

RESEARCH PAPER

Controllable Synthesis of Nitroaryl Functionalized Carbon Nanotubes under Mild and more Efficient Conditions

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ABSTRACT

In this research, the controllable synthesis of carbon nanotubes (CNTs) functionalized with derivatives of diazonium salts containing $-\text{NO}_2$ was carried out under mild and more efficient conditions (i.e. lower reaction temperature, shorter reaction time, assisting microwave and using radical scavenger) to study the morphology of these compounds before and after functionalization. For this purpose, the reactions of single-walled (SWCNT) and multi-walled (MWCNT) carbon nanotubes with 2-nitroaniline, 4-nitroaniline and 2,4-dinitroaniline in the presence of isoamyl nitrite as diazotization agent were performed at different conditions (i.e. solvent free, in dimethylformamide (DMF) solvent, thermal and microwave). The nitroaryl functionalized CNTs were characterized by X-ray diffraction (XRD) measurement, field emission scanning electron microscopy (FE-SEM), Raman spectroscopy, Fourier transform infrared (FT-IR) spectroscopy, ultraviolet-visible (UV-Vis) spectroscopy, energy dispersive X-ray (EDX) technique and elemental map analysis. The results clearly confirmed the successful controllable functionalization of CNTs by nitroaryl diazonium ions without any byproducts. The morphology of CNTs after functionalization is tubular. Functionalization of SWCNT by nitroaryl diazonium ions improves the crystallinity of starting material; while the crystallinity of MWCNT decreases with functionalization. The samples synthesized under microwave are more amorphous than samples synthesized under thermal conditions.

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INTRODUCTION

Since the discovery of CNTs, these compounds have been considered as one of the most promising materials for a wide range of applications in molecular electronics, materials science, nanotechnology, chemistry, etc. [1]. The surface modification of CNTs plays an important role in their use in the fields of nanomechanic devices, molecular electronics, energy storage, sensing and composite materials [2]. Therefore, the chemical modification of CNTs can open a way to modify the properties of these compounds.

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Aryl diazonium salts ($\text{Ar}-\text{N}_2^+\text{X}^-$) are one of the most important highly reactive organic compounds, which have very useful applications in organic synthesis and industry [3]. These compounds are starting materials for attachment of halogens, CN, OH, H, etc. into an aromatic ring in nucleophilic aromatic substitution reactions [4]. Also, they are widely used for synthesis of azo materials, which are extraordinary importance as dyes [5].

It was reported that diazonium salts can react with CNTs via chemical and electrochemical



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methods [6, 7]. All of these methods generate reactive intermediates from the aryl diazonium salts, which can then react with the CNTs surface to form covalent bonds [8]. Ellison and Gasda [9] performed the functionalization of SWCNTs by 4-amino (NH_2) substituted aniline in a single-step diazonium reaction using sodium nitrite and H_2SO_4 at 60 °C. Bahr and Tour [10] reported the thermal reaction of SWCNTs with diazonium compounds generated by action of isoamyl nitrite on 4-substituted aniline derivatives (with Cl, t-Bu, COOMe, NO_2 and COOH substituents) at 60 °C in acetonitrile solvent. Dyke et al. [11, 12] developed the thermal functionalization of SWCNTs for a series of 4-substituted anilines (with Cl, Br, t-Bu, COOMe and NO_2 substituents) and isoamyl nitrite in solvent free conditions at 60 °C. Also, they studied the reaction product analysis of SWCNTs functionalized by solvent free (isoamyl nitrite, 60 °C) and aqueous-based aryl diazonium species (sodium nitrite/acid, 60 °C) [12]. Price and Tour [13] performed the functionalization of SWCNTs on water in the presence of 4-substituted anilines (with F, Cl, Br, I, SO_3H , n-Bu, t-Bu, COOH, COOMe and NO_2 substituents) and isoamyl nitrite at 80 °C. Abrahamson et al. [14] reported the functionalization of SWCNTs with 4-nitro and 2,4-dinitrobenzenediazonium tetrafluoroborates in aqueous solution of sodium dodecyl sulfate (SDS) at 50 °C as well as reaction of 2,4,6-trinitroaniline with sodium nitrite in $\text{H}_2\text{SO}_4/\text{AcOH}$ at 25 °C. Shiraki et al. [15] observed unique photoluminescent solvatochromism for functionalized SWCNTs via 4-nitrobenzenediazonium salt in $\text{D}_2\text{O}/\text{SDS}$. Liu et al. [16] studied the functionalization of SWCNTs by diazonium salts generated by 4-methoxy (OCH_3) substituted aniline and isoamyl nitrite through thermal (solvent-free, 60 °C) and microwave-assisted (150 W, in o-xylene solvent) reactions. Mamane et al. [17] investigated the effect of microwaves on the functionalization of SWCNTs by the diazonium method. The functionalization was carried out by treating SWCNTs with 4-chloro (Cl) substituted aniline and isoamyl nitrite under microwaves at 200 °C. Powell et al. [18, 19] shown that functionalization of SWCNTs using diazonium salts can be significantly accelerated by optical excitation of carbon nanotubes. Lipińska et al. [20] studied the functionalization of MWCNT by reaction of 4-substituted anilines (with F, Cl, I, NH_2 , NO_2 , OH, COOH, COOEt and Et substituents) in the presence and absence of isoamyl nitrite in

DMF solvent at 80 °C. Salice et al. [21] reported the functionalization of MWCNTs by addition of aryl diazonium salts generated by treatment of 4-methoxy (OCH_3) substituted aniline with isoamyl nitrite at 60 °C in 1-cyclohexylpyrrolid-2-one as solvent. Benschgaier et al [22] developed the modification of MWCNT by 4-azido (N_3) substituted aniline in isoamyl nitrite at 60 °C.

Nowadays, the synthesis of energetic materials has been increasingly used in defense and non-defense industries. Organic compounds containing nitro group have high energy content and they are one of the most usable compounds for military applications [23]. For this reason, researchers in the world try to develop easier and more efficient methods to prepare and characterize high energy materials. It was reported that functionalization of carbon nanomaterials by high energy substituents increases the energy content and enhances the energetic properties of these compounds [24-29]. The nitroaryl functionalized CNTs can be considered potentially as highly promising nanoenergetic materials [14]. Among these compounds, 4-nitrophenyl functionalized CNT (p-MNP/CNT) has been the most studied [10-15, 18-20]; while no or few studies on 2-nitrophenyl (o-MNP/CNT), 2,4-dinitrophenyl (DNP/CNT) and 2,4,6-trinitrophenyl (TNP/CNT) functionalized CNTs were reported [14] (especially for MWCNT). Also as far as we know, the characterization of these compounds were limited to XPS (X-ray photoelectron spectroscopy), FT-IR, ATR-IR (attenuated total reflectance infrared spectroscopy), UV-Vis-NIR (ultraviolet-visible-near infrared absorption spectroscopy), Raman, photoluminescence spectroscopy, TGA (thermogravimetric analysis) and DSC (differential scanning calorimetry) for the selected ones (see Table 1).

After studying the literature reports, it is found that there are several problems in the functionalization of CNTs by diazonium salts. The diazotization methods which used sodium nitrite and benzenediazonium tetrafluoroborates at room temperature under aqueous conditions increase the risk of the generation of phenolic byproducts which may adsorb on the surface, rather than covalently attach as would be expected of radical coupling [30]. Therefore, the diazotization in nonpolar media with isoamyl nitrite even at higher temperatures is more convenient for functionalization of CNTs by

Table 1. Bibliography of recently literature reports about the synthesis of nitroaryl functionalized carbon nanotubes in different conditions, compared to the present study.

