Structural elucidation of Multi-walled Carbon Nanotube—Diferuloylmethane Conjugate: a pre-requisite for validating applications in water purification

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Keywords: carbon nanotubes, diferuloylmethane, functionalization, characterization, reinforcement, water treatment

Abstract
Carbon nanotubes (CNTs) with its exceptional properties are considered a material of choice for use in various water treatment processes. The functionalization of the CNTs helps fine-tune its properties to achieve desired performances and/or overcome the limitations in processability to satisfy the requirements as per the application. Diferuloylmethane (DFM), a plant derived polyphenolic diarylheptanoid is a bioactive compound intriguingly exploited for use in environmental remediation. In this paper we report the functionalization of CNTs with DFM to craft a novel carbon conjugate suitable for use as reinforcement in membrane fabrication. The experimental results showed that the prepared conjugate retained the integrity of nanotube structure on functionalization and also showed lesser agglomeration in comparison to the pristine nanotubes. The formation of conjugate was further confirmed by the changes in functionalities of DFM. The thermal and colloidal stability of the conjugate have also been reported. The prepared conjugate with synchronized properties of the individual constituents is proposed to be an ideal option for enhancing the performance of membranes used in water treatment processes.

1. Introduction

Purification of water by membrane filtration has gained sustained attention over the years. However, factors such as stability, fouling, flux decline, membrane life and operational costs remain to be a cause of concern in the practical application of membranes [1, 2]. Carbon, an eco-rich element exhibits allotropy and exists in different molecular forms. In the nanoscale, carbon allotropes are distinguished from bulk by structures having at least one dimension in the nanometer range [3]. The general classification of carbon structures is depicted in figure 1. The use of carbon nanostructures and/or their derivatives in water purification has been shown to not only efficiently separate contaminants from water but also offer improved chemical stability, mechanical robustness and fouling resistance, consequently resulting in membrane life extension and lower operation costs [1, 2, 4].

CNTs, an intriguing one dimensional allotrope of carbon is a hollow cylindrical tube-like framework made up of rolled up graphite sheets, another allotropic form of nanostructured carbon. Structurally, the nanotube surface consists of a hexagonal network of interconnected sp² hybridized carbon atoms contributing to the unique strength of nanotubes. CNTs have lengths in the range of tens to ten-thousands of micro meter and diameters of one to tens of nanometer depending on the number of layers of graphite, classified accordingly as single-walled (SWCNT), double-walled (DWCNT) and multi-walled (MWCNT) nanotubes. The distinctive structure induced properties make CNTs a lucrative option in a wide spectrum of applications [5–7].

In environmental remediation processes involving the removal of contaminants (such as small molecules, organics, metal ions) from water the use of CNTs have gained a lot of attention owing to its material properties [5]. However, due to the small size, high surface energy and strong intermolecular forces existing between the tubes give rise to increased agglomeration of the CNTs and as a consequence, the practical application of CNTs is
limited [3, 5, 6]. This is especially a major concern in CNT containing functionalized membrane based water treatment systems as the agglomeration of CNTs results in reduced solubility of the nanotubes in solvents, restricted interaction with other organic or inorganic material and/or reduced dispersibility in matrices [6, 8]. In order to speculate the sustained use of CNTs, functionalization of nanotubes, a phenomenon by which specific molecules or functional groups are incorporated into the nanotube structure is usually done to make them processable. The introduction of functional groups renders the nanotubes with significant properties different from those of the original nanotube and also enables tailoring the physicochemical attributes of CNTs. Functionalization can either be covalent (covalent linking of nanotube carbon and functional moiety) or non-covalent (complexation using forces) and can be done by chemical methods (polymer-assisted, surfactant-assisted, solvent and bio molecular dispersion) or by physical methods (ultra-sonication, high shear mixing) [6, 9, 10]. The modified CNTs in particular the multi-walled nanotubes have been reported to present enormous potential for use in water purification applications [5, 8, 11].

