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CNT based nanomaterials for food industry: a review

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Abstract: CNT-based composites can exhibit exceptional physical, chemical, and mechanical properties, and their tiny addition enhances activity significantly. These captured the eyes of food industrial sector due to its promising characteristics. Biosensing, gas sensing, antimicrobial properties, antibody immobilization, are key factor here. CNTs of various diameters, lengths, and functionalization processes were utilized to show antibacterial effect. By this effect these can be used in food packaging. By sensing ethylene, CNTs can be used in food ripening. As CNTs in pure water improves heat transmission, these can be used in controlled pasteurization which is needed for food safety. CNTs can sense cholesterol, vitamin B_6 and others food ingredients. So, these can be utilized in improvement of food quality. The germination of seedlings can be helped along by CNT, which is a positive impact in food quality. The application of CNT-based nanomaterials in food industry is the focus of our research.

Keywords: CNTs; food packaging; antibacterial property; biosensing; gas sensing.

1. INTRODUCTION

CNTs are a kind of carbon allotropes which have intermediate qualities between graphite and fullerenes. These are mainly nanomaterials and are utilized in a variety of applications [1]. The kinds of CNTs are as follows: single walled CNTs (SWCNTs) and multi walled CNTs (MWCNTs). In the applied sciences, both of these nanostructures have positive effects, for instance, large active surface area, thermochemical stability, chemical inertness, improved electrical properties, low charge transfer resistance [2]. The attachment of nanoparticles to the surface of external CNTs has resulted in the creation of a composite material including CNT-NPs. The functionalization of CNTs may result in the formation of a composite CNT-NPs material. It is possible to form covalent or noncovalent bonds between the surface of a CNT and a covering nanoparticle [3]. CNT are utilized in different sectors of food industry, such as, food packaging, food protection and conservation [4], coloring, increasing food life, flavoring, food safety, and nutritional additives etc. With the use of CNTs, it has been noticed that the rate of growth of plants, including the roots, has been increased. Food items, particularly processed foods, must be closely monitored to ensure that they are safe for consumption and that people are protected against infectious illnesses, which are mostly caused by pathogenic bacteria found in food. CNTs can be utilized in the development of gadgets which can identify biomolecules and diagnose illnesses has become essential in order to provide consumers with early warnings of potential dangers [5]. Because of its capacity to detect changes at its interface caused by the adsorption of charged species, SWCNT-FET biosensors have been used for the sensation of food pathogens in a variety of applications [6]. CNT enhances sensor performance because it has a high surface-to-volume ratio, which allows for more enzyme loading and more effective interaction between enzyme active sites that are deeply buried and the electrode. Water pollution, malic acid, and glucose have all been detected using biosensors in which CNTs can be utilized [7]. CNTs have an incredible elasticity. CNT can be bent, buckled, kinked, and twisted without destroying itself when subjected to axial compressive stresses. The addition of MWCNT led

to a considerable improvement in tensile strength and a reduction in the elongation at breakage of the packaging material. MWCNTs can be used in increasing elasticity in food packaging [8]. CNTs have CO2 adsorption capabilities [9]. CNTs can detect CO2 and thus these can be utilized in measurement of rotten food. SWNTs biosensors can exhibit substantial variations in electrical impedance and optical characteristics in response to their surroundings, which is generally regulated by the adsorption of a target on the surface of the CNT. Products currently under development include inkjet-printed test strips for the detection of estrogen and progesterone, microarrays for the detection of DNA and proteins, and sensors for the detection of NO2 and cardiac troponin. Similar CNT sensors have been utilized in the food sector to monitor gas and toxin levels [10]. Overall, CNTs has vast applications in food industries and this utilization of CNTs has been described in this article.