Compound	Preparation method	Temperature (°C)	Diazotization agent	Solvent	Characterization techniques	Ref.
TNP/SWCNT	Thermal	25	Sodium nitrite/Acid	H ₂ O/SDS	DSC, Raman, FT-IR	[14]
<i>p</i> -MNP/SWCNT	Thermal	60	Sodium nitrite/Acid	H ₂ O	-	[12]
<i>p</i> -MNP/SWCNT	Thermal	25	4-Nitrobenzenediazonium tetrafluoroborate	H ₂ O/SDS or D ₂ O/SDS	Photoluminescence	[11, 15]
<i>p</i> -MNP/SWCNT	Thermal	25	4-Nitrobenzenediazonium tetrafluoroborate	D ₂ O/SDS	UV-Vis-NIR, XPS	[18, 19]
DNP/SWCNT	Thermal	45	2,4-Dinitrobenzenediazonium tetrafluoroborate	H ₂ O/SDS	DSC, Raman, FT-IR	[14]
<i>p</i> -MNP/SWCNT	Thermal	50	4-Nitrobenzenediazonium tetrafluoroborate	H ₂ O/SDS	DSC, Raman, FT-IR	[14]
<i>p</i> -MNP/SWCNT	Thermal	60	Isoamyl nitrite	Acetonitrile	UV-Vis-NIR, Raman, TGA	[10]
<i>p</i> -MNP/SWCNT	Thermal	60	Isoamyl nitrite	Solvent free	UV-Vis-NIR, ATR-IR, Raman, TGA	[11, 12]
<i>p</i> -MNP/SWCNT	Thermal	80	Isoamyl nitrite	H ₂ O	UV-Vis-NIR, XPS, TGA	[13]
<i>p</i> -MNP/MWCNT	Thermal	80	Isoamyl nitrite	DMF	XPS, TGA, IR	[20]
<i>o</i> -MNP/SWCNT						
<i>p</i> -MNP/SWCNT						
DNP/SWCNT	Thermal	60		Solvent free	XRD, FE-SEM, Raman, FT-	
<i>o</i> -MNP/MWCNT	Microwave	180 W	Isoamyl nitrite, DPPH	and DMF	IR, UV-Vis, EDX, elemental map	This work
<i>p</i> -MNP/MWCNT						
DNP/MWCNT						

diazonium compounds (see Table 1). However, this method also has some problems due to the formation of azo bridges on the surface [20, 30] and polymerization of aryl moieties [30-33], especially where the microwave conditions were used [17, 30]. Therefore, the morphology of nitroaryl functionalized carbon nanotubes maybe poorly defined as a consequence of the attachment of byproducts to the CNTs surface.

In this article, the controllable synthesis of high energy nanomaterials based on CNTs (MWCNT and SWCNT) and nitroaryl diazonium ions are performed under mild and more efficient conditions (i.e. lower reaction temperature, shorter reaction time, assisting microwave and using radical scavenger for blocking radical polymerization and preventing any further couplings). The various instrumental techniques including XRD, FE-SEM, Raman, FT-IR, UV-Vis, EDX and elemental map are used for characterization of nitroaryl functionalized CNTs. Also, four methods are used for attachment of nitroaryl groups to both of MWCNT and SWCNT in similar conditions with focus on the morphology of these compounds using XRD, FE-SEM, EDX and elemental map techniques which were not reported before. We think this study is important for the development

of chemistry and applications of CNTs.

MATERIALS AND METHODS

Materials and instruments

MWCNTs (purity >95%, outside diameter: 20-30 nm, inside diameter: 5-10 nm, length: 10-30 μm) and SWCNTs (purity >90%, average diameter: 1.1 nm, length: 5-30 μm) were purchased from US Research Nanomaterials Inc. 2-Nitroaniline, 4-nitroaniline, 2,4-dinitroaniline and isoamyl nitrite were purchased from Merck. DPPH (2,2-diphenyl-1-picrylhydrazyl) radical scavenger was purchased from Sigma-Aldrich. The organic solvents (diethyl ether, acetone and DMF) were prepared from Merck Chemical Co.

The XRD patterns were recorded in the range of 10-75° (2θ) by Bruker D8-Advance diffractometer with CuKα radiation. The FE-SEM images were obtained by TE-SCAN MIRA III Field Emission Microscope. Raman spectra in the range 400-3500 cm⁻¹ were carried out using Teksan. The FT-IR spectra in the range 400-3500 cm⁻¹ were obtained using KBr pellets on a Perkin-Elmer RXI Fourier transform infrared spectrophotometer. The UV-Vis absorption spectra in the range 200-800 nm were monitored by Analytik Jena SPECORD-205 UV-Vis spectrophotometer. Semi-

quantitative elemental analysis were done by EDX analyzer as well as elemental map analysis.

Functionalization of CNTs under thermal and solvent free conditions

6 mg of CNTs (MWCNT and SWCNT) and 250 mg of amine (2-nitroaniline, 4-nitroaniline and 2,4-dinitroaniline) were added to a flask and then 1 mL of isoamyl nitrite containing radical scavenger (1 μ M) was added dropwise. The reaction mixture was heated at 60 °C under stirring for 48 h. The nitroaryl functionalized CNTs were filtered by sintered glass filter and washed with solvents (diethyl ether, DMF and acetone) until the filtrate became colorless. The collected products were dried at room temperature for 24 h.

Functionalization of CNTs under thermal and solvent conditions

6 mg of CNTs (MWCNT and SWCNT) were dispersed to 5 mL of DMF solvent in a flask under sonication for 10 min. Then, 250 mg of amine (2-nitroaniline, 4-nitroaniline and 2,4-dinitroaniline) and 1 mL of isoamyl nitrite containing radical scavenger (1 μ M) were added and the reaction mixture was heated at 60 °C under stirring for 48 h. The nitroaryl functionalized CNTs were filtered by sintered glass filter and washed with solvents (diethyl ether, DMF and acetone) until the filtrate became colorless. The collected products were dried at room temperature for 24 h.

Functionalization of CNTs under microwave and solvent free conditions

6 mg of CNTs (MWCNT and SWCNT) and 250 mg of amine (2-nitroaniline, 4-nitroaniline and 2,4-dinitroaniline) were added to a flask and then 1 mL of isoamyl nitrite containing radical scavenger (1 μ M) was added dropwise. The reaction mixture was placed in a microwave oven at 180 W for 50 min. The nitroaryl functionalized CNTs were filtered by sintered glass filter and washed with solvents (diethyl ether, DMF and acetone) until the filtrate became colorless. The collected products were dried at room temperature for 24 h.

Functionalization of CNTs under microwave and solvent conditions

6 mg of CNTs (MWCNT and SWCNT) were dispersed to 5 mL of DMF solvent in a flask under sonication for 10 min. Then, 250 mg of amine (2-nitroaniline, 4-nitroaniline and

2,4-dinitroaniline) and 1 mL of isoamyl nitrite containing radical scavenger (1 μ M) were added and the reaction mixture was placed in a microwave oven at 180 W for 50 min. The nitroaryl functionalized CNTs were filtered by sintered glass filter and washed with solvents (diethyl ether, DMF and acetone) until the filtrate became colorless. The collected products were dried at room temperature for 24 h.

RESULTS AND DISCUSSION

Controllable functionalization of CNTs by nitroaryl diazonium ions

The nitroaryl functionalized CNTs are controllably synthesized using reaction of CNTs (MWCNT and SWCNT) and nitroaryl diazonium ions under mild and more efficient conditions to investigate the morphology of these compounds before and after functionalization without any byproducts attached to the CNTs surface. The nitroaryl diazonium ions are generated *in situ* using reactions of 2-nitroaniline (*o*-nitroaniline), 4-nitroaniline (*p*-nitroaniline) and 2,4-dinitroaniline with isoamyl nitrite. These compounds are used for attachment of mononitrophenyl (*o*-MNP and *p*-MNP) and dinitrophenyl (DNP) substituents to CNTs under thermal and microwave conditions, in DMF solvent or solvent free (Fig. 1). A micromolar concentration of DPPH radical scavenger is added to the reaction medium for blocking radical polymerization and preventing any further couplings. It was reported that the addition of radical scavenger to diazonium solution effectively limits the formation of polyaryl layer [34].

According to Table 1, the synthesis of nitroaryl functionalized CNTs is performed at different protocols compared to previous reports, i.e. lower reaction temperature under thermal and shorter reaction time under microwave conditions. It can be seen that the synthesis of nitroaryl functionalized MWCNTs under thermal solvent free, microwave solvent free and microwave DMF conditions, and the synthesis of nitroaryl functionalized SWCNTs under thermal DMF, microwave solvent free and microwave DMF conditions have not been reported so far. Also, functionalization of MWCNT is carried out at milder thermal conditions (i.e. lower temperature, 60 °C) than previous literature reports (80 °C, Table 1) in DMF solvent. Moreover, the preparation methods are developed for functionalizing both of MWCNTs and SWCNTs by nitroaryl diazonium ions in similar conditions,

