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## Bioengineered multi-walled carbon nanotube (MWCNT) based biosensors and applications thereof

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The emergence of carbon nanotubes (CNTs) in the past decade has greatly promoted the development of biosensors, which provide a possible alternative to conventional detection systems. CNTs possess outstanding properties including good mechanical strength, photostability, better electrical conductivity, tunable photonic properties, ease of surface modification with functional groups, and the ability to conjugate with metal or organic components. The expanding family of CNTs, particularly multi-walled carbon nanotubes (MWCNTs), has been used for developing highly reliable and sensitive sensor systems. Bioengineered MWCNTs were fabricated by coupling with biological entities such as antibodies, aptamers, proteins, DNA, etc. as novel biosensing platforms. The present review aims to provide an overview of the recent developments in the field of bioengineered MWCNT-based biosensors. Recent research on CNT-based immunosensors, aptasensors, and enzymatic sensors is also discussed, along with some practical examples of such sensors. Finally, the applications of bioengineered gold nanoparticle–MWCNT (bio–AuNP–MWCNT) composites for the detection of analytes in food analysis, environmental monitoring, and clinical diagnosis have been discussed. The review concludes with a perspective on future developments in the field of bioengineered MWCNT-based sensors and their commercialization potential.

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### 1. Introduction

Carbon nanotubes (CNTs) have been an intensively discussed topic of research for nearly more than two decades. They were first discovered by a Japanese scientist Sumio Iijima in the year 1991. The developments in the field of CNTs has come a long way as one of the highly investigated


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nanostructured materials with thousands of scientific research studies published every year.<sup>1-4</sup> CNTs are structural allotropes of carbon in which the carbon atoms are arranged in an assembly of seamless hollow cylinders with one or more layers with open or closed ends. CNTs have been broadly classified into two groups: single-walled carbon

nanotubes (SWCNTs) and multi-walled carbon nanotubes (MWCNTs). SWCNTs are cylindrical shells with a single atomic thickness and are considered the functional unit of material. Further, SWCNTs form the architecture of MWCNTs containing multiple co-axial cylinders of SWCNT constituents with increasing diameters around one axis.<sup>5,6</sup> In short, CNTs



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can be perceived as graphene sheets with  $sp^2$  hybridized carbons rolled around themselves to produce robust long cylindrical structures. They are unique materials with diameters from a few nanometers and lengths of several nanometers to micrometers. They have been known to possess outstanding thermal, electrical, and mechanical properties. The functionalization of CNTs can improve their dispersibility in solvents and can enhance their interaction with other materials thereby increasing their scientific usage.<sup>7–9</sup> Some production methods such as chemical vapor deposition (CVD), arc discharge, laser ablation, electrolysis, and hydrothermal synthesis have been developed for large-scale manufacturing of CNTs.<sup>8,10–12</sup> The magnitude of properties and size of CNTs is usually dependent on the synthesis method, purification strategy, and post-synthesis functionalization. CNTs have been extensively researched worldwide for their applications in materials sciences,<sup>13,14</sup> electrochemistry,<sup>15,16</sup> electronics, superconductors,<sup>17–19</sup> catalysis,<sup>20,21</sup> energy storage,<sup>22</sup> water and environmental remediation,<sup>23–26</sup> textiles,<sup>27</sup> biosensors,<sup>28–31</sup> biomedicine and drug delivery,<sup>32–34</sup> *etc.*

Biosensing is an emerging area in different fields of contemporary research. Biosensors are powerful analytical devices for the detection of analytes in a myriad of applications including environmental remediation, clinical diagnosis, biomedicine, healthcare, agriculture, food industry, pharmaceuticals, industrial processing, and monitoring.<sup>35–38</sup> Biosensors are widely popular because of their amazing features such as high selectivity towards the target analyte, short detection time, ultralow detection limits, point-of-care testing, the potential to be miniaturized for portable use, and require less sample processing procedures as compared to conventional analytical techniques.<sup>39</sup> The most significant trend in sensor research during the last decade is the application of nanomaterials in biosensor fabrication. Nanomaterials, such as carbon nanotubes, metallic nanoparticles, semiconductor quantum dots, nanocrystals, nanowires, and carbon-based nanomaterials including CNTs, graphene, and carbon dots, have been exploited for the construction of high throughput biosensors with practical utility.<sup>37,40–45</sup>

Among all the applications of carbon nanomaterials, CNT-assisted biosensing platforms are garnering significant attention for real-time applications in sensing. The chemical, physical, biological, and mechanical properties of CNTs make them one of the smart nanomaterials for the development of robust sensing systems for environmental monitoring and analytical chemistry. CNT materials show prominent use as biorecognition elements, reaction supporters, or carriers in different sensors.<sup>46,47</sup> Different surface functionalities have been achieved by functionalizing the surface of CNTs through chemical adsorption. For instance, CNTs can serve as good platforms for conjugating other molecules *via* exohedral functionalization, while in the case of endohedral functionalization, the CNT's walls can be opened and filled with metals or organic materials.<sup>48</sup> Non-covalent

functionalization of CNTs can be attained either through sonication or  $\pi$ - $\pi$  interactions. Functionalized CNTs are known to cross biological barriers including cell membranes and can enter the cells. This process of internalization and release of CNTs in the cells is of particular interest in biology and biosensor research.<sup>49</sup> Moreover, several studies suggested that functionalized CNTs can resolve issues related to biocompatibility and toxicity.<sup>50–53</sup>

MWCNTs can be easily modified by hydroxyl, amino, and carboxyl groups for conjugation with biomolecules to develop immunosensors, aptasensors, and enzymatic sensors. MWCNTs have been explored as appropriate carriers for immobilizing antibodies and aptamers.<sup>54–58</sup> Enzyme immobilization of MWCNTs can also be performed using physical adsorption, with the assistance of surfactants, or direct covalent linking.<sup>59</sup> Recently, the combination of MWCNTs and gold nanoparticles (AuNPs) to create a hybrid composite (MWCNT-AuNP) has also been researched for applications in biosensing.<sup>60–64</sup> AuNPs can be directly conjugated to MWCNTs by physical adsorption without any chemical bonding between the two counterparts, or they can be chemically linked together to produce a stable structure through covalent bonding *via*  $\pi$ - $\pi$  stacking and hydrophobic and electrostatic interactions.<sup>65</sup> These materials have been particularly utilized in sensing applications for the detection of biomolecules, gases, food contaminants, and water pollutants.

The present review aims to document the recent development in the applications of MWCNT-based biosensors. Great efforts have been made in scientific research in which MWCNTs have been conjugated with antibodies, aptamers, and enzymes to develop immunosensors, aptasensors, and enzymatic sensors. Also, the exploration of novel advancements for developing functionalized AuNPs and MWCNTs with their utilization for biosensing is a dynamic research territory. Further, the review article focuses on developments of MWCNT-AuNP composites for biosensing applications in environmental remediation, food analysis, and others.

## 2. Significance of carbon nanotubes in biosensing applications

CNT-based biosensors are proving to be very beneficial in analytical sensor development. The construction of a simple CNT-based biosensor requires two components: the biorecognition element and the transducer. The CNT's surface is modified with bio-elements (such as proteins, antibodies, aptamers, enzymes, cells, *etc.*) working as the biological receptive part. The transducer converts the concentration of analyte used to a measurable physical signal including optical and electrochemical signals. The purification of CNTs after the synthesis process needs treatment with oxidizing acids that can create carboxyl moieties on the surface of CNTs. These carboxyl functionalities can further provide sites for possible covalent



functionalization of CNTs to a bio-recognition element. CNTs are mostly used as working electrodes in biosensors due to their astonishing low detection limit. The successful performance of CNT-based biosensors requires the optimization of various physicochemical properties, along with their surface functionalization and immobilization.

The use of MWCNTs in sensor development has its advantages and disadvantages as compared to the use of SWCNTs. MWCNTs are known to show better mechanical strength and stability than SWCNTs, which is an important point to be considered during sensor development.<sup>66–68</sup> Since the performance of the sensing material is dependent on the material structures, such material should possess high mechanical and thermal stability.<sup>69</sup> Hence, MWCNTs offer a greater opportunity to construct sensors with good performance and stability. Furthermore, MWCNTs are cheaper to produce in bulk synthesis without the use of any catalyst material. Also, they can be integrated with a suitable polymer or composite to enhance the mechanical, physical, and chemical properties. On the other hand, SWCNTs generally produced in the presence of catalysts are of poor purity. From the manufacturing point of view, MWCNTs are therefore preferred over SWCNT biosensors. Overall, it can be deduced that SWCNTs are more expensive and are often less pure than MWCNTs.<sup>70</sup> Besides, it is also observed that MWCNTs show better performance in rogue and corrosive environments. They can be therefore well suited in complex and real-world samples without any effect on sensor sensitivity and performance. However, there are certain applications, where SWCNTs are more preferred over MWCNTs. For instance, SWCNTs are more efficient in drug delivery applications since they have an ultra-high surface area and good drug loading capacity than their multi-walled counterparts.<sup>71–73</sup> Due to their amazing electronic properties, SWCNTs have gained great attention in electrochemical biosensors.

