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Structural and optical properties of functionalized multi-walled carbon nanotubes

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ABSTRACT

Herein, we report the functionalization of multiwalled carbon nanotubes (MWCNTs) using *meta*-Chloroperoxybenzoic acid (*m*CPBA) as an oxidizing agent. Epoxy groups are incorporated into the sidewall of MWCNTs and the prepared functionalized multiwalled carbon nanotubes (F-MWCNTs) were characterized using FT-IR spectroscopy, X-ray diffraction, Raman spectroscopy and UV–visible spectroscopy. Morphology of MWCNTs and F-MWCNTs was determined using Scanning electron microscopy (SEM) and transmission electron microscopy (TEM). TEM results clearly indicated that the diameter of F-MWCNTs is increased by 120% as compared to neat MWCNTs. From UV–visible spectroscopy data, band gap of F-MWCNTs was calculated using Tauc equation and it was found to be 3.9 eV. Photo emission property of F-MWCNTs was analyzed using photoluminescence spectroscopy. F-MWCNTs showed nice emission in the visible region and it depended upon the excited wavelength. These functionalized carbon nanotubes could find use as tunable optoelectronic devices in future nanotechnology.

1. Introduction

Carbon nanotubes (CNTs) have been attracting much attention from the researchers and industrialists for the last few years because of its diverse applications in various fields such as polymer nanocomposites [1–19], electronic, gas sensors [20–47], functional materials with excellent electronic and optical properties [48–59]. Moreover, recent years of research have given a powerful witness which emphasizes that CNTs are being used as 1D nanofillers in polymer nanocomposites. Many of these reports revealed remarkable applications of hybrid nanocomposites as compared to the conventional materials especially in terms of modulus and strength. Carbon nanotubes are made up of hexagonal ring structures of carbon atoms in which each carbon atom undergoes sp^2 hybridization and thus having one free pure p_z electron. It can easily undergo delocalization leading to the formation of double bond character between adjacent carbon atoms present in the hexagonal ring. As a consequence, the reactivity of CNTs towards chemical reagents is almost similar to the alkenes (olefins) chemistry. However, due to their inherent solubility in various organic and inorganic solvents, the applications of MWCNTs in practical use are limited to a certain extent. In this regard, extensive studies, including covalent and non-covalent functionalization of CNTs have been carried out to improve the compatibility with other organic or inorganic components for diverse applications [60–66] and to promote the practical applications of CNT based materials. The main discrepancy between covalent and non-covalent functionalization is that the original properties of CNTs were not altered by non-covalent modification. However, certain properties mainly the electrical conductivity of CNTs can be decreased by covalent functionalization owing to the interruption of conjugation by functional moieties. On the other hand, the inherent structural properties of pristine CNTs were not altered by non-covalent functionalization. Core amount of work has been devoted to decorating the epoxy groups on the sidewall of the CNTs [67–72] using various organic reagents. However, the optical properties like photoluminescence and band gap calculations of CNTs were lacking in those reports. *Meta*-Chloroperbenzoic acid is a commercially available and efficient epoxidizing agent for olefins. Trakakis et al. [72] reported the epoxidation of MWCNTs using *m*CPBA; nevertheless, they did not reveal the involvement of epoxy groups in tuning the band gap and optical properties.

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In this work, epoxy functionalized MWCNTs were prepared using *m*CPBA and confirmed the structural characterization of F-MWCNTs using FT-IR, X-ray, UV–visible and Raman spectroscopy. For the first time optical properties such as band gap and photo emission behavior of epoxy functionalized MWCNTs were discussed in detail in connection with functionalization process.

2. Materials and experimental methods

MWCNTs ($\geq$90%) were obtained from Nano shell Company Belgium, *meta*-Chloroperbenzoic acid (*m*CPBA) ($\leq$77%), Dichloromethane (DCM) ($\geq$99%) and Dimethylformamide (DMF) ($\geq$99%) were procured from Sigma Aldrich.

2.1. Fourier transform spectroscopy (FT-IR)

Shimadzu IR prestige 21 FT-IR spectrometer with ZnSe attenuated total reflectance (ATR) attachment was used between a frequency range of 4000–500 cm^{-1}. All the spectra were baseline corrected using IR solution software Shimadzu.

2.2. Raman spectroscopy

Bruker Senterra dispersive Raman microscope spectrometer was used with a laser excitation wavelength of 532 nm. All peaks are normalized using spectrum software prior to analysis of the data.

2.3. Wide angle X-ray diffraction (XRD)

XRD analysis was carried out to understand the change in nanostructures of MWCNTs and F-MWCNts using D8-Advance of Bruker (Germany) using CuKα radiations, in a 2θ range of 5–40°. The energy of the radiation was 8.04 keV and wavelength of 1.54 Å.

