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Simultaneous purification and oxidation of the as-synthesized MWCNTs with $KMnO_4$ using phase transfer catalyst at three different pH medium by the hydrothermal method

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HIGHLIGHTS

- Several approaches for the functionalization of CNTs have been developed, in both molecular and supramolecular chemistry.
- The effort to chemically oxidize CNTs is made in order to enhance the degree of attachment of the CNTs with various inorganic or organic functional groups, and harsh oxidizing agents like nitric acid or strong bases that are frequently used.
- Study evidenced that $KMnO_4$ with PTC is desired to selectively attack some of the π–bonds, without causing a total destruction of the graphene structures of the nanotubes.

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ABSTRACT

Improving and streamlining current oxidation techniques for experimental is the main goal of the research described in the present article. By applying the pressure created while on the hydrothermal process to an autoclave walled with Teflon, simplifying the procedure was accomplished. By comparing the degrees of functionalization attained with the dispersibility in the substantially pure and functionalized multi-walled carbon nanotubes (MWCNTs) final product, the beneficial effect of the procedure was evaluated. In order to achieve this, the study looked at and investigated how as-synthesized MWCNTs from Fe-Mo/MgO catalyst were simultaneously purified and oxidized using the chemical vapor deposition (CVD) method. Aliquot-336 was used as phase transfer catalyst (PTC) by hydrothermal method under three different pH conditions. Following functionalization, nanotubes of carbon might easily combine with various chemical reagents to generate homogeneous dispersions or even well-aligned structures because of the functional groups linked to their surfaces. In this case, a chemical called reagent potassium permanganate ($KMnO_4$) is necessary in order to target particular π-bonds while entirely destroying the nanotubes' graphene structures. The techniques have been explained in terms of mechanism, and the Fourier transform-infrared (FT-IR) spectroscopy has confirmed the functionalizations of the CNTs. These approaches were further explored through FT-Raman spectrum analysis, thermal assessments, energy dispersive X-ray spectroscopy (EDX), TEM (transmission electron microscopy) along with the help of EDX, and visible-near IR absorption and UV–visible absorption spectroscopy (ABS) procedures.

1. Introduction

Investigations have long been interested in the chemical functionalization of carbon nanotubes, also known as CNTs, in a number of scientific and technological domains, notably the circumstances that design nanoelectronics, colloids, polymer composites, hydrogen power engineering, bioengineering, supercapacitors, sensors, drug delivery, etc. The chemical surface modification of CNTs is necessary for controlling their morphological features when they assemble in the aforementioned new supramolecular assemblages [1]. The chemical modification of the CNTs surface, which involves the direct impregnation of special elements and inorganic or organic functional groups into

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the graphene sidewalls, is considered to be the most effective approach [2]. Although there has been significant advancement in this area, it is important to remember that specific control over the surface chemical reaction is necessary to achieve the desired degree of nanotube the functionalization process. Unfortunately, due to excessive matrix material viscosity, poor dispersion, and significant porosity within it nanocomposite treatment continue to be restricted to bench-top processing.

Generally speaking, functionalized carbon nanotubes (CNTs) are incapable of passing through any observable solid-to-liquid transition and instead behave like solids when there is no solvent or suspending media involved. The necessary conditions are created for enabling the synthesis of potential uses for these nanostructures by the functionalization of CNTs, or through the bonding of suitable chemical functions onto their conjugated sp^2 carbon compounds scaffolding [3,4]. The most effective way to solve this issue has been proposed to be chemical alteration of the carbon nanotube surfaces. As a result, functionalization with chemicals is critical for modifying CNT characteristics and application adaptability. The chemically driven covalent bonding mechanisms, within especially, has been shown to be extremely beneficial in maintaining stable bonds, and substantial attempts have already been made to build chemical functions on the outermost surfaces of CNTs [5]. However, supramolecular [6] and also molecular chemistry have yielded a number of strategies for functionalizing CNTs. Some of these techniques comprise endohedral functionalization [7] utilizing CNTs, non-covalent exohedral functionalization [8] such as the creation of supramolecular adducts adopting surfactants or polymers, covalent functionalization of the side walls [9], and functionalization of imperfections [10]. As a result, it is difficult to distribute them equally in a liquid matrix. The modification of surfaces together with homo polymers and possibly block copolymers, which involves surface-targeted grafting [11], in situ polymerization [12,13], polymer securing [14], and stacking interactions [15–17], has boosted the capability to dissolve for non-soluble CNTs in the presence of organic solvents. Bourlinos et al. demonstrated the production of meltable functionalized CNTs by connecting a canopy of short, flexible polyethylene glycol (PEG) chains to the nanotubes [18].

The research article published by [19] addresses microwave-assisted irradiation as a method for speeding up nanotube functionalization process. The results of these investigations found an insignificant amount of functionalization and solubility identical to that of wrapping agents by default. Pristine CNTs are often insoluble in a range of liquids, including water, polymer resins, and most solvents, since the sidewall of MWCNTs tends to be highly hydrophobic, making it extremely difficult to investigate their characteristics and uses without functionalization [17,20].

The relative reactivity of certain nanotube sites is exploited to induce functionalization employing a chemical oxidation technique despite conserving nanotube morphology. These sites are the end caps and the defect sites. Because of their 2D curvature and localized C=C bonds, the end caps are intrinsically extremely reactive, whereas chemical assaulting on the less curved sidewalls often necessitates the existence of sidewall defects, such as Stone-wales defects [21]. Chemical oxidation converts end caps and defect sites into carboxylic acid (R-COOH) groups, allowing for further functionalization [22]. By using amide coupling, the carboxyl groups at the open ends of severely oxidized CNT pieces of fullerene-pipes have been utilized to connect gold nanoparticles [23]. To enhance the interaction between CNTs and foreign molecules, the nanotubes' surfaces must be modified. Chemical treatments such as nitric acid or a mixture of sulfuric acid and hydrogen peroxide (piranha) have demonstrated that SWCNTs are capable of being reduced within a method that is controlled under particular circumstances [24,25]. Nonetheless, of the several purifying techniques, CNT oxidation treatments are among the best [26]. In order to produce shorter nanotubes, piranha was shown to target the damage sites already present in the graphene sidewall at high temperatures. This resulted in the generation of vacancies and the consumption of oxidized vacancies [27].

Zhang et al.'s comprehensive observation and analysis in 2003 revealed that imperfections on CNTs, whether originally or subsequently produced, played a significant part in the process of oxidation [28]. After identifying the processes that produce and consume defects, they investigated potential oxidation reactions and made predictions about the intermediate and end products. The oxidized material's electrical characteristics are determined by the existence of inefficiencies on the CNTs surface, which also impact the compound's stability as a structure. For example, Kovtyukhova et al.'s wet oxidation investigation shown that disrupting the interconnected structure of the tubes results in a three-order improvement in resistance. Conversely, less data exists about the structural modification of graphitic materials by simple oxidative processes [29]. Hiura et al. (1995) found that CNTs were functionalized throughout the purifying procedure. In the study, $KMnO_4$ had been utilized as the oxidant while H_2SO_4 served as a solvent [30]. The reactive edge of the tips and maybe the outer (or inner) layer of the nanotube undergo chemical alterations as a result of this oxidation. Various oxidant reagents, including conc. HNO_3, conc. H_2SO_4, aqua regia, super acid HF/BF3, aqueous OsO_4, OsO_4–$NaIO_4$, and others [31], have been used to attach functional groups to nanotube surfaces. However, many of the approaches discussed above suffered from low functionalization yield and high costs, making it impossible to obtain interesting outcomes across numerous domains.

