

Application of Functionalized Multi-Walled Carbon Nanotubes for Growth Enhancement of Mustard Seed Germination

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Abstract: Multi-walled carbon nanotubes (MWCNTs) are one of the nanomaterials that can be applied to agriculture. This work investigates the beneficial effects of MWCNT function on mustard plants. In this study, the material of MWCNTs is functionalized with nitric acid to attach the carboxylic group onto the tube wall. The functionalized MWCNTs were characterized by SEM, TEM, XRD, and FTIR. The MWCNT diameter produced ranges from 20 to 50 nm and the inner diameter is 5 to 10 nm at the pyrolysis temperature of 900 °C. It was found that crystallites of the MWCNTs have (002) and (100) directions. There is a weak peak in MWCNTs prior to the functionalization process due to the presence of metal carbide (Fe₃C), which serves as an active catalyst. FTIR results clearly indicate the presence of hydroxyl and carboxylic groups. These functionalized MWCNTs were dispersed into distilled water with various concentrations at 25, 50 and 75 µg/mL. By utilizing an immersion time of 24 h, mustard (*Brassica juncea*) seeds were soaked in each functionalized and non-functionalized MWCNT solution. Functionalized MWCNT solution at a concentration of 50 µg/mL was found to affect the growth of mustard seeds more significantly.

Keywords: multi-walled carbon nanotubes; functionalization; mustard; seed; germination

■ INTRODUCTION

Currently, the application of nanotechnology in agriculture is important. Various problems related to agriculture have been solved by utilizing nanotechnology. Such technology has supported modern agriculture in terms of providing, for example, pesticide sensor technology as well as both pesticide and fertilizer delivery systems [1]. Nanoparticles can reduce the loss rate of fertilizer nutrients into the soil by leaching and/or leaking and can extend the effective duration of the nutrient supply of fertilizers into soil [2]. Nano-sized material of mineral micronutrients may improve solubility and dispersion of insoluble nutrients in the soil, reduce soil

absorptional fixation, and increase bioavailability. Nanometer-sized fertilizers have been used to increase yields [3]. The use of nano silica fertilizer to improve the yield of rice and horticulture can be implemented by spraying onto the leaves through the mouth of the leaf. Nanosilica particles enter the mouth of a micrometer-sized leaf with relative ease [4].

Several nanoparticles with different characteristics have recently gained interest because of the possibility of their application in the treatment of plant growth [5]. Nanoparticles of varying composition, size, concentration, and other physical/chemical properties have been reported to provide positive or negative effects, particularly with respect to influencing growth

and development of various plant species. Multi-Walled Carbon Nanotubes (MWCNTs) is a nanomaterial with new interest for many scientists in terms of agricultural applications as a biosensor, fertilizer, catalyst, and pesticide adsorbent [6-12]. Penetrating MWCNTs in seed as well as the root system significantly affects their biological activity by enhancing the amount of water present inside the seed during the germination period [13]. However, it is necessary to optimize the diameter size of MWCNTs to allow them to enter into the seed and root walls. There are several methods used for the production of MWCNTs including arc discharge, laser ablation, chemical vapor deposition and spray pyrolysis [14-19]. One of the easier methods used to produce MWCNTs by adjusting its diameter is spray pyrolysis. The length and diameter of MWCNTs can be determined by growth temperature, which is a crucial consideration for MWCNT applications.

MWCNTs produced by several methods of growth as mentioned above have hydrophobic properties meaning that it is difficult to disperse them, particularly in water. This fundamental issue becomes a technical barrier to its wider application. To overcome this problem, the functionalization of MWCNTs or SWCNTs needs to be done through the reflux process, which increases its biocompatibility capabilities, particularly in terms of adsorption ability, electrostatic interactions, and covalent bonds by the presence of carboxylic groups on the walls [20-21]. However, the reflux process carried out using nitric, sulfuric, and peroxide acids or a combination of them causes significant damage to MWCNT bonds if it is not optimally controlled [22-24]. Therefore, the acid concentration and duration of the reflux process are still a substantial challenge to be addressed by future research.

