

Electrochemical Sensors Based on Architectural Diversity of the π -Conjugated Structure: Recent Advancements from Conducting Polymers and Carbon Nanotubes

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Conjugated conducting polymers and carbon nanotubes, both of which possess a conjugated structure of alternating carbon–carbon single and double bonds for the delocalization of π -electrons, are two important classes of electrochemical sensing materials. The combination of carbon nanotubes with conducting polymers or other functional materials (e.g., DNA chains, proteins, metal nanoparticles, carbon fibres) was found to create synergetic effects, that provide the basis for the development of numerous novel sensors with a high sensitivity, good selectivity, excellent environmental stability, and low power consumption. This article reviews recent developments in this exciting new area of electrochemical sensing by presenting the rational strategy of the author's group in the design and characterization of these new electrochemical sensors based on architectural diversity of the π -conjugated structure.

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The recent development of nanotechnology has opened up novel fundamental and applied frontiers in materials science and engineering.^[1] At the nanometer scale, the wave-like properties of electrons inside matter and atomic interactions are influenced by the size of the material.^[2] As a consequence, changes in the size-dependent properties (e.g., melting points and magnetic, optic, and electronic properties) may be observed even without any compositional change.^[2] Due to the high surface-to-volume ratio associated with nanometer-sized materials, a tremendous improvement in chemical properties is also achievable through a reduction in size.^[2] Furthermore, new phenomena, such as the confinement-induced quantization effect, could also occur when the size of materials becomes comparable to the de Broglie wavelength of charge carriers inside.^[2] By creating nanostructures, therefore, it is possible to control the fundamental properties of materials through the surface/size effect. This should, in principle, allow us to develop new materials and advanced devices of desirable properties and functions for numerous applications.

Polymers offer a class of materials in which the natural length of polymer chains and their morphologies in the bulk lie precisely in the nanometer length scale.^[2] This, together with the large number of possible configurations/conformations available to a macromolecular chain, indicates a considerable space for

creating polymeric materials of new properties and functions without any change in their chemical composition.^[3] The above description is particularly true for a class of macromolecules having conjugated structures of alternating carbon–carbon single and double bonds with different molecular symmetries, including conjugated polymers, (buckminster)fullerenes, and carbon nanotubes (Fig. 1).^[4]

Polymers have been traditionally used as electrically insulating materials; after all, metal cables are coated in plastic to insulate them. The visit of MacDiarmid to Shirakawa at Tokyo Institute of Technology in 1974 and, later, Shirakawa to MacDiarmid and Heeger at University of Pennsylvania, however, led to the discovery of conducting polyacetylene in 1977—a prototype conjugated conducting polymer (Fig. 1a).^[5] This finding opened up the important new field of polymers for electronic applications and was recognized by the 2000 Nobel Prize in Chemistry.^[6] The subsequent discovery of the electroluminescent light emission from conjugated poly(*p*-phenylene vinylene), by Friend's group at Cavendish Laboratory in 1990,^[7] revealed the significance for the use of conjugated polymers in photonic devices. Various conjugated polymers can now be synthesized to show the processing advantages of plastics and the optoelectronic properties of inorganic semiconductors or metals; with a



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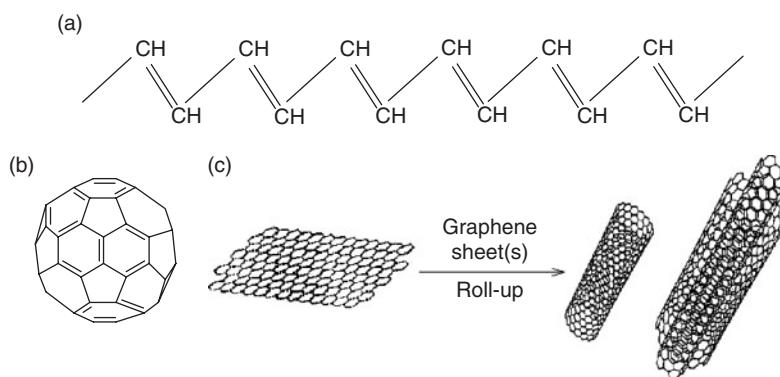


Fig. 1. Conjugated structures with different dimensionalities: (a) polyacetylene, (b) buckminsterfullerene C_{60} , (c) single- and double-wall carbon nanotubes.

Table 1. Some conjugated conducting polymers^[4]

Polymer (date conductivity discovered)	Structure	π - π^* gap [eV]	Conductivity ^A [$S\text{ cm}^{-1}$]
Polyacetylene and analogues			
Polyacetylene (1977)		1.5	10^3 – 1.7×10^5
Polypyrrole (1979)		3.1	10^2 – 7.5×10^3
Polythiophene (1981)		2.0	10 – 10^3
Polyphenylene and analogues			
Poly(paraphenylene) (1979)		3.0	10^2 – 10^3
Poly(p-phenylene vinylene) (1979)		2.5	3 – 5×10^3
Polyaniline (1980)		3.2	30–200

^AThe range of conductivities listed is from that originally found to the highest values obtained to date.

conductivity even up to $1.7 \times 10^5\text{ S cm}^{-1}$ comparing favourably with the value of 10^6 S cm^{-1} for copper or silver^[8] (Table 1).

Metals have high conductivity due to the free movement of electrons through their structure, and similarly in order for organic materials to be electronically conductive they must possess not only charge carriers but also an orbital system which allows the charge carriers to move.^[4] The conjugated structure can meet the second requirement through a continuous overlap of π -orbitals. Most organic materials, however, do not have intrinsic charge carriers. The required charge carriers may be provided by partial oxidation (p-doping) of the organic (macro)molecules with electron acceptors (e.g., I_2 , AsF_5) or by partial reduction (n-doping) with electron donors (e.g., Na, K).^[4] Through such a doping process, charged defects are introduced, which could then be available as the charge carriers (Fig. 2).

The early work on the conductivity measurements of polyacetylene films upon doping with vapours of I_2 , Br_2 , or AsF_5 , and subsequent compensation with NH_3 , therefore, constitutes

the simplest conducting polymer gas sensors.^[9] Indeed, metal (e.g., Cu or Pd) doped electrodeposited polypyrrole and poly(3-methylthiophene) films have recently been used for the detection of reducing gases such as NH_3 , H_2 , and CO .^[10] Besides, the interaction of a doped conjugated conducting polymer (e.g., D,L-camphorsulfonic acid-doped polyaniline emeraldine) with certain organic solvents (e.g., *m*-cresol) could cause a conformational transition of the polymer chain from a 'compact coil' to an 'expanded coil' through the so-called 'secondary doping' process,^[11] which was found to be accompanied by a concomitant change in conductivity. The conformation-induced conductivity changes have also been observed when conjugated conducting polymers were exposed to some common organic vapours (methanol, hexane, chloroform, THF, benzene, toluene, acetone), providing the basis for developing conjugated conducting polymer-based sensors for the detection of hydrocarbon vapours.^[12] Conjugated polymers have also been used as electrodes for electrochemical sensors with other electrical

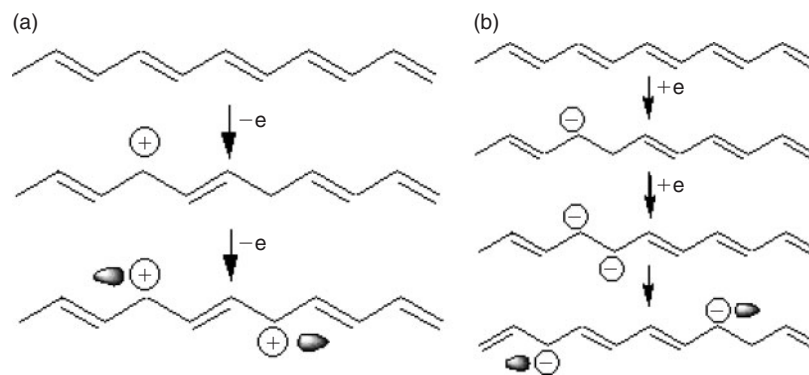


Fig. 2. A schematic description of the doping of *trans*-polyacetylene chain: (a) p-doping and (b) n-doping.