Chemically oxidizing CNTs is often done to increase the degree of attachment of the CNTs to various inorganic or organic functional groups, and severe oxidizing agents such as nitric acid or strong bases are commonly utilized. These procedures cannot be used to functionalize CNTs on electrical or mechanical devices because the chemicals target the underlying metal layers [32]. As a result, organic modification of CNTs is still a relatively new subject. More specifically, the targeted oxidation of CNTs to produce molecules with oxygen in them (alcohols, acids, aldehydes, ketones, etc.) is a critical and valuable process in the field of chemical manufacturing. Since oxidation significantly reduces the chemical inertness of the CNT systems, it makes CNT oxidation a particularly interesting process. Furthermore, oxidation has been considered as probably the most feasible scientific approach for the initial step of CNT chemically the functionalization process [33].

In many oxidation processes, permanganate yields good results when utilized in a variety of homogeneous and heterogeneous environments, on solid supports, and without the need for solvents. Green chemistry has recently placed more emphasis on the environmentally benign permanganate oxidation method [34]. There are two distinct kinds of response sites in CNTs: end caps as well as sidewalls. No matter the diameter of the CNTs, the end-caps, which have a hemispherical fullerene-like appearance, are always highly reactive [35]. As of right now, it is not possible to selectively conduct a reaction on the side walls or merely at the end caps. A few research studies use $KMnO_4$ oxidation to modify the fullerene surface in order to create these types of functionalizations, or CNTs which are composed up of a hemispherical cap and a planar wall [36–38]. Hong et al. (2008) investigated a unique chemical oxidation performed by certain groups; the functionalization and solubilization of MWCNTs were enhanced by utilizing $KMnO_4$ as an oxidant and tetrapropyl ammonium bromide (TPABr) as a phase transfer catalyst (PTC) [39]. Zhang et al. investigated the functionalization of CNTs by $KMnO_4$ assisted by PTC [40]. The advantages of the PTC methodology over other conventional methods are as follows:

(i) The efficiency of oxidation is drastically increased.
(ii) A better product preference is achieved between the hydroxyl group and carboxylic acid.
(iii) The reaction to this condition is comparatively low.
(iv) It assists in the transition of $KMnO_4$ from the solid to the organic phase, reducing CNT degradation.

(v) The simultaneous existence of a pair of phases at the interface (liquid-liquid or solid-liquid) creates continuity between each of them [41]. Furthermore, this kind of functionalization offers the great advantage of producing well dispersed and easy-to-handle CNTs.

Generally, the as-synthesized CNTs contain impurities such as amorphous carbon, metal catalyst residuals, bucky onions, spherical fullerenes and polyhedron graphite nano-particles [42]. These impurities significantly influence the properties of CNTs and limit their applications. Thus, purification has been an important synthetic effort since the discovery of CNTs, and there are many publications discussing different aspects of the purification process. The various methods of purification are oxidation methods such as thermal, wet, size selective, fixed air and wet air oxidation, acid treatment, microwave treatment, annealing, ultra-sonication, micro filtration, ferromagnetic separation, cutting, ball milling, functionalization and chromatography. However, CNTs suffer from uneconomical large scale purification, % purity, defects, and time consumption. Therefore, the effectiveness of the method must be assessed, using comparison levels of functionalization and dispersion in the highly purified MWCNTs end product. Maintaining the integrity of the nanotubes is necessary to activate the relative reactivity of specific sites on them, which is necessary to start the functionalization process via chemical oxidation. For this purpose we examined the simultaneous purification and oxidation of as-synthesized CNTs with $KMnO_4$ using Aliquot-336 as PTC by hydrothermal method in various pH conditions. This so-called hydrothermal method has been used in the synthesis of mesoporous [43,44], micro and nanoporous materials [45], and it was applied for the first time in the surface chemistry of the CNTs, modified by introducing carboxylic acid (−COOH) and hydroxyl (−OH) groups by means of $KMnO_4$ with PTC in three various pH medium, such as acidic, basic and neutral. Here, a reagent that targets specific π-bonds while sparing the nanotubes' graphene frameworks from complete disintegration is needed. Additionally, the mechanical explanation of this strategy has been provided.

2. Experimental section

2.1. Materials

The chemicals used for the oxidation of CNTs are as follows: Potassium permanganate ($KMnO_4$) purchased from Sigma Aldrich was used as an oxidizing agent; Tricapryl methyl ammonium chloride (Aliquot-336) from SRL, Mumbai, was used as a phase transfer catalyst (PTC); dichloromethane (CH_2Cl_2) from Merck, Mumbai, was used as a dispersing agent; potassium hydrogen phthalate ($KHC_8H_4O_4$; abbreviated as KHP), sodium bicarbonate ($NaHCO_3$), and potassium dihydrogen phosphate (KH_2PO_4) from Merck were used to prepare buffers in order to adjust the pH of the solution. Sodium hydroxide (NaOH), sodium sulphite (Na_2SO_3), and sulfuric acid (H_2SO_4) from Merck were used to remove the deposited manganese oxide (MnO_2) from the functionalized CNTs. All the chemicals used in this work were of analytical grade. No further purification was performed on the purchased chemicals, except $KMnO_4$ and CH_2Cl_2. The $KMnO_4$ was recrystallised from a saturated aqueous solution under nitrogen, and CH_2Cl_2 was double distilled before use.

2.2. Functionalization of CNTs under hydrothermal method

A typical experimental procedure examined for simultaneous oxidation and purification of MWCNTs with $KMnO_4$ using PTC in various pH mediums by the hydrothermal method is as follows: MWCNTs were produced from a 1:1:50 mol ratio of Fe-Mo/MgO catalyst via the chemical vapor deposition (CVD) technique by following the procedure given in our previous report [46]. Initially, 0.36 g of as-synthesized MWCNTs and 60 mL of distilled dichloro methane (CH_2Cl_2) were taken in a 100 mL round bottom (RB) flask. It was then kept in an ultrasonic bath at room temperature for 30 min, to allow the CNTs to disperse uniformly. Then it was stirred magnetically at room temperature for 2 h. Meanwhile, about 1 g (i.e., 1:3 ratios) of recrystallised $KMnO_4$ was added. Thus, the $KMnO_4$ was recrystallised from a saturated aqueous solution under nitrogen, resulting in a more stable solution than the as-received $KMnO_4$. Then 1 g of Aliquot-336, as PTC, was added to the above suspension. Now, the pH of the solution is less than 3. The influence of pH on the $KMnO_4$ oxidation of CNTs was examined in three various pH media, such as acidic, basic; and neutral. For this purpose, various buffer solutions were prepared. The procedures used for the preparation of pH 3.4, 10.8, and 7.0 buffers are as follows:

2.2.1. For acidic medium (pH 3.4)

100 mL of 0.1 M potassium hydrogen phthalate and 20.8 mL of 0.1 M HCl solution were prepared separately, and then they were mixed thoroughly. The solution was added to the above reaction mixture, until the pH reached 3.4 (for checking the pH, a Merck "Neutralit" pH indicator strip was used).

2.2.2. For basic medium (pH 10.8)

A solution of 100 mL 0.05 M $NaHCO_3$ and 42.4 mL 0.1 M NaOH was prepared separately, and thoroughly mixed to get a homogeneous solution. This solution was added to the reaction mixture until the pH reached 10.8.

2.2.3. For neutral medium (pH 7.0)

100 mL of 0.1 M KH_2PO_4 and 58.2 mL of 0.1 M NaOH solution were mixed to set the pH at 7.0.

Approximately 30 mL of the buffer solution was required to set the pH. After 2 h stirring, the mixture had been transferred to a 500 mL (mL) cleanable stainless-steel autoclave with a Teflon lining. After being tightly closed and heated to 110 °C for 6 h, the autoclave was then allowed to cool down naturally to ambient temperature. Following the procedure of hydrothermal treatment, the resulting specimens have been collected by filtering and rinsed using 1 M H_2SO_4, 0.4 g/L NaOH and 1 M Na_2SO_3 solutions for acidic, basic and neutral mediated oxidized CNTs respectively. Mainly those chemicals were employed to remove manganese oxides (MnO_2) from CNTs surface. This rinsing stage was repeated until no brown colour was visible in the resulting residue, which was then followed by a final rinse with concentrated HCl to remove any remaining MnO_2.