Biological and bioactive species such as proteins, carbohydrates, and nucleic acids can be conjugated with MWCNTs [5]. MWCNTs can be applied as a nutrient transfer path within the plant tissue. Soaking plant germination seeds in carbon nanotube material which has been dispersed in aquadest assists the growth process [25]. However, issues arise if the MWCNT concentration is excessive, and it is thus necessary to optimize the concentration of carbon nanotubes in various types of

plants. Khodakovskaya et al. [20] reported the increasing tomato seed germination through better moisture permeation using carbon nanotube material. MWCNTs function as providing new pores to allow water to permeate by penetrating the seed layer and acting as a part to channel water.

The use of MWCNTs as a pore medium for water canals is interesting because excessive MWCNT use also causes toxicity to plants [26]. Srivastava and Rao [13] explored the potential influence of 0–50 µg/mL of MWCNT on different seeds at varying concentrations on wheat, maize, peanut, and garlic. MWCNTs at low doses were able to increase water absorption and have an impact on the faster germination process and hence shorten germination time.

In this study, the influence of functionalized MWCNT material for the treatment of mustard plants by soaking mustard seeds in a functionalized MWCNT solution at various concentrations was analyzed. The growth temperature of MWCNTs, the process of functionalized MWCNTs, their characterization using X-ray diffraction (XRD), Fourier transform infrared spectrometry (FTIR), scanning electron microscopy (SEM), transmission electron microscopy (TEM) were also studied. The mustard plants were soaked in nanotubes, and their impact was then investigated by observing the growth of the plants and analyze differences in root and cell sizes. Based on this research, particular characteristics of MWCNTs will be obtained, especially the dimension and composition of the functionalized MWCNTs for treatment of mustard plant growth.

■ EXPERIMENTAL SECTION

Materials

Materials used in this study were benzene (CAS 71-43-2, 109646 - Merck Millipore) as a carbon precursor for MWCNT, ferrocene (Aldrich-F408; Ferrocene 0.98; CAS No.: 102-54-5) as a precursor for Fe catalyst, argon gas, nitric acid solution, and distilled water.

Instrumentation

A spray pyrolysis system was used to make the MWCNT material. The morphology images of the

functionalized MWCNTs were obtained using SEM (JEOL JSM-6390A) equipped with an Energy Dispersive X-ray (EDX) system which permits sub-micrometer elemental identification and compositional analysis. The structures of the functionalization of MWCNTs were obtained using XRD (Phillip analytical X-Ray B.V) with CuK α radiation ($\lambda = 1.5418 \text{ \AA}$) at 40 KV. TEM images were obtained on a JEOL 2011. The functionalized groups present in the MWCNTs were obtained using FTIR (Thermo Scientific Nicolet IS 10).

Procedure

MWCNT material was produced using a spray pyrolysis method (Fig. 1) at varying temperatures (800, 900, 1,000 °C). The source of the material used for making the MWCNTs was benzene and ferrocene. The optimal parameter of benzene as a carbon source and ferrocene as a catalyst was 3 g of ferrocene and 50 mL of benzene. The solution of ferrocene in benzene was introduced into the quartz reactor. MWCNTs produced from this method were still relatively difficult to disperse, and there were still residual Fe impurities from ferrocene. To resolve these issues, the work was directed towards developing methods to modify surface properties of MWCNTs with functionalization. This work was carried out using a reflux process with a nitric acid solution for 3 h to attach the carboxylic group to the tube wall. The MWCNT was washed with nitric acid only using MWCNT grown at the optimum temperature of 900 °C. Another effect of this reflux process is that the MWCNT wall will be damaged and lead to the attachment of the carboxylic group on the outer tube wall. For the application of the seed germination method, functionalized MWCNTs were dispersed into distilled water at various concentrations (0,

25, 50, and 75 $\mu\text{g/mL}$). By utilizing an immersion time of 24 h, the mustard (*Brassica juncea*) seeds were soaked in each functionalized MWCNT solution. Monitoring of seed growth of mustard seeds was performed, and growth of roots and stems was recorded.