transducers, including potentiometry, amperometry, and voltammetry. The fundamental principle and the advantages and disadvantages for each of the electrical transduction modes have been reviewed elsewhere.^[4]

Sometimes history repeats itself. The visit made by Kroto in 1985 to Smalley and Curl at Rice University led also to a Noble Prize winning discovery of buckminsterfullerene C_{60} —a conjugated molecule with a soccer-ball like structure consisting of 12 pentagons and 20 hexagons facing symmetrically (Fig. 1b).^[13] Although Ōsawa^[14] had theoretically predicted the structure of C_{60} in 1970 and Huffman^[15] might have produced the C_{60} molecules in his ‘graphite smoke’ as early as 1973, it was the 1985 discovery that generated a great deal of interest and created an entirely new branch of carbon chemistry.^[16] The subsequent discovery of carbon nanotubes (CNTs) by Iijima^[17] in 1991 opened up a new era in material science and nanotechnology.^[1] Carbon nanotubes (CNTs, Fig. 1c) may be viewed as a graphite sheet that is rolled up into a nanoscale tube form (single-walled carbon nanotubes, SWNTs) or with additional graphene tubes around the core of a SWNT (multi-walled carbon nanotubes, MWNTs).^[1]

In view of the large number of well defined carbon–carbon single- and double-bonds in their molecular structure, fullerenes and carbon nanotube are polymeric in essence. Just as conjugated polymers have widely been regarded as quasi one-dimensional semiconductors,^[4] fullerenes and carbon nanotubes can be considered as a quantum dot and quantum wire, respectively.^[1] Having a conjugated all-carbon structure with unusual molecular symmetries, fullerenes and carbon nanotubes have also been shown to possess some similar optoelectronic properties to conjugated polymers.

Just as conjugated conducting polymers have been demonstrated to show good sensing performance, the high surface area and good electronic properties provided by carbon nanotubes are also an attractive feature in the advancement of chemical- and bio-sensors.^[18] Indeed, carbon nanotubes and their derivatives have recently been reported as gas-sensing materials.^[19–21] In most of these studies, non-aligned carbon nanotubes are used for gas sensing, and the detection of the gases is accomplished by measuring the change in electrical properties of the carbon nanotubes induced by the charge transfer with the gas molecules (e.g., O_2 , NO_2 , NH_3) or the mass change due to physical adsorption of the gas molecules. Consequently, the number of analytes that can be determined using a carbon nanotube based sensor is hampered by the limited transduction mechanisms employed. It is a significant advancement to use perpendicularly aligned carbon nanotubes as the sensing material, which provides a

well-defined large surface area for a sensor with an enhanced sensitivity. These sensors can be built on each of the constituent aligned carbon nanotubes while they can be addressed collectively through the common electrode. The alignment structure also facilitates surface modification of the carbon nanotubes with various transduction materials for broadening the scope of analytes detectable by the nanotube sensor. Micropatterning of the aligned carbon nanotubes could further allow for the development of nanotube sensor chips. For both non-aligned and aligned carbon nanotube electrodes, carbon nanotubes have been demonstrated to enhance the electrochemical reactivity of biomolecules^[22] and promote the electron-transfer reactions of redox proteins such as myoglobin,^[23] cytochrome *c*,^[24] and microperoxidase MP-11.^[25] Recent studies, notably by Gooding’s group^[26] in Sydney and Compton’s group^[27] at Oxford, have demonstrated that much of the enhanced electrochemical reactivity and electron transfer of carbon nanotube electrodes arose from the edge-plane like nanotube ends with the side walls of carbon nanotubes comparable to the basal plane of pyrolytic graphite. In this regard, the perpendicularly aligned carbon nanotube arrays with all the nanotube top-ends fall on one plane at the interface between the electrode and electrolyte solution should provide additional advantages for the development of highly sensitive electrochemical sensors. Some of our recent studies on aligned carbon nanotube electrochemical sensors are summarized below.

While working in CSIRO Molecular Science (now CSIRO Molecular and Health Technologies) in Melbourne, we have prepared aligned carbon nanotubes by pyrolyzing iron(II) phthalocyanine (FePc) under an Ar/H_2 atmosphere at 800–1100°C.^[28] We have also developed several lithographic and plasma patterning methods for generation of the perpendicularly aligned carbon nanotube arrays with resolutions down to a micrometer scale.^[29–31] Our methods allow not only the preparation of micropatterned films of the perpendicularly aligned nanotubes but also their transfer onto various substrates, including those which would otherwise not be suitable for nanotube growth at high temperatures (e.g., conducting substrates for electrochemistry and polymer films for flexible devices). Fig. 3a shows the steps of the photolithographic process, in which a patterned polymer film after an appropriate carbonization treatment acts as a shadow mask for the patterned growth of the aligned carbon nanotubes.

On our further investigation of the aligned carbon nanotubes produced by the pyrolysis of FePc, we have recently developed a simple but effective method for preparing aligned carbon nanotube–DNA sensors by chemically

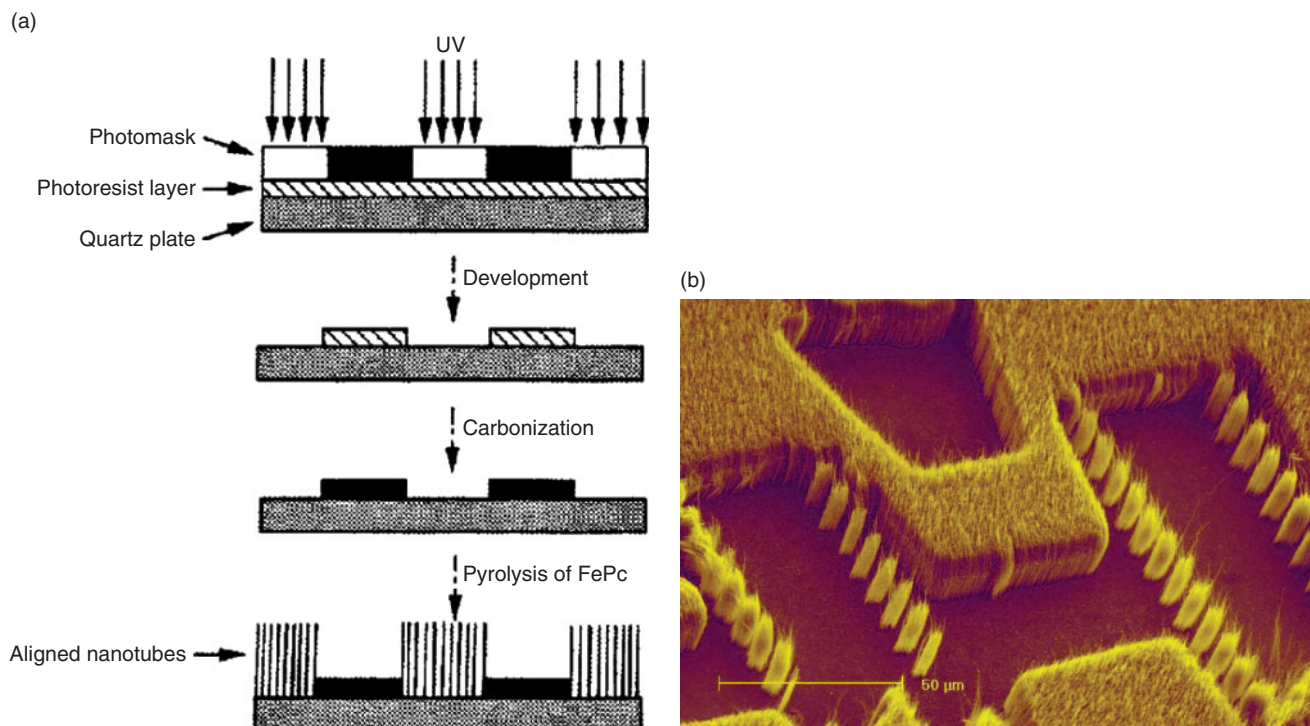


Fig. 3. (a) Schematic representation of the micropattern formation of aligned carbon nanotubes by a photolithographic process. (b) A typical SEM micrograph of patterned films of aligned nanotubes prepared by the pyrolysis of FePc onto a photolithographically prepatterned quartz substrate.^[29]