Diarylheptanoids, are a group of compounds responsible for the biological activity of natural products derived from plants. Structurally, these are identified by the presence of a 1, 7-diphenylheptane skeleton and may have linear or cyclic conformations. Among the hundreds of diarylheptanoids identified so far, the earliest reported structure is DFM, a linear diarylheptanoid. DFM commonly known as curcumin is the major curcuminoid occurring in dried rhizomes of Turmeric (Curcuma longa) along with smaller proportions of its two natural analogues [12–14]. The bright yellow colour of DFM is attributed to its unique structure consisting of two methoxylated phenols connected by a seven carbon linker having an \(\alpha, \beta\)-unsaturated \(\beta\)-diketone moiety. This configuration allows DFM to interact covalently (involving \(\alpha, \beta\)-unsaturated \(\beta\)-diketone moiety) or non-covalently (involving hydrogen bonds and hydrophobicity) with target molecules. The activity of DFM is directly influenced by the existence of keto enol tautomeric structures and its stability is pH dependent with the dominance of the keto-form in acid or neutral pH and the enol form in alkaline pH [12, 15, 16]. Therapeutically DFM is commonly used as an antimicrobial, antioxidant, anticancer, anti-inflammatory and anti-mutagenic agents [12–15]. The structural aspects of DFM give rise to interesting oxygen related photosensitizing properties. Owing to the intense absorbance band between 420–580 nm in the visible region of the electromagnetic spectrum, DFM is used to widen the photo activity of materials and has been applied in dye-sensitized solar cells, dye degradation and microbial decontamination [17–20]. DFM also can form stable complexes with a variety of metals, thereby reducing the metal toxicity in certain cases and has been reported for use in boron quantification [21, 22]. Therefore, DFM may be considered as a valid candidate for use in water treatment applications due to its spectrum of properties including heavy metal complexion, antifouling and photo activity.

The ultimate goal of water treatment is to remove chemical and biological pollutants from water making it safe for use and thereby steers research towards the identification of novel materials with high potential for use in water remediation. These materials are either used directly (as adsorbents/freestanding membranes) or indirectly (as reinforcements in membranes). In this paper, we report functionalization of MWCNTs with the multifaceted DFM and evaluate the structural aspects of the conjugate for suitability of use as reinforcement in the preparation of functionalized membranes for wastewater treatment processes. The conjugate is expected to possess synergistic material properties relevant for water treatment including high adsorption capacity, photocatalytic activity and anti-fouling ability.

Figure 1. Classification of carbon nanostructures based on its dimensions at the nanoscale.
2. Experimental section

2.1. Materials
Carbon nanotubes, multi-walled (Type 5) and Diferuloylmethane were purchased from SRL chemicals. The sulphuric acid (H₂SO₄) and nitric acid (HNO₃) used were of analytical grade.

2.2. Preparation of MWCNT-DFM conjugate
The functionalization of MWCNTs using DFM was carried out in a mixture of H₂SO₄ and HNO₃. Briefly, MWCNTs and DFM were taken in the ratio 1:10 and allowed to react in a H₂SO₄-HNO₃ mixture with heating and constant stirring followed by incubation in the dark at room temperature overnight. The resulting material was then washed and dried to get the MWCNT-DFM conjugate.

2.3. Measurements
Surface images were recorded using a Scanning Electron Microscope (SEM, VEGA3 TESCAN, Czech Republic). X-Ray Diffraction analysis (XRD) was carried out using Powder XRD System (PANalytical X'Pert Powder XRD System, United Kingdom) with K-α source of 1.54 Å and scan range 10° – 90°. Attenuated Total Reflectance Fourier Transform Infrared (ATR-FTIR) spectroscopy analysis was done on a single crystal ATR accessory using a FTIR spectrometer (JASCO FT/IR-6600, Japan). Raman spectra were recorded using a Raman Spectrometer (Desktop H-Peak Seeker PRO-532, United States) using a green light laser of wavelength 532 nm. X-ray photoelectron spectroscopy (XPS) analysis was recorded using a photoelectron spectrometer (PHI 5000 Versa Probe III, Japan). Proton Nuclear Magnetic Resonance (H1 NMR) measurement was carried out using a NMR spectrometer (Bruker NMR 400MHz, United States) with deuterated chloroform (CDCl₃) as solvent. Thermogravimetry (TG) analysis was done using a Thermo Gravimetric Analyzer (TGA Q50 V20.13 Build 39, United States). The Zeta Potential was determined using Dynamic Light Scattering instrument (Malvern Zetasizer, United Kingdom) using water as dispersant. All measurements were done at room temperature.

3. Results and discussion

3.1. MWCNT-DFM conjugate preparation
The reactants, MWCNT and DFM were taken in the ratio 1:10. This is done in order to enable formation of esters by shifting the equilibrium. Also, the polyphenol is used in excess (higher ratio) as it is less complicated to remove it than the nanotubes [23]. The use of HNO₃ initiates the oxidation of the MWCNTs to oxidized MWCNTs (o-MWCNTs) containing carboxyl (–COOH) functional groups [24]. The use of H₂SO₄ aids in CNT oxidation and also catalyses the esterification reaction between o-MWCNTs and DFM to form the MWCNT-DFM conjugate at room temperature [25, 26]. The conjugate was washed and dried completely before being used for further structural characterization. The schematic representation of the plausible chemical reaction between MWCNT and DFM during modification is given in figure 2.

