REVIEW

Review: carbon nanotube for microfluidic lab-on-a-chip application

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Abstract Microfluidic lab-on-a-chip allows chemical and biochemical analysis to be conducted in a miniaturized system. Miniaturized analysis reduces the reagent consumption while decreasing the overall size of the device, but the small dose of the sample make detection more demanding and is more sensitive to adsorption of species on the surface. Integration of carbon nanotubes into microfludic devices is a promising approach. This review addresses recent advances in the application of carbon nanotubes for microfluidic lab-on-a-chip. The literature review shows that carbon nanotubes have been used to achieve superlubrifying microchannels, act as high density nanoporous membranes, electrical transducers mainly in flow sensors and biosensors, and mimics of living systems. In addition, extensive work has been carried out to investigate the tunable mechanical, chemical and electrical properties of carbon nanotubes in order to manipulate and analyse extremely small volumes of fluid effectively.

Keywords Carbon nanotube · Microfluidic · Lab-on-a-chip

Introduction

Microfluidic systems are designed to handle and manipulate small volume of fluids in microchannels. Today, this technology is finding increasing application, particularly in chemical, biological and medical fields, which leads to a significant reduction in the cost per analysis. The volume of

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liquid used for one experiment can be reduced by three orders of magnitude by replacing a batch process (processing of liquid in wells) into a continuous flow process in microfluidics [17, 20]. One of the long term goals is to integrate this microsystem into lab-on-a-chip devices, where different operations and analysis normally performed in a lab are done on a single microdevice. As these miniaturized analytical systems are used to manipulate and analyse extremely small quantities of fluid with trace amount of targets (e.g. DNA, chemical and cells), great challenges arise in designing the functional elements such as channels, valves, mixers, separation and extraction units, and sensors [5].

Among different micro- and nano-materials, carbon nanotubes have received considerable attention in microfluidic application due to their physical electrical and chemical properties. Apart from some common properties desired for other applications such as high surface-to-volume ratio, excellent electrical conductivity, thermal conductivity and mechanical strength, there are several other properties of carbon nanotubes which make them very interesting for microfluidic applications.

First, their tubular structure allows liquid to flow either on their outer surface or through the hollow inner core (nanochannel of less than 10 nm diameter pore size), as in Whitby and Quirke [47]. This expands the possibilities to handle small molecular size proteins and biological molecules. Further, small liquid droplets are ideal for manipulation on dense arrays of carbon nanotubes where only the nanotube tips are in contact with the liquid, minimizing the contact area greatly [26].

Secondly, chemical functionalization of carbon nanotubes can be used to attach almost any desired chemical species to them in order to enhance the molecular selectivity and biocompatibility of the tubes for a wide

range of specific tasks. The most common example is sidewall functionalization. However, scientists have already established methods to coat the inner walls with polymer [29] and selectively functionalise each end of the nanotube [8].

This review aims to give an overview of the work that has been done in integrating carbon nanotubes in various parts of a microfluidic lab-on-a-chip, particularly in channel walls, membranes and sensors. The information is presented in the way which demonstrates the efforts of scientists and engineers to improve the interaction of carbon nanotubes to liquids and biological solutions physically, chemically and electrically.

Superhydrophobic surface

Most of microchannels require a superhydrophobic surface (contact angle, CA>150°, sliding angle<5°) to ensure that liquids flow smoothly while they are in minimal contact with channel walls. Therefore, small dose samples can be preserved during transportation in the microchannel. Another area of microfluidics which requires superhydrophobic substrates is digital devices, where microdrops instead of continuous microflows are involved [4]. In general, an artificially hydrophobic surface can be obtained by increasing the surface roughness, which allows air to be trapped more easily underneath the water droplet so the droplet essentially rests on a layer of air. In microfluidic devices where the volume of the microdrop may be as low as 0.05 μL, it is critical that surface roughness is at the nanometer scale, because otherwise, the droplet would lose levitation.