2. SPECIAL FEATURES OF CNT

Several attractive characteristics of CNTs point to their potential use in the industries of food products. In terms of electrical resistance, CNTs are incredibly low. The electrons within a CNT are less likely to be dispersed because of the CNT's tiny width and high aspect ratio. CNTs have an extremely low band gap, for example, SWNTs have a band gap of 0-0.5 eV and MWNTs have a band gap of 2.9-3.7 eV [8]. CNTs can show thermoelectric performances also [11]. Phonons have a strong influence on the thermal characteristics of CNTs, including their specific heat and thermal conductivity. Because of the strength of the atomic bonds in CNT, they can tolerate high temperatures and operate as excellent thermal conductors [8]. In industry, effective cooling is difficult technological problems. At ambient temperature, the thermal conductivity of aligned bundles of SWNTs is more than 200 W/mK, which is much higher than that of bulk nanotubes. Measurement of the average nanotube diameters of samples with various average nanotube diameters confirms this interpretation of K(T) linearity up to roughly 40 °C [12]. These can revert to their previous shape. However, its flexibility has a limit and may be temporarily warped by a high force. CNTs can be relatively durable materials. The Young's modulus is

between 270 and 950 GPa, while the tensile strength is between 11 and 63 GPa. It has been shown by a number of studies that CNTs are soft in the radial direction [8]. The hydrophobic characteristic of CNTs makes them so little water soluble. Nonetheless, they might be dissolved by means of modification and treatment [13]. Modified CNTs (e.g. Polystyrene/CNT (PS/CNT) composites [14], Cu/CNT [15], Alumina—CNT/SiC Nanocomposite, CNT-graphene heterostructure [16] etc.) have particular properties including thermal, mechanical, chemical etc. that may be used in numerous industrial sectors.

3. CNT FOR FRUIT RIPENING

Plant growth regulators such as ethylene are the most extensively utilized since they are essential in the stimulation of fruit ripening. It is a gaseous plant hormone that, in conjunction with other hormones and signals, plays role in the ripening process of fruit varieties [17]. The ethylene release profile of naturally ripened fruits and artificially ripened fruits differs. While the fruit is going through its natural ripening process, the rate of releasing ethylene slows down gradually over a lengthy period. As a result, naturally ripened fruits will have a longer shelf life than ripened fruits. The rate at which ethylene is released from fruits increases during artificial ripening is greater than that of natural ripening [18]. So, the detection of ethylene is critical in fruit ripening. The detection of ethylene is critical in differentiating between natural and artificial fruit ripening processes. Several scientific studies on the detection of ethylene using CNTs have been conducted throughout the previous decade. In 2014, a researcher presented a sensor for the detection of ethylene that was built on multiwall CNTs (Figure 1) [19].



Fig. 1. Ethylene detection mechanism using MWCNT in food ripening.

The combination of SWCNTs with copper (I) complex, according to recent research, may be effective in the detection of ethylene. A sensor based on SWCNTs has been created to monitor the amount of ethylene produced by fruit ripening at a ppm level. This sensor has a sensitivity of 1.8 percent for ethylene at a concentration of 50 ppm [20]. According to the findings of a research, the performance of MWCNT sensors is superior to that of SWCNT sensors in terms of ethylene feeling. It is necessary to use a reference ethylene sensor to maximize the effectiveness of the newly designed MWCNT sensor. With the help of a peristaltic pump, it will be possible to

create ethylene gas in the ethylene producing chamber, which will house the fruits, and then pump it into the test cell. The ethylene created by the fruits will also be sent via a reference ethylene sensor, which will be used to measure the concentration of ethylene. The efficiency of a newly created sensor may be determined by comparing the sensing results of the sensor with those of a standard reference sensor [18].