SWCNT-derived biosensors are known to have limited specific surface area to interact with larger bio-elements like mammalian cells, have an uncontrolled manufacturing process, and undergo chemical modification.<sup>74</sup> Moreover, the insolubility of SWCNTs can largely restrict their importance in biological and biomedical sensors. To improve the solubility of SWCNTs in aqueous solutions, nanocomposites with biocompatible properties have been particularly designed.<sup>75</sup> MWCNTs can be used as the modified scaffolds for electrodes. The electron transfer process in MWCNTs is greater with excellent conduction and electro-catalytic characteristics. Many of the enzymatic biosensors have incorporated MWCNT-modified electrodes as multifunctional scaffolds.<sup>76–78</sup> The surface of MWCNTs can be chemically modified with –SH groups, –OH groups, and –COOH groups to improve the uniformity of film on the electrode surface. MWCNTs also provide a better platform for immobilizing different biomolecules that can exhibit complementary activities.<sup>47,74</sup> Therefore, MWCNT biosensors have proved to be more promising in sensor fabrication.

There are some key advantages that CNTs have over graphene oxide (GO) and graphdiyne (GDY) for use in biosensors. One of the biggest advantages of CNTs is their high electrical conductivity. This makes them ideal for use in electrochemical biosensors, where they can be used to transfer electrons between the biomolecule and the electrode.<sup>15</sup> GO and GDY are also electrically conductive, but not to the same extent as CNTs. This can lead to slower electron transfer rates and lower sensitivity in electrochemical biosensors.<sup>16,79</sup> CNTs are very strong and lightweight. This makes them ideal for use in portable and wearable biosensors. CNTs have a high aspect ratio, which means they are long and narrow structures.<sup>80,81</sup> This property allows for a large surface area and enhances their interaction with biomolecules, increasing the sensitivity of biosensors, as compared to GO- and GDY-based sensors.<sup>82</sup> The tailored electronic properties and structural diversity of GDY hold promise for future biosensor development, although it is less explored compared to CNTs and GO.

There are still some challenges that need to be addressed before CNTs can be widely used in biosensors. The main challenge is that CNTs can aggregate in solution.<sup>83</sup> This can make it difficult to disperse CNTs evenly in the sensing matrix and can lead to decreased sensitivity of the biosensor. They are also susceptible to oxidation reactions.<sup>83</sup> This can lead to changes in their electrical properties and can reduce the sensor's performance and lifespan. The cost of CNTs can be a barrier to their widespread and large-scale use in biosensors. The fabrication of biosensors often requires CNTs of specific sizes and helicities. However, it is difficult to control the size of CNTs during manufacturing.<sup>84</sup> Additionally, it is challenging to produce CNTs that are both cost-effective and high-purity at scale. As a result, the current market prices of CNTs are too high for most commercial applications. The reproducibility of CNT-based biosensors can be a challenge. This is because the properties of CNTs can vary depending on the manufacturing process.<sup>85</sup> New manufacturing methods that can produce CNTs with more consistent properties should be developed. Despite these challenges, CNTs have the potential to be a valuable material for biosensing applications. The development of CNT-based biosensors have many different aspects which require cooperation between materials scientists and engineers who fabricate the biosensors.

### 3. Bioconjugation of multi-walled carbon nanotubes and applications

Different categories of MWCNT-biosensors have been designed to date to attach MWCNTs with biological elements such as DNA, proteins, antibodies, aptamers, and enzymes (Fig. 1). The majority of these biosensors are based on electrochemical detection that comprises the reference electrode, working electrode, and counter electrode. To completely take advantage of the MWCNT materials in biosensing, the MWCNTs must be properly functionalized



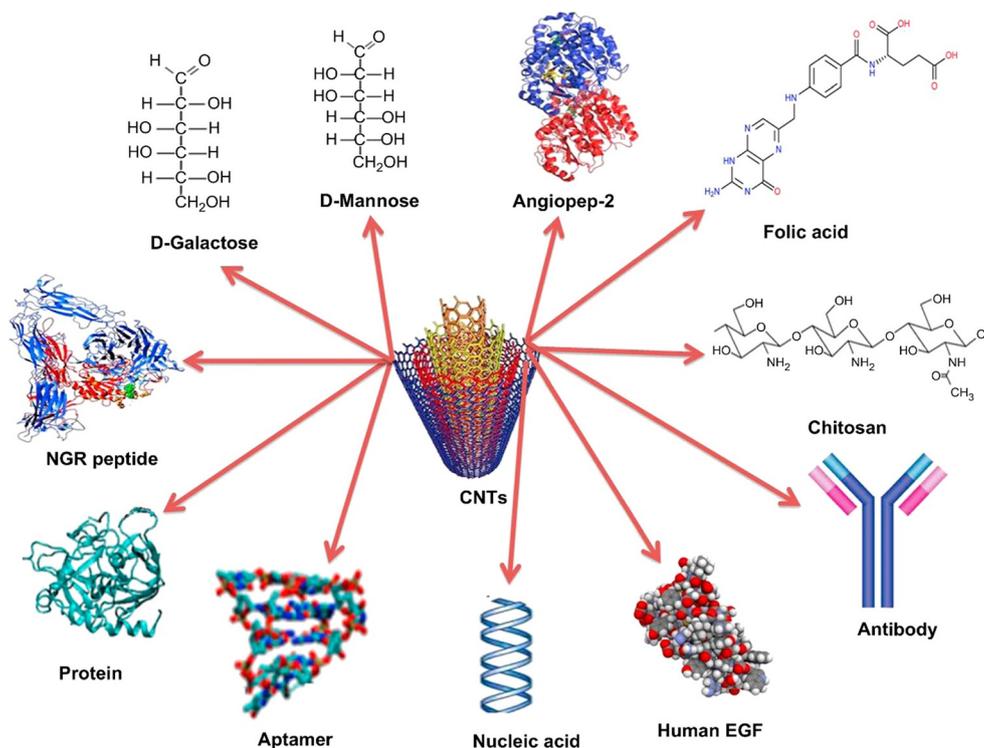


Fig. 1 Various biological molecules that can be conjugated to CNTs in the construction of biosensors. Reprinted with permission from Mehra et al.<sup>86</sup> Copyright© Elsevier.

and immobilized for better solubility, biocompatibility, and functionality. In the following section, different sensors based on the bioconjugation of antibodies, aptamers, and enzymes with MWCNTs are discussed with a special focus on their sensing applications (Table 1).

### 3.1 Immunosensor development

Immunosensors are analytical devices that utilize the immunochemical recognition between antigens and

antibodies to selectively detect several biomolecules such as proteins, hormones, and drugs. The detection is based on ligand affinity where the antibody interacts with the antigen to produce different signals on the base material and this signal is measured by the transducer.<sup>105,106</sup> Immunosensor technology is gaining high prominence in clinical medicine while diagnosis is also becoming an important area of research. An electrochemical immunosensor combines the immunological reaction between antibody-antigen and the electrochemical technology to produce high-performance

Table 1 A summary of studies on MWCNT-based biosensors

Order	Sensor material	Types of biosensor	Analyte	LOD	Sensitivity (range)	Ref.
1.	MWCNTs/Fe <sub>3</sub> O <sub>4</sub>	Immunosensor	PSA	0.39 ng mL <sup>-1</sup>	2.5 pg mL <sup>-1</sup> to 100 ng mL <sup>-1</sup>	87
2.	MWCNTs/cobalt phosphide	Immunosensor	Carcinoembryonic antigen	10 fg mL <sup>-1</sup>	10 <sup>-4</sup> –100 ng mL <sup>-1</sup>	88
3.	MWCNTs/Si <sub>3</sub> N <sub>4</sub>	Immunosensor	CYFRA21-1	2 fg mL <sup>-1</sup>	0.01–1 pg mL <sup>-1</sup>	89
4.	MWCNTs	Immunosensor	Alpha-feto protein	1.1 ng mL <sup>-1</sup>	10 ng mL <sup>-1</sup> –50 µg mL <sup>-1</sup>	90
5.	MWCNTs/PDDA	Immunosensor	Aflatoxin B <sub>1</sub>	0.03 ng mL <sup>-1</sup>	0.05–25 ng mL <sup>-1</sup>	91
6.	MWCNTs/Fe <sub>3</sub> O <sub>4</sub> /chitosan	Immunosensor	Carbohydrate antigen	0.163 pg mL <sup>-1</sup>	1 pg mL <sup>-1</sup> –100 ng mL <sup>-1</sup>	92
7.	MWCNTs/L-glutamic acid	Aptasensor	Tetracycline	3.7 × 10 <sup>-17</sup> M	10 <sup>-16</sup> –10 <sup>-6</sup> M	93
8.	MWCNTs/Ce-MOF	Aptasensor	Zearalenone	10 <sup>-5</sup> ng mL <sup>-1</sup>	5 × 10 <sup>-5</sup> –50 ng mL <sup>-1</sup>	94
9.	MWCNTs/Au nanoshell	Aptasensor	Profenofos	0.052 ng mL <sup>-1</sup>	0.1–1 × 10 <sup>5</sup> ng mL <sup>-1</sup>	95
10.	MWCNTs/Nafion	Aptasensor	Ochratoxin A	1 pg mL <sup>-1</sup>	0.005–10 ng mL <sup>-1</sup>	96
11.	MWCNTs/Ni-Fe LDH/BiVO <sub>4</sub>	Aptasensor	Ofloxacin	0.03 nM	0.1–16 000 nM	97
12.	MWCNTs/MoS <sub>2</sub>	Aptasensor	Kanamycin	0.21 pg mL <sup>-1</sup>	10 <sup>-3</sup> –10 <sup>3</sup> ng mL <sup>-1</sup>	98
13.	MWCNTs/TiO <sub>2</sub>	Aptasensor	Malachite green	8.68 pg mL <sup>-1</sup>	0.01–1000 ng mL <sup>-1</sup>	99
14.	MWCNTs/chitosan	Aptasensor	Exosomes	1 particle per mL	10 <sup>-2</sup> –10 <sup>10</sup> particles per mL	100
15.	MWCNTs/polyvinyl alcohol	Enzymatic sensor	Glucose	0.15 µM	0.1–20 mM	101
16.	MWCNTs/copolymer	Enzymatic sensor	Glucose	0.36 µM	1 µM–5 mM	102
17.	MWCNTs/nickel-cobalt	Non-enzymatic sensor	Glucose	—	0–1.25 mM	103
18.	MWCNTs/WS <sub>2</sub>	DNA biosensor	Hepatitis B viral genome	2.5 fM	10 fM–1 nM	104



