

Electrochemistry and Electroanalytical Applications of Carbon Nanotubes: A Review

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This review addresses recent developments in electrochemistry and electroanalytical chemistry of carbon nanotubes (CNTs). CNTs have been proved to possess unique electronic, chemical and structural features that make them very attractive for electrochemical studies and electrochemical applications. For example, the structural and electronic properties of the CNTs endow them with distinct electrocatalytic activities and capabilities for facilitating direct electrochemistry of proteins and enzymes from other kinds of carbon materials. These striking electrochemical properties of the CNTs pave the way to CNT-based bioelectrochemistry and to bioelectronic nanodevices, such as electrochemical sensors and biosensors. The electrochemistry and bioelectrochemistry of the CNTs are summarized and discussed, along with some common methods for CNT electrode preparation and some recent advances in the rational functionalization of the CNTs for electroanalytical applications.

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1 Introduction

Carbon nanotubes (CNTs) have been proved to be a novel type of nanostructure with unique structural, electronic and mechanical properties and have drawn extensive attention since their discovery.¹⁻³ Research over the past decade has revealed that the CNTs constitute a new form of carbon materials that are finding striking applications in many fields, such as energy conversion and storage,^{4,5} electromechanical actuators,^{6,7} chemical sensing⁸ and so forth. Generally, the nanotubes can be divided into two categories: single-walled carbon nanotubes (SWNTs) and multi-walled carbon nanotubes (MWNTs). The former can be regarded as a graphene cylinder formed by rolling seamlessly a single graphene sheet along an (*m,n*) lattice vector in the sheet. The (*m,n*) indices is a central parameter governing the metallicity and chirality of the tubes. The latter is composed of coaxial multilayer graphene tubes with interlayer space of 0.34 nm. The diameter varies from 0.4 nm to 3 nm for the SWNTs and from 1.4 nm to 100 nm for the MWNTs (typical

transmission electron microscopic images of the CNTs are shown in Fig. 1).

Due to the unique physical and chemical properties and thus the striking applications in various research and industrial fields, the CNTs have drawn extensive interest over the past decade. To date, we have witnessed great successes in the synthesis of the CNTs and in understanding of their chemical and physical properties. Several excellent reviews concerning these issues have appeared in the literature.^{9,10} Currently, increasing interests are being focused on the construction of the CNT-based functional nanodevices with novel properties for practical applications.

On the other hand, the CNTs represent a new kind of carbon-based materials and are superior to other kinds of carbon materials commonly used in electrochemistry, such as glassy carbon (GC), graphite and diamond, mainly in the special structural features and unique electronic properties. As a result, besides their striking applications in other fields, study of the CNT electrochemistry thus far has revealed that these unique properties of the CNTs substantially make them useful for electrochemical investigations, *e.g.*, electrocatalysis, direct electrochemistry of proteins and electroanalytical applications such as electrochemical sensors and biosensors.^{11,12} The electroanalytical applications of the CNTs for construction of

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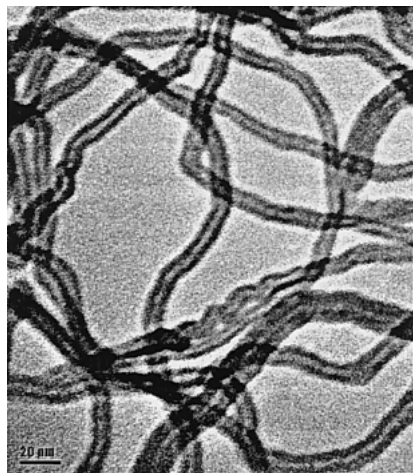


Fig. 1 Transmission electron microscopy image of the MWNTs (unpublished result).

electrochemical sensors and biosensors have been reviewed in the literature.^{6,13,14}

This review mainly aims at recent developments in electrochemistry and electroanalytical chemistry of the CNTs, highlighting several key issues in the electrochemistry and electroanalytical applications of the CNTs. Such issues include: (i) preparation of the CNT electrodes, (ii) electrochemistry and electrocatalysis of the CNTs, (iii) rational functionalization of the CNTs for electroanalytical applications, (iv) CNT-based bioelectrochemistry, and (v) CNT-based biosensors.

2 CNT Electrode Preparation

CNTs tend to aggregate together in almost all kinds of aqueous and organic solutions due to the van der Waals forces between tubes. This property is inherent in the CNTs and imposes the difficulties in making homogeneous CNT composite and thus greatly hampers electrochemical studies and electroanalytical applications of the CNTs. So far, significant progress has been made in covalent and noncovalent functionalization of the CNTs. Those strategies can also be used for solubilizing the CNTs and further facilitating their manipulations.^{15–18} However, methods for the preparation of the CNT electrodes from an electrochemical point of view are still needed. It is fair to say that the CNT electrodes used in most of the hitherto-reported electrochemical studies were simply prepared by randomly dispersing the CNTs onto a substrate electrode or by confining the CNTs on a substrate with polymers such as Teflon,¹⁹ Nafion or paste.^{20,21} Although those CNT electrodes have been demonstrated to be useful for practical electrochemical applications, they may not be very suited for fundamental electrochemical studies, since the random confinement of the CNTs onto the electrodes without any favorable orientation essentially causes the difficulties in determining the contributions of the ends and the sidewall of the nanotubes to the electrochemical properties (*e.g.*, electrocatalytic activity) of the CNTs. As a result, new methods, *e.g.*, aligned CNTs, have been recently developed and have proved to be useful for electrochemical studies and electroanalytical applications.^{11,22–24} Since these methods, including cast-coating, chemical deposition and chemical linkage, have been elegantly demonstrated in the literature for the preparation of CNT electrodes,^{22–25} we will only focus on the recently developed

methods for CNT electrode preparation, including confining the CNTs with polymers, paste, and sol-gel matrix or assembling the CNTs with layer-by-layer techniques.