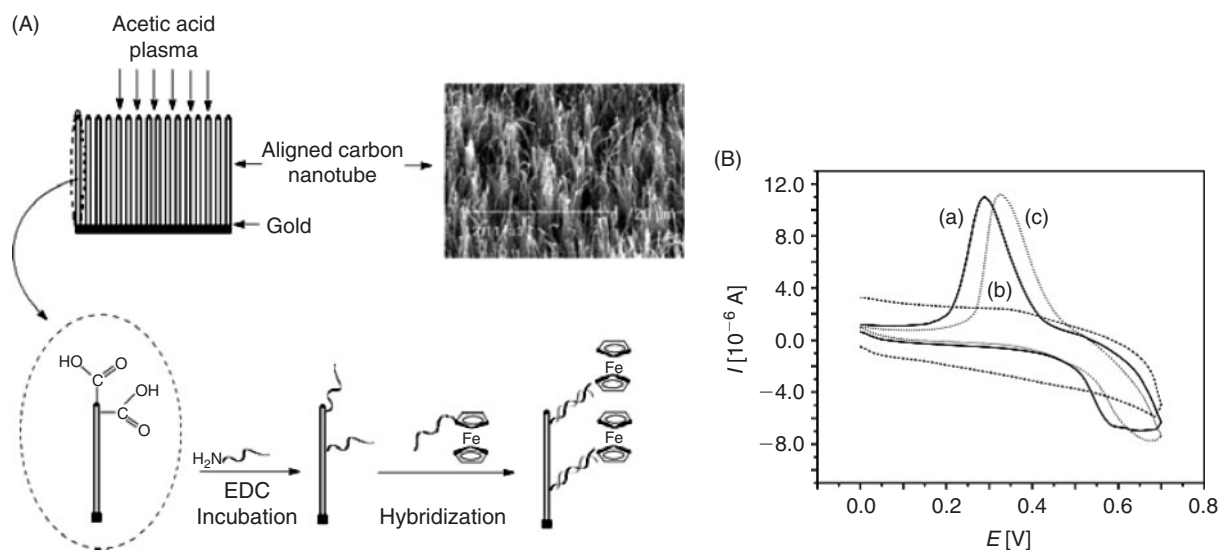


Fig. 4. (A) A schematic illustration of the aligned nanotube–DNA electrochemical sensor. The upper right SEM image shows the aligned carbon nanotubes after having been transferred onto a gold foil. For reasons of clarity, only one of the many carboxyl groups is shown at the nanotube tip and wall, respectively. (B) (a) The ssDNA (1)-immobilized aligned carbon nanotube electrode after hybridization with FCA-labelled cDNA (2) chains, (b) in the presence of FCA-labelled non-cDNA (3) chains, and (c) after hybridization with target DNA (4) chains in the presence of the FCA-labelled non-cDNA (3) chains.^[32]

coupling DNA probes on both the tip and wall of plasma-activated aligned carbon nanotubes in a patterned or non-patterned fashion.^[32] In particular, we carried out acetic acid plasma treatment on gold-supported aligned carbon nanotubes, followed by grafting single-strand DNA (ssDNA)

chains with an amino group at the 5'-phosphate end (i.e., [AmC₆]TTGACACCAGACCAACTGGT-3' **1**) onto the plasma-induced COOH group through the amide formation in the presence of the coupling reagent 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (EDC). Complementary DNA

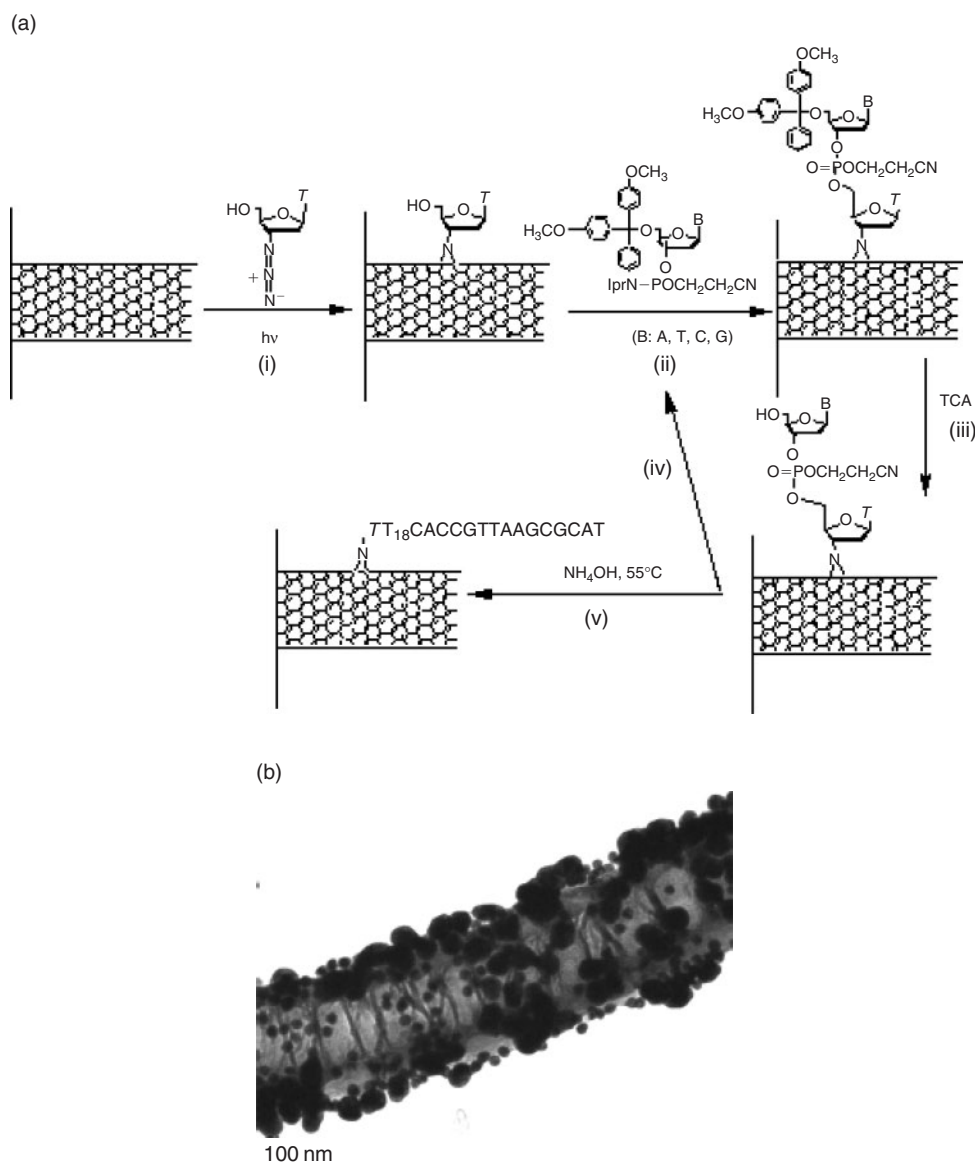


Fig. 5. (a) (i) Aligned MWNTs were coated with a solution of AZT, and UV-irradiated to produce photoadducts each with an OH group. (ii) The OH group reacted with a phosphoramidite mononucleotide to initiate synthesis of the DNA molecule. (iii) Trichloroacetic acid deprotected the OH group. (iv) Reaction with the next nucleotide followed, and the cycle was repeated until the molecule with the desired base sequence was made. (v) Finally, the nanotubes were heated in NH_3 solution to remove blocking groups from the nucleotides to produce the DNA-coated nanotubes. (b) DNA-directed modification of the nanotube surface with gold nanoparticles of different diameters (scale bar: 100 nm).^[33]

(cDNA) chains pre-labelled with ferrocenecarboxaldehyde (FCA, forming $[\text{FCA-C}_6]\text{ACCAGTTGGTCTGGTGTCAA-3}'$ **2**) were then used for hybridizing with the surface-immobilized oligonucleotides to form double-strand DNA (dsDNA) helices on the aligned carbon nanotube electrodes (Fig. 4A).