2.3. Characterization

In order to prove the success of the research work in the proposed way, the comparison of a series of data obtained from different characterization techniques is inevitable. Thereby, the above synthesized materials were characterized by various physico-chemical techniques, such as FT-IR, FT-Raman spectroscopy, EDX under TEM, Thermo Gravimetric Analysis – Differential Thermo Gravimetric (TGA-DTG), UV–visible spectroscopy, and Visible-near IR absorption spectroscopy, which have been used to establish the chemical modification during functionalization, quality, quantity, elemental composition,

morphological investigations, thermal stability, dispersion ability respectively.

2.3.1. Fourier transform-infra red (FT-IR) spectroscopy studies

The IR spectra of pristine, purified and functionalized CNTs were recorded on a PerkinElmer (Spectrum RX1) apparatus that makes use of the KBr pellet method. After around 4 mg of the sample and 200 mg of spectral grade KBr were crushed together, the resultant mixture was formed into a pellet form using a hydraulic pressing device with a 13 mm diameter self-supported wafer and an operating pressure of 5 ton/cm^2. The 400–4000 cm^{-1} band of the infrared spectrum was recorded with this powder.

2.3.2. Fourier Transform-Raman spectroscopy studies

Also for this characterization technique, to investigate the amorphous and crystalline phases, graphitization and possible damages on CNTs before and after the purification processes, FT-Raman spectra were recorded by FT-Raman spectroscopy. The Raman spectra were recorded with BRUKER: RF S27 using a laser excitation line at 532 nm (Nd-YAG), 100 mV, with 1 μm focus spot. The acquisition time for the spectrum was 90 s, and the spectral resolution was about 2 cm^{-1}.

2.3.3. Transmission electron microscopy (TEM) studies

The morphology, shapes, diameters, lengths, micro textures depending on the microscopic details of the oxidized CNTs, and chemical analysis by EDX were investigated by TEM observations. The TEM micrographs with EDX were performed using a transmission electron microscope (JEOL JEM 2100) operating at 200 kV. Samples for TEM were prepared by placing droplets of the sample suspended in methanol on a polymer micro grid supported on a Cu grid.

2.3.4. Thermogravimetry and differential thermogravimetry (TG-DTG) analyses

Thermogravimetric analyses were performed on a TA Instrument SDT Q600 $V_{8.0}$ Build 95 thermogravimetric analyzer, equipped with an EGA furnace. Samples were analyzed in platinum pans at a heating rate of 20 °C/min to 1000 °C in an atmosphere of N_2 flowing at 100 mL/min with the mass range of 3–4 mg.

2.3.5. UV–visible spectroscopy studies

The raw CNTs and functionalized CNT samples were dispersed in various solvents, and characterized by a UV–visible spectrophotometer, using the NEXUS 670 spectrometer. The absorbance at 600 nm (A600) of the samples with a concentration of 1 mg/10 mL was recorded.

2.3.6. Visible-near IR absorption spectroscopy studies

The covalent functionalization that occurred on the CNT surface was confirmed by a Visible-near IR absorption spectroscopy analysis. The spectra were recorded on Nano Spectralyzer with 10 spectral averages, and 0.5 s acquisition times.

3. Results and discussion

3.1. FT-IR analysis

FT-IR was performed on the purified CNTs (pristine CNTs) obtained from traditional method and functionalized CNTs by $KMnO_4$ treatment (f-CNTs), which were ground and pressed into KBr pellets (Fig. 1). FT-IR is commonly used to determine the chemical groups attached to the CNTs. Fig. 1. (a–d) shows the IR spectra of the pristine CNTs, and the ones functionalized with $KMnO_4$ using PTC in acidic (a-CNTs), basic (b-CNTs) and neutral (n-CNTs) pH medium respectively. The IR peak

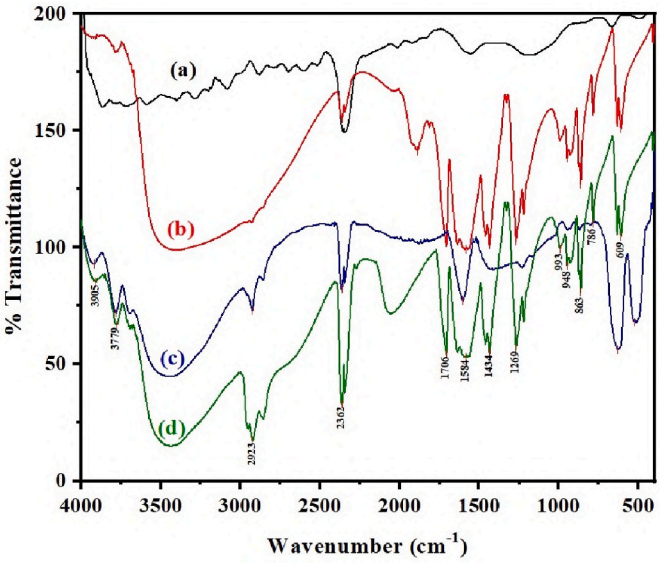


Fig. 1. FT-IR spectra taken using powdered KBr to form pellets with (a) raw-CNTs, (b) a-CNTs, (c) b-CNTs and (d) n-CNTs.

Table 1
Prominent FT-IR peak assignments of raw-CNTs, a-CNTs, b-CNTs and n-CNTs.

Wave number (cm^{-1})	Peak assignments [47,48]
3900 VW	Overtone/Combination
3779 W	OH bridging groups that are H bonded to the oxygen atoms
3395 B	A weak peak at 3480 cm^{-1} can be assigned to the vibrational modes of the –OH groups, indicating the presence of functional groups in the pure CNT
2923 M	C–H Asymmetric stretching
2850 VW	C–H Symmetric stretching
2362 M	C–C Asymmetric stretching
2100 VW	C–C Symmetric stretching
1888 S	Absorbance of C=C indicates oxidation of carbon with remarkably emergence as carbonyl of carboxyl group
1706 S	Absorbance of C=C indicates oxidation of carbon with remarkably emergence as carbonyl of carboxyl group
1603 S	Assigns to carbonyl of quinine type units along the side walls of the nanotubes
1584 S	Double bonding of carbon due to acid attack (C=C)
1434 S	The peak is the characteristic stretching vibrations of C–C bonds related to the expected nanotube phonon modes.
1269 S	Overlapping bands
1225 W	C–C Symmetric stretching/Purified MWCNT
1000 W	Overlapping bands
948 M	Presence of C–O bands in various chemical environments
863 S	It demonstrates the presence of C–O bonds in various chemical environments
786 W	Asymmetric hexagonal carbon
609 VW	Symmetric hexagonal carbon
500 W	Purified MWCNT

B-Broad; M-Medium; S-Strong; VS-Very Strong; VW-Very Weak; W-Weak.

