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Functionalization of single-walled carbon nanotubes with *N*-[3-(trimethoxysilyl)propyl]ethylenediamine and its cobalt complex

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Abstract

The reaction of *N*-[3-(trimethoxysilyl)propyl]ethylenediamine with fluorinated carbon nanotubes (F-CNT) produced the corresponding aminoalkylalkoxysilane functionalized carbon nanotubes. Cobalt salt is then complexed to this functionalized carbon nanotubes by the addition of cobalt chloride to form cobalt complexed nanocomposite in high yield. This composite and precursors were characterized by using Fourier transform infra-red spectroscopy (FTIR), transmission electron microscopy (TEM), energy dispersive spectral (EDS) and thermal gravimetric analysis (TGA). The nanoparticulate metal complexes of functionalized carbon nanotubes generate new nanostructure with several practical applications. The reaction of *N*-[3-(trimethoxysilyl)propyl]ethylenediamine with cobalt (II) chloride salt afford the cobalt complex nanoparticles, with particle sizes less than 10 nm.

Keywords

Carbon nanotubes (CNTs); Nanostructures; Thermogravimetric Analysis

1. Introduction

Synthetic biodegradable polymers are generally used in making scaffolds for bone tissue engineering but lack the desired mechanical properties especially when used in scaffolds of high porosity for guided bone growth under load bearing conditions.

Ceramics such as bioglass (Na₂O–CaO–SiO₂–P₂O₅), wollastonite, sintered hydroxyapatite (HAP) and sintered beta tricalcium phosphate (TCP) are known to bond to living bone. Unfortunately, their fracture toughness and elastic moduli are, respectively, lower and higher than those of human cortical bone. Bioactive materials with mechanical properties analogous to those of the human cortical bone are of great promise, especially in load bearing bone. Single walled carbon nanotubes (SWCNTs) have shown extremely high mechanical properties and aspect ratio [1–3]. Therefore, using SWCNTs as reinforcement agent in bioglass and ceramic should enhance the mechanical properties of bioglass while retaining bioactivity. The major

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challenge as mechanical reinforcement for SWCNTs is to overcome its tendency to aggregate due to van der Waals interactions and the π - π stacking, which usually leads to formation of large bundles of SWCNTs and poor dispersion, particularly more pronounced in inorganic matrixes, such as ceramics. Two of the key challenges in realizing the full potential of multifunctional nanocomposites based on carbon nanotubes are securing a reliable control over their surface chemistry, and achieving monodispersity in terms of length, diameter and helicity [4–5]. Several techniques are being employed to overcome the difficulties with regards to incorporation of carbon nanotubes in structural and functional ceramics, through covalent, electrostatic or non-covalent modification. Such techniques include coating CNTs with materials that eliminates the van der Waals interactions like hot pressing of nanoparticles of SiC with carbon nanotube [6–9]. In this paper, we present the side-wall functionalization of SWCNTs with *N*-[3-(trimethoxysilyl)propyl]ethylenediamine, and its chelation with cobalt salt to form SWCNT–cobalt complexed nanocomposite material.

2. Experimental section

2.1. Materials

The fluorinated SWCNTs (F-SWCNTs) were provided by Dr. Valery Khabashesku (RICE University) and characterized by elemental analysis and thermogravimetric analysis. The thermogravimetric, TGA and elemental analysis on the fluoro nanotubes confirmed about 20% side-wall functionalization of carbon nanotubes with fluoride. The following chemicals cobalt chloride hexahydrate, ($\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$) and *N*-[3-(trimethoxysilyl)propyl]ethylenediamine, (TPED) were obtained from Aldrich and were used as received. Pyridines, acetone (Aldrich) were dried with molecular sieves.

2.2. Instruments and measurements

Fourier transform infrared spectroscopy (FTIR, IR-200 Thermo-Nicolet 2.2) (KBr) in the range of 400–4000 cm^{-1} was used to confirm covalently bound amino group on SWCNT surface. Transmission electron microscopy (TEM) was performed at the Microscopy Laboratory at Texas A&M University on JEOL 6400 SEM @15KV. Thermal gravimetric analysis (TGA) was performed on Universal V3.4C TA instruments. The runs consisted of a ramp at a steady rate of 40°C/min, from 40 to 850°C. All elemental analysis were recorded by Schwarzkopf Analytical Services (NY) or qualitatively from energy dispersive spectral (EDS).

