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Nanostructured carbon electrodes

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Abstract

In its conducting form, carbon has proven to be a versatile, robust and high performing electrode material in areas such as energy conversion, energy storage and even medical bionics. In our laboratories we have been interested in the fabrication and utilization of nanostructured electrodes based on more recently discovered forms of carbon. These include carbon nanotubes and graphene.

Keywords

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Disciplines

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Nanostructured carbon electrodes

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In its conducting form, carbon has proven to be a versatile, robust and high performing electrode material in areas such as energy conversion, energy storage and even medical bionics. In our laboratories we have been interested in the fabrication and utilization of nanostructured electrodes based on more recently discovered forms of carbon. These include carbon nanotubes and graphene.

Introduction to carbon

Carbon can exist in a number of allotropes (different solid forms) commonly known as diamond, graphite, carbon nanotubes or fullerenes. In diamond, each carbon atom uses sp^3 hybrid orbitals to form strong covalent bonds (350 kJ mol^{-1}) to four other atoms. This gives rise to the incredible strength of diamond. Nanodiamond is a carbon material synthesized by detonation.[1] The use of nanodiamond as an electrode material is limited and therefore here we focus on the other three major types of electroactive carbon materials: carbon nanotubes, graphene, and fullerene.

In contrast to diamond, graphite comprises layers of 2D sheets of graphene in which the atoms are held together using sp^2 hybrid orbitals. While graphite itself is not strong since the graphene sheets can readily slide over each other, a graphene sheet is actually stronger than diamond due to the shorter (0.139 nm compared to 0.154 nm) and stronger bonds (>350 kJ mol^{-1}) made up of the sp^2 hybrid orbitals. Graphite is also different from diamond in that the overlap of the π orbitals resulting from sp^2 hybridisation produces a delocalised electron cloud giving rise to electronic conductivity as well as the absorption of visible light and a resulting black appearance. Synthesis of graphene (a single sheet of carbon atoms) has been achieved by vacuum graphitisation of silicon carbide or *via* direct epitaxial growth on metal substrates. Graphene has also been accessed by micromechanical cleavage of graphene or by oxidation of graphite to form a graphite oxide dispersion followed by chemical reduction.

Another allotrope of carbon discovered in 1985 (called Buckminsterfullerene and often referred to as buckyballs) involves discrete molecules with exactly 60 carbon atoms that are sp^2 hybridised. Each molecule involves alternating 5 and 6 member rings fused together to resemble a molecular soccer ball. Despite their sp^2 hybridised bonding and consequent π bonds, buckyballs have poor electrical conductivity as a result of their reduced π bond overlap. They are, however, excellent electron acceptors, and are considered promising n-type semiconductors. A number of molecules containing a different discrete number of carbon atoms (*e.g.* 70) have subsequently been discovered and are referred to as fullerenes.

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Carbon nanotubes (CNTs) are rolled up sheets of graphene. These can be single sheet cylinders giving single-walled carbon nanotubes (SWNTs), or multiple concentric cylinders of increasing diameter about a common axis separated by 0.34 nm (the same inter-plane distance observed in graphite) that are known as multi-walled carbon nanotubes (MWNTs). Single-walled carbon nanotubes comprise a seamless cylinder of one atomic layer of carbon consisting of a mixture of sp^3 and sp^2 bonds with the sp^3/sp^2 ratio varying from 15 to 40%. CNTs have overall diameters in the nanodomain and lengths in the micron to millimetre domain, providing an extremely high aspect ratio. The history of their discovery has been well-documented in the literature[2] with the first report appearing in 1978[3] and then subsequently in 1991.[4] The first well-characterized SWNT report was published in 1993.[5,6] Since then, SWNTs have been produced using the arc discharge process wherein the graphite electrodes were modified by transition metal catalysts. They have also been produced using laser ablation and chemical vapour deposition.

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Fullerenes

The Buckminsterfullerene molecule, commonly referred to as fullerene, was discovered in 1985 during experimental research aimed at understanding the mechanisms by which long-chain carbon molecules are formed.[7] The most famous and most stable of the fullerene molecules is C_{60} which consists of 20 hexagonal and 12 disjoint pentagonal faces, with a carbon atom at each corner of the individual polygons.[8]

Synthesis and functionalisation

The first studies on fullerenes were based on the clusters formed by laser heating of graphite; later fullerenes were produced in gram quantities using carbon evaporation equipment. Due to the typically low yield of fullerenes during the various synthesis methods, much research has gone into varying the starting material ranging from graphite rods to powdered carbon in attempts to improve the yield.[9] There are many articles describing the fullerene fabrication process and modifications thereof. However, there seems to be no standout process that is preferred, as the method of fabrication appears to be determined by the desired final application of the fullerene.

