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Review

Carbon nanotube based biosensors

Ning Yang[a], Xianping Chen[a,b,*], Tianling Ren[b], Ping Zhang[a], Daoguo Yang[a,**]

[a] The Faculty of Mechanical Engineering, Guilin University of Electronic Technology, 541004 Guilin, China
[b] Institute of Microelectronics, Tsinghua University, 100084 Beijing, China

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ABSTRACT

Carbon nanotube (CNT) based biosensors are recognized to be a next generation building block for ultra-sensitive and ultra-fast biosensing systems. This article provides an overview on the recent expansion of research in the field of CNT-based biosensors. We start by first introducing the material structures and properties of CNTs. The basic and some new developed synthetic methods of CNTs are presented. This is followed by a collection of working principle and performance of different CNT-based biosensors. The roles and the processing methods of functionalized CNTs are summarized. After that, some of the practical applications and concerns in the field are addressed. What is more, the scientific and technological challenges in the field are discussed at the end of this review.

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* Corresponding author at: The Faculty of Mechanical Engineering, Guilin University of Electronic Technology, 541004 Guilin, China. Tel.: +86 773 2290811.
** Corresponding author.
E-mail addresses: xianpignchen@tsinghua.edu.cn (X. Chen), daoguo_yang@vip.163.com (D. Yang).

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1. Introduction

The detection of biomolecules is crucial for many areas of healthcare, clinical medicine, food safety, environmental monitoring and homeland security, ranging from uncovering and diagnosing disease to the discovery and screening of new drug molecules and to giving off early warning against health agents [1–3]. Hence, the development of reliable and inexpensive devices that enable direct, high sensitive/selective, and rapid analysis of these species could impact mankind to have a more healthy and reliable life [4]. Central to detection is the signal transduction with selective recognition of the biological species of interest. Biosensors, which combine a biological recognition with a chemical or physical transduction [5], have proved to be promising the advantage in the utilization, and especially commercialization to satisfy the demands of the above-mentioned areas. Ever since the discovery of the CNTs in 1991 [6,7], they have quickly become a global research activity due to their ultra-high specific surface area and outstanding electrical, mechanical and electrochemical properties. It is well known that the material properties (e.g. electrical or optical) of CNTs is very sensitive to be affected by exposure to biomolecules and this has led to the investigation, by a number of groups [6,8–10], of these materials as sensing elements for biosensors [11]. The high surface-to-volume ratio of the CNT makes it possible to obtain ultra fast detection of biological species at low concentrations. Thus, CNT-based biosensors are recognized to be a next generation building block for ultra-sensitive biosensing systems. Comparing with the most of the commercially available sensors, based usually on metal oxides, silicon and other materials, the CNT-based biosensors have the following great advantages: (i) high sensitivity, because of the large surface area ratio and hollow pipe, CNTs can be used to immobilized enzyme [12] which keep high biological activity; (ii) fast response time, CNTs have an outstanding ability to mediate fast electron-transfer kinetics hence promote the electron-transfer reactions like NADH and hydrogen peroxide [11]; (iii) lower potential of redox reaction and less surface fouling effects; (iv) highly stability and longer life time. These improved characteristics have stimulated the increasing research interest in the applications of CNTs as components for biosensors. Fig. 1 gives the number of papers referring of biosensor based on CNTs (searching from Google Scholar) in last 15 years. It is clearly seen that the study of CNT-based biosensor was in an explosive growth since 2007. A previous, a review has described the state of the art in this field up to the year 2006 [11]. Since CNT-based biosensors have been seen rapid development as well as a substantial increase in activities and in the number of papers on this topic from 2007. The present review focuses on these more recent efforts and considers the developments up to the year 2014.

Here, we first introduce the structures and properties of CNTs in Section 2. The basic and some new developed synthetic methods of CNTs are represented in Section 3. This is followed by a collection of working principle and performance of different CNT-based biosensors, such as the CNT-based electrodes (the detection of physical and chemical signals) and CNT-field effect transistors (FETs), in Section 4. Section 5 discusses the roles of functionalized CNTs and summarizes the methods for functionalizing CNTs. After that, some of the practical applications and concerns in the field are traced in Section 6. Finally, the challenges and future work on developing CNT-based biosensor are presented at the end of the review.

2. The structure and property of CNTs

CNTs can be thought of as the seamless hollow tubes composed of rolling graphite sheet, according to the layer number of graphite sheet, the CNTs can be divided into single-walled carbon nanotubes (SWCNTs) and multi-walled carbon nanotubes (MWCNTs) [13,14], as shown in Fig. 2a and b respectively. In general, SWCNT is a single molecular nanomaterial, which is formed of only a layer that rolls a single sheet of graphite (graphene) into a seamless molecular cylinder. Its diameter distribution and length are at the range of 0.75–3 nm and l–50 μm respectively. While MWCNT is composed of more than two layers of curly graphite sheet, and its diameter is at the range of 2–30 nm and some even more than l00 nm (Fig. 2b) [15], the distance between each layer is approximately 0.42 nm.

You can image the structure of SWCNTs that the graphene plane is mapped into the cylinder without the deformation of hexagon graphene layer as shown in Fig. 3. The vector from A to A' can be illustrated in Eq. (1)

$$\hat{C}_h = n\bar{a}_1 + m\bar{a}_2 \quad (1)$$

where $\hat{C}_h$ is a linear combination of the lattice basis vectors, $\bar{a}_1$ and $\bar{a}_2$ are lattice basis vectors, and n and m are positive integers which are known as the chiral indices. In the process of rolling graphene sheet, the carbon atom A overlaps the carbon atom A', thus forming CNTs. Once integers (n, m) are affirmed, the structure of CNTs is completely determined. All structural parameters of SWCNTs can be determined by (n, m) index [16,17].

According to the different direction of winding, SWCNTs are divided into three different types of structure: armchair type, zigzag type and chiral type respectively [18]. The structure types of CNTs are related to their chiral vector (n, m) and the spiral angle θ. As shown in Fig. 4, when $n = m$, spiral angle is equal to 30° between chiral vector $\hat{C}_h$ and lattice vector $\bar{a}_1$, the type of CNTs is called armchair; when $m = 0, \theta = 0°$, the type of CNTs is called zigzag; and when $0 < \theta < 30°$, the type of CNTs is called chiral. The electrical properties of SWCNTs strongly depends on diameter and chirality [19], and the diameter d is given by Eq. (2)

$$d = \frac{|C|}{\pi} = a(n^2 + nm + m^2)^{1/2} \quad (2)$$

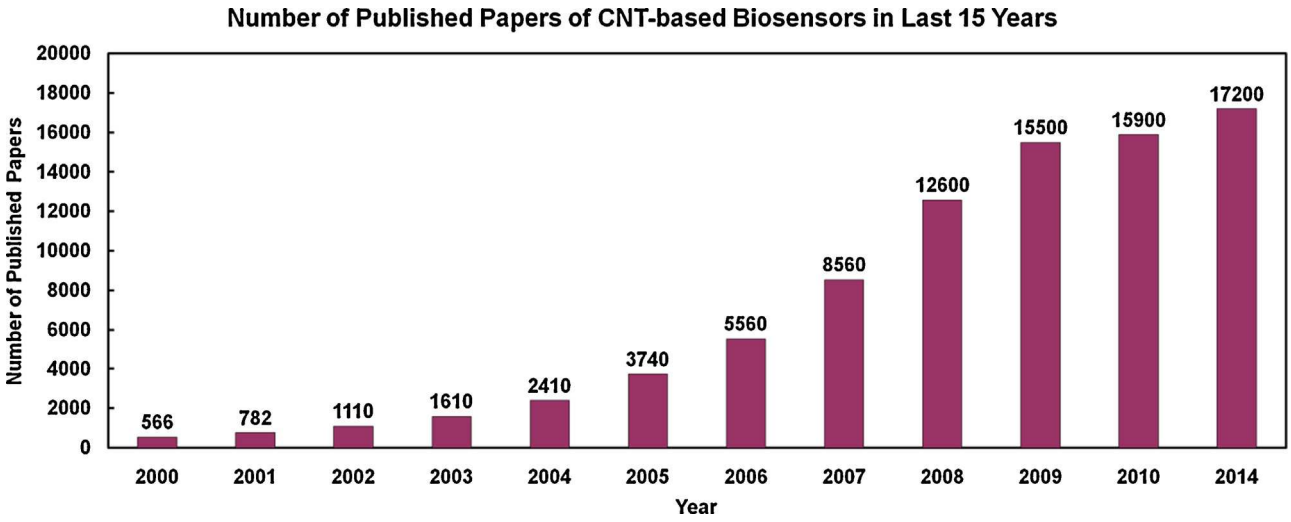

Fig. 1. Trend of investigation of CNT-based biosensor over the last decade.

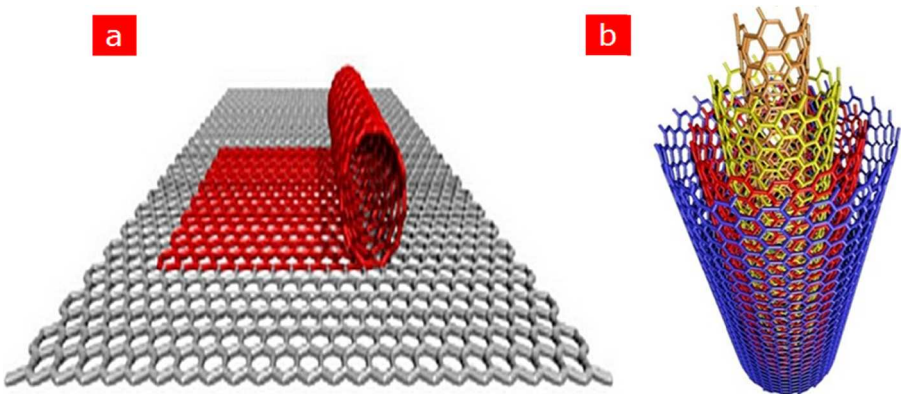

Fig. 2. (a) Schematics of SWCNTs which composed of a single layer of curly graphite. (b) Schematics of MWCNTs.

where a is the distance between two adjacent carbon atoms. All of the CNTs have metallic attribute when $n - m = 3r$ (r is an integer), or they are semiconductor. And the energy gap of semi-conductive SWCNTs is inversely proportional to the diameter d. If the diameter is too large, the energy gap is zero approximately, and the conductivity of SWCNTs will be turned into metallic attribute from semiconductor. The armchair CNTs are metallic attribute with the most stable structure [8].

3. Synthesis of CNTs

The application of CNTs in biosensors is becoming more and more widely. Therefore, the demand of CNT in industry has become increasingly urgent. Several synthesis schemes, such as arc discharge, laser ablation and chemical vapor deposition (CVD) [20], have been developed for the preparation of CNTs. With the research on CNTs is more and more extensively, the synthetic methods of CNTs have been improved. Table 1 lists the various methods for preparing all kinds of CNTs in recent years. The main synthetic methods are introduced briefly and their main advantages and disadvantages are discussed.

3.1. Synthetic methods of CNTs

3.1.1. Arc discharge

Arc discharge is one of the major methods for the preparation of CNTs, and it was introduced to grow CNTs firstly by Iijima in 1991 [6]. The principle of this method is that CNTs are deposited on the graphite cathode under the action of current in a vacuum reactor as shown in Fig. 5. The bulky graphite rod is used as cathode, while the fine graphite rod is used as anode; the distance between the two graphite electrodes is remained within 1 mm and the arc is kept steady. The vacuum reactor is filled with a certain amount of inert gas, such as helium or argon for avoiding the oxidation

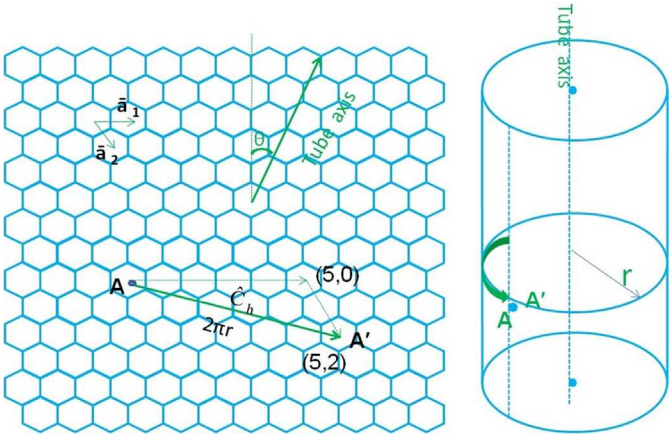

Fig. 3. The structure schematic diagram of carbon nanotubes, all structural parameters of SWCNTs can be determined by (n, m) index and the structure of CNTs is completely determined by (n, m).

Table 1
The synthetic methods of CNTs.

Method	Progress	Consequence	Refs.
Arc discharge	Synthesized they between two graphite rods in water bath at different voltage	Good quality and high yield CNTs are obtained	[21]
	Two graphite electrodes submerged in different liquid media	Yielding various dimensional nanocarbon structures	[22]
	Using strong oxidizing agent HNO_3/H_2O_2 instead of metal catalyst and vacuum devices	Improving purity of MWCNTs	[23]
	The discharge is maintained in a magnetic field	High quality MWCNTs are obtained	[24]
	Using physical forces both during synthesis	Relatively straight and defect free MWCNTs are obtained	[25]
Laser ablation	Dynamic light scattering, micro-Raman and high-resolution transmission electron microscopy were used	Controlling their nanostructures	[26]
	Using binary catalysts combining the transition metals Fe, Co and Ni	Different carbon nanostructures can be obtained	[27]
	Direct synthesis using pulsed laser ablation	SWCNTs show fast and strong photoresponse (as high as 1350% at 405 nm)	[28]
	Irradiating of a CO_2 laser in continuous wave mode onto a boron-containing graphite target at room temperature	The fine crystalline structure of MWCNTs can be obtained	[29]
	Ablating a nickel/carbon composite target in ethanol or ambient air	MWCNTs	[30]
CVD	Growing on iron catalyst film using plasma enhanced chemical vapor deposition (PECVD) system	Vertically aligned single wall carbon nanotubes of diameter 0.8–1.5 nm can be obtained	[31]
	Co was used as catalysts, at 700 °C using hydrogen to acetylene gas ratio at 25:25 Sccm	High yield of MWCNTs	[32]
	Using NiO powder as catalysts and LPG as carbon source	The yield of CNTs increased	[33]
	$AlPO_4$ was used as catalysts	Y-shaped CNTs	[34]
	Taking iron nanoparticles as catalyst	SWCNTs	[35]
	Taking Co–Mo as catalyst and using CH4 at 900 °C	SWCNTs	[36]
	Metal catalyst-free mist flow	SWCNTs can be synthesized without any treatments	[37]
	Ni over Cr layer as a catalyst at 600 °C	CNTs	[38]
	Taking Ni/MgO as catalyst and using CH4 in micro-fluidized bed	CNTs exhibited relatively small and mean outer diameter, less defect, and high purity	[39]
	Photochemical deposition	MWCNTs	[40]
Others			
Low-temperature plasma	The plasma causes the dissociation of carbon resource	CNTs with highly distributed active species and catalyst activation	[41]
Low-temperature plasma reduction	Facile glow discharge plasma reduction operated at room temperature	CNTs	[42]
Solvothermal	At the low temperature of 180 °C	MWCNTs bundles	[43]
Low-temperature solvothermal	Dichlorobenzene as a carbon source was catalyze by a solvothermal approach at 200 °C	Well-aggregated carbon nanotubes are achieved	[44]
Solvothermal	At the temperature of 200 °C and a reaction for 10 h	Magnetic MMWCNTs with alterable structure	[45]
Sol–gel	The mixed solution was evaporated at 80 °C for 8 h	MWCNT–$LiMn_2O_4$	[46]
Hydrothermal	The solution was transferred into a 100 mL autoclave and kept at 160 °C for 8 h	CNTs with well-dispersed Fe_3O_4	[47]
Hydrothermal	The solution was transferred into a 30 mL autoclave and kept at 150 °C for 4 h	CNT core/porous MnO_2	[48]
Flame	Diffusion flames were acted as reaction environments, using catalysts as aerosols and supported upon substrates	CNTs	[49]
Flame	CNT growth occurs via the decomposition of flame-generated carbon precursors	CNTs with higher physical properties	[50]
Flame	Using rotating opposed flow ethylene diffusion flames and a catalytic Ni substrate	Controlling the synthesis of CNTs	[51]
Flame	Taking $Fe/Mo/Al_2O_3$ as catalyst	Self-oriented CNTs	[52]

of CNTs. The synthesis of CNTs is usually under certain loading conditions, such as the current (50–120 A), voltage (20–30 V) and temperature (>3000 °C) and the reduced pressure (50–700 mbar). In the process of arc discharge, the graphite and metal catalyst of anode graphite rod is vaporized and consumed constantly under a high-temperature plasma; after the action of metal catalysts, the CNTs are deposited on the graphite cathode [53]. The selection and control of these process parameters including arc voltage,