sensors with fast detection time and high precision as compared to traditional immunoassays.<sup>107,108</sup> MWCNTs are often coupled with antibodies to develop immunosensors. To improve the sensor sensitivity of MWCNT-based immunosensors, scientists have coupled MWCNTs with metal or organic materials to produce nanocomposites. The combination of metallic NPs, bimetallic NPs, or metal oxide NPs with MWCNT-modified electrodes can largely enhance detection sensitivity. Apart from that, MWCNTs can be modified with functional groups (amino, hydroxyl, *etc.*), magnetic nanoparticles (MNPs), ionic liquids, mesoporous silica, fullerenes, and graphene to develop highly sensitive immunosensors.<sup>109</sup> Electrochemical immunosensors based on MWCNTs have been developed to recognize cancer biomarkers,<sup>88,89,110,111</sup> biomolecules,<sup>90,112</sup> clinical diagnosis,<sup>92,113</sup> microbial pathogens and toxins,<sup>91,114,115</sup> antibiotics,<sup>116</sup> and environmental pollutants.<sup>117,118</sup> Electrocatalytic labels (nanocatalysts) are also being utilized for fabricating sandwich-type electrochemical immunosensors due to the generation of high catalytic current to improve the sensor sensitivity. MWCNTs can be utilized as signal labels and can provide a large surface area for the immobilization of secondary antibodies in sandwich immunosensors. For instance, a sandwich-type immunosensor was proposed for the detection of prostate-specific antigen as shown in Fig. 2. Other sensors have also been fabricated to detect different classes of analytes using the same approach.<sup>88,119–121</sup> The main challenges suffered by MWCNT immunosensors are miniaturization of biosensors and cost-effectiveness. In the near future, MWCNTs show a promising approach for fabrication of point-of-care devices for sensing purposes.

### 3.2 Aptasensor development

Aptasensors have gained increasing attention in sensing applications. Aptamers are generally ssDNA molecules that bind to a specific complementary sequence. Aptamers can efficiently compete with antibodies as recognition elements. DNA aptamers are more stable and easier to synthesize with high selectivity. MWCNTs offer many opportunities for the development of electrochemical as well as optical aptasensors based on aptamer assembly.<sup>122,123</sup> Aptamer immobilization on the surface of MWCNTs can provide a better sensitive signal and less noise. Aptamer immobilization is usually based on three mechanisms: physical adsorption, covalent bonding, and affinity binding.<sup>57,124</sup> Recently, electrochemical aptasensors developed with MWCNT composites have been utilized in the detection of microbial pathogens and toxins,<sup>56,94,125–127</sup> bisphenol A,<sup>128–130</sup> pesticides,<sup>95,131</sup> antibiotics,<sup>93,132–134</sup> and biomolecules.<sup>135–139</sup> MWCNT-based aptamers provide certain advantages such as good sensitivity, portable nature, rapid detection, simple instrumentation, and low fabrication costs, as compared to traditional immunoassays.

### 3.3 Enzymatic sensor development

Enzymatic sensors based on MWCNTs are a popular class of biosensors in which the tubular structures of MWCNTs provide a large surface area that can be efficiently used to immobilize enzyme molecules. This can largely improve the response signal of biosensors. These sensors utilize the biomolecular conjugation and specificity of the enzyme to direct electrochemical reactions between the enzymes and bulk CNT materials.<sup>59,140,141</sup> There have been several

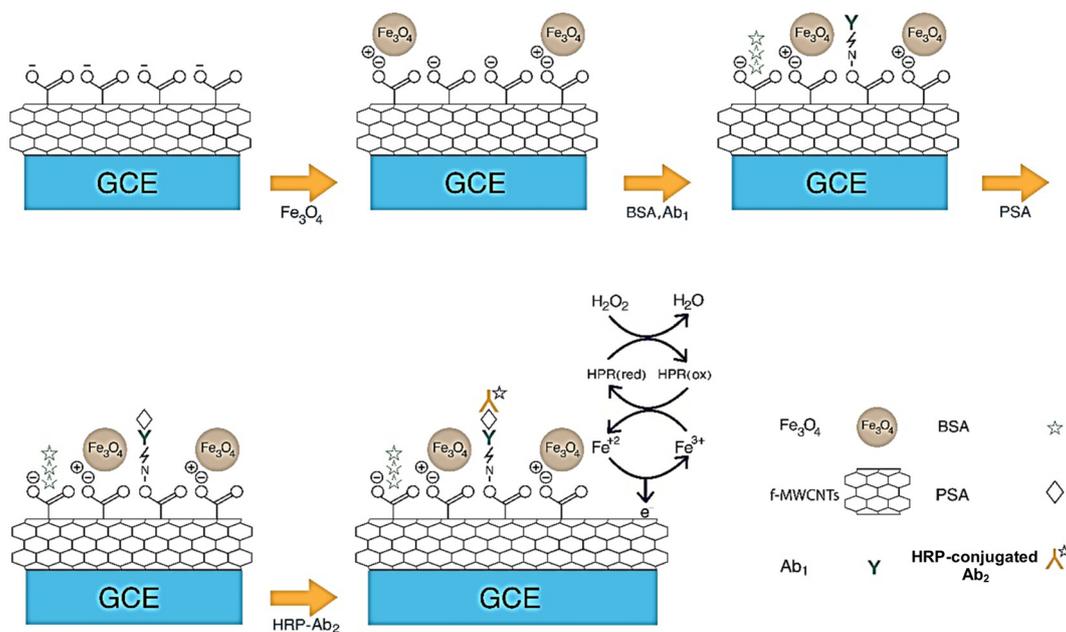


Fig. 2 Development of a highly sensitive sandwich-type electrochemical immunosensor using MWCNTs and magnetic NPs for detection of prostate specific antigen (PSA). Reprinted with permission from Shamsazar *et al.*<sup>87</sup> Copyright© 2021 Elsevier.



studies published on MWCNT-based enzymatic sensors developed with glucose oxidase (GO), horseradish peroxidase (HRP), tyrosinase, cholesterol oxidase (CO), cholesterol esterase (CE), alkaline phosphatase, acetylcholinesterase, urease, lactate oxidase, dihydrofolic acid reductase (DHFR), *etc.* A number of these enzymes catalyze substrate reactions including glucose, lactate, cholesterol, amino acids, urate, pyruvate, glutamate, alcohol, folic acid, and hydroxybutyrate to produce products such as NADH and hydrogen peroxide that can be detected electrochemically.<sup>142–145</sup> An enzyme can be immobilized on MWCNTs *via* covalent bonding, physical adsorption, cross-linking, and even entrapment. Physical adsorption between the enzyme and MWCNTs can be achieved by one of the interactions such as hydrogen bonding, van der Waals, hydrophobic, hydrophilic, or ionic interactions. In this method, there are high chances of the release of the enzyme from the material support due to weaker bonds.<sup>146,147</sup> In cross-linking, the enzyme is linked to support material (*i.e.* CNTs) *via* cross-linking agents (glutaraldehyde, glyoxal, epichlorohydrin, and 1-ethyl-3-(3-dimethyl aminopropyl) carbodiimide (EDC)) together with *N*-hydroxysuccinimide (NHS) to enhance attachment.<sup>148</sup> The covalent bonding leads to a stronger attachment between the enzyme and the carrier.<sup>149</sup> The majority of prior research has applied the application of MWCNT-enzymatic sensors in sensing glucose,<sup>101–103</sup> cholesterol,<sup>62,150,151</sup> urea,<sup>152,153</sup> catechol,<sup>154</sup> *etc.*

### 3.4 DNA biosensor development

DNA biosensors have been particularly used in clinical diagnosis, medical sciences, forensics, drug discovery, and testing of genetic and infectious diseases. In sensor development, the nucleic acid (dsDNA) can adsorb strongly on the MWCNT surface and hence can be used to construct MWCNT–DNA bio complex for sensing applications in many scientific areas.<sup>155,156</sup> DNAs are ideal biorecognition elements. DNA biosensors are used for the detection of metal ions, small metabolites, organic dyes, peptides, proteins, cancer cells, and pathogenic microorganisms.<sup>157,158</sup> The covalent attachment of MWCNTs and DNA in electrochemical biosensors leads to fast electron transfer. Moreover, MWCNTs can also be self-assembled or can be deposited vertically on gold (Au) substrates followed by adsorption of DNA molecules.<sup>155,159,160</sup> A literature survey shows that MWCNT–DNA biosensors have been exploited for the detection of DNA methyltransferase and site-specific DNA sequences,<sup>161,162</sup> viral genomic DNA,<sup>104</sup> miRNA,<sup>163</sup> gender determination in fish,<sup>164</sup> pirazon,<sup>165</sup> bacteria,<sup>166</sup> and food contaminants.<sup>167,168</sup> Recently, polypyrrole and hydroxyapatite nanoparticles with MWCNTs were used in the construction of an electrochemical DNA biosensor for *Mycobacterium tuberculosis*.<sup>169</sup> The response surface methodology (RSM) operations were performed to optimize the best conditions for maximum performance of the biosensor (Fig. 3). It can be anticipated that the clinical diagnosis and pathology will be

