

Functionalisation of MWCNTs with piperazine and dopamine derivatives and their potential antibacterial activity

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Functionalised multi-walled carbon nanotubes (MWCNTs) are exclusively used in antibacterial activity due to their high aspect ratio and surface penetration characteristics. This study reports the synthesis of piperazine and dopamine functionalised MWCNTs to investigate antibacterial activity against strains like *Staphylococcus aureus* and *Micrococcus luteus*. MWCNTs were activated through acid oxidation and then refluxed at 75°C for 10 and 8 h in the presence of piperazine and dopamine, respectively. The functionalised MWCNTs were characterised by scanning electron microscopy, Fourier-transform infrared spectroscopy, X-ray diffraction and Raman spectroscopy. Moreover, functionalised MWCNTs were subjected to zone inhibition assay on agar plates. Results revealed the significant antibacterial activity against various bacteria up to 50%. Similarly, it was observed that the effect of different solvents, such as dimethyl formamide (DMF) and dimethyl sulfoxide (DMSO) was non-prevalent to the bacterial zone of inhibition. Such facile nano-modifications provide passage to nano-antibacterials for advanced studies.

1. Introduction: Carbon nanotubes (CNTs) are exclusively significant nanomaterials due to their amazing broad spectrum physicochemical, mechanical and electrical properties [1]. Previously, it is well documented that the CNT's size and surface area play important role in their biological and toxicological investigations. Specifically, the CNTs upon size reduction show an increase in surface area which permits their biological interaction with living cells [2–10]. This phenomenon clearly highlights remarkable interest to monitor the potential of this material for antibacterial study.

Several studies have shown single-walled carbon nanotubes (SWCNTs) as significantly cytotoxic to human and animal cells, whereas toxicity developed due to multi-walled carbon nanotubes (MWCNTs) was not prevalent. However, conclusions obtained from several previous cytotoxicity studies are often contradictory due to CNT's surface properties, purity and utilisation of different cell culture and cell types. Therefore, understanding the development of more research knowledge about the synthesis, purification and physicochemical characterisation of both SWCNTs and MWCNTs are required for better understanding of cytotoxicity [11–17]. In 2013, Hanqin Chen and co-workers worked on broad-spectrum CNTs and suggested that rigid and thin SWCNT showed more effective in terms of cell wall/membrane piercing of bacteria (spherical) than MWCNTs. However, compromising to safety, CNTs are toxic to the microbial flora of the human gut [18]. Similarly, various research efforts were conducted to improve the antibacterial impact of CNTs by combining them with several metallic nanoparticles as well as with various bioactive functionalities [19].

The bio-functionalised CNTs give biocompatible nature rendering them to be more environment-friendly. For instance, CNTs functionalised with poly-lysine [20] and other biomolecules [21]

have shown very low or negligible toxicological environmental impact [22]. Few reports support positively-charged groups at CNT ends, responsible for effective adsorption and damage to negatively-charged phospholipid membranes present in bacteria [23–25]. Piperazine and substituted piperazines belong to an important class of pharmacophores [26]. Among them, the well-known piperazine category is indinavir (trade name: Crixivan), capable to act as HIV protease inhibitor. The piperazinyl cross-linked ciprofloxacin dimers exhibited low antibacterial activity against resistant bacterial strains. Additionally, when benzimidazole and benzotriazole molecules were linked with piperazine derivatives strong antifungal activity was observed [27, 28]. Therefore, the fabrication of CNTs with piperazine makes it partially soluble in organic and inorganic solvents and facilitates its use in cancer therapy and other biological applications [29–34].

Dopamine is also an important neurotransmitter that plays a significant role in the central nervous system, renal and hormonal systems [35]. Piperazine and dopamine are interesting bioactive moieties which are present in various drugs [36]. The polar nitrogen atom in the piperazine ring and the amine nitrogen in the dopamine enhance favourable interaction with biomolecules and enzymes and confer biological activity [37]. The functionalisation of MWCNTs with the biologically active molecule is predominantly playing an important role in the emerging field of nanomedicine [38]. Thus, extensive research has been focused on MWCNTs surface modification through esterification [39], fluorination [40], oxidation [41] and amidation reactions [42].