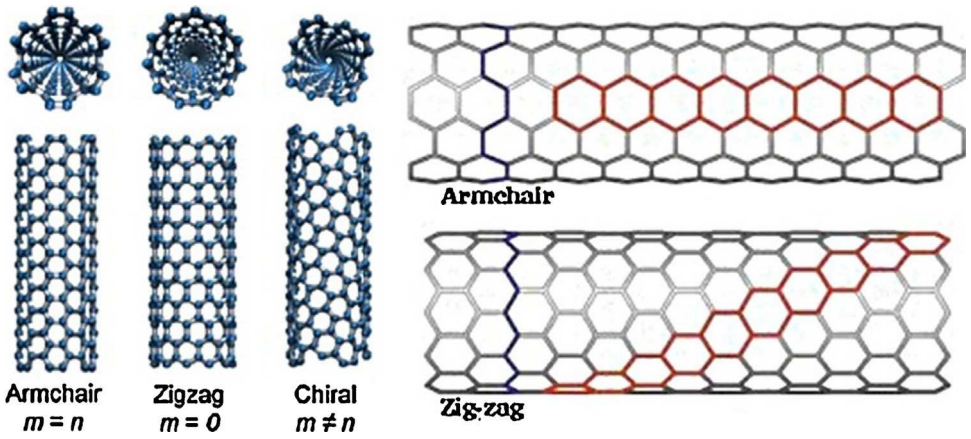

Fig. 4. Different types of SWCNTs: the armchair, the zigzag and the chiral.

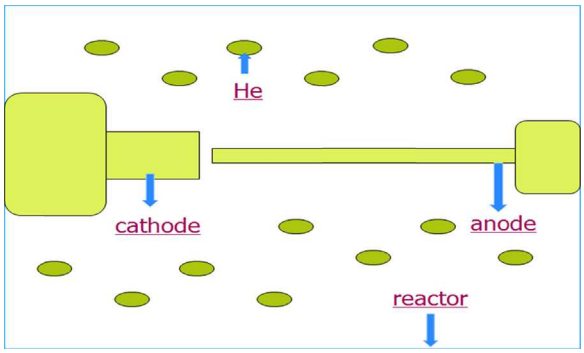

Fig. 5. The schematic diagram of arc discharge. The bulky graphite rod is acted as cathode and CNTs are deposited on the graphite cathode.

current, pressure of inert gas and electrode cooling speed is the key to the synthesis of CNTs. The choice of the metal catalysts to the synthesis of CNTs is also very important, and it will affect the efficiency of the preparation. The synthesis of CNTs using arc discharge with fewer defects has better thermal conductive performance and greater mechanical strength. But there are also some problems, for example, the synthesis of CNTs is required to under the vacuum environment, but the vacuum environment is hard to maintain and it is also very expensive [54]. In addition, low current arc is conducive to the formation of CNTs, but this will make the arc unstable. However, if the arc current is higher, the generated impurities such as amorphous carbon and graphite of CNTs will be increased. Moreover, because the electrodes need continuous change, it will result in discontinuity of the process. Therefore, the yield of CNTs via arc discharge is lower.

Arc discharge is one of the most mature synthetic methods for SWCNTs and it is also used more extensively. Researches showed that different catalysts for the synthesis of SWCNTs would cause the different diameter distribution [55–57]. Ferrocene was found to be a better catalyst precursor, and it can form the SWCNTs product with very high purity [57], and an overview and high-resolution TEM images (inset) of the CNT product is presented in Fig. 6.

3.1.2. *Laser ablation*

Laser ablation is a simple and effective new method [58] developed from the arc discharge by Smalley and his co-workers [59]. The principle of this method can be described by Fig. 7. Firstly, a piece of graphite is placed in a vacuum furnace which is filled some inert gas (e.g., helium) under the condition of high temperature. After that, using high energy laser beam to irradiate the metal catalyst and carbon atoms of targeted graphite, the high temperature will be produced instantly to prompt them to evaporate, and then the carrier gas will brings these carbon molecules and catalyst particles to the high temperature zone. Finally, the carbon atom clusters are deposited on the collector to create the CNTs. The most significant advantage of the laser ablation is that the produced CNTs have high

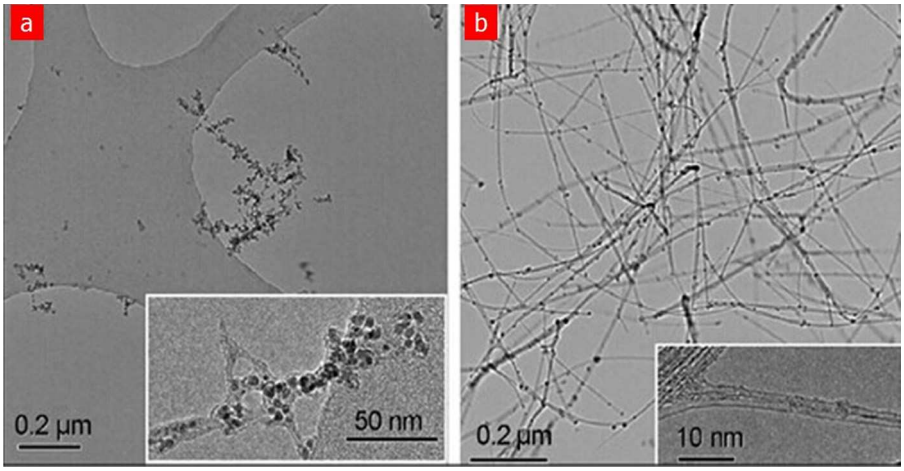

Fig. 6. Overview and high-resolution TEM images (inset) of the CNT product. (a) $Fe(CO)_5$ (TF = 1300 °C, x = 18 cm, QTOT,CO = 910 cm^3/min, $pFe(CO)_5$ = 0.3 Pa). (b) $FeCp_2$ (TF = 800 °C, x = 7.5 cm, QTOT,CO = 410 cm^3/min) [57].

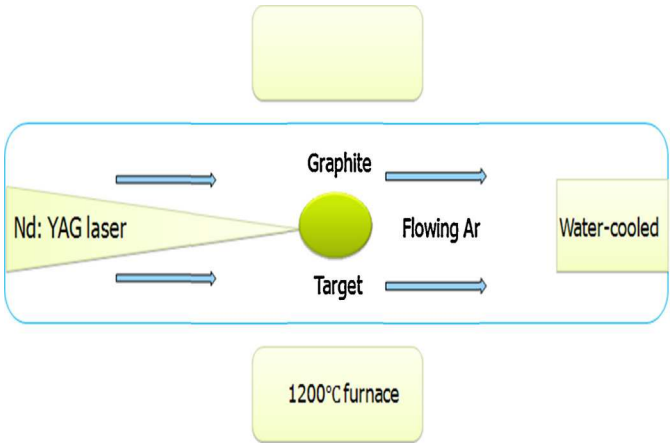

Fig. 7. The schematic diagram of laser ablation. Metal catalyst and carbon atoms of graphite target are evaporated via laser ablation, and CNTs are deposited on the water-cooled collector.

purity and very few defects. Furthermore, the yield of CNTs can up to 70–90%. However, using this method to grow CNTs requires high investment cost and energy consumption, hence it is difficult to be applied in commercial production.

3.1.3. Chemical vapor deposition (CVD)

CVD is one of the most widely used and the most in-depth investigated method for the synthesis of CNTs, actually it is essentially a thermal dehydrogenation reaction which needs a transition metal catalyst [60]. The principle of CVD is presented in Fig. 8: firstly, the carbon source gas enters into the reaction chamber together with carrier gas under the temperature of 600–1000 °C, and the gas will be decomposed to produce the carbon atoms on a coated catalyst substrate under the high temperature, finally CNTs are generated. The often-used transition metal catalysts are Co [32], Fe, Ni, Cu, Cr, Mo [61], sometimes are their alloy. The carbon source generally use carbon gases, such as methane, ethanol, ethylene, acetylene, benzene and so on. This can help in reducing the required temperature for the decomposition of gaseous hydrocarbon into carbon

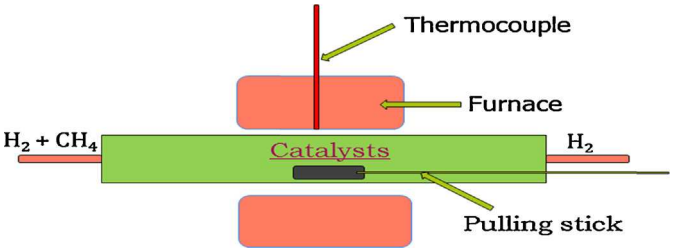

Fig. 8. The schematic diagram of CVD. Carbon source gas enters from one end and is converted into CNTs after catalytic action.

and hydrogen [39]. The key process parameters of CVD are carbon source, gas flux, carrier gas flux, growth temperature and catalyst concentration. According to the loading and dispersion methods of catalyst, CVD is divided into matrix method and floating catalyst method [62]. The advantages of CVD are that CNTs can grow on the substrate directly, and the equipment is simple and low cost. It is worth noting that this method can be operated continuously for mass production.

At present, the production of MWCNTs accounted for more than 90% of the output. Therefore, how to synthesize MWCNTs effectively with more yields has become a particularly important issue. As the MWCNTs can be grown effectively, CVD has become the main synthetic method of MWCNTs. Camilli et al. developed a new method for synthesizing MWCNTs by CVD using a stainless steel as catalyst [63]. It is worth noting that a continuous production of CNTs from the same substrate is achievable, and the stainless steel substrate can be reused after carefully removing the synthesized CNTs. As shown in Fig. 9a, the presence of native nanoscale substrate structure which look like hills, while these hills still exist after the substrate has used for the synthesis of CNT in Fig. 9b. Fig. 10 shows the growth process of the MWCNTs on stainless steel [63].

3.1.4. Others

Except the above three main synthetic methods, there are some other emerging methods for the preparation of CNTs, such as low temperature plasma [41,42]/solvothermal [43,44] process,

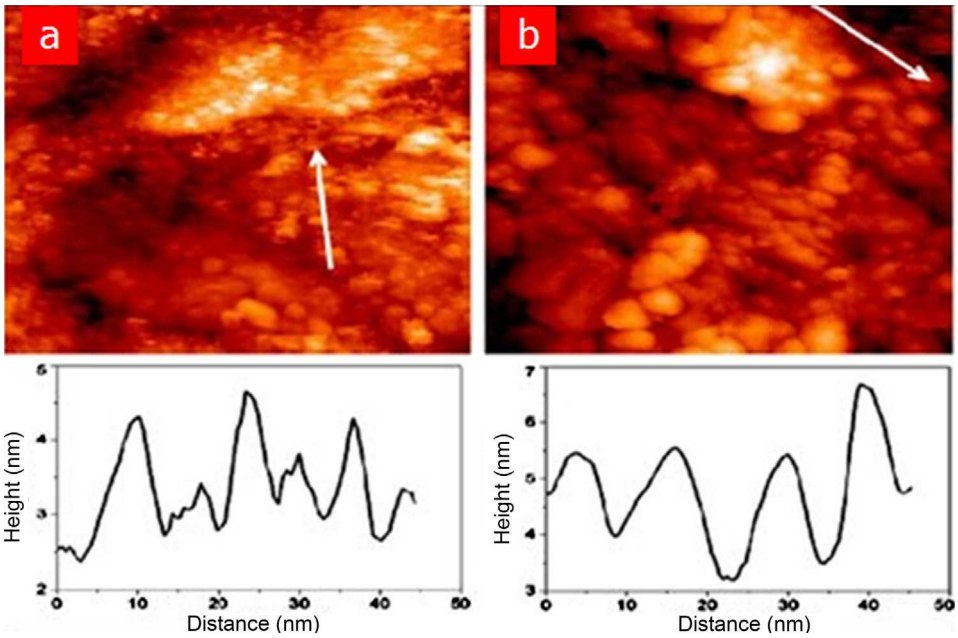

Fig. 9. 150 nm constant current STM images of the stainless steel surface before (a) and after (b) use for the CNT growth. The lower panels show the relative cross section, corresponding to the white arrows in the STM images. $I = 0.3$ nA, $V_{Sample} = 700$ mV [63].

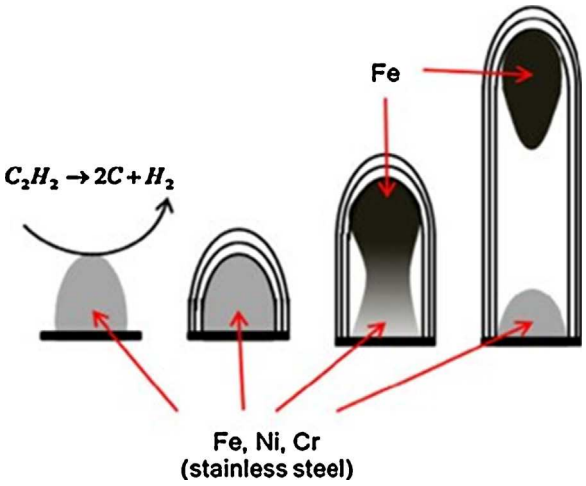

Fig. 10. Schematic depiction of the growth process of MWCNTs on stainless steel. At the working temperature (730 °C), the nano-hills on the stainless steel surface are in liquid state, so the stretching force applied on them during the formation of the CNT make them elongated and finally broken into two parts. According to this model the tube grows upward, leaving the nano-hill (or, at least, a part of it) on the stainless steel surface [63].

hydrothermal [47,48], flame [50,51], and the microwave [64,65]. But the yield of these methods is relatively lower and the process conditions are very difficult to control.