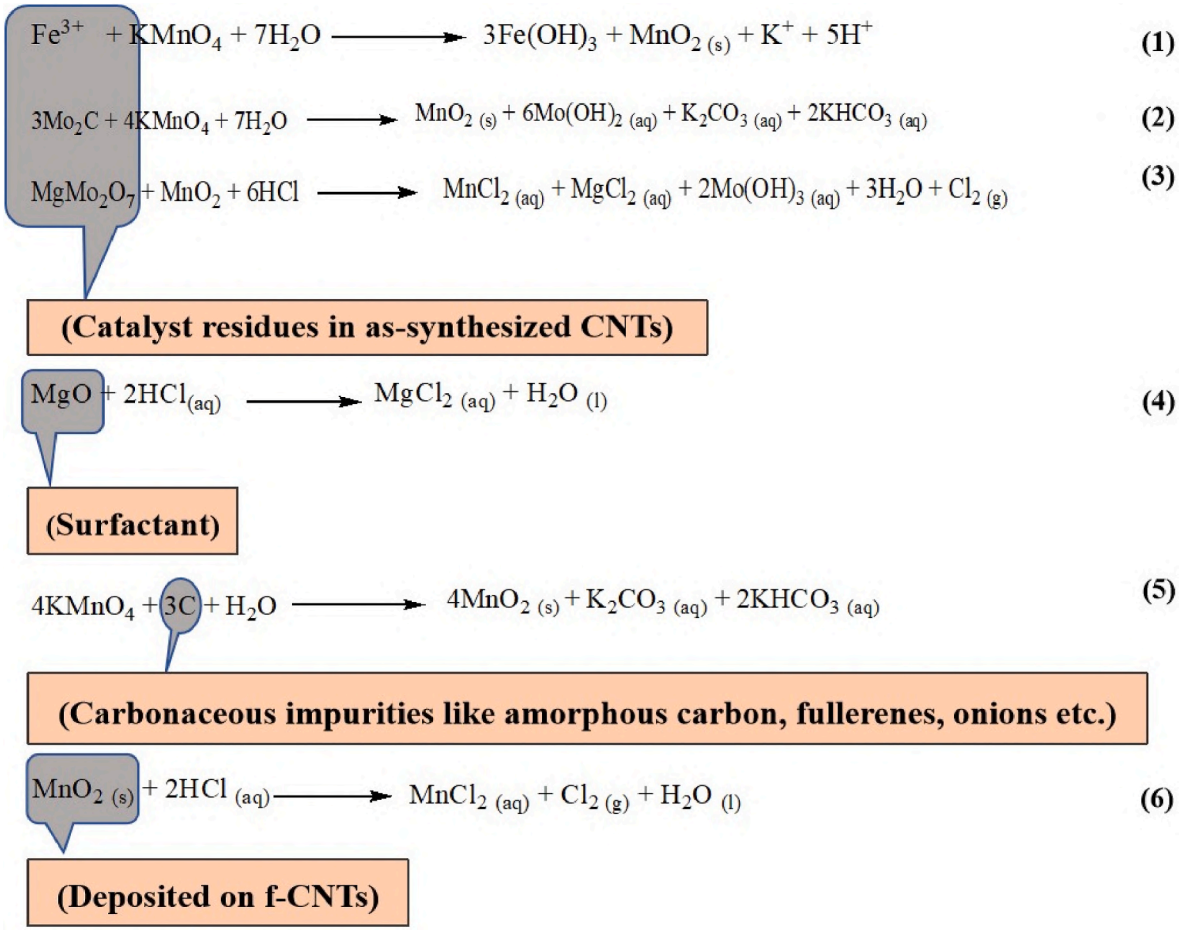
assignments are given in Table 1. The IR spectrum of the pristine CNTs is practically featureless and shows extremely low infrared absorption intensities; the very weak peak seen at 2352 cm^{-1} is due to the terminal C=C stretching present in the CNT framework. It was confirmed that most of the C=C bonds exist in the non-terminal; i.e., the surface sites and other functional groups were not present in the pristine MWCNTs. In contrast, a number of IR peaks are present in the spectra of the functionalized MWCNTs (Fig. 1b–d). The figure shows a very broad and intense absorption peak at 3395 cm^{-1} due to the intermolecular H-

bonded O–H stretch, present in all the f-CNTs. The small and less intense peak at 1584 cm^{-1} is associated with the absorption frequency of the olefinic double bond in conjugation with the carbonyl group. The peak at 1384 cm^{-1} is due to the O–H bending deformation in –COOH groups.

The less intense and very weak peak seen at 2352 cm^{-1} is due to the terminal C=C stretching present in the CNT framework [49]. This intensity of the peak is shifted to 2362 cm^{-1} in all the FT-IR spectra of f-CNTs. Therefore, it proves that the C=C groups in the CNTs are readily bonded with the carboxylic acid (–COOH) groups or hydroxyl (–OH) groups. Adding functional groups, such as hydroxyl (-OH) or carboxyl (-COOH), to CNTs improves their dispersibility in different liquid solvents and interactions with other chemicals, including polymeric materials [50]. Thus, the generation of the –OH and –COOH groups on CNTs due to their functionalization was confirmed. Furthermore, it showed that $KMnO_4$ was capable of opening the π–bonds of MWCNTs. The significant absorption characteristics seen at 1300 cm^{-1} and 1150 cm^{-1} have been correlated to the symmetric and asymmetric lengths of the C=C containing groups within nanotubes. The absorbance at 1225 cm^{-1} corresponds to a C−C stretching. The broad yet intense absorption at 3395 cm^{-1} suggests a large concentration of −OH groups.

The sharp and very intense peaks at 1706 cm^{-1} indicated the presence of carbonyl groups (C=O stretch), indicating carboxylation was the predominant functionalization reaction that occurred (C(sidewall)-(O)-COx(H)) particularly in a-CNTs and n-CNTs (Fig. 1b and d). The peak arising due to the C=O stretch was not observed in the b-CNTs samples (Fig. 1c). Therefore, it was further confirmed that b-CNTs report the hydroxyl group as the dominant group for basic permanganate oxidation reactions. According to the publications, tests have been conducted utilizing thermal oxidation, chemical-based and UV/Ozone treatment, especially aimed at achieving carboxylation of MWCNTs; an examination in these cases revealed that hydroxyl functionalization had happened [51].

In 2008, Yuan et al. provided an easy method to purify MWCNTs, involving chlorine water and ammonia water [52]. However, in the current innovative approaches to the purification and functionalization of MWCNTs, examination of current materials revealed that selective oxidization of carbon nanotubes can be accomplished by employing a hydrothermal process, opening up an entirely new route to the intended specific chemical-based manipulation of nanotubes. Additionally, the IR studies gave evidence of the –COOH groups, −OH groups, −COOH combined with –OH groups being attached during the hydrothermal oxidation of MWCNTs with $KMnO_4$, using PTC in acidic, basic and neutral media respectively. The selectivity of the above processes was confirmed according to the proposed reaction schemes for the purification and oxidation of MWCNTs by using $KMnO_4$ in the hydrothermal and filtration stages are given in the following equations 1–6.



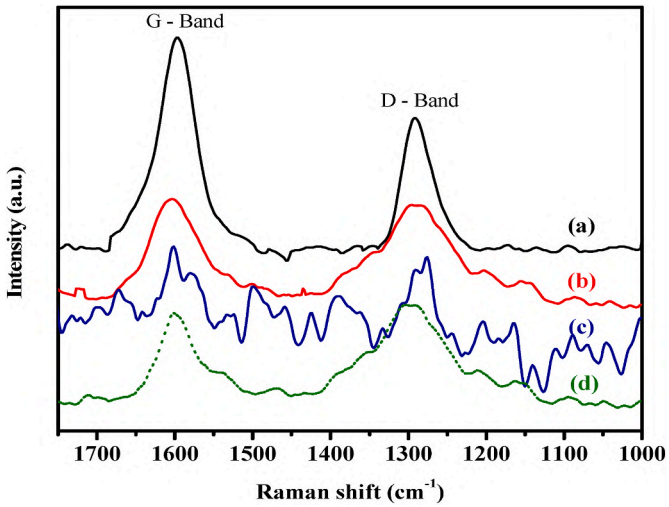


Fig. 2. FT-Raman spectra of (a) raw-CNTs, (b) a-CNTs, (c) b-CNTs and (d) n-CNTs.

