Sidewall modification of multiwalled carbon nanotubes by *Allivum sativum* (garlic) and its effect on the deposition of gold nanoparticles

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ABSTRACT

Sidewall modification of multiwalled carbon nanotubes (abbreviated as MWCNTs) was achieved using *Allivum sativum* (garlic) extract by an acid-free green process. These organo-sulfur modified-MWCNTs were then decorated with gold nanoparticles and examined by transmission electron microscopy. The presence of organosulfurs over the modified nanotube surface was confirmed. Nanotube surface modification and subsequent presence of thiols as an active linker was confirmed by Raman spectroscopy, Fourier transform infrared spectroscopy, energy dispersive X-ray and X-ray photoelectron spectroscopy. In the absence of these organosulfurs (thiols), no gold nanoparticle attachment was observed. Both small (1–8 nm) and large (12–20 nm) gold nanoparticles were found to decorate the modified nanotube surface suggesting coalescence among nanoparticles.

1. Introduction

In recent years, nanoscience and nanotechnology has made considerable progress towards synthesis and characterization of new materials due to their wide-spread application in everyday life. Much of this success was possible due to chemical modifications or functionalization of carbon nanotube (CNT) surface [1]. This combination of chemically modified nanotubes decorated with nanoparticles has found tremendous usage in electronics, sensors, biomedical applications, catalysis, H_2 storage, etc. [2]. Gold nanoparticles (Au NPs) in particular, happens to be a key material and building block for newer technologies owing to their unique set of properties at nanoscale [3]. Several methods for functionalizing CNTs followed by Au NP deposition on the modified nanotube surface were proposed recently. Satishkumar et al. [4] showed that CNTs upon harsh acid treatment allowed tagging of metal nanoparticles (including Au NPs) on the modified nano-

tube surface. Also, Jiang et al. [5] showed selective attachment of Au NPs on nitrogen-doped multi-walled carbon nanotubes (MWCNTs) with H_2SO_4–HNO_3 chemical treatment. Similarly, surface activation by carboxylic acid [6] and thio-amide-carboxyl [7] surface has been reported for immobilization of metal NPs. The general idea which prevailed was that pristine CNTs are inert structures and harsh pre-treatment is needed to create 'openings' on the CNT surface for attaching other chemical groups. However, Ellis et al. [8] demonstrated weak hydrophobic anchoring of Au NPs by utilizing thiol capping on acetone (–OH group) activated CNT surface. Similarly, other techniques were also reported [9–11] for Au NP attachment on CNT surface. However, most of these techniques were without any chemical modification of nanotube surface thereby limiting the binding strength and capacity of Au NPs over the nanotube surface. Since, CNTs are not ideal structures and contain defect sites and impurities [12], this makes them ideal site for addition reactions [13]. These defect sites

can be exploited to tag metal nanoparticles onto the CNT surface without any harsh treatment as demonstrated by Zanella et al. [14] to tag gold nanoparticles via thiol linkages [15–17]. These sulfur linkages when attached to the defect sites, open new possibilities for attaching other chemical groups (including nanoparticles) at the vacancy defect sites. Although, considerable efforts have been made in pre-treatment of CNTs as discussed previously, most of these techniques require excessive usage of toxic solvents, acid pre-treatment and rigorous process control at high temperatures. Thus, there is a need to functionalize CNTs in a more benign and eco-friendly manner. With this aim, we hereby provide a novel biogenic method for CNT surface thiolation and subsequent attachment of Au NPs by utilizing organosulfur plant extract. Garlic is one such natural source of organosulfur compounds [18] where total sulfur content ranges from 0.35% to 1% of its dry weight [19]. Here, we report CNT surface modification by utilizing natural organosulfurs from *Alllium sativum* (Garlic) and its effect on the deposition of Au NPs onto the modified CNT surface under ambient reaction conditions with an acid-free green process. This biogenic study has the potential to evolve into biomimetic study with advanced interdisciplinary research to provide innovative surface modification strategies for carbonaceous materials in future.