The wettability of a forest of vertically aligned carbon nanotubes has been extensively studied due to its brush-like nanoscale roughness which exhibits a perfect air–water interface—the water droplet can remain nearly spherical at the tips of the nanotubes [11]. However due to the high surface free energy of carbon nanotubes, the nanotube array inhibits the flow of water droplets and the spherical droplets stick on the surface. Therefore, most of the work has looked at coating the forest templates with low surface energy material, intended to achieve the self-cleaning or Lotus effect —water droplets move easily on the surface, carrying along undesirable particles. One example used a thin conformal coating of layer of polytetrafluoroethylene (PTFE) on carbon nanotube forests as demonstrated by Lau et al. [18].

For practical integration into microfluidic systems, Journet et al. [16] studied the effect of fluid pressure against the robustness of nanotube forests. His experiment showed that superhydrophobic nanotube forests coated with gold-thiol affinity are able to withstand high excess pressures (larger than 10 kPa)—the water droplet remains at the top of the rough nanotube forest even under high

pressure. This is in contrast to superhydrophobic surfaces obtained using more conventional lithography, where contact angle decreases with the applied pressure- the droplet seeps into the microscale texture surface at high pressures.

Li et al. [21, 22] introduced a novel strategy for achieving a superhydrophobic surface without additional chemical modification. His group grew aligned carbon nanotubes (10 μm height) on the wall of a honeycomb structure of diameter 3~5 μm (Fig. 1). The experimental results showed that this honeycomb-like nanotube structure exhibited higher CA (163.4°) than that of a densely packed nanotube array (136.5°) with a sliding angle less than 5°— water droplets started to slide with little tilt on the substrate. Patankar [33] explained theoretically that this effect was attributed to the two-tier (micron- and nanoscale) roughness, which not only amplified the contact angle, but also made the water droplet rolls off more easily (Fig. 2).

Sun et al. [40] further highlighted the importance of optimizing the geometry of the double structured roughness. In their experiment, they created the dual-scale roughness by growing nanotube forests on a 10 μm× 10 μm×30 μm pillar array patterned on a silicon substrate. By simply varying the spacing between pillars, an abrupt transition from a superhydrophobic to superhydrophilic state was observed; the CA for 15 μm and 10 μm spacing is 153° (superhydrophobic) and 27° (superhydrophilic), respectively. The significance of microscale roughness (the size, height and spacing of pillars) was again emphasized by Zhu et al. [55]. More importantly, they discovered that the main role of nanoscale roughness is to stabilize the superhydrophobic surface rather than to enhance the super-hydrophobicity. By combining the dual-scale tier nanotube array and the fluorocarbon coating, a superlubrifying surface was achieved- the water droplet rolls across the horizontal surface and only can be stopped by a barrier. This means water droplets can move in microchannels without using any external force e.g. pumps.

However, Xu et al. [48] pointed out that aligned nanotube arrays are not essential for the surface super-hydrophobicity of films. In their work, the randomly aligned alkyl-modified carbon nanotube films prepared by chloroform suspension exhibited comparable CA and sliding angle (163° and <5°, respectively), as has been reported on vertically aligned nanotubes. Although the randomly distributed nanotube film showed no well-arranged pattern, the double structured surface roughness was formed naturally during the drying process of the nanotubes. The nano-scale and micro-scale roughness were generated by individual non-aligned nanotubes and nanotube bundles, respectively.