4. Working principles of different CNT-based biosensors

The concept of CNT-based biosensor was derived from the description of the enzyme electrode by Clark in 1962 [66]. In general, the composition of CNT-based biosensor includes two parts: biological sensitive element and transducer as shown in Fig. 11. The CNT functionalized with biomolecules or bioreceptors, such as proteins (e.g., cell receptors, enzymes, antibodies), oligo- or polynucleotides, microorganisms, or even whole biological tissues, are working as the biological sensitive element [67–69]. The role of transducer is to convert the concentration of analytes to other detectable physical signals, such as currents, absorbance, mass or acoustic variables for testing and detecting. According to the interactions between analytes and the biological sensitive materials, CNT-based biosensors will be separated into two categories: chemical and physical, and they are discussed in the following sections. Among of them, the CNTs-field effect transistors will be highlighted at the end of this section owing to its superior properties.

4.1. Chemical

Currently, the electrochemical biosensors mainly have three types: amperometric-based, potentiometric-based and impedimetric-based, the amperometric-based mode is the most widely used [70,71]. Its principle is to change chemical signals into electrical signals, once enzyme electrode is immersed in the test solution, the analytes will come into the enzyme layer through diffusion effect and have enzymatic reaction immediately. At present, most of the working principles of CNTs-based biosensors are fit this. The following content about working principle of amperometric-based type of electrochemical CNTs-based biosensors will be introduced.

The hollow structure of CNTs is good for the adsorption of enzyme. Therefore, in amperometric CNTs-based biosensors, CNTs are always used to functionalize with enzyme to generate the enzyme CNT electrodes or to modify the surface of electrodes. The sensing mechanism of amperometric CNTs-based biosensors is using the enzyme fixed CNT electrode to catalyze oxidation or reduction. According to different analytes, different enzymes are selected, such as nicotinamide adenine dinucleotide (NADH) [72,73], glucose oxidase (GOD) [74], aflatoxin-oxidase [75], cholesterol oxidase [76], urease [112], lactic acid oxidase [153] and horseradish peroxidase [77] and so on. Through the effect of enzyme, oxidizable hydrogen peroxide (H_2O_2) or reduced nicotinamide adenine dinucleotide (NADH) is easily to generate [78], as described in Eqs. (3) and (4):

$$\text{Substrate} + O_2 \overset{\text{oxidase}}{\longrightarrow} \text{Product} + H_2O_2 \quad (3)$$

$$\text{Substrate} + \text{NAD} \overset{\text{dehydeogenase}}{\longrightarrow} \text{Product} + \text{NADH} \quad (4)$$

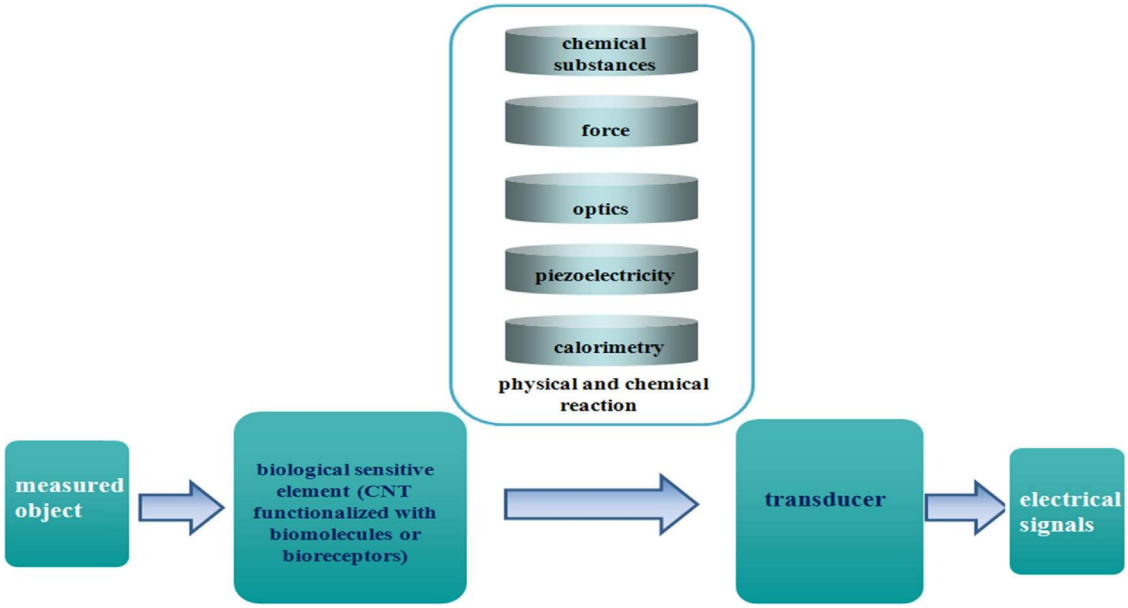

Fig. 11. Schematic depiction of different CNTs-based biosensors. The physical or chemical reaction is transformed into electrical signals after the target molecule was detected by detection device.

The peroxide or NADH species can be liberated to generate the cations and electrons as illustrated in Eqs. (5) and (6), so that they could be detected by using CNT electrodes.

$$H_2O_2 \rightarrow O_2 + 2H^+ + 2e^- \quad (5)$$

$$NADH \rightarrow NAD^+ + H^+ + 2e^- \quad (6)$$

At present, the CNTs-based biosensors research on the determination of glucose is the most widespread. The glucose can be catalyzed by glucose oxidase (GOD) containing FAD as a cofactor, and Eqs. (7) and (8) give an example of the reaction mechanism of glucose of YSI 23A [74]. According to the Eqs. (5), (7) and (8), the glucose could also be detected by using GOD CNTs electrodes. Manso et al. used Aucoll–CNT–Teflon electrode to detect GOD and find that the composite CNTs-electrode shows significantly improved responses to H_2O_2 when compared with other CNTs-electrode [79].

$$\text{Glucose} + \text{GOD(FAD)} \rightarrow \text{Gluconolactone} + \text{GOD(FADH2)} \quad (7)$$

$$\text{GOD(FADH2)} + O_2 \rightarrow \text{GOD(FAD)} + H_2O_2 \quad (8)$$

4.2. Physical

In the following content, the physical biosensor includes optical, piezoelectric and calorimetric biosensors are summarized and discussed.

4.2.1. Optical

Detection of biomolecules using near-infrared light between 0.9 and 1.3 eV has important biomedical applications because of greater tissue penetration and reduced auto-fluorescent background in thick tissue or whole-blood media [79]. CNTs have excellent luminescence properties [80–82], high luminous intensity [83], excellent wavelength conversion function [84], especially the tunable near-infrared emission that responds to changes in the local dielectric function but remains stable to permanent photobleaching [85]. Based on these advantages, CNTs are quickly applied in optical biosensor. Barone et al. developed near-infrared optical sensors based on SWCNTs that modulate their emission in response to the adsorption of specific biomolecules [85]. Two distinct mechanisms of signal transduction – fluorescence quenching and charge transfer for SWCNTS was elucidated by using a ultraviolet–visible–near-infrared spectrophotometer as shown in Fig. 12a. The sensing mechanism of CNT optical sensor for glucose detection is illustrated in Fig. 12b, and the porous dialysis capillary of the enzyme/SWCNT solution is shown in Fig. 12c.

4.2.2. Piezoresistive

Piezoresistive effect is the change of resistance in the effect of external force. Experimental research shows that CNTs have high strength and toughness, and their Young's modulus greater than 1 TPa [86] which is 100 times than steel while the density is only about 1/6 of the steel [87]. Therefore, CNTs have become the promising candidate material for piezoresistive CNTs-based sensor. Furthermore, it is interesting that there is no any sign of the break when the deformation of CNTs reaches to 40% [88]. The resistance and band gap relationship of the carbon nanotubes is expressed in Eq. (9). Where E_{gap} is band gap, R is the contact resistance, and t is the electronic transmission probability.

$$R = R_s + \frac{1}{|t|^2}\frac{h}{8e^2}\left[1 + \exp\left(\frac{E_{gap}}{KT}\right)\right] \quad (9)$$

E_{gap} can be expressed in Eq. (10) in the deformation of σ.

$$E_{gap} = \left|\left(\frac{\gamma\alpha^2}{16\gamma^2} - \frac{ab\sqrt{3}}{2}\sigma\right)\sin(3\Phi)\right| \quad (10)$$

Energy gap changes with the deformation can be expressed in Eq. (11).

$$\frac{dE_{gap}}{d_\sigma} = sign(2p+1)3t_0(1+\nu)\cos(3\Phi) \quad (11)$$

where $\alpha = 2.5$ Å, r is the radius of the CNTs, $b = 3.5$ eV/Å, $t_0 = 2.74$ eV, Φ is the chiral angle, r is Poisson's ratio and $p = 0$ or $p = 1$ or $p = -1$.

It is well known that the signal-to-noise ratio (SNR) is an essential performance parameter of FET-based sensors. For exploring the performance metric, a study on the SNR of piezoresistive transducers based on CNTFETs has been conducted by using a piezoresistor made of small band gap semiconducting SWCNTs (SGS-SWCNTs) as presented in the middle of Fig. 13 [89]. The results indicated that the SNR of SGS-SWCNTs had a very strong dependence on the gate bias voltage, and the best operating condition of this SWCNT-based piezoresistor was at device off-state, where strain resolution was maximal.

4.2.3. Calorimetric

The principle of thermometric measurement is that when the immobilized biological materials takes reaction with the corresponding measured objects often accompanied with the change of the heat, which generate heat effect. The sensing mechanism of the thermal CNTs-based biosensors is shown in Fig. 14a. As the changes of temperature will alter the size of CNT and create a different amount of strain on the CNT network [84], according to this principle, another thermal CNTs-based biosensor, which is similar to piezoresistive sensor, has been designed, and the sensing mechanism is illustrated in Fig. 14b. A layer of CNTs would be placed across a material containing a large coefficient of thermal expansion.

4.3. CNTFET biosensor

CNTs configured as FETs offer the advantages of possible biocompatibility, size compatibility, and sensitivity toward minute electrical perturbations for the detection of biological species [69]. In addition, the effective detect area can be made into the size of a single biomolecules or virus. What is more, the biosensor can recognize some kind of specific molecular or distinguish testing response from different types of samples by means of chemical and biological modification in the subsequent moment. In the other side, it is also low-cost, low-noise and portable [90]. Because of these unique characteristics, CNTFET biosensor has been widely used in the field of biology, such as protein, glucose, enzyme, antigen and antibody molecules, DNA molecules, bacteria and hormone [91,92]. In CNTFET biosensor, the preparation of metal electrodes as source and drain electrode are prepared on the surface of silicon substrate coated with silicon dioxide insulating layer. The connection of specific CNTs between the two electrodes is acted as conductive channel, and introducing a gate electrode, importing gate source voltage to control conduction or close [93] as shown in Fig. 15a. The CNTs were synthesized by CVD and the distance between the two electrodes is approximately 3 μm. Fig. 15b elucidates the mechanism of CNTFET biosensor. The specific antibodies can be coated with CNTs, specificity adsorption between antigen and antibody could generate an electric signal that is observed and recorded [69,94].

According to the different reactants, CNTFETs are divided into different types of FET including enzyme FET, immune FET, organization FET, cell FET, and DNAFET. Over the past decade, many groups have brought significant contributions to promote the development of CNTFET biosensors. For instance, Star et al. [95] prepared nanoscale FET devices with SWCNTs as the conducting channel for the electronic detection of specific protein binding. To avoid non-specific binding, the SWCNTs were coated with a PEI/PEG polymer layer attached with biotin for specific molecular recognition.

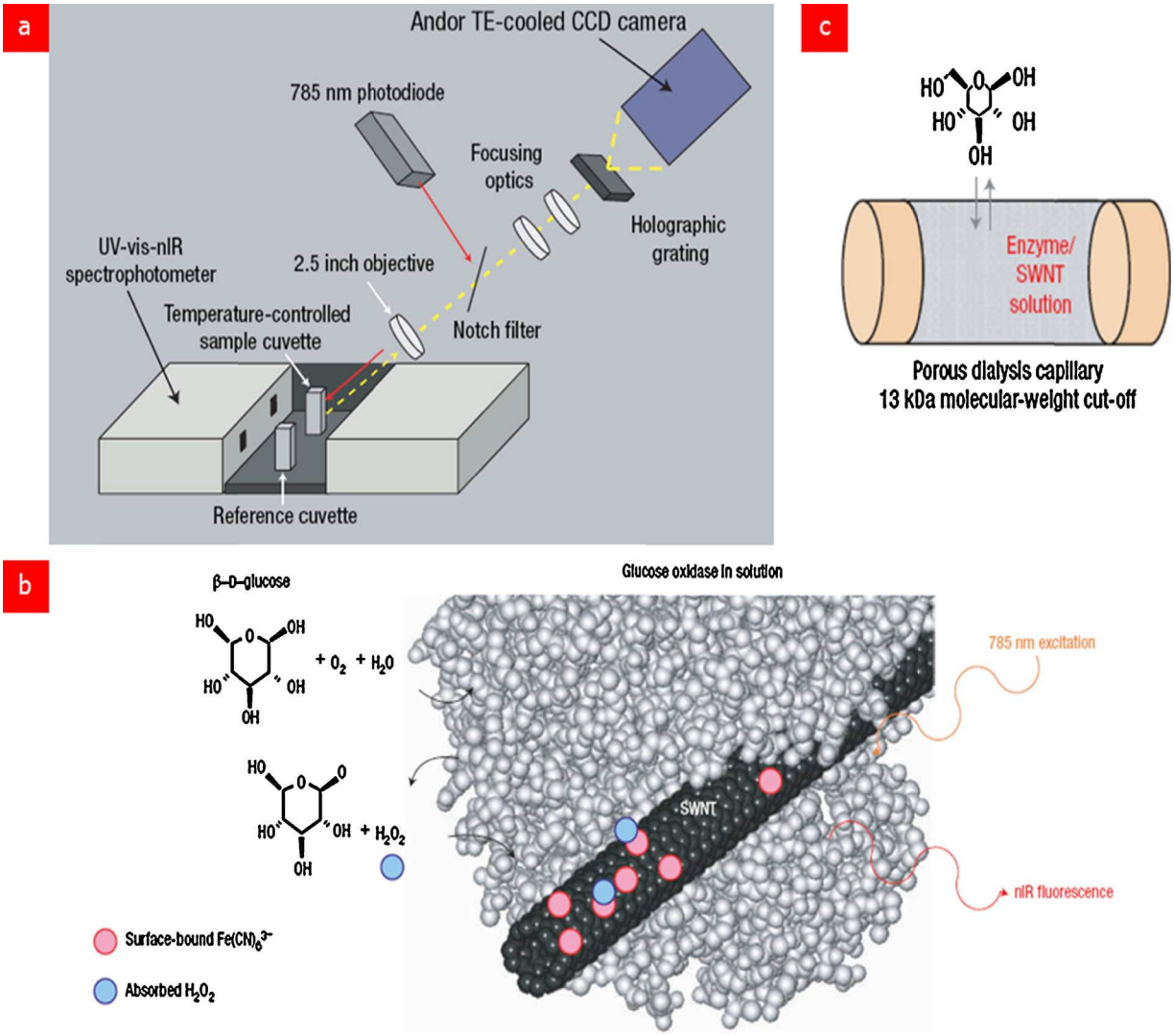

Fig. 12. (a) The schematic diagram of ultraviolet–visible–near-infrared spectrophotometer. (b) Reaction at the enzyme converts glucose to the gluconolactone with the hydrogen peroxide co-product detected by interaction with the $Fe(CN)_6^{3}$-functional groups on the exposed nanotube surface between enzyme monomers. (c) The schematic diagram of porous dialysis capillary [85].