2. Experimental

2.1. CNT surface modification

Prepared MWCNTs from chemical vapor deposition (CVD) process (Aldrich, USA; 95% purity, 6–9 nm; 5 μm) were used. CNT surface modification was carried out by freshly chopped garlic (100 g) cloves, which were crushed and extracted with 20 mL aqueous solution of water:ethanol (95:5 v/v). This extract was centrifuged at 3500g to remove any suspended solids and the supernatant was retained. It is important to note that 80% of organosulfurs in garlic cloves convert to allicin (diallyl thiosulfinate) by enzymatic activity of allinase (naturally present in garlic) which converts alliin (3-(2-propenylsulfinyl)alanine) upon being cut in the presence of water in a period of 10–15 s [20]. At elevated temperatures, alliin rapidly converts to diallyl trisulfide (DATS) and diallyl disulfite [21]. Since, CNT sidewall functionalization is affected with the curvature of carbon nanotubes [22], we preferred small diameter MWCNTs for thermal activation in plastic vials by solvent-free process [23] of baking reactant mixture at elevated temperature. MWCNTs (10 mg) were placed together with organosulfur extract (2 mL, 80 mg dry weight) and heated at 110 °C for 4 h in sealed vials. This reaction mixture was sonicated for 15 s at every hour to homogenize the reaction solution. Excess of organosulfur extract was removed from the reaction mixture by centrifugation at 3500g for 2 min. Finally, organosulfur modified multi-walled nanotubes (to be referred as OS-MWCNT) was obtained.

2.2. Decoration of gold nanoparticles on CNTs

Gold nanoparticles were prepared by the reaction of HAuCl$_4$ (Sigma) and citric acid (Aldrich). In a typical experiment,

5 mg of OS-MWCNT was dispersed in 1-butanol (5 mL) and sonicated for 10 min. Then, 0.016 g of HAuCl$_4$ and 0.017 g citric acid, both dissolved separately in 5 mL of 1-butanol were stirred for 30 min to produce Au NPs [24] before being added dropwise into the dispersion of OS-MWCNTs. Final volume was set to 10 mL. This dispersion was vigorously stirred at room temperature for 3 h with intermittent sonication of 15 s at every 30 min. After this procedure, solid phase was separated by centrifugation (3500g for 10 min) and washed six times with 1-butanol to remove any non-linking Au NP from the CNT surface. Finally, we obtained our desired product of OS-MWCNTs decorated with Au NPs (Au-OS-MWCNT) which were dried at 60 °C and stored away from light in a vacuum desiccator. As a control test, same procedure of Au NP deposition was performed with pristine MWCNTs.

2.3. Characterization of Au-CNT nanocomposite

Preliminary analysis of Au NP deposition over the modified CNT surface was done by NanoDrop 3300 Fluorospectrometer operated at 400–600 nm with relative fluorescence units (RFU) at 540 nm. MWCNTs – with and without Au NP attachment dispersed in 1-butanol were transferred to carbon coated grid for transmission electron microscopy (TEM) measurements by Hitachi H-7100 transmission electron microscope and Jeol JEM 1011 electron microscope operated at 100 and 200 kV, respectively. Images obtained were analyzed using ImageJ 1.43M software. Transmission mode Fourier transform infrared (FT-IR) spectroscopy was carried out using Jasco FTIR-680 plus coupled to a high performance computer. The results reported here were obtained from 200 scans at a 4 cm^{-1} resolution and were verified five times with different nanocomposite samples prepared and stored under identical conditions. Energy dispersive X-ray (EDX) analysis was done to confirm sulfur linkages present over the nanotube surface using JEOL JSM6400 operating at an accelerating voltage of 15 kV and working distance of 15 mm; resulting spectra were analyzed using Spectra Manager ver. 1.06.02. Raman spectra was obtained by using the 514.5 nm line of an Ar$^+$ laser (100 mW) analyzed by a JOBIN-YVON monochromator Model U-1000 for 10 cycles each of 16 s. Confirmatory analysis for sidewall addition of thiol onto CNT surface was done by X-ray photoelectron spectroscopy (XPS) obtained from JEOL JPS9010 MC photoelectron spectrometer operating at 10 kV and 30 mA. The results obtained were analyzed by SpecSurf ver. 1.7.3.9 software.

3. Results and discussion

Fig. 1a shows fluorospectra of OS-MWCNT decorated with Au NPs and spectra of Au NPs alone (Fig. 1b).