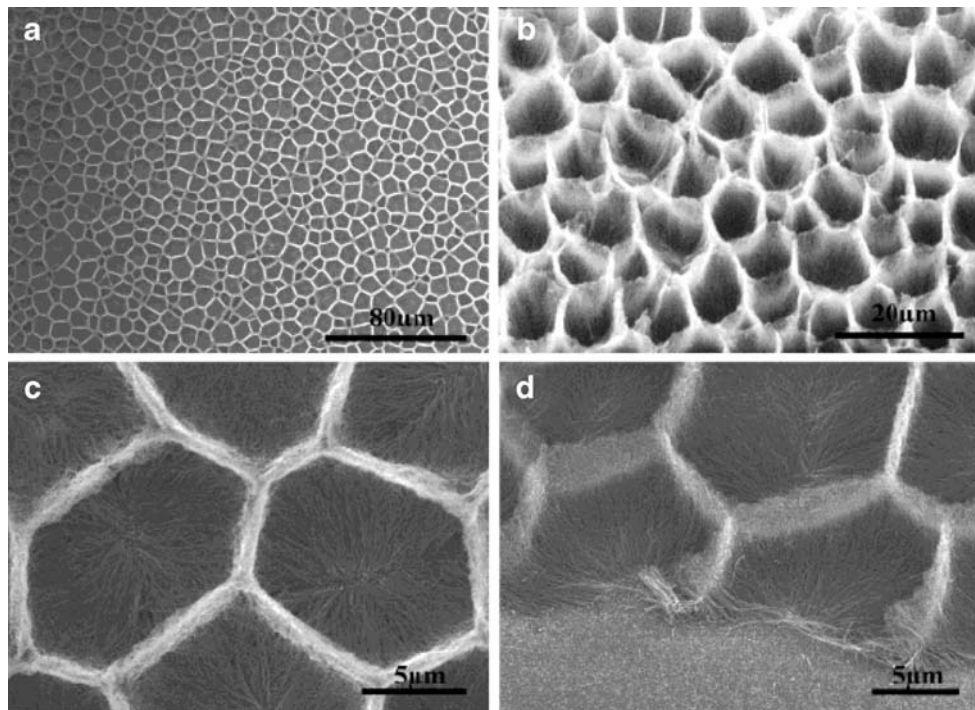As discussed, surface modification using three dimensional structures of both aligned and non-aligned carbon

Fig. 1 a–d SEM images of honeycomb pattern aligned carbon nanotubes to achieve superhydrophobic surface by creating two-tier (micro- and nanoscale) roughness. Hexagon honeycombs of diameter 3~5 μm ware composed of carbon nanotubes of 10 μm heights. Reprinted with permission from Li et al. [21, 22]. Copyright American Chemical Society

nanotube arrays have been extensively studied. Today's trend is towards switchable hydrophobicity in carbon nanotubes to dynamically control the interaction of liquids with the superhydrophobic surface through external stimuli. In addition to liquid manipulation in microchannels, this ability can be extended to fabrication of smart microfludic devices such as temperature-controlled valves, as shown in the work done by Sun et al. [39] using a temperature responsive polymer, poly(N-isopropylacrylamide) (PNI-PAAm). By coating the carbon nanotubes with PNIPAAm, they turned the superhydrophobic nanotube forest to a superhydrophilic state (CA~0)—the water droplet wetted the substrate almost completely. However, the CA increased to 63.7° when its temperature rose to 40°C. Alternatively, an electrical method provides a non-destructive and selective way to alter the wettability of a surface.

This is particularly suitable for carbon nanotubes which are naturally highly conductive electrically. Wang et al. [47] also demonstrated that water can be efficiently wet the superhydrophobic nanotube array by applying a small positive dc bias to the substrate.

Membrane separation

Bakajin et al. [2] demonstrated a simple physical filtration technique which utilized a nano-porous structure (10 to 50 nm tube-to-tube spacing) of carbon nanotubes as a separation media. Nanotubes arrays that were grown perpendicular to the direction of flow on a microfluidic channel allowed the passage of molecules smaller than the wall-to-wall spacing of the nanotubes.

