

# Preparation of Soluble Chitosan Modified Single-Walled Carbon Nanotubes

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**Abstract:** Functionalized carbon nanotubes hold a lot of promise application in many research fields. We covalently linked octadecylamine and chitosan to single-walled carbon nanotubes by a double functionalization method. The functionalized single-walled carbon nanotubes have substantial solubility in organic solutions such as dichloromethane, chloroform or toluene, etc. Fourier transform infrared spectroscopy, Raman spectroscopy, thermogravimetric analysis and transmission electron microscopy were used to analyze the samples, showing an attachment of octadecylamine and chitosan to carbon nanotubes, and end-to-side or end-to-end interconnections among nanotubes.

**Keywords:** single-walled carbon nanotubes; chitosan; modification; soluble

## 1. Introduction

Biological application of carbon nanotubes (CNTs) has started to emerge [1, 2] since their landmark research by Iijima in 1991 [3]. To improve their solubilities, many attempts have been made to functionalize single- or multi-walled carbon nanotubes (SWCNTs or MWCNTs) [4-7]. Bioactive molecule grafted CNTs with improved solubilities could even be used as drug carriers [8-10].

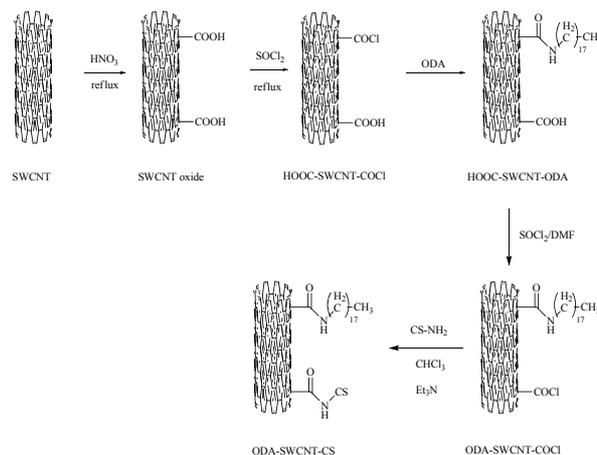
Chitosan (CS) is a kind of controlled releasing carriers [11], and several procedures have also been developed to functionalize CNTs with CS [12-14]. However, with these methods the levels of functionalization are usually not so satisfying. Herein we demonstrated a new approach to double functionalize SWCNTs with octadecylamine (ODA) and CS, and soluble CS/ODA functionalized SWCNTs (ODA-SWCNT-CS) composites could be obtained. Fig. 1 shows the synthetic route of preparing ODA-SWCNT-CS composites.

## 2. Experimental

### 2.1. General

SWCNTs were purchased from Shenzhen Nanotech Port Co., Ltd.. Oxidized SWCNTs were obtained according to the references [15,16]. With the goal of obtaining ODA-SWCNT-CS composites, we carried out a stepwise synthesis technique to functionalize oxidized SWCNT with ODA firstly [15], then with CS.

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**Figure 1. The synthesis route of functionalization of SWCNTs with ODA and CS.**

### 2.2. Functionalization of oxidated SWCNTs with ODA and CS

The oxidized SWCNTs (100 mg) and 20 mL  $\text{SOCl}_2$  were kept in a round bottomed flask and heated to  $75^\circ\text{C}$  for 24 hours. The solution was distilled to remove  $\text{SOCl}_2$  and DMF, then filtered and washed with anhydrous THF, dried at  $60^\circ\text{C}$  under vacuum overnight to gain HOOC-SWCNT-COCl.

The so obtained HOOC-SWCNT-COCl and 3.50 g of ODA was added to the reaction and heated to  $95^\circ\text{C}$  for another 96 hours, the further purification procedure was carried out according to reference [15] to gain HOOC-SWCNT-ODA.