Both samples showed distinct surface plasmon resonance peak (SPR) at 540 nm when laser excitation was made in the white light region. This characteristic absorbance at 520–540 nm suggest towards the presence of gold nanoparticles linked over the modified CNT surface. The SPR peak remained after repeated washing and vigorous sonication. This preliminary result indicated that Au NPs may be attached onto the modified nanotube surface. Also, retention
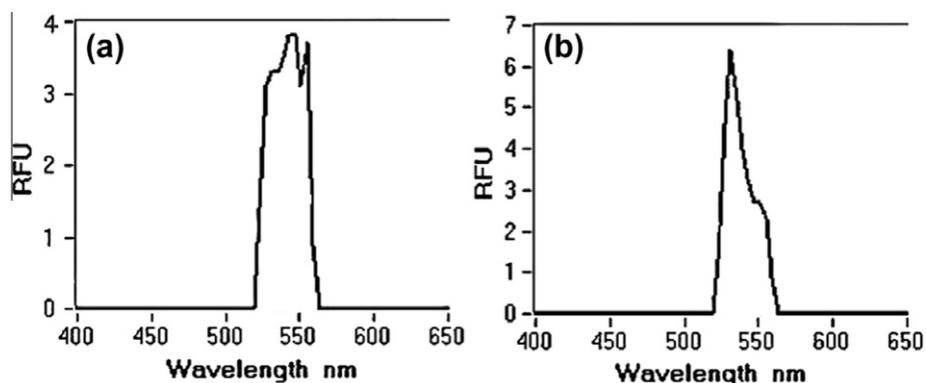
Fig. 1 – (a) SPR observed in Au-OS-MWCNT; (b) SPR observed in Au NP solution.

of optical absorption spectra suggested that there is no adverse influence on the nanoparticles. We noted that Au NPs do not attach to pristine MWCNT (control) when observed after same amount of washing as stated above. Likewise, TEM, EDX and XPS analysis also confirmed the same that no Au NP attachment was done over the pristine MWCNTs under the same set reaction conditions (data not shown).

TEM images of Au-OS-MWCNTs showed gold nanoparticles on the surface of organosulfur modified MWCNTs, as is evidenced in Fig. 2.

Fig. 2b shows TEM micrograph of OS-MWCNT decorated with gold nanoparticles of size 5–15 nm. A micrograph of pristine MWCNT (control) is shown in Fig. 2a for comparison. Gold nanoparticles (without being deposited onto the modified nanotube surface) exhibited face-centered cubic (fcc) structure as indicated by {111} and {200} facet diffraction pattern in Fig. 2d. Fig. 2c shows adherence of several Au NPs along the sidewall of OS-MWCNT. Au NPs attached on the OS-MWCNT surface showed similar fcc-type diffraction pattern associated with Au NPs alone along with the interlayer
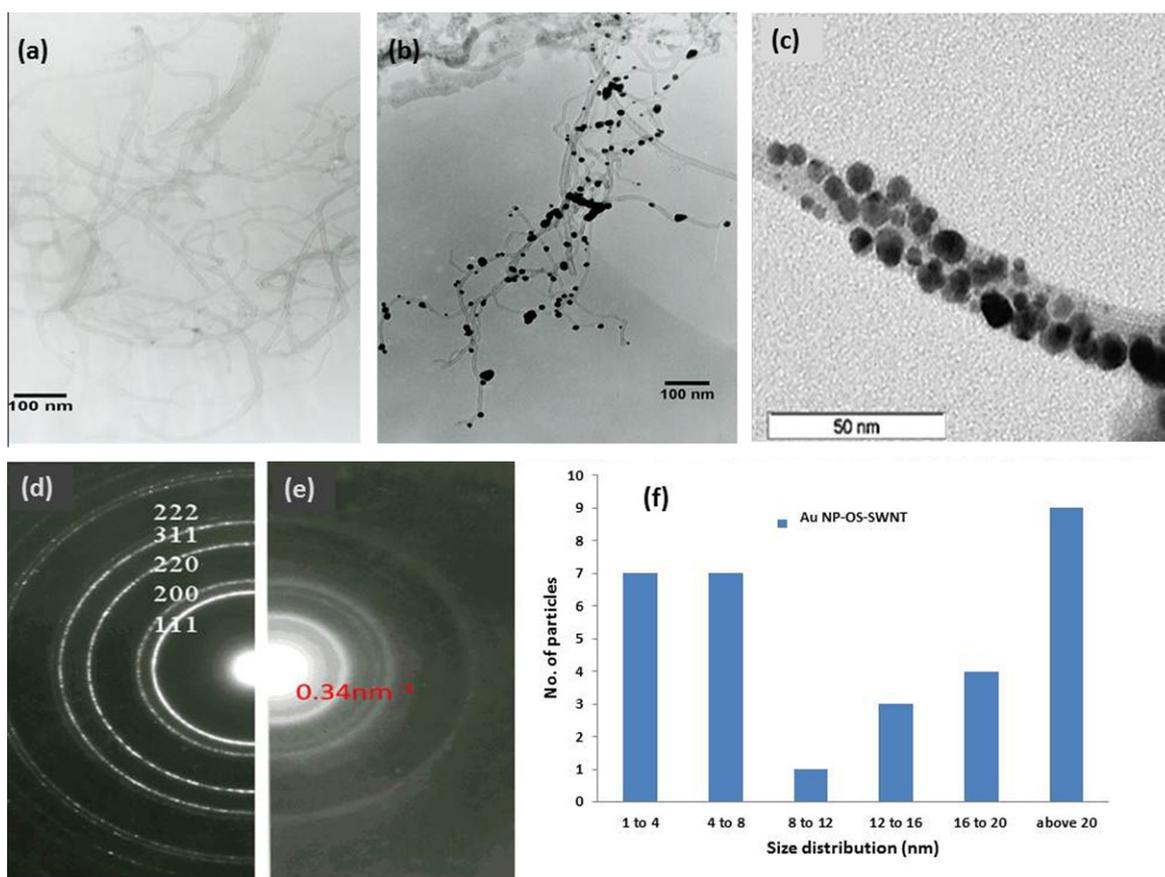