RESULTS AND DISCUSSION

Temperature determines the pyrolysis process of hydrocarbon compounds and catalyst into its constituent carbon elements. Using varying temperatures affects the diameter and length of MWCNTs. It was found that lower temperatures of 800 °C will produce shorter MWCNTs, which were larger in diameter compared to when using higher temperatures. Low temperatures not only produce shorter MWCNTs but also bend the resulting MWCNTs (Fig. 2(a)). If the temperature is increased to 900 and 1,000 °C, the pyrolysis process takes place more rapidly and effectively, leading to MWCNT tubes being formed that are longer (Fig. 2(b) and 2(c)). At these temperatures, the

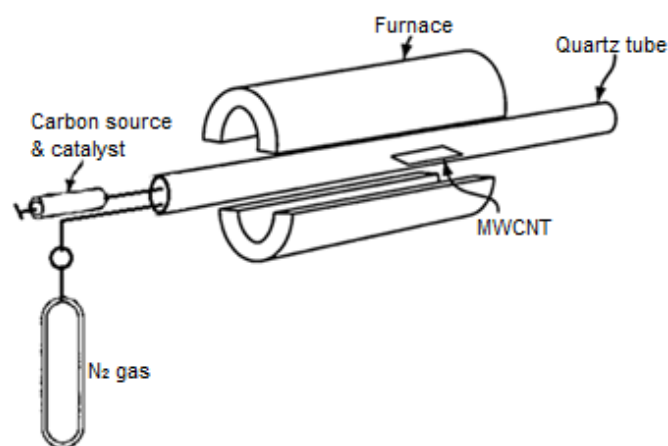


Fig 1. Schematic representation of spray pyrolysis method

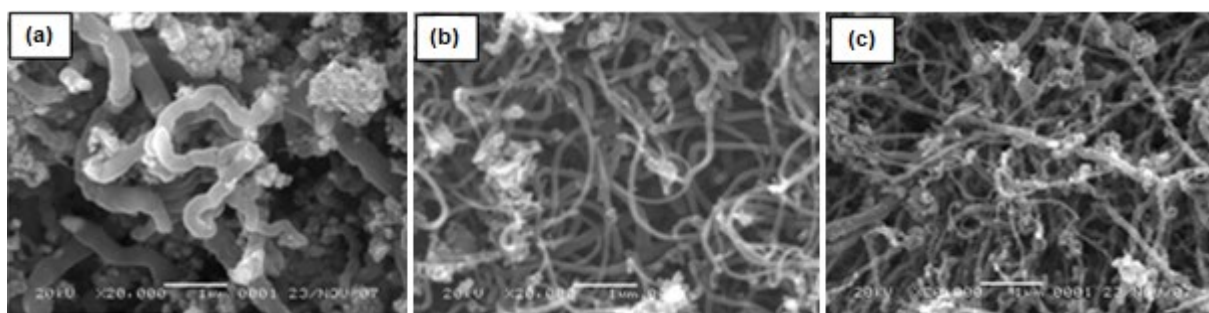


Fig 2. SEM images of MWCNTs with varying temperatures of growth: (a) 800, (b) 900 and (c) 1,000 °C

source will split into more constituent carbons, a process which causes increasing diffusion of carbons on the surface of the catalyst metal [19]. Therefore, more MWCNTs form and their diameters will be smaller. MWCNTs produced at a growth temperature of 1,000 °C are slightly damaged; other studies have also determined that structural graphite cannot be formed at such temperatures [5].

The reflux process, as shown in Fig. 3, illustrates that nitric acid treatment releases Fe particles and attaches COOH groups to the walls of the MWCNT tubes. The reflux process leads to defects in the MWCNT wall due to the presence of nitric acid. These intrinsic defects are supplemented by oxidative damage to the nanotube framework. In particular, the treatment of MWCNTs with strong acids such as HNO₃, H₂SO₄ or a mixture of them will tend to open these tubes that serve to tether many different types of chemical moieties onto the ends and defect sites of the tubes. MWCNTs functionalized using this method have an advantage in that they are soluble in various organic solvents due to possessing many functional groups such as carboxylic (COOH) ones derived from the reflux process with nitric acid [27-28]. The longer reflux process tends to produce increased Fe particle content derived from ferrocene catalysts and a decreasing Fe particle content between the before and after the reflux process, as explained from the EDX characterization.

