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Mini-Review

Implication of Wood-Derived Hierarchical Carbon Nanotubes for Micronutrient Delivery and Crop Biofortification

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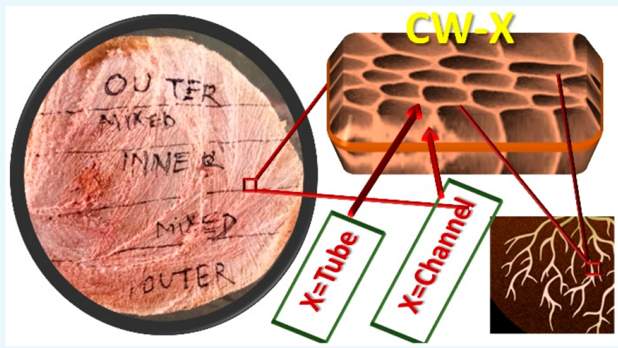

ABSTRACT: A similarity of metal alloy encapsulation with the micronutrient loading in carbon nanoarchitecture can be fueled by exploring carbon nanocarriers to load micronutrient and controlled delivery for crop biofortification. A wood-derived nanoarchitecture model contains a few-graphene-layer that holds infiltrated alloy nanoparticles. Such wood-driven carbonized framework materials with legions of open porous architectures and minimized-tortuosity units further decorated carbon nanotubes (CNTs), which originate from heat treatment to carbonized wood samples. These wood-derived samples can alleviate micronutrient nanoparticle permeation and delivery to the soil. A rapid heat shock treatment can help in distributing N−C−NiFe metal alloy encapsulation in carbon frameworks uniformly in that case; higher heating and rapid extinction of heat shock have led to formation of good dispersion of nanoparticles. The wood-carbon framework decorated with metal alloys displays promising electrocatalytic features and cyclic stability for hydrogen evolution. Envisaged from this strategy, we obtain enough evidence to form an opinion that a singular heat shock process can even lead to a strategy of faster growth of a wood-carbon network with well-dispersed micronutrient metal salts in porous matrices for high-efficiency delivery to the soil. Having envisaged the formation of ultrafine nanoparticles with a good dispersion profile in the case of transition metals and alloy encapsulation in the carbon network due to the rapid heating and quenching rates, we anticipate that the loading of micronutrients in the wood-derived nanoarchitecture of carbonized wood derived carbon nanotube (CW-CNT), which can offer an application in seed germination and enhance growth rates of crops. The experience of controlled experiments on germination of tomato seeds on a medium containing CW-CNT that can diffuse the seed coat with the promotion of water uptake inside seeds for enhanced germination and growth of tomato seedlings can be further extended to cereal crops.

■ INTRODUCTION

Significant development for increasing crop yields to match the global food requirement due to escalating inhabitants warrants the development of agriculture to adopt new technologies for chemicals and fertilizer delivery. To date, numerous silica, carbon, and metal/metal oxide based nanostructured functional materials have been applied for pesticide delivery and pesticide/mycotoxin detection.[1] However, comparatively less is known about nanomaterials for crop growth regularization and crop production security via enhancing the efficiency of nutrient delivery by carrying bioactive agents to targets to maximize the bioavailability of nutrients.[2] New ideas are needed for improving the existing crop system, to solve the global food crisis security challenges to overcome applications of functional nanomaterials in plant productivity, especially fiber-producing and ornamental species.[3a] This is initiated by active seed germination upon exposure to CNTs or graphene resulting from higher root and seedling growth in plants and plant cell cultures.[3b,d] Therefore, application of carbonaceous nanomaterials (CNMs) has rapidly increased, which also includes graphene and carbon nantotubes.[3b,e] Applications such as agricultural land use and remediation of soil for fertilizing and crop protection are major areas of focus for CNMs.[3a,f] Design of hierarchical structure derived from natural wood and similar biomass-derived materials is known for water and energy applications.[4] This starts from bottom-up assembly using nanocellulose into various forms such as 1D, 2D, and 3D including a top-down strategy for introducing novel functionality to wood-derived hierarchical structure.[5a] Besides nanocellulose materials, naturally found hierarchical structures can span wide magnitudes in dimension to enhance new functions.[5b]

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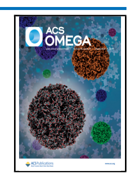

Given the surge of interest in exploring the use of wood-derived nanomaterials for a number of areas such as bioengineering, energy, and electronics,[4c] wood-derived CNTs are scarce in the area of micronutrient delivery for crop production.[5c] Wood can be chemically transformed to a carbon-based composite in a sequence of steps including lignin removal, carbonization, and filling of chemical components into resulting carbonaceous nanoarchitecture.[1,2,6a] Thermal treatment of wood results in channels of carbonized wood (CW) which improves the stability, elastic nature, and tractableness of wood carbon sponge (WCS).[5a,6a,d] Wood-derived fabrication of a highly compressible CNT with wave-shaped/reduced graphene oxide (rGO)−carbon nanofiber (CNF) aerogel by freeze-casting in which CNF enhances the interaction between rGO and CNTs.[6e] How a wood-derived CNT architecture can be accessible is an unanswered question even after development of conventional pyrolysis. Herein, we describe a method to access a CW-CNT (Figure 1)[4c] network