The current report focuses on the functionalisation of MWCNTs with piperazine and dopamine derivatives and their anti-bacterial activity against common bacterial strains like *Staphylococcus aureus*, *Micrococcus luteus* and others. For this purpose, MWCNTs were first activated through acidic treatment to activate

–COOH groups on their surface. Then carboxylated MWCNTs were reacted with thionyl chloride (SOCl_2) to produce MWCNTs-acid halide intermediate. This intermediate was further reacted with substituted piperazine and dopamine to produce MWCNTs-piperazine and MWCNTs-dopamine derivatives. As synthesised derivatives were characterised by energy-dispersive X-ray spectroscopy (EDX), Fourier transform infrared spectroscopy (FTIR), X-ray diffraction spectroscopy (XRD), scanning electron microscopy (SEM) and Raman spectroscopy. Later on, zone inhibition assay results on agar plates showed antibacterial activity against *Escherichia Coli*, *Klebsicella pneumonia*, *Staphylococcus bacter*, and *S. aureus* up to 56.25, 56.25, 50 and 43.3% respectively by MWCNTs-piperazine. While against *S. aureus* and *M. leutius* 20 mm inhibition zones were produced by MWCNTs-dopamine derivatives.

2. Materials and methods: All the reagents and chemicals such as MWCNTs (95% purity), nitric acid (HNO_3), sulphuric acid (H_2SO_4), thionyl chloride (SOCl_2), dimethyl formamide (DMF), acetonitrile (CH_3CN), potassium carbonate (K_2CO_3), dopamine, 1-(pyridin-4-yl) piperazine, acetone (CH_3CO), methanol (CH_3OH) and toluene ($\text{C}_6\text{H}_5\text{CH}_3$) were purchased from Sigma–Aldrich and used as received without any further purification.

2.1. Synthesis of MWCNTs-COCl: The preparation of MWCNTs-COCl is a two-step procedure. In the first step, pristine MWCNTs were surface-functionalised with –COOH group. For this purpose, 200 mg of MWCNTs were added to a mixture of HNO_3 and H_2SO_4 (60 ml: 10 ml) in a 250 ml round bottom flask and refluxed at 120°C for 48 h as shown in Fig. 1 (step a). This treatment facilitated the introduction of –COOH group at MWCNTs surface [41]. After 48 h, the reaction mixture was allowed to cool down to room temperature prior than filtration and several washing steps. The black precipitates were separated as MWCNTs-COOH. In the second step, 100 mg of MWCNTs-COOH was added in 10 ml of thionyl chloride (SOCl_2) and refluxed at 45°C for 6 h as (Fig. 1, step b). After reflux, the crude compound was obtained as MWCNTs-COCl intermediate which was immediately used for the next steps.

2.2. Synthesis of MWCNTs derivatives

2.2.1. Synthesis of MWCNTs-piperazine derivative: For this purpose, 163 mg of substituted piperazine, 50 mg of MWCNTs-COCl, 5 ml of DMF and 160 mg of K_2CO_3 were taken in a 250 ml round bottom flask and refluxed at 75°C for 10 h (Fig. 1, step c). The resulting mixture was allowed to cool to room temperature, filtered off and washed several times with ethyl methanol and deionised water. The resulting black solid product of MWCNTs-piperazine was vacuum dried and stored for further characterisation.

2.2.2. Synthesis of MWCNTs-dopamine derivative: For the preparation of MWCNTs-dopamine derivative, 140 mg of dopamine was mixed with 160 mg of K_2CO_3 in a round bottom flask. Then 5 ml of DMF was added and subjected to reflux at 75°C for 8 h. 50 mg of

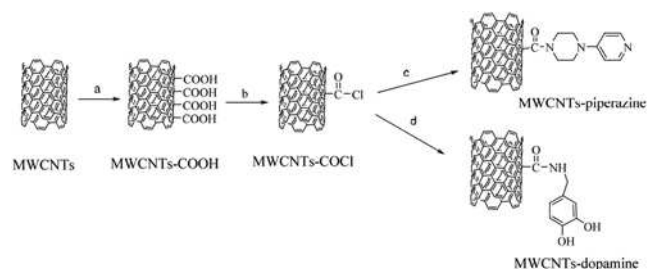


Fig. 1 Corresponding steps for the synthesis of MWCNTs-piperazine and MWCNTs-dopamine

MWCNTs-COCl was added to this solution and refluxed for 24 h (Fig. 1, step d). The mixture was then cooled to room temperature, washed thrice with ethyl acetate, dichloromethane, methanol and deionised water to remove unreacted precursors and stored for further characterisation.