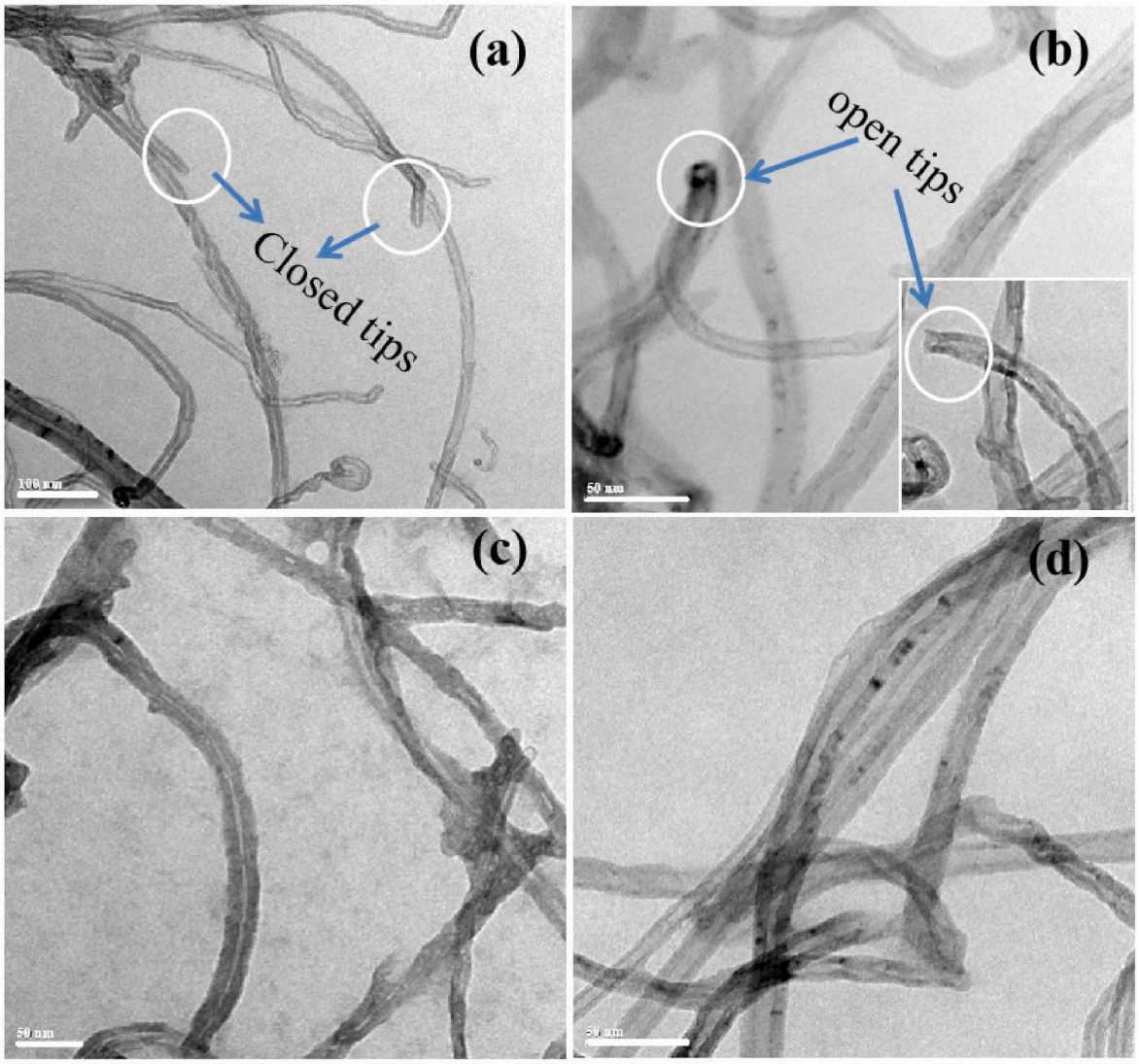
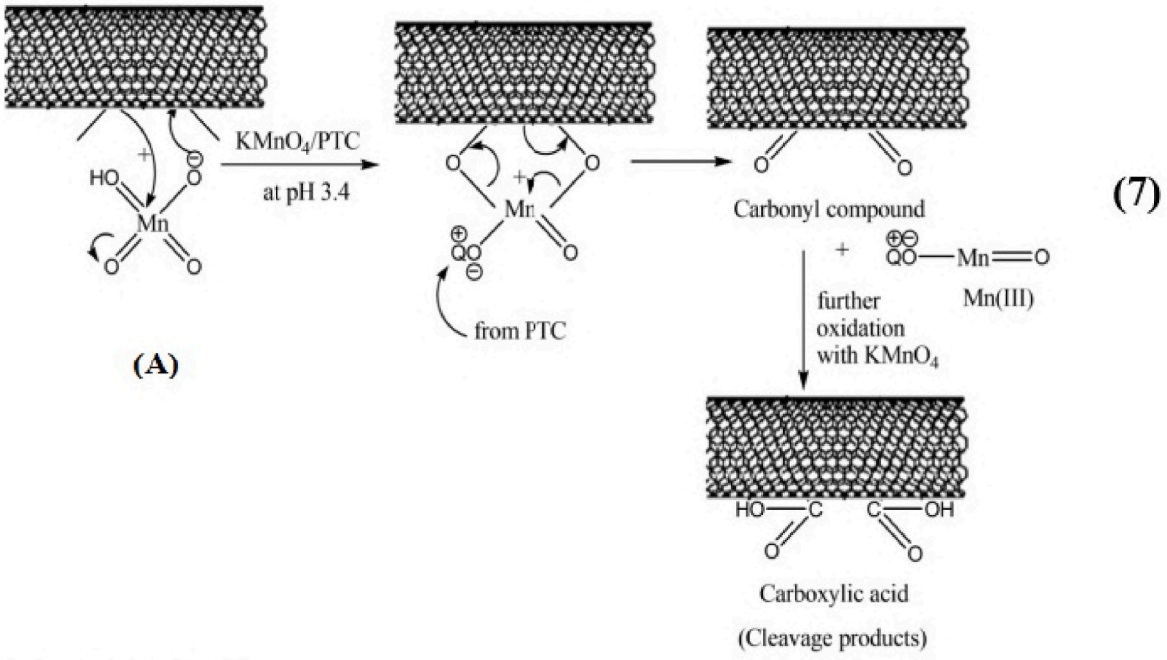
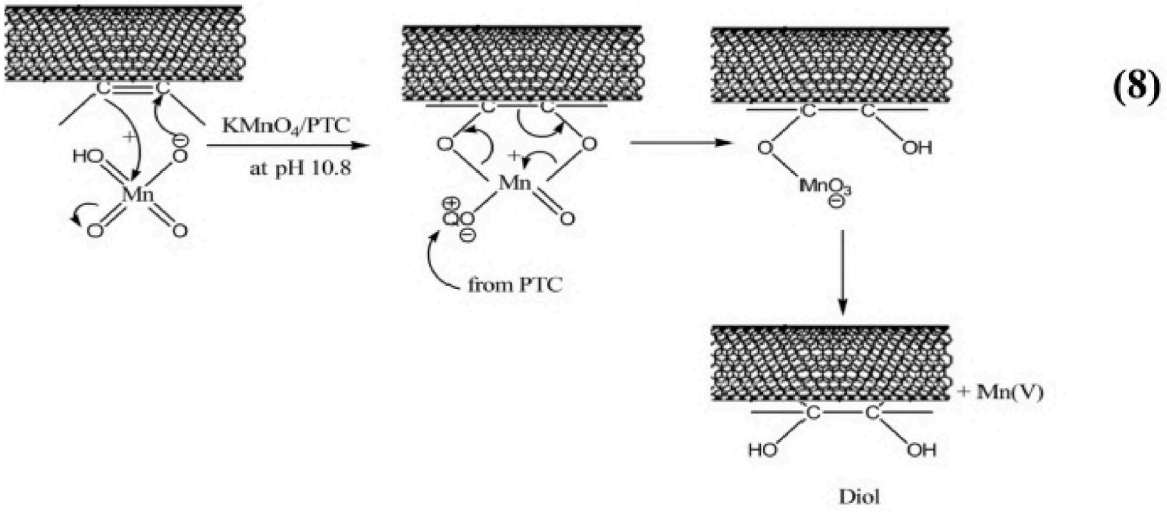


Fig. 3. TEM images of (a) raw-CNTs, (b) a-CNTs, (c) b-CNTs and (d) n-CNTs.