4. SENSING APPLICATION OF CNT IN FOOD INDUSTRY

The CNT has long been recognized as a remarkably successful approach in the realm of food safety. CNTs have a number of beneficial properties for bio detection with having property for antibody immobilization and a low absorption in the visible range, both of which are important for bio detection [21,22]. Staphylococcal enterotoxins (SEs) are a useful model toxin system for determining the relevance of various biodetection methodologies, especially in the context of food safety, and for testing these approaches. They have been suggested to be potential bioweapons in the future [23]. The detection of Staphylococcal enterotoxin B (SEB) in food has been tested using CNTs in recent research. They used a straightforward CCD detector in conjunction with CNTs to create a cheap and portable point-of-care immunosensor [24]. Polyphenols in flow systems may be detected using glassy carbon electrodes (GCEs) and MWCNTs [25]. The glucose oxidase enzyme was detected using electrodes modified with boron-doped [26]. The MWCNT-doped titania-Nafion composite-modified GCE (CNT-titania-Nafion/GC) has been designed to detect bisphenol A in a variety of environments (BPA). The results of the experimental tests demonstrate that this nanosensor has high selectivity and repeatability [27]. The detection of nitrite in milk has been accomplished using a novel ionic liquid-SWNT (IL-SWCNT) based nanosensor [28]. The development of a fructose dehydrogenase (FDH) immobilized CNT biosensor for the quick measurement of fructose in food has been completed. Experimental investigations in honey, fruit juices, soft drinks, and energy drinks were carried out to assess the detection performance of the novel fructose biosensor, and the findings were found to be in good agreement with those obtained using a commercial reference kit [29]. To detect sulfonamides (SAs) in egg samples using magnetic multi-walled CNTs (MMWCNTs) has been used. The findings of the experiments show that MMWCNTs can identify SAs in the incurred egg samples with an acceptable level of accuracy [30]. MWCNTs/GCE can also detect Sudan red I (up to 2.01×10^{-8} M) [31]. Chitosan-CNT (CS) modified electrodes can determine selective Br within the range of 36×10^{-7} to 14×10^{-5} g/mL [32]. The incorporation of carbon tubes into nanosensors has resulted in an increase in the antimicrobial effect of the sensor, which may be ascribed to the penetration of these tubes into microbial cell walls, resulting in permanent damage and cell death [33]. As a result of the incorporation of carbon tubes into nanosensors, it has been shown that the antibacterial activity of the carbon tubes has been increased significantly. This may be due to the penetration of carbon tubes into microbial cell walls, which results in

permanent damage and cell death, according to certain theories [4,33]. When it comes to electrochemical micro sensor systems, CNT-based devices are mostly used in field effect transistors [34]. Malic acid nanosensors based on NADP specific malate dehydrogenase (malic enzyme) mounted on functional c-MWCNT electrodes have been developed (0.12 cm²). With the help of EDC-NHS coupling, malic enzyme has covalently immobilized onto a c-MWCNT electrode [7]. In recent years, noteworthy progress has been made in the development of a screenprinted carbon electrode/CNT that can detect E. sakazakii at concentrations ranging from 103 to 109 CFU/mL and with detection limits as low as 7.7×10⁻¹ CFU/mL, as well as having long-term preservation capabilities. It was pointed out that the development of E. sakazakii in milk powder following the addition of water resulted in a limitation, and the product's use had to be postponed until the problem was resolved [35] SWCNTs was therefore proposed to use the GOx-AuNP-CNT Teflon sensor to determine the glucose content in sports beverages using the conventional addition technique. Results were compared to those obtained using a spectrophotometric flow injection approach that used immobilized glucose oxidase on a Controlled Pore Glass reactor, and there was a strong correlation [36]. A direct oxidation test at electrode surfaces may be used to detect whether or not BPA is electrochemically active. It is possible to modify electrodes with metal nanoparticles or carbon-based nanoparticles in order to improve their detecting capabilities. With the use of MWCNTs and a molecularly imprinted polymer (MIP), a GCE was modified to allow for sensitive electrochemical detection of BPA in which the MWCNTs served as an electrically conductive layer and the MIP served as a particular site for BPA binding [37].

5. CNT FOR FOOD SAFETY

CNT can contribute to food safety purposes. For the measurement of pirimicarb insecticide, it has been suggested to use laccase-modified multiwall CNTs (MWCNT) [13]. In computational fluid dynamics, a CNT-water nanofluid has been observed. Adding a tiny percentage of nanoparticles to pure fluid improves heat transmission, according to the research team [38]. Heat transfer technologies are used in food industry to control fluid temperatures in processing systems in order to meet the requirements for pasteurization, filling operations, and food safety standards [39]. Freshness indicators, on the other hand, are meant to provide precise information on the quality of a food product as it is being kept, transported, and presented. The interaction between microbial metabolites and the markers that have been included offers visual information about the microbiological quality of the product that is being assessed. The spoilage components or microbial metabolites that are created during the deteriorating of a food product, such as volatile sulfides and ammonia, are sensitive to the new freshness indicators that have been established. When it comes to the detection of diseases in the food supply chain, the isolation of pathogens from their natural environment in the food system is important to success [40]. Escherichia coli O157:H7 and Enterobacter sakazakii have been detected using