2.1 CNT-polymer nanocomposite electrodes

Nafion, a perfluorinated ionomer, has been widely used to confine electrocatalysts and/or biomacromolecules (*e.g.*, enzymes and proteins) on electrode surfaces to prepare chemically modified electrodes with electrochemical properties distinct from those of bulk electrodes. This kind of insulating polymer has been recently demonstrated to be particularly useful for preparing the CNT-based electrodes because of its capability of confining the CNTs onto substrate electrodes and of solubilizing the CNTs in solution.^{12,26} These properties, combined with the electrocatalytic activities of the CNTs, have been proved to be very useful for construction of CNT-based amperometric sensors and biosensors. Wang *et al.* prepared CNT/Nafion nanocomposite electrodes and found that the as-prepared electrode possesses excellent electrocatalytic activities toward carbohydrates, hydrogen peroxide (H_2O_2) and NADH.¹² The catalytic activities toward H_2O_2 and NADH were further exploited for construction of oxidase- or dehydrogenase-based biosensors with a good reproducibility and high stability as well as minimized interference. The CNT/Nafion nanocomposite electrode was also found to be able to accelerate the oxidation of homocysteine and can be used for the detection of such species at a low potential.²⁶

Alternatively, conductive polymers, such as polypyrrole (PPy) and polyaniline (PAN) can also be used for fabrication of CNT/PPy and CNT/PAN nanocomposite electrodes due to the ease in preparation through co-polymerization by a chemical or electrochemical approach and that the resulting nanocomposites exhibit high conductivity and stability.^{27,28} The nanocomposite electrodes can be used for stable electrocatalysis and thus for construction of electrochemical sensors. For example, Guo *et al.* used PAN to prepare the CNT-based electrode and found that the prepared CNT/PAN electrode possesses a good electrocatalytic activity toward the reduction of nitrite.²⁸ In addition to the striking applications in confining the CNTs onto macro-sized electrodes, the strategy through the use of conductive films to confine the CNTs may also be applicable for preparing CNT-based microelectrodes, because the procedures for the preparation of CNT/PPy and CNT/PAN nanocomposites can be easily conducted on the microelectrodes through electrochemical polymerization. The small size and good electrochemical properties of the CNTs could make the CNT-based microelectrodes available for the electrochemical measurements in micro-environments such as biological tissues.

It should be noted that the uses of insulating polymers such as Nafion to prepare the CNT-based electrodes may be advantageous over those of conductive polymers when the as-prepared electrodes are employed for cyclic voltammetric measurements. This is because the former electrodes exhibit a more discernable faradaic response for the redox species from the low charging current, compared with the latter ones. Furthermore, the CNTs in themselves are highly conductive, with a fine structure of several μm in length (Fig. 1) and can actually act as nanowires. This property essentially compensates the poor conductivity of the insulating polymer used. Moreover, the noncovalent attachment of insulating polymers onto the CNTs to prepare the CNT/polymer nanocomposite does not seriously distort the unique electronic and structural properties of the CNTs. As a result, the CNT/insulating polymer nanocomposite electrodes are anticipated to retain the conductivity and electrochemical properties of the CNTs and are therefore

envisaged to be very attractive for electrochemical studies and electroanalytical applications.

2.2 CNT paste electrodes

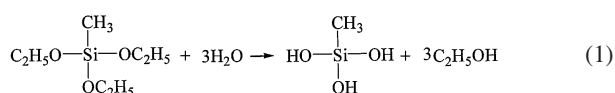
Similar to the procedures for the preparation of carbon paste electrodes, CNT paste electrodes are generally prepared by first mixing the CNTs with mineral oil into paste and then packing the paste into a cavity. For example, Valentini *et al.* prepared a CNT paste electrode;²⁰ in their procedure, the paste was hand-mixed in a mortar and then packed into a micro-cavity at the end of a Teflon tube terminated with an electrical conductor. The electrochemical properties of the prepared CNT paste electrode were investigated by using cyclic voltammetry with $\text{Fe}(\text{CN})_6^{3-/4-}$ couple as the redox probe. They found that the reversibility of the redox couple was dependent on the content of the CNTs in the paste. For instance, a good reversibility of the $\text{Fe}(\text{CN})_6^{3-/4-}$ couple was achieved when the ratio of CNT-to-oil ratio was 75:25 (w/w), while a sluggish voltammetric response was recorded when the CNT content was reduced to 37%. The poor electrochemical property of the CNT paste electrode was considered to result from the very high resistance of the CNT paste. Possible applications of the CNT paste electrode with an appropriate content of the CNTs were demonstrated for the electrochemical detection of some biologically important species, *e.g.*, dopamine (DA), serotonin, epinephrine and ascorbic acid (AA).

2.3 CNT/sol-gel nanocomposite electrodes

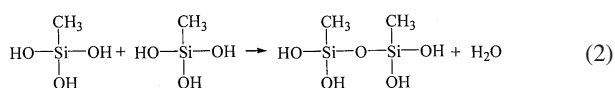
The sol-gel technique has been widely used in electrochemistry because of the combined advantages from the intersection between sol-gel chemistry and electrochemistry. Over the last decades, sol-gel electrochemistry has drawn extensive interest because of its remarkable facilitation of electrochemical studies and applications.²⁹⁻³¹ Among those studies, increasing interest is being focused on sol-gel derived ceramic carbon electrodes (CCEs) that are generally prepared by doping carbon or graphite powder into a silicate gel matrix. The CCEs have been demonstrated to be very useful for electrochemical investigations, *e.g.*, electroanalysis, biosensors, electrocatalysis, and energy conversion and storage.

Similar to the CCEs, ceramic-carbon nanotube nanocomposite electrodes (CCNNEs) could also be prepared by doping the CNTs into a silicate gel matrix.^{32,33} The formation of silicate gel (with methyltriethoxysilane (MTEOS) precursor as an example) has been known to undergo the processes of hydrolysis, condensation, polycondensation and drying through the following reactions.³⁴

Hydrolysis:



Condensation:



Polycondensation:

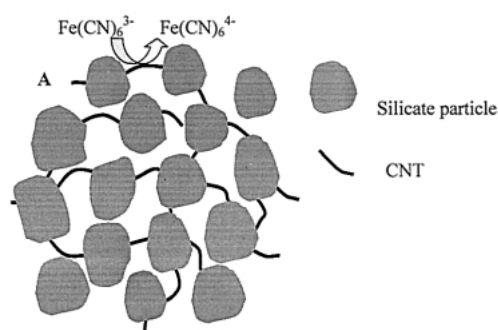
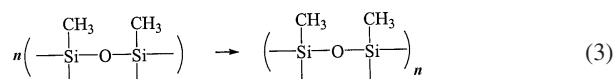


Fig. 2 Schematic illustration of the CNT/sol-gel nanocomposite electrode with tunable electrode dimensions.