The so obtained HOOC-SWCNT-ODA was mixed with 20 mL  $\text{SOCl}_2$  [containing 1 mL anhydrous dimethylformide (DMF)] and heated to 75 °C for 24 hours. The solution was distilled to remove  $\text{SOCl}_2$  and DMF, then filtered and washed with anhydrous THF, dried at 60 °C under vacuum overnight to gain ODA-SWCNT-COCl.

A mixture of 100 mg ODA-SWCNT-COCl, 800 mg of chitosan, 20 mL of anhydrous chloroform ( $\text{CHCl}_3$ ), 1 mL of anhydrous  $\text{Et}_3\text{N}$  (triethylamine) was heated to 60 °C for 96 h. The solution was treated with 50 mL deionized water and extracted with  $\text{CHCl}_3$ . The organic layer was collected, distilled to remove  $\text{CHCl}_3$ , washed with ethanol (10min sonication at 40 KHz). The remaining solid was dissolved in dichloromethane ( $\text{CH}_2\text{Cl}_2$ ) and centrifugated, the black-colored supernatant was decanted and filtered, the filtrate was distilled to remove  $\text{CH}_2\text{Cl}_2$ , dried at 60 °C under vacuum overnight to gain 60 mg ODA-SWCNT-CS composites.

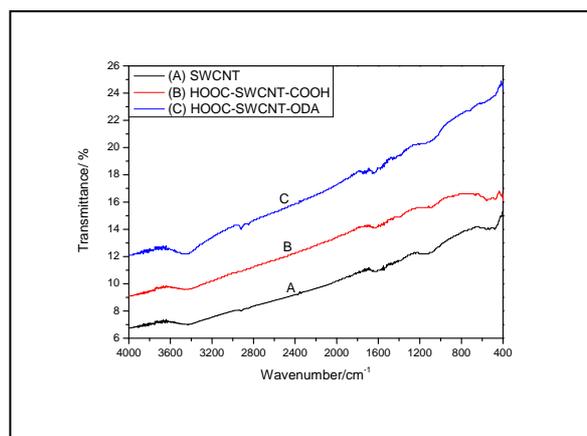
### 2.3. Functionalization of oxidated SWCNTs with ODA and CS

The microstructures of the samples were observed with transmission electron microscopy (TEM) on JEOL JEM-1230 (operated at 100 kV). Fourier transform infrared (FT-IR) spectrum was recorded on Nicolet AVATAR360 FT-IR spectrometer. Raman spectrum was obtained using a Renishaw micro-Raman system 2000 spectrometer operated at a laser wavelength of 514.5 nm generated by an argon laser.