Fig. 2 – (a) TEM image of unmodified CNT; (b) TEM image of Au-OS-MWCNT; (c) High resolution image of Au-OS-MWCNT; (d) XRD pattern obtained from Au NP; (e) XRD pattern obtained from Au-OS-MWCNT; (f) Au NP particle size distribution on OS-MWCNT surface.
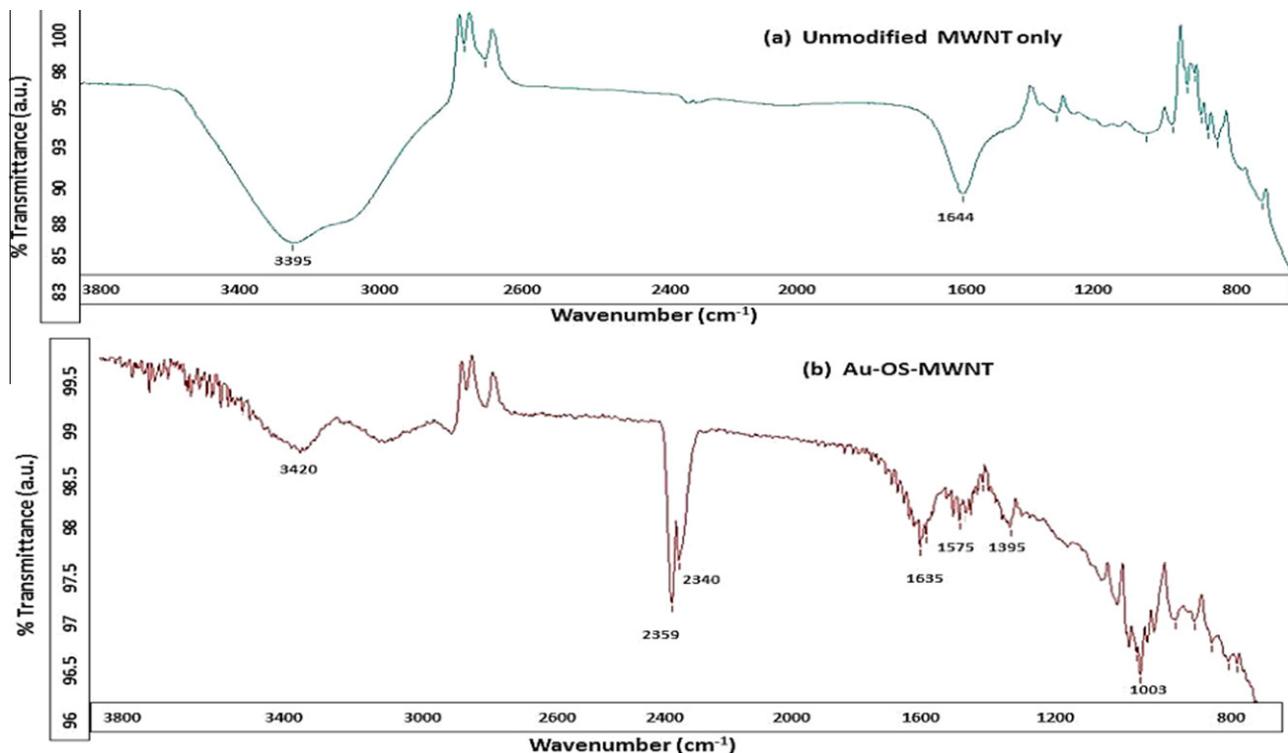
Fig. 3 – (a) FT-IR spectra of unmodified MWCNT; (b) FT-IR spectra of Au-OS-MWCNT.
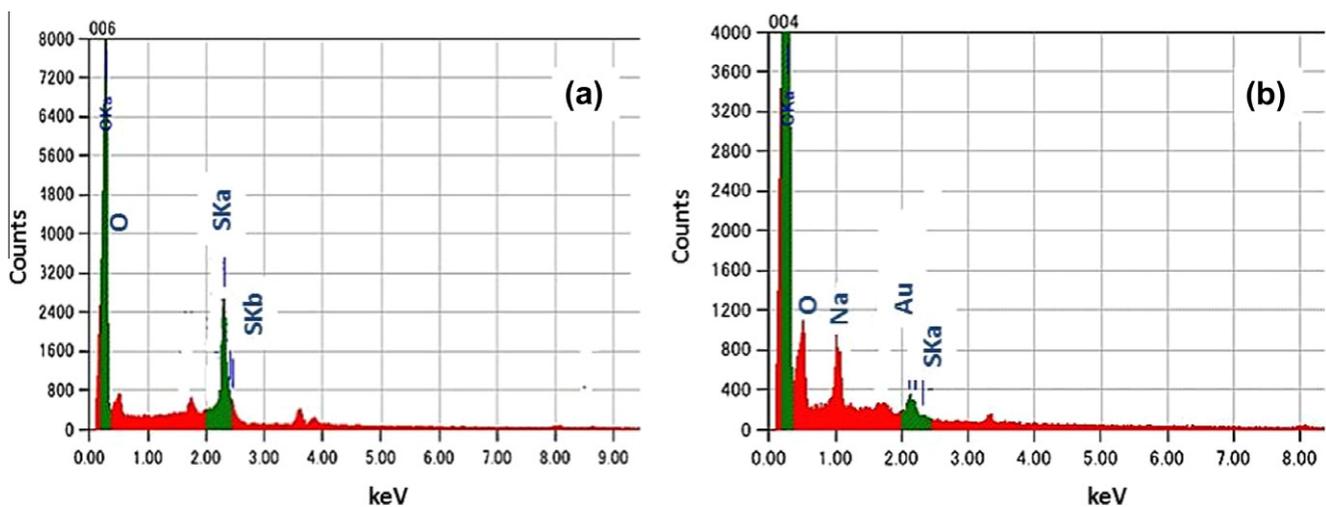