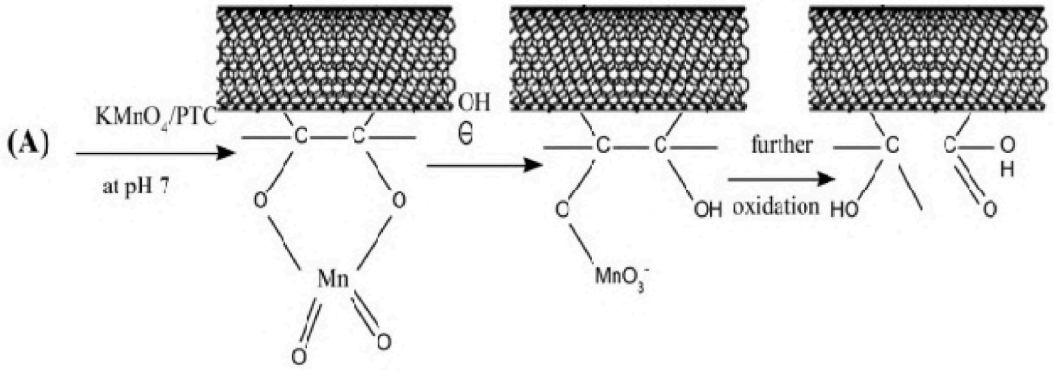
The proposed reaction mechanisms for the oxidation of MWCNTs by using $KMnO_4$ with PTC in hydrothermal stage under various pH media, such as acidic pH 3.4, basic pH 10.8 and neutral pH 7.0, are given in the schemes 7, 8 and 9 [53] respectively.



(7)



(8)



(9)

3.2. FT-Raman analysis

The investigated substances were subjected to several Raman studies, with typical spectra provided in Fig. 2. The Raman spectrum of the unprocessed CNT solid are displayed in the upper plot of Fig. 2. The graphitic G-band does not separate at the high frequency ultimately of the Raman spectrum, other than the G-peak fails to appear as a shoulder on the main G′-peak. This phenomenon was explained by two factors: first, a broadening prompted by the concurrently processed excitation of numerous tubes, which resulted in a combining with G′; and secondly, the existence of larger-dimension tubes and resulting in mostly provided primarily broad bands identical to the structure of graphite. All of the Raman spectra's D-band at 1302 cm^{-1} revealed an ID/IG ratio of 1.6 % for the virgin specimen, which is 5–12 % more than for the f-CNTs generated from functionalized CNTs. This suggested a significantly greater level of dimensional organization in the as-grown outcome, owing to fewer defect locations.

The Raman spectra of functionalized MWCNTs (f-CNTs) are presented in Fig. 2. The ID/IG ratio fluctuates with pH medium, indicating that further functionalization has occurred on the surface of the material. The drop in the G-band (1592 cm^{-1}) has been attributed to a decrease in resonant Raman intensification following functionalization, since the incorporation of an irregular configuration of sp^2 bonded side groups to the MWCNTs produces a lack of symmetry in the bonded nanotube framework [54]. This resulted in a widening and decrease in the van Hove singularity states (vHs), diminishing the resonance impact

Table 2
Weight % of elements present in CNTs after oxidation with $KMnO_4$ at various pH medium.

pH medium	Weight %[a]							% purity of carbon
	C	O	Fe	Mo	Mg	K	Mn	
Raw	94.53	2.88	0.92	1.3	0.24	0.12	–	94.53
Acidic	94.36	5.24	0.04	0.36	–	–	–	99.82
Basic	94.31	4.27	0.42	1.0	–	–	–	99.77
Neutral	93.74	3.65	0.29	–	0.28	–	2.05	99.16

[a] From EDX under TEM analysis.

[55]. In addition to the loss of symmetry, the covalent attachment of electron withdrawing groups, such as carboxylate or hydroxyl groups, resulted in the removal of electrons from the valence vHs in MWCNT. Increased lattice disorder generated by side wall functionalization intensifies the D-band, increasing the ID/IG ratio [56]. Functionalization reduces symmetry and electronic resonance in the C-C tangential mode, resulting in lower G-band intensity in f-CNT spectra.

3.3. TEM observation

TEM (Transmission electron microscopy) micrographs of MWCNTs before and after the required functionalization by $KMnO_4$ using PTC are presented in Fig. 3a and b respectively. The Fe-Mo/MgO catalyst retains the crystallinity and shapes of MWCNTs in the starting CNT material (i.e. raw-CNTs) confirmed from Fig. 3a. Moreover, no amorphous carbon was

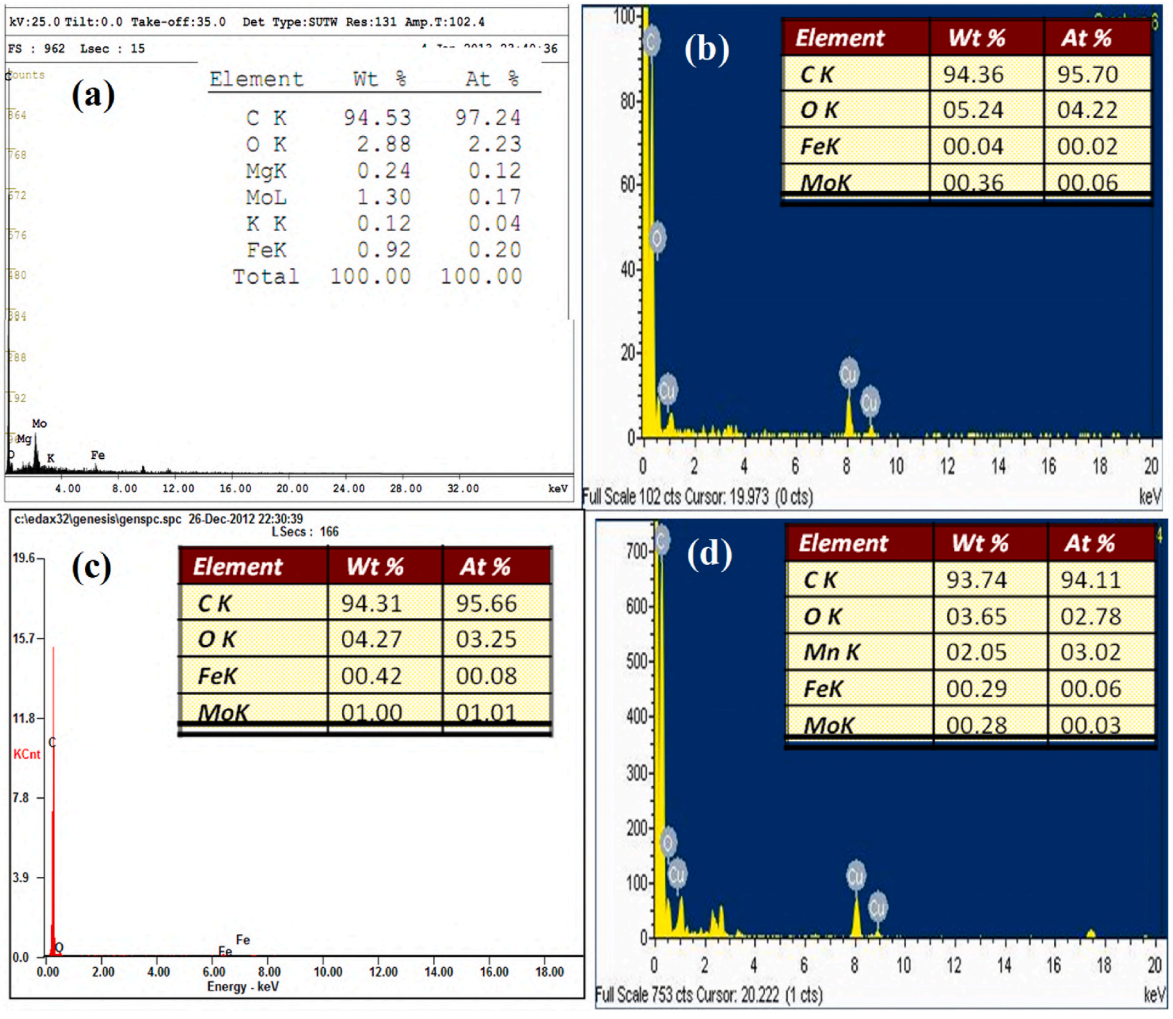


Fig. 4. Atomic % ratios from the surface of (a) raw CNTs, (b) a-CNTs, (c) b-CNTs and (d) n-CNTs (EDX spectroscopy measurements under TEM analysis).