For fullerenes to be useful in these applications they are usually constructed as functional materials such as fullerene nanowires, nanotubes and nanofilms.[10] They have been shown to act as electron mediators and thereby operate as electron relays for activation of oxidations or reductions of target substances. In order to realise the full potential of fullerenes in these proposed applications, it is necessary in most cases to functionalise the fullerene molecule to improve its processability. Therefore, much effort has been invested into developing routes to functionalise the fullerene molecule.

It is well established that fullerenes and their derivatives possess a unique capacity for scavenging reactive oxygen species (ROS).[11] Because underivatised fullerenes are insoluble in water and biological systems, hydroxylated and other derivatised fullerenes have been utilized due to their increased water solubility and resulting increase in payload of ROS-scavening activity to target cells and tissues.[12] Fullerene functionalisation with such complexes as amino acids also has the potential to provide greater interaction between the fullerene and the

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biological environment, yielding potential new medical and pharmacological applications.[13] The use of functionalised fullerenes for medical applications is an exciting prospect with much effort being made into designing fullerenes for use in cancer therapies due to their RSO capabilities. dos Santos *et al.*[14] describe the preparation, characterization and photophysical properties of a novel fullerene derivative chemically modified with a tetrazole (Fig. 1). The results suggest that this derivative can be used in biological applications, for example as a photosensitizer, in topical photodynamic therapy (PDT).

One area of intense research that has driven the functionalisation of fullerenes is photovoltaics (involving bulk heterojunctions). Functionalised soluble fullerene derivatives are known as some of the best n-type organic semiconductors (Fig. 1). Moreover, molecular heterojunctions made by covalently linking fullerenes with electron donating or photoactive macromolecules show promise as intrinsic p/n-type semiconductors and even artificial mimics of biological photosynthesis.[15] Methanofullerene phenyl-C61-butyric acid methyl ester ([60]PCBM) is an effective solution processable n-type organic semiconductor and has been blended with p-type conjugated polymers to make photovoltaic (PV) cells[16,17] and thin-film organic field effect transistors (OFETs),[18,19] and has also shown promise for use in photodetectors.[20] The never-ending quest to improve the efficiencies of PV cells has resulted in extensive research into using functionalised fullerene as an active component of the cell. The role of the functionalised fullerene in this case is to increase the photoinduced electron transfer between distinct molecular networks within the PV cell and hence construct a device with high performance. Fukuda *et al.*[21] investigated the functionalisation of C_{60} with phthalocyanines (Pc), and anticipated that the possibility of developing new devices such as organic transistors and photovoltaic cells will increase if Pc and C_{60} are combined, since Pcs themselves have rich electronic properties. Ozoemena *et al.*[22] reported the synthesis, electrochemistry and oxygen reduction properties of FePc and CoPc species peripherally substituted with $-SO_2Bu$ or C_{60} moieties. Cathodic reduction of oxygen is essential in the design and development of fuel cells.

Fullerene derivatives have also been investigated as active components of lithium ion batteries in attempts to increase performance. Chen *et al.*[23] produced a novel fullerene-functionalised terthiophene monomer, *N*-methyl-2-(2-[2,2′;5′,2″-terthiophen-3′-yl]ethenyl)fullero[3,4]pyrrolidine (TTh-BB), that could be successfully electropolymerised to form the homopolymer, P(TTh-BB). The conducting polymer-fullerene homopolymer showed increased capacity when used as the anode material in a lithium-ion battery. as well as electrocatalysis for the oxygen reduction in fuel cell development.

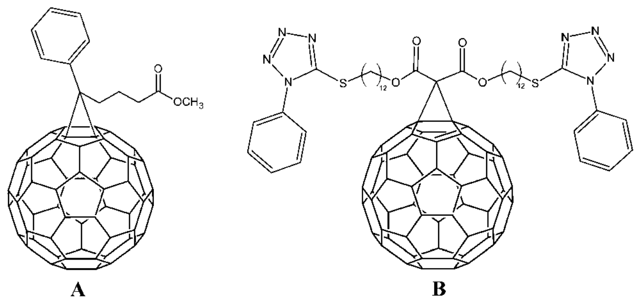

Fig. 1 Examples of functionalised fullerenes: A, PCBM[16,19] and B, tetrazole.[14] Effective n-type semiconductor PCBM is soluble in organic solvents.

Functionalisation has proven to be a very attractive means of improving fullerene processability. However, fabricating these functionalised fullerenes into electrode structures is not straightforward and researchers have consequently had to develop ways to produce these electrode structures.