Fig. 4 – (a) EDX data of OS-MWCNT (without Au NP deposition); (b) EDX data of Au-OS-MWCNT.

spacing of graphite sheets (0.34 nm) as shown in Fig. 2e. The close proximity of Au NPs to OS-MWCNT despite constant washing suggests certain level of adherence between them. Average Au NP particle size distribution on OS-MWCNT is depicted in Fig. 2f where variation in the Au NP size happened due to the presence of other organic moieties in garlic extract. This is in accordance with Zhong's [25] finding that the position of nano-gold surface plasmon band depends on particles size, distance between the Au NPs and interaction of Au NPs with molecules on the surface. Red shift (SPR @ 520–540 nm) indicates that either the interparticle spacing is short, or the particle aggregation is bigger. In our cases, if CNTs are suc-

cessfully modified with organothiol groups on the sidewall of MWCNTs, gold nanoparticles should be closely packed along with certain level of particle aggregation due to other organic moieties present in the garlic extract. This was verified when gold nanoparticle solution was subjected to garlic extract under similar reaction conditions which resulted in particle aggregation. To understand more about active functional groups present over the modified nanotube surface, we carried out transmission mode FT-IR measurements. FT-IR spectrum of unmodified MWCNT is shown in Fig. 3a.

OS-MWCNT decorated with Au NPs (Fig. 3b) showed signature bands at 1635, 1575 and 1395 cm^{-1} associated with the
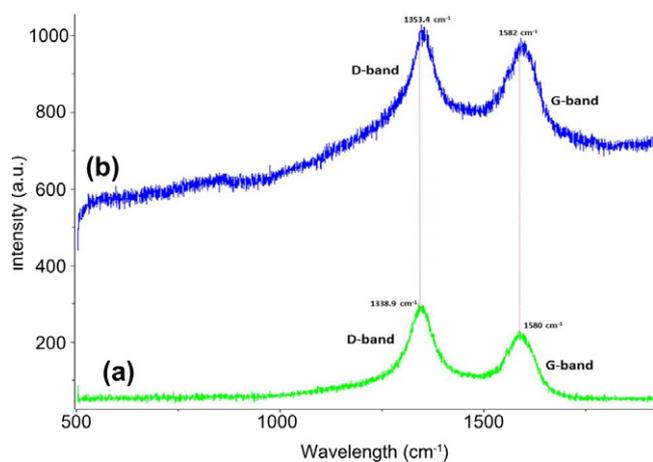
Fig. 5 – Raman spectra of (a) pristine MWCNT and (b) organosulfur modified MWCNT.

note that the band obtained at 1003 cm^{-1} confirms the presence of thiocarbonyl center whose presence was detected by absorption in 1250–1000 cm^{-1} region. Since, absorption occurs in the same region as C—O stretching, considerable interactions can occur within these vibrations within a single molecule. EDX study (Fig. 4) further confirmed the presence of sulfur in functionalized MWCNT.