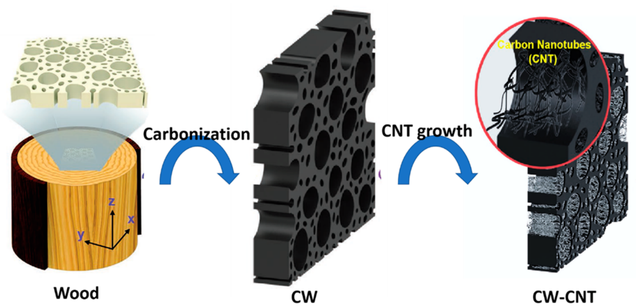

Figure 1. CNTs produced from wood carbon network (adapted with permission from ref 4c. Copyright Wiley VCH 2020).

for loading micronutrients ($FeSO_4$, $ZnSO_4$) by constructing CNT nanochannels in the CW-framework via thermal treatment. In these attempts, we have described the significant role of CNTs in promoting plant growth, the process of deriving 3D-CNT frameworks from 3D-morphology of woods, and role of tortuosity for diffusion of micronutrients in the CW-CNT frameworks. Mechanistic interpretation of passage of water through CNT materials introduced into plant cell are depicted. Finally, a proposal of nutrient loading and delivery through the CW-CNT network is presented. The idea of the CW-CNT network as a candidate for the nutrient carrier has been developed from the ever-increasing multifold application including charge-storage capacity,[7a,b] intrinsic ion adsorption mechanism,[7c] and building materials.[7d]

We envisaged that the contribution from the CW-CNT nanoarchitecture for micronutrient delivery can be multifold-backed by experimental evidence. To prevent agglomeration of nutrient metal salts and nanoparticles, CNTs are a smart vehicle for micronutrient delivery to seeds during germination.[8a] The penetration feature of CNTs to cells supports the delivery of micronutrients (Zn atoms) in a controlled manner.[8b] Zn uptake and translation in the plant system is dependent on bioavailability in the growth media. CNTs enters into the roots, stems, and leaves of seedlings within tissues and cells of roots. CNT nanoarchitecture is even capable of penetrating a seed coat with significant thickness which makes this layer permeable to micronutrients.[9] This can directly improve seed germination linked to the germination rate (%), the energy of germination (%), and the length of the roots and stems. Due to the regular periodic packing of carbon atoms, identifiable from the electron diffraction pattern, the penetration levels of CNTs derived from wood nanochannels would enhance the bioavailability of nutrients in the growth media due to significant penetration in seeds. In addition, there is a decrease in peroxidase activity by CNTs by inactivation of peroxidase molecules by CNTs due to sorption related chemical interactions.[10a] In addition, ion−CNT interaction may induce redox changes; MWCNTs can perforate the seed coat and affect the mineral nutrient supply to the seedlings via the mutually opposing forces of inflow with water and retention in the growth media by the ion−CNT transient−dipole interaction.[10b] Overall, CNT−ion interaction in the growth media improves the water absorption and concentration of essential nutrients. Therefore, stimulation of the growth of roots and stems is apparent by using CNT nanoarchitecture derived from woods. Since carbonized wood (CW) is known for producing CNTs, such advantages will be unlikely with existing candidates for nutrient delivery.

CARBON NANOTUBES (CNTS) FOR PLANT GROWTH

The synthesis strategy of single-walled carbon nanotubes (SWCNTs) and similar nanomaterials has improved and become scalable for manufacturing to realize their application profile including biomass production in plants.[11a] Toward delivery of DNA, herbicides and similar biomolecules to the plants MWCNTs can penetrate the plant cell wall. They act as a smart treatment, gene delivery, and nutrient delivery vehicle to plants.[11b] Pumpkins are grown in an aqueous medium with nano-Fe_3O_4 particles. Zhu et al. reported that pumpkins can absorb, translocate and accumulate nano-Fe_3O_4 in plant cell tissue.[11c] The uptake of C_{70} nanoparticles and their distribution in rice plants was exposed.[11d] The C_{70} particles form small aggregates in vacuoles and leaf cell walls with dark layered structures. Recently, it was explored that multiwalled carbon nanotubes can be absorbed from medium or soil by the root system of tomato plants and thereafter distributed inside plants and reach the leaves and tomato fruits. Thus, carbon nanotubes were identified by Raman spectroscopy in tomato fruit plants grown in soil supplemented with MWCNT during regular watering.[11e] A high concentration of MWCNT ($\geq$500 μg/g of soil) could have bearing on the soil microbial activity. However, it was found that fullerene (C_{60}) exhibits minimum impact on the functional and structural features of the soil microbial community.[12] It has long been known that exposure of CNTs to seeds of tomatoes enhances the seed germination level by increasing the growth rate of seeding. A significant increase in vegetative biomass was witnessed by using CNTs due to a faster germination rate, which is due to CNT-driven water accumulation.[13a] In this process, the nanoarchitecture of certain materials can penetrate seeds for facilitating seed water uptake which was confirmed by Raman spectroscopic analysis with strong scattering properties of graphitic materials.