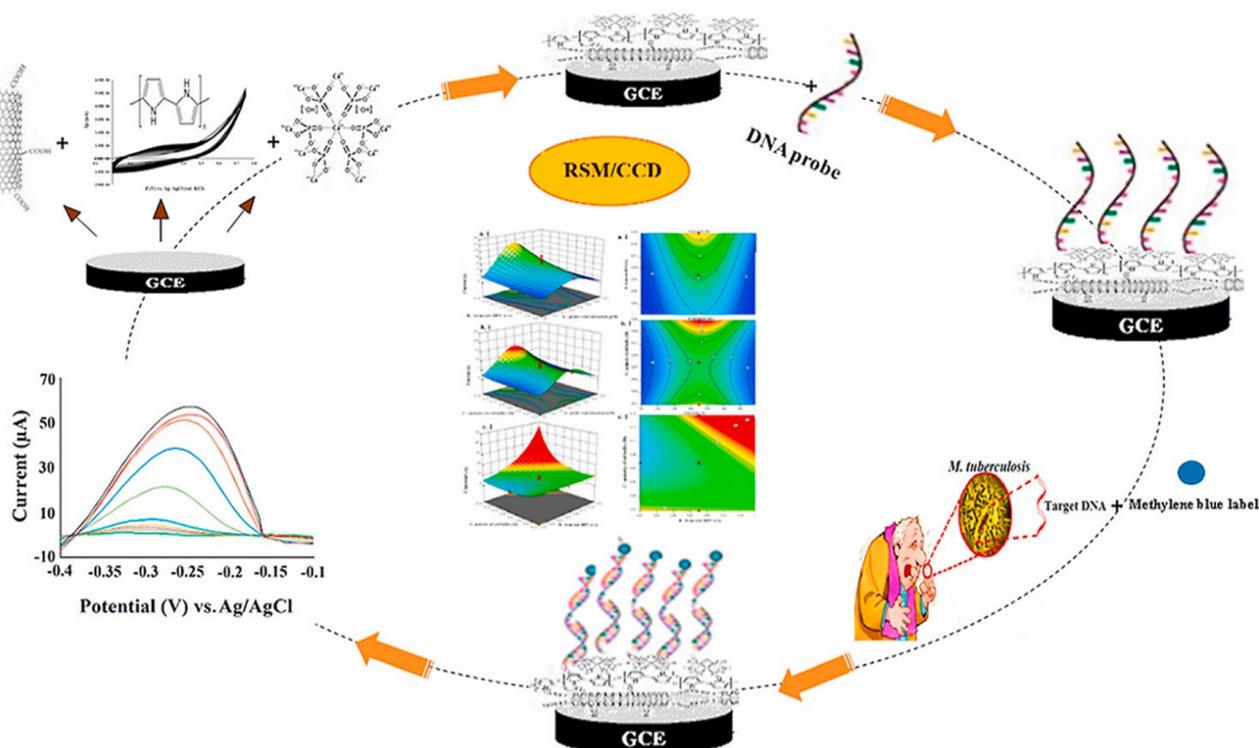


Fig. 3 A representation of an electrochemical DNA biosensor for the detection of *Mycobacterium tuberculosis*, whose conditions are optimized using the RSM technique. Reprinted with permission from Rizi *et al.*<sup>169</sup> Copyright© 2021 Elsevier.



largely dependent on the successful development and implementation of DNA biosensors.

## 4. Multiwalled carbon nanotube–gold nanoparticle composites (MWCNT–AuNP composites)

Nanocomposites are described as hybrid materials consisting of a nanomaterial incorporated into a mixture with a suitable polymer, matrix, ceramics, inorganic materials, *etc.* to improve and enhance its properties. The composites of MWCNTs and AuNPs have attained significant attention for applications in biosensors (DNA, proteins, glucose), gas sensors (oxygen, water vapor), and heavy metal sensors.<sup>170,171</sup> A detailed discussion on the synthesis and biosensing applications of MWCNT–AuNP composites is provided in the following sections.

### 4.1 Synthesis of MWCNT–AuNP composites

The integration of MWCNTs and AuNPs to generate nanocomposites can generate novel properties not found earlier in their counterparts. The use of AuNPs in these composites provides the advantages of facile synthesis, excellent electrical conductivity, and good catalytic properties. Also, the AuNPs possess unique properties such as strong adsorption ability, good biocompatibility, and conductivity.<sup>172,173</sup> Thus, the combination of MWCNTs and AuNPs can aid in the enhancement of immunosensor sensitivity. In addition, the MWCNT–AuNP nanocomposites exhibit huge surface areas to immobilize plentiful biomolecules along with an enhanced electron transfer process. Different methods exist for the synthesis of MWCNT–AuNP composites such as physical adsorption, *in situ* chemical deposition, and *ex situ* chemical deposition. The AuNPs can be directly decorated on the CNT support material by physical absorption. In the direct deposition of AuNPs on MWCNTs, the AuNPs are attached to modified or unmodified MWCNTs without any linking molecule. Surface functionalization of MWCNTs can be performed to generate new functional groups (–COOH) on their surface to facilitate the linking process. Physical deposition of AuNPs is generally performed in an ultrahigh vacuum environment and produces MWCNT–AuNP composites with good yield and high purity.<sup>174</sup> The direct deposition process possesses some disadvantages including weak bonding between AuNPs and MWCNTs, high chances of detachment, less uniformity, and longer reaction times. In chemical deposition, the *in situ* procedure deposits AuNPs on CNTs during AuNP synthesis, whereas AuNPs are synthesized before the deposition in the *ex situ* method.<sup>175</sup> Also, wet chemical deposition can be done which involves covalent/non-covalent bonding between the modified MWCNT surface and AuNPs due to hydrophobic,  $\pi$ – $\pi$  stacking, and electrostatic interactions. Several studies have reported the chemical attachment of AuNPs onto MWCNTs.<sup>61,176,177</sup> Furthermore, proteins can also mediate

the formation of assembly between AuNPs and MWCNTs to produce various hybrids of MWCNTs.<sup>178</sup> One novel approach for producing AuNP decorated MWCNTs was also reported recently using cysteaminium chloride *via* the formation of a zwitterionic acid–base bond (as shown in Fig. 4).<sup>65</sup> Though several methods have been developed for the synthesis of MWCNT–AuNP composites, still there is a need for research on the controlled deposition of Au nanostructures on the CNT surface.

### 4.2 Applications of MWCNT–AuNP composites in biosensors

MWCNT–AuNP nanocomposites have been reported for several sensing applications for environmental monitoring and food analysis as discussed in detail in the following subsections and summarized in Table 2.

**4.2.1 Sensing of biomolecules.** MWCNT–AuNP composites have been extensively used for detecting several biological and chemical molecules. A large number of studies have investigated the potential of MWCNT–AuNP composites in the detection of different biomolecules such as glucose,<sup>217–221</sup> cholesterol,<sup>222</sup> uric acid,<sup>184,223</sup> ascorbic acid,<sup>224</sup> human chorionic gonadotrophin,<sup>225–227</sup> carcinoembryonic antigen,<sup>228–230</sup> hormones<sup>231,232</sup> and target DNA.<sup>161,233</sup> Since MWCNTs are excellent fluorescence quenchers and possess a large surface area for loading nanoparticles, they can be used for the development of fluorescent biosensors. In this context, a fluorescent biosensor for the detection of miRNA was fabricated owing to the fluorescent quenching properties of the fluorophore-labeled complementary DNA conjugated MWCNT/AuNP complex and integrated with a signal amplification system.<sup>179</sup> A good fluorescent signal was observed due to the formation of DNA–RNA duplex on the addition of miRNA, leading to their desorption from the complex. Recently, a nanocomposite of Ni-MOF/MWCNTs/AuNPs was reported in the construction of a flexible paper-based biosensor for HIV (human immunodeficiency virus) DNA detection.<sup>180</sup> The developed electrode showed good performance in the detection of HIV DNA with a LOD of 0.13 nM.