3.2. Characterization of the prepared conjugate
3.2.1. SEM imaging
The surface morphology of materials can be illustrated using SEM analysis. The SEM micrographs of MWCNT and the MWCNT-DFM conjugate are shown in figure 3. The unmodified MWCNTs show smooth tubular morphology without amorphous particles on their surface (2 μm scale). In addition, these pristine tubes show agglomeration at 5 μm scale. However, the DFM-MWCNT conjugates reveal amorphous particles on the tubular surface (2 μm scale). Interestingly, the agglomeration was lowered in DFM-MWCNTs as compared to
pristine MWCNTs (5 μm scale). The reduction in agglomeration due to the functionalization makes the conjugate suitable for use as reinforcements in fabrication of membranes for water treatment [8].

3.2.2. XRD analysis

The structural components of materials can be examined using the XRD analysis. CNTs have been established to exhibit a (002) reflection diffraction peak at values slightly lower than the graphitic peak ($2\theta \approx 26.5^\circ$). This is a direct consequence of the decrease in crystalline structure with an increase in sp² carbon layer spacing in CNTs [27]. In a study by Bhaumik et al it was shown that the intensity of diffraction peaks of CNTs decreased upon the incorporation of polypyrrole upon nanocomposite formation [28]. The characteristic diffraction pattern of DFM reveals the presence of peaks between $2\theta$ values 10°–30° [29]; while the absence of these characteristic peaks represent the distribution of DFM at a molecular level in hybrid systems [30]. In a study by Moussawi & Patra, it was reported that on conjugation DFM exhibited peaks at 37.03°, 37.80°, 43.23° and 64.35° [31]. From the figure 4, it can be seen that the diffraction pattern of MWCNT-DFM conjugate revealed a sharp peak at $2\theta = 36.7^\circ$, relatively lower intensity peaks at $2\theta$ values of 42.97°, 63.32°, 76.45°, 80.64° and a broadened peak at $2\theta = 24.6^\circ$. Thus, from the XRD analysis it can be confirmed that the MWCNT-DFM conjugate was formed. The average crystallite size (D) was calculated using the Scherer formula given by,

$$D = \frac{K\lambda}{\beta \cos \theta}$$

where, K is a dimensionless shape factor; λ is the x-ray wavelength; β is the full width at half maximum of the peak; and $\theta$ is the Bragg angle. It was found to be 42.86 nm for the prepared conjugate.

3.2.3. Raman spectral analysis

The Raman Spectroscopic analysis provides specifics on the ordered/ disordered crystal structure and intermolecular interactions of materials. Raman spectra of CNTs exhibit characteristic D, G and 2D bands at around $1350 \text{ cm}^{-1}$, $1580 \text{ cm}^{-1}$ and $2700 \text{ cm}^{-1}$, respectively. The D and G bands each represent the defective and graphitic nature of the nanotubes; while the 2D band arises from two phonon second order scattering processes [32]. In a study on covalent functionalization of MWCNTs, Wang et al reported that any increase in intensity of the D band due to grafting of functional molecules onto the surface of MWCNTs is counteracted by a simultaneous decrease in intensity due to purification [33]. Also, the existence of similar spectral observations for pristine and functionalized MWCNT with unchanged relative peak intensity ratios confirms encapsulation of the MWCNT without any distinct changes in the graphitized structure [34]. The Raman spectrum of MWCNT shows the characteristic D, G and 2D peaks at 1329 cm$^{-1}$, 1573 cm$^{-1}$ and 2686 cm$^{-1}$. The spectrum of the prepared MWCNT-DFM conjugate showed the presence of a G band of nanotubes at $\sim 1540 \text{ cm}^{-1}$ and an insignificant D band on DFM interaction (figure 5). It can be observed that the
D band intensity is clearly less than that of the G band and the consequent $I_D/I_G$ ratio was found to be approximately 0.12. Thus, on functionalization of the MWCNT with DFM, the disorder in the CNT structure reduced to form a reliable conjugate structure for use in functionalized membranes.

