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Preparation of semiconductor-enriched single-walled carbon nanotube dispersion using a neutral pH water soluble chitosan derivative

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ABSTRACT

Debundling and selective dispersion of semiconducting single-walled carbon nanotubes (SWNTs) has been demonstrated using a neutral pH water soluble chitosan derivative, N-acetylated chitosan (NACHI), which is synthesized by controlled N-acetylation of chitosan using acetic anhydride. The SWNT–NACHI supernatant solution demonstrated semiconductor-enriched property owing to the preferential adsorption of N-groups of the NACHI on semiconducting nanotubes with a fairly weak charge transfer. The dispersion of nearly individualized SWNTs achieved by surface modification of nanotubes with a biocompatible polymer can be utilized for electronic and biomedical applications such as field effect transistor, biosensor, cell culture medium and SWNT-biomacromolecule hybrid materials.

1. Introduction

Single-walled carbon nanotubes (SWNTs) have drawn great attention of researchers on account of their unique electrical, mechanical, and thermal properties which are significant to various potential technological applications [1–5]. As produced SWNTs exist as large bundles or ropes of 30–50 nm diameters due to the strong intertube van der Waals attraction, along with the hydrophobic property make them insoluble in most of the common solvents and in polymer matrix [6]. As synthesized SWNTs usually contain about 1/3 metallic and 2/3 semiconducting SWNT species. Separation as well as individual solubilization of SWNTs is essential for many of the realistic applications which are particular to one or the other type of nanotubes in order to explore their unique and extraordinary properties. There have been tremendous amount of efforts for the separation, solubilization and hence the processing of SWNTs by means of covalent, noncovalent, ionic or free radical modifications of nanotube surfaces [7–11]. The noncovalent approach is considered to be the most promising technique, because it allows surface modification of carbon nanotubes (CNTs) without much disturbing the π-system of the graphene sheet, therefore it preserves intrinsic electronic structure of the nanotubes [12]. Different types of surfactants, aqueous and organic solutions of polymers have been widely employed for the solubilization and hence processing of CNTs [13–17]. In order to separate semiconducting from metallic tubes, several methods including density gradient induced centrifugation, AC dielectrophoresis, gel electrophoresis, selective adsorption of semiconducting SWNTs on agarose gel, selective electrical breakdown of metallic CNTs, selective flocculation assisted by octadecylamine or porphyrins have been investigated [18–24]. Recently, Cao et al. demonstrated percolation theory based methods to reduce the metallic conduction paths in a random network CNT circuit [25]. The nanotubes dispersed in biocompatible media are of special interest for applications such as biosensor, template for cell culture, SWNT-biomacromolecule hybrid, etc. Various biomolecules, biosurfactants and biopolymers including DNA, proteins, poly(L-lysine), starch, gelatin, steroids and chitosan have shown capability for the effective debundling and individual dispersion of SWNTs in water [26–30].

In this contribution, we present debundling and diameter selective dispersion of small diameter SWNTs possessing semiconductor-enriched property with the assistance of a neutral pH water soluble chitosan derivative. The chitosan, (poly-β-(1–4)-D-glucosamine), is a deacetylated product of chitin and is a naturally abundant polysaccharide. However chitosan has been used for various functional materials, including biomaterials, its applications are limited because of insolubility in water, it can only be dissolved in acidic medium [31,32]. The chitosan has demonstrated capability for dispersing SWNTs in acidic medium and it also has shown tendency to preferentially disperse smaller diameter nanotubes [33,34]. Recently, Zhang et al. reported the debundling and individual dispersion of SWNTs in neutral pH aqueous solutions of chitosan derivatives such as O-carboxymethyl chitosan and O-carboxymethyl chitosan modified with poly(ethylene glycol) [35]. Herein, we demonstrate effective debundling and suspension of

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individual or thin bundles of semiconductor-enriched SWNTs using a neutral pH water soluble chitosan derivative, N-acetylated chitosan (NACHI), which is synthesized by a simple functionalization process reported in literature [31]. The lone pair of electrons on the electron rich N-groups such as amine and amide groups of NACHI plays a vital role in the isolation of SWNTs into thinner bundle or individual tubes as well as selective dispersion of semiconducting nanotubes [24,36]. Compared to unsorted nanotubes, the semiconductor-enriched SWNTs hold great potential for applications such as thin film transistors and display applications owing to their high mobility, high ratio of semiconductor nanotubes, and compatibility for room-temperature processing [37]. The suspension of nearly individualized semiconductor-enriched nanotubes obtained by wrapping with biocompatible polymer opens up new prospects for diverse electrical and biomedical applications including thin film transistors, biosensor, SWNT-biomacromolecule hybrids, cell culture, and drug delivery applications.

2. Materials and methods

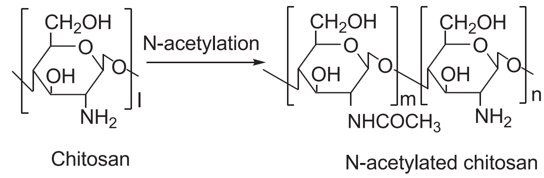
2.1. Materials and instrumentation

The SWNTs synthesized by HiPco process were purchased from Unidym, USA. Low molecular weight chitosan (degree of deacetylation: 75–85%, $M_n = 1.2 \times 10^5$ Da), acetic anhydride, pyridine and sodiumdodecylbenzenesulfonate (SDBS) were purchased from Sigma–Aldrich. Acetic acid, acetone and ethanol were obtained from Samchun chemicals, Seoul, Korea.