Fig. 2 a Microscopic image of the surface of superhydrophobic lotus leaf showing the dual scale roughness structure. **b** A composite mercury drop on top of the leaf remains spherical at the tips of double roughness structure [33]. Courtesy of Prof. W. Barthlott, University of Bonn. Copyright American Chemical Society
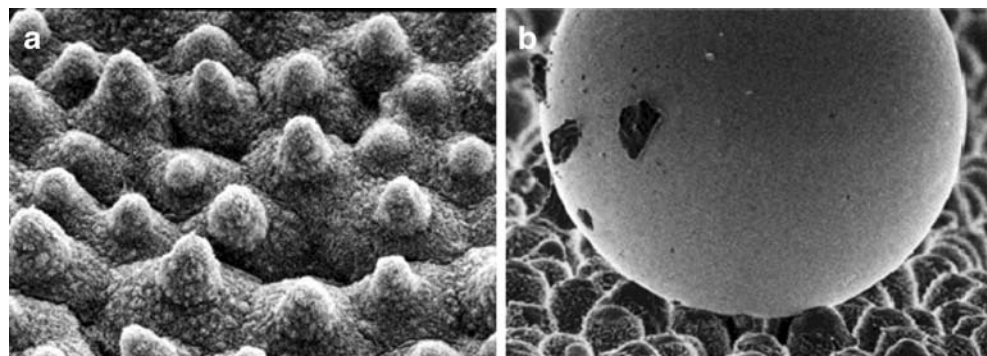
This idea was conceptualized by Doktycz and Simpson [10] after 2 years and the group patented the invention in 2004 with support from the US Government. The first embodiment of the invention illustrated a simple membrane structure which was based on nanotube arrays as barriers. The system is solely driven by diffusion which can be controlled by the separation of the nanotubes. Other embodiments were derived from this concept; one was chemical functionalization of the nanotubes membrane to enhance its molecular selectivity. Additionally, individually addressable nanotube electrodes can be integrated with the membrane to provide an electrical driving force for transport, and an electronic interface to the fluid for control and detection.

Hinds et al. [14] were the first to introduce a novel aligned multi-wall carbon nanotube (MWCNT) membrane with pore size below 10 nm. In their work, open ended nanotubes were aligned parallel to the fluid flow direction to allow the fluid to flow through the hollow tube inner core. The pore size of the membrane was determined by the hollow inner core diameter of the nanotubes, which was well controlled at 4.3±2.3 nm. This nano-scale membrane consisted of a nanotube array grown by CVD on a quartz substrate. A polystyrene solution was then spin coated onto the nanotubes array to fill the gaps between the tubes, followed by plasma etching to remove the top layer of the composite and to open the nanotube central pores. They observed that overall, the fluid velocities of water and a variety of solvents are four to five orders of magnitude faster than in any other materials with nanometer-scale pores. These rapid transport rates exist because the walls of nanotubes are much smoother (on the atomic scale) than other materials [28]. This method was further investigated by Holt et al. [15] using double-wall carbon nanotube (DWCNT) membranes to attain smaller pore sizes in the 1.3 to 2.0 nm range.

At the same time, researchers were looking for ways to control the transport through nanotube membranes. Miller and Martin [29] developed a way to modulate the direction and magnitude of the electro-osmotic flow through carbon nanotube membrane. They coated the inner-wall of carbon nanotube membranes with a redox-active polymer film, poly (vinylferrocene) or PVF, which can be reversibly and electrochemically switched between an electrical neutral and a polycationic state to control surface charges induced on the nanotube inner walls. Therefore it controlled both the direction and magnitude of the electroosmotic flow through the carbon nanotube membrane with redox modulating the flow.

Recently, Li et al. [24] demonstrated a novel strategy to reversibly tune the pore size of nanotube membranes as they are mechanically compressed and released. This application was based on the super-compressibility and full elasticity of an aligned MWCNT membrane. The membrane was size-selective (5 to 20 nm in their work to separate proteins) based on the compression level and exhibited excellent resilience (elastically cycled hundreds of times without any significant reduction in the membrane thickness) and easily cleaned (Fig. 3).

