT-IR and blue shift in UV-visible spectra of nanohybrid-A compared to pure CuTAP confirms the covalent linkage. 38% weight loss observed in the TGA due to the extent of CuTAP functionalization. Nano hybrid-A shows the hypso- and hypo- chromic shift compared to reported TAP or Zn-TAP due to Cu ion substitution.

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