2.3. Preparation of *N* – [3 – (trimethoxysilyl)propyl] ethylenediamine, (TPED) modified single-walled carbon nanotubes

The F-SWCNT (80.0 mg) was charged into a round bottom flask followed by the addition of the functionalizing reagent, in excess (3.0 ml) and the Pyridine (2.0 ml) was added to the reaction flask. The mixture was heated in a closed tube at 120 °C for 24 h. After cooling, the mixture was filtered through a 0.2 μm membrane filter under vacuum. The black residue obtained was washed several times with large excess of acetone and then dried at 100 °C for 24 h, to yield TPED-SWCNTs, **1**. To 10 mg of **1** was added 50 mg of cobalt chloride in THF and stirred at room/or hydrothermal to yield brown solid **2**, the cobalt complex of the functionalized SWCNT. The reaction of cobalt (II) chloride with *N*-[3-(trimethoxysilyl)propyl] ethylenediamine without the SWCNT was also carried out for comparison to yield compound **3**. All of the compounds were characterized by TGA, FTIR and TEM.

3. Results and discussion

Scheme 1 summarizes the reactions leading to products **1**, **2** and **3**, respectively. The reaction of fluorinated carbon nanotubes (F-CNT) with *N*-[3-(trimethoxysilyl)propyl]ethylenediamine

was carried out following a slight modification of a general procedure reported in the literature [10].

3.1. FTIR

The infrared spectrum (IR) for the F-SWCNT (not shown) is characterized by a vibration mode at 1220 cm^{-1} indicative of the C–F vibration with no other so obvious vibration [11]. The FTIR of **1** shows CH_2 stretching vibrations centered around 2955 cm^{-1} (Fig. S2). The stretching vibrations of the vicinal silanol groups overlap the NH asymmetric stretching vibration position around 3251 cm^{-1} . The mode at 1559 cm^{-1} corresponding to N–H in plane [12], and the Si–O stretching vibration appears around 1091 and 1006 cm^{-1} [13].

In **2**, the OH deformation peak that appeared at 1052 in **1** seem to have been reduced in intensity, and shifted to lower wave number, while the NH vibration slightly shifted to higher wave number. Otherwise, no other differentiating features are expressed.

3.2. Thermal analysis

The comparative TGA and DSC analysis of **1** and **2** are shown in Fig. 1 (and 3 is shown in Supplementary Fig. S1). In **3**, which contain only the cobalt complex without carbon nanotubes, 3–4 stepwise weight losses are observable with associated heat flow. The initial weight loss (24%) commenced from room temperature to about 250°C and associated with an endothermic peak around 250°C . This weight loss is associated with loss of volatile materials and condensation products of the triethoxysilane to produce diethyl ether, ethanol, and water. Comparative TGA of sample prepared hydrothermally, where presumably all of the alkoxy silane groups were either converted to silanol groups or siloxane, showed reduced weight loss in this region (12%) and mostly from loss of water. The second weight loss commenced from 250 to 350°C (approx. 8%), and associated with this is a very sharp endothermic peak around 350°C , likely due to loss of propyl linkage group, followed by a third weight loss from 350 to 670°C (approx. 28%) with two endothermic peaks, one at 420°C , and the other at 630°C . The weight losses are likely due to the total loss of the hydrocarbon and nitrogen groups, and possible phase change to produce a metal salt or combination of cobalt–silicate system. The latter endothermic peak is likely the heat change associated with phase change. The residual weight of about 40% primarily is composed of this product. The comparison of TGA of the fluoro-CNTs precursor to the TGA of **1** allows us to estimate 12–15% side-wall functionalization of the CNTs.

3.3. Transmission electron micrograph

The TEM and EDS analysis of **1** and **2** confirms the functionalization of the sidewall of the carbon nanotubes and the presence of cobalt in **2**. In addition to that, the presence of chloride atom in the EDS spectrum of **2** suggests that the other two ligating atoms are likely to be the Cl.

The TEM and EDS analyses of **3** show the images of cobalt complex nanoparticles with particle sizes obviously less than 10 nm , and particle shape appears to be spherical. The EDS agrees with the elements present.

4. Conclusions

Amino alkyl trialkoxysilane functionalized SWCNTs are synthesized via reaction of F-SWCNTs with the amino alkyl functionalizing reagents. The uniform dispersion of these functionalized SWCNTs in ceramics to form monolith has also been accomplished. These nanocomposite materials that incorporate superstrong lightweight carbon nanotube structures

into inorganic matrix (bioglass) are an attractive approach to design of high performance composite materials with superior mechanical properties.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgements

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Fig. 1. SWCNT-diaminosilyl compound **1** in dashed line, while in bold is the SWCNT-diaminosilyl-Co complex compound **2**.

Fig. 2.
TEM and EDS of **1**.

Fig. 3.
TEM and EDS of **2**.

Fig. 4.
TEM of Cobalt-*N*-[3-(trimethoxysilyl)propyl]ethylenediamine.

Scheme 1.