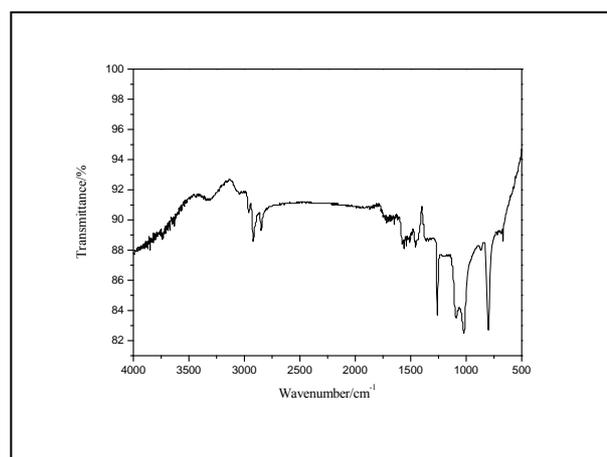
## 3. Results and discussion

FT-IR spectroscopy is one of the powerful analytical tools for the characterization of SWCNT samples [17], and most detailed information of the surface grafted molecules could be provided by the FT-IR observation. Fig.2 shows FT-IR spectrum of pristine SWCNTs, HOOC-SWCNT-COOH, and HOOC-SWCNT-ODA. FT-IR spectrum of HOOC-SWCNT-ODA shows the broad peak at  $3433\text{ cm}^{-1}$  which dues to the O-H and N-H stretch vibration; the new peaks at  $2920$  and  $2948\text{ cm}^{-1}$  ( $\nu(\text{C-H})$  and  $\nu_{\text{as}}(\text{C-H})$ ) of  $-\text{CH}_3$ ,  $1728\text{ cm}^{-1}$  ( $\nu(\text{C=O})$  stretch of the carboxylic acid),  $1637\text{ cm}^{-1}$  ( $\nu(\text{C=O})$  stretch of the amide I),  $1581\text{ cm}^{-1}$  ( $\nu(\text{C=O})$  stretch of the amide II), and  $715\text{ cm}^{-1}$  ( $\nu(\text{CH}_2)$ ,  $-\text{[CH}_2\text{]}_n-$  ( $n \geq 4$ ) of long alkyl group of the attached ODA molecule) are also confirmed. Fig. 3 shows FT-IR spectrum of ODA-SWCNT-CS: the peak at  $3324\text{ cm}^{-1}$  dues to the broad O-H stretch of grafted CS; the peaks at  $2918$  and  $2845\text{ cm}^{-1}$  due to C-H stretch of the alkyl chain; and the ODA-SWCNT-CS composites also show peaks at  $1670\text{ cm}^{-1}$  ( $\nu(\text{C=O})$  stretch of the amide I),  $1695\text{ cm}^{-1}$  ( $\nu(\text{C=C})$  stretch of the SWCNT),  $1567\text{ cm}^{-1}$  ( $\nu(\text{C=O})$  stretch of the amide II),

$1450\text{ cm}^{-1}$  ( $\delta$  (C-H) bend of the alkyl chain),  $1247\text{ cm}^{-1}$ ,  $1091\text{ cm}^{-1}$  and  $1020\text{ cm}^{-1}$  ( $\nu$  (C-O) stretch, which suggest that the primary hydroxyl groups participated partly in the reaction); the characteristic peaks at  $867\text{ cm}^{-1}$  and  $1120\text{ cm}^{-1}$  are two characteristic bands of the glucopyranose rings, respectively. FT-IR spectrum is implying that CS and ODA have been simultaneously attached to the surface of SWCNTs.



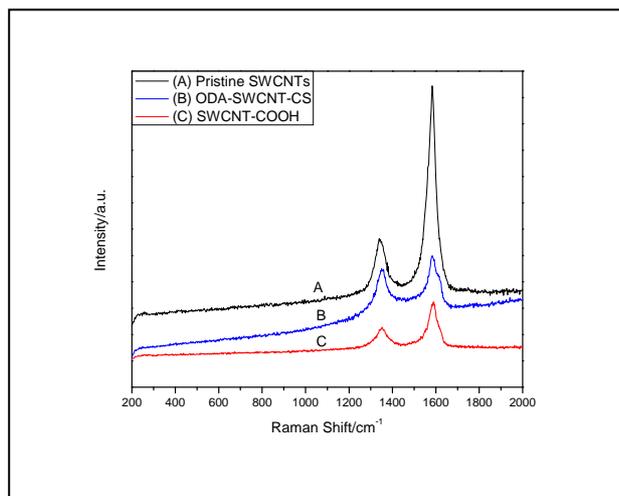
**Figure 2. FT-IR spectrum of SWCNT samples: pristine SWCNT, HOOC-SWCNT-COOH, and HOOC-SWCNT-ODA composites.**



**Figure 3. FT-IR spectrum of ODA-SWCNT-CS composites.**

The structural integrity of the obtained products was further verified by Raman spectroscopy. Fig. 4 shows Raman spectrum for pristine SWCNTs, oxidized SWCNTs and ODA-SWCNT-CS composites. Raman spectrum of the pristine SWCNTs exhibits the characteristic tangential ( $1588\text{ cm}^{-1}$ ) modes of SWCNTs and a relative weaker disorder band ( $1352\text{ cm}^{-1}$ ), indicating the presence of a small number of  $\text{sp}^3$  hybridized carbons within the SWCNTs framework. Significant increases in

the intensity of the disorder band in the SWCNT-COOH and the ODA-SWCNT-CS composites are observed. The increase in the intensity of the disorder band indicates that parts of  $sp^2$  hybridized carbons have been changed into  $sp^3$  hybridized carbons.