The hydrolysis, condensation and polycondensation reactions initiate as soon as the mixing of METOS, HCl, alcohol and H_2O occurs. Hydrolysis (reaction 1) results in the formation of silanol groups ($\text{Si}-\text{OH}$) that react further to produce siloxane ($\text{Si}-\text{O}-\text{Si}$) polymers in the condensation and polycondensation (reactions 2 and 3). These reactions form a colloidal suspension of small particles (a sol) that interconnect to eventually form a rigid and porous structure (a gel). Some kinds of siloxane polymers formed in the condensation and polycondensation reactions are hydrophobic (*e.g.*, that with METOS as a precursor) and can thus interact with the hydrophobic sidewall of the nanotubes through hydrophobic interaction. The noncovalent adsorption and the growth of the silicate particles on the nanotubes were considered to effectively separate the aggregated nanotubes into single nanotubes or small bundles of nanotubes. Moreover, the growth of sol particles on the separated nanotubes eventually separates the formed single nanotubes or small bundles of nanotubes into several independent parts, as schematically depicted in Fig. 2. The parts shielded by the silicate particles are not electrochemically accessible and thereby can not be used for electrode reactions. In contrast, the exposed parts of the nanotubes are readily accessible for solution species and actually serve as nanoelectrodes for electrode reactions. As a consequence, the intersection of CNT science with sol-gel chemistry not only provides a facile protocol for the preparation of CNT-based electrodes (*i.e.*, CCNNEs) that are relatively useful for electrochemical studies, but also allows the prepared CCNNEs to efficiently integrate the advantages both from the CNTs and from sol-gel electrochemistry. More importantly, such an intersection provides the CCNNEs with another striking point of superiority, *i.e.*, tunable electrode dimension from conventional to microscopic dimensions. We have found that a high content of the CNTs (*i.e.*, higher than 1.5 mg/mL in the sol) leads to the formation of the CCNNE characteristic of an electrode of a conventional dimension, while a low content (typically lower than 0.10 mg/mL) essentially yields the CCNNE similar to a nanoelectrode ensemble. Both kinds of CCNNEs are very useful, *e.g.*, for electrocatalysis toward AA and glutathione (both reduced and oxidized forms).³³

Furthermore, the CNT/sol-gel nanocomposite electrodes can be further exploited for development of biosensors by entrapping enzymes or proteins into the CNT/sol-gel nanocomposite because of the excellent biocompatibility of the sol-gel matrix and the good electrochemical properties of the CNTs.³⁵ Gavalas *et al.* prepared CNT/amino acid oxidase/sol-gel bio-composites that could be used for biosensing of amino acids.³⁶ As another example to demonstrate such striking applications, we have prepared CNT/horseradish peroxidase (HRP)/sol-gel

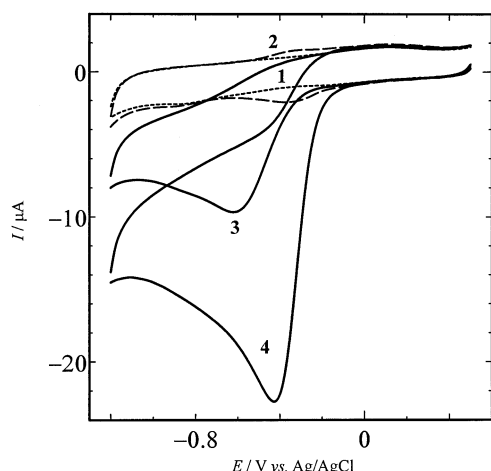


Fig. 3 Typical cyclic voltammograms of SWNT/APTOS-modified (curves 1 and 3) and HRP/SWNT/APTOS-modified (curves 2 and 4) GC electrodes in 0.10 M phosphate buffer (pH 7.0) saturated with N_2 (curves 1 and 2) or air (curves 3 and 4). Scan rate, 300 mV/s. A 5 μ L of 3-aminopropyltrimethoxysilane (APTOS) was mixed with 5 μ L of single-walled carbon nanotubes (SWNTs, 1 mg/mL in DMF) and 5 μ L of 20 mg/mL horseradish peroxidase (HRP) in aqueous solution. The mixture was sonicated to give a homogenous solution, which was kept for 1 h at room temperature. HRP/SWNT/APTOS-modified electrode was prepared by applying 1 μ L of the mixture to a glassy carbon electrode (3-mm diameter) and the electrode was dried at ambient temperature (unpublished results).

bioelectrochemically functional nanocomposite and found that the electronic communications between HRP and the CNTs entrapped within the sol-gel matrix were well conducted. Figure 3 displays typical cyclic voltammograms obtained with CNT/sol-gel-modified (curves 1 and 3) and CNT/HRP/sol-gel-modified (curves 2 and 4) GC electrodes in 0.10 M phosphate buffer (pH 7.0) saturated with N_2 (curves 1 and 2) or air (curves 3 and 4). The redox wave obtained at the CNT/HRP/sol-gel-modified electrode (curve 2, dashed) at -0.40 V was ascribed to the redox process of Fe^{III}/Fe^{II} heme groups in HRP molecules entrapped into the nanocomposite, suggesting that the direct electron transfer between HRP and the CNTs was successfully conducted. Such direct electron transfer property could be further used for bioelectrocatalysis, *e.g.*, toward the reduction of oxygen, as shown in Fig. 3 (curves 3 and 4). As shown, the presence of O_2 in solution clearly increased the cathodic peak current, while the reversed oxidation peak current of HRP (curve 4) was decreased compared with its absence (curve 2, dashed). This observation, along with the positive shift in the potential for O_2 reduction at the CNT/HRP/sol-gel-modified GC electrode compared with that at the CNT/sol-gel-modified GC electrode (curve 3), indicates that the CNT/HRP/sol-gel nanocomposite electrode possesses a good catalytic activity toward the reduction of O_2 .

2.4 Layer-by-layer assembly of CNT film electrodes

Layer-by-layer self-assembly is one of template-driven approaches based on the deposition of oppositely charged species and has already found widespread applications in modification chemistry. Layer-by-layer technique has also been used for preparing CNT multilayer films assembled onto solid substrates.^{37,38} Mamedov *et al.* and Rouse *et al.* reported the CNT/polyelectrolyte multilayer films through alternate adsorption of the polyelectrolyte poly(diallyldimethylammonium chloride)

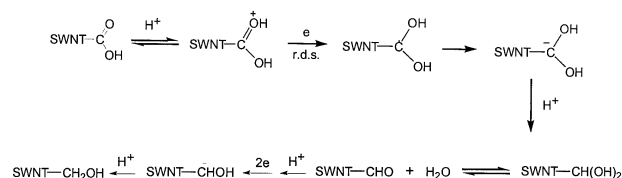
(PDDA) and single-walled carbon nanotubes (SWNTs) onto substrates.^{39,40} The method was essentially based on the electrostatic interaction between positively charged PDDA and negatively charged oxygenated groups at the tube ends. As demonstrated, the uses of the layer-by-layer method could produce uniform and homogeneous SWNT multilayer films with excellent physical and mechanical properties.