Electrode fabrication

The electrochemistry of the fullerenes, *e.g.* C_{60}, is of interest because it provides information about the energetics and kinetics of electron-transfer processes and chemical reactions associated with them. Thus, studies of the reduction of C_{60} in solvents where it is moderately soluble (*e.g.* toluene, *o*-dichlorobenzene)[24] produces a series of (up to six) diffusion-controlled, Nernstian reduction waves showing the successive addition of electrons to the molecule.[25,26] The electrochemistry of fullerenes has been extensively studied with a comprehensive review provided by Echegoyen *et al.*[27] More recently studies have addressed the long running debate on the "electrocatalytic" properties of C_{60}. There is evidence to suggest that responses earlier attributed to alkali cation insertion into C_{60} from aqueous electrolytes are due to formation of oxygenated species[28,29] and that C_{60} itself is not reduced in the aqueous potential window.

The use of fullerenes as electrode materials has been demonstrated in a range of applications such as the counter electrode in a dye-sensitized solar cell[30] and as electrodes in double-layer capacitors.[31] In addition, by lowering the potential of electroreduction of many different redox substrates and increasing the reaction rates, thus improving sensitivity and selectivity, fullerenes have proved useful as both redox catalysts and mediators in electrochemical catalysis,[32] electroanalytical investigation of pharmaceuticals,[33] and sensor applications.[34]

Fullerene based electrodes are typically fabricated from composite blends of fullerenes and some binder (surfactant, solvent, polymer, *etc.*) that are then cast onto supporting substrates such as glassy carbon electrodes. The performance of these electrodes can be limited by the homogeneity of the fullerene blend as well as the uniformity of the formed film. In order to improve the homogeneity of the blends, much effort has been invested into functionalising the fullerene molecule. Functionalisation is intended to enhance solubility and hence improve integration with the binder. Efforts to improve film uniformity have centred on spin coating[35] whereby the fullerene material is placed on the substrate and spun at high speed in order to form a uniform thickness film, in most cases of micron thickness. This method is preferred when the electrode material is to be used in such devices as photovoltaic cells (bulk heterojunctions, BHJ) where some level of transparency is desirable.[36] To date, all significant improvements in BHJ power conversion efficiency have occurred by control over their morphological properties.[37]

Despite the improvements brought about by functionalisation and spin coating, researchers have employed alternative fabrication methods to produce fullerene-based electrodes. One such technique is layer-by-layer (LbL) deposition[38] that utilizes electrostatic contacts between oppositely charged species, in association with van der Waals interactions to form a layered film. This approach is attractive as it permits fine tuning of the overall composite properties since the researchers can tailor each layer of the structure during the fabrication process. Unfortunately, this LbL approach is very time consuming and tedious, requiring careful control over the environment in which the LbL film is formed. As a result, this approach has not been widely adopted for the fabrication of fullerene structures.

Inkjet printing technology as a fabrication tool has been investigated for the manufacture of highly efficient polymer : fullerene bulk heterojunction solar cells.[39] Inkjet printing is a commonly used technique for controlled deposition of solutions of functional materials in specific locations on a substrate and can provide easy and fast deposition of polymer films over a large area. The inkjet printing technique is very promising due to its compatibility with various substrates, because the ink material is transferred from the writing head to the substrate without direct contact with the surface. This permits defined areas to be precisely printed with high resolution very easily by drop on demand (DOD) and, thus, a post patterning of the coated layer can be eliminated.[40] Hoth *et al.*[40] demonstrated that by adjusting the chemical properties of a poly(3-hexylthiophene) polymer donor and by using inkjet solvent mixture, they were able to gain control over the nanomorphology of poly(3-hexylthiophene) : fullerene blends during the printing process. They report a new record power conversion efficiency of 3.5% for inkjet printed poly-(3-hexylthiophene) : fullerene based solar cells.

Carbon nanotubes

Since their discovery, carbon nanotubes have generated global scientific and industrial activity because of their unique properties. Many are interested by their unprecedented mechanical[41] and transport properties.[42] Their wide electrochemical potential window, chemical stability and large surface area give them very attractive properties as electrode material candidates in energy storage[43,44] (capacitors and batteries) and energy conversion (fuel cells[45] and electromechanical actuators[46]) applications. Recent advances in combining soft biological materials with carbon nanotubes have provided an extra dimension in enabling carbon nanotube-based electrodes to interface with biological systems. In this section, we will briefly review the recent progress in the synthesis and fabrication of carbon nanotube-based electrodes and provide insight in each related application.