3.2.4. ATR-FTIR spectral analysis
The FTIR Spectroscopy revealed details on the structural functionalities and possible interaction sites of materials. The DFM infrared spectra, in general exhibits signature functionalities including: phenolic-OH stretch ($3503 \text{ cm}^{-1}$), methyl C–H ($2847 \text{ cm}^{-1}$), benzene ring stretching ($1594 \text{ cm}^{-1}$), C=O bonding ($1496 \text{ cm}^{-1}$), olefinic C–H bend ($1429 \text{ cm}^{-1}$), aromatic C–O stretch ($1271 \text{ cm}^{-1}$), methyl–CH$_3$ rocking ($1149 \text{ cm}^{-1}$), C–O–C stretch ($1023 \text{ cm}^{-1}$) with other peaks including benzoate trans C–H vibration ($956 \text{ cm}^{-1}$) and C–H vibration of aromatic ring ($717 \text{ cm}^{-1}$) [35–37]. The weakening of the main absorption peaks on interaction of DFM with phospholipids has been reported earlier [38]. Also, shifts in peak positions may be considered as indicators of minor structural changes at the molecular level [39]. The ATR-FTIR spectra of conjugate (figure 6) appears to be highly similar to that of DFM with a distinctive reduction in the peak intensities and slight shift in positions, indicating the interaction of DFM with o-MWCNT. The pronounced weakening of the peak at $\sim 3500 \text{ cm}^{-1}$ representing the phenolic-OH group (as indicated by the arrow in
Figure 6 hints it to be the site of possible interaction for the o-MWCNTs. This is in accordance with a study by Hatamine et al reporting the considerable reduction of oxygen-containing groups of DFM on rGO binding while retaining the characteristic peaks of DFM projecting that the DFM was bound on the surface of the rGO sheets [40]. Thus, on functionalization the phenolic –OH group in DFM bonds covalently with the carboxyl groups in the o-MWCNT thereby forming the functionalized MWCNT-DFM conjugate. This is further confirmed by XPS and H1 NMR analysis.

3.2.5. XPS spectral analysis
XPS analysis was used to confirm the oxygenated functionalization on the MWCNTs. The XPS survey spectra of the conjugate showed the presence of peaks at two positions relating to the presence of two elements, carbon and oxygen (figure 7(a)). It can be clearly seen that the relative intensity of C1s peak is higher than O1s peak. The C1s XPS spectrum of CNTs in general exhibit a core peak at ~284.5 eV and a relatively close peak at ~285.1 eV representing the sp2 carbon atoms and sp3 carbon atoms, the relative intensities of which can be correlated with the degree of graphitization [41]. Another peak at ~291.5 eV is representative of the π-π* transition loss [42]. The O1s spectrum of CNTs identify the peaks at regions between 531.6 eV – 531.9 eV and 533.3 eV – 533.8 eV representing the presence of C=O and C–O bonds [43]. On the other hand, in DFM, the peaks at ~284.8 eV, ~286.5 eV and ~288.8 eV in the C1s spectrum represent the carbon in alkane/alkene or benzene ring, C-OH/ ether or in conjunction of aromatic ring/main backbone of DFM and characteristic C=C bond in DFM, respectively [44]. DFM O1s spectral peaks at ~533.5 eV and ~532.1 eV represent C=O and C–O bonding oxygen atoms [45]. For the MWCNT-DFM conjugate, deconvolution of C1s spectra (figure 7(b)) reveals a core peak at 284.6 eV representing sp2 carbon and two peaks at higher binding energies 286.3 eV and 286.9 eV representing the carbon bound to electronegative atoms of oxygen. Deconvolution of the O1s spectra (figure 7(c)) reveals two peaks at 533.3 eV and 531.4 eV corresponding to C=O and C–O bonding oxygen atoms. It was observed that the intensity of the C=O peak was relatively higher in comparison to C–O bonds. The increased intensity in C=O bond peaks may be due to the formation of ester bonds on conjugation between the phenolic –OH in DFM and the –COOH in o-MWCNTs further confirming the formation of the MWCNT-DFM conjugate.