The layer-by-layer assembled CNT multilayer films have also been demonstrated to be very useful for electrochemical studies and electroanalytical determinations. We have prepared multilayer films of multiwalled carbon nanotubes (MWNTs) and PDDA onto GC electrode by virtue of the electrostatic interaction between purified MWNTs and PDDA. The assembled MWNTs were found to be mainly in the form of single nanotubes or small bundles of the nanotubes, with almost the same loading in each layer. Moreover, the assembled MWNT multilayer films were characterized to well retain the electrochemical properties inherent in the MWNTs. These properties substantially enabled the prepared CNT electrode to be very useful for efficient electrocatalysis, *e.g.*, toward AA oxidation and O_2 reduction and further to be available for selective square voltammetric detection of DA without interference from AA and for the development of novel alkaline air electrodes with a high performance.⁴¹

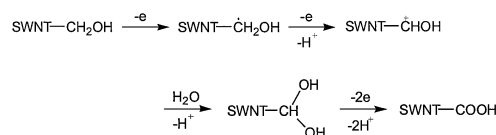
3 Electrochemistry of CNTs

Similar to other kinds of carbon-based materials frequently used in electrochemistry, *e.g.*, GC, graphite and diamond, CNTs are electrochemically inert and do not exhibit voltammetric response in the potential window commonly used. However, it is known that the methods used for synthesis of the CNTs inevitably introduces some impurities, such as nanocrystal metal catalysts, amorphous carbon, and carbon nanoparticles, into the CNT samples. Thus, the raw CNTs have to be subject to purification, such as chemical oxidation or thermal treatment before they are put into use. The pretreatments shorten the CNTs and lead to the partial oxidation of the CNTs to produce functional oxygenated groups at the open ends and defects along the sidewall, in particular, which dramatically modify the electronic and structural properties of the nanotubes.⁴²⁻⁴⁷ As a consequence, also very similar to other kinds of carbon-based materials mentioned above, the CNTs generally bear some functional oxygenated groups, of which some are electroactive. Li *et al.* have observed a pair of redox waves at purified CNTs and ascribed them to the redox process of oxygenated groups produced at the CNTs, as shown below.⁴⁸

For the reduction process:



For the re-oxidation process:



Barisci *et al.* studied electrochemical properties of the CNTs

in aqueous and non-aqueous solutions.⁴⁹⁻⁵¹ Consistent with those reported by Li *et al.*, they also observed a couple of broad redox peaks at *ca.* -0.15 V (*vs.* Ag/AgCl, 3 M NaCl) at the SWNTs, which were attributed to the functional oxygenated groups. They further found that the observed responses disappeared upon thermal treatment of the CNTs at 1173 K. Very recently, the same group has also investigated electrochemical properties of CNTs in ionic liquids.

4 Electrocatalysis of CNTs

Considerable interest has been focused on electron transfer processes at various substrates, since the electron transfer kinetics is known to largely depend on electrode materials and their surface properties. Such investigations are both fundamentally interesting and practically useful. This case is particularly suitable for the carbon-based materials because those materials, such as GC, graphite, fullerene and diamond, with different electronic and structural properties, have been proved to possess distinct electrochemical properties from each other. CNTs, as a novel class of carbon family, are known to have a distinct structure and thus may be envisaged to exhibit different forms of electrochemical behavior from other kinds of the carbon-based materials. In general, CNTs bear two kinds of carbon atoms: those at the tube ends and those at the sidewall of the nanotubes. In electrochemistry, both components behave very differently; the former behaves like the edge plane of highly orientated pyrolytic graphite (HOPG) and possesses favorable electrochemical properties, while the latter resembles the basal plane of HOPG and shows very slow electron transfer kinetics. So far, the CNTs have been demonstrated to possess good electrocatalytic activities, as summarized in Table 1, compared with other kinds of the carbon-based materials. Recent results tend to ascribe the observed electrocatalytic activities of the CNTs to the edge-plane-like component of the CNTs. Thus, from a mechanistic point of view, the CNTs are not distinct from the edge planes of the HOPG in their electrocatalytic activities. In spite of this, the good electrocatalytic activities of the CNTs do constitute some new electroanalytical methods, especially for biological determinations.^{11,72,73} For example, Britto *et al.* reported a first example of electrocatalysis of the CNTs toward the oxidation of DA; in this work the MWNT paste electrode was prepared in bromoform.⁷⁴ The redox process of DA was found to be improved at the MWNT electrode compared with the results at the graphite electrode, in both the reaction reversibility and the electron transfer rate constant. Ajayan *et al.* investigated the electrochemistry of the CNT electrode with $\text{Fe}(\text{CN})_6^{4-}/\text{Fe}(\text{CN})_6^{3-}$ as redox probe.⁷² They found that the redox process of the probe was enhanced at the CNT electrode; this result was similar to that of DA. They further ascribed the observed accelerated electron transfer to two possible reasons: (i) better wetting properties due to porous structure of bundle CNTs, and (ii) surface electronic structure of nanotube layers, because it is not entirely basal-plane-like graphite due to the helicity, low dimensionality, and possible topological defects. Li *et al.* systematically investigated the electrocatalytic activity of the CNTs toward biologically important species, such as monoamines and their metabolites.⁴⁸ Wang *et al.* observed marked electrocatalytic activity of the CNTs embedded in Teflon toward H_2O_2 and NADH, which could be used for construction of enzyme electrodes.¹²

Recently, Compton *et al.* demonstrated that the CNTs and graphite powder confined onto basal plane pyrolytic graphite

Table 1 Species that can be detected through electrocatalysis of CNTs

Species	Media	CNTs	Ref.
Catechol	PBS (pH 7.0)	MWNT	52, 53
Dopamine	PBS (pH 6.9)	SW/MWNT	21, 54 - 56
Epinephrine	B-R buffer (pH 6.9)	SWNT	57
AA	PBS (pH 7.0)	MWNT	33
DOPAC	PBS (pH 7.0)	MWNT	58
Nitric oxide	PBS (pH 7.0)	MWNT	59, 60
Cysteine	0.2 M H_2SO_4	CNTPE	61 - 63
Glutathione	PBS (pH 7.0)	MWNT	33
Homocysteine	PBS (pH 7.0)	MWNT	26
NADH	PBS (pH 7.4)	MWNT	19, 64 - 67
H_2O_2	PBS (pH 7.4)	MWNT	19, 64
Uric acid	PBS (pH 7.0)	SWNT	56
Oxygen	0.1 M NaOH	MWNT	41
Glucose	0.1 M NaOH	MWNT	68
Adenine	Acetate buffer (pH 5.0)	CNTPE	69
Guanine	Acetate buffer (pH 5.0)	CNTPE	70, 71
Insulin	PBS (pH 7.4)	MWNT	71