Exposure of crops to MWCNTs during crop growth (barley, soybean, corn) with an enhancement of photosynthesis was reported.[13b] The response of plants to such treatment for 20 weeks was tracked by phenotypical experiments, the photosynthetic potential and translocation of MWCNTs was measured, and an enhancement by 10% was found. The Raman spectroscopic mapping technique was explored for seed exposure experiments to MWCNTs for 24 h for hydrophonics as compared to the control, possibly due to the phenotypic changes of treated plants. Soybeans grown in soil amended

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Table 1. Effect of CNTs on Plant Growth

sample no.	plant species	CNT	CNT synthesis	effect	ref
1	*Glycine max*	SWCNTs	Synthesized by a radio frequency catalytic chemical vapor deposition technique at 720 °C.	Enhanced root length and biomass production	15a
2	*Solanum lycopersicum*	SWCNTs	Synthesized by a radio frequency catalytic chemical vapor deposition technique at 720 °C.	Increased plant height, flowering, fruiting, accelerates leaf senescence and inhibits root formation	15b
3	*Allium cepa*	SWCNTs	SWCNTs synthesized by the chemical vapor deposition (CVD) method.	Promotes root elongation	15c
5	*Hyoscyamus niger*	SWCNTs	SWCNTs synthesized by the chemical vapor deposition (CVD) method.	Provides drought resistance by enhancing water uptake; activates defense system	15c
6	*Oryza sativa*	Hollow MWCNT, Fe-filled CNTs, Fe co-filled CNTs	Chemical vapor deposition (CVD), laser ablation, and pyrolysis.	Cell wall penetration, favors seedling growth, increases phytohormone	15d
7	*Brassica oleracea*	MWCNTs	Commercial source	Maintains ionic balance in plant	15e
8	*Cucumis sativus*	MWCNTs	Commercial source	Favors seed germination, helps root growth. Promotes resistance to sludge and sewage stress	15f
9	*Brassica napus*	MWCNTs	Commercial source	The enhanced moisture content of germinating seeds and increases water absorption of root tissues	15g
10	*Cucurbita cylindrica*	MWCNTs	Chemical vapor deposition (CVD), laser ablation, and pyrolysis.	Increases root length	15d
11	*Zea mays*	MWCNTs	Chemical vapor deposition (CVD), laser ablation, and pyrolysis.	Increases leaf length and biomass. Accumulates in cytoplasm, cell membrane, chloroplast, specific cell phloem, xylem.	15d
12	*Cucumis sativa*	MWCNTs	Commercial source	Increases biomass, reduces shoot length	15h
13	*Brassica juncea*	oxidized-MWCNT	Commercial source	Enhanced germination, root and shoot growth.	15i
14	Barley, Soybean	MWCNT	Synthesized using a radio frequency catalytic chemical vapor deposition technique at 720 °C.	Increased germination, shoot and leaf length	15j
15	Hydroponic mustard	Oxidized-MWCNT	Commercial source	Reduced germination and dry biomass.	15i

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Table 2. Effects of CNTs on Soil Microorganism

sample no	organism	CNTs	treatment	effect	ref
1	Microbial communities	MWCNT	10−100 mg/kg	No visible effects	16a
2	Microbial communities	MWCNT	0,50,500, and 5000 mg/g	Reduced enzyme activity, microbial biomass, and extracellular enzyme activity	14e
3	Microbial communities	Raw and acid treated, functionalized MWCNTs	0−5000 mg/kg	Bacterial community composition affected but recovered afterward	16b
4	*Escherichia coli*	SWNTs	1−50 mg/mL	Strong antimicrobial properties.	16c
5	Gram-negative *Escherichia coli*, *Pseudomonas aeruginosa*, and gram-positive *Staphylococcus aureus*, *Bacillus subtilis*	SWCNT dispersed and SWCNT agglomerates in saline solution	5 g/mL	Higher antibacterial activity to gram-positive bacteria compared to agglomerates.	9b
6	Bacterial and fungal communities	Carboxyl-functionalized SWCNTs	0.5 mg/L	Alteration on *Pseudomonas putida* (Gram-negative) phase transition temperatures. Higher doses had maximum biomass loss.	16d
7	Gram-positive, Gram-negative bacteria, and fungal population	SWCNT	0.03−1 mg/g	Reduced biomass of microbe and fungal population	14g

with MWCNTs, graphene nanoplatelets (GNPs), or carbon black (CB) with reduced leaf area was exhibited as compared to the control including complete plant N_2 fixation.[3f] Nodulation and N_2 fixation are negatively affected by CNMs with stronger effects at low CNM concentrations. CNM dispersal in aqueous soil extracts has explained the inverse dose−response relationships and showed more agglomeration at higher concentrations of CNMs (over 90% CNMs found to be settled as agglomerates >3 μm after 12 h). Herein, we summarize how CNTs can tune the growth of various plants for a wide range of plant species (Table 1), which involves influencing the water flux/intake and moisture content. Results summarized in Table 1 describe how CNTs play their role as micronutrient distributor and stabilizer in crop biofortification under varied environments.