Synthesis and functionalisation

The three main synthesis techniques for CNT production are arc discharge,[47] laser ablation[48] and chemical vapour deposition (CVD).[49] They differ in the ability to control the quantity and quality of the carbon nanotubes, and also in the substrates upon which they can be collected. For example, the former two methods use a solid-state carbon precursor for nanotube growth and produce only entangled nanotubes. The use of a hydrocarbon gas as carbon source and metal particles as catalysts in the CVD method enables the production of regularly patterned and highly orientated CNT arrays. All of these methods, however, produce a heterogeneous mixture of metallic and semiconducting carbon nanotubes with varying degrees of amorphous carbon impurities and catalyst residues. The removal of impurities by electrophoretic or chromatographic methods can be quite challenging.[50,51] The density-gradient ultra-centrifugation technique is proving to be a scalable process to separate carbon nanotubes based on their electronic structure.[52]

In terms of CNT processability, most of the available nanotube raw materials are in the form of intractable carbon soot that spontaneously aggregates in both aqueous and organic environments. Their poor solubility in most solvents has also severely restricted their uses in the development of effective procedures for characterization. Hence, many recent studies are devoted to improving their solvent compatibility. In response to this problem, a variety of functionalization methods have been proposed and demonstrated to ensure efficient debundling and dispersion. Covalent or non-covalent attachment of functional molecules (*e.g.* polymers, surfactants, biopolymers, zwitterions, *etc.*) has been found essential to produce stable (agglomerate-free) CNT dispersions.[53–56]A number of approaches have been taken in order to process these dispersions into useful electrode structures.

A variety of surfactants (including Triton X-100, sodium dodecylsulfate and sodium dodecylbenzenesulfonate) have been used to assist carbon nanotube dispersion in water. This widely used process involves high power sonication to initially break the CNT bundles. The surfactant is believed to be adsorbed onto the CNT surface (randomly or through micelle formation), which facilitates CNT stabilizsation in aqueous environment. Due to batch-to-batch variation of CNT production, many parameters in this procedure (including sonication duration and power and nanotube-to-surfactant concentration ratios) are required to be constantly optimised. Inefficient dispersion results in the formation of aggregates which compromises the quality of the material (*e.g.* mechanical properties of a composite) and reproducibility of results. Recent interest in introducing CNTs into biological systems has led to the use of biopolymers (peptides, polysaccharides, DNA, *etc.*) to facilitate CNT stabilisation in aqueous media.[57–59] Some amphiphilic α-helical peptides have been specifically designed to maximize their affinity for CNT surfaces through π–π interactions. The same principle allows SWNT bundles to be solubilised by certain conjugated polymers including poly(*m*-phenylenevinylene) and its derivatives.[60,61]

Electrode fabrication

A free-standing electrode comprised of a planar mat of entangled CNT (more commonly known as "bucky paper") can be fabricated by filtration of a carbon nanotube dispersion (Fig. 2a).[62,63] This method results in a robust, stand-alone material (up to several hundred μm thick) that can be easily peeled from the filter support. Although this simple method may not be practical for large-scale production, bucky paper electrodes have been useful in providing new insights into the fundamental properties of CNTs and some have been valuable in pointing to practical applications. Apart from the obvious applicability as electrode materials for batteries and supercapacitors, this electrode configuration enables the study of the electromechanical actuation behaviour (expansion and contraction to do mechanical work) of CNTs upon application of appropriate potentials.[64]

Another simple electrode fabrication method involves casting the CNT dispersion on an existing electrode. We have shown that

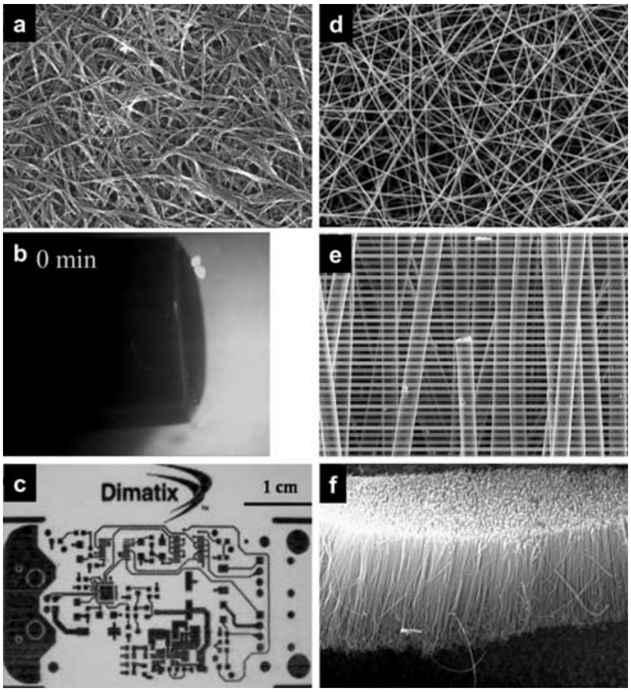

Fig. 2 Various carbon nanotube electrodes: (a) SEM of a single wall carbon nanotube "bucky paper" electrode; (b) optical image of a carbon nanotube biogel; (c) optical image of a printed CNT-PAn dispersion on a PET substrate; (d) SEM of an electrospun nanofiber mat from SWNT/PEO/DNA dispersion; (e) SEM of wet-spun SWNT-HA bio-fibers; (f) SEM of aligned MWNT array produced *via* CVD process.