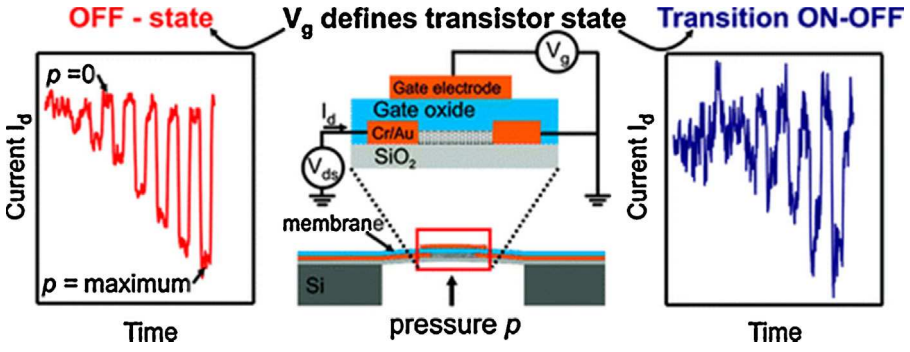

Fig. 13. SNR of a SWCNT-based piezoresistive sensors: left side is at off-state, middle is the schematic diagram of the sensor, and the right side is at transition on-off [89].

Only the biotin–streptavidin binding has been detected by changes in the device characteristic of the SWCNT-based FET nanodevices. Villamizar et al. [96] reported a fast, sensitive and label-free FET-based biosensor based on polymer coated SWCNTs for the selective determination of *Salmonella infantis*. In order to prevent the non-specific binding of other bacteria or proteins, the anti-*Salmonella* antibodies functionalized SWCNTs were treated with Tween 20. In addition, Oh et al. [97] developed a CNT film-based biosensor with a metal semiconductor FET structure for detection of amyloid-beta in human serum. Tseng et al. used CNTFET to detect DNA hybridization at the single-molecule level [88]. A single stranded probe DNA sequence was immobilized at a point defect in a SWCNT by

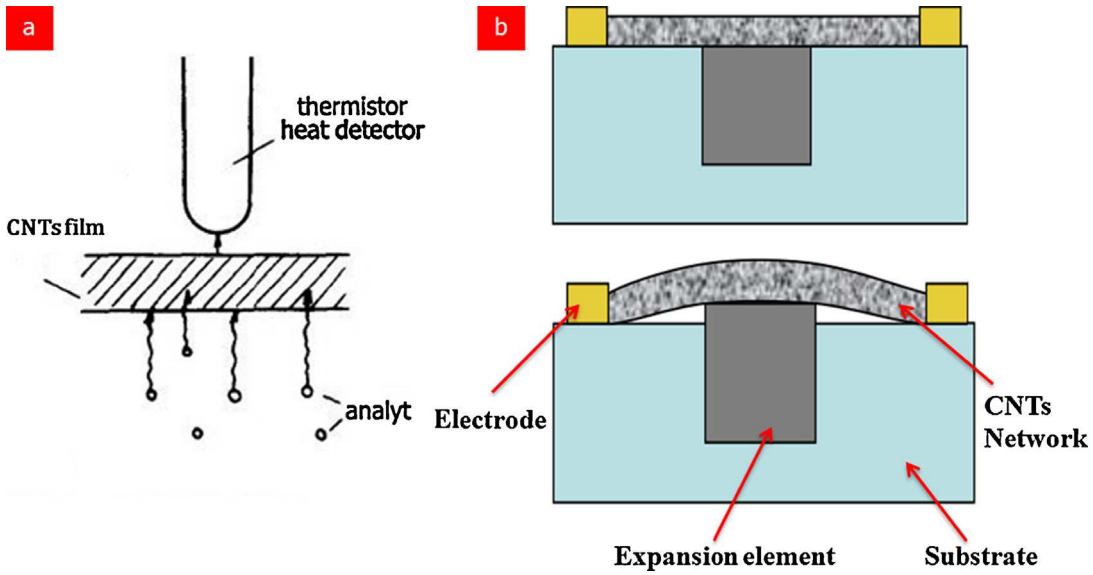

Fig. 14. (a) The reaction between biological materials and corresponding measured objects will generate heat then could be detected by tranducer. (b) When the temperature changes, the expansion element will also change, result in the deformation of CNTs.

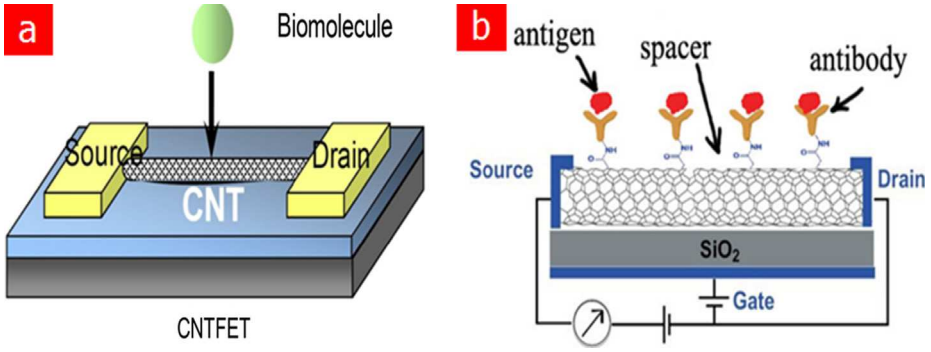

Fig. 15. (a) Exhibiting a structural model, CNTs is acted as conductive channel between the two electrodes to absorb biomolecules. (b) A schematic illustrates the working principle of CNTFET.

covalently attaching; and the DNA functionalized SWCNTs were able to measure two-level fluctuations in the conductance of the nanotube in the presence of a complementary DNA target [92].

However, it is worth noting there are still many factors can affect the accuracy of CNTFET especially the charge noise. Sharf et al. used the CNTFET biosensor platform to examine the noise generated by substrate interactions and surface adsorbates, and demonstrated that contact with substrates and adsorbates will significantly increase the charges noise in CNTFET biosensors as compared in Fig. 16 [98]. Fig. 16a shows the charge noise when the CNTs without surface adsorbates, by contrast, Fig. 16b is opposite. It is clearly observed that the charge noise in Fig. 16a is approximately the same while the charge noise in Fig. 16b fluctuates up and down between −4 and 4 mV.

In the future, the development of CNTFET biosensor will be toward these aspects: (i) CNTFET biosensor of epitaxial grid electrode; (ii) miniaturization of reference electrode; (iii) Composite multi-functional CNTFET biosensor; (iv) CNTFET biosensor Combines with flow injection system.

5. Functionalization of CNTs for biosensor

The CNTs structure is very stable due to their large intertube attraction energy, so that it is insoluble in most solvents. Therefore, the major challenge for the preparation of CNTs for biosensors is the solubility of CNTs [99]. In order to solve this problem, Functionalization of CNTs with other nanomaterials, such as polymer, proteins, DNA, enzyme, as shown in Fig. 17, to improve their dispersibility and compatibility with the target biological species [100]. Functionalized CNTs have many improved characteristics [101], such as large edge plane, high surface activity, high catalytic efficiency and more functional groups. Using the functionalized CNTs can improve the fixed efficiency of biological recognition of molecules (enzymes, DNA, antigen/antibody, etc.) in biosensors as listed in Table 2. Compared with the conventional solid-state carbon biosensors, the biosensors made of functionalized CNTs have higher sensitivity, faster response, and wider detection range. This section can be divided into two parts: (i) the roles of functionalized CNTs to address why they are important for the biosensors and (ii) how to prepare the functionalized CNTs.

5.1. The roles of functionalized CNTs

5.1.1. Immobilized enzyme

The special hollow tube structures of CNTs lead to a larger specific surface area and a lot of surface atoms of them [151]. The carboxyl on the surface of CNTs is easy to combine with protein amino via covalent binding. Hence they could be used to immobilize enzyme molecules and enhance the response signal of biosensors made of these materials [152,153].

Table 2
Detection of biomolecules using functionalized CNTs.

Analyte	Functionalized CNT for biosensors	Detection range	Sensitivity	Refs.
Proteins				
Glutamate	Glutamate dehydrogenase (GLDH) immobilized on thionine–SWNTs	0.5–400 μM	137.3 ± 15.7 μA mM^{-1} cm^{-2}	[72]
BSA	Self-assembly of oxidative SWCNTs on Au	0.1–1.2 mM	3.89 μA $μM^{-1}$	[102]
PSA	SWCNT forest bound anti-PSA	0.04–5 ng mL^{-1} (LOD 40 pg mL^{-1})	2864 mL ng^{-1}	[103]
A-fetoprotein	Glassy carbon electrode (GCE) modified with Au NPs	1–55 ng mL^{-1} (LOD 0.6 ng mL^{-1})	4.5 × 10^{-2} μA mL ng^{-1}	[104]
IL-6	SWCNT forests modified electrodes	40–150 pg mL^{-1} (LOD 30 pg mL^{-1})	3 nA cm^{-2} (pg mL^{-1})$^{-1}$	[105]
Alpha thrombin	MWCNTs were used as modifiers of SPCEs	0.39–1.95 nM	105 pM	[106]
Virus NS1	Anti-NS1 antibodies were covalently linked to CNT–SPE	40 ng mL^{-1}–2 μg mL^{-1}	85.59 μA mM^{-1} cm^{-2}	[107]
Uric acid	MWCNTs modified with AuNP	0.01–0.8 mM	10 and 20 mg L^{-1}	[108]
Carbofuran	MWCNTs modified with acetylcholinesterase	10^{-10}–10^{-3} g L^{-1}	10^{-12} g L^{-1}	[109]
Oxalate	Immobilized sorghum leaf oxalate oxidase on carboxylated MWCNT	8.4–272 μM	0.0113 μA $μM^{-1}$	[110]
Lysozyme	DNA aptamer-recognizing lysozyme was immobilized on MWCNT	2.5 mM $[Fe(CN)6]^{3-/4-}$	12.09 μg mL^{-1}	[111]
Con A	Lectin–carbohydrate biospecific interactions	3.3 pM–9.3 nM	1.0 pM	[112]
IgE	MWCNT/ionic liquid/chitosan nanocomposite modified electrode	0.5–30 nM	37 pM	[113]
Dengue virus	Anti-NS1 antibodies are immobilized on the electrode surface	0.1–2.5 μg mL^{-1}	0.035 μg mL^{-1}	[114]
Protein C	Dendrimer modified 8-channel screen-printed electrochemical array	0.64 pmol of 20 μL	1.81 μg mL^{-1}	[115]
Serotonin	Functionalized CNTs/ionic liquid nanocomposite	5.0–900.0 μM	2 μM	[116]
Myoglobin	Carbon ionic liquid electrode modified with Fe_3O_4	0.2–11.0 mmol L^{-1}	0.18 mmol L^{-1}	[117]
Dopamine	MWCNT–nafion–cysteamine modified tyrosinase	0.05–100 μM	1 μM	[118]
Glucose				
	GOx immobilized on a hybrid film of AgNPs/CNTs/chitosan	0.5–50 μM (LOD 0.1 μM)	135.9 μA mM^{-1}	[119]
	GOx bound to ZnO NPs/MWCNTs	0.1–16 mM	12.5 mA M^{-1} cm^{-2}	[120]
	Cu NPs in a self-assembled CNT film	50 μM–1.8 mM (LOD 0.1 μM)	602.04 μA mM^{-1} cm^{-2}	[121]
	Silicon dioxide Fe_3O_4@SiO_2/MWNTs	1 μM–30 mM	800 nM	[122]
	NiO-modified multi-walled carbon nanotubes	2 μM	1.77 mA mM^{-1} cm^{-2}	[123]
	Amperometric biosensor based on GOx-SWCNT	0.5–8.0 mM	32 μA mM^{-1} cm^{-2}	[124]
	CNTs modified Pt/Pd	0.062–14.07 mM (LOD 0.031 mM)	112 μA mM^{-1} cm^{-2}	[125]
	Multilayer films containing CNT, a nano-thin plasma-polymerized film (PPF)	4.9–19 mM	5.1 ± 0.9 μA mM^{-1} cm^{-2}	[126]
	Immobilize GOD onto a GCE	0.01–15.2 mM	57.0 μA mM^{-1} cm^{-2}	[127]
	MWCNTs–SnS_2 modified GCE	2.0 × 10^{-5} M–1.95 × 10^{-3} M	21.65 mA M^{-1} cm^{-2}	[128]
	SWCNTs-$PhSO_3^-$	0.02–6 mM	6 μA mM^{-1} cm^{-2}	[67]
	Composite films combine with polyaniline, SWCNTs and Prussian Blue	10^{-5} M–5 × 10^{-3} M	15.5 μA mM^{-1} cm^{-2}	[129]
	Ni3S2 were dispersed over MWCNT surface	30–500 μM	3345 μA mM^{-1}	[130]
	G/MWCNTs hybrid material	4.8 μM cm^{-2} (LOD)	29.72 mA M^{-1}	[131]
DNA/gene				
	Probe DNA immobilized on aligned MWCNT thin films	50–200 nM	0.02 μA nM^{-1}	[132]
	Combine SWCNTs with Pt	Up to 510 μM	45.6 nA mM^{-1}	[133]
	Chitosan and MWNTs was coated on a GCE	1.0 × 10^{-13}–5 × 10^{-10} M	8.5 × 10^{-14} M	[134]
	p-Aminobenzoic acid was immobilized on the surface of the electrode modified with SWCNTs with carboxylic acid groups	1.0 × 10^{-12}–1.0 × 10^{-7} M	3.5 × 10^{-13} M	[135]
	PANF-MWCNT-CHIT-DNA modified CPE	1.0 × 10^{-13}–1.0 × 10^{-7} mol L^{-1}	2.7 × 10^{-14} mol L^{-1}	[136]
Test DNA	Layer-by-Layer MWCNT-PABA-AuNP modified GCE	1.0 pM–5.0 nM		[137]
miRNA	DNA probes were immobilized onto the surface of MWCNT-modified glass carbon electrodes		4.963 μA cm^{-2} $decade^{-1}$	[138]
Others				
Acrylamide	c-MWCNT/CuNP/PANI	5 nM–75 mM	72.5 μA nM^{-1} cm^{-2}	[139]
Fructose	D-fructose dehydrogenase (FDH) bound to MWCNTs	5–40 mM		[140]
Galactose	A laponite clay film coated on a Pt electrode surface	1.0 × 10^{-6}–1.6 × 10^{-3} M	85 mA M^{-1} cm^{-2}	[141]
Shigella flexneri	HRP–anti-*S. flexneri* immobilized by physical adsorption on the MWCNT	10^4–10^{11} cfu mL^{-1}	3.1 × 10^3 cfu mL^{-1}	[142]

Table 2 (*Continued*)

