Progress in Organic Coatings 77 (2014) 679–684

Contents lists available at ScienceDirect

Progress in Organic Coatings

journal homepage: www.elsevier.com/locate/porgcoat

A facile, efficient, and rapid covalent functionalization of multi-walled carbon nanotubes with natural amino acids under microwave irradiation

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ARTICLE INFO

Article history:
Received 10 January 2013
Received in revised form
13 November 2013
Accepted 9 December 2013
Available online 27 December 2013

Keywords:
Carbon nanotubes
Amino acids
Functionalization
Electron microscopy
Thermogravimetric analysis

ABSTRACT

Covalent surface functionalization of multi-walled carbon nanotubes (MWCNT)s with different natural amino acids was successfully carried out under microwave irradiation. The process is fast, one-pot, simple and resulted in a high degree of functionalization as well as dispersibility in organic solvents. Surface functionality groups and morphology of MWCNTs were analyzed by Fourier transform infrared spectroscopy, diffuse reflectance ultraviolet–visible spectroscopy, thermogravimetric analysis, X-ray diffraction, field emission scanning electron microscopy, and transmission electron microscopy. The results consistently confirmed the formation of amino acid functionalities on MWCNTs which is available for further chemistry, while the structure of MWCNT has remained relatively intact. These results illustrate a direct pathway to functionalize MWCNTs for building nanostructures. The amino acid-functionalized MWCNTs could be easily dispersed in common organic solvents.

1. Introduction

There is currently great interest in the potential use of carbon nanotubes (CNT)s and other carbon nanomaterials in biomedical and engineering applications [1]. This interest is due to the stable cylindrical surface morphology of CNTs and their unique electronic, mechanical, and thermal properties as well as chemical stability of these materials [2,3]. However, native multi-walled CNTs (MWCNT)s have poor solubility and biocompatibility. In order to improve solubility in physiological solutions, processing, and selective binding affinity to biotargets, these carbon nanomaterials need to be surface-functionalized with conjugating molecules such as amino acids, peptides, proteins, lipids, carbohydrates, nucleic acids, and polymers [4–8]. To date, various approaches for functionalization of CNTs have been proposed due to the recent expansion and availability of chemical modification and bio-functionalization methods with the aim of 'bottom-up' nanoscale device constructions. There are also several comprehensive review papers that describe the chemistry of functionalized CNTs and the reaction mechanisms between the CNTs and functional groups [9–12]. These methods can be conveniently divided into chemical functionalization and physical methods based on the interactions between the active molecules and carbon atoms on the CNTs. Some conventional methods such as sonication and mixing have already employed. A simple chemo-mechanical method was used to achieve in situ amino functionalization of CNTs using ball milling [13,14]. Some useful functional groups, like amine and amide terminals, were attached onto the CNT surface after milling, allowing covalent bonding to polymers and biological systems. Sidewall functionalization of CNTs including cycloaddition, such as Diels–Alder reaction, carbene and nitrene addition [15,16], fluorination, chlorination, bromination [17,18], hydrogenation [19], azomethine ylides [20], have also been successfully employed in recent years. All these methods can be regarded as the derivative of sidewall functionalization. Defect functionalization is another method for covalent functionalization of CNTs. The defects on CNTs created by oxidants are stabilized by bonding with carboxylic acid (—COOH) or hydroxyl (—OH) groups. These functional groups have rich chemistry and the CNTs can be used as precursors for further chemical reactions, such as silanation [21], polymer grafting [22], esterification [23], thiolation [24], alkylation and arylation [25] and even some biomolecules [26]. The CNTs functionalized in this way are soluble in many organic solvents because the hydrophobic nature

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http://dx.doi.org/10.1016/j.porgcoat.2013.12.003

of CNTs is changed to hydrophilic one due to the attachment of polar groups. However, these methods are often time-consuming, comprising multiple steps. Therefore, development of simple and cost-effective chemical methods for covalent functionalization of CNTs has become an important area of research both from fundamental and application standpoints. In recent years, the microwave irradiation is suggested as a simple, inexpensive and rapid approach for functionalization of CNT [27–29]. This method also resulted in lower structural defects on CNTs surface compared with the conventional methods [30].

Based on the above considerations, we aim to exploit an easy and feasible method to form amino acid-functionalized multi-walled CNTs (MWCNT)s by amino-functionalization with seven different amino acids [L-leucine (Leu), L-isoleucine (Ile), S-valine (Val), L-alanine (Ala), S-methionine (Met), L-phenylalanine (Phe), and L-tyrosine (Tyr)] in a one-pot procedure. The MWCNTs samples were characterized from the viewpoint of functionality and morphology.

2. Experimental

2.1. Materials

Carboxyl-modified MWCNT (purity > 95% and carboxyl content 2.56 wt.%) used in this study was purchased from Neutrino Co. (Iran), have outer diameters of 8–15 nm and lengths of ~50 μm. Natural L-α-amino acids were purchased from Merck Chemical Co. (Germany). N,N′-dimethylacetamide (DMAc) (d = 0.94 g cm^{-3} at 20 °C) were distilled over barium oxide under reduced pressure. Other reagents were obtained commercially and were used without further purification.