electrodes formed in this way where the dispersion contains CNTs and a biopolymer (*e.g.* chitosan) actually form a swellable, conducting biogel (Fig. 2b).[65] This highly electroactive biogel has lower impedance than the host substrate and can be made to contain bioactive molecules and can support cell growth, making them excellent candidates for use as bionic electrodes. They can also be used as host carrier films for drug delivery where electrical stimulus modulates the release of a small drug molecule.[66] Others have used electrode modification methods, such as drop-casting,[67] inkjet-printing,[68] screen-printing[69]and self-assembly techniques,[70,71] to deposit stable CNT integrated redox-active films on other electrode substrates for use as electrochemical and bionic devices.

Flexible, transparent, conductive CNT films may be fabricated from CNT dispersions by non-contact deposition onto substrates (paper or plastic) with the use of an inexpensive off-the-shelf commercial inkjet printer and cartridge (Fig. 2c).[72–75] Patterns having a sheet resistance of 100 kohm/square and an optical transparency of 85% were obtained from a single printed layer. An increase in the number of printed layers improved resistance and reduced transparency. A major drawback of this method, however, is the increased sensitivity to the quality of nanotube dispersions compared to other methods and the roles that the chemical and physical properties of the substrate play in determining the quality of the final printed material. Inkjet deposition and characterisation of transparent conducting electroactive polyaniline (PAn)-carbon nanotube composite films with high CNT loading fraction (up to 32 wt.%) displayed improvement in electrochromic behaviour, and could be switched between yellow, green and blue. The PAn-CNT dispersion could be readily deposited onto substrates such as photopaper, PET, Pt-ITO glass and Au-PVDF.

Some carbon nanotube dispersions are also amenable to electro-spinning to produce nanofibrous mats.[76–82] Electrospinning provides a low-cost and rapid one-step integrated processing platform to produce continuous ultra-fine fiber electrodes. Filaments (50 to 250 nm diameter) prepared from DNA/SWNT/PEO blends (Fig. 2d) are potentially useful in the development of new electrode materials for enzyme biosensing.[83] In other studies, low volume fractions of carbon nanotubes incorporated in electrospun PLA and PAN filaments displayed increased thermal stability and mechanical reinforcement. "Bio-nanowebs" electrospun from a biostable elastomer (SIBS, poly(styrene-β-isobutylene-β-styrene)) containing SWNTs yielded conductive and electroactive nanofiber mats, which showed a much higher charge capacity and surface area than the bare ITO-glass substrate.[84] These useful combinations of properties, combined with promising success during cell culturing, open up the possibility of using these conductive materials as substrates for investigating the effects of electrical stimulation on cell growth.

Similar CNT dispersions may also be formed into long lengths of micron dimension electromaterials by wet-spinning.[55,85–90] This process involves injection of the dispersion into a coagulation bath to induce fiber formation. Depending on the spinning formulation used, fiber formation can be induced by coagulation, precipitation, cross-linking, or polyelectrolyte complexation of the polymers used in the spinning and coagulation solutions.[91] Shown in Fig. 2e are bundles of micro-fibers prepared from a CNT-hyaluronic acid dispersion. Recently, we have developed several approaches to produce carbon nanotube fibers of high strength and with excellent conductivity and electrochemical properties.[92,93] Cyclic voltammetry measurements of CNT biofibers showed capacitive behaviour with measured specific capacitance of up to 44 F g^{-1}. This method offers great opportunities for large-scale production of electrodes that can be woven in electronic textiles or as components in artificial muscles.

Integrated carbon nanotube-based electrodes may also be fabricated in geometrically well-assembled configurations without the use of a solution processing route. A powerful method to assemble carbon nanotubes in a pre-determined orientation on planar substrates is chemical vapour deposition (CVD) synthesis. This method can produce a highly ordered, vertically oriented high surface area CNT array ("CNT forest") (Fig. 2f).[94,95] Recently, we have shown that either sputtered Pt or an inherently conducting polymer can be used to produce a robust lateral interconnect. A modified CVD approach (Fig. 3) enables production of an entangled nanoweb electrode integrated into a conformable layer of conducting activated carbon.[96]

CNT electrodes have been shown to provide enhanced electron transfer characteristics with electrochemical activity known to take place at the edge-plane sites, on the tube surface, on the tube ends and defects (holes).[97,98] Electroactivity is also influenced by the chemical functionality (*i.e.* oxygen-containing groups) on the CNT surface.[99,100] Favourable electrocatalytic responses have been observed for simple redox species (*e.g.* ferric/ferricyanide couple)[101] and even for biomolecules such as dopamine, epinephrine, NADH, and ascorbic acid.[102–106] Carbon nanotube