Fig. 4 provides SEM images of MWCNT material before and after purification. It can be seen that many

material morphologies are not patterned (amorphous) and white spots are present. Clearly, these white lumps and spots are not a representation of MWCNTs, but rather other materials which are by-products or waste materials from the process of MWCNT synthesis, namely amorphous carbon. The red circle insert is part of amorphous carbon. Removal of Fe impurities and amorphous carbon can be done through a reflux process with several acid solutions. The use of strong acids to reflux MWCNT materials such as hydrochloric acid (HCl), nitric acid (HNO₃) and sulfuric acid (H₂SO₄) is particularly effective in reducing Fe particles and amorphous carbon. In this research, HNO₃ was used to reflux MWCNT.

Fig. 5 demonstrates that MWCNT material that has been refluxed has tube ends not covered by Fe impurities. During spray pyrolysis, Fe particles typically

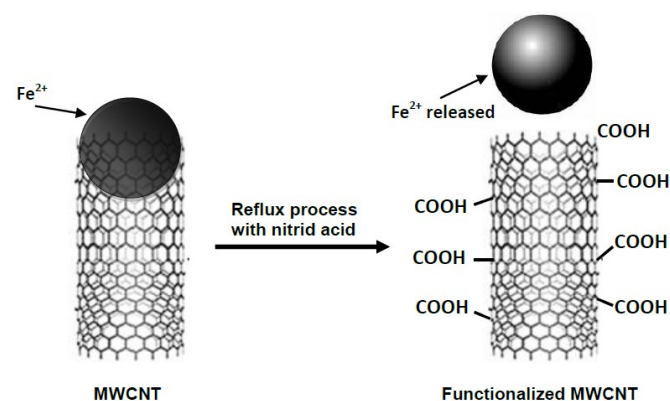


Fig 3. Illustration of MWCNT reflux process — from MWCNTs to functionalized MWCNTs

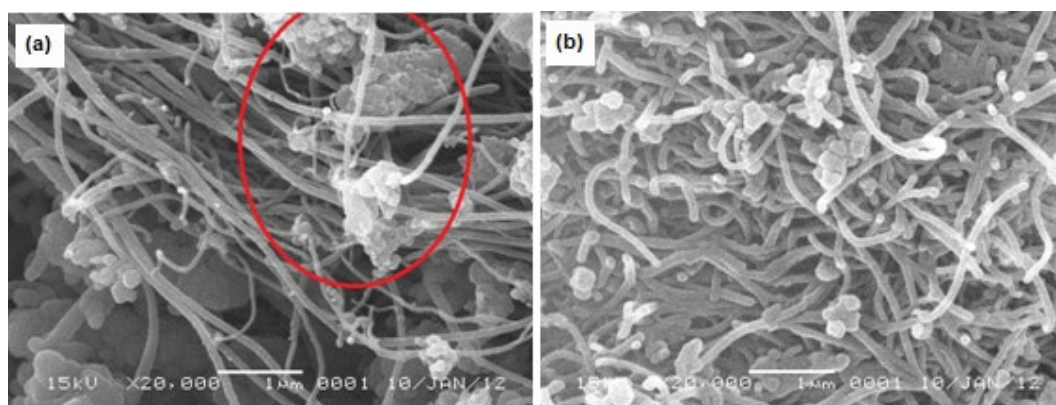


Fig 4. SEM images of MWCNT with temperature of growth of 900 °C (a) without reflux process and (b) with reflux process following spray pyrolysis. The red circle insert is part of amorphous carbon

move and act as the head followed by the tail in the form of carbon bonds so that the position of Fe particles is at the end of the tube. The reflux process is intended to release Fe particles from the end of tubes. Furthermore, for MWCNTs that have been purified, the morphological form appears more orderly and uniform; the morphology that is not patterned disappears completely, with only a few white spots remaining. As reported by Edward et al. the purification of carbon nanotubes using acids can reduce Fe attached to the end of the MWCNT surface [29]. In addition, purification with acid is also able to reduce amorphous carbon which is not shaped as nanotubes [30].