integrated electrodes that have been coated with MWCNTs, sodium alginate (SA), and carboxymethyl chitosan (CMC) composite sheets, according to the research [41]. The MWCNT/Nafion modified glassy carbon electrode has used to detect the hydrolysis product, p-aminophenol, in the solution. Because of its quickness and sensitivity, the approach may be utilized for the detection of E. coli in river water, and it can be applied in the food manufacturing industry [36]. The amperometric immunosensor for the detection of carbofuran, a pesticide, was developed using MWCNTs and a graphene sheet-ethyleneimine polymer-Au (GS-PEI-Au) synthesized GCE [42]. AuNPs and a CNT-based nanocomposite film were coated on a glassy carbon electrode, increasing the electron transfer rate while also improving antibody immobilization and stability. To detect the presence of ochratoxin A in grape juice and wine, researchers developed a sensor that uses silver nanoparticles (AgNP) and reduced graphene oxide (rGO)-enhanced electrodes with MIP as the recognition element [43]. When it came to the detection and quantification of Staphylococcal enterotoxin B and cholera toxin, the researchers employed silicon nanowire transistors and CNTs, respectively. The same nanosensors were also used for the detection and quantification of food coloring in the laboratory [44].

6. IMPROVEMENT IN FOOD QUALITY BY UTILIZING CNT

It is vital to assess the amount of cholesterol present in meals to preserve food quality. A biosensor made of CNTs can detect the presence of cholesterol. CNT nanosensors are capable of detecting food pathogens and labeling microorganisms, which is a crucial characteristic of food quality detection [45]. These food-grade nanotubes have the potential to act as transporters for nutrients, vitamins, and fragrance components [46] [47]. The development of a multi-wall CNT film coated glassy carbon electrode for the detection of melatonin has been observed. Using the sensor, researchers were able to determine the amount of melatonin present in Naobaijin capsules. These are salable sanitarian food product [36]. Electrochemical detection employing CNTs can be utilized to detect flavor-producing chemicals and antioxidants in foods, for instance, beans and apples, food colorants such as Ponceau 4R and Allura Red in drinks and Sudan-1 in ketchup [31] [48]. Food value may be determined by analyzing vitamin B₆ levels in food samples. It is also necessary for the assessment of vitamin B₆ in the blood. The amplification of CPE by two conductive mediators has been used to produce a sensor for the first time. This catalyst, composed of NiO-CNTs and MOHFPE and CPE, had a catalytic impact on the determination of vitamin B₆ and increased the oxidation current of vitamin B₆ by about 2.5-fold. As a result of this, the recovery data for the NiO-CNTs/MOHFPE/CPE sensor for the measurement of vitamin B_6 in food samples ranged from 97.33 percent to 103.86 percent, indicating that the sensor's capacity to detect vitamin B₆ in actual samples is very strong [49].

7. CNT IN FOOD PACKAGING

Food packaging is a critical and integral aspect of the food industry, the food supply chain, food safety, and public health, among many other things [50]. MWCNTs and PLA composites has been blended in a melt furnace to increase the elasticity of the PLA polymer in the case of food packaging [51]. Carbon dioxide (CO₂) is one of the most prevalent by-products produced when food spoils, and it is produced because of increased microbial activity. Due to the minimal quantity of CO₂ emitted by the decaying food within the packaging, a gas sensor of this kind would need to have a sensitivity of just a few parts per million to be effective in this application. CNTs have the potential to be utilized in CO₂ sensing (Fig. 2) [52]. An further development has been the development of a CNT with perfluorosulfonated polymer sensor for the quick detection of E. coli in food [53]. It has been discovered that adding CNTs as fillers to packaging materials may result in materials with extraordinarily high tensile strength, toughness, and barrier qualities, including polypropylene, polyamide, and polyvinyl alcohol, among other materials [33,54,55].