observed on these nanotubes. It was also clear from the images, that the CNT end caps, which were present in the TEM image of the raw-CNTs, are not present in the TEM image of the f-CNTs (shown by circular area). This implies that the end caps of the CNTs were broken due to hydrothermal oxidation, in the functionalization of MWCNTs (shown in the inset Fig. 3b).

The EDX performed on the samples of raw and f-CNTs taken under TEM images in Fig. 3 are given in Fig. 4. The surface element compositions of different CNTs were analyzed by EDX, and the results are summarized in Table 2. Signature emissions of C, O, Mg, Mo and Fe were observed in the raw CNTs (Fig. 4a). After functionalization, the oxygen content of all the samples increased significantly. For the sample oxidized in an acidic medium, the oxygen amount increases nearly 2 times that of the raw CNTs and for those oxidized with $KMnO_4$, the oxygen sharply increased to 5.24 %. The differences in the increase degree of the oxygen content were due to different activities of $KMnO_4$ in various pH medium. Based upon its pH levels a solution containing $KMnO_4$ transforms into various chemical compounds. It is converted to a colorless solution, Mn^{2+} under pH lower than 7. It generates a brown precipitate, MnO_2 at pH = 7. At pH > 7, it produces a green solution MnO_{2-4}.

Fig. 4b shows 94.36 % carbon, 5.24 % oxygen, 0.36 % molybdenum and 0.04 % iron by weight was present, accounted for by the presence of surface functional groups on the CNT structures. Less than 1 wt % iron was detected, which can be attributed to the $KMnO_4$ used in the present hydrothermal method that was used to oxidize, and removed as iron oxide. In acidic pH 3.4 seemed to be much more functionalized and easier to be oxidized than other pH medium. Therefore, only in the acidic pH medium, MWCNTs were more suitable for the covalent functionalization with the carboxyl groups [57]. Table 2 lists the weight % ratios that range found for each of the MWCNTs depicted in Fig. 4. The findings reveal that the surfactants causes zero amounts of manganese and potassium, these may be totally eliminated as a result of the washing process. But, in the n-CNTs, and the samples displayed a weight % ratio of manganese at 2.05 %, which was detected by EDX (Fig. 4 d). Therefore, the present results gives strong evidence, that the removal of the MnO_2 from nanotube is quite easy by the present novel approaches.

3.4. Thermal analysis

The thermogravimetric investigation was carried out on the functionalized MWCNTs depicted in Fig. 5. These specimens were subjected to heating in an inert surroundings using a 50 mL min^{-1} supply of the nitrogen at an average rate of 10 °C min^{-1}, until they reached a maximum desired temperature of 1000 °C. The TG data reveals a mass loss ranging from ~10 % to ~15 % for a-CNTs (Fig. 5a), which indicates steady mass reduction across the whole temperature range. The f-CNT curve indicates an overall mass degradation of 40 % up to 1000 °C, including about 30 % mass drop below 400 °C with two discrete phases. The following graphs show temperature-induced reductions in mass according to inert circumstances for unprocessed CNTs, wherein the bulk of the carbon and MWCNTs remains during combustion. On the other hand, the f-CNT samples' elevated loss suggests that the side-wall as well as tube end functional molecules have been eliminated. The progressive losses below 400 °C give some insight into the existence of various functional groups [58]. TG analysis of information reveals that heating to 400 °C in an inert surroundings will be enough to completely eliminate carbon nanotube functioning. The results obtained are fairly similar to the DTG spectrum analysis (Fig. 6).

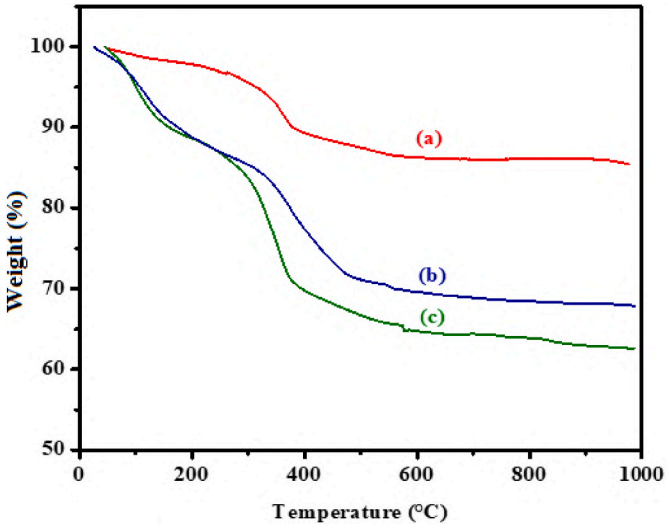


Fig. 5. TG spectra lines of MWCNTs at various temperature rates of (a) a-CNTs, (c) b-CNTs, and (d) n-CNTs.

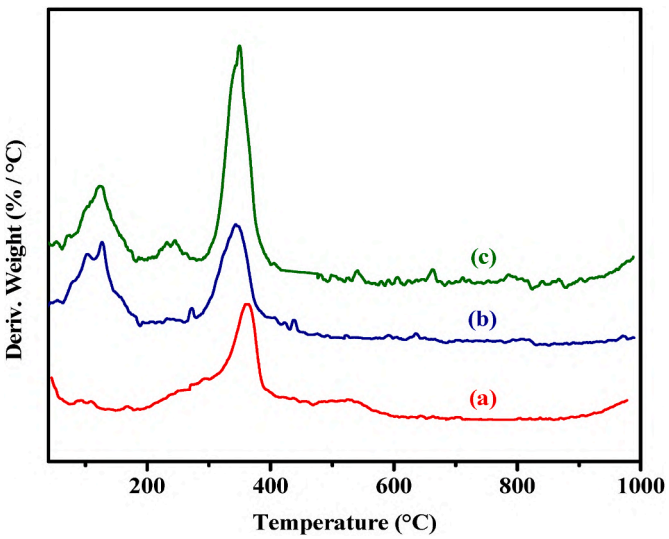


Fig. 6. DTG spectra lines of MWCNTs at various temperature rates of (a) a-CNTs, (c) b-CNTs and (d) n-CNTs.