Generally, MWCNTs is a micronutrient distributor as well as a nutrient stability provider under arid environment. The concentration of 15 μg/mL of ZnO/MWCNTs showed the best response for onion seed germination with a decrease in the water requirement for germination. The maximum numbers of telophase via mitotic cell division were also observed. Increased concentration of ZnO/MWCNTs does not exert any harmful effect on plant growth compared to MWCNTs.[14a] The effect of MWCNTs on beans (*Phaseolus vulgaris*) grown in hydroponics and soil microbes showed that at a concentration of 50 μg/mL, plants showed a tolerance to MWCNTs at 250 μg/mL, and at 500 μg/mL MWCNTs plant growth decreased or plants died.[14b] Aliquots of 750 μg/mL concentration of MWCNTs reduced microbial biomass. Thus, higher concentrations of CNT create stress and contact of MWCNTs to microbes may damage the microbial cell membrane, causing cell death. The MWCT exerts a significant effect on plant phenotype and soil microbiota composition. Tomato plants with CNT application produced twice as much fruit compared to the control. The relative abundance of Bacteroidetes and Firmicutes increased, but Proteobacteria and Verrucomicorbia decreased with increasing CNT concentration.[14c] Yatim et al. studied the roles of MWCNTs and functionalized MWCNTs in increasing the efficacy of urea fertilizer on paddy.[14d] It was reported that growth of plants treated with FMU1 (0.6 wt % fMWNTs) and FMU2 (0.1 wt % fMWNTs) was significantly enhanced by 22.6% and 38.5% compared to plants with MU (0.6 wt % MWNTs). The paddy treated with FMU1 produced 21.4% more panicles and 35% higher grain yield than MU, and FMU2 resulted into 28.6% more panicles and 36% more grain yield than MU, which indicates the advantage of fMWNTs over MWNTs to be combined along with urea fertilizer for plant nutrition.

Chung et al. have shown that high MWCNT concentrations reduce soil microbial features and biomass. Microbial biomass carbon and nitrogen at 20 days were found to be significantly reduced in soils treated with MWCNTs@5000 mg g^{-1} soil.[14e] Therefore, the release of MWCNTs in soil should be regulated. Radkowski et al. in a pot experiment evaluated the effect of MWCNTs and carboxylated MWCNTs on microorganisms in soil and root.[14f] The highest number of most microorganisms was found from the control, and the lowest values were in treatments with carboxylated MWCNTs, intermediate from raw MWCNTs. Thus, soil contamination even with relatively high amounts of MWCNTs or carboxylated MWCNTs does not lead to high mortality of soil microorganisms (Table 2). The single-walled carbon nanotubes (SWCNTs) are among the most used carbon nanomaterials. In a soil incubation experiment, upon addition of powder or suspended form of SWCNTs, the biomass of Gram-positive and Gram-negative bacteria and fungi revealed a significant negative relationship, and relative abundance of bacteria showed a positive relation with SWCNT concentration. Results further indicated that a higher concentration of SWCNTs may negatively affect soil microbial communities.[14g]

CNTs can affect plant productivity in both hydroponics and soil besides the effects on plant morphology and physiological and molecular processes beyond full understanding until recently.[17a,b] Understanding the influence of biological parameters on the response to CNT incorporation using exposure conditions, both in soil and in seedling stage, are rarely known. In the context of CNT phytotoxicity at the different biological levels, an evaluation of plant morphology (germination rate, plant height, biomass content) and plant metabolism and plant biomacromolecule composition using infrared spectroscopic techniques was reported to determine the response of crop species exposed to CNT in the soil.[17c] The sensitivity level of areas such as seed surface, plant clade, and plant genus undergoes an enhancement of biomass including the overall surface charge modification of accumulated CNTs from soil to plant. In this process, CNT interacts with pectins and fucosylated xyloglucans to accumulate in plant cell walls and results in overall surface charge modification from negative in soil to plant cell walls, which alters plant sensitivity due to negatively charged sites by pectins and polysaccharides on cell walls. At the level of gene expression restoration under abiotic stress (drought and high salinity), crops with CBNs can be linked with CBN-induced gene expression. This rice and tomato crop proceeds under salt stress and water-deficit stress, respectively, wherein the RNA-Seq approach allowed for gene expression of CBN-treated rice and tomato.[17d] More details on the mechanistic side are not yet revealed on the influence of CNTs on gene expression.