The performance of the surface-bound ssDNA (**1**) chains on the plasma-treated nanotube electrode for sequence-specific DNA diagnoses was demonstrated in Fig. 4B. The strong oxidation peak seen at 0.29 V in curve a of Fig. 4B can be attributable to ferrocene and indicates the occurrence of hybridization of FCA-labelled cDNA (**2**) chains with the nanotube-supported ssDNA (**1**) chains, leading to a long-range electron transfer from the FCA probe to the nanotube electrode through the DNA duplex. In contrast, the addition of FCA-labelled non-cDNA chains (**3**) under the same conditions did not show any redox response of FCA

(curve b of Fig. 4B). This indicates that, as expected, there was no specific DNA pairing interaction with the non-cDNA chains, and that physical adsorption of the FCA-labelled DNA chains, if any, was insignificant in this particular case. Subsequent addition of target DNA chains (**4**) into the above solution, however, led to a strong redox response from the FCA-labelled DNA (**3**) chains (curve c of Fig. 4B) because the target DNA (**4**) chain contains complementary sequences for both **1** and **3** chains. More interestingly, the electrochemical responses seen in Fig. 4B were revealed to be highly reversible. These results demonstrated that specific DNA sequences could be covalently immobilized onto plasma-activated aligned carbon nanotubes for sensing cDNA and/or target DNA chains of specific sequences with a high sensitivity and selectivity. Along with the techniques for micropatterning aligned carbon nanotubes, these results should

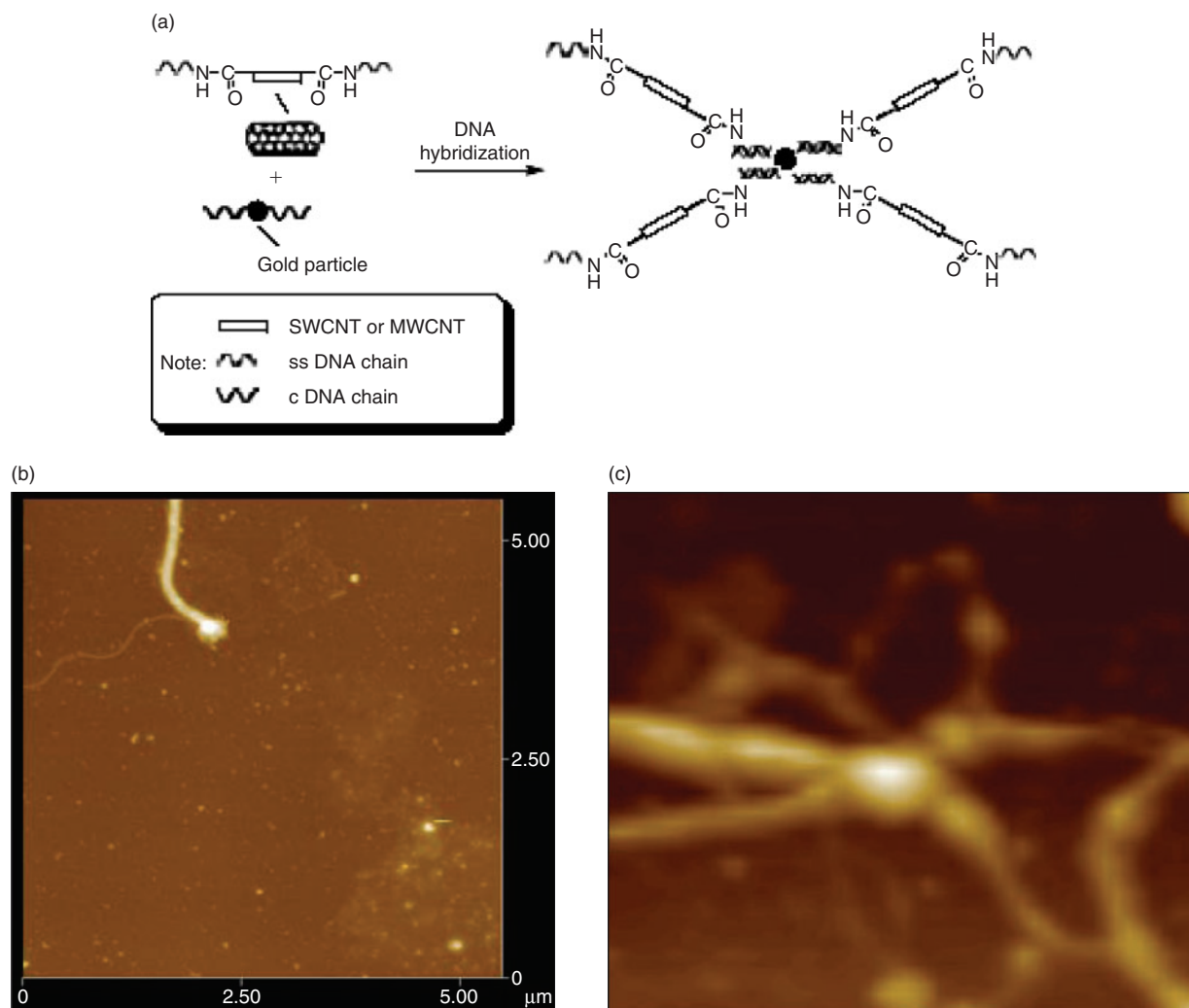


Fig. 6. (a) Schematic representation of procedures for DNA-directed self-assembly of multiple carbon nanotubes and nanoparticles. Typical AFM image of (b) the self-assembly of an ssDNA-SWNT and ssDNA-MWNT through a cDNA-Au nanoparticle (scanning area: $5.60 \mu\text{m} \times 5.60 \mu\text{m}$) and (c) multiple ssDNA-SWNTs and ssDNA-MWNTs connected with a cDNA-Au nanoparticle core (scanning area: $1.10 \mu\text{m} \times 1.10 \mu\text{m}$).^[34]