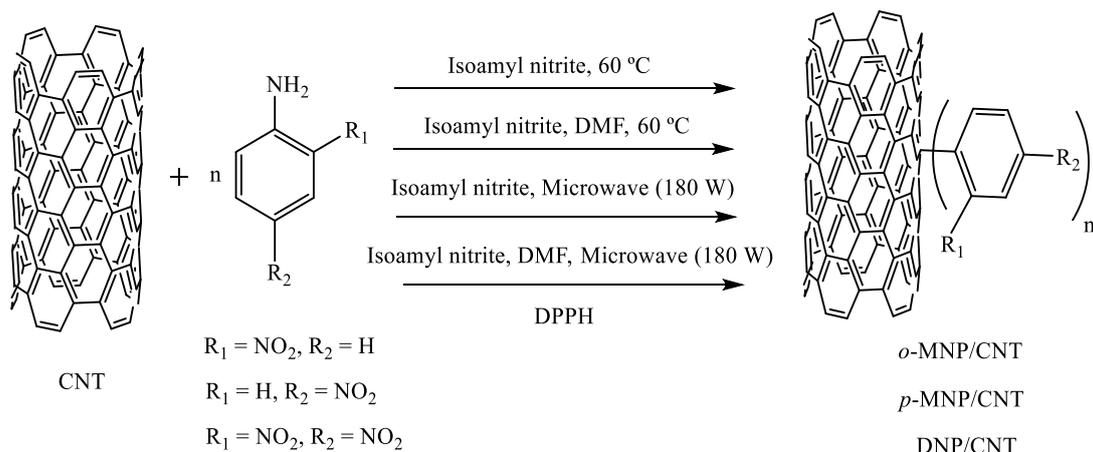


Fig. 1. The controllable functionalization of CNTs by nitroaryl diazonium ions produced insitu using reaction of nitroaromatic amines with isoamyl nitrite containing radical scavenger.

which are not reported elsewhere. As MWCNTs are less reactive than SWCNTs [20], this feature of the present study can be important. Comparison of the methodologies used for functionalization of CNTs by nitroaryl diazonium ions indicates that the reactions can be achieved in only 50 min using microwave instead of 48 h, necessary for the thermal conditions. Therefore, microwave is more rapid and efficient method for attachment of nitroaryl groups to CNTs.

Following the reaction mechanism

The proposed mechanism for the formation of aryl diazonium ions from aromatic amines and isoamyl nitrite involves the generation of aryl diazohydroxide intermediate which can convert into the corresponding diazonium ion or decompose to aryl radical [35]. Based on the previous reports for CNTs [36], it is investigated that the first step of the addition of diazonium

ions to CNTs involves the reductive dissociation of diazonium ion with releasing nitrogen gas and the formation of an aryl radical which can react with C=C double bonds of CNTs in order to functionalize them.

To follow-up the reaction mechanism and ensure the formation of nitroaryl radicals, the DPPH radical scavenger is added to the reaction medium. This molecule is a stable synthetic free radical which is widely used to evaluate the ability of compounds to act as free radical scavengers or radical hydrogen donors [37]. It was reported that DPPH blocks radical polymerization and prevents all couplings further from the surface [34]. The DPPH contributes in homolytic dissociation of diazonium ions and reacts with additional nitroaryl radicals (Fig. 2). During this reaction, the purple color of DPPH solution ($\lambda_{\text{max}} = 520 \text{ nm}$) turns to yellow ($\lambda_{\text{max}} = 330 \text{ nm}$). The coupling product of this reactions has been characterized previously [34].

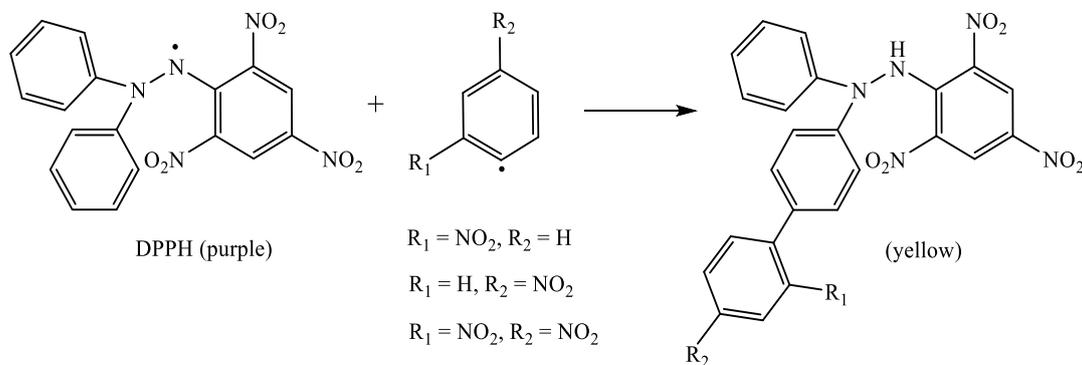


Fig. 2. Reaction of DPPH radical scavenger with the additional nitroaryl radicals produced insitu by homolytic dissociation of diazonium ions.

Therefore, the Controllable functionalization of CNTs by insitu generated nitroaryl radicals become possible, where the additional nitroaryl radicals are captured by DPPH radical scavenger.

Characterization of nitroaryl functionalized CNTs XRD measurement

The XRD measurement is widely used for study of the crystallinity and the phase composition of carbon nanomaterials [38]. In general, two peaks are detected in the XRD patterns of these compounds at around $2\theta = 26$ and 43° , which could be assigned to (002) and (100) reflections of typical graphite, respectively [39].

The XRD pattern of pure MWCNT versus diffraction patterns of p-MNP and DNP functionalized samples over the range of 2θ angles from 10 - 75° is shown in Fig. 3. The XRD pattern of MWCNT displays a sharp diffraction peak at $2\theta = 25.9^\circ$ (with d-spacing of 3.4451 \AA) as well as a weak diffraction peak at $2\theta = 42.5^\circ$ (with d-spacing of 2.1284 \AA), corresponded to (002) and (100) reflections, respectively. This pattern has agreement with diffraction peaks of purified MWCNT at $2\theta = 26$ and 44° [39].

The sharp and obvious diffraction peaks observed in the XRD pattern of pure MWCNT could be attributed to its well-crystallized structure. The same areas of varying intensity and width have also been observed for functionalized MWCNTs,

i.e. $2\theta = 26.2$ ($d = 3.3964 \text{ \AA}$) and 43.2° ($d = 2.0957 \text{ \AA}$) for p-MNP/MWCNT, and $2\theta = 26.3$ ($d = 3.3839 \text{ \AA}$) and 43.1° ($d = 2.0981 \text{ \AA}$) for DNP/CNT. This analysis is not used before for characterization of nitroaryl functionalized CNTs. The average crystallite sizes determined from X-ray line broadening of (002) and (100) peaks through the Scherrer equation for DNP and p-MNP functionalized MWCNTs are 8.4 and 9.7 nm , respectively; which are larger than the corresponding value related to pure MWCNT (7.4 nm). These results show that the precise 2θ location, d-spacing, average crystallite size and relative intensity of the peaks change after the functionalization process. Also, the samples synthesized under microwave appear to be more amorphous than samples synthesized under thermal conditions.

The XRD pattern of pure SWCNT versus diffraction patterns p-MNP and DNP functionalized samples is shown in Fig. 4. The XRD pattern of pure SWCNT displays the low intense broad peaks at around 26.0 (with d-spacing of 3.4315 \AA) and 44.7° (with d-spacing of 2.0263 \AA), which reveals the amorphous nature of this compound. In agreement with literature (i.e. 26.6 and 43.45° [40]), these peaks are related to the (002) and (100) carbon planes, respectively.

XRD patterns of functionalized SWCNTs show the drastic changes in the intensity. The (002) and (100) peaks become sharper and more intense

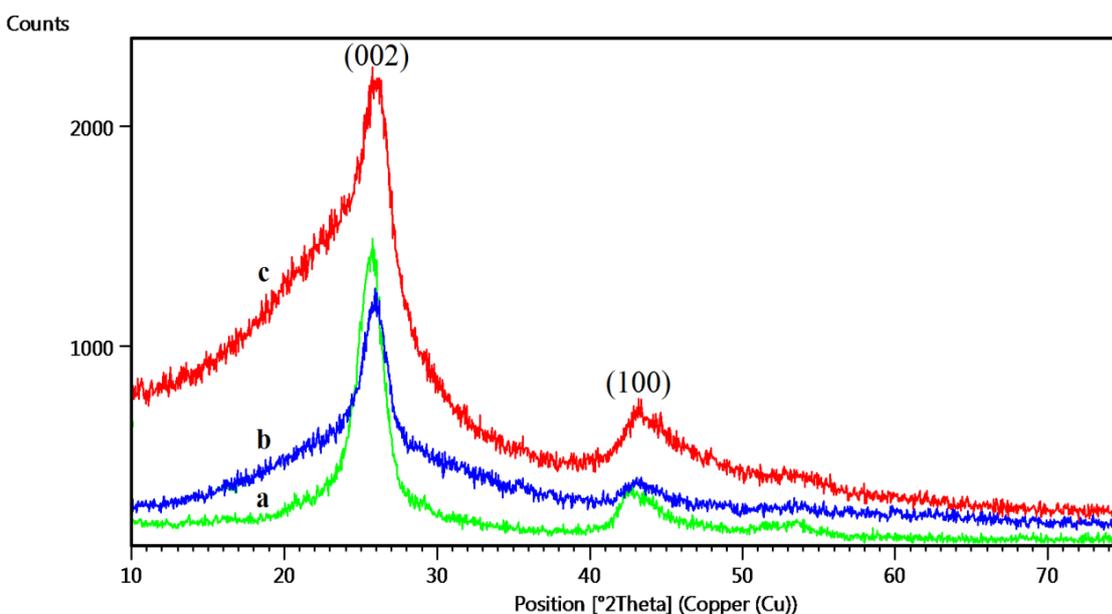


Fig. 3. XRD pattern of pure MWCNT (a) versus DNP functionalized MWCNT synthesized under thermal and solvent free conditions (b) and p-MNP functionalized MWCNT synthesized under microwave and solvent free conditions (c).