2.2.3. Antibacterial test: Antibacterial activity was tested with MWCNTs-piperazine and MWCNTs-dopamine derivatives. For this purpose sample was introduced in the form of a small disc on R2A plates pre-inoculated with $100\ \mu\text{l}$ of inoculum containing 10^7 – 10^8 CFU ml^{-1} of cultured bacteria (approximately). Later, plates were incubated at 30°C for 48 h. Lastly, the diameters of the inhibition zones around MWCNTs-piperazine and MWCNTs-dopamine were determined.

3. Results and discussion

3.1. Characterisation of MWCNTs derivatives: As prepared derivatives of MWCNTs were characterised through various techniques such as SEM, FTIR, XRD and Raman spectroscopy. The morphology of MWCNT's derivatives was investigated by SEM analysis. Fig. 2 shows the SEM images of MWCNTs-piperazine and MWCNTs-dopamine derivatives. The SEM images of MWCNTs exhibited rough surface, suggesting the successful incorporation of piperazine (a) and dopamine (b) molecules [42]. After incorporation, the average thickness of MWCNTs was estimated at around 51.20 nm as evident in Fig. 2.

FTIR study of MWCNTs and MWCNTs-COOH is presented in Fig. 3. FTIR spectra of acid oxidised MWCNTs (Fig. 3b) shows a

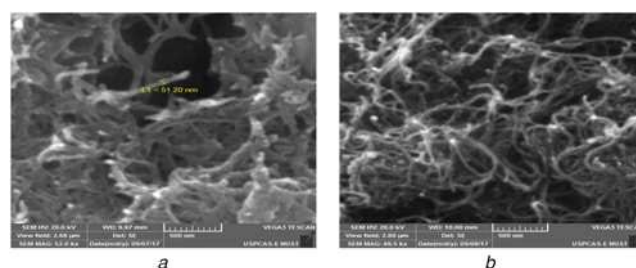


Fig. 2 SEM images of
a MWCNTs-piperazine
b MWCNTs-dopamine derivatives

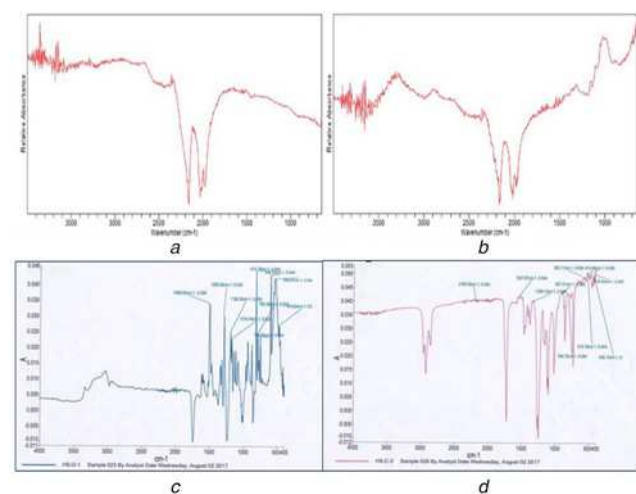


Fig. 3 FTIR spectra of
a Pristine MWCNTs
b MWCNTs-COOH
c Pure dopamine
d MWCNTs-dopamine derivative

broad peak at 3536 cm^{-1} , which is referred to OH stretchings of carboxyl groups ($\text{O}=\text{C}-\text{OH}$ and $\text{C}-\text{OH}$). This peak was absent in the spectra of pristine MWCNTs (Fig. 3a) [43]. After functionalisation of MWCNTs with piperazine and dopamine derivatives, the broad peak around 3536 cm^{-1} disappeared due to the involvement of carboxyl group (Figs. 3c and d) during derivatisation. To further validate the phenomenon of functionalisation of MWCNTs with piperazine and dopamine derivatives Raman spectral studies were performed.

Raman spectra in Fig. 4 are representing MWCNTs-piperazine and MWCNTs-dopamine materials exhibiting two extensive sections. In the first-order section $500\text{--}2000\text{ cm}^{-1}$, three peaks around 870 , 1360 , and 1604 cm^{-1} were observed. Whereas, two asymmetric and broad peaks around 2712 and 2949 cm^{-1} in the second-order section $2000\text{--}4000\text{ cm}^{-1}$ were also noticed.

The G band frequency was found to be existing around 1604 cm^{-1} , which is featured due to the tangential vibrations of carbon atoms [44]. In Fig. 4a, the additional peak at 870 cm^{-1} may correspond to structural defects [45]. The D band observed at 1360 cm^{-1} arises from structural defects or sp^3 -hybridisation of carbon [46]. In the Raman spectrum of MWCNTs-dopamine (Fig. 4b) two prominent peaks around 2712 and 2940 cm^{-1} are observed in the second-order region. The peak present at 2940 cm^{-1} is assigned to the intrinsic CH_2 stretching band directly linked to the amide linkage of dopamine [47].