The diameter of MWCNTs produced by spray pyrolysis ranges from 20 to 50 nm. There are several walls forming a tube with an inner diameter of 5 to 10 nm, as shown by TEM characterization in Fig. 6(a). The MWCNT production using a ferrocene catalyst on the spray pyrolysis method will leave Fe as an impurity at the end of the tube (Fig. 6(b)). Therefore, the purification process of MWCNT from Fe catalyst residue needs to be carried out using a reflux treatment.

Table 1 shows the results of the EDX analysis of MWCNT treatment with and without reflux. It can be seen that reflux treatment will reduce the atomic percentage of Fe compared to without reflux. The mechanism of Fe reduction has been explained previously.

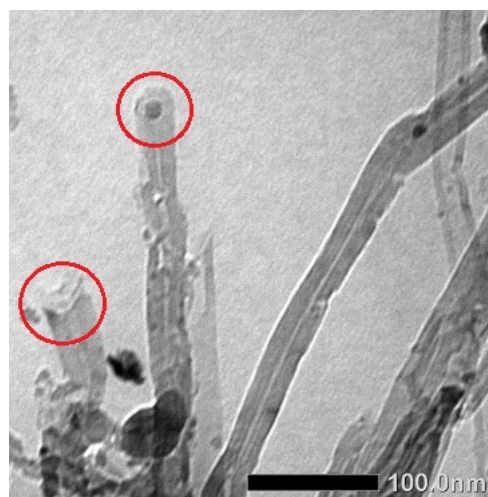


Fig 5. TEM image of MWCNT material which was refluxed. The insert red circle shows that the Fe particle has escaped from the end of tube after reflux process

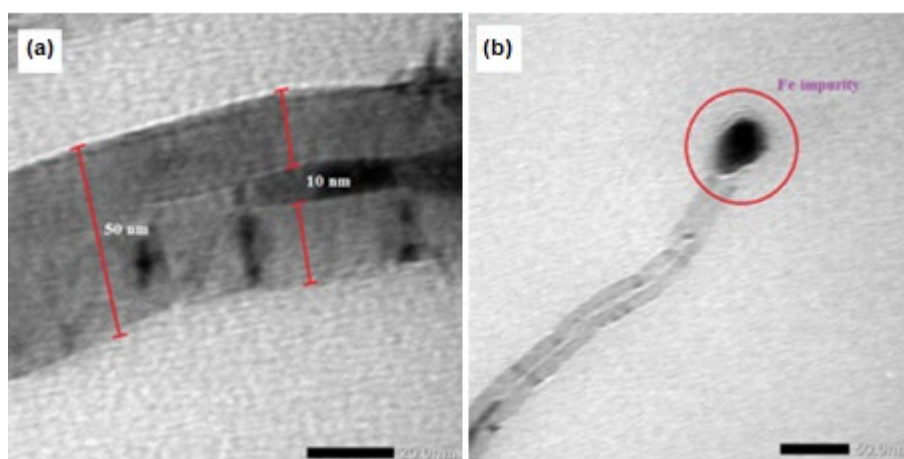


Fig 6. TEM image of (a) inner and outer diameter of MWCNT tube and (b) the presence of Fe impurities at the end of the MWCNT tube EDX was used to identify the quantitative amounts of different elements present in MWCNTs

Table 1. Results of EDX analysis of MWCNT treatment with and without reflux

No	Sample	Chemical composition in atomic %	
		C	Fe
1	MWCNT without reflux	96.40	3.60
2	MWCNT reflux	99.64	0.36

Fig. 7(a) and 7(b) illustrate XRD analysis of MWCNTs before and after the functionalization process, respectively. There are two graphite crystal orientations at 2 theta angles of 26.4 and 43.7° corresponding to the main plane of (002) and the additional plane of (100) [31]. The results also show that the peaks of CNT (002) are in symmetry, indicating good crystallite dimensions and in agreement with Das et al. [32]. MWCNT has different chiralities, consisting of different layers and shows the same peak diffraction pattern (002) with a graphite sheet. In addition, the honeycomb lattice structure of a single graphene cell caused the peak family (hk0) to be related to the (100) plane. The peak (hk0) is generated because of the curved nature of nanotubes [33]. The small peak at 37.4° in the MWCNTs prior to functionalization suggests the presence of Fe₃C in the sample. The metal carbide acts as an active catalyst in the formation of tubular structures of graphitic carbon and indicates the impurity of the sample [19].