Fig. 4a shows EDX spectra of OS-MWCNT (without Au NP attachment) and Fig. 4b shows Au-OS-MWCNT. Gold loading of around 0.78 atomic wt.% was obtained in Au-OS-MWCNT while no such result was obtained from control sample. We also observed the characteristic 2:1 stoichiometric ratio between sulfur and gold at some reaction sites over the Au-OS-MWCNT suggesting formation of dithiols as active biolinker. However, this ratio varied from reaction site being observed over the Au-OS-MWCNT surface. We found that OS-MWCNT can have sulfur content in the range of 0.4–1 atomic wt.%. Upon pyrolysis, the garlic extract confirmed the presence of around 0.17% of sulfur left in the reaction mixture. Further, the initial sulfur concentration in the organosulfur extract was found to be around 1.8%.

Surface modification was confirmed by Raman spectroscopy as shown in Fig. 5.

stretching of nanotube backbone. Also, evidence of utilizing openings/defects in graphite wall of MWCNT was denoted by characteristic absorbance of —C≡C at 2200–2400 cm^{-1} region. Similar result was obtained by Zhang et al. [26] with nitrile group addition on the sidewall of CNT. It is important to
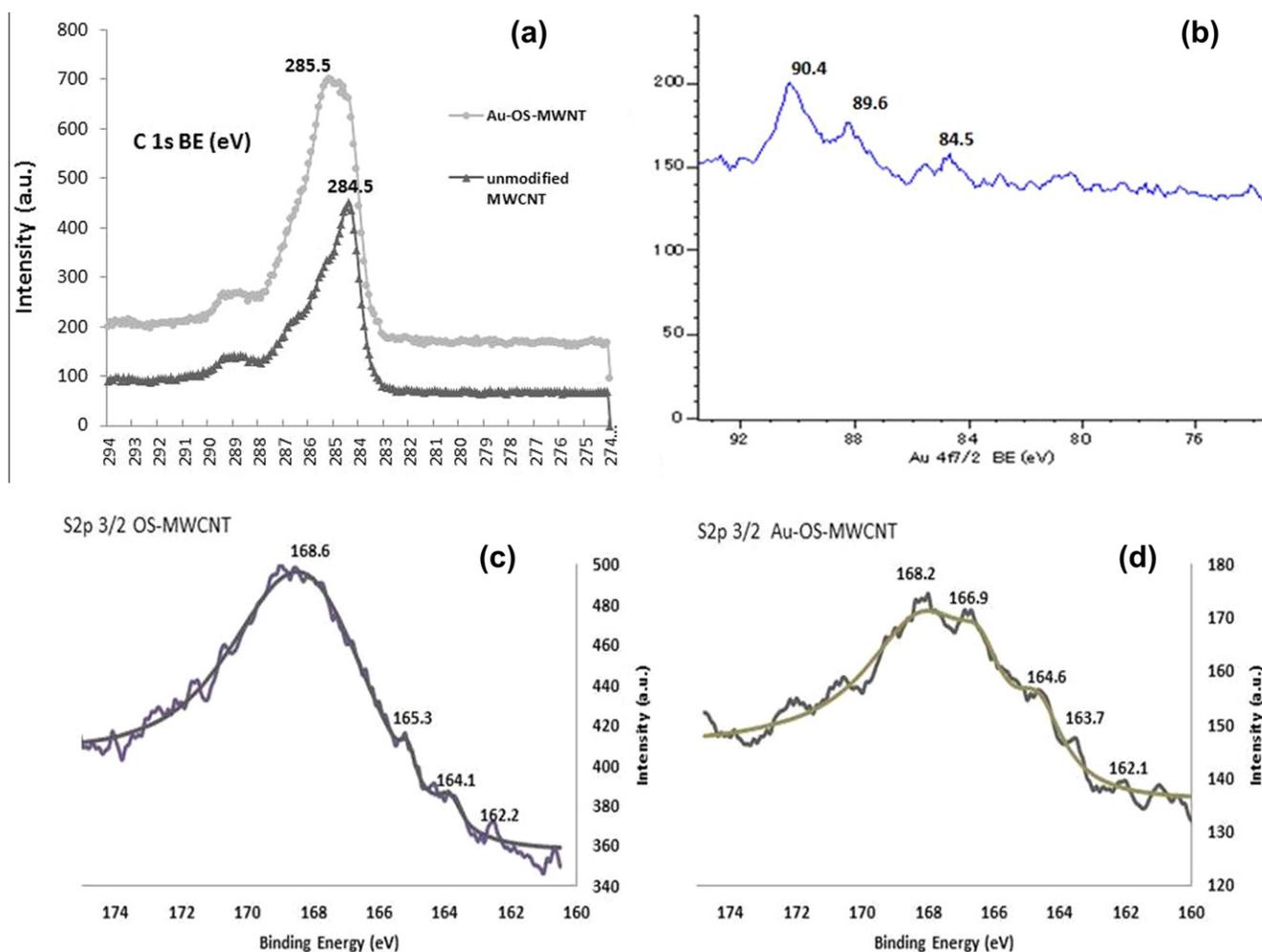