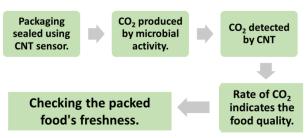


Fig. 2. Detection of CO₂ to measure freshness while Packaging.

Polypyrrole and silver nanoparticles in conjunction with CNT has been used to provide good microbial elimination activity [56]. The addition of CNTs to chitosan resulted in a considerable improvement in antibacterial activity against *E. coli* [57]. It has been discovered that TiO₂/branched CNT nanostructures are very efficient antifungal materials when exposed to visible light [58]. These antifungal and antibacterial properties make CNT and their composites feasible in the case of food packaging.

8. WATER TREATMENT BY CNT FOR FOOD INDUSTRY

The contamination of water bodies by organic compounds is becoming a prominent issue that must be addressed. It is important to treat water before using in food industry. It is a concerning issue. Many researchers in the field of organic wastewater treatment have been more interested in CNT-based materials. They may be used as adsorbents to efficiently extract organic contaminants from wastewater. These may also be used in AOPs to decompose organic contaminants. So, these materials may have potential applications in the water treatment [59]. In water treatment and desalination, CNT -based filters have been used to remove bacteria and viruses from polluted water intended for human consumption or for food production. Nitrite in water has been detected using AuNP multi-wall CNTs, allowing for the prevention of contaminating the environment [60].

Because of its fibrous form and strong conductivity, CNT filters are effective in removing germs and viruses. Through size exclusion and depth filtering, the thin layer of CNTs may successfully remove bacteria and viruses from the environment; the bacteria that do not be removed are substantially inactivated within hours after being collected. A modest voltage was applied to MWNTs, resulting in the oxidation of bacteria that had been adhered to the nanotubes. Aside from that, the applied voltage has the potential to enhance viral transmission to anodic CNTs [61]. CNTs have been combined with a variety of recognition components and employed as materials for electrochemical sensors that detect heavy metals, according to the research team. Using SWCNTs functionalized with thiophenol groups (SWCNT-PhSH) and an Au electrode, a sensor for the detection of Hg²⁺ has been produced [62]. Ho₂O₃/MWCNT has been used for UV-driven photocatalytic removal of tetracycline in the case of water treatment for food industry [63].

9. APPLICATION AS FOOD INGREDIENTS AND ADDITIVES

GO and CNT nanocomposite films has been reported to have significant electrocatalytic activities toward the oxidation of three food additives (NaNO₂, HQ, and CC) and to have simultaneous detection abilities for the three analytes when cast on glass ceramic electrodes (GCE). Because the conductive CNT was dispersed in the GO/CNT/CS nanocomposite films with excellent GOassisted dispersion, the elevated electrocatalytic activities of the modified electrodes were ascribed to this. It was discovered that by substituting carbon black with silicon dioxide, the GO/CNT/sCS/GCE displayed much higher electrocatalytic activity than the GO/CNT/CS/GCE toward the oxidations of the three analytes. The increased electrocatalytic activities of the GO/CNT/sCS films were due to the expansion of the expandable sCS in aqueous solutions of analytes, which resulted in increased porosity in the films. A GCE with the modifications GO/CNT/sCS 5/5/5/50 showed linear concentration ranges for NaNO2, HQ, and CC detections in the ranges of 1.25-357, 1.25-533, and 1.25-878 M for the three components. NaNO2, high-purity water (HQ), and chlorinated chloride (CC) had sensitivities of 0.481, 0.594, and 0.734 Acm² M1, respectively. The LOD values for NaNO₂, HQ, and 0.020 M were 0.048, 0.022, and 0.020 M, respectively (CC) [64]. L-glutamate can be oxidized in this experiment by a glutamate enzyme that was attached to the SWCNT devices, and one of the byproducts of this process was ammonia, which impacted how well the devices conducted electricity. Thus Lglutamate can be detected by SWCNT devices [65]. CNT has a favorable influence on the germination of tomato seedlings. Additionally, this technique may be used in the production of plants that are resistant to drought and salt, as well as plants that are tolerant of excessive rainfall [1].