than those of pure SWCNT after functionalization. Therefore, functionalization of SWCNT by nitroaryl diazonium ions improves the crystallinity of starting material. The XRD pattern of p-MNP functionalized SWCNT displays diffraction peaks at 26.1° ($d= 3.4158 \text{ \AA}$) and 43.4° ($d= 2.0853 \text{ \AA}$). The corresponding values related to DNP functionalized SWCNT are 25.6° ($d= 3.4791 \text{ \AA}$) and 43.6° ($d= 2.0776 \text{ \AA}$). The average crystallite sizes determined from X-ray line broadening of (002) and (100) peaks through the Scherrer equation for p-MNP and DNP functionalized SWCNTs are 6.0 and 6.3 nm, respectively; which are smaller than the average crystallite size of pure SWCNT (7.0 nm). The change in 2θ location, d-spacing, average crystallite size and intensity of the peaks for nitroaryl functionalized SWCNTs are accompanied with changes in morphology and crystalline structure of SWCNT.

FE-SEM

FE-SEM provides powerful information about the morphology of nanomaterials [41]. This analysis is not used before for characterization of nitroaryl functionalized CNTs. The FE-SEM images of DNP functionalized MWCNT at different magnifications are shown in Fig. 5. It can be seen that the morphology of MWCNT after functionalization is tubular. The outer diameter of DNP functionalized MWCNTs is 20-30 nm, similar to that reported for

starting material. FE-SEM images reveal clearly that functionalized nanotubes are agglomerated after the functionalization. The greater tendency of these compounds to agglomeration than pristine nanotubes is the consequence of the stronger polar interactions between functionalized MWCNTs.

According to XRD and FE-SEM data, the morphology changes induced by functionalization of CNTs are shown in Fig. 6. The homogeneous bundles of MWCNTs (high crystalline) convert into heterogeneous bundles (low crystalline) after functionalization; while the heterogeneous bundles of SWCNTs (amorphous) convert into homogeneous bundles (crystalline) after functionalization. Therefore, functionalization of SWCNT by nitroaryl diazonium ions improves the crystallinity of starting material; while the crystallinity of MWCNT decreases with functionalization. Both of the functionalized MWCNTs and SWCNTs retain their tubular nature.

Raman spectroscopy

The nitroaryl functionalized MWCNTs are further studied with Raman spectroscopy to provide insights into the effects of functionalization onto structure of carbon nanotubes. Raman is a powerful spectroscopic technique for characterization of different forms of carbon materials [42]. The main feature in Raman spectra

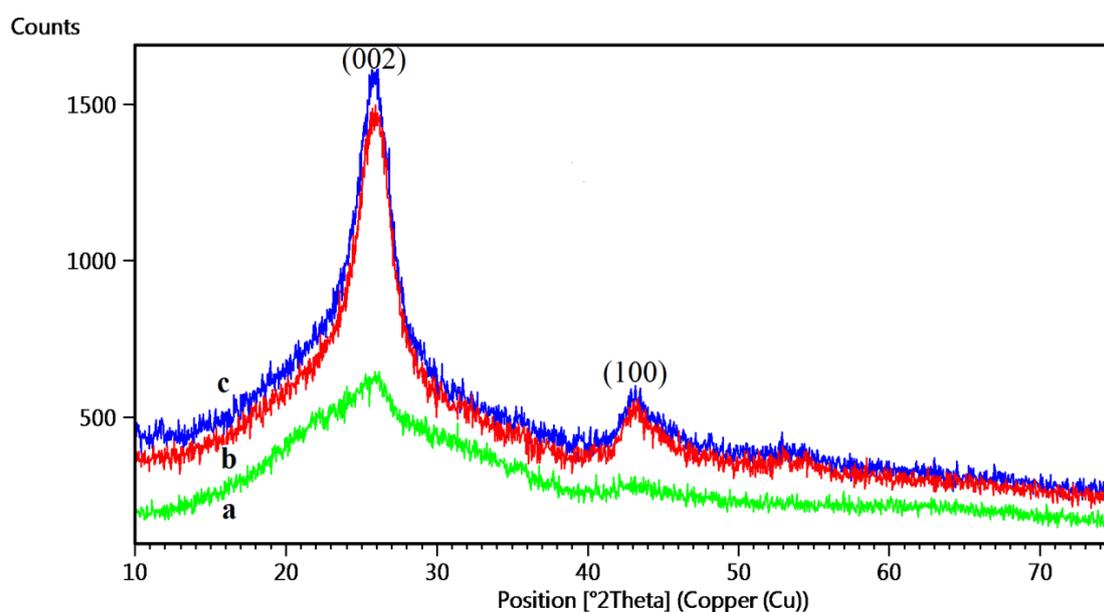


Fig. 4. XRD pattern of pure SWCNT (a) versus p-MNP functionalized SWCNT synthesized under thermal and solvent free conditions (b) and DNP functionalized SWCNT synthesized under thermal and solvent free conditions (c).

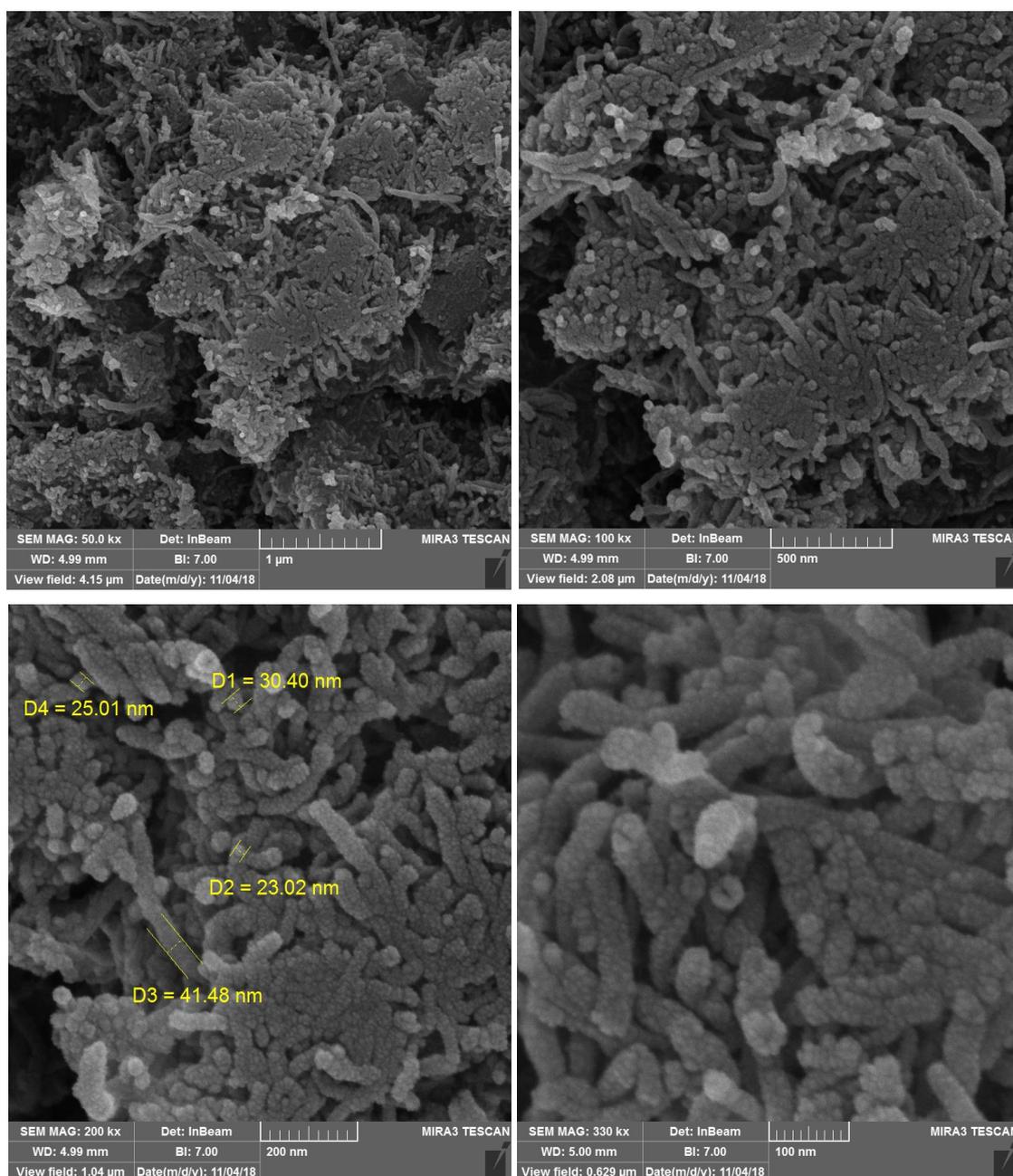


Fig. 5. FE-SEM images of DNP functionalized MWCNT synthesized under thermal and solvent free conditions.

of carbon allotropes are the D and G bands, which appear at about 1350 and 1580 cm^{-1} , respectively [43]. The G band arises from the vibrations of the sp^2 carbon, while the D band is due to disorder or defects in sp^2 -hybridized carbon systems [43]. The modification of carbon surfaces is confirmed by the ratio of the D band intensity to the G band [43].