Detection of certain biomolecules is significant for early disease diagnosis and therapy (like insulin, cholesterol, and uric acid) has also been reported using the MWCNT–AuNP nanocomposite. For instance, an electro-chemiluminescent sensor for insulin was designed using MWCNTs/rGONRs-Cds: Eu NCs as the ECL signal generators and copper-modified AuNPs as the quenchers.<sup>181</sup> The intensity of the ECL signal reduced with a corresponding increase in insulin concentration within the linear range of 0.5 to 50 ng mL<sup>–1</sup> and a detection limit of 0.04 pg mL<sup>–1</sup>. Another study reported a voltammetric enzymatic biosensor using cholesterol oxidase enzyme immobilized MWCNTs as shown in Fig. 5.<sup>62</sup> The sensor presented a sensitivity of 10.12  $\mu\text{A mM}^{-1} \text{cm}^{-2}$  and a LOD of 0.1 mM. In another work, the detection of choline was reported for monitoring brain-related disorders. The amperometric sensor was developed through the deposition



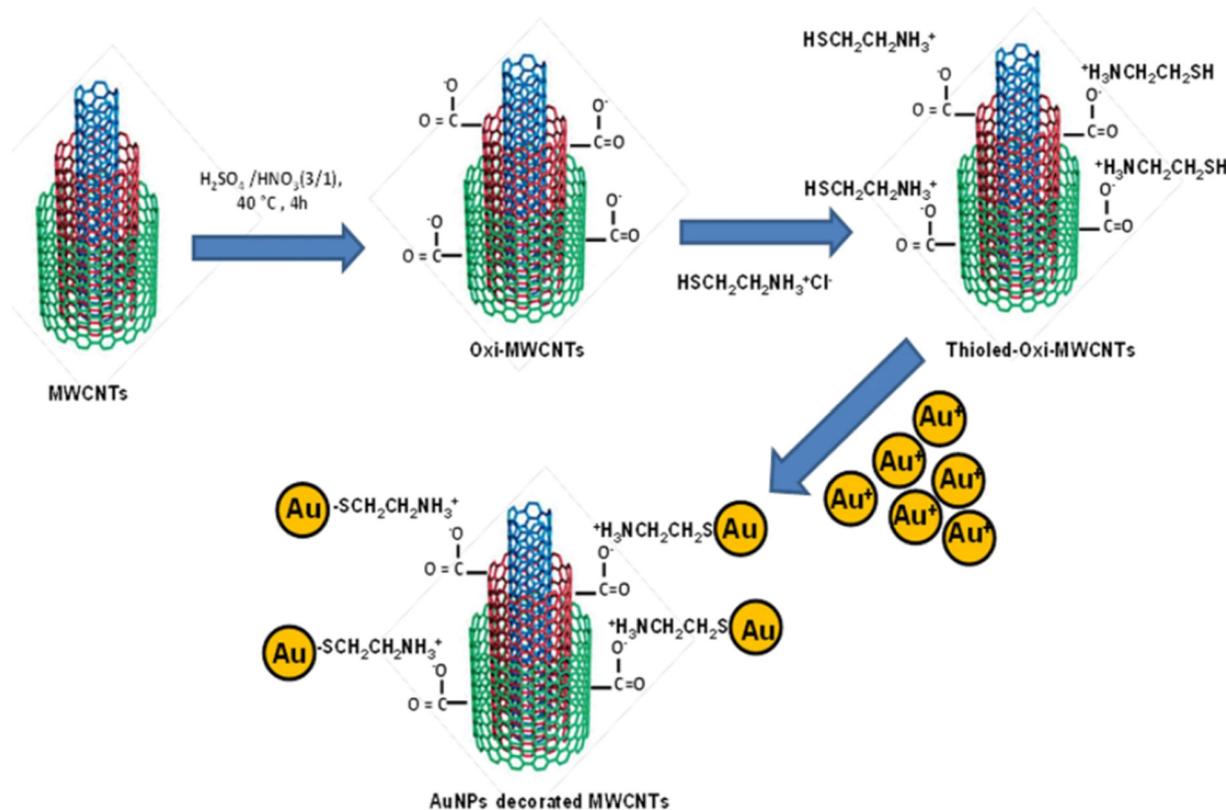


Fig. 4 Decoration of MWCNTs with AuNPs using cysteamine chloride functionalization. Reprinted with permission from Chinh *et al.*<sup>65</sup> Copyright© 2019 Springer Nature.

of MWCNTs and AuNPs on an electrode.<sup>182</sup> Chitosan polymer was used to disperse MWCNTs followed by immobilization of the choline oxidase enzyme *via* glutaraldehyde linking. The sensor showed a LOD of  $0.6\text{ }\mu\text{M}$  and a linear detection range from 3 to  $120\text{ }\mu\text{M}$ . Also, silicate molecule-capped AuNPs and functionalized MWCNT (MWCNT-EDAS-AuNP) network nanocomposite was used for the simultaneous detection of dopamine and ascorbic acid.<sup>183</sup> Another study developed an electrochemical sensor using graphene foam/MWCNT/AuNP composite-modified electrodes.<sup>184</sup> The developed sensor was employed for the detection of dopamine in brain tissue and uric acid in human urine with high sensitivities. Similarly, a dopamine sensor was designed using AuNP decorated MWCNT composites as the modifier for GCE, with a detection limit of  $35\text{ nM}$ .<sup>185</sup> Recently, Guan *et al.* demonstrated an electrochemical sensor comprising a covalent organic framework, amino-modified MWCNTs, and AuNPs modified on GCE.<sup>186</sup> The practical application of this sensor was demonstrated in the detection of dopamine and uric acid with LOD of  $0.21$  and  $0.29\text{ }\mu\text{M}$ , respectively. Moreover, a screen-printed electrode biosensor based on AuNP/MWCNT nanocomposites has also been reported for exocytosis dopamine detection. The applicability of this system was also demonstrated as an evaluation tool for cell viability and drug activity evaluation.<sup>215</sup>

3-Nitrotyrosine is a crucial protein related to the pathology of many diseases such as Alzheimer's disease, Parkinson's

disease, and other cardiovascular diseases. A highly sensitive electrochemical sensor for 3-nitrotyrosine was constructed using electropolymerized pyrrole MIP doped with AuNPs modified on a GCE modified with MWCNTs and graphene oxide nanoribbons.<sup>187</sup> The sensor produced a linear detection range from  $0.2$  to  $50.0\text{ }\mu\text{M}$  with an LOD of  $50\text{ nM}$ . Recently, an electrochemical neuro biosensor for the detection of protein DJ-1/Park7 was constructed using MWCNT-AuNP composite doped indium tin oxide electrode.<sup>188</sup> The sensor was successfully checked for the presence of DJ-1/Park7 in cerebrospinal fluid and saliva.

Detection of human serum albumin (HSA), the most abundant protein in human serum, is necessary for clinical diagnosis and pre-treatment of various diseases. An impedimetric immunosensor was designed using the electrodeposition of AuNPs on an MWCNT-ionic liquid electrode using a 6-hexane dithiol (HDT) monolayer as a cross-linker.<sup>189</sup> The detection range and LOD were found to be  $0.1\text{--}100\text{ }\mu\text{g mL}^{-1}$  and  $15.4\text{ ng mL}^{-1}$ , respectively.

Determination of purines and their derivatives in body fluids can assess the pathological conditions in humans. In a study, a ceramic carbon electrode was fabricated by incorporating AuNPs and MWCNTs in a thiol-modified ceramic gel.<sup>190</sup> This sol-gel sensor was able to detect purine-based compounds such as uric acid (UA), xanthine (XA), and caffeine (CA) because the gel matrix provided a good platform for encapsulating these materials for sensing purposes. The