Today, scientists are taking a great step forward to engineer the biological membrane in living systems and carbon nanotubes are the natural choice for interfacing with the biological world. The first success was demonstrated by Nednoor et al. [30] with a carbon nanotube-based ion membrane to mimic biological protein channels regulated by phosphorylation or dephosphorylation. The membranes consisted of an array of aligned carbon nanotubes (CNTs) with hollow graphitic cores passing across a solid polymer film. They functionalized the open tips of carboxylate-terminated carbon nanotubes in the membrane with a bulky peptide, which was subsequently used for the receptor attachment (phosphanoryl groups and antibody) to regulate the flow through the pore entrance (Fig. 4).
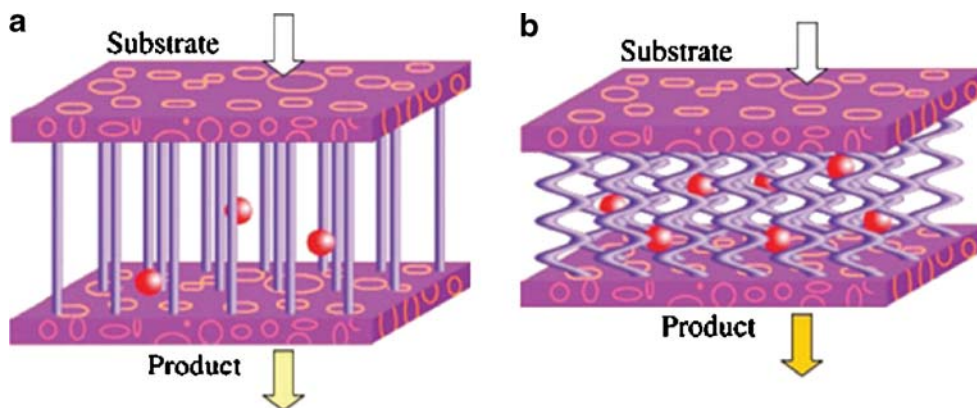

Fig. 3 Schematic illustrations of molecules entrapment in the compressed carbon nanotube membrane. **a** The straight and uncompressed nanotube membrane with larger tube-to-tube spacing allows most of the molecules to pass through it. **b** When the nanotube membrane is partially compressed, tube-to-tube spacing is reduced accordingly, and more molecules are entrapped [24]. Copyright Wiley-VCH Verlag GmbH & Co.KGaA. Reproduced with permission
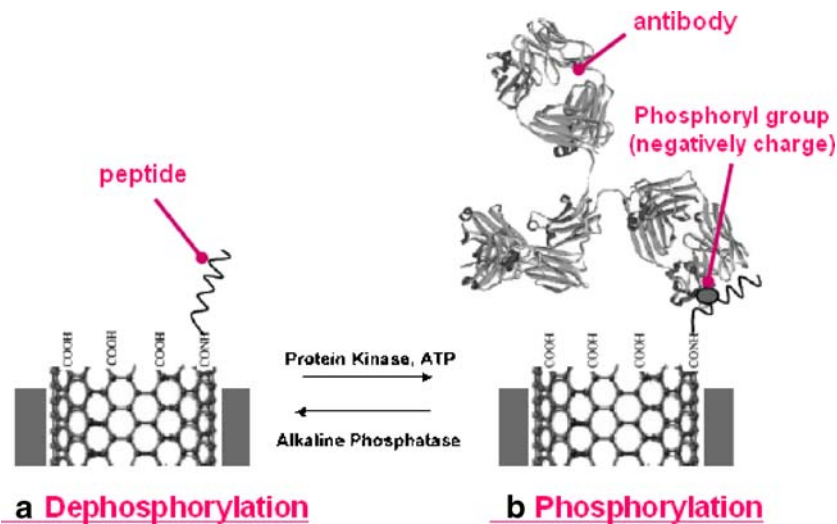
Fig. 4 Schematic of phosphorylation based ionic channel. The phosphorylated peptide tethered to the nanotube core entrance binds the antibody to modulate ionic flux through the nanotube core, as shown in (**b**). In contrast, **a** shows no antibody binding to peptide without phosphoryl group. The flux behavior is dominating by the electrostatic effect, and it is independent on the size of the antibody. *Grey region* represents the polystyrene membrane that forces ionic flow through the nanotube core. Reprinted with permission from Nednoor et al. [30]. Copyright The Royal Society of Chemistry

Sensor

Previous sections reviewed the use of carbon nanotubes, mainly their surface chemistry and mechanical properties, to control and manipulate the buffer (carrier) fluid flow and the extraction of reactants. This section is dedicated to discuss the application of carbon nanotubes as electrical transducers mainly in flow sensors and biosensors.