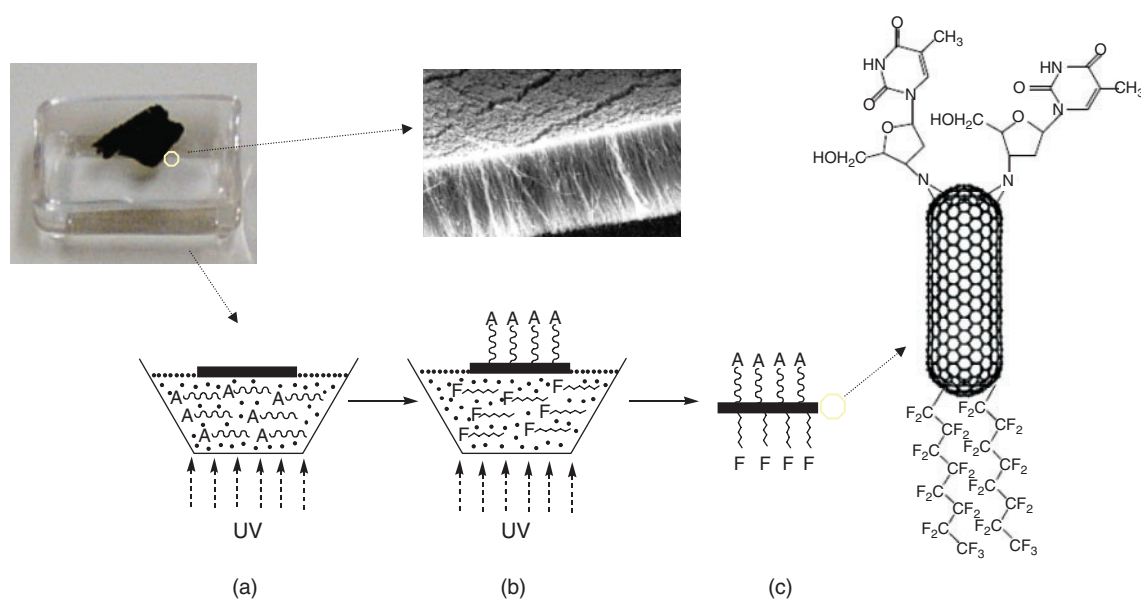


Fig. 7. A free-standing film of aligned MWNTs floating on the top surface of (a) an AZT solution in ethanol for UV irradiation at one side of the nanotube film; (b) a perfluorooctyl iodide solution in trichloroethylene for UV irradiation at the opposite side of the nanotube film;^[35] and (c) the asymmetrically end-functionalized carbon nanotube film.

have important implications not only for the sequence-specific analyses or diagnoses of DNA chains but also for the use of carbon nanotubes in advanced sensing chips.

Sensor chips (or sensor arrays) consist of many different sensors on a single chip, allowing the identification of complex mixture systems even without separation. The construction of sensor chips requires multidimensional integration of functional components. Self-assembly could facilitate the development of sensor chips by adding multifunctional supramolecular structures to the existing sensing devices and systems. In collaboration with McCall and Moghaddam at CSIRO in Australia, we have developed a photochemical method to functionalize carbon nanotubes with photoreactive reagents (e.g., aziridothymidine, AZT), followed by the coupling of ssDNA chains onto the carbon nanotube through the photo-adduct and coating the nanotube sidewalls with cDNA-modified gold nanoparticles by means of DNA hybridization (Fig. 5).^[33]

The locations of the DNA molecules thus attached onto the carbon nanotubes can be determined by a visual assay using cDNA-modified gold nanoparticles and transmission electron microscopy (TEM). Fig. 5b shows gold nanoparticles positioned in close proximity to the surfaces of the nanotubes; the sample was prepared by binding cDNA-attached 16-nm diameter gold nanoparticles to the ssDNA chains grafted on the nanotubes, followed by a further hybridizing of the remaining unbound cDNA on the 16-nm gold nanoparticles to their cDNA chains attached to 38-nm diameter gold nanoparticles.

Therefore, the highly specific DNA hybridization reaction can be used not only to develop the visual assay to check the exact locations of DNA molecules attached to the nanotubes, but also to provide a means of self-assembling functional components on the nanotube surface for potential applications, including in sensor chips. Furthermore, we have also prepared a wide range of multicomponent structures of carbon nanotubes (Fig. 6) through DNA-direct self-assembly of carbon nanotubes and gold nanoparticles in solution for multifunctional material and device applications.^[34]

In somewhat related work, our^[35] and Hinds' group^[36] independently reported asymmetric end-functionalization of carbon nanotubes. In particular, we developed a simple but effective photochemical approach to directly grafting different chemical reagents onto the opposite tube-ends of individual carbon nanotubes, as schematically shown in Fig. 7. The resultant nanotubes with different chemical reagents (e.g., ssDNA and cDNA chains) attached onto their opposite tube-ends should be very useful for site-selective self-assembly of carbon nanotubes into many novel functional structures even without the involvement of nanoparticles.

More recently, we have developed a facile yet versatile and effective substrate-enhanced electroless deposition (SEED) method for decorating CNTs with various metal nanoparticles, including those otherwise impossible by more conventional electroless deposition methods, in the absence of any additional reducing agent.^[37,38] By simply supporting carbon nanotubes with a metal substrate of a redox potential lower than that of the metal ions to be reduced into nanoparticles, we have recently used the SEED method to deposit metal (Cu, Ag, Au, Pt, and Pd) nanoparticles onto SWNTs and MWNTs (Fig. 8).^[37] In conjunction with shape- and size-controlled metal nanoparticle syntheses, the SEED technique described above further enabled us to successfully deposit the shape/size-controlled metal nanoparticles either on the nanotube outer or inner wall (Fig. 9).^[38] Our preliminary results have also demonstrated that

the SEED method can be used to graft metal nanoparticles onto the aligned/micropatterned carbon nanotubes, either along the nanotube length or on nanotube tips, while largely retaining their structural integrity (Fig. 10).

To study the electrochemical activity of the CNTs modified with metal nanoparticles, we used the FePc-generated aligned CNTs modified with Pt nanocubes as the working electrode for electrocatalytic oxidation of methanol. As can be seen in Fig. 11, the pristine, aligned CNT electrode showed a capacitive current only due to the double layer capacitance (Fig. 11a), whereas the Pt nanoparticle modified, aligned CNT electrode showed two strong redox peaks at 0.45 and 0.7 V, characteristic of methanol oxidation.^[38] These results indicate the usefulness of the metal nanoparticle modified, aligned CNT arrays as efficient electrodes in methanol direct fuel cells and perhaps many other electrochemical systems, including sensors and sensor chips.

Furthermore, we have successfully prepared multicomponent and multifunctional hybrid structures based on micro-sized carbon fibres (CFs) sheathed with aligned carbon nanotubes and their derivatives (Fig. 12),^[39] which were demonstrated to be an effective means for connecting nanoscale entities to the outside world and to possess interesting electrochemical properties attractive for a wide range of potential applications, including in methanol direct fuel cells, highly sensitive chemical- and bio-sensors.^[39]

Fig. 13 shows amperometric responses for a glucose oxidase immobilized aligned CNTs on the CF substrate (curve a) and the pristine CF electrode (curve b) to each successive addition of 3 mM glucose. As can be seen, a stepwise increase in the current signal upon each successive addition of glucose (curve a) was observed, while the CF electrode showed no obvious current change with the addition of glucose (curve b). Also included in the inset of Fig. 13 is the current increment with the glucose concentration for the CNT-CF electrode, which shows a pseudo-linear relationship indicating a high sensitivity and reliability. The linear response to the glucose concentration extends beyond 20 mM, which is higher than the 15 mM required for practical use in the detection of blood glucose.^[40] The CNT-CF glucose sensor also shows a fast response, reaching to a steady-state current signal within about 20 s upon each addition of the glucose to the detecting solution. Given that many enzymatic reactions are associated with the generation of hydrogen peroxide, the methodology developed in this study should be applicable to sensor many other biologically important substances. Judicious modification of the CF-supported aligned carbon nanotubes with various functional moieties could lead to a class of novel multidimensional, multicomponent, and multifunctional materials of practical significance.