■ WOOD-DERIVED CNT FRAMEWORK

As we have seen, the CNT morphology of carbon materials was successfully explored for plant growth applications by delivering DNA, herbicides, and similar biomolecules. However, micronutrient delivery by means of a CNT network of carbon materials in plant biofortification is not known. When the natural wood is dissected to the direction of growth and carbonized to result in a porous framework of carbonized wood, it was shown that the CNT arrays could be grown in inner microchannels through facile in situ pyrolysis deposition, which increases the accessibility of active centers for immobilization of transition metals or metal alloys.[18a] In a wood cell wall, the dominant constituent lignin of the bond line between cells is responsible for the aggregation of cells in the tissue; therefore, lignin removal causes an increase in cell wall porosity. Besides spheres, sponge, and fibrils, wood-derived components can be carbonized to a well-tuned morphology to result in novel carbon materials based on temperature, heating speed, and concentration of starting material. One of the most challenging parts is the morphology that results from CW, which is not smooth enough to further tune due to inherent microcrystalline orientation (Figure 2).[18b] Morphology tuning of wood-derived carbon materials is what was required to access CNT nanoarchitecture in the carbonized wood.

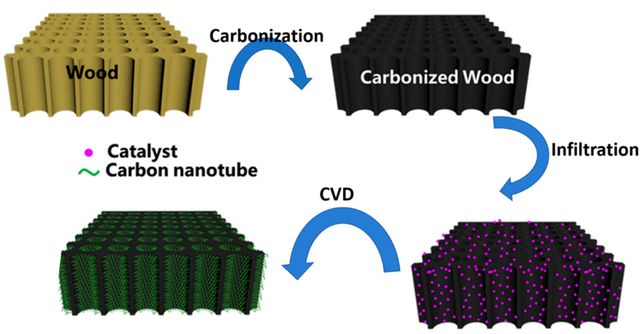

Figure 2. Process of CNTs/AWC slices from wood (adapted and reproduced with permission from ref 18b. Copyright Elsevier 2019).

The carbonized wood transformed the carbon framework into higher conductivity, lighter weight, and lower tortuosity.[3,4] In the case of few-graphene-layer morphology (one to four layers), encapsulation takes place in metal salts in the carbon nanotube channels.[18c] Top-down wood-derived soft materials depend on wood scaffolds with layered structure along with aligned micro−nanochannels within which MWCNT is formed which acts as a conductive component within the wood-derived carbon nanoarchitecture.[18d] In certain cases, uniform embedding of MWCNT on wood scaffold is driven by the presence of hydroxyl groups that induce hygroscopicity.

■ WOOD-DERIVED NANOARCHITECTURE FOR NUTRIENT LOADING

Free-standing porous carbon frameworks can offer self-supported open and porous electrode assembly for enhancing mass transfer by loading micronutrient metal salts. The heat shock treatment method through ultrafast Joule heating generates porous carbonized wood (CW).[18c] The thermal shock induced thinner graphene shells (multiple layers) result in more controlled wood derived carbon microchannels. The thermal shock process was optimized at 900 °C for 2 h at a ramp rate of 10 °C min^{-1} with natural cooling afterward. Mechanistically, when the CW-CNT sample dipped into metal Ni and Fe salts, self-assembly of N−C−NiFe electrolyte occurs rapidly in the CW-CNT framework by ultrafast heat pulse. This causes permeation of electrolyte into the porous framework by generating hydrogen gas on the metal catalyst surface, and such gas is released from microchannels without blocking mass transfer pathways. This offers a new horizon for the nanoarchitecture creation through graphene channels which can induce in situ self-assembly of micronutrient nanoparticles in the graphene channels with a deposition to increase the number of active sites for immobilization or loading micronutrient salts. By dissecting perpendicularly toward the growth direction of wood followed by heat shock, carbonization gives access to the porous and aligned carbon framework. This also helps to grow CNT arrays inside the microchannels through in situ pyrolysis which results in increased active sites for immobilization of metal salts. The resulting CW-CNT network of the materials can be used for the adsorption of nutrient salts such as $FeSO_4$ and $ZnSO_4$ (Figure 3). In the case of N−C−NiFe electrocatalysts, CW-CNT was dipped into the precursor solutions of Ni and Fe salts and dried to allow rapid self-assembly of CW-CNT by heat shock. Considering the results of electrolyte assembling into CW-CNT networks, in the low-tortuosity wood structure,[18e] micronutrient salts can diffuse into generated framework architecture in which $FeSO_4$ salts are anchored on the CNTs for rapid release.

All wood devices are known for their biodegradabilities such as supercapacitor with significant capacitance electrodes derived from natural wood via carbonization and electro-deposition.[19a,b] Fully wood-based flexible electronic device components (wood film from lignin carbon nanofiber) involves tailoring of nanoarchitecture followed by collapsing the cell walls by preserving the original alignment of cellulose-based cell walls.[19c] Similarly, due to anaerobic biodegradability of woods and generation of CNT channels under heat shock and natural abilities of woods to contain nutrients related to the wood density, we are prompted to examine the capacity CW-CNT to load nutrients and their delivery to the soil which can directly influence the fertility of soil.[19d]