FTIR is generally used to investigate the functionalization of MWCNTs, particularly for assaying the existence of groups attached to MWCNT tube walls. The level of functionalization would change MWCNTs properties and lead to them dissolving in water if it were used for appropriate applications. In this research, FTIR analysis was carried out to determine the functional groups present in both non-functionalized and functionalized MWCNTs. The resulting MWCNTs typically contain C-H, C=C, and C-O groups due to the spray pyrolysis process [24,31]. The reaction between

benzene and ferrocene as a catalyst at high temperatures produces carbide bonds. The carbides formed will tend to bind themselves in chains or rings, not only with one bond (C-C) but also as double bonds (C=C).

Fig. 8(a) presents spectra of functionalized MWCNTs, comprising C-O groups at the wave number of 1,027 cm⁻¹, the wide transmission band at 3,450 cm⁻¹ indicates the presence of O-H groups [17]. Wave numbers of 2,350 cm⁻¹ are characteristic of C=C groups [34]. The weak peak at around 2,850 cm⁻¹ is assigned to vibration modes of C-H or C-H₂ while the wave number of 1,720 cm⁻¹ is attributed to C=O stretching vibrations in carboxyl groups [35]. Fig. 8(b) shows the spectra of non-functionalized MWCNTs. The band at wave number 1,157 cm⁻¹ is the absorption of C-O groups, while the wave number of 2,850 cm⁻¹ is associated with the vibration modes of C-H or C-H₂. Wave numbers of 2,350 cm⁻¹ are characteristic of the C=C group due to the integrity of the hexagonal MWCNT structure.

In the case of functionalized MWCNTs, the characteristic O-H band appeared significantly broad and with higher intensity. This higher intensity is attributed to the increase in the number of hydroxyl groups on the MWCNT surface after functionalization. Decreasing the absorbance of C=C at 2,350 cm⁻¹ indicates oxidation of carbon with the emergence of a peak at 1,645 cm⁻¹ as carbonyl (C=O) stretching vibration of carboxyl groups, indicating the expansion of carboxylation on the surfaces of functionalized MWCNTs. The FTIR results

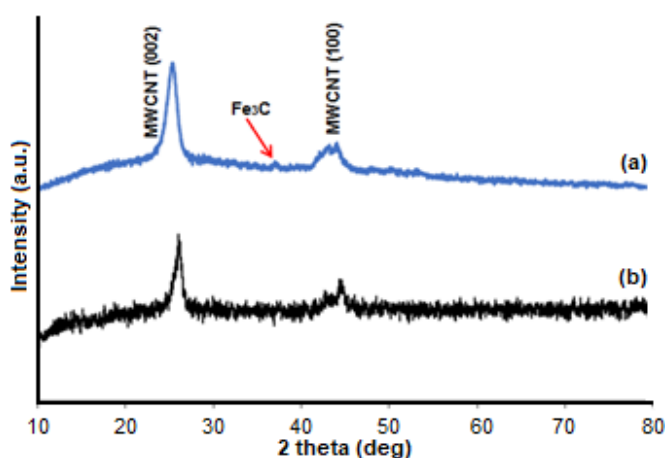


Fig 7. X-ray diffraction pattern of MWCNTs (a) before and (b) after functionalization