**Table 2** A compilation of different studies on MWCNT-based biosensors for detection of analytes

Order	MWCNT- and AuNP-based material	Analyte	LOD	Sensitivity (range)	Ref.
19.	MWCNT/AuNC composite	miRNA-155	35 pM	100 pM–2 nM	179
20.	Ni-MOF/MWCNTs/AuNPs	HIV DNA	0.13 nM	10 nM–1 μM	180
21.	MWCNTs/rGONRs-CdS: Eu NCs and Cu@AuNPs	Insulin	0.04 pg mL <sup>-1</sup>	0.5 pg mL <sup>-1</sup> –50 ng mL <sup>-1</sup>	181
22.	Au-MWCNTs-PPy network	Cholesterol	0.1 mM	2–8 mM	62
23.	MWCNTs–AuNPs/chitosan	Choline	0.6 μM	3–120 μM	182
24.	MWCNT–EDAS–AuNPs	Dopamine	0.07 μM	0.1–9 μM	183
		Ascorbic acid	0.08 μM	0.1–8 μM	
25.	Graphene foam/MWCNTs/AuNPs	Dopamine	1.36 nM	0.1–48 μM	184
		Uric acid	33.03 nM	0.50–60 μM	
26.	AuNP decorated MWCNTs	Dopamine	35 nM	—	185
27.	COF/MWCNTs/AuNPs	Dopamine	0.21 μM	0.7–108 μM	186
		Uric acid	0.29 μM	0.97–200 μM	
28.	MIP/AuNPs/MWCNTs/GO nanoribbons	3-Nitrotyrosine	50 nM	0.2–50.0 μM	187
29.	MWCNT–AuNP/ITO electrode	DJ-1/Park7	0.5 fg mL <sup>-1</sup>	4.7–4700 fg mL <sup>-1</sup>	188
30.	AuNPs/MWCNTs/6-hexanedithiol	Human serum albumin	15.4 ng mL <sup>-1</sup>	0.1–100 μg mL <sup>-1</sup>	189
31.	AuNPs/MWCNTs/thiol-modified ceramic gel	Uric acid	50 nM	—	190
		Xanthine	63 nM		
		Caffeine	354 nM		
32.	AuNPs/Zr-MOF/MWCNTs	Adenine	0.09 μM	0.8–60 μM	191
		Guanine	0.08 μM	0.8–60 μM	
33.	Magnetic MWCNT/AuNP/antibody	α-Fetoprotein	3.33 fg mL <sup>-1</sup>	10 fg mL <sup>-1</sup> –100 ng mL <sup>-1</sup>	192
34.	MWCNT decorated AuNPs	TP53	10 <sup>-17</sup> M		193
35.	MWCNTs and AuNPs/HER 2 antibody	HER2	7.4 ng mL <sup>-1</sup>	10–110 ng mL <sup>-1</sup>	194
36.	MWCNTs, AuNPs/calixarenes	Paracetamol	0.2 μM	1–150 μM	195
37.	Carboxylated MWCNTs/AuNPs	Cyproterone acetate	1.66 × 10 <sup>-8</sup> M	9.9 × 10 <sup>-8</sup> M –1.15 × 10 <sup>-5</sup> M	196
38.	MIP/MWCNT–AuNP composites	Velpatasvir	0.21 ng mL <sup>-1</sup>	0.649–80.0 ng mL <sup>-1</sup>	197
39.	AuNPs/MWCNTs/chitosan nanocomposite	Chlorpyrifos	0.06 × 10 <sup>-6</sup> mg mL <sup>-1</sup>	0.1–40 × 10 <sup>-6</sup> mg mL <sup>-1</sup>	198
40.	Polyaniline/MWCNTs/AuNPs	Zn <sup>2+</sup>	0.039 μg L <sup>-1</sup>	—	199
		Pb <sup>2+</sup>	0.037 μg L <sup>-1</sup>		
		Cu <sup>2+</sup>	0.017 μg L <sup>-1</sup>		
41.	PANI/MWCNTs/AuNPs	Hg <sup>2+</sup>	0.08 ppm	0.01–10 ppm	200
42.	Chitosan/MWCNTs@GONRs/GCE	Dibutyl phthalate	7 ng mL <sup>-1</sup>	—	201
43.	AuNPs/MWCNTs/hydrogel	4-Nitrophenol	—	1 × 10 <sup>-8</sup> –5 × 10 <sup>-5</sup> M	202
44.	Graphene/MWCNTs/AuNPs	Nitrite	0.9 μM	10–140 μM	203
45.	MWCNT/copper–polyaniline/AuNPs	Nitrate	0.09 μM	0.8–30 μM	204
46.	AuNPs–MWCNTs–chitosan nanocomposite	<i>Salmonella typhimurium</i>	5 × 10 <sup>2</sup> CFU mL <sup>-1</sup>	10 <sup>3</sup> –10 <sup>7</sup> CFU mL <sup>-1</sup>	205
47.	MWCNTs, AuNPs/MIP	Diethylstilbestrol	24.3 fg mL <sup>-1</sup>	10 <sup>-10</sup> to 10 <sup>-6</sup> mg mL <sup>-1</sup>	206
48.	MWCNTs/AuNPs/anti-ZEA antibody	Zearalenone	0.15 pg mL <sup>-1</sup>	10 <sup>-4</sup> –10 <sup>-1</sup> ng mL <sup>-1</sup>	207
49.	Polyethyleneimine/MWCNTs/AuNPs	Kidney bean	0.023 μg mL <sup>-1</sup>	0.05 to 100 μg mL <sup>-1</sup>	208
		Lectins			
50.	p-Aminothiophenol/MWCNTs/AuNPs	Quercetin	3.3 × 10 <sup>-10</sup> M	—	209
		Rutin			
51.	AuNPs/MWCNTs	Tetracycline	42 ppb	0.2–0.6 ppm	210
52.	MWCNTs, AuNPs, chitosan, and GO	Sunset yellow	0.032 mg mL <sup>-1</sup>	10–90 mg mL <sup>-1</sup>	211
53.	MWCNTs/graphene/AuNPs	Antioxidants	—	—	212
		Glucose			
		Alcohol			
54.	Prussian blue/MWCNTs/chitosan–AuNPs cryogel	Histamine	1.81 μM	2.50–125.0 μM	213
55.	Fe <sub>3</sub> O <sub>4</sub> /MWCNT–COOH/AuNP–AFP antibodies	AFP	1.09 pg mL <sup>-1</sup>	1 pg mL <sup>-1</sup> –10 μg mL <sup>-1</sup>	214
56.	AuNPs/MWCNT nanocomposites	Cell viability and drug evaluation (exocytosis dopamine sensing)	—	—	215
57.	MWCNTs/AuNPs-acetaminophen	<i>E. coli</i>	3.02 CFU mL <sup>-1</sup>	—	216

detection limits were determined to be 50, 63, and 354 nM for UA, XA, and CA, respectively. In another study based on AuNP-modified Zr-MOF and carboxyl-functionalized MWCNTs, a voltammetric sensor (Fig. 6) was designed for the detection of purines such as adenine and guanine in DNA.<sup>191</sup> The sensor achieved a LOD of 0.09 and 0.08 μM for guanine and adenine, respectively.

Cancer biomarkers are the indicators of the progression of diseases such as pancreatic, breast, liver, and ovarian cancer. Biomarkers have possible applications in oncology, disease diagnosis, prediction of response to disease, and disease monitoring. One of the important biomarkers is α-fetoprotein found in the serum of patients suffering from liver cancer. The AuNP/CNT hybrid material was developed



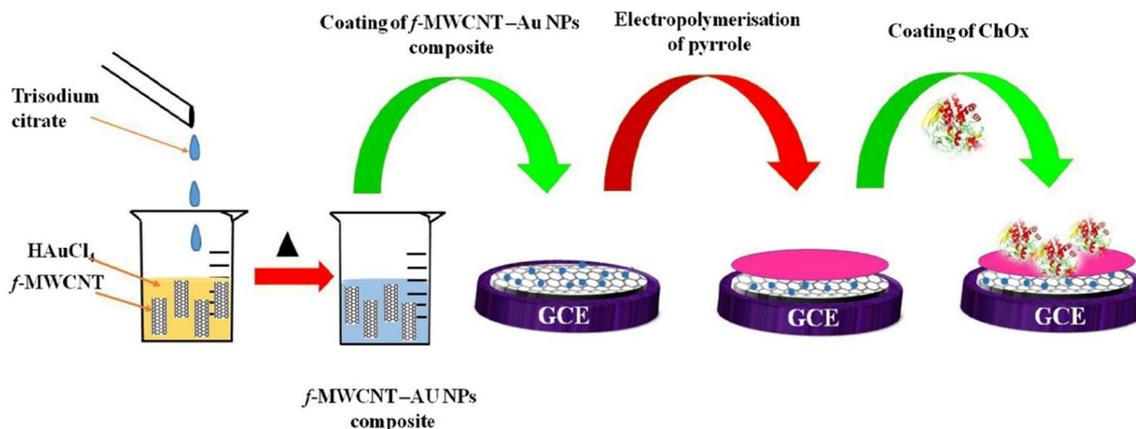


Fig. 5 A cholesterol biosensor synthesized from immobilization of cholesterol oxidase enzyme (ChOx) on AuNP modified MWCNT-PPy electrode. Reprinted with permission from Alagappan et al.<sup>62</sup> Copyright© 2020 Elsevier.

for amperometric sensing of  $\alpha$ -fetoprotein (AFP) with a low detection limit of  $0.6 \text{ ng mL}^{-1}$ .<sup>234</sup> Similarly, a sandwich-type electrochemical immunosensor was fabricated for AFP detection.<sup>192</sup> Recently, an advanced  $\text{Fe}_3\text{O}_4/\text{MWCNT-COOH}/\text{AuNP}$ -based electrochemical sensor was developed for the detection of trace liver cancer biomarker AFP in the picogram range (LOD  $1.09 \text{ pg mL}^{-1}$ ).<sup>214</sup> Magnetic MWCNTs modified with AuNPs were produced and loaded with  $\text{Pb}^{2+}$  ions and secondary antibodies. The generated hybrid composite  $\text{Pb}^{2+}@\text{Au}@\text{MWCNTs-Fe}_3\text{O}_4$  produced a linear detection range of  $10 \text{ fg mL}^{-1}$  to  $100 \text{ ng mL}^{-1}$  and a LOD of  $3.33 \text{ fg mL}^{-1}$ . *TP53* is an important early diagnostic cancer marker. In a study, AuNPs grown on aligned MWCNTs served as a label-free DNA biosensor for the detection of mutations in the *TP53* gene.<sup>193</sup> The improved performance of the sensor was attributed to highly synergistic interactions between the MWCNT array and AuNPs. The sensor showed a good response to target DNA related to *TP53* mutation detection

with a low LOD of  $10^{-17} \text{ M}$ . The HER2 gene levels in the serum of patients can be beneficially used in the early detection of breast cancer. In this regard, an impedimetric immunosensor was fabricated by using MWCNTs and AuNPs decorated on an ionic liquid electrode.<sup>194</sup> The monoclonal HER2 antibody was immobilized on AuNPs/MWCNTs and the antigen-antibody interactions were measured through impedance response. The sensor produced a low LOD of  $7.4 \text{ ng mL}^{-1}$  for HER2 detection.