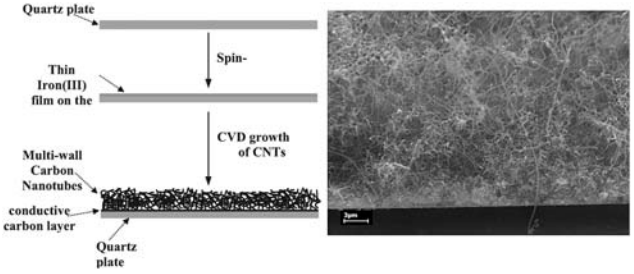

Fig. 3 Left: schematic of the procedures for CNT nanoweb growth on a quartz plate; right: SEM image of CNT nanoweb (cross section).

electrodes have also been used to facilitate direct electron transfer with redox proteins such as cytochrome c.[107] The use of CNT electrodes in the development of a selective glucose biosensor has been described[108] and we have used aligned carbon nanotubes coated with polypyrrole-GOD (Fig. 4) to do likewise.[109] The dispersant used in the preparation of CNT electrodes also provides a potential platform for creation of bio-sensors. For example, chitosan has been shown to be an effective dispersant,[110] and novel electrode structures can be formed from chitosan.[65] The same molecule provides an excellent platform for immobilization of biomolecules for biosensor applications.[111] Attachment of antibodies directly to carbon nanotubes has also enabled development of electrochemical based immunoassay systems.[112]

The high surface area of CNT electrodes has made them attractive candidates for use as electrodes in a number of different energy conversion and storage devices.[113] They have, for example, been used to develop new capacitor electrodes[114] and excellent charge storage capabilities have been obtained by utilizing CNTs on composites involving metal oxides.[115]

Novel aligned carbon nanotube electrode structures have been used to achieve charge storage in a Li-ion battery configuration, with a discharge capacity of 265 mAh g^{-1} reported.[116] This perhaps pales into insignificance given the more recently reported discharge capacity of 546 mAh g^{-1} for a carbon nanoweb electrode produced by coating a carbon fiber paper.[117]

Carbon nanotube electrodes have been shown to be capable of undergoing electromechanical actuation[118] and, given their inherent mechanical properties, provide a basis for super-strong artificial muscles. Even the addition of small amounts of carbon nanotubes to polyaniline-based artificial muscles has been shown to provide unprecedented performance under load.[119,120]

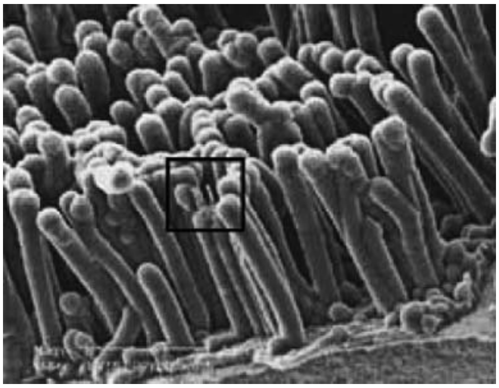

Fig. 4 SEM image of polypyrrole coated CNT array. Two exposed tips are highlighted by a square.

The wet-spinning technique used to produce long lengths of micron dimensional fibers is a simple route to the production of carbon nanotube-based microelectrode structures[121,122] for use in conventional electrochemical applications such as energy storage or in less conventional areas such as artificial muscles.

Graphene-based electrodes

In the family of carbon nanostructures, graphene is the youngest member but has attracted enormous recent interest. Like carbon nanotubes, graphene is promising for applications in a wide range of areas: sensors, high-performance nanocomposites and electrodes for optoelectronic and electrochemical devices.[123] Compared to CNTs, the production and processing of graphene appears to be easier and more economic. A number of approaches have been proposed to produce graphene sheets, including mechanical cleavage of graphite,[123] epitaxial growth on SiC substrates at high temperatures,[124] chemical vapour deposition,[125,126] bottom-up organic synthesis,[127] solvothermal reaction[128] and chemical conversion of graphite oxide.[129] Among these methods, the graphite oxide route has received the most attention. This method allows the large-scale production of graphene at relatively low cost and particularly graphene oxide-derived graphene can be readily made solution-processable through several strategies.[130] This section will outline the recent progress in large-scale synthesis and processing of graphene using the graphite oxide route and will briefly highlight its applications in transparent conductors and electrochemical electrodes.

