Electrochemistry of Graphene: New Horizons for Sensing and Energy Storage

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Received 15 May 2009

ABSTRACT: Graphene is a new 2D nanomaterial with outstanding material, physical, chemical, and electrochemical properties. In this review, we first discuss the methods of preparing graphene sheets and their chemistry. Following that, the fundamental reasons governing the electrochemistry of graphene are meaningfully described. Graphene is an excellent electrode material with the advantages of conductivity and electrochemistry of sp² carbon but without the disadvantages related to carbon nanotubes, such as residual metallic impurities. We highlight important applications of graphene and graphene nanoplatelets for sensing, biosensing, and energy storage. © 2009 The Japan Chemical Journal Forum and Wiley Periodicals, Inc. Chem Rec 9: 211–223; 2009: Published online in Wiley InterScience (www.interscience.wiley.com) DOI 10.1002/tcr.200900008

Key words: graphene, graphene nanoplatelets, electrochemistry, electron transfer, batteries

1. Introduction

Graphene is a single-atom thick, two-dimensional sheet of sp² bonded carbon. Experimentally discovered in 2004, graphene sheets captured the interest and imagination of physicist and chemists alike arising from their unique electronic, optical, mechanical, thermal, and electrochemical properties. Graphene is a new form of carbon, as shown in Figure 1. While 0-dimension carbons, such as fullerenes, act as insulating materials, 1-dimensional carbon structures, such as single-walled carbon nanotubes (SWCNTs), which are basically wrapped-up graphene sheets, possess excellent uniaxial electron conductivity and fast heterogeneous electron transfer rates at their ends. Two-dimensional graphene sheets offer a unique two-dimensional environment for electron transport and offer fast heterogeneous electron transfer at their edges (Figure 1). The 3-dimensional structure based on sp² hybridized carbon is, of course, graphite. Graphene shows many advantages for electrochemical applications when compared to graphite or to carbon nanotubes. Graphene exhibits a surface area of 2630 m² g⁻¹, which is much greater than that of graphite (~10 m² g⁻¹) and even that of carbon nanotubes (1315 m² g⁻¹). The electrical conductivity of graphene is excellent. When comparing graphene to graphite, one should note that graphene sheets are flexible as opposite to brittle graphite, which is beneficial for use in flexible electronic and energy storage devices. Electrodes made from graphene have significantly more uniform distribution of electrochemically active sites than do those made from graphite. Their electrochemical properties are similar to those of carbon
nanotubes. However, graphene has one huge advantage over carbon nanotubes: it is usually prepared from graphite and does not contain any heterogeneous materials. This is in contrast to the preparation of carbon nanotubes, which are typically grown from carbon-containing gas with the use of metallic catalytic nanoparticles. It is well documented that such nanoparticles remain in the carbon nanotubes even after extensive purification procedures, leading to two very significant problems. It has been shown that such residual metallic impurities are electrochemically active even when intercalated within the carbon nanotubes and that they can dominate the electrochemistry of carbon nanotubes. This is a significant problem for the construction of reliable sensors and energy storage devices. In addition, such residual metallic impurities possess toxicological hazards because they can participate in the redox activities of biomolecules, such as within biological samples, even down to 50 ppm levels of impurities in CNTs. Graphene precludes the problems associated with carbon nanotubes while outperforming their properties in many ways.

Research on graphene is a very young field having explosively started in 2004 after the development of a simple technique of preparing a single-layer graphene sheet. The enormous progress in this field is because the relevant research can be built on the wealth of techniques and knowledge available from decades of research on graphite and carbon nanotubes. However, not only graphene is in the forefront of materials research. Graphene nanoplatelets formed by stacked graphene sheets with a typical thickness of 2–10 graphene layers are an equally important research topic in chemistry, physics, and materials science. We should note that graphene nanoplatelets with more than 100 layers possess the electronic properties of graphite and should be thought of as thin layers of 3D graphite rather than as graphene nanoplatelets.

Here, we wish to detail the exciting area of electrochemistry of graphene and graphene nanoplatelets and the advantages that they bring for the development of sensors and energy storage systems. We start with a description of the methods for preparing graphene and graphene nanoplatelets, followed by a discussion of the chemical properties of graphene. Then, we will describe the fundamental electrochemistry and important electrochemical applications in the areas of sensing, biosensing, and energy storage.