■ TORTUOSITY AND DIFFUSION

In wood nanoarchitecture, lowering of the tortuosity of the materials accelerates the ion transfer when used as the electrode.[5] Higher mass load and lower tortuosity influence the high ionic and electronic conductivity of ions with low deformability.[19e,f] This part has been considered as the critical and major challenge in creating thick CW-CNT-based channel development under heat shock. In our case of CW-CNT nanoarchitecture, CNT network creation is dependent on the diffusion of $FeCl_2$ and Fe_2Cl_2+$ZnCl_2$ salts at the time of

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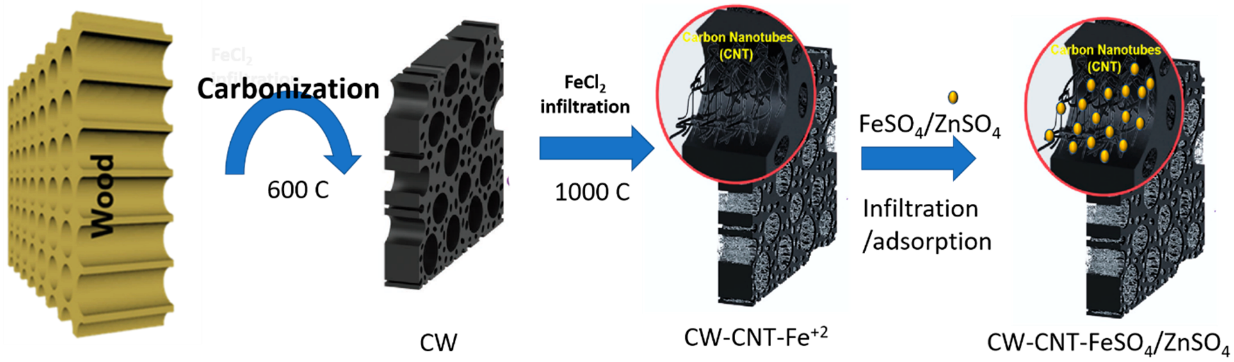

Figure 3. Proposed strategy of wood-nanoarchitecture based nutrient loading and delivery for seed germination and biofortification of crops. (Sections of the figure are adapted with permission from ref 18c. Copyright Wiley-VCH 2018).

carbonization of CW loaded with salts. Minimizing the tortuosity route transport of the ion and electron in channels loaded with metal ions results in faster transport of ions by reducing the diffuse distance. Tortuosity as defined herein, $\tau = \varepsilon(D/D_T)$ in which ε(porosity), D_T(macroscopic diffusivity), and D(conductivity) of electrolyte where anisotropic pores are aligned in the transport direction.[19a] Therefore, CW-derived CNT nanoarchitectures with straight, aligned channels are highly desirable to achieve a low tortuosity and expected high metal diffusivity.[20a] At the same time, ultrathick 3D carbon framework is also a result of wood carbonization.[14c] Such wood-derived low tortuosity nanostructure contributes to a significant reduction in ion diffusion and electron transport distance with a much faster kinetics as reported. The question that arises if we wish to use such low-tortuosity carbon nanotube architecture for the micronutrient's salts (Zn^{2+}, Fe^{2+}, Cu^{2+}, Mn^{4+}) loading and delivery to soil is what are the important factors that should be considered for plant growth and seed germination dependent biofortification of crops. In this regard, what we can find from a recent report is that in vitro studies with onion seedlings in the presence of SWCNT (single wall carbon nanotube) and fSWCNT (functionalized SWCNT). However, SWCNR and MWCNT, wherein the coaxial graphitic cylinders present in MWCNTs affect the porosity network, result into altering the water flux required by the onion seedlings.[20b] It is found that when MWCNT enters, being hydrophobic, it slips to the endocarp, the bilipid layer, and when it enters the seed, the diffuse flux of water inside the plant changes. Therefore, the flow of water will be affected by the friction of MWCNT when it is vertically aligned. Therefore, change of density in MWCNT leads to change in porous network and water flux. However, the proposal of micronutrient delivery will be organized by loading the metal salts into the CNT network of the CW to result in nutrients@ CW-CNT in water flux given the fact that MWCNT accumulates to modulate the flow of water, resulting in retardation.[8a] As found for ZnO/MWCNTs, transport of water due to the capillary action in a seedling, in which interaction of water molecule with the supported Zn causes water to cling at the edges of the pore consisting of Zn atoms through hydrogen bonding, is responsible for originating the charge (Figure 4). This promotes water entry as evidenced by the growth with a vegetative fresh mass of seedlings with ZnO/MWCNTs for both MWCNTs and ZnO/MWCNTs.