Flow sensor

In 2003, Ghosh et al. [12] reported the experimental observation of the voltage generated by the flow of a polar liquid over single-wall carbon nanotube (SWCNT) bundles when the liquid flowed along the nanotubes surface. Due to the one-dimensional nature of the SWCNT, a voltage of 0.65 mV was generated even at the very low velocity of 5×10^{-6} ms^{-1}, a sensitivity which is more than ten times better than that when using MWCNTs and has never occurred (no electrical signal detected) in graphite. Otherwise the voltage response of SWCNT and MWCNT bundles to the flowing liquid is similar, a logarithmic velocity dependence, which is also dependent on the ionic charge (higher sensitivity for HCl than water), and the viscosity of liquid [12, 53]. Later, Sood and Ghosh [37] patented their SWCNT-based flow sensor.

Recently, Qu et al. successfully integrated carbon nanotube-based flow sensors into a polydimethysiloxane (PDMS) microfluidic channel. The flow sensing element, Electronic-Grade nanotubes were aligned between the gold microelectrodes using AC dielectrophoretic on the glass substrate. The preliminary result showed that the sensor was reliable (good adhesion of the deposited nanotubes to the electrodes) and consumed ultra-low-power (~1 µW) to detect the DI-water flow rate at 0.8 to 2.1 ms^{-1} range [35].

Bourlon et al. [6] were the first to develop a flow sensor that can be easily integrated into the newly emerging nano-scale channels using a sensing element of about 2 nm height. In their work, a 2 nm diameter, semiconducting SWCNT that bridged the Pd/Au source and drain contacts, and was integrated on a microfluidic channel was able to detect a NaCl flow rate of about 8.3×10^5 ms^{-1} with a 1 Hz bandwidth.

Biochemical sensor

Electrochemical (EC) biosensors are currently the most popular of the various types of biosensors and carbon is one of the common materials used as the EC electrode; the conventional carbon electrodes are glassy carbon (GC), graphite and carbon fibers, and the new form uses carbon nanotubes. Its high surface-to-volume nanoscale structure, excellent conductivity and high chemical stability make the CNT-based EC electrode superior to traditional carbon electrodes. A great amount of research has been performed on biosensing CNT electrodes and the results have been reviewed by several authors [1, 3, 42].

Several methods, as summarized in Table 1, have been explored to fabricate the CNT electrode, basically to improve its sensitivity and selectivity to various types of biological molecules. The simplest strategy is to add CNTs onto conventional electrodes by confining the nanotubes on the electrode with binders such as Teflon, Nafion or paste. Nafion, a perfluorinated sulfonic acid ionomer with good

Table 1 Examples of carbon nanotubes-based biosensing electrodes [3]

CNT-based electrode	Principle	Variables	Examples
CNT paste electrode	Mixing CNTs powder with binder into paste then pack it into a cavity- same as the preparation of conventional carbon paste electrodes.	Binder: mineral oil, bromoform or Teflon Ratio of CNT-to-binder Enzyme incorporation	CNT-Teflon-GOx for glucose [43] MWCNT-mineral oil for nucleic acids [34] SWCNT-mineral oil for ferricyanide etc [41]
CNT-modified electrode	Modify conventional EC electrodes (GCE or metal Au, Pt or Cu or carbon fiber) with CNT- CNT deposition on conventional EC electrode	Spin casting a solution of CNT dispersion or soldering of CNT bundles onto conventional electrodes Solvent: phosphate buffer, concentrated sulphuric acid, acetone Surfactant: DHP and DCP Mechanical binder: Nafion Direct growth of CNT on electrode	$Ru(bpy)_3^{2+}$;MWCNT-Nafion/GCE for difedol [32] MWCNT-Nafion/CFE for liver mitochondria [45] CNT bundle/Cu for prostate cancer cells [51] Heat-treated MWCNT tower [21, 22] PVA-MWCNT/Si for cholesterol [36] PPy-CNT/Si for PC12 cell [31]
Metallic catalysts decorated CNT electrode	Adding metallic nanoparticles or complexes onto CNT electrodes- an alternative to use transition metallic thin films with high catalytic activity but are prone to severe poisoning and corrosion	Pt, Cu, Co nanoparticles, metal complexes (e.g. Cobalt porphyrin, Iron phthalocyanines), Au colloids.	CoP-SWNT-Nafion/GCE for dioxygen reduction [9] Cu-SWCNT-Nafion/GCE for glucose [27] Cu-CNT-mineral oil-carbohydrates [44]
Enzyme immobilized CNT electrode	Immobilize enzyme on CNT modified electrode. Nanotubes serve as transducers to communicate from enzyme centers to substrate- improve selectivity and sensitivity	Non-covalent—binding through a medium (i.e. hydrogel/ sol gel/ polymer matrix) or a binder Covalent-direct binding of enzyme to nanotubes	ssDNA-PPy-MWCNT/GCE [7] GO_x@POAP/FePc-MWNT[50] GOx-HRP-CNT-PAMAM [52] FAD-GOx/SWCNT/Au substrate [25] ADTZ-MWCNT/Au for ST [49] HRP-EDC/MWCNT [19]
Nanoscale CNT electrode	Use individual nanotube as nanoelectrode e.g. FET with single SWCNT	Immobilize enzyme on CNT covalent and non-covalently Type of electrodes (source and drain) Type of gate (metal gate or liquid gate)	Lipid bilayer-SWCNT for cell membrane [54] PSA-AB-SWCNT for PSA [23] Starch-SWCNT [38]