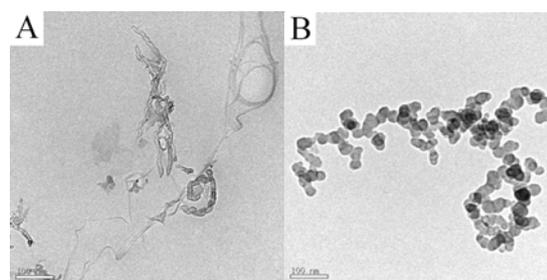


**Figure 4.** Raman spectrum (514.5 nm excitation) of pristine SWCNTs, SWCNT-COOH and the ODA-SWCNT-CS composites.

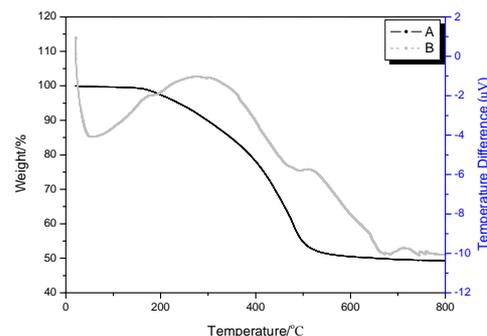
The presence of pristine SWCNTs is observed in the form of bundles, and their surfaces are very smooth (Fig. 5A). In contrast to pristine SWCNTs (Fig. 5A), amounts of organic components can be observed as protuberances in ODA-SWCNT-CS composites after the surface decoration (Fig. 5B). The modified SWCNTs are becoming thicker, indicating that ODA and CS wrap around the nanotubes. End-to-side or end-to-end nanotube interconnections could also be found (Fig. 5B).

The amounts of grafted CS and ODA were determined by thermogravimetric analysis (TGA). The TGA and differential scanning calorimetry (DSC) data were recorded under a flow of  $N_2$  from room temperature up to 800 °C. Four weight-loss regions are observed (Fig. 6): the first section from room temperature to 172 °C is ca. 1.1% and this is mainly attributed to the desorption of weakly bound water from the surface and the inner walls of nanotubes; the second step of mass-loss takes place in the range of 182.1 °C to 288 °C which has relation to decomposition of the grafted ODA and the weight loss is ca. 8.0%; the decomposition reaction in the third step from 288.1 °C to 520 °C is considered as decomposition of grafted CS, and the weight loss is ca. 38.4%; the decomposition reaction in the fourth step from 520.1 °C to 723 °C is considered as decomposition of unreacted residual carbonyl groups of oxidated SWCNTs and the weight loss is ca. 3.0%. TGA further confirms the covalently attachment of CS and ODA.

In contrast to pristine SWCNTs, ODA-SWCNT-CS composites have substantial solubility in dichloromethane, chloroform and toluene. No precipitation was observed upon prolonged standing of the solution of ODA-SWCNT-CS composites. The solubilities of ODA-SWCNT-CS composites in above-mentioned solutions are about 0.5 mg/mL. And in contrast with simultaneously double functionalization of CNTs, the step by step modification is also an effective method to functionalize CNTs [18, 19].



**Figure 5.** TEM images of pristine SWCNT (A) and SWCNT bundles functionalized with ODA and CS (B) (scale bar = 100 nm).



**Figure 6.** The TGA (A) and DSC (B) of ODA-SWCNT-CS composites

## 4. Conclusions

In summary, functionalization of SWCNT using ODA and CS was carried out by a standard stepwise technique. And ODA-SWCNT-CS composites were fully characterized. ODA-SWCNT-CS composites can dissolve in organic solvents (dichloromethane, chloroform, THF and toluene, etc.). Due to their solubilities and attached bioactive molecule moieties, ODA-SWCNT-CS composites may have potential applications in drug delivery as well as other biological applications.

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