Analyte	Functionalized CNT for biosensors	Detection range	Sensitivity	Refs.
E. coli	Porous pseudo-carbon paste electrode modified with carboxylic MWNTs	1.0×10^3–1.0×10^7 cells m:$^{-1}$	8.0×10^2 cells mL^{-1}	[143]
NADH	PolyXa/FAD/MWCNTs	5×10^{-6}–1.7×10^{-4} M	155 μA mM^{-1} cm^{-2}	[144]
Hypoxanthine	Xanthine oxidase was immobilized carbon film and on CNT-modified CF		0.75 μM	[145]
D-Xylose	Xylose dehydrogenase/MWNTs composite film-modified electrode	0.6–100 μM	0.5 μMd-xylose (S/N = 3)	[146]
Guanine	MWCNTs decorated with Fe_3O_4	0.05–8 μM	5 nM	[147]
Cholesterol	Nanocomposites MWCNTs–GO–Thi–Au	0.15–828 μM	50 nM	[148]
Lactate	Bionanocomposite was immobilized on the surface of a GCE	2.0 μM–0.40 mM	6.0 μA mM^{-1}	[149]
Ethanol	The electrode surface was modified with the polymer and f-MWCNTs	5.0×10^{-6}–30×10^{-4} mol L^{-1}	150 μA mM^{-1} cm^{-2}	[150]

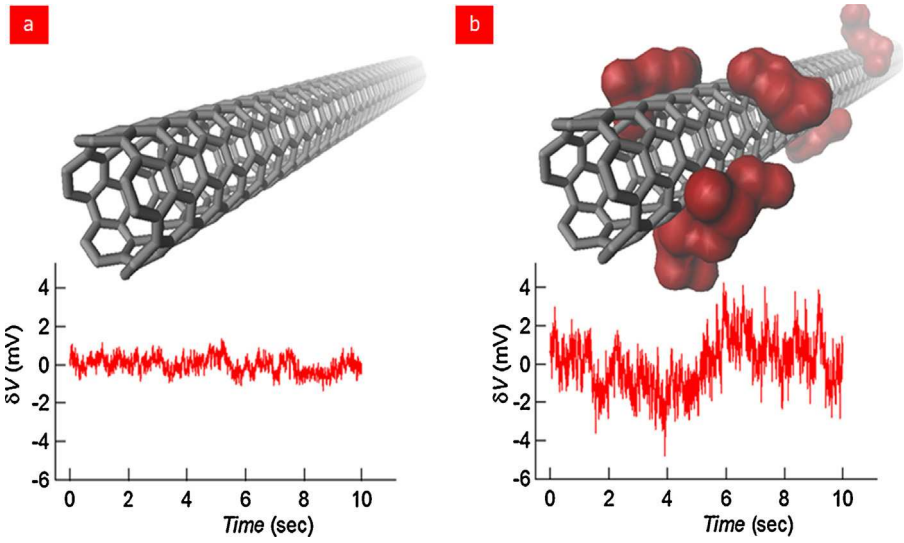

Fig. 16. (a) A schematic of charge noise when the CNTs without surface adsorbates. (b) A schematic of charge noise when the CNTs with surface adsorbates [98].

5.1.2. Electrical catalysis of biological molecules

It is well-known that the acidification treatment can introduce a lot of functional groups (—OH, —CHO, —COOH, etc.) [154] to the surface of CNTs to create surface defects [125]. The difference of surface microenvironment will result in the different distribution of the surface energy of CNTs and this can provide a large number of active site to make the functionalized CNTs have good catalytic activity for biomolecules.

5.1.3. Improve the reversible oxidation–reduction of biological molecules

Many investigations suggest that introduction of some functional groups (e.g. —COOH) can significantly facilitate the electron transfer processes to enhance the reversible oxidation–reduction, by providing more active sites for the reactions. For example, the oxidation–reduction reaction process, which can be described respectively by using Eqs. (12) (reduction process) and (13) (oxidation process), and can be improved by introducing the carboxyl onto the surface of CNTs. Compared with the glassy carbon, the efficiency of the functionalized CNTs is much higher [155].

$$\text{MWNTs-COOH} + 4e^- + 4H^+ \rightarrow \text{MWNTs-CH}_2\text{-OH} + H_2O \quad (12)$$

$$\text{MWNTs-CH}_2\text{-OH} + H_2O - 4e^- \rightarrow \text{MWNTs-COOH} + 4H^+ \quad (13)$$

5.1.4. Reduce the overpotential of redox reaction

Many enzyme biosensors utilize oxidase to oxidize the substrate, at the same time, produce hydrogen peroxide [156]. Due to their special nanotubes structures and abundant surface functional groups, CNTs can enhance its bioelectrocatalytic activity for redox reaction, generally presents a negative shift of the oxidation peak, namely lower oxidation potential [78,157].

5.1.5. Direct electron transfer

The enzymes can transfer electron effectively and directly on the surface of functionalized CNTs and maintain its bioelectrochemical activity [158,159] without the need to add electronic media or promoter to determine the substrate, which can greatly simplify the fabrication steps of relevant sensors [160]. The high surface activity is advantageous to the electron transfer between the biological sensing materials, such as enzyme and proteins and the CNTs [161], this makes CNTs can achieve a direct electronic transmission [161]; on the other hand, because of the unique nanostructures of CNTs, they can act as "molecular wires" to transfer electrons to the redox center of the biological sensing materials [162].

5.2. The methods for the functionalizing CNTs

The functionalizations of CNTs can be achieved by physical and chemical approaches. Physical modification utilize the mechanical means such as ultrasonic, milling, crushing and friction to activate CNTs surface to change their surface physical and chemical structure [163]. This method can increase CNTs' internal energy and surface activity and then make the tubes react with or attached to other materials, to attain the purpose of the surface modification. At present, the large shear force or ultrasonic processing is often used to disperse CNTs [164,165]. In addition, high-energy

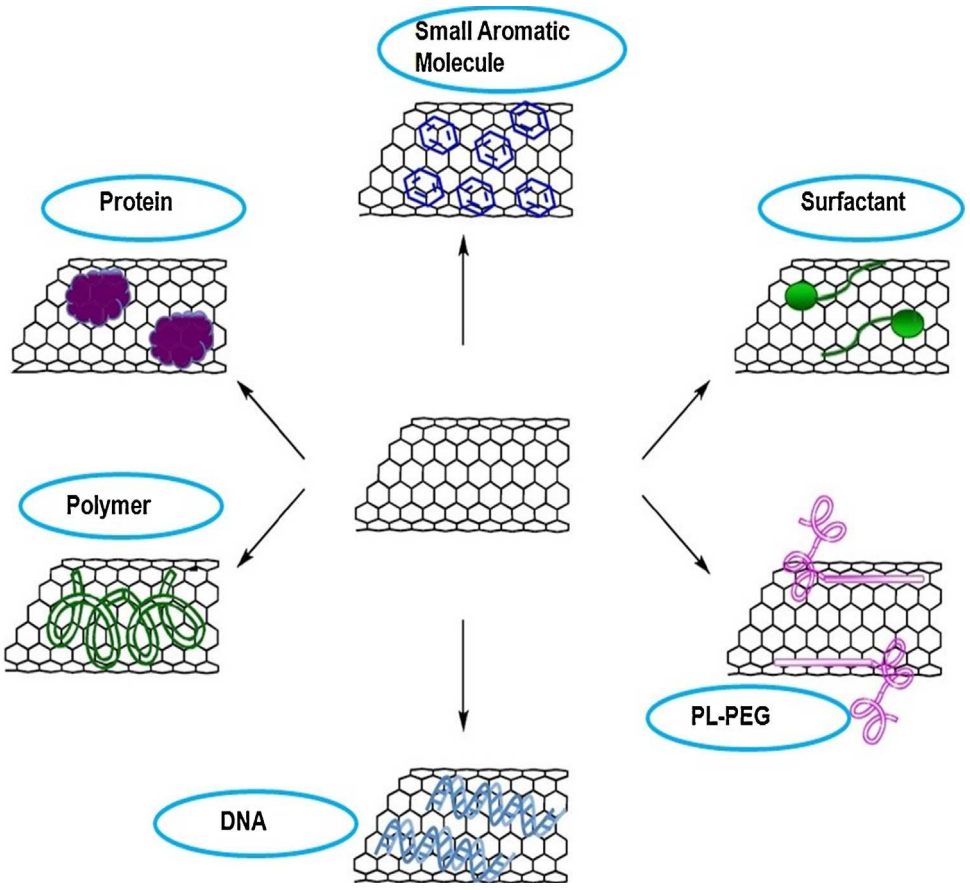

Fig. 17. Functionalization of CNTs with various nanomaterials.

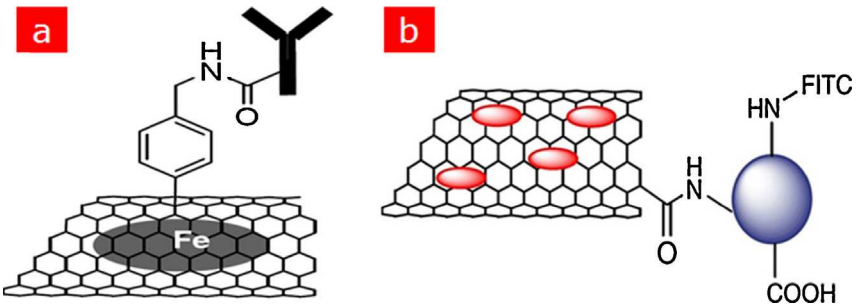

Fig. 18. Covalent modifications of CNTs. (a) Covalent modification occurs in side-wall while (b) Occurs in tip defects.

modification (i.e., ultraviolet, plasma beam [166], electron beam, high-energy corona discharge, μ ray) is also a kind of effective surface modification method of CNTs.

In general, chemical approach mainly has two methods: covalent modification and non-covalent modification. However, only non-covalent modification can remain the original structure and properties of CNTs, and does not damage the π system [167,168] while the structure of covalent modification is more stable. And they are discussed in the following sections.

5.2.1. Non-covalent modification

The highly delocalized π electron via sp^2 hybridization of carbon atoms in CNTs can be combined with other compounds containing π electrons through the π–π non-covalent bonding effect. According to this principle, functionalization of CNTs can be realized by non-covalent modification [158]. Non-covalent modification of CNTs will not damage the π system of tubes, and the tubes are expected to be reassembled into orderly network. Intact structure of CNTs can be obtained even if a large number of functional groups are coated on their surface. But the non-covalent bond is much weaker than covalent bonding. Non-covalent modification generally uses conjugated polymers [169], bioactive molecules (e.g. DNA, enzyme, protein) [170] and conjugated polycyclic aromatic hydrocarbons (e.g. pyrene and its derivatives) [171] to disperse and functionalize CNTs. Non-covalent modification using conjugated polymers has been applied to many areas in developing CNT-based biosensors. DNA is an often used bioactive molecules for the non-covalent modification of CNT [172], and the DNA/CNTs biosensors have been widely applied in the detection of all kinds of biospecies such as HIV virus. Besides, such as GOD, and horseradish peroxidase also have been wrapped in MWCNTs by layer-by-layer assembly to modify the CNTs [173]. CNTs can be dispersed via means of physisorption use the surfactants including gum arabic, amylose, polyvinyl pyrrolidone, or Triton X-100 and so on. The

poly(carbonate-urea) urethane has been used to wrap MWCNTs to improve their dispersibility [174]. Proteins are the commonly used material to disperse CNTs efficiently in aqueous medium. Iancu et al. utilized functionalized MWCNTs with serum albumin to detect liver carcinoma cells [175].

5.2.2. Covalent modification

Covalent modification often occurs in tip defects as well as side wall of CNTs (see Fig. 18). The principle of the method is that the CNTs are first oxidized by high concentration acid and are cut into short tubes, and this followed by introducing functional groups (e.g. carboxyl) onto in the terminal or the defect sites of lateral wall of CNTs. Therefore, CNTs can be functionalized with different functionalities by covalent modification to meet the different requirements of biosensing applications [176]. Covalent modification in tip mainly includes carboxylation and subsequent derivatization, such as amidation and esterification reaction. By contrast, covalent modification in side wall generally includes fluorination, alkylation reaction, cycloaddition. Although, covalent modification can improve the properties of CNTs, to a certain extent it will destroy the sp^2 structure of the CNTs, thus influence their stability.

5.2.2.1. Carboxylation and subsequent derivatization reaction. Carboxyl reaction refers to oxidized CNTs through chemical reaction to generate activating group like carboxyl. It is relatively simple and mature method to modify the CNTs. The usually used high concentration acid for oxidizing and cutting CNTs is HNO_3 [177], H_2O_2/H_2SO_4, K_2CrO_4/H_2SO_4, $KMnO_4/H_2SO_4$ [178], or OsO_4. Coupling agents, such as hydroxybenzotriazole and carbodiimides: N-(3-dimethylaminopropyl)-N-ethylcarbodiimide and N,N-dicyclohexylcarbodiimide [179] are also used. After the carboxylation, the hydrogen-bonding still exists in the surface of the CNTs and leads to the gather of CNTs, thus affecting their solubility and dispersion. Therefore, it needs further carboxyl derivatization and destroys the hydrogen-bonding to improve the dispersity. The carboxyl derivatization can be achieved by esterification or amidation with alcohol or amine moieties respectively for introducing the function group —COOH, which can be converted to ester or amide.

5.2.2.2. Lipidation or phthalein amination. Biosensors based on lipidation or phthalein amination CNTs have been applied in the detection of many biomolecules, such as proteins, DNA, carbohydrates, enzymes. For instance, tumor lysate protein has been conjugated to MWCNTs by amidation reaction to enhance the efficacy of an antitumor immunotherapy [180], and the functionalized CNTs had the potential to improve the prognosis of cancer treatment. Yoshimura et al. demonstrated a covalent coupling of a protein of interest to the end of CNTs with an azide group without disturbing the function of protein by using a modified Staudinger–Bertozzi ligation [181]; they also observed that the calmodulin can be attached to the end of the CNTs without affecting the ability to bind to the substrate in a calcium-dependent manner (see Fig. 19), which can be used for developing Ca^{2+}-biosensor. It is also known that using poly ethylene glycol to modify CNTs can improve its biocompatibility of CNTs [182]. DNA can also be attached to CNTs by amidation to enhance the sensitivity of CNTs to DNA recognition [68]. Through the introduction of carbohydrates, the surface properties of CNTs can be modified not just to improve their water solubility but also to enable these versatile nanostructures to interact selectively with biological systems for biosensor applications [183]. For example, galactose-tethered amino groups modified SWCNT was found highly efficient in capturing *Escherichia coli* in physiological solutions. In addition,

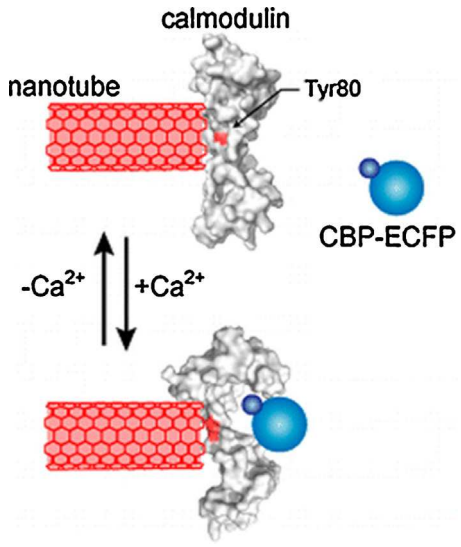

Fig. 19. CNTs attached with calmodulin protein for Ca^{2+}-biosensor [181].