ion exchange and biocompatibility properties, is the most commonly used surfactant to solubilize the CNTs and serves as a binder to strengthen the mechanical network of CNTs to the electrode. Other surfactants used were dihexadecyl hydrogen phosphate (DHP) or dicetyl phosphate (DCP) [3].

In addition, some work has been done to improve the catalytic activity of the CNT-modified electrodes by decorating them with transition metal nanoparticles or complexes on the nanotubes. In the recent work performed by Choi et al. [9], the glassy carbon electrode (GCE) modified by single walled

carbon nanotubes (SWNTs) and Nafion, and homogeneously coated with Cobalt porphyrin (CoP) showed a higher electrocatalytic activity for the reduction of dioxygen to hydrogen peroxide or water.

The selectivity of electrodes can be further enhanced with enzyme immobilization. This is particularly important in electrochemical DNA sensors, where the principle relies upon immobilizing one single-stranded DNA, probe/target DNA, onto a transducer surface, and these DNA sequences have the ability to precisely recognise their partner with a complementary base sequence, target/prope DNA [13]. Another fre-

quently used enzyme is glucose oxidase (GOx) for glucose detection. Ye et al. [50] immobilised GOx on a poly-*o*-aminophenol (POAP)-electropolymerized, Iron-phthalocyanines (FePc) decorated MWCNT electrode surface. SEM images indicated that GOx enzymes trapped in the POAP film tend to deposit primarily at the tips of nanotubes and evenly disperse along the sidewalls. This is non-covalent binding; the enzyme is attached with the help of a binder or incorporated into a polymer matrix, hydrogels or sol-gels.

By contrast, covalent immobilization allows direct anchoring of the enzymes to the carbon framework, which enables direct electron transfer to the active center of the enzyme. However, the covalent bond of certain enzymes will possibly impair the enzyme activity during the immobilization process. Therefore different strategies have been employed to maintain the correct conformation of the enzyme to compensate for the negative influence of the covalent linkage. Yao et al. [49] showed in their work that for an aflatoxin–detoxifizyme (ADTZ) enzyme, which was connected to a Sterigmatocystin (ST) substrate during immobilization on the MWCNT modified gold electrode (Fig. 5), the sensitivity had been improved by two orders of magnitude, compared to the corresponding results obtained from the MWNT modified gold electrodes when ADTZ was directly adsorbed onto them.

An effective approach to improve the electrical contact between the active sensing material (CNTs) and the conducting substrate electrode is direct growth of CNTs onto the substrates. This also ensures that the sensor is free of impurities originating from the surfactant or the binder.

Nguyen-Vu et al. [31] demonstrated a novel electrical–neutral interface between the brush-like nanotube arrays and the neural network of a rat pheochromocytoma, PC12 cell. The array of vertically aligned CNT was grown directly on a silicon substrate using PECVD and then grafted with the conducting polypyrrole (PPy) thin films to prevent the nanotubes from collapsing into microbundles. This three-dimensional robust nanoelectrode exhibited very low impedance and makes it an ideal electronic device for long-term implantation into the brain.