There has been a continuous need for the analysis of pharmaceutical compounds and drugs. Monitoring paracetamol (PCM) levels in biological matrices is important for its regulation. In this context, an electrochemical sensor was reported based on GCE modified with MWCNTs, AuNPs, and calixarenes.<sup>195</sup> The electrode showed good electrocatalytic activity and high electrochemical response toward PCM with a detection limit of  $0.2 \text{ }\mu\text{M}$ . In another study, the detection of cyproterone acetate (CPA) drug in

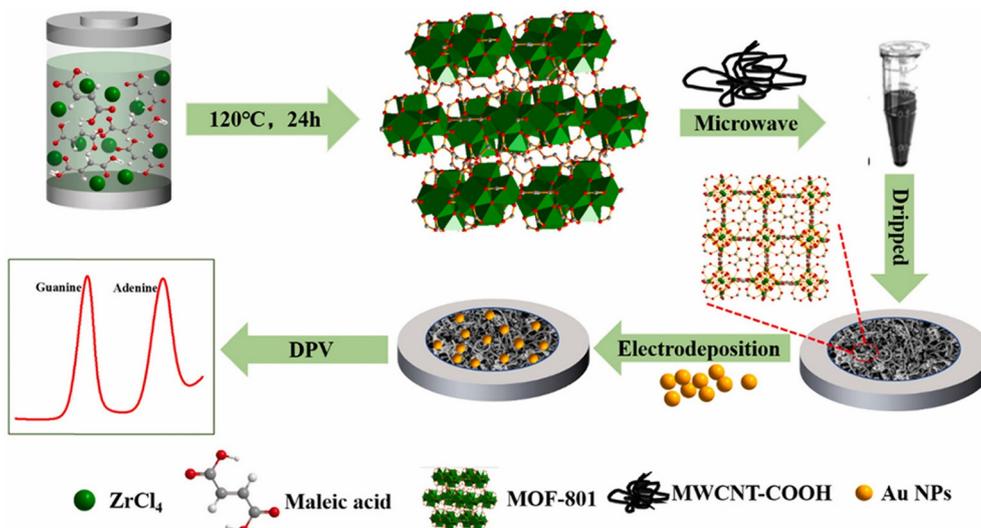


Fig. 6 A schematic representation of the fabrication of guanine and adenine sensor using Zr-MOF, carboxylated MWCNTs, and AuNPs. Reprinted with permission from Guo et al.<sup>191</sup> Copyright© 2021 Elsevier.



pharmaceutical and body fluids was studied with a voltammetric sensor based on carboxylated MWCNT and AuNP modified carbon paste electrode.<sup>196</sup> The sensor produced a linear response with CPA concentration in the range from  $9.9 \times 10^{-8}$  to  $1.15 \times 10^{-5}$  M with an LOD of  $1.66 \times 10^{-8}$  M. Another report successfully synthesized a novel MIP and MWCNT–AuNP composite-based structure for the analysis of velpatasvir drug in body fluids.<sup>197</sup> The developed material showed a 3D starfish-like hollow skeleton that could detect VELPR with an LOD of  $0.21 \text{ ng mL}^{-1}$ . As already discussed, studies on applications of MWCNT–AuNP composite in biomolecules and protein detection are well documented.

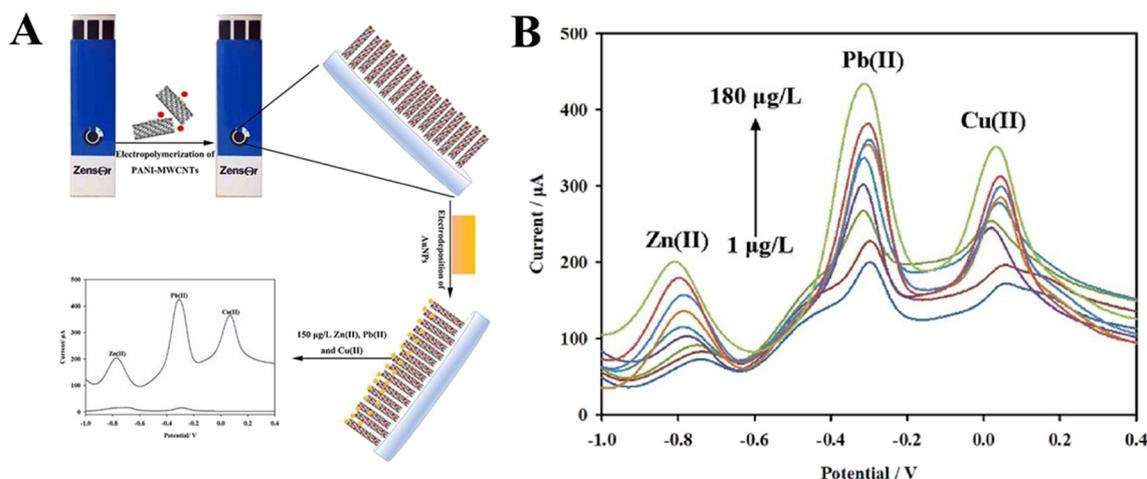
**4.2.2 Sensing of environmental pollutants.** MWCNT–AuNP nanocomposites have greatly shown potential in environmental sensing applications for the detection of pesticides, heavy metals, organic dyes, nitrites, hazardous chemicals, radionuclides, and emerging contaminants.<sup>235–237</sup>

Pesticide residues are a huge threat to human health causing acute and chronic toxicity. Detection of pesticide residues in the environment is a serious concern for environmental protection. Chlorpyrifos is a common organophosphate pesticide extensively used in agricultural practices but harmful to human health. Detecting chlorpyrifos is therefore important for promoting environmental safety. In this context, an electrochemical multilayered immunosensor was designed with AuNPs and MWCNTs/chitosan nanocomposite for chlorpyrifos sensing.<sup>198</sup> AuNPs were used as a platform for the immobilization of chlorpyrifos antibody. Under optimal conditions, the immunosensor displayed a wide linear range from  $0.1$  to  $40 \times 10^{-6} \text{ mg mL}^{-1}$  with a detection limit of  $0.06 \times 10^{-6} \text{ mg mL}^{-1}$ . Detection of heavy metals in environmental samples has also been reported using screen-printed carbon electrodes modified with polyaniline/MWCNT/AuNP composite.<sup>199</sup> The sensor was further utilized for

simultaneous sensing of  $\text{Zn}^{2+}$ ,  $\text{Pb}^{2+}$ , and  $\text{Cu}^{2+}$  ions using anodic stripping voltammetry with detection limits of  $0.039$ ,  $0.037$ , and  $0.017 \text{ } \mu\text{g L}^{-1}$ , respectively, as shown in Fig. 7. Also, a recent study reported the synthesis of PANI/MWCNT/AuNP composites for electrochemical detection of mercury in cosmetic products using methylene blue as a redox indicator.<sup>200</sup>

Furthermore, there has been a certain focus on the analysis of emerging contaminants in the environment. For example, dibutyl phthalate (DBP) is present in the environment as a toxic compound found in trace levels. It is produced by the excessive use of plastics and food packaging materials. A study reported a novel impedimetric immunosensor for DBP detection by utilizing chitosan/MWCNTs@GONRs/GCE-induced signal amplification with a good detection limit of  $7 \text{ ng mL}^{-1}$ .<sup>201</sup> Also, a hydrogel nanocomposite mixed with AuNPs and MWCNTs was prepared for the electrochemical sensor in the detection of 4-nitrophenol (4-NP) with good sensitivity.<sup>202</sup> Similarly, nitrite and nitrate are prominent environmental contaminants mainly produced due to the excessive use of nitrogen-containing fertilizers. Recently, a graphene-based electrode modified with MWCNTs and AuNP films was examined for the detection of nitrite in water samples ranging from  $10$  to  $140 \text{ } \mu\text{M}$  with a detection limit of  $0.9 \text{ } \mu\text{M}$ .<sup>203</sup> The sensor electrode oxidized nitrite at low potential and higher currents, thereby making it insensitive to the presence of common interfering ions. Also, a nanocomposite based on electrosynthesis of AuNPs on MWCNT/copper–polyaniline (Cu–PANI) was effectively examined for the presence of nitrate ions in environmental samples with a good LOD of  $0.09 \text{ } \mu\text{M}$ .<sup>204</sup> All these studies have shown that the MWCNT–AuNP composites have great potential in the screening of environmental pollution.

**4.2.3 Food analysis.** Maintenance of food safety and quality is an important part of the food processing industry.



**Fig. 7** Electrochemical detection of heavy metal ions ( $\text{Zn}^{2+}$ ,  $\text{Pb}^{2+}$ , and  $\text{Cu}^{2+}$ ) using AuNP/polyaniline–MWCNT modified carbon electrode. (A) Construction of the sensing platform. (B) Stripping voltammograms for various concentrations of  $\text{Zn}^{2+}$ ,  $\text{Pb}^{2+}$ , and  $\text{Cu}^{2+}$ . Reprinted with permission from Shao *et al.*<sup>199</sup> Copyright© 2021 Elsevier.



A variety of sensors have been produced to date for the detection of a range of different toxicants present in food. Seminal contributions have been made by the scientific community in developing sensors based on MWCNT–AuNP nanocomposites for the detection of food contaminants such as bacteria, microbial toxins, neomycin, *etc.*<sup>216,238–241</sup> Detection of microbes such as *E. coli* in foodstuffs has been achieved using PPy/AuNP/MWCNT/Chi hybrid nanocomposite (Fig. 8). Detection of *Salmonella typhimurium* in foodstuffs is important. In this context, an impedimetric immunosensor utilized the immobilization of anti-*Salmonella* antibodies on AuNP–MWCNT–chitosan nanocomposite modified on a glassy carbon electrode.<sup>205</sup> The sensor achieved a detection limit of  $5 \times 10^2$  CFU mL<sup>-1</sup>.