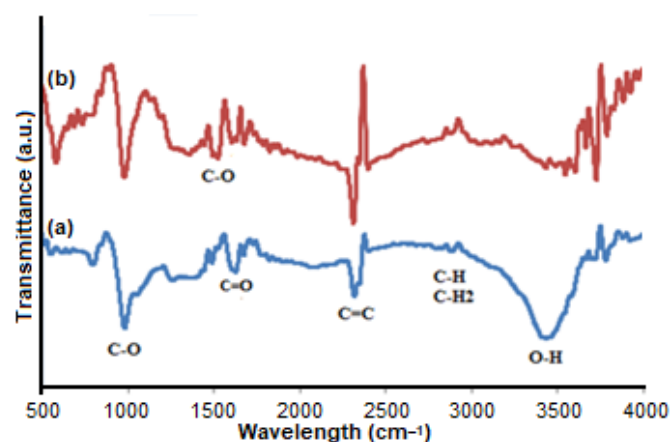


Fig 8. FTIR spectra of (a) functionalized and (b) non-functionalized MWCNTs

clearly demonstrate that the hydrophilic groups such as hydroxyl and carboxylic have been introduced onto the treated MWCNT surfaces. Thus, the functionalization of MWCNTs by the change in properties from hydrophobic to hydrophilic with the emergence of hydroxyl and carboxylic groups on its surface can be utilized as a nutrient transfer path within the plant tissue.

Fig. 9 illustrates non-functionalized and functionalized MWCNT solutions at several concentrations used for immersion of mustard seeds. Non-functionalized MWCNT cannot be dissolved in water and tend to float on the surface. At the functionalized MWCNT solution with a concentration of 25 $\mu\text{g}/\text{mL}$, the solution still appears clear because several MWCNTs are still dissolved, while at concentrations of 50 and 75 $\mu\text{g}/\text{mL}$, it appears black due to the presence of more MWCNT material. This result shows that the functionalization process of MWCNTs has been able to help the dispersion process in water because

there is a carboxylic group on the surface of MWCNTs which will increase the surface energy and reduce chemical affinity with dispersing media [36]. Surface functionalization can be developed to improve their dispersion, stability, and biocompatibility by introducing carboxylic groups.

Observations on the growth of germination of mustard plants are shown in Fig. 10. A significant positive effect on root and stem growth was seen to be very different between seeds treated by immersion in non-functionalized MWCNT solution of (a) 50 $\mu\text{g}/\text{mL}$ and functionalized MWCNT solutions with different concentration of (b) 25 $\mu\text{g}/\text{mL}$, (c) 50 $\mu\text{g}/\text{mL}$ and (d) 75 $\mu\text{g}/\text{mL}$. The functionalized MWCNT solution of 50 $\mu\text{g}/\text{mL}$ has an effect on maximum growth compared to concentrations of 25 $\mu\text{g}/\text{mL}$ and 75 $\mu\text{g}/\text{mL}$. This result demonstrates that a concentration of 50 $\mu\text{g}/\text{mL}$ is the

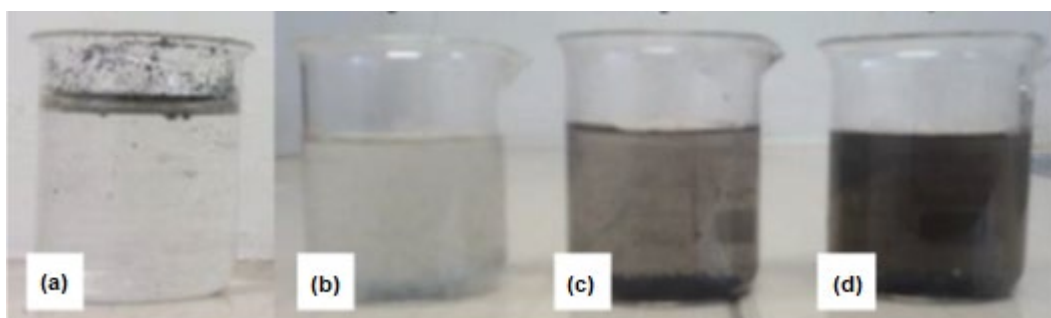


Fig 9. Photos of non-functionalized MWCNT solution of (a) 50 $\mu\text{g}/\text{mL}$ and functionalized MWCNT solutions with different concentration of (b) 25 $\mu\text{g}/\text{mL}$, (c) 50 $\mu\text{g}/\text{mL}$ and (d) 75 $\mu\text{g}/\text{mL}$