Another advantage of direct growth of CNTs on electrodes is the ability to fabricate nanoscale CNT electrodes using at least one carbon nanotube. Due to its small diameter and hence higher sensitivity of SWCNTs, there is a considerable interest in using a single or a network of semiconducting SWCNT nanotubes serving as an active electron channel between the source and drain in a FET; every carbon atom is on the surface and exposed to the environment. Therefore even small changes in the charge environment can cause dramatic changes to their electrical properties [1]. Zhou et al. fabricated a SWCNT FET to probe the properties of lipid bilayer systems, which serves as an artificial model to study the mechanism of living cell membranes [54].

Conclusion

Carbon nanotubes have many desirable properties as materials to realise a microfluidic lab-on-a-chip. Various forms of carbon nanotubes have been integrated into different micro-
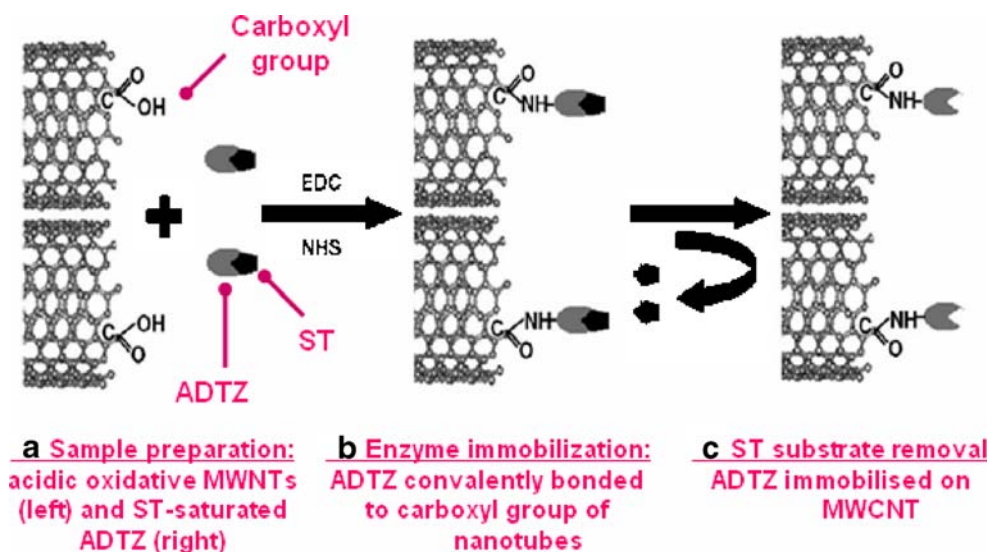

Fig. 5 **a**–**c** Schematic illustration of the covalent immobilization of enzyme ADTZ onto MWNTs with EDC and NHS via covalent bond. The enzyme ADTZ, which is saturated with its substrate ST prior to the immobilization is covalently linked to the carboxyl group on oxidative MWNTs via acid amide bond. After removing the ST substrate, the active-remained ADTZ is immobilized onto the MWNTs-modified gold electrode, the ST biosensor is then assembled. Because the enzyme active site was protected by the substrate, the covalently immobilization remain the enzyme bioactive well. Without this substrate protection strategy, only a weaker electro-signal can be produced on the ADTZ immobilized MWNTs biosensor. Reprinted from Yao et al. [49]. Copyright 2006, with permission from Elsevier

fluidic functional elements to enhance their surface chemistry, biocompatibility and electrical sensing. In addition, controlled growth of carbon nanotubes using catalytic chemical vapour deposition (CVD) or plasma enhanced CVD (PECVD) onto various substrates enable these materials to be integrated into current microfluidic systems.

So far, the direction has been to utilise the carbon nanotubes as an individual microfluidic element with a single function. Future work should be directed at incorporating carbon nanotubes elements with multiple functions to enhance microfluidic lab-on-a-chip, or even form a complete system. For example, a microanalysis system can be formed by integrating a carbon nanotube membrane into capillary electrophoresis or dielectrophoresis systems to perform multiple/multiplexed functions of physical filtering, electric field separation and molecule detection. This could potentially lead to lab-on-chip devices with smaller size, less functional elements, and lower power consumption.

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