Synthesis and functionalisation

Graphite is made of stacks of graphene layers and is abundant in nature and industry. Graphite seems to be the ideal source for large-scale production of graphene. However, high-yield direct exfoliation of graphite has proven to be difficult due to inter-sheet van der Waals interactions. Although it has been recently demonstrated that sonication treatment of graphite in certain organic solvents or in water in the presence of surfactants can lead to partial exfoliation of graphene sheets,[131–133] the yield is still unsatisfactory. In contrast, it has long been known that graphite oxide, a layered material that can be produced by controlled oxidation of graphite, can be well dispersed in water due to the presence of hydrophilic hydroxyl, epoxide, carbonyl and carboxyl functional groups. Ruoff and co-workers have recently confirmed that graphite oxide can be fully exfoliated in water as individual graphene oxide sheets by sonication.[129] Although graphite oxide is electrically insulating, it can be conveniently converted back to conducting graphene *via* chemical reduction or thermal treatment (Fig. 5).[129,134] Rapid thermal expansion can also cause graphite oxide to delaminate into individual graphene sheets.[135]

In addition to high yield conversion, solution processability can be easily achieved through the graphite oxide route. By simply adjusting some synthetic conditions, the resulting graphene can be readily dispersed in various solvents during the synthetic process, making it solution processable. Chemical

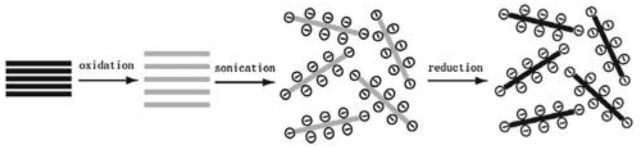

Fig. 5 Schematic showing the chemical route to graphene dispersions from graphite: (1) chemical oxidation of graphite to graphite oxide; (2) exfoliation of graphite oxide in water by sonication; and (3) chemical reduction of graphene oxide to graphene.

conversion from graphene oxide leaves a small amount of residual oxygen-containing groups, which make the resulting graphene surfaces negatively charged when dispersed in water. We have found that by controlling the colloid chemistry, graphene sheets can form stable aqueous colloids *via* electrostatic repulsion without the need for foreign polymeric or surfactant dispersants.[134] Ruoff and co-workers have observed that stable dispersions can be obtained if the reduction of graphene oxide is conducted in certain organic solvents, such as *N*,*N*′-dimethylformamide.[136] Kaner and co-workers have found that graphene oxide can be dissolved in pure liquid hydrazine while being deoxygenated. The resulting graphene can remain dispersed in hydrazine through the formation of a hydrazinium graphene complex in the absence of any surfactants.[137]

The solubility of graphene in a broader range of solvents can be further achieved by chemical modification. Thanks to the oxygen-containing groups that exist in graphite oxide (*i.e.* carboxyl and hydroxyl), a variety of functional groups can be anchored onto the surface of graphene oxide by reacting with alkylamines,[138] isocyanates[139] and diazonium salts[140] or by polymer grafting.[141]

The prevention of aggregation of graphene can also be realized by adding other stabilizing agents such as surfactants and polymers into the graphene oxide dispersion prior to deoxygenation.[142–144] Through this strategy, other soluble electrically active molecules can be easily incorporated into graphene during its synthesis to create novel composite electrodes.

Electrode fabrication

Successful dispersion of graphene in various solvents enables using low-cost solution processing techniques to fabricate graphene-based electrodes. Graphene films can be made simply by drop-casting, spraying,[145] and dip- or spinning-coating[146] of graphene dispersions or graphene oxide dispersions. Vacuum filtration is another simple method for assembling graphene sheets into highly ordered macroscopic electrodes. We and other groups have recently demonstrated that during vacuum filtration, graphene sheets in solution can interlock together in a near-parallel manner, yielding ultra-strong, electrically conductive and thermally stable graphene paper (Fig. 6).[134,143,147,148] This unique carbon paper could find applications in flexible batteries. Uniform thin graphene films can also be prepared by filtration for use as transparent electrodes.[149]

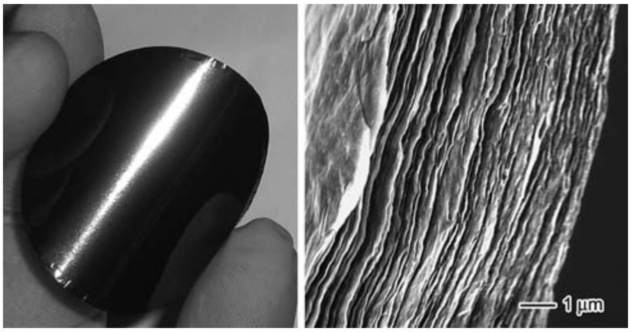

Fig. 6 (Left) Photograph of graphene paper prepared by vacuum filtration of a graphene dispersion; (right) SEM image of the cross-section of graphene paper showing a layered structure.