10. CONCLUSION

When CNT was first invented, its primary function was to transport electricity; nevertheless, its applications are becoming more diverse as time goes on. CNT even has its applications in the food industry, such as fruit ripening,

food detection, food safety, increase in food quality, food packaging, food preservation, water treatment, food component, food additive, and many more. CNT even has its applications in the food sector (Table 1). CNT has applications almost everywhere in the food sector, ranging from eliminating pathogens to the components of packaging and even the process of its sealing. It offers a

wider range of potential applications. If the use of CNT in the food industry receives greater attention, then the possibility of continued development is increased. As a direct consequence of this, not only will we get the most nutritious meals possible, but also their prices will be lowered.

Table 1. Uses of CNT nanomaterials in food industry.

CNT Nanomaterials	Application in food industry	Reference
Electrodes modified with Boron doped CNT	Detection of glucose oxidase enzyme	[26]
CNT-Titania-Nafion/GC	Detection of glucose oxidase enzyme Detection of bisphenol	[20]
IL-SWCNT Based nano sensor	NO ₂ ⁻ detection in milk	[28]
FDH immobilized CNT biosensor	Quick measurement of fructose in food	[28]
Magnetic MWCNT	Detection of sulfonamide in egg samples	[30]
MWCNTs/GCE	Detection of summation B_{12}	[30]
MWCNTs/GCE	Detection of Vitalian B ₁₂ Detection of Sudan Red I	[48]
Chitosan-CNT modified electrodes	Detection of selective Br	[32]
SWCNT-FET biosensor	Detection of selective Bi	[6]
MWCNT	Detection of those pathogen Detection of ethylene	[18]
SWCNT combination of Cu(I) complex	Detection of ethylene	[20]
CNT-SPE	Food preparation	[2]
CNT in combination with Teflon	To stabilize the activity of glucose oxide as well as	[2]
CIVI III combination with Torion	ethanol dehydrogenase in cell tissue	[2]
CNT based electrochemical sensor	To monitor the amount of glucose & NADH	[2]
Glassy Carbon electrode (GCE) & micro wafer CNT	Detection of polyphenols in flow system	[25]
(MWCNT-GCE)	Detection of polyphenois in 110 w system	[20]
MWCNT/Chitosan modified electrodes	Detection of Pb & Cd	[2]
MWCNT/Chitosan modified electrodes	Detection of glutamate	[2]
MF/MWCNT-SH/GCE	Detection of Sudan red I	[2]
Hybrid CNTs/Nafion	Detection of toxic ractopamine & salbutamol	[2]
	presence in pork	
CS/PB/MWCNTs/HGNs	Detection of Malathions chlorpyrifos	[2]
	monostrophes & carbofuran	
MWNT-CS & sol-gel MIP film fabricated GCE	Detection of QCA	[2]
(MIP/sol-gel/MWNTs-CS/GCE)		
SWNT/FET/ORP	Detection of trimethylamine	[2]
Screen printed carbon electrode/CNT	Detection of E. sakazakii	[35]
NiO-CNTs and MOHFPE	determination of vitamin B ₆	[49]
, MWCNTs and PLA composite	To increase the elasticity of the PLA polymer	[51]
CNT	Sensing CO ₂	[52]
CNT with perfluorosulfonated polymer sensor	Quick detection of E. coli in food	[53]
CNT-titania-Nafion/GC sensor	Detection of BPA in food packaging samples	[2]
CNT gas sensor	To monitor carbon dioxide and ammonia levels	[33] [55]
Polypyrrole and silver nanoparticles in conjunction with CNT	To provide good microbial elimination activity	[56]
TiO ₂ /branched CNT nanostructures	yery officionay entifyngel meteriels	[50]
SWCNT-FET	very efficiency antifungal materials Detection of Salmonella infantis	[58] [36]
AuNP multi-wall CNT	Detection of Satmonetta injunits Detection of Nitrite in water	
		[60]
(SWCNT-PhSH) and an Au electrode Ho ₂ O ₃ /MWCNT	Detection of Hg ²⁺ UV-driven photocatalytic removal of tetracycline	[62] [63]
	Seed germination	
biotransformation of CNTs and other metals	Seed germination	[2]

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