DOPAC, 3,4-dihydroxyphenylacetic acid; NADH, β -nicotinamide adenine dinucleotide (reduced disodium salt hydrate); PBS, phosphate-buffered solution; B-R buffer, Britton-Robinson buffer.

via either abrasive attachment or "film" modification have the same electrocatalytic effects toward NADH, epinephrine, and norepinephrine.⁷⁵⁻⁷⁷ They compared the redox processes of epinephrine and $\text{Fe}(\text{CN})_6^{3-}$ at the CNTs with other kinds of electrodes, *i.e.*, C_{60} -modified electrode, basal plane pyrolytic graphite and edge planes pyrolytic graphite, and found that the CNT electrode exhibits almost the same electrochemical response as that at the edge plane electrode. This observation suggests that the electrocatalytic nature of the CNTs originates from the ends of nanotubes, rather than from the sidewall of the nanotubes or from their unique nanostructure.

Gooding *et al.* compared the electrochemical properties of $\text{Fe}(\text{CN})_6^{4-}/\text{Fe}(\text{CN})_6^{3-}$ couple at the CNTs randomly dispersed onto substrate with those at the aligned CNTs.⁷⁸ The peak-to-peak potential separation was 105 mV at the randomly dispersed SWNTs and 72 mV at the aligned SWNTs. This difference revealed that the aligned SWNTs show better electrochemical properties than the randomly dispersed SWNTs. They further studied the correlation between electrochemical properties and the length of the nanotubes and the presence of oxygenated groups at the tube ends. The results imply that the favorable electrochemical properties of CNTs may arise from the presence of oxygenated groups, carboxylic acid moieties, in particular, at the ends of CNTs.

Wang *et al.* studied electrochemical oxidation of NADH, AA, and H_2O_2 at the CNTs prepared by different methods, such as chemical vapor deposition (CVD) and ARC discharge.⁶⁴ The CNTs prepared by CVD show better electrocatalytic activities than those prepared by ARC discharge. The electrocatalytic properties of the CNTs prepared by ARC discharge were improved by electrochemical pretreatment of the CNTs because the pretreatment breaks the end caps of the CNTs to expose new edge-plane-like sites. The edge-plane-like sites show good electrocatalytic activity, consistent with the observations described by Compton *et al.* and Gooding *et al.* The researchers have also compared the electrochemical activities of CNTs from different sources and found that the electrochemical activities are closely associated with the sources of the CNTs and the strategies for confining CNTs onto electrode.⁷⁹

5 Rational Functionalization of CNTs for Electrochemical Applications

Different from other kinds of carbon-based materials used in electrochemistry, the CNTs possess a framework structure with sp^2 carbon. The sidewall of the nanotubes is very hydrophobic and enriches π -stacking. Such properties make it possible to rationally functionalize the CNTs through either covalent or noncovalent chemistry so as to modulate molecule architecture towards bulk nanodevices.^{9,80,81}

5.1 Functionalization with nanoparticles

Attachment of metal (oxide) nanoparticles onto the CNTs to form functional nanocomposites is receiving great attention because of the structural properties of the CNTs, such as nanometer size and high surface area, and the potential applications of formed nanocomposites.⁸² The unique properties of the CNTs make them particularly useful as metal catalyst supports since the high surface area is essential to disperse catalyst particles and to maintain the catalytic activity of the catalysts. Earlier efforts have been devoted to the preparation of functional nanoparticles (NPs)/CNT nanocomposites and to their applications in electrochemical sensors and fuel cells. For example, Pt-NPs/SWNT nanocomposite electrode prepared by attachment of Pt-NPs onto the SWNTs has been used for electrochemical biosensing.^{83–85} The high surface area of the nanocomposite electrode was demonstrated to improve mass transport, resulting in an enhanced amperometric response, *e.g.*, toward H_2O_2 . This property was further used for the construction of sensitive enzyme-based biosensors. For example, by using glucose oxidase (GO_x), Hrapovic *et al.* constructed a Pt-NPs/CNT-based biosensor that responded more sensitively than the GO_x /GC, GO_x /Pt/GC, and GO_x /CNT/GC electrodes.⁸³ The response time of this electrode was determined to be 3 s and the detection limit was determined 0.5 μ M. Besides, the Pt-NPs/CNT nanocomposite electrode can be used as a sensitive electrochemical oxygen sensor and a cathode of direct methanol fuel cells. Recently, the nanoparticles of copper and nickel have also been attached onto the CNTs and the prepared nanocomposite electrodes have been used for amperometric detection of carbohydrates, amino acids and peptides with sensitivities higher than those at metal nanoparticles or the CNTs alone.^{86–89}

Besides the functionalization of the CNTs with metal nanoparticles to form electrochemically functional nanostructures, quantum dots have also been used to functionalize CNTs to constitute another platform for electroanalysis. For instance, functionalization of the CNTs with CdS essentially offers an electrochemical protocol for DNA analysis. Wang *et al.* reported a sensitive stripping voltammetric technique for the detection of DNA hybridization with CdS-functionalized CNT electrodes.⁹⁰

5.2 Functionalization with organic compounds

The π -stacking interaction between the aromatic compounds and flat graphite always results in a stable adsorption of such compounds onto graphitic surface.⁹¹ Such a strategy has been extensively used for preparing durable and functional chemically modified electrodes that have greatly facilitated various electrochemical studies and electroanalytical applications. Compared with other kinds of carbon-based materials mentioned above, the CNTs exhibit a special sidewall curvature and possess a π -conjugative structure with a highly