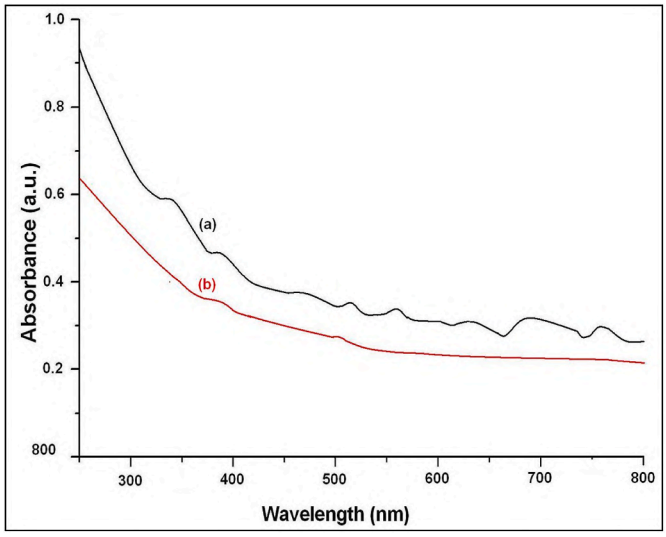


Fig. 7. Visible-near IR absorption spectra of (a) before and (b) after functionalization with $KMnO_4$ using PTC in acidic medium.

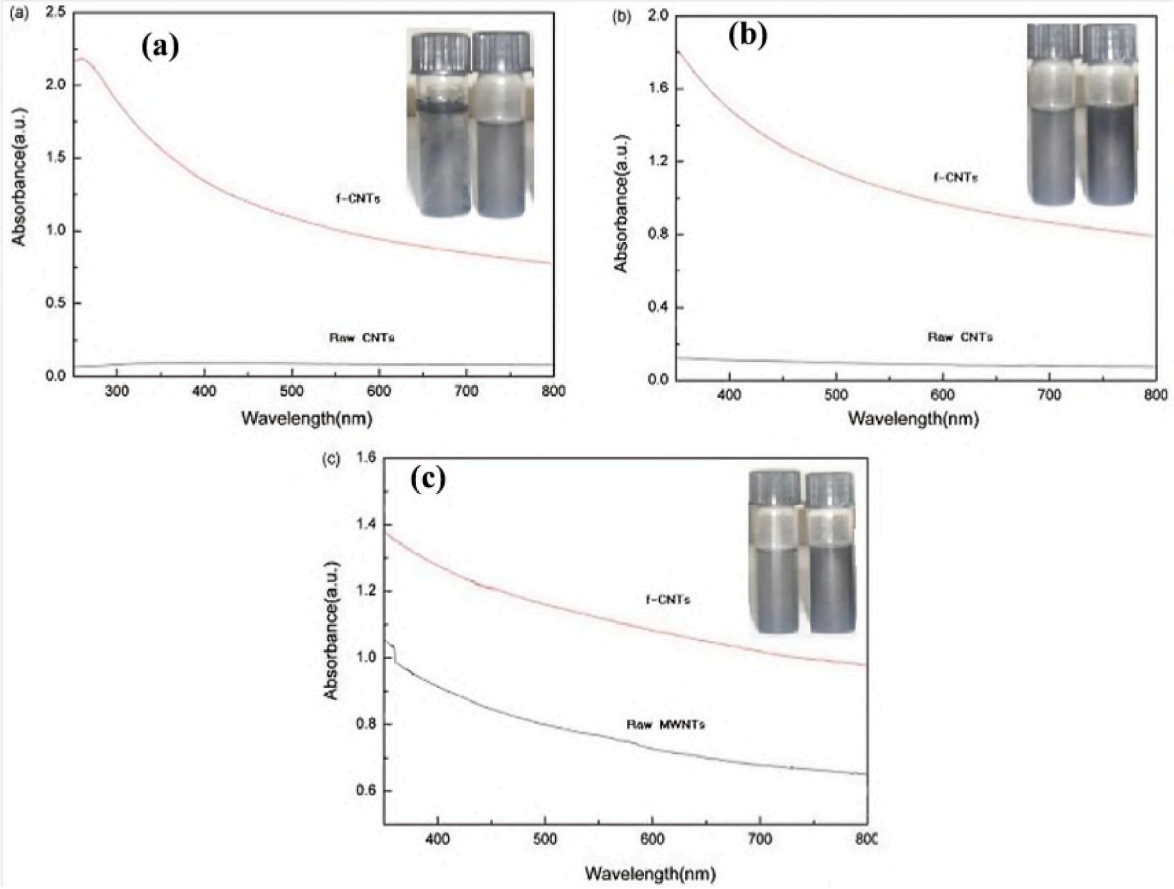


Fig. 8. UV–visible spectra of the samples in: (a) H_2O, (b) ethanol and (c) dichloromethane at a concentration of 1 mg/10 mL collected 6 h following the solution was successfully sonicated for 1 h.

Table 3
Specimen absorbance at 800 nm was measured at a concentration of 1 mg/10 mL.

Solvent	Raw-CNTs	a-CNTs
H_2O	0.0842	0.9451
Ethanol	0.0886	0.9684
CH_2Cl_2	0.7258	1.0830

3.5. Visible-near IR absorption spectroscopy analysis

The representative visible-near IR absorption spectra of raw CNTs and a-CNTs are shown in Fig. 7. It is well known that the visible-near IR absorption spectra show the common signs of covalent functionalization [23]. The trace in Fig. 7a shows the characteristic van Hove singularities (vHs) of raw (unfunctionalized) materials that disappear after functionalization in the trace (Fig. 7b), which confirmed, that the covalent functionalization occurred on the surface of the MWCNTs.

3.6. UV–visible spectroscopy studies

The functionalized CNTs solid material obtained from the permanganate oxidation by the hydrothermal the scale-up experiment was evaluated for dispersibility in various solvents such as H_2O, ethanol, and dichloromethane (shown in Fig. 8), and the samples were assessed using a UV–visible spectrophotometer to acquire quantitative results. To determine maximal dispersibility, use light absorbance measurements and assume a Beer-Lambert relation [59,60]. Plotting the UV–visible absorbance (at 800 nm) vs. concentration (1 mg/10 mL) produced the calibration curves. These findings are presented in Table 3. The dispersibility of MWCNTs was remarkably changed after the oxidation with $KMnO_4$ with PTC in an acidic medium. Optical micrographs of the samples in various solvents are also given in the inset of Fig. 8. For further confirmation of the above phenomenon, it was observed that MWCNTs terminated with carboxylic acid groups in a-CNTs, and the dispersibility of raw MWCNTs decreased substantially in each of the aforementioned solvents. This phenomena is particularly fascinating in the field of CNT functionalization. It is critical because a-CNTs are thought to have great promise in delivering medications, biological products technology, and medical diagnostics.

4. Conclusions

In this particular investigation, we demonstrated methods to effortlessly perform sequential purification and oxidation adopting $KMnO_4$ as well as PTC in three separate pH media: acidic, basic, and neutral. We achieved the aforementioned through employing the hydrothermal approach. The obtained materials have discussed by various physicochemical methods along with EDX data. From the accumulated results, the new method developed for simultaneous purification and oxidation of MWCNTs in acidic medium when compared to the second step purification by air oxidation followed by 36 % HCl treatment (90.07 %), it was efficient in eliminating the majority of the catalyst particles and amorphous carbon, leaving high purity CNTs with a maximum of 98.6 %. The raw CNTs from Fe-Mo/MgO catalysts, together with the purification process, presented a promising method for synthesizing extremely pure MWCNTs. This was proved from the comparison of the FT-IR, TEM and EDX results of the present materials with raw CNTs. The morphology of the CNTs after functionalization has been preserved. The

hydrothermal procedures of the functionalization of CNTs generated mainly the –COOH groups in a-CNTs, –OH groups in b-CNTs, and both functional groups are presented in n-CNTs, more easily at the caps than at the walls. Furthermore, the present study evidenced that $KMnO_4$ with PTC aims to target certain π-bonds without destroying the carbon nanotubes' graphene as its frameworks that exist. The enhanced oxidation process made possible by PTC is predicted to be a cost-effective way to produce high-grade multifunctional carbon nanotubes on huge quantities

CRediT authorship contribution statement

J. Logeswari: Writing – original draft. **T. Kamatchi:** Writing – review & editing. **P. Kumaresan:** Supervision.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

The authors do not have permission to share data.

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