The Raman spectra of pure and DNP

functionalized MWCNT are shown in Fig. 7. In accordance with literature (1337 and 1577 cm^{-1} [44]), Raman spectrum of MWCNT exhibit two signals at 1339 (D band) and 1571 (G band) cm^{-1} . While, these signals for DNP functionalized MWCNT appear at 1345 and 1576 cm^{-1} , respectively. It can be seen that both of the D and G bands, are shifted to higher frequency for DNP functionalized MWCNT. As the D band

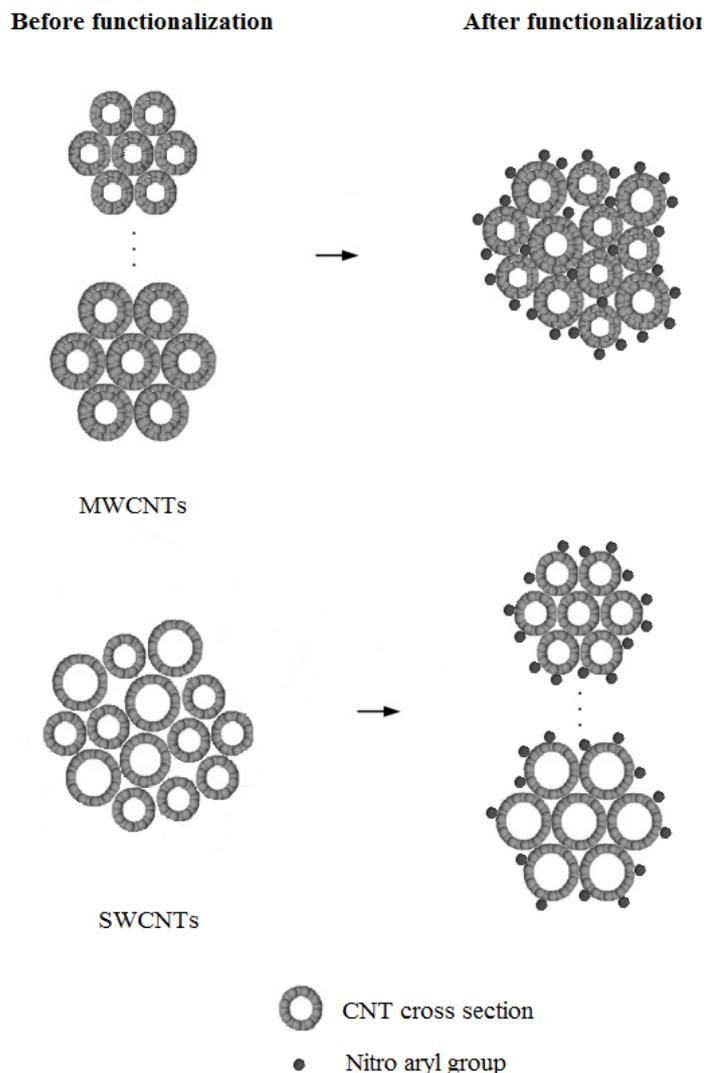


Fig. 6. Effect of functionalization on the morphology MWCNTs and SWCNTs.

represents surface defects originating from the functionalization, the increasing of D/G intensity ratio from 1.157 for pure MWCNT to 1.165 for functionalized compound can be attributed to the functionalization of MWCNT. It is well known that the ratio of D and G band are more significant to indicate the functionalization in SWCNT, while in the case of MWCNT it is less significant (because MWCNT has several layers of carbon sheets more than SWCNT). This analysis is not reported before for nitroaryl functionalized MWCNTs. However, it was shown that the covalent attachment of nitrophenyl groups to SWCNT increases the disorder mode (D-peak, $\sim 1300\text{ cm}^{-1}$) in Raman spectra when compared to the graphitic mode

(G-peak, $\sim 1590\text{ cm}^{-1}$) in all p-MNP, DNP and TNP/SWCNT cases [14].

FT-IR spectroscopy

As every type of bond has a different natural frequency of vibration, the molecules with different structures have different infrared absorption pattern [45]. Therefore, the nitroaryl functionalized CNTs exhibit different vibrational properties in comparison to non-functionalized compounds.

In Fig. 8, the FT-IR spectrum of pure MWCNT in the range $1000\text{-}2000\text{ cm}^{-1}$ is compared with FT-IR spectra of p-MNP functionalized MWCNT synthesized under different conditions. The FT-IR

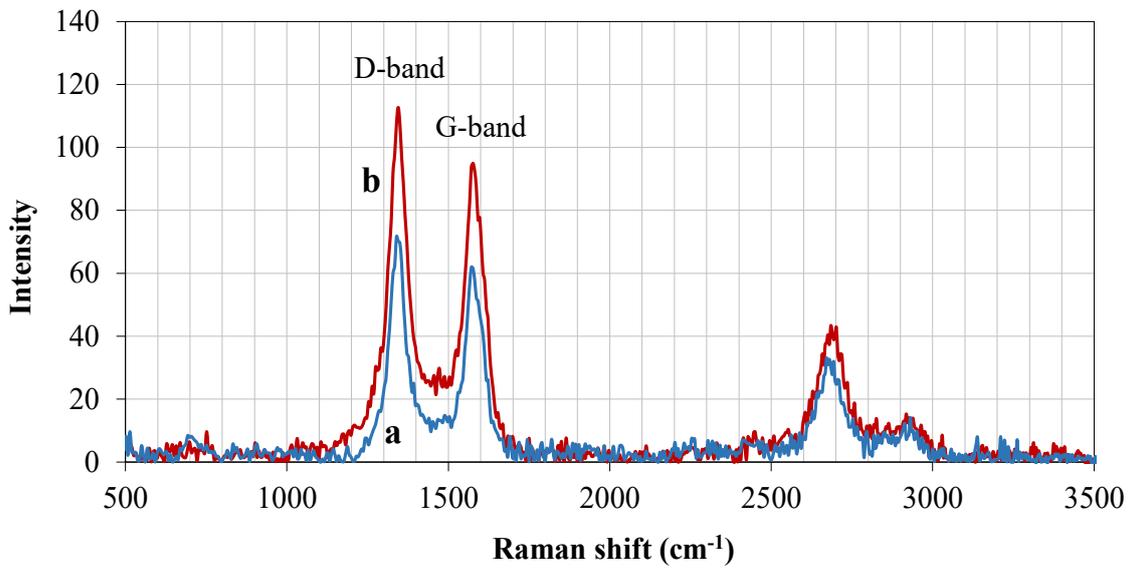


Fig. 7. Raman spectrum of pure MWCNT (a) versus DNP functionalized MWCNT synthesized in thermal and solvent free conditions (b).