Table 2 Compounds that could be functionalized onto CNTs

Compound	Nanotube	Ref.
NiTMATAA	SWNTs	92
CuTMATAA ^a		92
Thionine	SWNTs	93
Tetraaza[14]annulenes	SWNTs	94
Aryl diazonium	SWNTs	95
Pyrene	SWNTs	96
9,10-Phenanthraquinone	MWNTs	97
1,2-Naphthaquinone		97
4-Nitrobenzylamine	MWNTs	98
Porphyrin	SWNTs	99
Anthracene	SWNTs	100
Surfactant	SWNTs	101
Polymer		102
Polyaniline	SWNTs	102

a. NiTMATAA and CuTMATAA: Ni(II) and Cu(II) complexes of 5,7,12,14-tetramethyldibenzo-1,4,8,11-tetraazacyclotetradeca-3,5,7,10,12,14-hexaene.

hydrophobic surface property. These unique properties of the CNTs produce remarkable differences in the interactions of the aromatic compounds with the CNTs from those with the flat graphite. For instance, the π -stacking and hydrophobic interactions between the aromatic compounds and the CNTs are expected to be stronger than those with the flat graphite. These intrinsic structure-associated interactions between the compounds and the CNTs, on one hand, are very attractive for the fabrication of stable and functional CNT-based nanodevices and, on the other hand, substantially endow novel electrochemical properties to the resulting adsorptive nanostructures that are believed to be relatively different from those of the initial compounds and the CNTs alone.

Currently, noncovalent and covalent functionalization of the CNTs with organic compounds has become the subject of intensive investigations on the fabrication of novel nanostructures with new functions and applications. Increasing interest is being focused on this field and so far many kinds of organic compounds have been attached onto the CNTs to generate functional nanostructures, as summarized in Table 2. Typically, Zhang *et al.* and Star *et al.* systematically studied the adsorption of (polynuclear) aromatic compounds onto the SWNTs and the interactions between the compounds and the SWNTs.^{92,100} The strong adsorption of those aromatic compounds and the formation of the resulting adduct were primarily attributed to the charge-transfer and hydrophobic interactions between the molecules and the SWNTs, in which the former is an electron acceptor and the latter is an electron donor.

The electrochemistry of the formed CNT-organic adsorptive nanostructures has been investigated. Melle-Franco *et al.* reported a strategy to solubilize the CNTs by covalently functionalizing the CNTs with pyrrolidines.¹⁰³ They further studied the electronic properties of the functionalized CNTs with cyclic voltammetry over a wide potential range. Compton *et al.* studied the effect of lithium cation on the electrochemical behavior of anthraquinone adsorbed onto MWNTs.¹⁰⁴ Zhuang *et al.* immobilized *tetra*-phenylporphyrin (TTP) onto SWNTs and studied the interaction between hemoglobin (Hb) and the TTP/SWNT film electrochemically.¹⁰⁵ Dong *et al.* prepared a novel nanohybrid by attaching Pt nanoparticles and tetrakis(*N*-methylpyridyl)porphyrin cobalt onto the CNTs.¹⁰⁶ The electrode exhibited a remarkable electrocatalytic activity toward the reduction of oxygen.

Table 3 Electron transfer properties of proteins at CNTs

Protein	CNT electrode	E^0/V	ET rate/s ⁻¹	Analyte	Ref.
Cyt. <i>c</i>	CNT paste	<i>ca.</i> 0.06	NA	NA	115
HRP	Poly-L-lysine/SWNT	NA	NA	H ₂ O ₂	116
Hb	CNTPME	-0.278 (SCE)	0.062	H ₂ O ₂	117
Hb	CNT film	-0.343 (SCE)	1.25 ± 0.25	H ₂ O ₂	118
Mb	MWNT film	NA	NA	H ₂ O ₂	119
Mb	MWNT film	-0.248 (SCE)	5.4	NO	120
MB	Oriented SWNT	-0.21 (SCE)	NA	H ₂ O ₂	121
HRP	Oriented SWNT	-0.25 (SCE)	NA	H ₂ O ₂	121
HRP	CNTPME	-0.643 (Ag/AgCl)	2.48 ± 0.03	H ₂ O ₂	122
Cyt. <i>c</i>	SWNT film	NA	NA	Adenine	123
Catalase	SWNT film	-0.414 (SCE)	NA	H ₂ O ₂	124
MP-11	MWNT film	-0.26 (Ag/AgCl)	38	H ₂ O ₂ , O ₂	125
MP-11	Aligned SWNT/Au	-0.390 (Ag/AgCl)	2.8 – 3.9	NA	11
GOx	CTAB-CNT	-0.466 (SCE)	1.53 ± 0.45	NA	126
GOx	Aligned SWNTs	-0.422 (Ag/AgCl)	0.3	NA	127
GOx	Aligned SWNTs	-0.45 (SCE)	NA	Glucose	128
GOx	CNTPME	-0.659 (Ag/AgCl)	1.61 ± 0.3	NA	129
GOx	SWNT film	-0.441 (Ag/AgCl)	1.7	Glucose	130

E^0 , formal potential; NA, not available; MP-11, microperoxidase 11.

We have described the adsorption of redox-active Methylene Blue (MB) dye onto the SWNTs to form an electrochemically functional nanostructure and its layered nanocomposite. MB essentially interacts with the SWNTs through charge-transfer and hydrophobic interactions, leading to the formation of a MB-SWNT adsorptive nanostructure which exhibits distinct electrochemical properties from those of MB adsorbed onto GC electrode. The interactions between MB and the SWNTs were demonstrated to closely associate with the structural properties of the SWNTs. The stable adsorption of water-soluble and positively charged MB molecules onto SWNTs was further demonstrated to solubilize the formed nanostructure in water and to fabricate functional nanocomposites by layer-by-layer assembling of the formed nanostructure on solid substrate.¹⁰⁷

5.3 Functionalization with biomaterials

Integration of biomaterials such as proteins, enzymes, antigens, antibodies or DNA with the CNTs essentially provides new hybrid systems that combine the conductive or semi-conductive properties of the CNTs with the recognition or catalytic properties of the biomaterials. Superior to other kinds of carbon-based materials, the internal cavities or external sides of CNT walls provide the platform for the accommodation of the biomolecules. That is, the CNTs can be used as a good host of biomolecules, which is a key issue to CNT-based bioelectronic nanodevices.