Fig. 6 – XPS spectra (a) C 1s spectra of modified and unmodified MWCNTs; (b) Au 4f spectra of Au NPs attached onto Au-OS-MWCNTs; (c) S 2p spectra of OS-MWCNT; (d) S 2p spectra of Au-OS-MWCNTs.

Fig. 5a shows Raman spectra of pristine MWCNTs while Fig. 5b shows that of OS-MWCNTs. Pristine MWCNTs showed G and D bands at 1580 and 1338.9 cm^{-1}, respectively. These G and D bands got shifted to 1582 and 1353.4 cm^{-1}, respectively in case of OS-MWCNTs. The higher upshift in D-band region towards the higher wavelength and lower shift in G-band is commonly observed in case of dopants containing oxygen atoms in their structure. It is known that oxygen can easily get attached to the defect sites in nanotube network leading to greater modification in defect band [27]. Further, the G/D intensity ratio of pristine MWCNTs (1.18) as compared to OS-MWCNTs (1.16) suggests decrease in relative sample purity due to CNT surface modification. These chemical modification results in the upshift of G and D bands which are related to direct electron charge transfer process from the nanotube to the acceptor molecule and are generally time-dependent [28]. Thus, Raman spectra confirmed the surface modification took place while FT-IR and EDX suggested towards the presence of sulfur (organothiols) in the reaction mixture. Confirmatory proof of organosulfur modified nanotube surface with facilitating Au NP attachment was obtained by XPS data as shown in Fig. 6.

In present case (Fig 6a), unmodified MWCNT C1 component of C 1s spectrum was represented at 284.5 eV [29]. This when compared to Au-OS-MWCNT composite showed an increase of C 1s spectral peak width upon functionalization, from 1.4 to 1.9 eV. This is expected when electron delocalization becomes limited [30,31] as a result of interactions between thiols and CNT sidewall. Broadening is also observed due to overlapping of CNT and organosulfur C 1s spectral envelopes, which

causes an increased intensity in binding energy region around 286.5 eV [32] (C-SH) as observed in our case. Both contributions are manifested as increases in peak width and asymmetry. OS-MWCNTs after treatment with Au NP solution exhibits a new peak at Au 4f region (Fig. 6b) together with C 1s peak at 285.5 eV and S 2p peak between the regions 162–164 eV responsible for thiol interactions. In Fig. 6b, component at 84.5 eV (88.2 for the 4f5/2 component) is assigned to Au^0. In particular, the positions of the Au 4f7/2 signal assigned to the Au^0 peak present a binding energy sensitively higher respect to the 84 eV value of bulk gold (88 eV for the 4f5/2 component). This is an indication of the presence of very small gold nanoclusters in the samples due to the presence of metallic nuclei that acts as centers for the successive grow of the gold nanoparticles. This can also result from the coalescence of Au NPs when deposited over the OS-MWCNTs as observed in this study. Further, decrease in relative peak intensities between the two S 2p spectra (Fig. 6c and d) can be clearly observed after Au NP attachment which further supports that S-moieties are responsible for Au NP attachment. Characteristic sulfur–oxygen interaction at around 168 eV region was also observed which is common in case of natural organosulfurs. This confirms that the attachment of Au-NPs to modified CNT surface can be achieved via thiol and thiocarbonyl linkages. Similar results were reported by Nakamura et al. [33] for carbon surface modification via elemental sulfur and subsequent interaction with Au NPs.