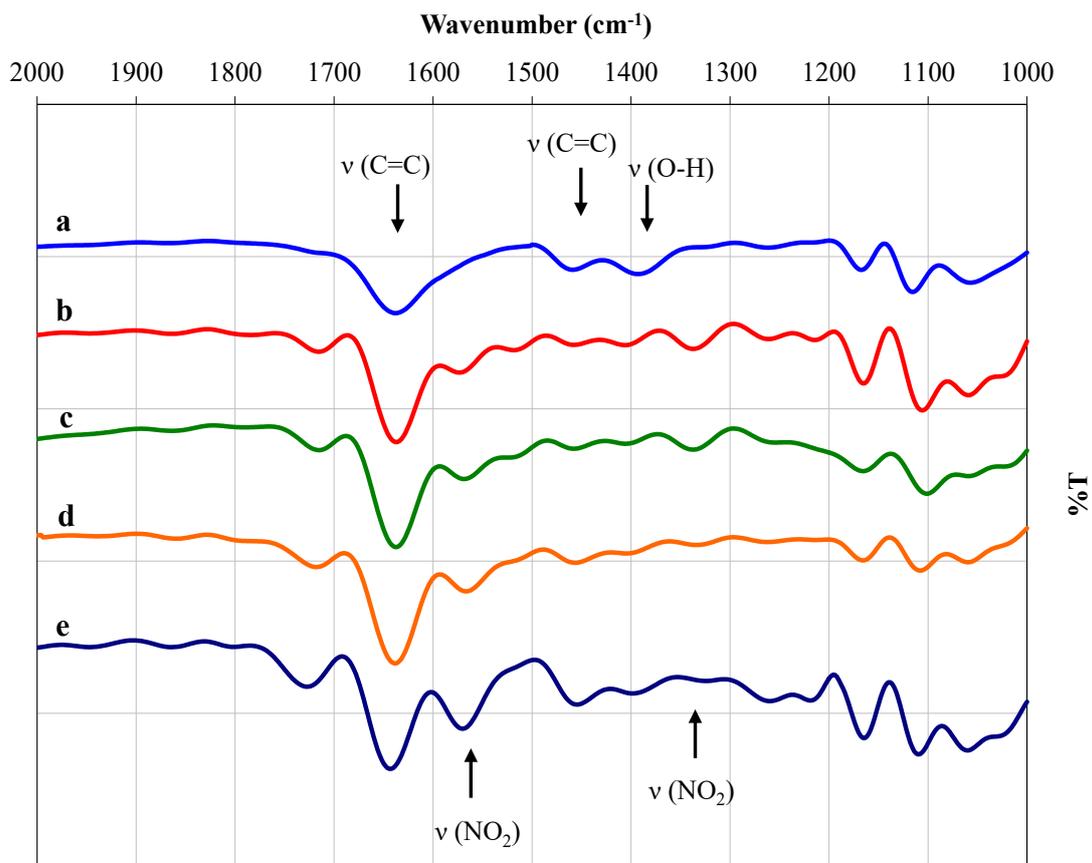


Fig. 8. FT-IR spectrum of pure MWCNT (a) versus p-MNP functionalized MWCNT synthesized under different conditions, i.e. solvent free (b, e), in DMF solvent (c, d), thermal (b, c) and microwave-assisted (d, e).

spectrum of MWCNT displays two peaks at 1458 and 1638 cm^{-1} arise from C=C stretching modes of aromatic rings and a peak at 1392 cm^{-1} related to OH bending vibration of adsorbed water. The observed peaks are matched with the values previously reported for pristine MWCNT, i.e. 1410 and 1636 cm^{-1} [46]. The C=C stretching bands in functionalized MWCNTs appear in the range 1400-1500 and 1600-1700 cm^{-1} . New bands observed at 1300-1400 and 1500-1600 cm^{-1} are attributed to the symmetric and asymmetric bond vibrations of NO_2 in nitroaryl functionalized compounds, which confirm the successful functionalization of MWCNTs.

The FT-IR spectra of o-MNP and DNP functionalized MWCNTs synthesized under different conditions in the range 1000-2000 cm^{-1} are shown in Fig. 9. The spectra exhibit two absorbing peaks at 1300-1400 and 1500-1600 cm^{-1} for NO_2 stretching vibrations along with the C=C stretching bands at 1400-1500 and 1600-1700 cm^{-1}

¹.

The FT-IR spectrum of pure SWCNT versus p-MNP and DNP functionalized SWCNTs synthesized under different conditions is shown in Fig. 10, which displays two peaks at 1436 and 1630 cm^{-1} corresponding to C=C stretching modes and a peak at 1364 cm^{-1} for OH bending vibration. The successful functionalization of SWCNT by nitroaryl groups is confirmed by the observed changes in the FT-IR spectrum of SWCNT after functionalization, and the appearance of some new peaks at 1300-1400 and 1500-1600 cm^{-1} for NO_2 groups. According to the literature, the characteristic absorption peak for pristine SWCNT appears at 1624 cm^{-1} [47]. Also, FT-IR spectroscopy verified the existence of NO_2 groups on all three kinds of nitrophenyl/SWCNTs at 1300-1350 and 1500-1550 cm^{-1} [14].

UV-Vis spectroscopy

UV-Vis spectroscopy is a qualitative method

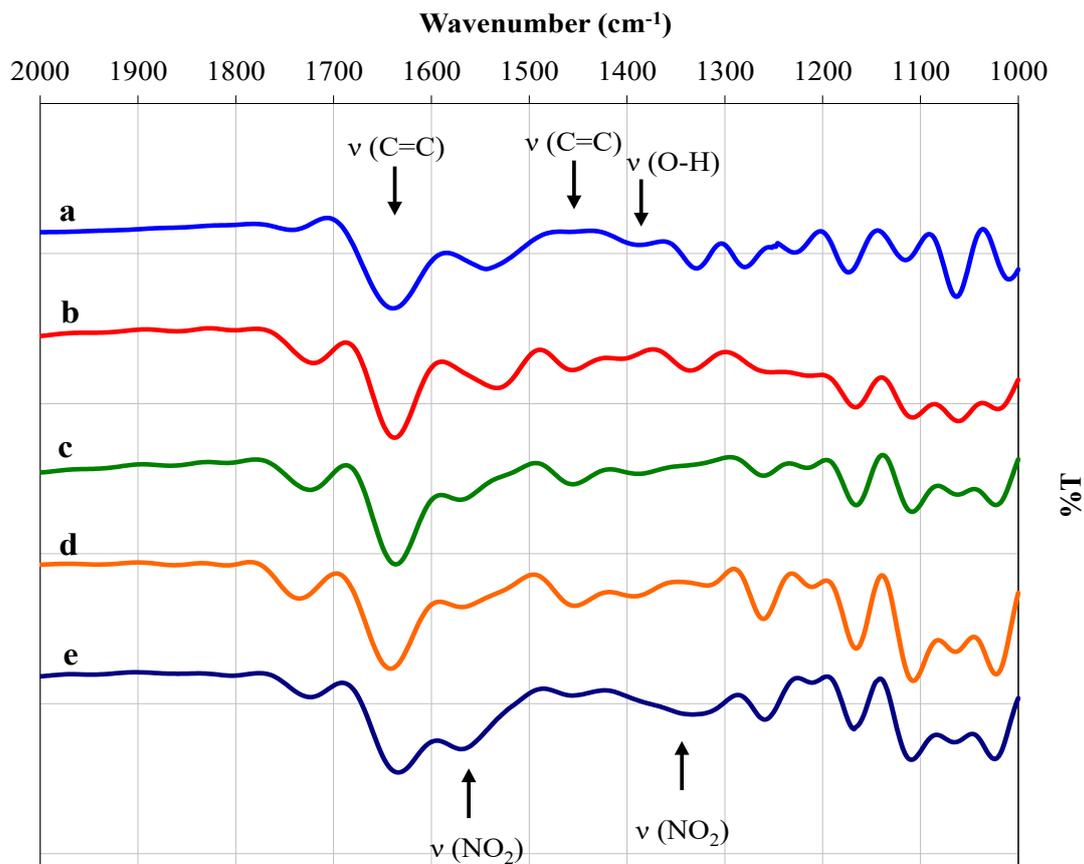


Fig. 9. FT-IR spectra of o-MNP functionalized MWCNT (a) and DNP functionalized MWCNT (b-e) synthesized under different conditions, i.e. solvent free (a, b, d), in DMF solvent (c, e), thermal (b, c) and microwave-assisted (a, d, e).