2.4. Scanning electron microscopy (SEM)

Scanning electron microscope model JEOL (JSM-6390) with an accelerating voltage of 15 kV was used to understand the morphology of both MWCNTs and F-MWCNTs.

2.5. Transmission electron microscopy (TEM)

The morphology of MWCNTs and F-MWCNTs was analyzed by TEM (JEOL). MWCNT powder (1 mg) was sonicated using a bath sonicator for 5 min in water as solvent and then drop cast on TEM grid prior to analysis. The elemental analysis was done using Oxford INCA x-sight energy-dispersive X-ray spectroscopy (EDX) system.

2.6. UV–visible spectroscopy

Absorption spectra were recorded on a JascoV-650 spectrometer; samples (1 mg/3 ml) were dissolved in DMF solvent prior to analysis.

2.7. Photoluminescence spectroscopy

Horiba scientific Fluromax-4spectrometer was used to evaluate the emission spectra of F-MWCNTs. The sample preparation was same as in the case of absorption spectra.

2.8. Preparation of functionalized carbon nanotubes

MWCNT powder (250 mg) was added to DCM (50 ml) in a round bottom flask (RBF). After dispersing the MWCNTs powder in DCM, *m*CPBA (1.5 g) was slowly added to the reaction mixture and the stirring was continued up to 24 h. Next, the solid was filtered using Whatman filter paper from the reaction mixture and washed with sodium bicarbonate (1.5 g) solution. The black solid obtained was dried in a hot air oven at 40 °C.

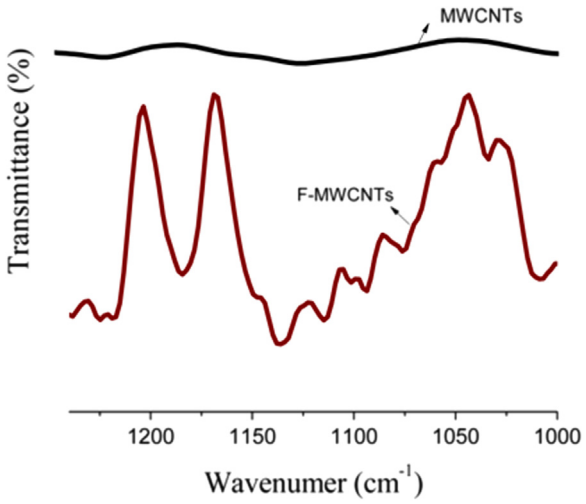

Fig. 1. FT-IR spectra of neat MWCNTs and F-MWCNTs.

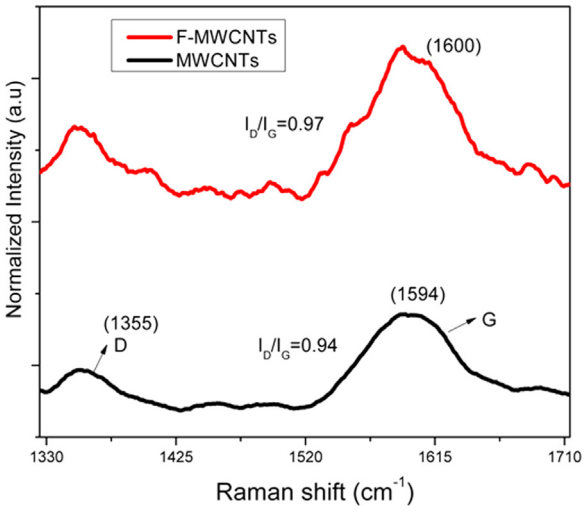

Fig. 2. Raman spectra of neat MWCNTs and F-MWCNTs.

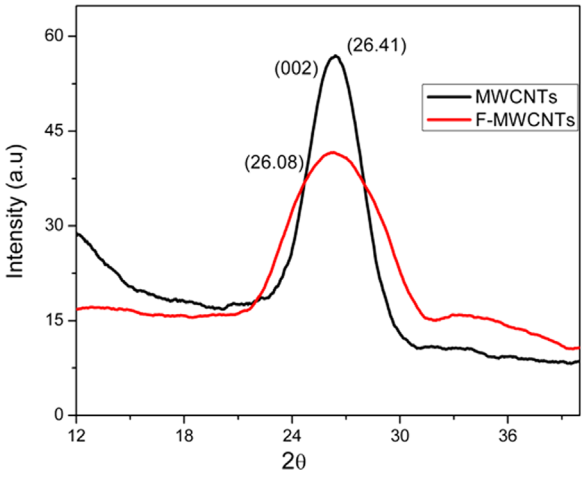

Fig. 3. X-ray spectra of MWCNTs and F-MWCNTs.