In general, the biomolecules can be functionalized onto the CNTs through a covalent or noncovalent way. In order to meet the requirement for coupling biomolecules, chemical modification or functionalization of the CNTs is essential. For example, the carboxylic groups at the tube surface was used to covalently bind the biomaterials, such as sugar moieties,¹⁰⁸ oligonucleotides,^{109–111} peptide nucleic acids,¹¹² and proteins¹¹³ via carbodiimide coupling of the respective amino-functionalized biomolecules or using heterobifunctional coupling reagents.¹¹⁴ In addition, a bifunctional linker was also utilized to anchor the biomolecules onto the CNTs. Chen *et al.* reported an elegant method for protein immobilization by irreversibly attaching 1-pyrenebutanoic acid succinimidyl ester onto the sidewall of the SWNTs via π - π stacking of the pyrene group. The active ester group of such a compound was used to covalently bind the lysine residue of proteins.⁹⁶

6 CNT-based Bioelectrochemistry and Biosensors

6.1 CNT-based bioelectrochemistry

The electronic and structural properties of the CNTs make them very attractive for bioelectrochemical studies and applications. As summarized above, the CNTs exhibit a good conductivity (depending on the kind of the CNTs), high chemical stability and excellent electrochemical properties. More remarkably, the CNTs have been demonstrated to be able to facilitate direct electron transfer of enzymes and proteins such as glucose oxidase (GOx) and heme proteins including Cyt *c*, HRP, hemoglobin (Hb), myoglobin (Mb) and catalase. These properties not only make it possible to understand the intrinsic thermodynamic and kinetic electron transfer properties of enzymes and proteins at new interfaces, but also pave a new way to bioelectronic nanodevices. To date, the bioelectrochemistry of the proteins have been investigated at the CNT electrodes, *e.g.*, CNT paste electrode, randomly dispersed CNTs, and the CNTs chemically linked to substrate electrode, as summarized in Table 3. The mechanism for the observed facilitated electron transfer of heme proteins on the CNTs has been proposed to be a result of nano-sized structural properties of the CNTs, or of the surface defects produced during the treatment,¹²² or of direct hem-nanotube π - π communication.¹³¹

As demonstrated, the CNTs have been proved to be capable of facilitating protein electrochemistry; a combination of such electron transfer properties with the specific enzyme-substrate reactivity could generate various functional nanohybrid systems that may pave an effective way for the development of new bioelectronic nanodevices. However, such potential is still limited by the facts that: (i) the CNTs tend to aggregate in most solvents, producing difficulties in manipulation of the CNTs for practical applications, integration with biomacromolecules, in particular; (ii) electronic communication between the proteins and the CNTs, which is a critical step for developing redox protein-based bioelectronic nanodevices, is rather slow at the pristine CNTs; and (iii) the strong interactions between the proteins and the CNTs could distort the proteins, leading to the loss of their biocatalytic activities toward substrates. Therefore, the bioelectrochemical applications of the CNTs, such as

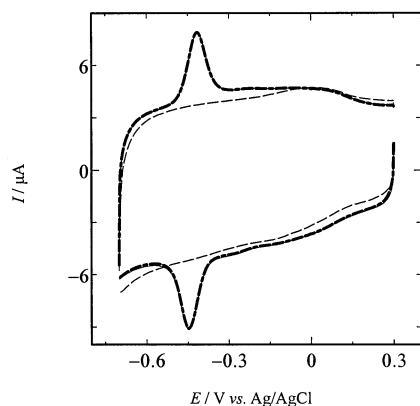


Fig. 4 Cyclic voltammograms of GOx/MWNT-modified GC electrode in 0.10 M N_2 -saturated phosphate buffer (pH 7.0) in the absence (dotted curve) and presence (solid curve, overlapped with dotted curve) of 5 mM glucose. The dashed curve represents the voltammograms of MWNT-modified electrode in 0.10 M N_2 -saturated phosphate buffer. Scan rate, 50 mV/s. The GOx/MWNT-modified electrode was prepared by coating 1 μL of 40 mg/mL glucose oxidase (GOx) onto the MWNT-coated electrode. The MWNT-coated electrode was prepared by applying 4 μL of 1 mg/mL MWNTs onto GC electrode (unpublished results).

bioelectrochemistry and biosensors require rational functionalization of the CNTs to improve their solubility and biocompatibility. By using HRP and SWNTs as examples, we have tried to address these limitations by rationally functionalizing the CNTs through covalent and noncovalent ways so as to facilitate direct electronic communication between the proteins and the CNTs. In our case, the CNTs were functionalized through a covalent approach with hydroxyl and carboxyl groups and a noncovalent approach with block copolymer (*i.e.*, Pluronic P123). The functionalized CNTs were found to possess improved solubility in aqueous solution and possibly enhanced biocompatibility. We found that both kinds of the functionalized CNTs were capable of facilitating the direct electron transfer of HRP, in which the noncovalently P123-functionalized CNTs were found to be advantageous over those covalently functionalized with $-\text{OH}$ and $-\text{COOH}$ groups. These approaches would be very useful for investigating protein electron transfer at new interfaces and may offer a straightforward way to bioelectronic nanodevices, such as electrochemical biosensors and enzyme-based biofuel cells.¹³²

Other types of enzymes, such as GOx were also studied to check the possibility of conducting their direct electrochemistry on the CNTs. Willner *et al.* covalently coupled the FAD cofactor to the carboxylic groups of the SWNTs aligned onto the Au electrode.¹²⁸ The reconstitution of the apo-GOx onto the functionalized electrode got a turnover rate of electrons to the electrode to be about 4100 s^{-1} , which was about six-fold higher than the turnover rate of electrons from the active site of native GOx to its natural oxygen electron acceptor (700 s^{-1}). The bioelectrocatalytic oxidation of glucose was observed at a potential higher than 0.18 V (vs. SCE). Willner *et al.* also found a dependence of the electron transfer rate constant on the length of the SWNTs and ascribed this dependence to the defect sites introduced into the SWNTs. Such sites act as local barriers to charge transport. Gooding *et al.* achieved the direct electron transfer of GOx onto the CNT array and calculated the electron transfer rate of GOx.¹²⁷

Direct electron transfer of GOx was also observed at the

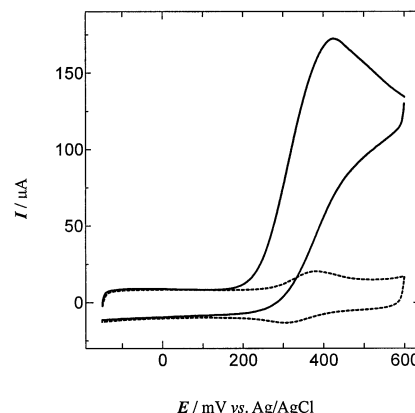


Fig. 5 Cyclic voltammograms of GOx/MWNT-modified glassy carbon (GC) electrode in 0.10 M phosphate buffer (pH 7.0) containing 2 mM ferrocene monocarboxylic acid before (dotted curve) and after (solid curve) addition of 10 mM glucose in solution. The GOx/MWNT-modified electrode was prepared by coating 1 μL of 40 mg/mL glucose oxidase (GOx) onto the MWNT-coated electrode. The MWNT-coated electrode was prepared by applying 4 μL of 1 mg/mL MWNTs onto the GC electrode. Scan rate, 20 mV/s (unpublished results).