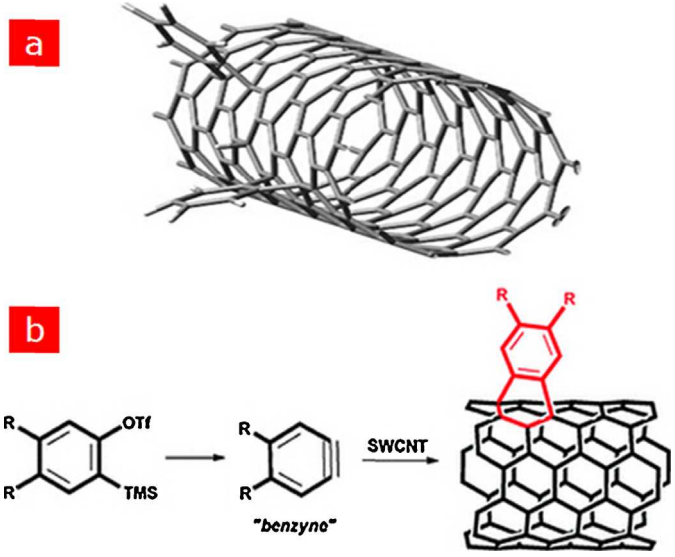

Fig. 20. (a) The structure stereogram of CNTs cycloaddition. (b) The cycloaddition scheme of CNTs, R is the compound that we need [185].

polymers also have been functionalized into CNTs for delivery, imaging, and sensing in cancer research [184].

5.2.2.3. Cycloaddition. Cycloaddition refers to the reaction that makes molecular of olefins or conjugated olefins become a cyclic compound. As the same as amidation, the function groups generated by cycloaddition are also mainly happened at the tips and defect sites of CNTs. Langa et al. has firstly carried out the cycloaddition of benzyne to SWCNT [185], and the three-dimensional stereogram of this CNT cycloaddition product is given in Fig. 20a. The general procedure for the covalent functionalization of SWCNT can be schemed in Fig. 20b. There are two key steps: (i) preparing the benzynes which linked the required compound, and (ii) attaching the benzyne to SWCNTs though cycloaddition. Cycloaddition reaction has the advantages of good stability, mild, high yield, and easy to get the product. Ali-Boucetta et al. utilized cycloaddition to obtain well-dispersed short and individualized MWCNTs [186]. It was found that the highly functionalized MWCNTs did not accumulate in any tissue and could be excreted in the urine. And Al-Jamal et al. took in vivo experiments to indicate that the degree

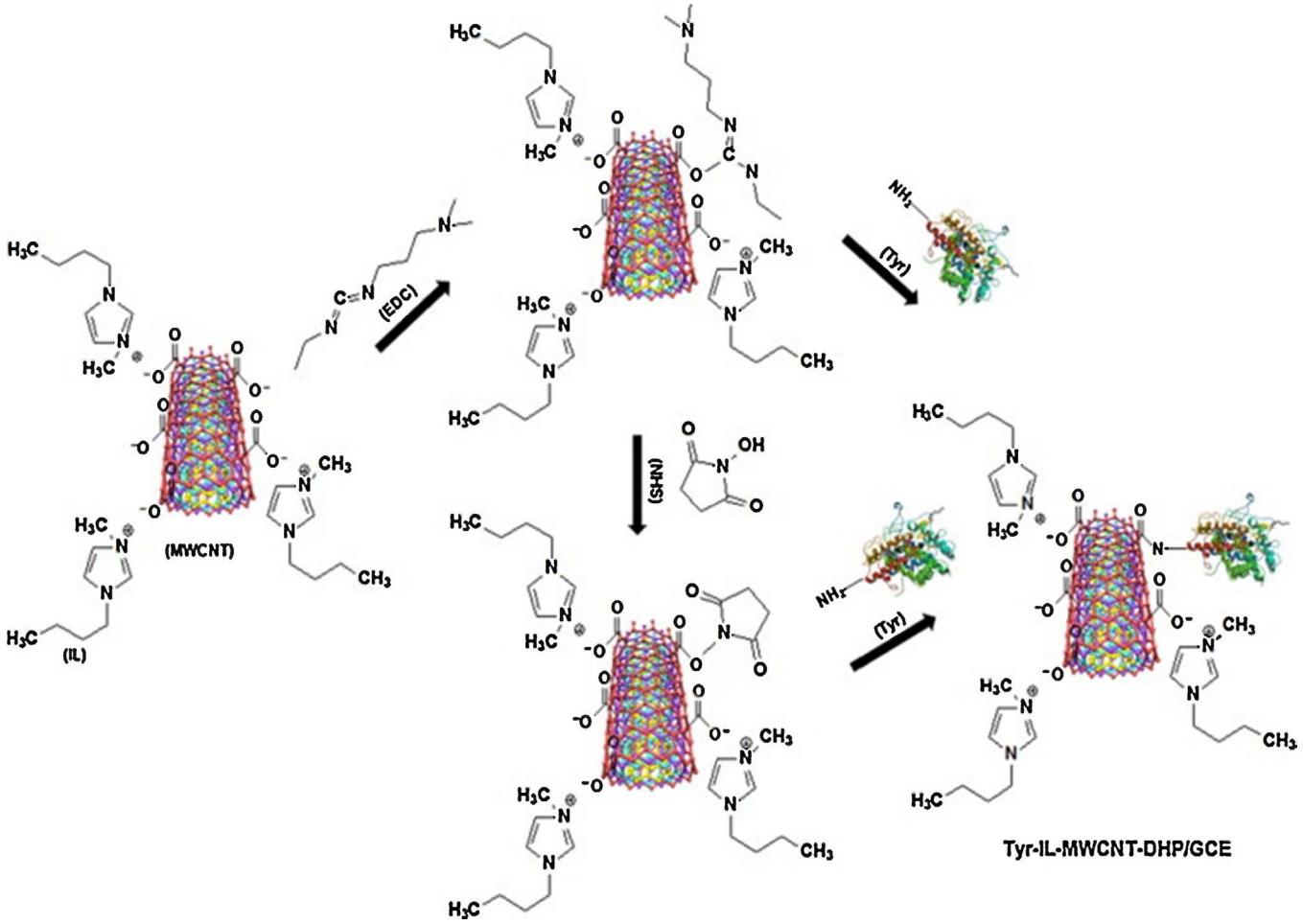

Fig. 21. Scheme displaying the preparation and functioning of the Tyr-IL-MWCNT-DHP/GCE biosensor.

of chemical functionalization of CNTs will determine tissue distribution and clearance profiles [187]. Controlling these properties is very important for the potential design of CNT-based biosensors for diagnostics.

6. Applications of CNT-based biosensor

6.1. Enzyme biosensors

Enzyme biosensors are the most popular type of biosensors, and many commercialized biosensing devices are based on it. The large surface area of CNTs is contributed to biomolecular conjugation, and this unique characteristic has been used for constructing the enzyme biosensors [158]. For example, Vicentini et al. developed a tyrosinase biosensor based on a GCE modified with functionalized MWCNT, 1-butyl-3-methylimidazolium chloride (ionic liquid = IL) and tyrosinase (Tyr) within a dihexadecylphosphate (DHP) film [188]. The fabrication process of the tyrosinase biosensor is illustrated in Fig. 21. The use of MWCNT and IL led to a synergistic effect by combining the high conductivity and biocompatibility of the IL with the electrocatalytic activity of MWCNT and enhanced the response signal of the biosensors. This biosensor also exhibits high stability and long lifetime. In addition, an enzyme biosensor was developed for the detection of androsterone by using 3α-hydroxysteroid dehydrogenase immobilized onto a CNTs/IL/NAD^+ composite electrode [189].

Glucose detection is one of the important applications of enzyme biosensors because the concentration of blood glucose is one of the important indicators of human health. The glucose biosensor is widely used and investigated [190]. A novel, excellently stable glucose biosensor based on a chitosan-bovine serum albumin (Chi-BSA) cryogel with incorporated MWCNTs, ferrocene (Fc), and GOD was successfully fabricated by Fatoni and his coworkers [191]. The MWCNTs/Chi-BSA-Fc/GOD biosensor showed high operational stability with a wide linear range and a low Michaelis–Menten constant. For the detection of glucose, this biosensor was not affected by dissolved oxygen and showed no response to the common interferences in blood samples such as, ascorbic acid and uric acid, in physiological levels [191]. Meanwhile, a highly selective amperometric glucose biosensor based on GOD dispersed at MWCNT/graphene oxide hybrid composite modified electrode was developed by Chen et al. [192]. There is a new trend to develop non-enzymatic CNT-based biosensors for glucose detection. For instance, a highly sensitive non-enzymatic glucose biosensor was prepared by dispersing nickel and copper nanoparticles instead of enzyme on the MWCNT electrode as illustrated in Fig. 22 [193]. These biosensors can effectively analyze glucose concentration in human serum samples, avoiding interference, with a ultra-low detection limit, and it is a promising non-enzymatic glucose sensor due to its low overpotential, high sensitivity, good selectivity, good stability, fast response, and low cost. Another kind of non-enzymatic glucose biosensor was developed by depositing

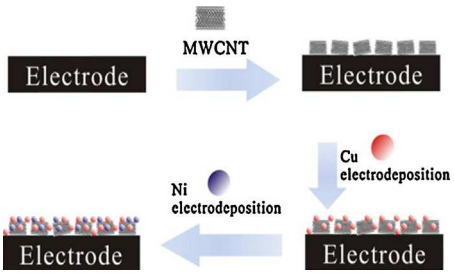

Fig. 22. The diagram of manufacturing operation of non-enzymatic glucose biosensor. The process is bare, MWCNT, Cu/MWCNT, Cu/Ni/MWCNT step by step.

gold nanostructures onto CNT electrode via pulsed laser and also showed a remarkable performance [194].

6.1.1. Immobilization of enzyme

In enzyme biosensor, the enzyme acts as a biological recognition element, thus its immobilization directly affects the performance of the enzyme biosensor, such as lifetime, selectivity and sensitivity [158]. Immobilized enzyme on CNTs can keep good biological activity and has good stability, durability. Therefore, immobilization of enzyme is a key step for the preparation of CNT-based enzyme biosensor. There are a variety of immobilized methods [195], mainly including: physical activity adsorption, cross-linking, covalence, and embedding. Here, we will introduce them one by one in the following sections. Table 3 lists the various immobilization methods of enzyme in CNTs-based biosensors in recent years.

6.1.1.1. Physical adsorption. Physical adsorption is the simplest method for the immobilization of enzyme, and the biological sensitive reagents are adsorbed on the surface of the substrate through van der Waals force, ion inter-atomic force or hydrophobic interactions. This method does not need chemical reagent and has small influence on enzyme activity. Pastorin et al. have contributed a wonderful work to analyze the influence of CNTs on enzyme activity and structure by investigating the different immobilization procedures through enzyme kinetics and circular dichroism studies (see Fig. 23) [195]. Their results indicated that the enzyme physically adsorbed (see Fig. 23a) onto CNTs has much higher activity than the other methods like covalent bonding (see Fig. 23b). Yao et al. have developed a simple, rapid and highly sensitive SWCNT-based enzyme biosensor for the detection of sterigmatocystin (ST) [212]. In their study, a new enzyme named aflatoxin-oxidase (AFO) cloned from *Armillariella tabescens* was immobilized onto a chitosan-SWCNTs modified Au electrode via electrostatic interactions and hydrophobic interactions. But the enzyme physically adsorbed onto CNTs is very sensitive for the solution of the temperature, ionic strength, pH and substrate concentration [196]. At the same time, the adhesion strength between enzyme and electrode substrate surface is weak, biological molecules are easily pulled away from the electrode hence the average lifetime of the electrode is shorter. For addressing this issue, some new methods have been developed based on physical adsorption, for example, Yola prepared AuNPs/p-MWCNs nanocomposites and detected quercetin and rutin simultaneously by a new square wave voltammetry method [213].

6.1.1.2. Covalent bonding. Covalent bonding is that the enzyme molecules combined with the surface of CNTs via covalent bond. A procedure of the attachment of oxidized enzyme on CNTs is exhibited in Fig. 23c. In general, this process usually has some special requirements on the environment conditions, such as low temperature (0 °C), low ionic strength and physiological pH. Furthermore, it often joins the substrates of enzyme in order to prevent the enzyme's active site from bonding with the electrode surface [214]. For this purpose, chemical reagent (such as silane) is usually used to activate the electrode surface, and then the enzyme is directly bonded on the surface of active electrode. On the opposite, comparing with adsorption enzymes, covalently immobilized enzymes are combined closely with carrier, thus have high stability and repetition of usability [215,216]. It is worth mentioning that covalently immobilized enzymes have time operability longer than that of the adsorbed enzymes. Generally, the activity of adsorption enzymes is not big [217]. In Wang's experiment, between 3 and 4 h the activity of adsorption enzyme is highest, but the later time the activity will decrease sharply while the cross-linking enzyme begins to decline after 8 h [218]. In Arica's experiment, for the covalently immobilized enzymes, an increase in coupling time led to an increase in extent of immobilization, this relation leveled off after 18 h [219]. However, the formation of covalent bond will results in reducing the biological activity of enzymes to a certain extent, thus affecting the overall performance of the sensor. To solve these problems, covalent bonding has been improved [75,220]. For example, Tan et al. have showed that the lipase via covalent immobilization on the magnetic MWNTs exhibits a high activity [206].

6.1.1.3. Cross-linking. Cross-linking for the enzyme immobilization is to use bifunctional or multifunctional reagents to form cross-linked network structure between enzyme molecules or between the enzyme molecules and gel/polymer. The commonly used cross-linking agent is glutaraldehyde, which is a bifunctional reagent. The typical characteristic of this reagent is that the ends of their molecule structure have two aldehyde groups which can react with enzyme or protein amino to form similar Schiff base derivatives. CNTs film is also a powerful platform as a host of enzyme immobilization to improve the sensitivity of enzyme-based biosensors due to their good connectivity leading to the increased electron transfer rate [203,221]. The porous CNTs films with high network density provide not only the open pores to host more enzyme molecules, but also the ultra-high specific surface area of CNT as enzyme hosting sites [203]. Jung and co-workers have fabricated an excellent performance biosensors based on enzyme precipitate coating in gold nanoparticle-conjugated SWCNTs network films (see Fig. 24). The SWCNTs network films based biosensors have shown a high-performance for the detection of glucose with a remarkable sensitivity [203]. In addition, supramolecular self-assembly film, physical adsorption and gel/polymer embedding methods are often supplemented by cross-linking method to prevent leakage of enzyme.

6.1.1.4. Embedding. Embedding immobilization is to embed the biomolecules [210] in polymer gel, film or the substrate of surfactant [222]. For instance, embedding the GOD and CNTs in a bioadhesive film of chitosan can achieve a good performance of the lack of direct electron transfer. Generally, it does not need to bind with the biomass residues, therefore, embedding immobilization rarely changes the advanced structure of bioactive substances, which the biological activity loss rarely. So far, it is the most common used immobilization technology.