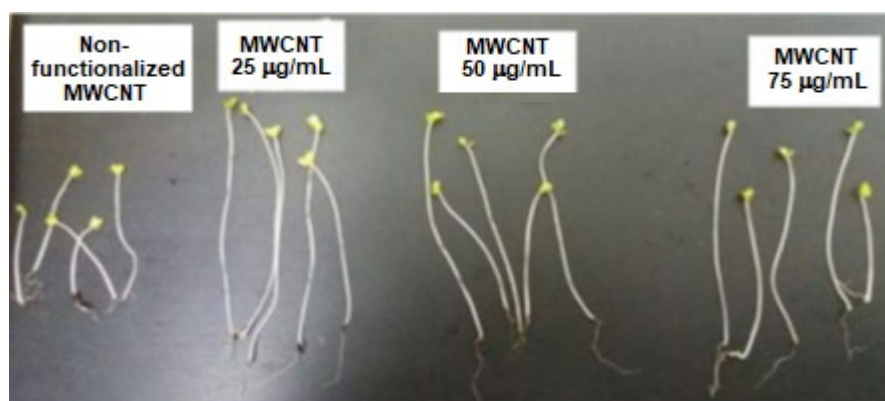


Fig 10. Photos of the effect of soaking mustard seeds for five days in non-functionalized MWCNTs solution of (a) 50 $\mu\text{g}/\text{mL}$ and functionalized MWCNTs solutions with different concentration of (b) 25 $\mu\text{g}/\text{mL}$, (c) 50 $\mu\text{g}/\text{mL}$ and (d) 75 $\mu\text{g}/\text{mL}$

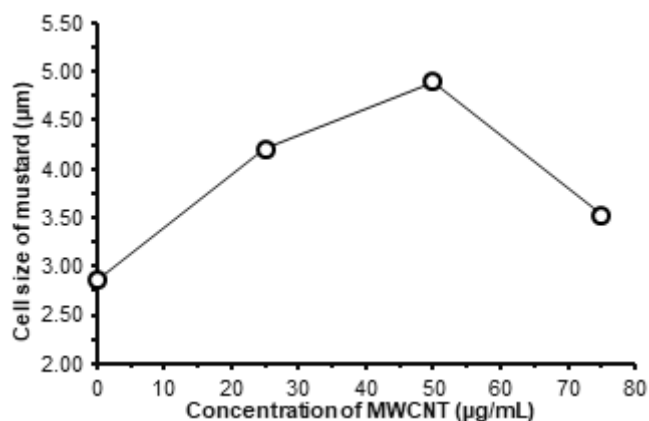


Fig 11. Effect of functionalized MWCNTs on mustard cell growth

optimum concentration where MWCNT material can enter the cell wall of mustard seeds and root systems and significantly affect their biological activity by increasing the amount of water that penetrates inside the seed during the germination period [13]. At the functionalized MWCNT solution of 75 µg/mL, aggregation of MWCNT within the roots can occur, potentially causing negative effects such as inducing nanotoxicity, inhibiting nutrient transport, and affecting plant growth [37].

Differences in the size of mustard plant cells were observed due to immersion treatment in functionalized MWCNTs (Fig. 11). Mustard plants soaked in the functionalized MWCNT solution of 50 µg/mL had a larger cell size than those soaked in concentrations of 25 µg/mL, 75 µg/mL, and control. The optimum concentration at 50 µg/mL gives the opportunity to transfer water into the wall of mustard seeds at a higher rate than other concentrations. However, the excess of MWCNTs in plants is still a question for researchers.

■ CONCLUSION

This work has demonstrated that the process of MWCNT functionalization can be successfully carried out to activate MWCNT walls in the presence of carboxylic groups. Functionalized MWCNT solutions at a concentration of 50 µg/mL led to the highest mustard seed growth rates. These functionalized MWCNTs enter the germination wall and allow the water absorption required for mustard germination to be more effective.

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