On the other hand, we have recently synthesized, in collaboration with Wan's group at the Chinese Academy of Sciences, polyaniline (PANI) nanotubes (Fig. 14a) through a self-assembled $C_{60}(OH)_6(OSO_3H)_6$ supramolecular template using $(NH_4)_2S_2O_8$ as an oxidant.^[41] This, together with the more recent discovery of patterned and non-patterned generation of conducting polymer micro-/nano-containers self-assembled around the surface of 'soap bubbles' produced on an electrode by electrolysis of appropriate electrolyte solutions (Fig. 14b),^[42] clearly indicates that supramolecular engineering has broadened the scope for developing multidimensional and multifunctional π -conjugated structures of significance for sensor and sensor chip applications.^[43]

In addition to the chemical grafting of DNA chains onto the carbon nanotube surface and DNA-directed self-assembling

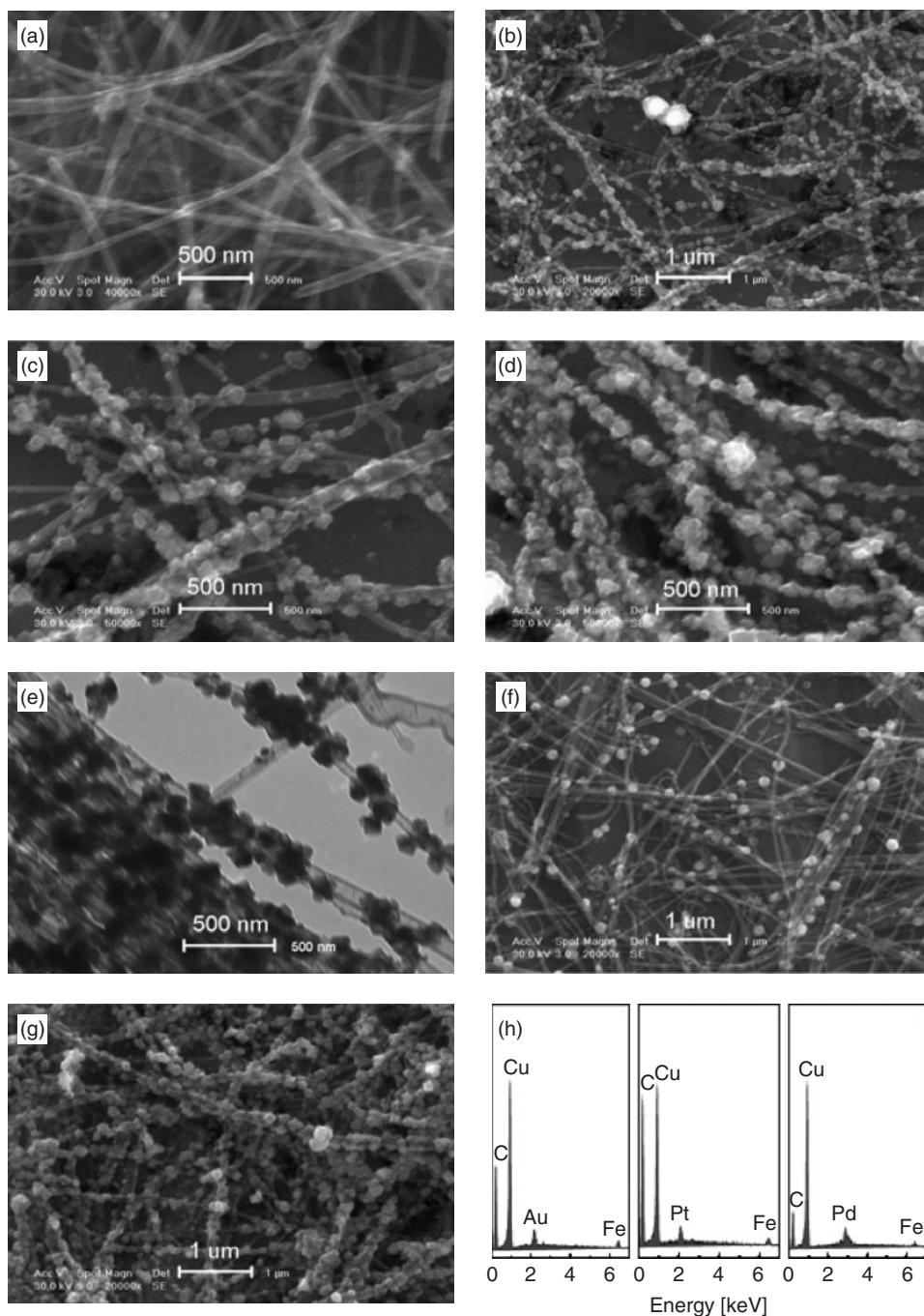


Fig. 8. SEM images of MWNTs supported by a copper foil after being immersed into an aqueous solution of HAuCl_4 (3.8 mM) for different times: (a) 0 s, (b) 10 s, (c) same as for (b) under a higher magnification, (d) 30 s. (e) A TEM image of Au nanoparticle coated MWNTs. (f) The Cu-supported MWNTs after being immersed in an aqueous solution of K_2PtCl_4 (4.8 mM) for 10 s, and (g) the Cu-supported MWNTs after being immersed into an aqueous solution of $(\text{NH}_4)_2\text{PdCl}_4$ (7.0 mM) for 10 s. (h) Energy-dispersive X-ray spectra for the Au, Pt, and Pd nanoparticle-coated MWNTs on Cu foils.^[37]

carbon nanotubes in solution for sensor and sensor chip applications, we, in collaboration with Wallace's group in Wollongong University, have also used the aligned carbon nanotubes as nanoelectrodes for making novel conducting polymer-coated carbon nanotube coaxial nanowires (CP-CNT) by electrochemically depositing a concentric layer of an appropriate conducting polymer uniformly onto each of the constituent aligned nanotubes (Fig. 15a).^[44] To demonstrate the potential sensing applications for the CP-CNT coaxial nanowires, we have

immobilized glucose oxidase onto the aligned carbon nanotube substrate by electropolymerization of pyrrole in the presence of glucose oxidase. The glucose oxidase containing polypyrrole-carbon nanotube coaxial nanowires were used to monitor the concentration change of hydrogen peroxide (H_2O_2) generated from the glucose oxidation reaction by measuring the increase in the electro-oxidation current at the oxidative potential of H_2O_2 .

As shown in Fig. 15b, a linear response of the electro-oxidation current to the glucose concentration was obtained for