Ultrathin graphene films with precisely controlled numbers of layers can also be fabricated by the traditional Langmuir–Blodgett (LB) technique. Huang and co-workers have recently discovered that graphene oxide dispersions in methanol–water can spread on the water surface to form LB films without any additional amphiphilic molecules.[150] Dai and co-workers have found that chemically exfoliated graphene LB films can be directly formed by spreading graphene in dichloroethane on water.[151]

Given that chemically prepared graphene sheets can be negatively charged when dispersed in water, single- or multi-layers of graphene sheets can be deposited on a positively-charged substrate by the electrostatic assembly technique.[134,152,153] By alternately immersing a substrate into a negatively charged graphene colloid and a positively charged polycation solution, graphene sheets can be integrated with other polycations at a molecular/nanometre scale through electrostatic interactions. Because many functional molecules and nanoparticles are (or can be made) positively charged, a wide range of exciting graphene-based composite electrodes can be created using this simple approach. The surface charges on chemically prepared graphene also enable assembling graphene films by electrophoretic deposition.[154]

The combination of high optical transmittance, low electrical resistivity, high chemical stability and mechanical strength makes thin graphene layers an ideal optically transparent electrode material for use in various optoelectronic devices. The use of graphene in both dye-sensitized and organic-based solar cells[155–157] as well as liquid crystal display devices[131] has recently been demonstrated. The ease of large-scale production and processing of graphene sheets through the graphite oxide route will significantly facilitate the utilization of graphene-based transparent electrodes in real devices.

Carbon materials such as graphite and carbon black are traditionally used in electrochemical electrodes for energy conversion and storage. Single graphene sheets have a high theoretical specific surface area of 2630 $m^2\ g^{-1}$, making graphene very attractive as a novel nanostructured electrochemical electrode. The use of chemically derived graphene or its composites in supercapacitors[158] and lithium-ion batteries[159] showed very promising results. For example, Ruoff and co-workers have recently demonstrated that a specific capacitance of 135 F g^{-1} for graphene-based electrochemical capacitors can be achieved in an aqueous electrolyte. Graphene electrodes could also be used for bio-sensing, as recently demonstrated by Niu and co-workers.[160]

Graphene is only one atom thick, offering very sharp edges. This appears to make graphene an excellent field emitter as well. Cheng, Ren and co-workers have recently demonstrated that electrophoretic deposition of chemically prepared graphene sheets can form a unique electrode structure in which many of the graphene sheets are normal to the substrate. The resulting electrodes exhibit excellent field-emission properties.[154]

It is noteworthy that because there are usually a certain amount of residual oxygen-containing groups existing in chemically prepared graphene, graphene electrodes prepared from the graphite oxide route could be different from other carbon materials. For example, we have found that as-prepared graphene paper electrodes exhibit a cyclic voltammogram different from the conventional graphite electrode when used in a lithium battery, and two cathodic peaks appeared during the lithiation process. Their charge/discharge behaviour is also different. The initial capacity of graphene-based electrodes is much higher than that of graphite-based ones but it is irreversible.[161] This result suggests that electrochemical properties of graphene-based electrodes can be readily tuned by chemical modification of individual graphene sheets.

Given that edge-plane defects and oxygen-containing surface groups in carbon nanotubes have been found to influence their electrochemical response,[99,100] in the future it would be of interest to study how these groups affect the electrochemistry of graphene. The oxygen-containing groups on chemically prepared graphene also provide useful reactive sites for surface modification to allow tailoring of electrochemical properties. Additionally, as the electronic transport in graphene films is dependent on the number of graphene layers, it would be interesting to study whether the thickness of graphene films affects their electrochemical properties. Accordingly, when one studies graphene-based electrodes, their surface chemistry as well as the thickness should be properly characterized.

Future developments

The discovery of nanostructured forms of carbon has had a dramatic impact on the design and utilisation of new electrode materials. Their application has been shown to be beneficial in areas such as energy conversion (solar cells and fuel cells) and storage (batteries and capacitors). In the biological area, nanostructured carbon nanotubes have been shown to have useful electrocatalytic properties that have propelled them into laboratories developing new biosensing technologies. An emerging area of activity is in the use of nanostructured carbon electrodes as platforms for mammalian cell growth, with the prospect of using electrical stimulation to enhance and/or direct growth.[162] It has been shown that mammalian cells will grow readily on CNT platforms[163] including fibers.[162,164] More recently nanostructured graphene electrodes have been shown to be non-cytotoxic.[148]

The unique combination of extraordinary mechanical properties of carbon-based nanostructures and composites together with their electrochemical properties and organic nature will undoubtedly lead to more applications in the medical bionics area.[165]

The continued development of synthesis, processing and material fabrication protocols that enable highly pure, reproducible structures to be produced is essential if the true potential of this exciting area is to be realised.

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