CNTs randomly dispersed onto the substrate, as shown in Fig. 4. However, the bioactivity of the GOx (possibly those closely attached to the sidewall of the nanotubes) may be seriously decreased, probably because of the strong interactions, such as hydrophobic interaction between GOx and the sidewall of the nanotubes that could seriously distort the structure of GOx. Davis *et al.* immobilized β -lactamase I onto the surface of the CNTs and found that only 19% bioactivity was maintained.¹³³ Consistent with this observation, we found that the GOx immobilized onto the CNTs did not exhibit remarkable bioelectrocatalytic activity toward the oxidation of glucose, as shown in Fig. 4 (solid and dotted curves), even though the direct electron transfer of GOx was clearly recorded (dotted curve). These results imply that the redox wave recorded for GOx at the CNTs may be ascribed to the free flavin moieties lost from the denatured enzyme. However, this conclusion may only be limited for the enzyme molecules closely attached onto the sidewall of the CNTs. Those indirectly attached onto the sidewall of the nanotubes may retain most of the biocatalytic activity. This assumption can be supported by the catalytic activity of GOx immobilized onto the CNTs toward glucose with electron transfer mediator in solution, as shown in Fig. 5. As shown, the GOx/CNT-modified electrode shows a good catalytic current response toward glucose with ferrocene monocarboxylic acid as an electron transfer mediator to shuttle the electron transfer between electrode and GOx, which is in a good agreement with earlier report.¹³⁴ The observed large response essentially indicates that GOx (possibly not closely attached onto the sidewall of the CNTs) are biochemically active.

6.2 CNT-based biosensors

Similar to the conventional electrochemical biosensors, CNT-based biosensors can also be generally divided into three categories: (i) first-generation based on the detection of H_2O_2 or O_2 involved in the enzymatic reaction, (ii) second-generation through the utilization of an electron transfer mediator, and (iii) third-generation based on direct electron transfer of enzymes or proteins. Superior to the conventional electrodes, *e.g.*, GC, Au

and Pt electrodes, the CNT electrodes have been proved to possess electrocatalytic activity toward the oxidation of H_2O_2 and reduction of O_2 and to possess capability for facilitating the direct electron transfer of proteins or enzymes, as mentioned above. These properties make the CNTs particularly attractive for the development of the first- and third-generation electrochemical biosensors, as summarized above.

In addition, organic electrocatalysts, such as polynuclear aromatic dyes can be stably immobilized onto the CNTs and can be further used to accelerate the oxidation of H_2O_2 or shuttle the electron transfer between the CNTs and enzymes or proteins. This, coupled with the good conductivity of the CNTs, makes the CNTs very useful for the construction of the first- and second-generation electrochemical biosensors. Ye *et al.* functionalized the MWNTs with iron-phthalocyanines to redox-catalyze H_2O_2 oxidation and, based on this, constructed a highly sensitive and selective glucose biosensor by co-immobilizing glucose oxidase onto the functionalized MWNTs.¹³⁵ Chen *et al.* co-immobilized Methylene Blue with HRP onto the CNTs to shuttle the electron transfer between HRP and the CNTs. The modified electrode showed a good bioelectrocatalytic activity toward H_2O_2 reduction.¹³⁶ By adding electron transfer mediator into solution, Davis *et al.* developed glucose biosensor with GOx nonspecifically adsorbed on the SWNTs.¹³⁴

In addition, electrochemical biosensors based on dehydrogenase have been developed through electrocatalytic oxidation of NAD(P)H cofactors onto the CNTs or functionalized CNTs. Antiochia *et al.* prepared CNT paste electrodes modified with electrodeposited film derived from 3,4-dihydroxybenzaldehyde and constructed glucose biosensors by successively coupling with glucose dehydrogenase.⁶⁵ Zhang *et al.* used chitosan to solubilize the CNTs and to create a biocompatible environment for enzyme immobilization onto the surface of CNTs.¹³⁷ Toluidine Blue O was further introduced into the functionalized CNTs and was used as an electrocatalyst for accelerating the oxidation of NADH. Such a scheme was used to construct a dehydrogenase-based electrochemical biosensor.¹³⁸

7 Concluding Remarks

We have addressed recent advances in electrochemistry and electroanalytical applications of the CNTs. As a new kind of carbon-based materials, the CNTs have been proved to be very useful for electrochemical studies and electroanalytical applications. The main advantages of the CNTs over other kinds of the carbon-based materials, such as GC, graphite, fullerene and diamond, with respect to their electrochemical properties and applications can be summarized in the following aspects. First, the CNTs are electrocatalytically active. Although this property is not distinct from that of edge plane of HOPG and thus the uses of the CNT electrodes for electrocatalysis may not be a new mechanistic contribution to electrochemistry, the high conductivity and excellent electrocatalytic activity of the CNTs substantially constitute new electroanalytical protocols for sensitive determinations. Second, the unique structural property of the CNTs makes them very attractive to accommodate electrochemically or biologically functional elements including electrocatalysts, *e.g.*, metal (oxide) nanoparticles, quantum dots and organic compounds, and biomaterials, *e.g.*, enzymes (proteins), antibodies and DNA. The prepared functional nanocomposites are particularly useful for electroanalytical purposes, *e.g.*, electrocatalysis and biosensor development. Third, the CNTs

can facilitate the direct electron transfer of some kinds of enzymes and proteins, *e.g.*, heme proteins. This property not only makes it possible to understand the intrinsic thermodynamic and kinetic electron transfer properties of enzymes and proteins at new interfaces, but also paves a new way to bioelectronic nanodevices. Finally, as demonstrated, the CNT electrode exhibits a three-dimensional architecture, provided the CNTs are properly confined onto substrate electrodes. This property, combined with other properties mentioned above, would make the CNTs valuable for practical applications. For example, the three-dimensional architecture of the CNTs can lead to a high loading of electrocatalysts or biomaterials onto the solid substrate and thus can enhance the efficiency for (bio)electrocatalysis. It is fair to say that these unique properties of the CNTs will certainly pave a way to new nanoelectrochemistry in the future.

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