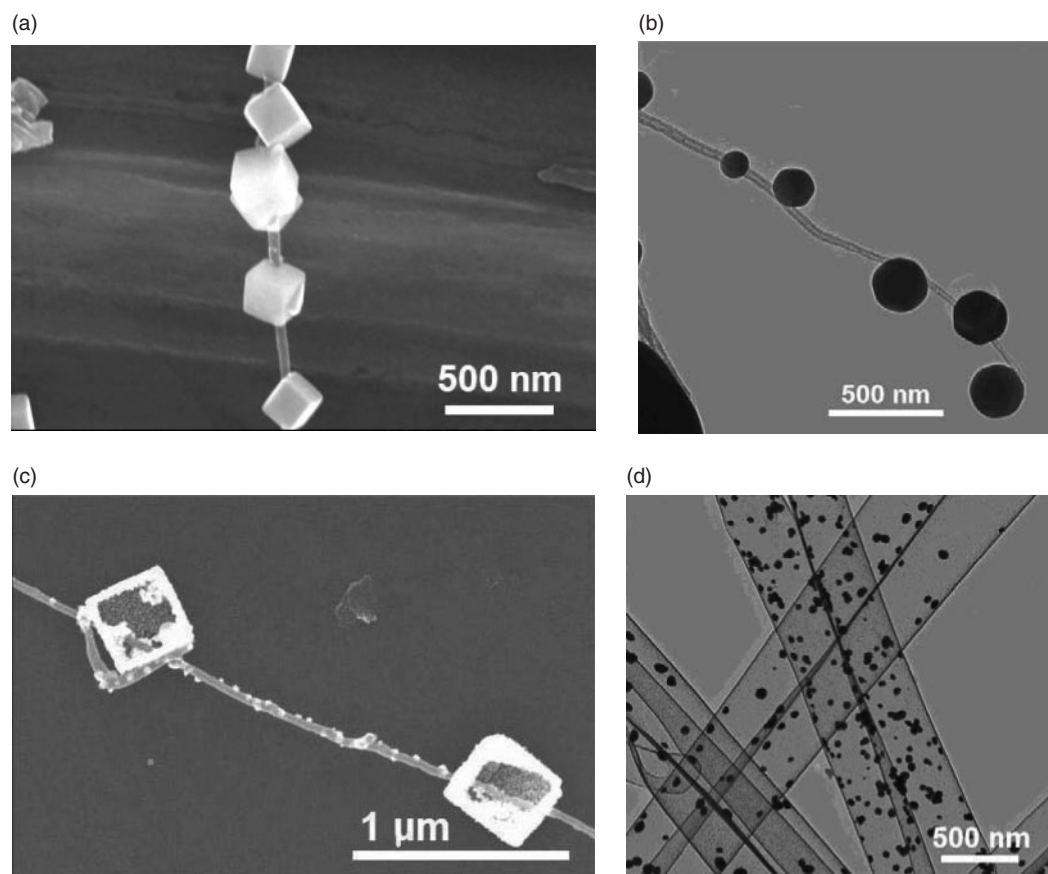


Fig. 9. SEM images of sidewall modification of carbon nanotubes with (a) Pt cubes, (b) spheres, (c) Au hollow nanoboxes, and (d) a TEM image of CNTs having their innerwall modified with Pt nanospheres by immersing the template-synthesized, perpendicularly aligned CNTs into an aqueous solution of 1.9 mM K_2PtCl_4 for 30 min.^[38]

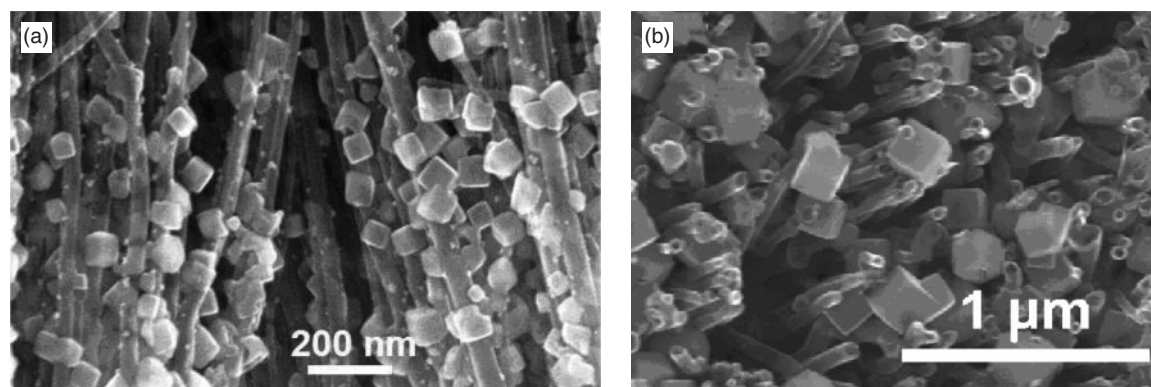


Fig. 10. SEM images of (a) aligned CNTs decorated with Pt nanocubes, prepared by immersing the Cu foil-supported aligned CNTs into an aqueous solution of 3.8 mM K_2PtCl_4 and 5 mM $CuCl_2$ for 1 min, and (b) an SEM image of Pt nanocubes deposited onto the nanotube tips by floating the Cu foil-supported aligned CNT films on an aqueous solution of 3.8 mM K_2PtCl_4 containing 5 mM $CuCl_2$ for 1 min.^[38]

the CP-CNT nanowire sensor. The linear relationship extends to glucose concentration as high as 20 mM. Furthermore, responses from the CP-CNT glucose sensors were found to be about an order of magnitude higher than that of more conventional flat electrodes coated with glucose oxidase containing polypyrrole films under the same conditions. Apart from the large surface/interface area obtained for the nanotube-supported conducting polymer layer, which is attractive for using them in sensing applications, the coaxial structure allows the nanotube

framework to provide mechanical stability and efficient thermal/electrical conduction to and from the conducting polymer layer. The CP-CNT nanowire sensors were also demonstrated to be highly selective for glucose with their electro-oxidation current responses being almost unchanged even in the presence of some interference species, including ascorbic acid, urea, and D-fructose. The well-defined nanochannels of the perpendicularly aligned carbon nanotubes could provide additional discrimination for the detection of single molecular in a complex

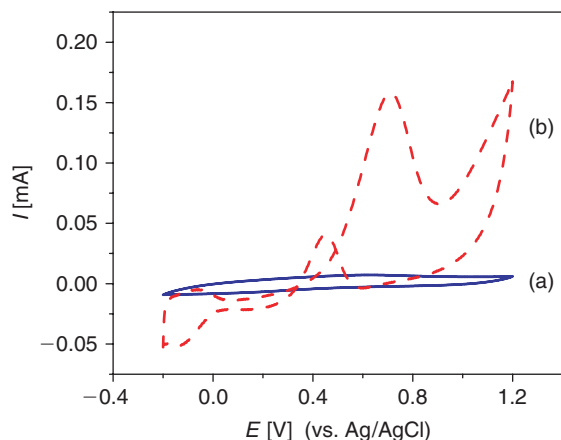


Fig. 11. Cyclic voltammograms of (a) the pristine aligned CNT and (b) Pt nanoparticle modified, aligned CNT electrodes supported by a sputter-coated Au layer in a N_2 -saturated aqueous solution of 2 M CH_3OH + 0.1 M H_2SO_4 solution (scan rate, 50 mV s^{-1}).^[38]

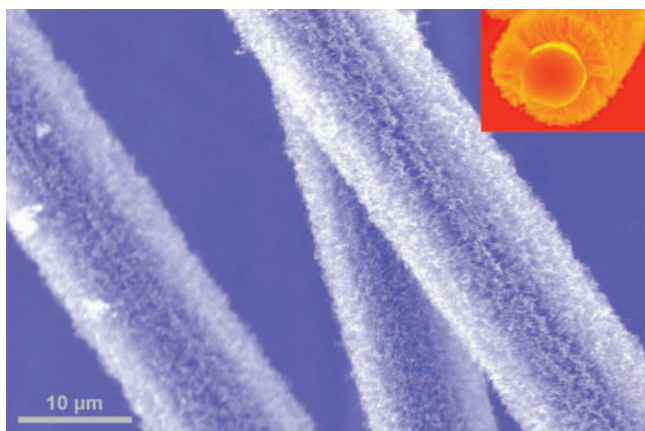


Fig. 12. SEM images of CFs after the growth of carbon nanotubes. Inset: cross-sectional view after deliberately breaking an aligned CNT-sheathed CF.

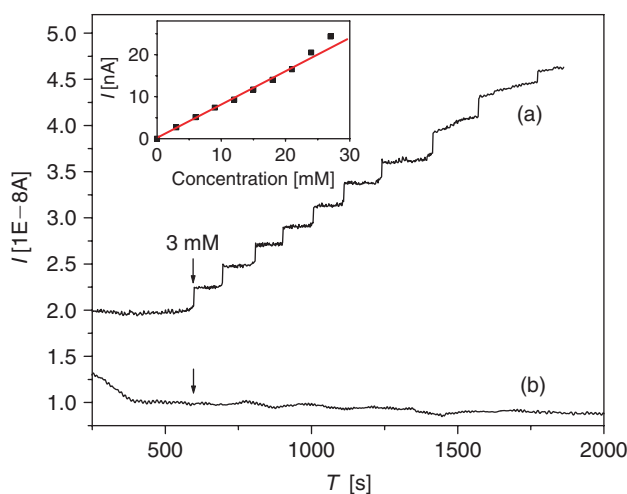


Fig. 13. Amperometric responses to the successive additions of 3 mM glucose for (a) the glucose oxidase attached aligned CNT-CF electrode and (b) the CF electrode after having been subjected to the same electrochemical oxidation and glucose oxidase immobilization processes. Inset: current increment against the glucose concentration for the CNT-CF glucose sensor.^[40]