Furthermore, to investigate the crystallinity of MWCNTs derivatives, XRD analysis was performed. Fig. 5 represents the XRD patterns of MWCNTs-piperazine and MWCNTs-dopamine samples. XRD patterns exhibit two general peaks at 26.25° and 44.20° , corresponding to (002) and (100) reflection planes of MWCNTs-dopamine and MWCNTs-piperazine, respectively. The intensity of these peaks is lower than pristine MWCNTs [48] which indicates the adsorption of piperazine and dopamine on MWCNTs-COCl surface. In the XRD spectrum of MWCNTs-piperazine, the first peak at 26.25° was shifted to 28.53° which can be easily attributed to the presence of stress or

surface modification by anchoring materials [43]. Apart from this, there is no observable shift in peak position suggesting MWCNTs-COCl retained their original structure. Overall the peak patterns validate that the crystallographic structure of MWCNTs-COCl was not altered much upon the incorporation of piperazine and dopamine derivatives.

3.2. Antibacterial activity of MWCNTs-derivatives: Fig. 6 shows the antibacterial activity of as synthesised MWCNTs-dopamine derivative against *E. coli*, *K. pneumonia*, *S. bacter*, and *S. aureus* at various concentrations. *E. coli* at 0.1, 0.5 and 1% concentration show 54.2, 37.5 and 56.25% biological activity (Fig. 6a). Whereas, *S. bacter* and *K. pneumonia* at 0.1, 0.5 and 1% concentrations exhibit 53.13, 34.37 (Fig. 6b) and 50% and 56.25, 31.25 and 50% antibacterial activity (Fig. 6c). Similarly, the antibacterial activity against *S. aureus* (Fig. 6d) at 0.5 and 1% concentrations displayed 43.3 and 34.37% impacts. In all above experiments, Ciprofloxacin (antibiotic) was used as standard. Details regarding the inhibition zone of MWCNTs-dopamine and standard against different bacterial strains are presented in Table 1 and Fig. 7a.

Similarly, for MWCNTs-piperazine the antibacterial activity against *S. aureus* and *M. leutus* was determined by examination of bacterial growth against standard ciprofloxacin as shown in Fig. 6b and 8.

The antibacterial activity was monitored at 0.1 and 0.5% concentration of MWCNT-piperazine derivative. Results show that the inhibition area of the microbe decreased particularly due to MWCNTs-piperazine action (Fig. 8). We also studied the effect of different solvents, i.e. DMF and DMSO on the antibacterial activity of MWCNTs-piperazine derivative. Results displayed that