2. Preparation of Graphene and Graphene Nanoplatelets

The preparation of graphene is a crucial issue and this area of research is very active since none of the existing methods is suitable for all applications. The methods of preparation can be classified into the following five categories. (i) Historically, the first method for the production of graphene is the “cellophane method,” which is capable of separating a single graphene sheet from crystalline graphite. Such dry mechanical exfoliation is useful for the investigation of physical properties.
and for selected applications (such as single-layer graphene in field-effect transistors),\textsuperscript{17,18} but for electrochemical applications, bulk quantities of graphene sheets are needed. (ii) Several methods of producing bulk quantities of graphene sheets and graphene nanoplatelets were developed based on chemical exfoliation of graphite. This involves intercalation of small molecules (typically sulfuric and nitric acid\textsuperscript{6} or small organic molecules such as tetrabutyl ammonium hydroxide\textsuperscript{19}) between the graphene layers in graphite and consequent separation of the graphene sheets (i.e., by either thermal evaporation of the intercalated molecules\textsuperscript{6} or sonication\textsuperscript{19}; see Figure 2). It is remarkable that this method is based on the 150-year-old work by Brodie.\textsuperscript{20} (iii) Unzipping carbon nanotubes by either electrochemically, chemically, or by physical methods. (a) Electrochemical intercalation of Li\textsuperscript{+} and ammonia within the lattice of graphite\textsuperscript{21,22} or multiwalled carbon nanotubes,\textsuperscript{23} increases the interlayer distance from ca. 3.35 Å to 6.62 Å, and consequently delaminates graphite or CNT to form a graphene nanoribbon (see an example in Figure 3, A). (b) A physical approach to the preparation of graphene nanoribbons (GNR)
was demonstrated by Dai and co-workers.\textsuperscript{24} Carbon nanotubes were opened by plasma etching of nanotubes partly embedded in a polymeric film (Figure 3, B). The resulting graphene nanoribbons exhibited smooth edges and a narrow width distribution (10–20 nm).\textsuperscript{23} (c) Tour and co-workers\textsuperscript{25} recently presented a solution-based oxidative process for producing a nearly 100% yield of nanoribbon structures by lengthwise cutting and unraveling of multiwalled carbon nanotubes (MWCNT) side walls. The CNT wall is subjected to permanganate oxidation to give the manganate ester which can oxidize further to the dione in the dehydrating medium. The next attack by permanganate eventually results in the fully cut nanotube (see the example in Figure 3, C). (iv) Epitaxial growth of graphene, which is useful for applications in nanoelectronics.\textsuperscript{26} (v) Chemical vapor deposition (CVD) for synthesis of graphene nanoplatelets and nanoribbons.\textsuperscript{27} We should emphasize here that the CVD method should be catalyst free to preclude similar problems that are associated with

**Fig. 3.** Graphene sheets from multiwalled carbon nanotubes. (A) Mechanism for intercalation and unwrapping of MWCNT; tridimensional representation (above) and cross-section view (below) of the initial stages. The dots represent ammonia-solvated lithium ions, which are attracted by the negatively charged MWCNTs (charges in the tubes are omitted for clarity). The intercalation expands the interlayer spacing almost twice and the resulting stress ruptures the walls. After HCl treatment, the tubes are exfoliated and disordered (stage not represented here). After thermal treatment, further exfoliation occurs together with some recrystallization of graphitic planes, producing nanoribbons, such as the idealized ex-MWCNT shown on the right. (B) Chemical route: a) Representation of the gradual unzipping of one wall of a carbon nanotube to form a nanoribbon. Oxygenated sites are not shown. b) The proposed chemical mechanism of nanotube unzipping. The manganate ester in 2 could also be protonated. c) TEM images depicting the transformation of MWCNTs (left) into oxidized nanoribbons (right). The right-hand side of the ribbon is partly folded onto itself. The dark structures are part of the carbon imaging grid. (C) Physical route: a) A pristine MWCNT was used as the starting raw material. b) The MWCNT was deposited on a Si substrate and then coated with a PMMA film. c) The PMMA–MWCNT film was peeled from the Si substrate, turned over and then exposed to an Ar plasma. d)–g) Several possible products were generated after etching for different times: GNRs with CNT cores were obtained after etching for a short time \( t_1 \) (d); tri-, bi-, and single-layer GNRs were produced after etching for times \( t_2 < t_3 < t_4 \); e)–g). h) The PMMA was removed to release the GNR. Reprinted with permission from Refs [23–30].
CNTs relative to intercalated metallic impurities, as discussed above. Given the significant amount of interest in graphene, the number of methods of preparation is expected to increase steadily.

There is a problem associated with the stability of individual graphene sheets since they tend to restack to form graphite nanoplatelets (<100 layers) or even thicker structures (>100 layers). Solutions to this problem include chemical functionalization or the use of nanoparticles (metallic, C<sub>60</sub>, or carbon nanotubes) to prevent such restacking. These methods are discussed in the following sections.