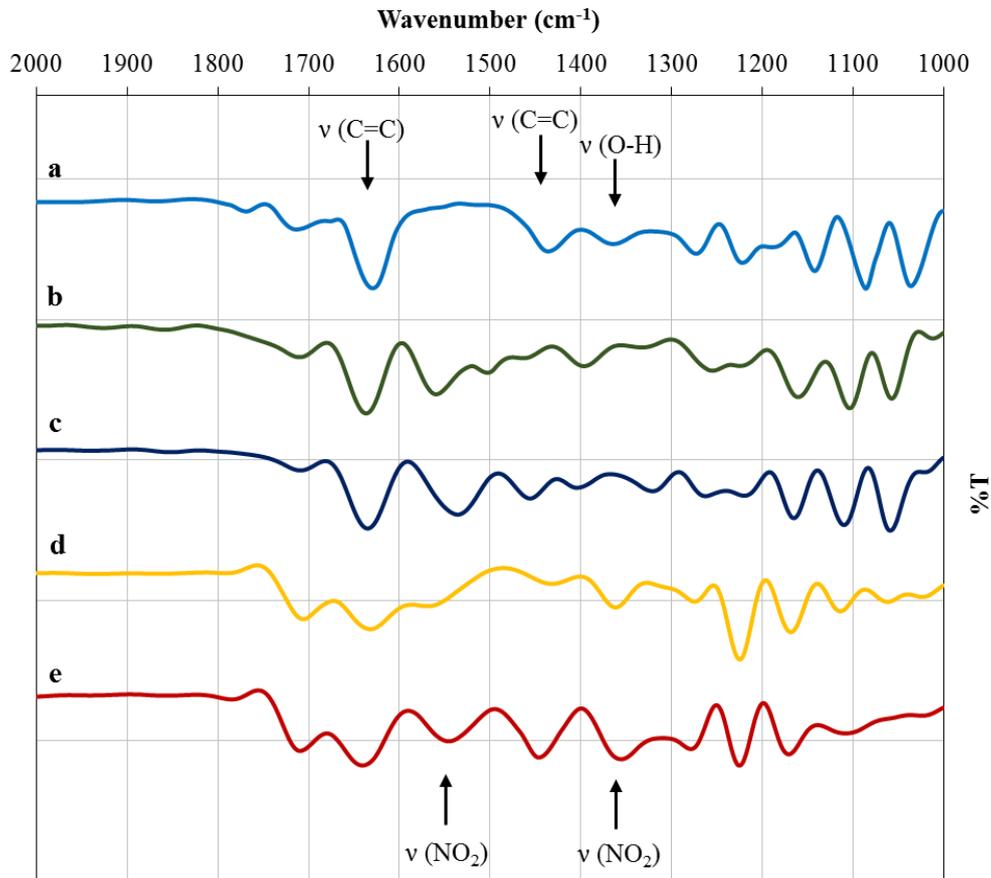


Fig. 10. FT-IR spectrum of pure SWCNT (a) versus p-MNP (b, d) and DNP (c, e) functionalized SWCNT synthesized under different conditions, i.e. solvent free (b, c, d, e), thermal (b, c) and microwave-assisted (d, e).

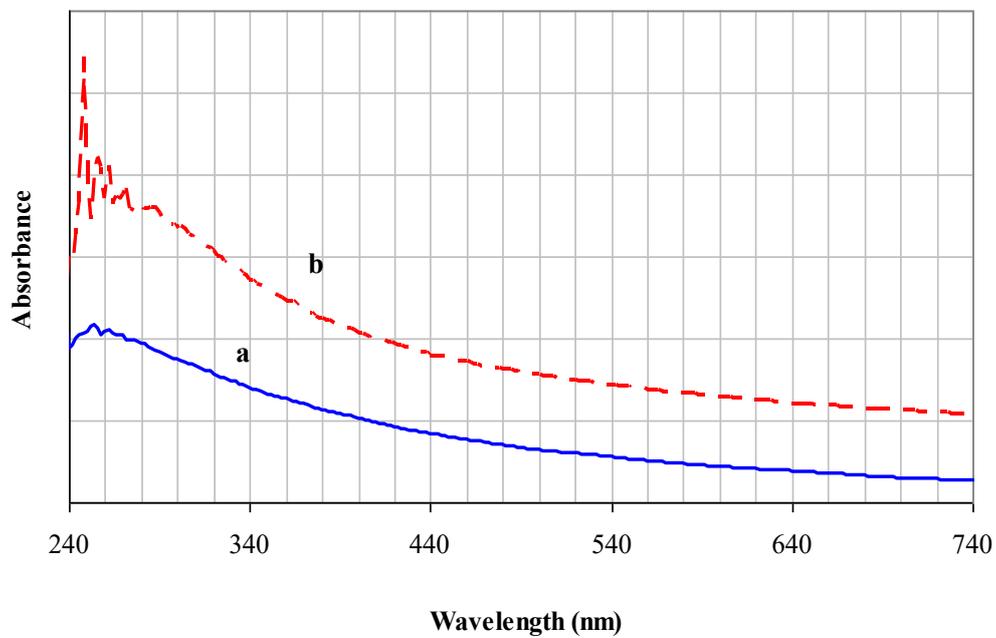


Fig. 11. UV-Vis absorption spectrum of pure MWCNT (a) versus DNP functionalized MWCNT synthesized under thermal and solvent free conditions (b).

for studying the electron transfer in molecules [45]. It was reported that the UV-Vis spectrum of MWCNT shows an absorbance with a maximum value occur at 250 nm [48]. The UV-Vis spectra of pure MWCNT and DNP functionalized MWCNT are shown in Fig. 11. The broad absorption band with absorption maximum at about 260 nm is ascribed to the $\pi \rightarrow \pi^*$ transitions of C=C bonds, which form

the carbon nanotube network. The absorption band at about 270 nm in the UV-Vis spectrum of functionalized MWCNT corresponds to the $n \rightarrow \pi^*$ transitions of NO_2 [45]. This result supports the attachment of nitroaryl groups to the MWCNT. Also, absence of azo species on the CNTs surface is clearly confirmed by this spectrum, because the absorption maximum of -N=N- linkages in the

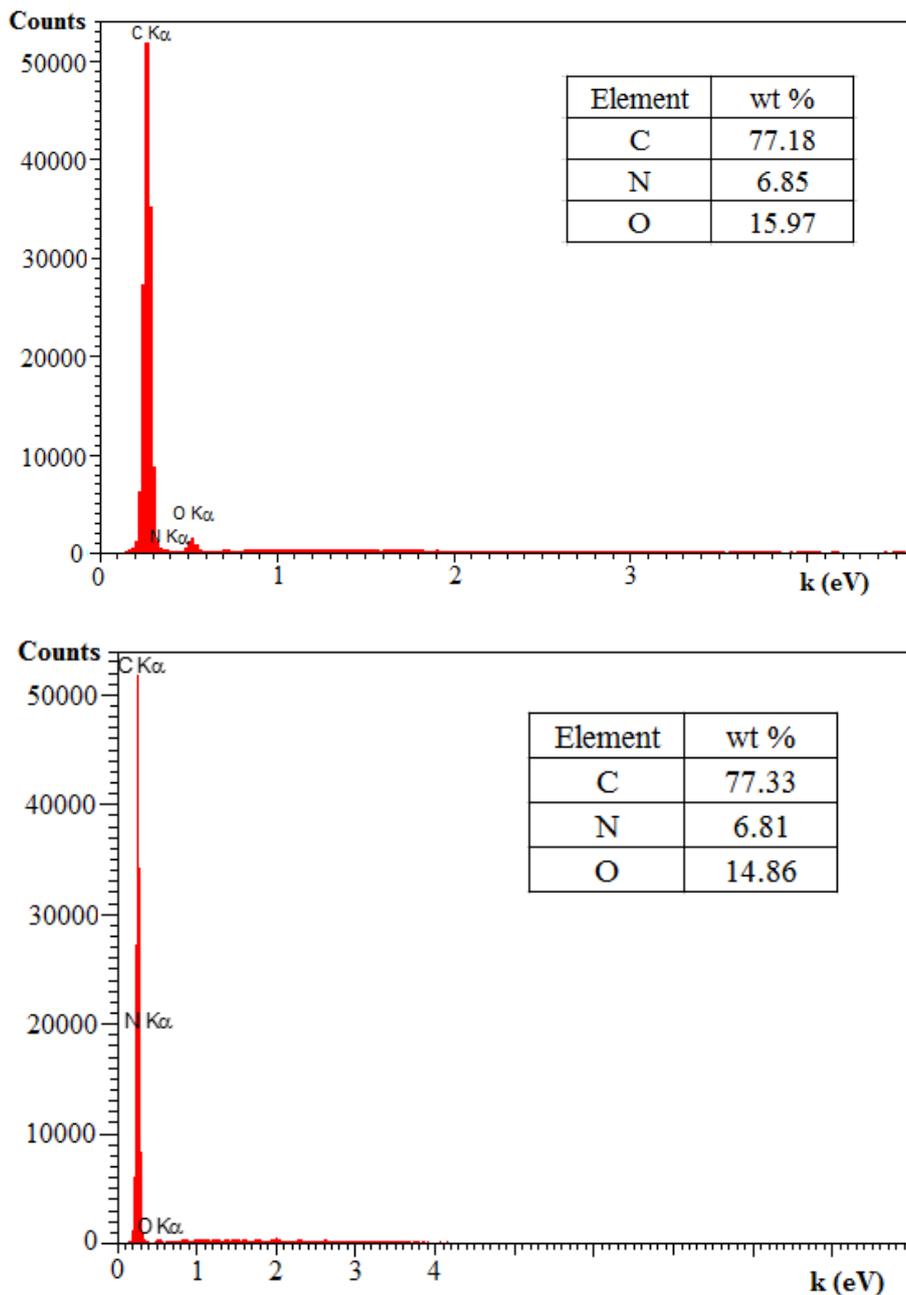


Fig. 12. EDX pattern of DNP functionalized MWCNT synthesized under thermal and solvent free (top) and thermal in DMF solvent (bottom) conditions.

absorption spectrum of functionalized MWCNT at around 350-550 nm [45] does not observed.