Finally, based upon our experimental observation, we were able to hypothesize a free-radical mechanism (Fig. 7) which may be responsible for CNT surface modification in presence of alliin/allicin as major organosulfur groups in garlic. The
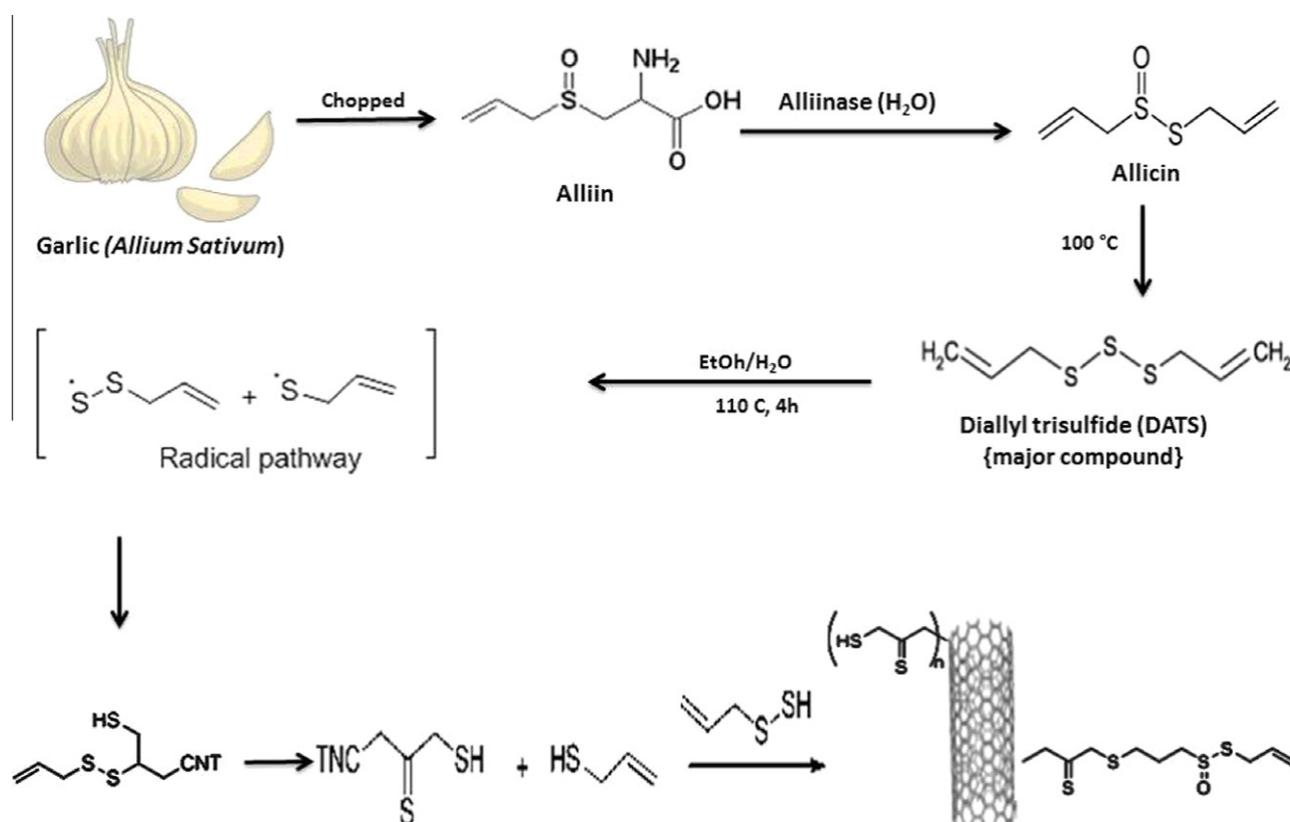

Fig. 7 – Schematic representation of MWCNT surface modification in presence of garlic organosulfur extract.

thiolated CNTs obtained as end-product can then be used for Au NPs deposition over the modified nanotube surface.

These results clearly demonstrate that organosulfur groups (alliin/allicin as major products) present in the garlic extract are responsible for attachment of Au NPs over the modified nanotube surface and in absence of these 'bio-linkers', no Au NP attachment was observed. We strongly believe that biogenic methods have the potential to provide advanced surface/material modification strategies in the growing field of carbonaceous materials.

4.　Summary

We have shown 'one-pot' sidewall attachment of Au NPs to MWCNTs treated with garlic plant extract (organosulfurs) by a facile eco-friendly process. As per our knowledge, this is the first study to effectively utilize plant phytochemicals for sidewall modification of CNTs under moderate temperature conditions. Such bio-inspired materials may facilitate novel synthesis and application routes in a more sustainable manner. Finally, an interdisciplinary research will aid in better understanding of underlying mechanism and properties this nanocomposite may possess.

Acknowledgements

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