6.2. DNA biosensors

The well known DNA biosensors have been used for medical diagnostics, forensic science, agriculture, or even environmental clean-up efforts just after there were developed. The heart of DNA biosensor is the sensing element – nucleic acid such as single-stranded DNA (ssDNA) or double-stranded (dsDNA). It is found that ssDNAs adsorb strongly on CNTs, while duplex DNAs cannot bind to CNTs stably [80]. This unique property has been employed to

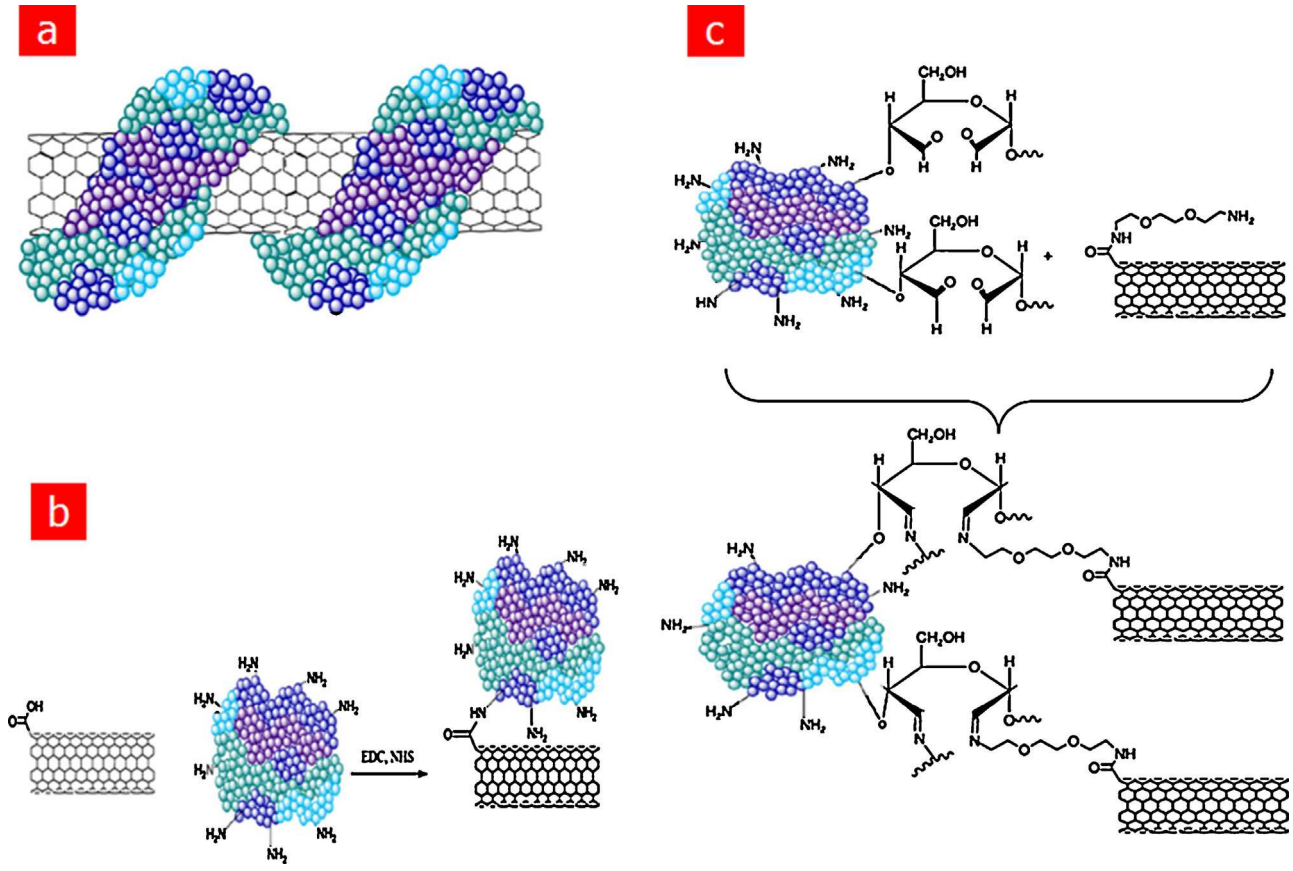

Fig. 23. The different immobilization approaches of enzyme on CNTs. (a) The schematic diagram of physical adsorption of enzyme around CNTs. (b) The covalent immobilization of the enzyme on CNTs through carbodiimide chemistry. (c) Functionalization of CNTs (SWNTs–NH_2 and MWNTs–NH_2) with oxidized enzyme (amyloglucosidas) [195].

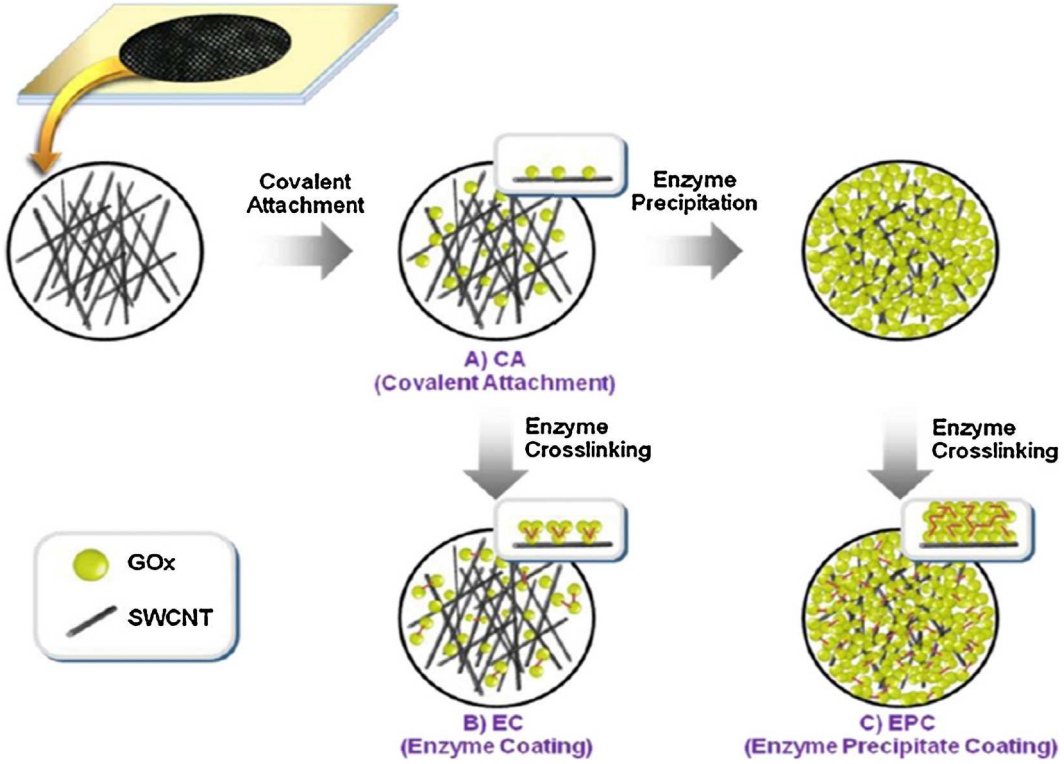

Fig. 24. Schematic illustration of enzyme immobilization methods on the SWCNT film: (A) CA, (B) EC, and (C) EPC were prepared by using three different methods of "covalent-attachment", "enzyme crosslinking", and "enzyme precipitation and crosslinking", respectively. The illustrations in the rounded rectangles are schematic configurations of SWCNT and GOX molecules for each type of specimens [203].

Table 3
The immobilization methods of enzyme.

Method	Enzyme	Immobilization	Refs.
Adsorption	GOD	In Pt-MWCNT-ACS	[196]
	Laccase	In modified screen-printed electrode	[197]
	Horseradish peroxidase	In MT-MWCNs	[109]
	GOD	In CNTs	[198]
	Lipase	In raw-MWCNT	[199]
	Acetylcholinesterase	In MWCNT	[109]
Crosslinking	Tyrosinase	In IL-MWCNT	[200]
	Tyrosinase	Tyrosinase layer with an electropolymerized film containing CNTs	[201]
	GOD	In MWCNT immobilized by 1-ethyl-3 together with EDC/NHS	[202]
	GOD	In SWCNT network films	[203]
	Horseradish peroxidase	HRP on a GCE modified with MWCNTs	[204]
	Laccase	In c-MWCNTs	[205]
Covalent bonding	Aflatoxin-oxidase	In MWCNTs-modified Pt electrode	[75]
	Lipase	In M-MWCNTs	[206]
	Catalase	Protective layer of inert carbon nanotubes	[207]
	GOD	CNTs chitosan-based porous membranes	[208]
	Xylanase	In MWCNTs	[209]
Embedding	Tyrosinase	In MWCNTs	[210]
	GOD	GOx and CNTs were embedded in a bioadhesive film of chitosan	[161]
	Horseradish peroxidase	Gr/f-MWCNTs/(Rd-GLD)/HRP	[211]

elaborately design CNT-DNA biocomplexes for applications in biosensing technology for various molecular targets. Tang et al. have fabricated completely electronic DNA sensors based on SWCNT-FET, which are readily amenable to integration with high-density sensor arrays in "system-on-chip" for microanalysis devices [92]. The SWCNT acts as the transducer which translates and amplifies DNA hybridization on Au into a directly measurable electrical signal. In comparison with most of the commercially available optical and other electrochemical DNA biosensors, this new developed sensing platform has shown much simpler chemistry and easier set up.

In addition, a simple and ultra-sensitive DNA biosensor based on MWCNT signal amplification and fluorescence polarization (FP) detection has been successfully developed for monitoring the activity and inhibition of DNA methyltransferase (MTase) in homogeneous solution [223], and the working principle of this MWCNT-based DNA biosensor is represented in Fig. 25. The DNA probe was consisted of dsDNA and restriction endonuclease. The FAM-labeled DNA probe is cleaved by restriction endonuclease without DNA MTase.

Recently, Zhang et al. designed a sensitive DNA biosensor based on a glassy carbon electrode modified with MWCNTs, polydopamine (PDA), and gold nanoparticles, for sequence-specific DNA detection [224]. Fig. 26 shows the immobilization and hybridization detection of probe DNA [224]. The Au-NPs/PDA/MWCNTs film sensor interface significantly enhanced the performance of the electrochemical DNA biosensor. This novel sensing platform exhibits excellent sensitivity and selectivity and has been utilized in human serum samples for an assay of complementary target DNA analysis with satisfactory results.

6.3. Other CNT-based biosensor

Immune sensor is the use of the function of combination and recognition between antigen and antibody to detect target biomolecules, such as protein [225], drug [226], and hormone [227]. Antigen will be specifically combined with the antibody, thus different signals change base on compound produced by the reaction of antigen and antibody. The application of immune sensor is mainly in clinical medicine. For instance, Yu et al. developed amplified electrochemical immunosensors based on SWCNT forest platforms with multi-label secondary antibody-nanotube bioconjugates for highly sensitive detection of cancer biomarkers in serum and tissue lysates [228]. These SWCNT immunoassay platforms show excellent accuracy for clinical screening and point-of-care diagnostics. In addition, an sensitive electrochemical immunosensor for the detection of cholera toxin (CT) using liposomes and poly(3,4-ethylenedioxythiophene)-coated CNTs has been fabricated [81]. Additionally, Faridbod et al. have developed a novel ultra-sensitive immunosensor for the detection of pesticide such as atrazine using antibody combined with Au nanoparticles, MWCNTs and ionic liquid on GCE surface (see Fig. 27a) [229]. This biosensor has shown excellent sensing performances such as low response time (<9 s), high sensitivity with repeatability (R.S.D. value of 3.7%) and long-term stability (40 days with a decrease of 8.9% in response) (see Fig. 27b).

Near-infrared light between 0.9 and 1.3 eV has significant potential for biomedical detection because of greater tissue penetration and reduced auto-fluorescent background in thick tissue or whole-blood media [85]. The other advantages of the near-infrared signaling there are no blinking, no bleaching and a large Stokes shift [230]. Strano and his co-workers have observed a tunable near-infrared emission of CNTs that responds to changes in the local dielectric function but remains stable to permanent photobleaching [85]. This excited result displays new opportunities of CNTs that modulate their emission in response to the adsorption of specific biomolecules for optical nanosensors, which can be operated in strongly absorbing media of relevance to medicine or biology. Several CNT-based optical biosensing platforms have been developed using the near-infrared signal [230–233]. Fig. 28a exhibits that the SWCNTs are functionalized with a chelated nickel ion and wrapped in chitosan, which acts as the docking site for a modulator of the SWCNT intensity and His-tagged lectin. Fig. 28b exhibits that nanotube gel is excited with a laser, SWCNT emission is collected via an inverted microscope [232]. When a free glycan or glycoprotein is detected, the signal is increased [232]. For example, Cao et al. used absorption spectra of SWCNTs to detect DNA hybridization. They had demonstrated that the DNA hybridization on the sidewall of SWCNT resulted in systematic red shifts while metallic species did not show any shift in the absorption spectra [233].

6.4. Practical concerns of CNT-based biosensor

Although CNT-based biosensor has been widely used because of better performance compared with previous one, it still has many practical concerns in application. The fabrication of biosensor

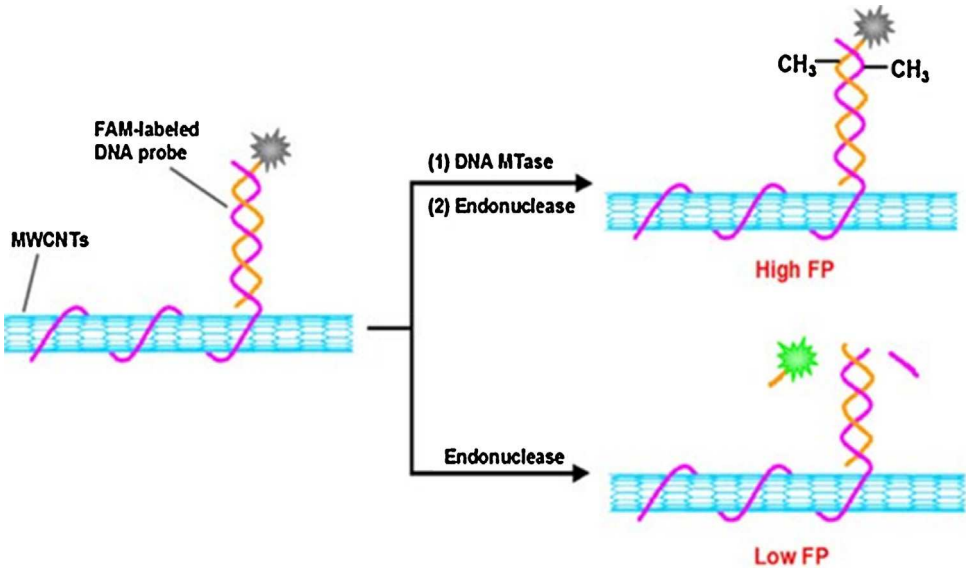

Fig. 25. The principle of the MWCNT-based FP sensing platform for the detection of methyltransferase [223].

usually needs specific size and helicity of CNTs [234]. However, it is a formidable task for the selection of the size and helicity of CNTs because it is difficult to control the size of CNTs in the manufacturing process. In addition, the existing technology is also difficult to make a cost-effective mass production of CNTs and achieve a high purity. Purity is crucial for CNT-based biosensor; some researches are required to arrive at highly purity (99.99%), but it hard to obtain it. That is the reason why the current market price of CNTs is too high for any realistic commercial application.