3.2.6. H1 NMR spectral analysis
The H1 NMR technique provides information on the stereochemistry of materials by means of changes in the chemical shift values of hydrogen nuclei in DFM. The H1 NMR spectra of DFM report the presence of characteristic peaks at ~3.8 ppm, ~6.74 ppm – 7.56 ppm, ~9.6 ppm and ~16.4 ppm corresponding to –OCH3, aryl – H, phenolic – OH and enol – H respectively [46, 47]. In CDCl3, DFM exists in its keto enol tautomeric form [48]. In the H1 NMR spectra of the MWCNT-DFM conjugate (figure 8), the presence of major peaks representing DFM can be observed. However, the spectra also reveals the absence of two peaks, the enol hydrogen (~16.4 ppm) and the phenolic -OH (~9.6 ppm) groups of DFM suggesting the possibility that these may be the primary interaction sites of the o-MWCNTs. Also, the shift in aromatic methyl peak from ~3.8 ppm to ~2.69 ppm can be related to the changes in structural conformation of the DFM molecule on binding the MWCNT. The disappearance of the DFM phenolic –OH on interaction with the MWCNTs further confirms it

Figure 6. FTIR spectra of DFM and MWCNT-DFM conjugate (arrow indicates the weakening of the significant phenolic –OH group of DFM on conjugation).
to be a primary bonding site in the formation of MWCNT-DFM conjugate, which is in accordance with the FTIR and XPS data reported.

3.2.7. TG analysis

The thermal behaviour of materials as a function of temperature can be studied using thermogravimetric analysis. It has been well established that the thermal oxidation pattern of carbon varies depending on its structure with the degradation onset temperature considerably lower for disordered carbons and is observed to increase with the degree of graphitization [49]. On the other hand, the thermal oxidation of DFM has been reported to occur in two stages: the decomposition of substituent groups between 94 °C–357 °C and the

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Figure 7. XPS spectral curves of MWCNT-DFM conjugate (a) Survey spectrum, (b) C1s spectrum and (c) O1s spectrum.

Figure 8. NMR spectrum of the MWCNT-DFM conjugates in CDCl₃ solvent.
decomposition of the aromatic rings between 357 °C–533 °C [50]. Also, the thermal behaviour of DFM mixed with nanomaterial show differential characteristics in that conjugated DFM showed rapid weight loss compared to physically adsorbed DFM [31]. The thermogram of pristine MWCNT and the MWCNT-DFM conjugate is shown in figure 9. It can be observed that for pristine MWCNT, there occurs a very little weight loss (<5%) upto 350 °C which may be attributed to the evaporation of adsorbed water molecules (moisture) and other impurities while in the case of the MWCNT-DFM conjugate, the weight loss occurs in multiple stages. A weight loss from 130 °C–250 °C corresponds to the elimination of a few functionalities and the major weight loss (∼50%) between 250 °C–450 °C corresponds to the rapid combustion of aromatic groups. The residual carbons are further oxidized at temperatures >450 °C. The observed results confirm the formation of the conjugate and also that the DFM is covalently bound with the MWCNTs rather than physically adsorbed as identified by the rapid weight loss of the MWCNT-DFM conjugate.

3.2.8. Zeta potential analysis

The magnitude of electrostatic interaction between colloidal particles in a suspension is given by the Zeta potential. Carbon-DFM conjugates such as SWCNT-DFM and reduced Graphene oxide-DFM with zeta potentials of −12.5 mV and −20.2 mV has been reported earlier [40, 51]. In general, the zeta potential of MWCNT is related to the density of acidic sites present on its surface and an increase in the zeta potential value of MWCNT/water suspension on functionalization has been correlated with an increase in the stability of the system [52]. The average zeta potential value recorded for the MWCNT in water was found to be −18.5 mV, while that of the conjugate was −15.6 mV, indicating an increase in the stability of the colloidal system making it suitable for use in water treatment membranes.

4. Summary and conclusion

The DFM functionalized MWCNTs were prepared by a simple single step acid-functionalization process. The characterization of the conjugate using XRD confirmed the loading of crystalline DFM nanoparticles on the nanotubes. The decrease in the D band intensity and the reduced I_D/I_G ratio indicate the improvement in structural integrity of the nanotube on binding with DFM by removal of amorphous carbons. The FTIR and H1 NMR spectra revealed the phenolic hydroxyl groups to be the major site of interaction and the shifts in peak positions were attributed to structural changes associated with the formation of the conjugate. The C1s XPS spectra confirmed the presence of carbon associated with the nanotube and the presence of carbon bound to electronegative oxygen atoms, while the O1s spectra showed a relatively higher ratio of C=O bonds which further confirm the ester formation. The TGA analysis shows the thermal behaviour of the conjugate while an increase in the zeta potential of MWCNT-DFM conjugate demonstrates a stable colloidal system. The prepared conjugate is expected to have complementary properties of both CNTs and DFM making it a compound of interest for use as reinforcement in preparation of functionalized membrane for water purification.
Data availability statement

The data generated and/or analysed during the current study are not publicly available for legal/ethical reasons but are available from the corresponding author on reasonable request.

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