2.2. Methods

The apparatus used for the MWCNT functionalization was a Samsung microwave oven (2450 MHz, 900 W) (Korea). Fourier transform infrared (FT-IR) spectra of the MWCNTs were recorded with a Jasco-680 (Japan) spectrometer [taken in potassium bromide (KBr)] at a resolution of 4 cm^{-1} and they were scanned at wavenumber range of 400–4000 cm^{-1}. Band intensities are assigned as weak (w), medium (m), strong (s), and broad (br). Vibration bands were reported as wavenumber (cm^{-1}). Diffuse reflectance ultraviolet–visible (DRUV) measurements were done with a Jasco-V-570 spectrophotometer (Japan) at room temperature. Thermal stability of the MWCNTs was evaluated by recording thermogravimetric analysis (TGA)/derivative thermogravimetric (DTG) traces (STA503 win TA TGA, Germany) in nitrogen atmosphere (flow rate 60 cm^3/min). A heating rate of 10 °C min^{-1} was used in each experiment. The X-ray diffraction (XRD) was used to characterize the crystalline structure of the MWCNTs. XRD patterns were collected using a Bruker, D8AVANCE (Germany) diffractometer with a copper target at the wave length (of) λ Cu Kα = 1.54 Å, a tube voltage of 40 kV, and tube current of 35 mA. The samples were scanned at a rate of 0.05°/min from 10° to 80° of 2θ. For XRD studies rectangular pellets prepared by compression molding were used. The morphology of the functionalized MWCNTs was observed using field emission scanning electron microscopy (FE-SEM). The images were taken at 15 kV using a HITACHI S-4160 instrument (Japan). Images were obtained from powders dispersed on conducting tape. Transmission electron microscopy (TEM) micrographs were obtained using a Philips CM 120 (Netherlands) microscope with an accelerating voltage of 100 kV. For TEM studies, ultrathin sections (30–80 nm) of the composites were prepared using Leica Ultramicrotome. Ultrasonic irradiation was carried out on a MISONIX ultrasonic XL-2000 SERIES, USA with the probe of the ultrasonic horn immersed directly in the mixture solution system with frequency 2.25 × 10^4 Hz and the power of 100 W.

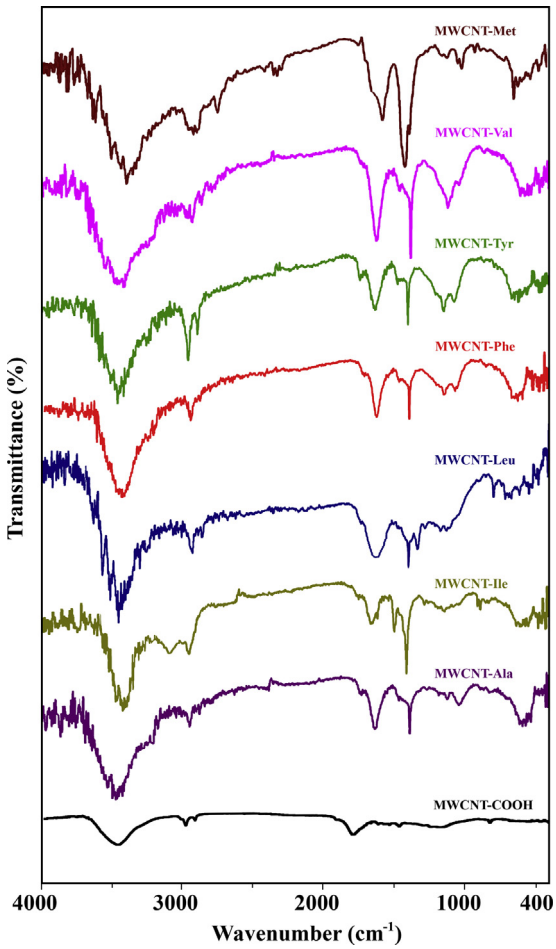

Fig. 1. FT-IR spectra of carboxyl and amino acid-functionalized MWCNTs.

2.3. Amino acid functionalization of MWCNTs

Fig. 1 shows the schematic diagram of functionalization procedure of MWCNTs with amino acids. Regarding amino acid-treated MWCNTs, each amino acid (200 mg) was mixed with DMAc (20 ml) for 2 h at 60 °C. The pristine carboxylated MWCNTs (100 mg) and $NaNO_2$ (100 mg) were sonicated with 20 ml DMAc solution for 2 h until a homogeneous suspension was obtained. The MWCNTs suspension was then poured into a porcelain dish (50 ml), and placed in a domestic microwave chamber. The abovementioned MWCNTs suspension was heated in microwave up to 120 °C for 15 min with output power of 700 W. Then the resulting suspension was cooled to room temperature and then poured into 200 ml HCl solution (5%, v/v). The mixture was stirred for 30 min at room temperature and then decanted to remove the solvent. When the amount of solvent became about 20 ml, the mixture was subjected to irradiation with high-intensity ultrasound for 1 h. The obtained homogeneous suspension was placed in an 80 °C oven overnight to evaporate most of the solvent. The filtration products was washed more than 7 times with DMAc and water for the removal of any unreacted residue amino acids and then dried for 48 h at 50 °C.

3. Results and discussions

A series of natural amino acids were explored to react with MWCNTs (Scheme 1). A condensation reaction occurred between