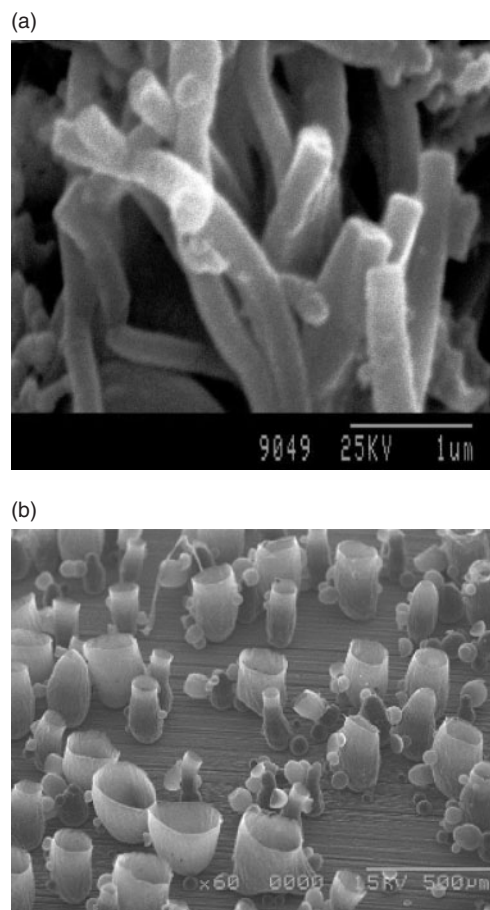


Fig. 14. SEM images of (a) PANI- $C_{60}(OH)_6(OSO_3H)_6$ nanotubes and (b) some of conducting polymer micro-/nano-structures prepared by the 'soap bubble' template technique.^[41,42]

environment, leading to highly sensitive and selective nanotube sensors.

In collaboration with Roy and Tia at the US Air Force Research Laboratory (AFRL), we have recently developed new sensors with high sensitivity, good selectivity, and excellent environmental stability yet low power consumption for the detection of a broad class of chemical vapours. These new sensors were prepared by partially coating of perpendicularly aligned carbon nanotube arrays with an appropriate polymer thin film along their tube length.^[45] As schematically shown in Fig. 16, the absorption and desorption of chemical vapours by the polymer matrix cause changes in the inter-tube distance, and hence the surface resistance across the nanotube film. Simple measurements of the resistance change, therefore, constitute the nanotube-polymer chemical vapour sensors. These rationally designed aligned carbon nanotube-polymer composite films are flexible and can be effectively integrated into many systems for a wide range of potential applications, including their use as multifunctional sensors for sensing chemical vapours, mechanical deformations, and thermal and optical exposure.^[45] This is clearly an area in which future work would be of value.^[46]

These are just some examples, which show advanced sensors and sensor arrays could be developed from conducting polymers and carbon nanotubes. The tiny size of nanotube sensors implies that they are very energy efficient and could move through the cell membrane without obvious harmful effect on the

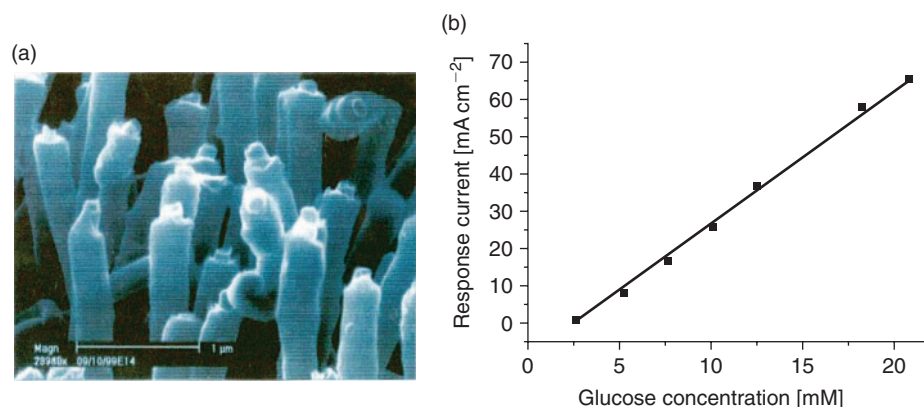


Fig. 15. (a) Typical SEM images of the CP-NT coaxial nanowires produced by cyclic voltammetry on the aligned carbon nanotube electrode, showing a thin layer of conducting polymer (polypyrrole) coating surrounding each of the constituent aligned carbon nanotubes. (b) The dependence of electrooxidation current at the oxidative potential of H_2O_2 on the glucose concentration for the CP-NT coaxial nanowire sensor.^[44]

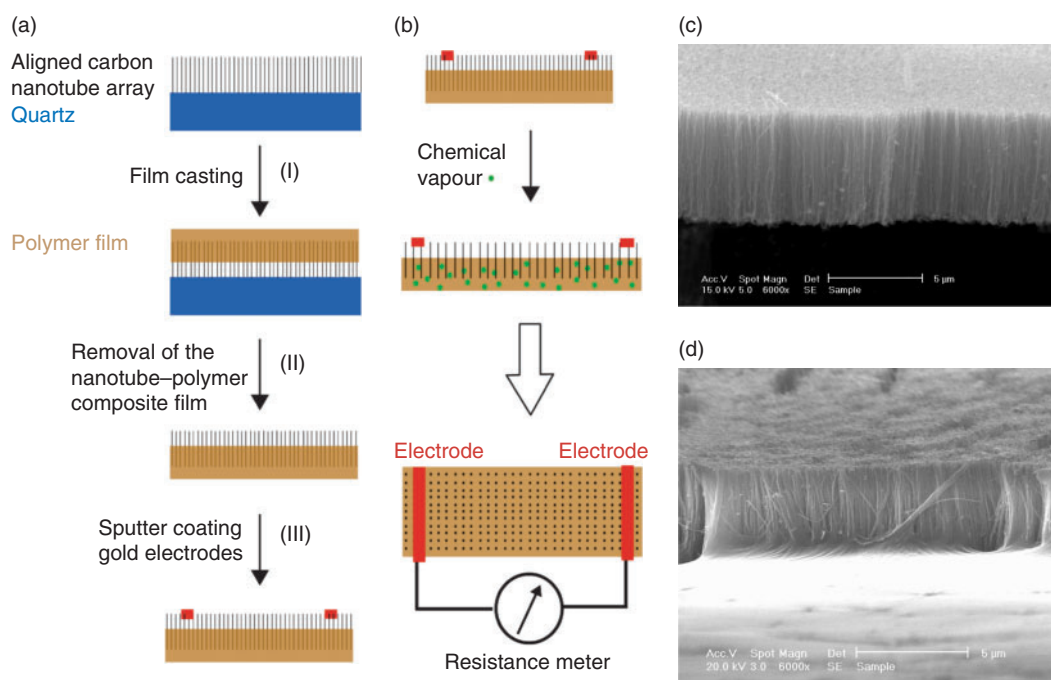


Fig. 16. Schematic illustration of the procedures for (a) fabricating and (b) characterizing the aligned carbon nanotube-polymer composite chemical vapour sensor. SEM images of the aligned carbon nanotube array (c) before and (d) after being partially coated with a polymer (PVAc) film on top and turned upside down (scale bars: 5 μm).^[45]

cell function. With so many transduction methods and micro-/nano-fabrication techniques already reported^[1] and more to be developed, there will be vast opportunities for developing numerous complex measurement devices of capabilities for various sophisticated analyte detections from chemical and biological sensors based on the architectural diversity of the π -conjugated structure. Continued research and development efforts in this exciting field will surely revolutionize the way in which future chemical and biomedical tests to be performed in both research and clinical diagnostic laboratories that could affect many aspects of our lives in the long term.

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