EDX and elemental map analysis

The EDX analysis is a technique coupled with SEM based on the generation of characteristic X-rays which used to identify the elements and their concentrations in the sample [49]. This analysis is not applied before for characterization of nitroaryl functionalized CNTs. The EDX patterns of DNP functionalized MWCNT synthesized under

different conditions are shown in Fig. 12, which reveal the characteristic peaks of carbon, nitrogen and oxygen atoms. The C, N and O elemental compositions for compound synthesized under thermal and solvent free conditions are 77.18, 6.85 and 15.97 wt%, respectively. The corresponding values for functionalized compound under thermal in DMF solvent are 77.33, 6.81 and 14.86 wt%, respectively. While, the certificate EDX analysis of pure MWCNT predicts the presence of 98.39 % carbon without any nitrogen and oxygen [50].

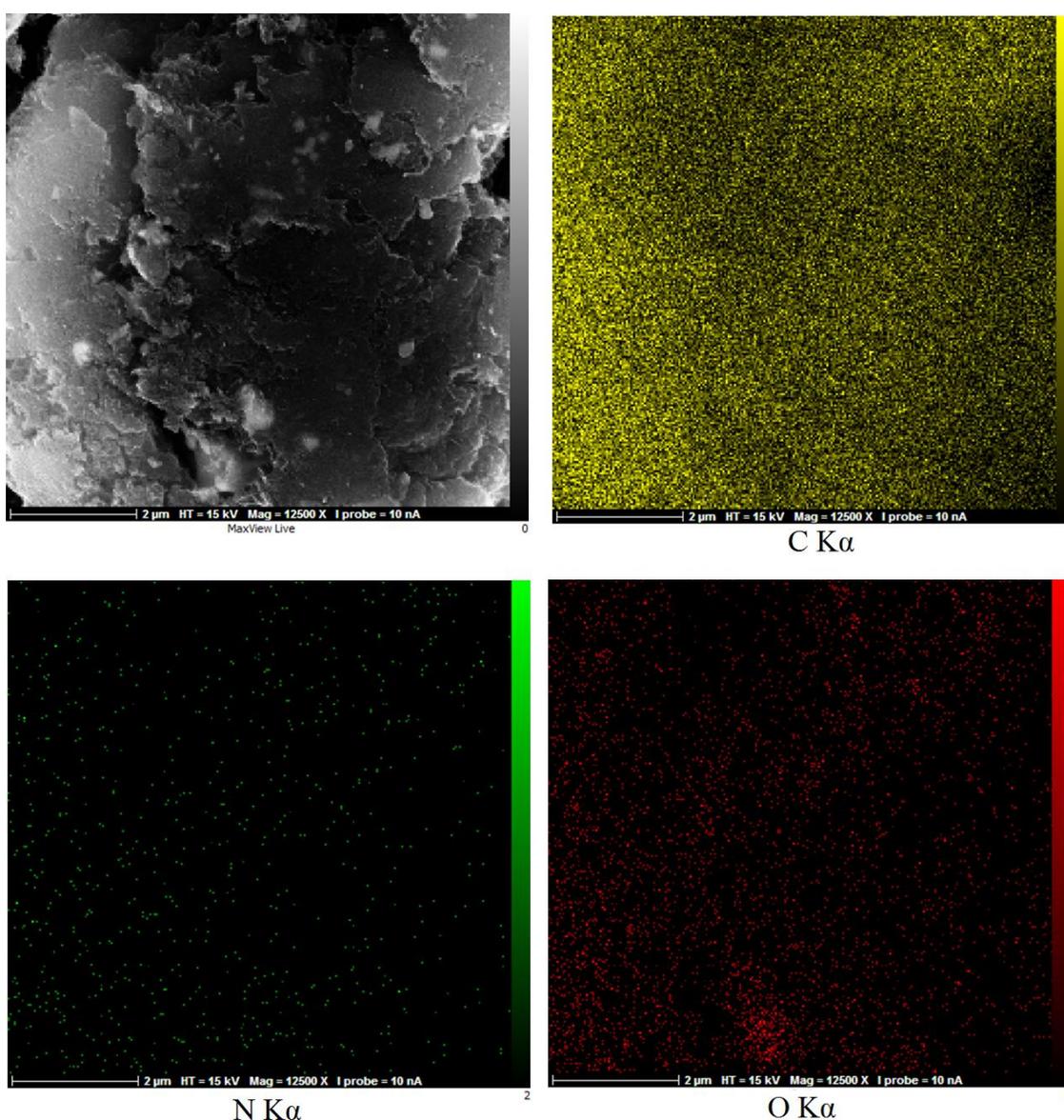


Fig. 13. SEM image of base and elemental mapping of C, N and O atoms for DNP functionalized MWCNT synthesized under thermal and solvent free conditions.

The elemental map of DNP functionalized MWCNT illustrates carbon, nitrogen and oxygen atoms (Fig. 13). According to this analysis, nitrogen and oxygen atoms are dispersed homogenous on carbon surface. The higher percentage of carbon than nitrogen and oxygen and the higher percentage of oxygen than nitrogen confirm the functionalization process. The results of EDX and elemental map analysis provide strong evidences for the presence of NO₂ groups on the composition of products and the successful functionalization of carbon nanotubes by diazonium ions.

CONCLUSIONS

In the present study, the nitroaryl functionalized CNTs were controllably synthesized using reaction of CNTs (MWCNT and SWCNT) and nitroaryl diazonium ions under different conditions (i.e. thermal, microwave, in DMF solvent and solvent free). The synthesis of these compounds was performed under mild and more efficient conditions (i.e. lower reaction temperature, shorter reaction time and assisting microwave). DPPH radical scavenger was added to the reaction medium for blocking radical polymerization and preventing any further couplings. The preparation methods were developed for nitroaryl functionalization of both MWCNT and SWCNT in similar conditions. The functionalization of MWCNTs were carried out at milder conditions (i.e. lower temperature) than previous reports. The reactions were done in only 50 min using microwave instead of 48 h, necessary for the thermal conditions. Therefore, microwave is more rapid and efficient method for attachment of nitroaryl groups to CNTs.

To follow-up the reaction mechanism, DPPH radical scavenger was added to the reaction medium and the formation mechanism of nitroaryl functionalized CNTs was discussed. Various approaches for characterization of nitroaryl functionalized single-walled and multi-walled carbon nanotubes via XRD, FE-SEM, Raman, FT-IR, UV-Vis, EDX and elemental map analyses were reported. Some of these techniques were used for the first time for characterization of the nitroaryl functionalized CNTs, i.e. XRD, FE-SEM, EDX and elemental map. Other techniques such as Raman and UV-Vis were applied for characterization of nitroaryl functionalized MWCNTs. Also, FT-IR analysis was used for characterization all of the synthesized compounds under different conditions.

The morphology changes due to the functionalization of CNTs were monitored by XRD and FE-SEM. The sharp and obvious diffraction peaks observed in the XRD pattern of pure MWCNT are attributed to its well-crystallized structure; while the low intense and broad diffraction peaks in the XRD pattern of pure SWCNT are associated with its amorphous nature. Functionalization of SWCNT by nitroaryl diazonium ions improves the crystallinity of starting material; while the crystallinity of MWCNT decreases with functionalization. The changes in width and intensity of XRD patterns as well as the average crystallite sizes confirm the morphological changes in the functionalized CNTs relative to the starting materials. The precise 2θ location and d-spacing of the XRD peaks change with the functionalization. The samples synthesized under microwave are more amorphous than samples synthesized under thermal conditions. FE-SEM images showed that nanotubes are agglomerated after the functionalization. The morphology of CNTs after functionalization is tubular. Raman spectra indicated that functionalization induces changes in CNTs band structure. The increase of D/G ratio in Raman spectrum was attributed to the functionalization of CNTs. FT-IR and UV-Vis spectra showed the presence of NO₂ group and supported the attachment of nitroaryl substituents to the CNTs. EDX pattern of products revealed the characteristic peaks of carbon, nitrogen and oxygen atoms. The elemental map of functionalized CNTs illustrated that nitrogen and oxygen atoms are dispersed homogenous on carbon surface. The obtained results clearly confirmed the successful functionalization of CNTs by nitroaryl diazonium ions under different experimental conditions.

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CONFLICTS OF INTEREST

The authors declare that there are no conflicts of interest regarding the publication of this manuscript.

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