For CNT-based biosensor, the enzyme always needs to immobilize onto the surface of CNTs. However, immobilization is bound to damage their biological activity, biocompatibility and structure stability. Therefore, their potential impact on the selectivity and sensitivity of CNT-based biosensors need to be considered. At the same time, it is need to study their cytotoxicity [235] toward biological species for the integration of CNTs into biological cells and tissues. Therefore, it is urgent need for standardization [236] of the structural and surface characteristics of CNTs and the standard guideline for cytotoxicity determination. At present, about the sensor fabrication and applications still stays in the experimental stage, if CNT-based biosensor wants to get promotion, the above problems must be solved.

Functionalization of CNTs with other functional materials [67,153,167,237], such as enzyme, proteins or nanomaterials, is a rational way to regulate their properties to fulfill different biosensing requirements. The development of new functionalized CNTs for biomedical detection is a rapidly growing field. The question is how this large number of materials could be quickly evaluated for their practical application in biosensors [4,238,239]. The experimental method in developing biosensors based on functionalized

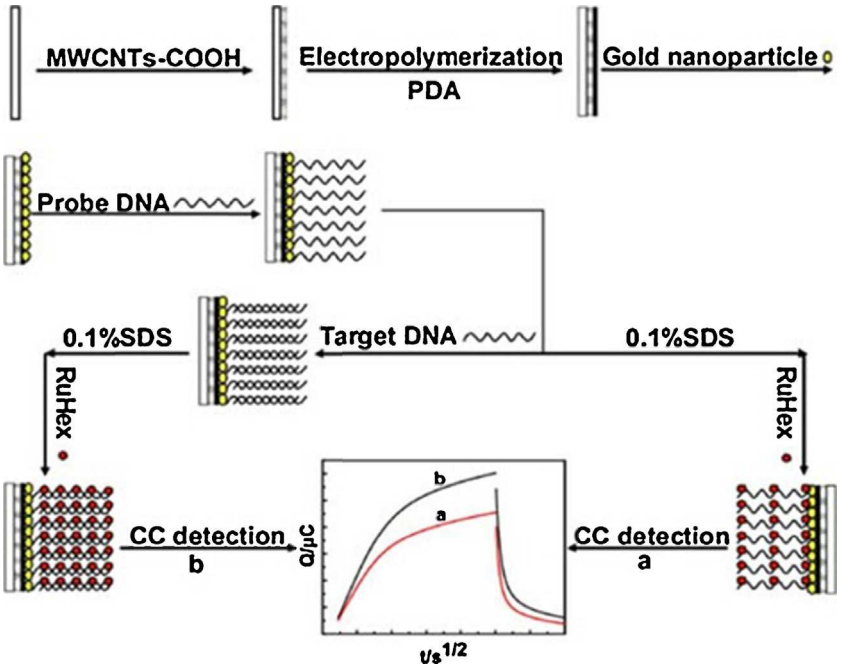

Fig. 26. Schematic illustrations of the immobilization and hybridization detection of probe DNA [224].

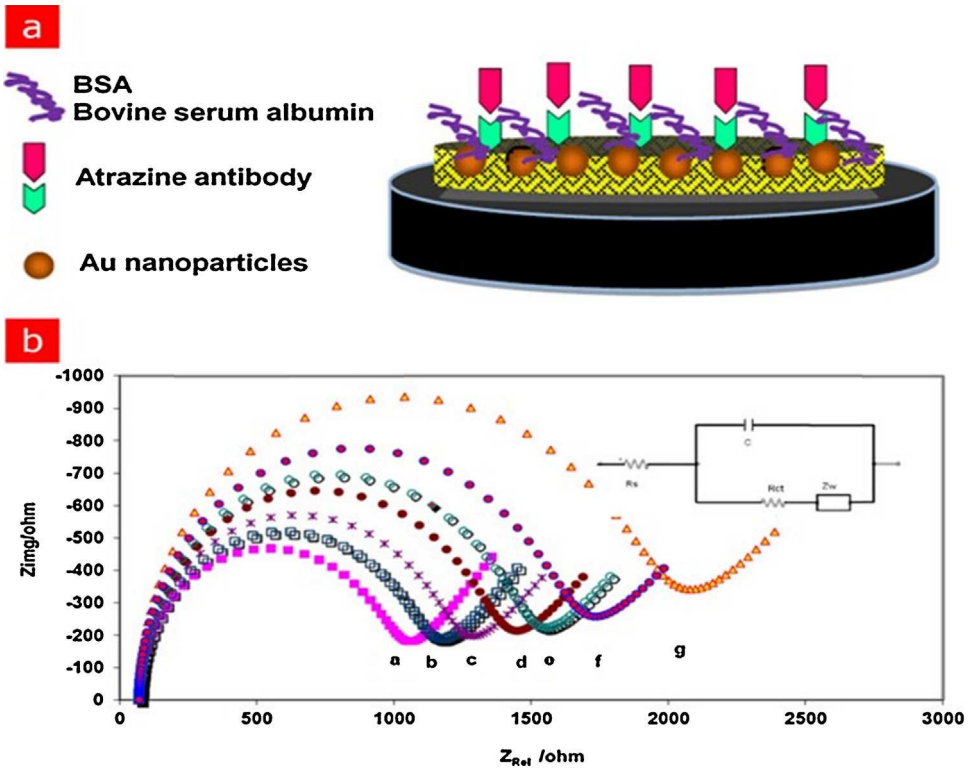

Fig. 27. MWCNT-based immune sensor for the detection of pesticide such as atrazine: (a) Schematic figures of the sensor preparation. (b) Nyquist plots of electrochemical impedance spectroscopy spectra of after interaction with different concentrations of atrazine [229].

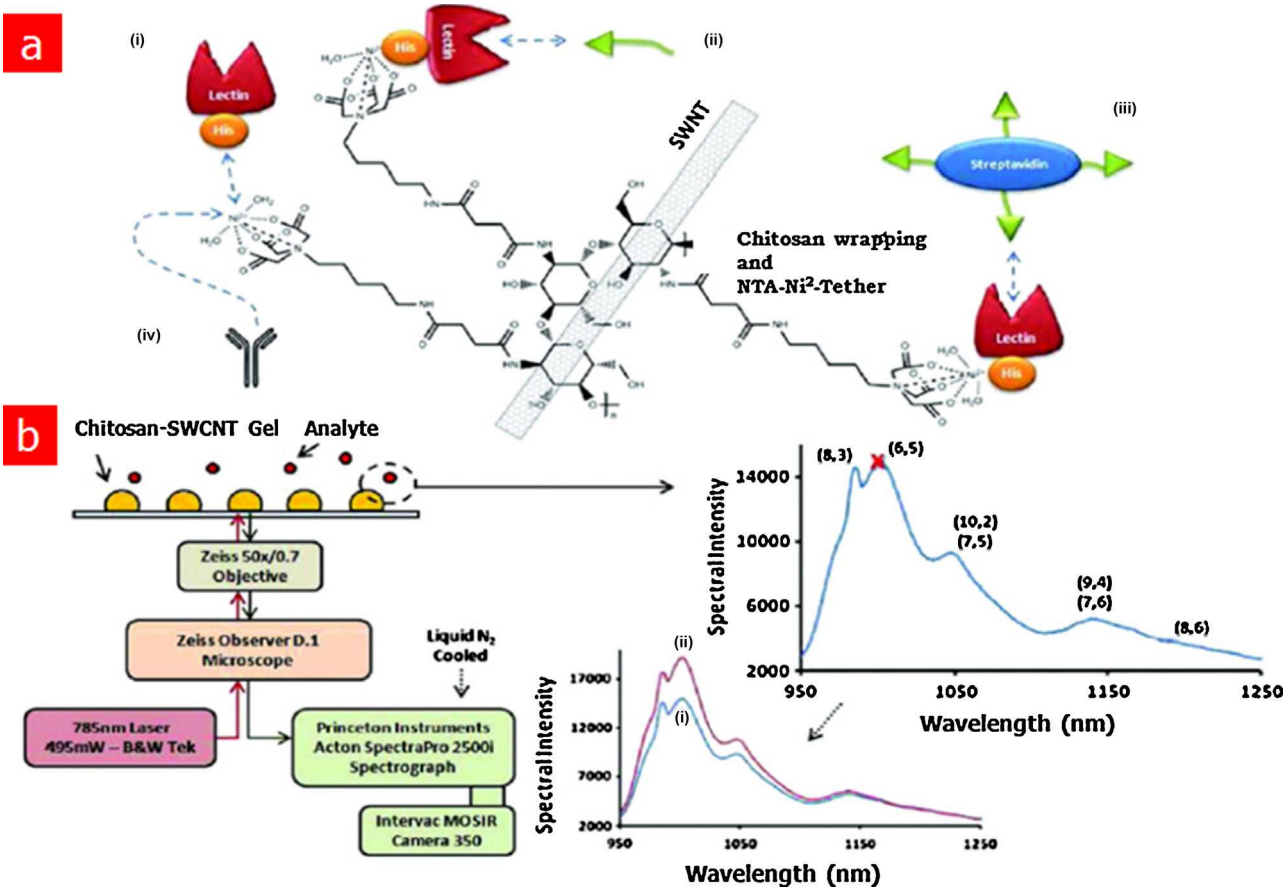

Fig. 28. Optical sensor for glycans based on CNTs: (a) the SWCNTs are functionalized with a chelated nickel ion and wrapped in chitosan. (b) Nanotube gel is excited with a laser, SWCNT emission is collected via an inverted microscope. When a free glycan or glycoprotein interacts with the sensor, the signal is increased [232].

CNTs is common but expensive, time consuming and labor intensive [239–242]. An approach to design and evaluation based on molecular modeling will help not only in providing a fundamental understanding of physical and chemical phenomena in sensors at atomic level but also in setting protocols for rational design, optimization and synthesis of functionalized CNTs at product scale with less extensive experimental testing [162,238–240,242,243].

7. Challenges and perspectives

CNTs are one of the most exciting areas in current materials sciences, and the development of CNTs for biomolecule detection is particularly important for bioengineering and biomedical applications. This review has sought to highlight the recent progresses in the rapidly developing domain of CNT-based biosensors. Although recent works have made many amazing advances in this field, there are still some challenges and further works may mainly include the following five aspects.

The first one is cost-effective. The high prices of CNTs materials and CNT-based enzymatic biosensors has become the main problems which seriously restrict their development and widespread applications [244]. Reducing these costs is a complex challenge will almost certainly require the integration of materials research and nanotechnology. Non-enzymatic sensor based on CNTs is a potential choice which has been attracted by some research groups [245]. Novel nanotechnologies such as nanoimprint lithography and soft lithography are also helpful.

Both chemical and physical properties of functionalized CNTs strongly depend on the ambient conditions, such as temperature and pH. Thus, the second challenge is how to prolong the thermal stability and lifetime of CNT-based biosensors in application of CNTs, and the main challenge to the researchers in the field. Using nanocomposite materials instead of the expensive and fragile enzymes to detect target molecular has shown some improved properties, like thermal tolerance, long-term stability, and cost effectiveness. Except that, some studies have indicated that the sensitivity and the detection limits is significantly enhanced using nanocomposite materials combine with CNTs and metal (Au, Pt, etc.) for biosensor.

With the sustainable development of new nanomaterials combined with CNTs, characterization of these new materials at the molecular level is essential and a key scientific challenge. In parallel with experimental studies, molecular modeling must be further developed as a tool to predict the performance of new materials for a given biomolecules. Such computational methods will enable a quick evaluation of new materials. Eventually, a clear understanding of the structure–function relationships will be convenient to support and guide experimental efforts toward the most promising structures with improved biosensing abilities.

What is more, CNTs-based optical biosensors have shown many unique characteristics and have been researched widely. Meanwhile, CNT fibers possess higher specific modulus strength and can be fabricated simpler [246]. It could be used as DNA probe to detect DNA molecular and put it into gene vector therapy. Thus, fabrication of new CNTs-based optical biosensors and synthesis of new CNT fibers is still a focus of future works in biosensing field.

Clearly, the development of CNT-based biosensors is a multifaceted challenging work that needs a well cooperation between materials scientists, who are developing new materials, and engineers, who are committed to fabricate the new micro/nanodevices such as bionanosensors. Therefore, the greatest and the last challenge is how to build a joint platform that allows the efficiently discussion, learning and cooperating between physists, chemists, and electrical/mechanical engineers.

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Biographies

Ning Yang is a master student at Guilin University of Electronic Technology, and he received B.Eng. degree from the same university. His current research focuses on thermal–mechanical reliability and degradation mechanism of CNTs-based sensors.

Xianping Chen (born 1979 in China) received degrees from the Chongqing University (B.Eng. 2002), Dresden University of Technology (M.Sc. 2006), Germany, and Delft University of Technology (Ph.D. 2012), The Netherlands. After his Ph.D. study, he was appointed to a high-level overseas talent at Guilin University of Electronic Technology, where is currently an associate professor of Nanomaterials & Nanoelectronics, based on the "Hundred Talents Program" in Guangxi Zhuang Autonomous Region of China. He is also currently a part-time researcher at Institute of Microelectronics, Tsinghua University, China. His current research is involved with theoretical research on Materials Chemistry and Physical Chemistry of materials specialization. He is also working on developing nanostructures (e.g. nanowires, nanotubes, and nanoparticles) materials based nanoelectronics.

Tianling Ren received his Ph.D. degree from Department of Modern Applied Physics, Tsinghua University, China in 1997. He has been a full professor of Institute of Microelectronics, Tsinghua University since 2003. He has been a visiting professor at Electrical Engineering Department, Stanford University from 2011 to 2012. His research is focused on novel micro/nanoelectronic devices and key technologies, including MEMS/NEMS, memories, RF devices, micro/nanomaterials and flexible electronics. He has published 300 journal and conference papers and 50 patents. He is administrative community member and distinguished lecturer of IEEE Electron Devices Society. He is also council member of Chinese Society of Micro/NANOTECHNOLOGY.

Ping Zhang (born 1981 in China) is associate researcher of Thermal Management & Nanomaterials at the Guilin University of Electronic Technology. He has received his master degree from the Guilin University of Electronic Technology in 2009, Ph.D. degree from the Nanjing University of Science & Technology in 2013. His research mainly focuses on the performance improvement of high power density electronics such as light-emitting diodes (LED) and micro/nanoscale electronics, heat transfer enhancement and thermal measurement techniques.

Daoguo Yang received master degree from Zhejiang University, China in 1989 and Ph.D. degree from Delft University of Technology, The Netherlands in 2007. After his doctoral research, he has worked as post-doctoral research fellow for two years in TUDelft. Afterwards, he joint Philips Semiconductors (NXP Semiconductors), the Netherlands and worked as a Principal Engineer and project leader is currently a professor and the dean of the College of Mechanical and Electrical Engineering, Guilin University of Electronic Technology, China. He is also the director of Research Center for Microelectronics Packaging and Assembly of GUET, and he was appointed as Distinguished Expert of Guangxi Province in 2011. Dr. Yang has over twenty years of working experience in the filed of electronics packaging and assembly. His scientific interests are mainly in microelectronics and Microsystems packaging and assembly technologies, LED packaging and system integration, reliability analysis, numerical and experimental mechanics. He has authored or co-authored over 100 scientific publications, three book chapters and two European patents. He was the chair of the technical committee of the 13th International Conference on Electronic Packaging Technology & High Density Packaging (ICEPT-HDP 2012). He is the technical committee member of EuroSimE. He was invited to present several keynote speeches in international conferences.