It was found that CW-CNT was accessed by dipping CW immersed in the nickel nitrate solution and ultrasonication to infiltrate CW before vertical placement in the quartz tube for

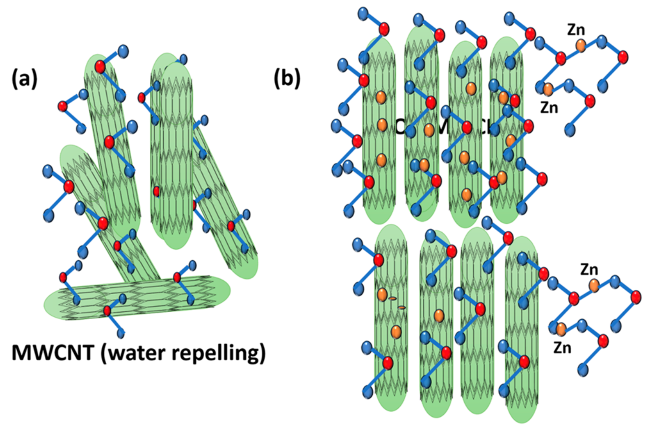

Figure 4. Depiction of water flow through MWCNTs) (a) and compared with that of ZnO/MWCNTs with hydrogen bonding influenced by Zn^{2+} while comparing with the water interaction mechanism for the vegetative mass enhancement of seedlings. (Image is drawn in Power Point; original image from ref 8a. Copyright American Chemical Society, 2018).

pyrolysis under argon. Self-assembly of CW-CNT with Ni and Fe salts followed by drying and ultrafast heat pulse treatment originated in the N−C−NiFe electrode on an open-framework CW structure. We have created a carbonized wood-derived nanoarchitecture by immersing CW into $FeCl_2$ (anhydrous) and a mixture of $FeCl_2$+$ZnCl_2$ aqueous solution followed by pyrolysis of salt infiltrated CW. We assume based on observation from loading of Ni−Fe salts that micronutrient salts (Zn^{2+}, Fe^{2+}, Cu^{2+}, Mn^{4+}) will self-assemble into a CW-CNT network and permeate through the open microchannels. We have performed the thermal process to access CW materials from at least 12 different high-altitude wood samples followed by adsorption of micronutrient salts from solution. During the process of adsorption of micronutrient salts on CW, further pyrolysis of salt-adsorbed CW undergoes tube and microchannel formation in the CW-CNT material. In such processes, $FeCl_2$ and $ZnCl_2$ are utilized, and such salt ions play major role in the interaction with the wood surface and create active sites for creating numerous microchannels and tubes.

■ SUSTAINABILITY WITH WOOD-DERIVED NUTRIENT CARRIERS

Highly crystalline nanocellulose-based building block requires top-down approaches adopted for wood-derived nanomaterials used for sustainable technologies such as energy storage, water

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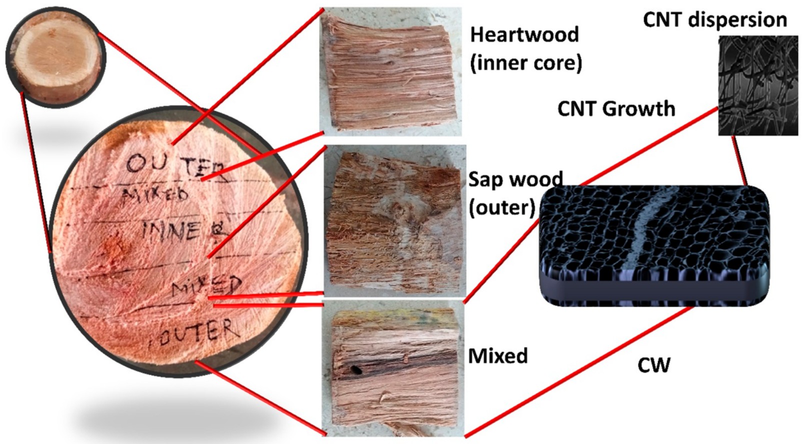

Figure 5. Proposed sequence of carbonized wood that was processed in the CNT growth study by varying sections of wood samples to determine the effect of CNTs on natural wood nanoarchitecture.

treatment, and engineering for advanced wood-based materials for attaining advanced sustainability.[20b] We envisaged that the large-scale biotemplate of the biomaterial wood can provide increased features to renewable and sustainable technology for nutrient storing bioresourced carbon nanoarchitecture. Such an attempt may compliment the emerging field of functional wood-derived materials in terms of the novel structural template and novel nanostructure-derived approaches for exploring wood-derived MWCNTs for advanced nutrient carrier profile. Even when a significant development toward the need of facile conversion of renewable wood-biomass to liquid fuels and other chemicals is already completed,[20c] the approach of wood-derived nanoarchitecture based nutrient carriers for plant growth was not explored sufficiently yet, except for limited strategies from biochar.[21a] Limited research in understanding the growth of CNTs from woods besides limited understanding of functional 3D cellulose architecture that undergoes thermal changes of anisotropic structures of wood to form carbon nanoarchitecture.[21b] Such a top-down fabrication strategy opened the scope for developing unconventional nanoarchitecture formation from natural wood with sustainable features such as lattice-like rigid wood architecture thermally transformed into repeated carbon channels like lamellar form with tube morphology.[22] In one of our initial experiments, from high-temperature pyrolysis (900 °C) of inner and mixed wood samples, nanotube-like architecture is achieved for further treatment with nutrient salts for loading micronutrients such as zinc and iron.

