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Spectroscopic studies on sidewall carboxylic acid functionalization of multi-walled carbon nanotubes with valine

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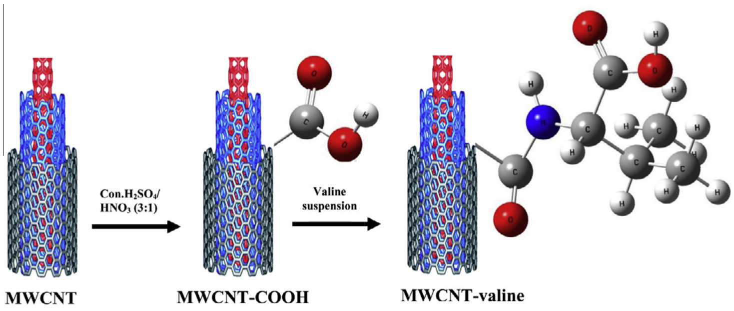
HIGHLIGHTS

- The convenient and simple method for sidewall carboxylic acid functionalization of MWCNTs with valine was demonstrated.
- The enhanced XRD peak (002) intensity was observed for valine functionalized MWCNTs.
- The blue shift was observed in the UV–Vis spectra of valine functionalized MWCNTs.
- The EPR absorption spectral data were found to be best fit for the Gaussian lineshape.
- SEM images show that the increase in the diameter of the MWCNTs was observed for valine functionalized MWCNTs.

GRAPHICAL ABSTRACT



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ABSTRACT

The valine functionalized multi-walled carbon nanotubes (MWCNTS) were prepared and characterized by using XRD, UV–Vis, FT-IR, EPR, SEM, and EDX, spectroscopic techniques. The enhanced XRD peak (002) intensity was observed for valine functionalized MWCNTs compared with oxidized MWCNTs, which is likely due to sample purification by acid washing. UV–Vis study shows the formation of valine functionalized MWCNTs. FT-IR study confirms the presence of functional groups of oxidized MWCNTs and valine functionalized MWCNTs. The ESR line shape analysis indicates that the observed EPR line shape is a Gaussian line shape. The *g*-values indicate that the systems are isotropic in nature. The morphology study was carried out for oxidized MWCNTs and valine functionalized MWCNTs by using SEM. The EDX spectra revealed that the high purity of oxidized MWCNTs and valine functionalized MWCNTs. The functionalization has been chosen because, functionalization of CNTs with amino acids makes them soluble and biocompatible. Thus, they have potential applications in the field of biosensors and targeted drug delivery.

Introduction

Carbon nanotubes (CNTs) are a newly discovered form of crystalline carbon, which forms cylinders of carbon having a diameter in the nanometer scale and a variable length [1]. The functionalization of CNTs is an actively discussed topic in contemporary nanotube literature since the modification of CNTs properties is

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believed to open the road toward real nanotechnology applications [2–7]. Due to their exceptional combination of mechanical, thermal, chemical, and electronic properties, MWCNTs are considered as unique materials, with very promising future applications, especially in the field of nanotechnology, nanoelectronics, composite materials and as well as in medicinal chemistry [8–21]. The researchers are still far from considering CNTs as entities easy to integrate into organic, inorganic, or biological systems. One of the most powerful approaches to improve CNTs handling is the carboxylic acid functionalization of their sidewalls, which enables chemical bonding between the MWCNTs and the material of interest [22]. The mixture of sulfuric acid/nitric acid or nitric acid can be used to form carboxylic acid groups on the surface of CNTs. The introduction of carboxylic acid groups to CNTs by oxidative procedures gives useful sites for further modifications as they enable the covalent coupling of molecules through the creation of amide and ester bonds. The presence of carboxylic acid groups in the CNTs leads to a reduction of van der Waals interactions between the CNTs, which strongly facilitates the separation of CNTs bundles into individual nanotubes [4]. Functionalization of CNTs with the assistance of biological molecules remarkably improves the solubility of nanotubes in aqueous or organic environment and, thus, facilitates the development of novel biotechnology, biomedicine, and bioengineering [23]. The functionalized MWCNTs can have higher sensitivity and better response towards electrochemical detection than pristine MWCNTs [24]. Ilie et al. reported that MWCNTs functionalized with nicotinamide leads to significant insulin production compared with individual administration of nicotinamide representing nanomediated treatment of diabetes mellitus [25]. Meng et al. reported that antitumor response can be increased by conjugating a tumor lysate protein to MWCNTs [26]. A novel biomaterial-MWCNT-chitosan-phycocyanin prepared by functionalizing MWCNTs with chitosan and conjugated to phycocyanin for photodynamic and photothermal cancer therapy were tested on breast and liver cancer cells. Liu et al. reported that the biomolecule-functionalized MWCNTs are expected to be more selective than untreated and oxidized-MWCNTs for the solid-phase extraction of metal ions. Functionalized CNTs are promising novel materials for a variety of biomedical applications. The potential applications of MWCNTs are particularly enhanced by their ability to penetrate biological membranes [27].