Diethylstilbestrol (DES) is a synthetic estrogen that is generally administered to meat and milk-producing animals. Analysis of DES residues is important for preventing its toxicity. In a study, a glassy carbon electrode was developed by decorating MWCNTs and AuNPs, electroplated by sol-gel MIP.<sup>206</sup> The sensor produced differential pulse voltammetric response with the addition of DES in the detection range of  $10^{-10}$  to  $10^{-6}$  mg mL<sup>-1</sup>. The sensor produced highly selective and sensitive results for the detection of DES in milk.

Zearalenone (ZEA) contamination can occur in food products including cereals, mainly maize, and manufactured foods. A study was conducted to determine ZEA by using carbon screen-printed electrodes modified with AuNPs (attached with anti-ZEA antibody), and MWCNT

dispersions.<sup>207</sup> The sensor was used in the amperometric detection of ZEA at an applied potential of  $-0.3$  V. The developed sensor showed a LOD of  $0.15$   $\mu\text{g mL}^{-1}$ .

Kidney bean lectins (KBLs) are carbohydrate-binding proteins, whose quantification is important for monitoring the allergic activity of KBL in foods. A study developed an immunosensor for highly sensitive detection of KBL activity.<sup>208</sup> The composite of polyethyleneimine functionalized MWCNTs and AuNPs coated on a GCE was immobilized with KBL antibodies. Under optimum conditions, the immunosensor extended a good linear response with KBL from  $0.05$  to  $100$   $\mu\text{g mL}^{-1}$  and LOD of  $0.023$   $\mu\text{g mL}^{-1}$ .

Detection of polyphenolic compounds such as flavonoids in food products is important for assessing food quality and safety. AuNPs functionalized on *p*-aminothiophenol modified MWCNTs were coated on a glassy carbon electrode (GCE) for simultaneous detection of quercetin and rutin in fruit samples.<sup>209</sup> Besides phenolic compounds, monitoring the levels of antibiotics in food products is important due to the adverse effects of antibiotics on humans. Palisoc *et al.* fabricated a highly sensitive tetracycline sensor by modification of GCE by AuNPs and MWCNTs *via* electrodeposition technique.<sup>210</sup> This electrode was employed as a working electrode in DPV to analyze tetracycline residues in organic and non-organic chicken with an LOD of 42 ppb.

Food colorant dyes have been widely used in the food industry to impart color and texture to food products.

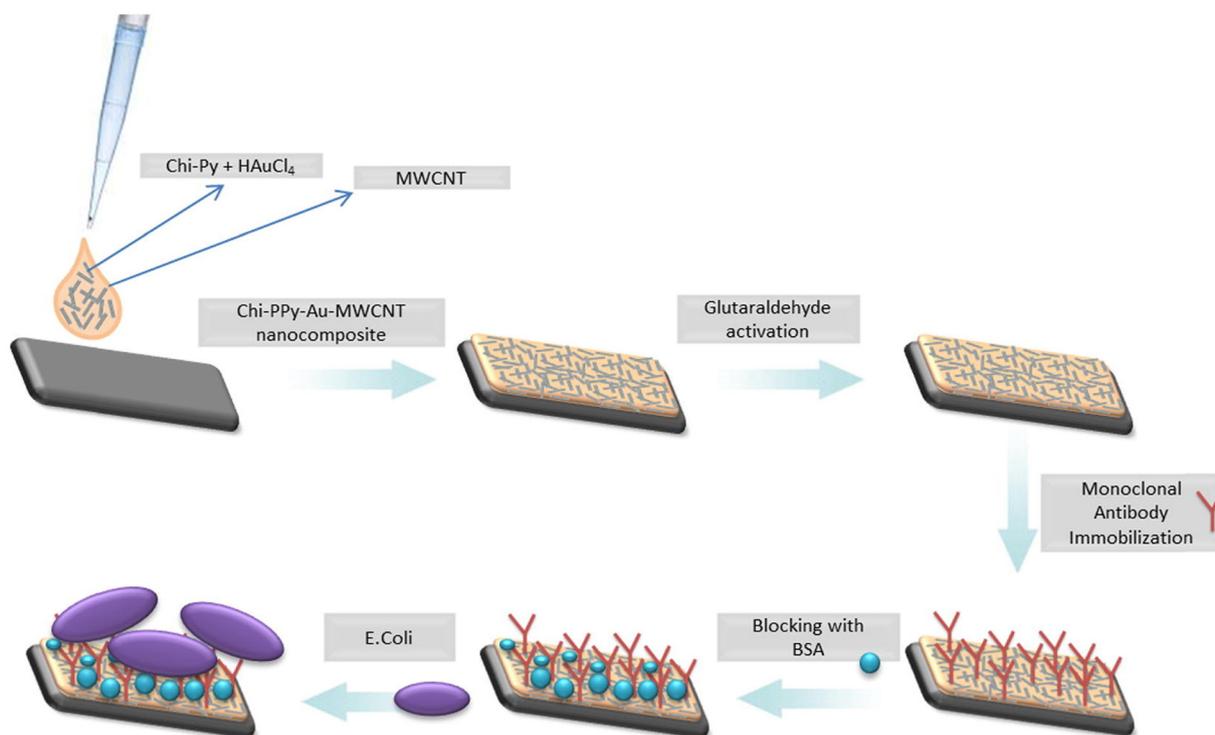


Fig. 8 Fabrication of an electrochemical immunosensor for sensing *E. coli* by using a nanocomposite made of PPy/AuNP/MWCNT/chitosan. Reprinted with permission from Güner *et al.*<sup>115</sup> Copyright© 2017 Elsevier.



## Sensors &amp; Diagnostics

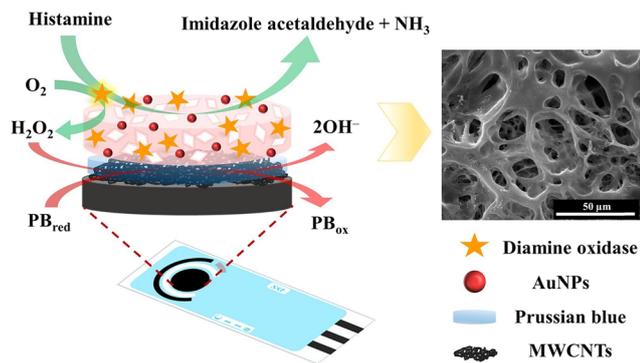


Fig. 9 Development of histamine biosensor using screen-printed carbon electrode modified with chitosan-AuNPs-cryogel on Prussian blue-coated MWCNTs. Reprinted with permission from Nontipichet et al.<sup>213</sup> Copyright© 2021 Elsevier.

However, they may cause allergies, anxiety, diarrhea, and even cancer. Detection of food colorants is necessary to prevent their hazardous effects. A biosensor based on the modification of electrodes with MWCNTs, AuNPs, chitosan, and GO was synthesized for sensing sunset yellow (SY) in foodstuffs.<sup>211</sup> The sensor employed a differential pulse voltammetric method for the detection of SY with an LOD of  $0.032 \text{ mg mL}^{-1}$  and was successfully validated with candy and soft drink samples.

Bioenzymatic sensors can be developed using different enzymes and can be applied in food analysis. For instance, a study reported the application of ionic liquids as media for electrode materials for the development of disposable amperometric biosensors.<sup>212</sup> The electrodes modified with MWCNTs, graphene, and AuNPs were modified with lipase, glucose oxidase, or alcohol dehydrogenase for sensing antioxidants, glucose, and alcohol in foodstuffs. Similarly, a study reported that the histamine levels in seafood can be detected by an enzymatic biosensor comprising a screen-printed carbon electrode (Fig. 9) modified with Prussian blue electrodeposited on MWCNTs covered with chitosan-AuNP cryogel.<sup>213</sup> It achieved a good LOD of  $1.81 \mu\text{M}$  and could detect histamine in fish and shrimps.

## 5. Conclusion and future perspective

The present review provides a comprehensive discussion regarding the biosensing applications of MWCNT-based nanocomposites for the detection of several analytes. The combination of two materials MWCNTs and AuNPs in nanocomposites imparts many benefits such as large surface area, tuneability, rich surface functionality, and chemical stability, that can be effectively introduced into the biosensor systems for detecting many analytes including biomolecules, proteins, environmental pollutants, food toxins, etc. Different methods such as direct attachment of AuNPs on MWCNTs, or wet chemical deposition for fabricating MWCNT-AuNP composites have been developed, but still there should be research on the controlled deposition of AuNPs on the

MWCNT surface and a uniform and efficient distribution of AuNPs on the MWCNTs. Furthermore, there should be enough room for modification and advancements of these composites so that several other nanomaterials can be attached to them to produce a better synergic effect. There should be a focus on the synthesis of multifunctional AuNPs and MWCNTs with diverse sizes for sensing multiple analytes with high selectivity and sensitivity. Additional applications need to be explored based on the characteristics of these two nanomaterials and the nanocomposites.

## Author contributions

Sandeep Kumar: conceptualization, review roadmap, investigation, writing – original draft, review & editing. H. K. Sidhu: review roadmap, critical investigation, writing, review & editing. Ashok K. Paul: review roadmap, critical investigation, writing, review & editing. Neha Bhardwaj: conceptualization, review roadmap, critical investigation, supervision, writing, review & editing. Neeraj S. Thakur: conceptualization, review roadmap, supervision, project administration, writing, review & editing. Akash Deep: conceptualization, review roadmap, writing, review & editing, supervision, project administration.

## Conflicts of interest

There is no conflict of interest.

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