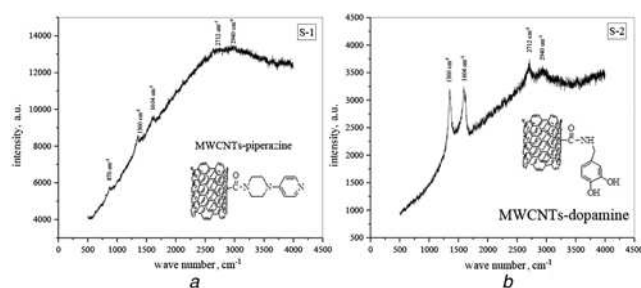


Fig. 4 Raman spectra of
a MWCNTs-piperazine
b MWCNTs-dopamine

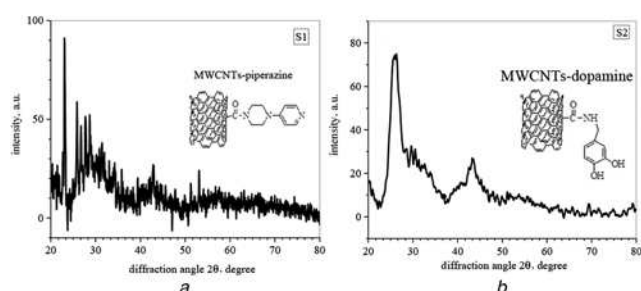


Fig. 5 XRD patterns of
a MWCNTs-piperazine
b MWCNTs-dopamine

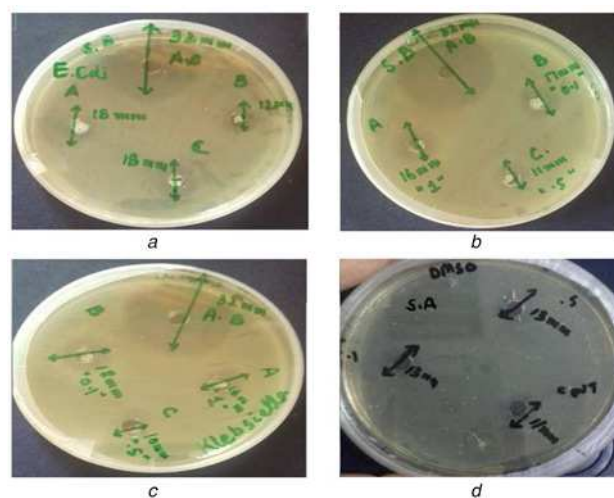


Fig. 6 Inhibition zones of MWCNTs-dopamine derivative against
a *E. coli*
b *K. pneumonia*
c *S. bacter*
d *S. aureus* at different concentrations

Table 1 Inhibition zones of MWCNTs-dopamine derivative and standards against different bacterial strains in DMSO

Bacterial strain	0.10%	0.50%	1%	Std.
<i>E. coli</i> , mm	12	18	18	32
<i>S. aureus</i> , mm	13	16	13	30
<i>K. pneumonia</i> , mm	18	11	10	32
<i>S. bacter</i> , mm	17	16	11	32

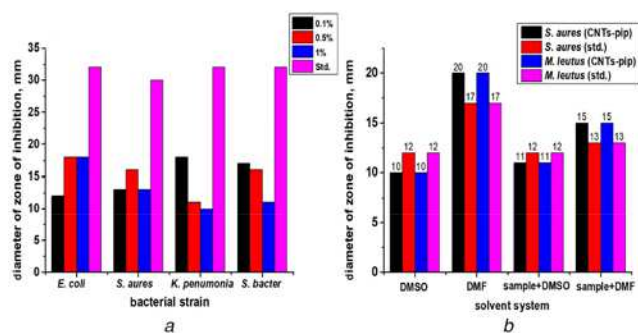


Fig. 7 Graphical representation of zone of inhibition effect of
 a Three different concentration of MWCNTs-dopamine derivative on different bacterial strains
 b Different solvents on MWCNTs-piperazine derivative on *S. aureus* and *M. leutius*

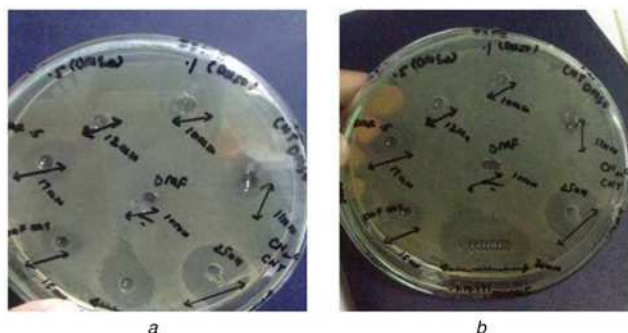


Fig. 8 Inhibition zone of MWCNTs-piperazine derivative against
 a *S. aureus*
 b *M. leutius*

Table 2 Inhibition zones of MWCNTs-piperazine derivative and standards against *S. aureus* and *M. leutius* in different solvents

Solvents	<i>S. aureus</i>		<i>M. leutius</i>	
	MWCNTs-pip.	Std.	MWCNTs-pip.	Std.
DMSO, mm	10	12	10	12
DMF, mm	20	17	20	17
SAMPLE-DMSO, mm	11	12	11	12
SAMPLE-DMF, mm	15	13	15	13

the effect of solvents was not prevalent on the antibacterial zone of inhibition (Fig. 7b and 8 and Table 2).

4. Conclusions: This work utilises simple steps to activate and functionalise MWCNTs with biologically active derivatives. Activation of MWCNTs was achieved with great ease with both piperazine and dopamine. Successful functionalisations were confirmed as well as exclusively elaborated with state-of-the-art spectroscopic techniques like SEM, Raman, FTIR, XRD and others. Moreover, the considerable antibacterial activity of MWCNTs-dopamine and MWCNTs-piperazine was achieved against common bacterial species like *E. coli* and *S. bacter* and *K. pneumoniae*. We believe that targetted functionalisation of MWCNTs to enhance the biological activity is undoubtedly a way forward for future bioapplications.

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