Amino acids are components of peptides, indispensable compounds in the life process and can also reflect the common chemical properties of complicated biomolecules. So, the interaction between CNTs and amino acid is very important for understanding the interaction mechanism between CNTs and biomolecules [28,29]. Valine is an essential branched chain amino acid, important for smooth nervous system and cognitive functioning. Valine is particularly important for gall bladder and liver function, as well as balancing nitrogen levels in the body. Valine enhances energy, increase endurance, and aid in muscle tissue recovery and repair. Valine also lowers elevated blood sugar levels and increases growth hormone production [30,31]. Valine functionalized MWCNTs has been researched because Valine has a high reactivity and wealth of chemistry. The aim of the present work is to develop a relatively simple and effective process of functionalizing MWCNTs with amino acids and carry out the characterization study. Here we report, the preparation and characterization of oxidized MWCNTs and valine functionalized MWCNTs. The characterization work has been extensively carried out by using X-ray diffraction (XRD), ultraviolet–visible (UV–Vis), Fourier transform infrared (FT-IR), electron paramagnetic resonance (EPR), scanning electron microscopy (SEM), and energy dispersive X-ray (EDX) techniques.

Materials and methods

The MWCNTs was purchased from Aldrich Chemical Co, St. Louis, MO, USA. Valine, H_2SO_4, and HNO_3 were purchased from Merck, Germany.

Sample preparation

Oxidized MWCNTs

Pristine MWCNTs were mixed with a mixture of 3:1 concentrated sulfuric and nitric acid and sonicated for 3 h at 40 °C in an ultrasonic bath to introduce carboxylic acid groups on the surface of MWCNTs. After sonication the mixture was added dropwise to cold distilled water and the resulting samples, oxidized MWCNTs were filtered and dried in vacuum at 80 °C for 4 h [32].

Valine functionalized MWCNTs

The oxidized MWCNTs were mixed with 0.3 M valine suspension and sonicated for about 1 h at room temperature. After sonication the oxidized MWCNTs/valine suspension was directly filtered and the solid sample was dried in a vacuum for about 16 h at room temperature [33]. In the similar way, valine functionalized MWCNTs (0.6 and 0.9 M concentration of valine) were also prepared. Fig. 1 shows the scheme for the synthesis of oxidized MWCNTs and valine functionalized MWCNTs.

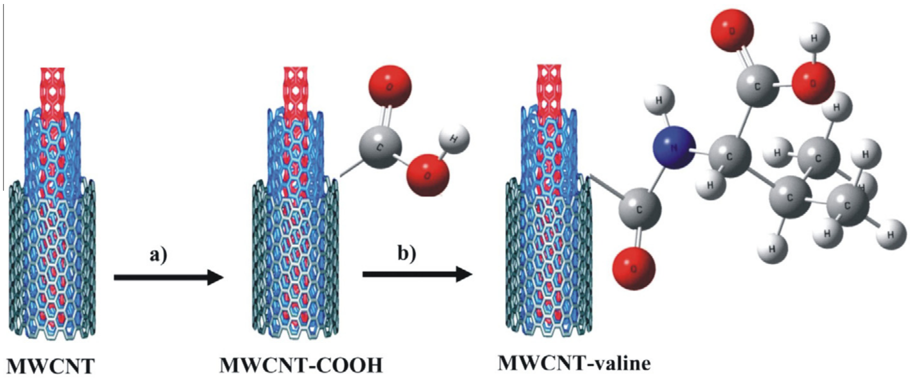

Fig. 1. Scheme for the synthesis of valine functionalized MWCNTs (a) pristine MWCNTs was mixed with (H_2SO_4/HNO_3 (3:1), sonicated for 3 h and the mixture was added to cold distilled water. The samples were filtered and dried in vacuum at 80 °C for 4 h. (b) The oxidized MWCNTs was mixed with valine suspension, sonicated for 1 h at room temperature. The samples were filtered and dried in vacuum at room temperature for 16 h.