A cup-horn type ultrasound sonicator (Sonics, VCX 750, Vibracell™, USA) was used for the preparation of SWNT dispersions. The Fourier transform-infrared (FT-IR) spectra of polymer and SWNT–NACHI samples were recorded on a Nicolet OMNIC 6700 FT-IR spectrometer (Thermo scientific, USA). Scanning electron microscope (SEM) images of SWNT dispersions drop-casted on silicon (Si) substrate were obtained using a LEO SUPRA 55, Genesis 2000 (Carlzeiss instrument, Germany) operated at 1.5 kV. Transmission electron microscope (TEM) image of SWNT supernatant dropped and dried on 400 mesh copper grid (G400, Gilder 400 mesh Grid, Cu, Ted Pella, Inc. CA) was obtained using a JEOL high resolution transmission electron microscope. Atomic force microscope (AFM) images were obtained using a silicon AFM tip with XE-100 instrument (Park system, Korea) in non-contact mode at atmospheric condition. Ultraviolet–visible–near infrared (UV–vis–NIR) absorption measurement was performed using a JASCO-V530 UV–vis–NIR spectrometer (Japan). Raman spectra were recorded on a Dongwoo 320i instrument using 785 nm diode laser beams with 1 s exposure time. The Raman fluorescence spectra were obtained using Raman RXN Kaiser Optical Systems. Inc. (USA) at an exposure time of 10 s at an excitation wavelength of 785 nm. The current–voltage characteristics of thin films were recorded using a Keithley 2612 SYSTEM sourcemeter.

2.2. Synthesis of N-acetylated chitosan

The water soluble chitosan derivative, NACHI, was prepared by controlled N-acetylation of chitosan according to a method previously reported in literature [31]. Briefly, low molecular weight chitosan sample (1 g) was dissolved in 25 mL of 2.8% acetic acid in a flask equipped with a plug, 25 mL of ethanol was added into it and stirred well. Pyridine (approx. 8 mL) was dropped into the mixing solution until the solution became clear. Acetic anhydride (10 mL) was charged into the reaction mixture with continuous stirring. After it was stirred for 4 h at ambient temperature, the reaction mixture was precipitated with ethanol. The precipitate was then washed with excess acetone to remove excess reagents.



Scheme 1. Preparation of water soluble N-acetylated chitosan.

The derivatized chitosan sample was dried overnight at 50 °C in a hot air circulating oven. The degree of deacetylation of the product was estimated to be 49.7 by acid–base titration [31]. Characterization of the derivatized sample was conducted by FT-IR spectroscopy. A schematic representation for the synthesis of water soluble chitosan derivative is shown below (Scheme 1).

2.3. Preparation of SWNT dispersion

In a typical experiment, 30 mg SWNTs were immersed into 100 mL aqueous solution of NACHI (5 mg/mL) and ultrasonicated using a cup-horn type ultrasound sonicator at 200 W for 10 min and 540 W for 30 min. The temperature of sonication bath was maintained below 10 °C by putting ice to avoid structural damages which may occur due to excessive heating effects. The dispersion was then centrifuged at 15,000 rcf (relative centrifugal force) for 5 h to remove aggregates and bigger bundles. The greenish colored supernatant solution was carefully collected. A reference sample was prepared using aqueous solution of an anionic surfactant, SDBS, under the same experimental conditions. Characterizations of the SWNT dispersions were carried out by SEM, TEM, AFM, UV–Vis–NIR absorption spectroscopy, Raman spectroscopy and by electrical measurements.

3. Results and discussion

3.1. Characterization of N-acetylated chitosan

To confirm the functionalization, FT-IR spectra of pristine chitosan and NACHI samples were recorded using KBr pellet in transmittance mode. Fig. 1 shows that the characteristic absorption bands of chitosan corresponding to $-CO-NH_2$ vibrations at 1655 and 1592 cm^{-1} became more enhanced when the chitosan was functionalized with acetic anhydride. Furthermore, the band II of amide group at 1592 cm^{-1} marked noticeable enhancement and a peak shift towards lower wave number region (1558 cm^{-1}), which indicate that the functionalization has been occurred at the amino groups of chitosan. N-acetylation causes destruction of intermacromolecular hydrogen bonds and interchain hydrogen bonds, which alter the secondary structure of chitosan, decreasing its crystallinity and unfolding its molecular chains, which in turn improve the solubility of NACHI in water [31].

3.2. Characterization of SWNT–NACHI dispersion

The characterization and evaluation of SWNT–NACHI dispersions were carried out in comparison with a reference sample prepared using an anionic surfactant SDBS under the same experimental conditions. Optical photograph of SWNT dispersions, which are used in this study, are shown in Fig. 2. The SWNT–NACHI supernatant has a greenish color, while the uncentrifuged SWNT–NACHI dispersion and SWNT–SDBS supernatant are black colored. The greenish coloration is due to the supernatant mainly consists of smaller diameter nanotubes, which is reflecting the separation of SWNTs [20].