Even though CNT-based nanotechnologies contain the potential to contribute to healthy nutrition of crops, associated health risks from nutrient chemicals ($FeSO_4$, $MnSO_4$) that are delivered through CNT-based carriers reduce nutrient loss, reduce chemical hazards, and improve crop yield. Therefore, micronutrient fertilization, in addition to enhancing crop yield, improves crop nutritional level, therefore addressing the challenges of micronutrient deficiency. However, possible increased exposure to the micronutrient nanoparticles and CNTs in roots of edible crops may cause nanotoxicity by inhibiting nutrient transport by affecting plant growth.[23] Therefore, aggregation of CNTs in roots must be avoided, and such possibilities of phytotoxicity in plant cells may also change gene expression of plants.[11e]

■ CONCLUSION AND PERSPECTIVE

In summary, the design principal, fabrication strategy, and potential features for nutrient loading into the CW-CNT nanoarchitecture have been discussed by taking guidance from the emerging nanowood-derived CNT network which can be achieved by the heat shock treatment method for developing a nanowood architecture system as the micronutrient delivery system. As seen in the case of wood-derived electrode-design, high heating rates and subsequent quenching can effectively offer ultrafine nanoparticles in a porous CW-CNT framework. This also contains many aligned microchannels that favor metal salt nutrient permeation and loading. Therefore, we expect that CW-CNT@micronutrients ($FeSO_4$, $MnSO_4$) will hold nutrients in aligned microchannels of CNT network and release those micronutrients in soil. Until this point, the mechanism of water uptake inside seeds is not clearly known even when SWCNT were well-explored. In this context, less water usage for enhancing the seed germination percentage was explained mechanistically. In addition to the effect of CNTs on the soil microbiota, these act as a growth regulator of plants in both laboratory and crop fields. A range of concentrations of CNTs are exposed to soil via agglomeration in soil water extracts, which explains the inverse-dose relationships. It shows that CNTs at higher concentrations were highly agglomerated and less bioavailable.[3a] The concept of less bioavailability of a higher dose of MWCNTs proved to be counter-productive for soil-cultivated soybean growth due to agglomeration of SWCNTs at higher doses. Therefore, inhibition of symbiotic N_2 fixation by agglomerated SWCNTs causes poor bioavailability of SWCNTs and therefore reveals the negative effect of a higher dose of SWCNTs. Contrary to this, ZnO/MWCNTs show that a higher dose offers the best seedling growth. When the CNT channels in CW-CNT act as nutrient carrier for $FeSO_4$ and $ZnSO_4$, mitotic cell divisions[24] are supposed to occur that could offer a maximum number of telophase as result of growth enhancement.

Our proposed approach of using CW-CNT-based CNT nanochannels for holding and delivering micronutrients can be developed as a unique technique that will enable the advantage of using it as a sustainable and biodegradable nutrient carrier. Advanced nanowood materials have been researched only recently. Any concept of utilizing such nanoarchitecture derived from wood for the crop experiments for either seed

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germination or nutrient delivery to soil was not explored.[24,25] Nanoarchitecture of wood can be transformed to a unique microstructure. We aim to explore the carbon nanotube (CNT) channels of carbonized wood, which may result in a unique type of nanoarchitecture for nutrient loading and delivery to soil. Our major aim is to understand the mechanism of nutrient delivery by the CW-CNT to soil and determine the factor responsible for holding the nanoarchitecture for carrying nutrients and their delivery to soil. To construct CNT-channels from natural woods, we have selected six high-altitude plant wood species and collected samples for carbonization from their outer, mixed, and inner sections with a strategy of growing CNT channels toward growth direction by infiltrating $Fe^{2+}$and Zn^{2+} salts (Figure 5). Due to the presence of lignin in the secondary cell wall, flexibility and porosity are low in the natural wood bond line for aggregation in tissues. Efforts can be made toward delignification of natural wood before carbonization, which might impart more flexibility and increase porosity offering more space for infiltration of metal salts for promoting CNT formation at a higher temperature that might also facilitate higher nutrient loading. A complete delignification can be attempted for eliminating the binding capacity of lignin during heat shock.[25b] For a partial lignin-removed wood sample, the presence of percentage of lignin can benefit the formation and distribution in CW framework. If wood cells remove lignin from the secondary cell walls, the assembly of biomacromolecule can be strongly affected by preserving the integrity of cell wall. Therefore, it will be interesting to find out the effect of lignin/hemicellulose matrix on the CNT growth for our varied range of high-altitude forest wood samples consisting of separated heart (inner), sap (outer), and mixed wood.

The CW derived CW-CNTs can be scaled up for the commercial purposes of micronutrient delivery vehicles to soil for production of cereal crops. The supply of raw materials for CW production can be accessed from high-altitude forests to obtain wood with a range of different morphologies of wood nanoarchitecture. Such nanoarchitecture will be studied by post-carbonization characterization using high-resolution microscopic techniques. Such CW-CNT networks may contain varied mechanical strength and tensile strength when the CNT network is incorporated into the carbonized scaffold. Therefore, more microscopic structural studies to reveal the pattern of tubes and microchannels are necessary for determining the commercial application of such CW-CNTs.

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