It should be emphasized that after the graphene sheets or graphene nanoplatelets are prepared, they should undergo extensive characterization before being used for any application to avoid incorrect claims and conclusions regarding their properties, as was sometimes the case in carbon nanotube research.9

**Chemistry of Graphene**

Graphene sheets can be functionalized by both non-covalent and covalent means. (i) *Non-covalent* functionalization by physisorption of aromatic molecules on a basal plane of graphene sheets leads to breaking the symmetry of graphene layers and is useful in the electronic application of graphene sheets.28 (ii) *Covalent functionalization* of graphene via a chemical route can take advantage of a wealth of methods available from graphite and carbon nanotube research. The starting point of functionalization is usually the oxygen-containing groups present at the
graphene edges and/or surface. For example, this can be used for covalent stitching of graphene layers via diaminoalkane to create nanoplatelets with a controllable distance between graphene layers (from 0.8 to 1.0 nm for “stitching” agents NH$_2$-(CH$_2$)$_4$-NH$_2$ and NH$_2$-(CH$_2$)$_{10}$-NH$_2$, respectively) (Figure 4, A).$^{29}$ Alternatively, graphene nanoplatelets can be assembled layer-by-layer from graphene sheets.$^{30}$ In such a case, the graphene surface is covalently modified with poly(acrylic acid) and poly(acrylamide). This introduces negative and positive charges on the graphene surface. The positively and negatively charged graphene sheets assemble into a multilayer structure through electrostatic interaction (Figure 4, B). The graphene sheets are then chemically modified to stabilize them and to promote their solubility. For example, anionic polymer poly(vinyl alcohol) can be attached to graphene sheet carboxylic groups via an ester bond to facilitate solubility without the addition of any additional foreign component (Figure 5).$^{31}$

The controllable attachment of functional elements (nanoarchitectonics) is a paramount topic of the current state-of-the-art nanotechnology. Oxygen-containing groups serve as starting points for functionalization and, as will be discussed in the following sections, they are also thought to be responsible for heterogeneous electron transfer from/to graphene sheets. Therefore, the issue of being able to locate these groups is of paramount importance. Yudasaka et al.$^{33}$ developed a method for the identification of site location of carboxyl groups via a Pt(NH$_3$)$_6$(OH)$_4$ complex as a stain (see Figure 6). When the Pt-ammine complex was mixed with graphene in ethanol, it was possible to observe, by transmission electron microscopy, that many Pt-ammine complex clusters with an average size of about 0.6 nm were present at the edges of the graphene sheets. This suggests that the carboxyl groups mainly exist at the graphene edges. We have developed a similar method using europium hydroxide as a staining agent for locating oxygen-containing groups (hydroxyl, carbonyl, carboxyl) on the surface of carbon nanotubes.$^{34}$ Such a method could be used in a similar fashion for locating such groups on graphene sheets.

**Electrochemistry of Graphene**

Research on the electrochemistry of graphene can take advantage of the enormous amount of work that has been published on graphite (especially on highly oriented pyrolytic graphite –
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HOPG) and carbon nanotube materials. Because it was shown previously that there is no difference in the electrochemical behavior of SWCNTs (rolled up single graphene sheet) and HOPG (stacked graphene sheets), it is possible to predict that the electrochemistry of individual graphene sheets and graphene nanoplatelets will also be similar.9,35

Fundamentals

Graphene sheets provide a 2D environment for electron transport. Heterogeneous electron transfer from/to a graphene sheet takes place on the edges of the graphene sheet, while heterogeneous electron transfer from the plane of a graphene sheet is very close to zero.36 The oxygen-containing groups at the edges of the graphene sheets influence its electrochemistry. However, there is a controversy over whether this influence is positive (i.e., enhances the heterogeneous electron transfer rate) or negative (slows the heterogeneous electron transfer rate). Chou et al. suggested that the carboxylic groups at electrodes modified by single-walled carbon nanotubes are responsible for increasing the heterogeneous electron transfer rate constant (and thus for increasing the speed of electron transfer) of ferro/ferricyanide.37 However, thereafter, we demonstrated the opposite for the same system.38 Ji et al. showed that with an increasing amount of oxygen-containing groups present on graphite microparticles, heterogeneous electron transfer between the graphitic material and ferro/ferricyanide decreases.39

Recently, we proved that oxygen-containing groups on carbon nanotubes and graphite possess preferential "electrocatalytic" properties for the oxidation of endiol groups (see Figure 7).40 The oxygen-containing species present on the graphene sheets generated during acid treatment are responsible for this enhancement of electron transfer. Heterogeneous charge transfer for oxidation of the endiol groups arises from a proton-coupled electron transfer mechanism. The oxygen-containing species withdraw two protons from the endiol group and aid the oxidation reaction, reducing the overpotential voltage.40

The effect of oxygen-containing groups on the electrochemistry of graphene cannot be overestimated. It is not just their influence on the heterogeneous electron transfer rate but also on the adsorption/desorption of molecules, which takes place before and after the electrochemical reaction. Recently, we experimentally and theoretically proved the reasons for, and mechanism of adsorption of β-nicotinamide adenine dinucleotide (NAD⁺) on graphene sheets.41 NAD⁺ is a major element in electrochemical enzyme biosensors and biofuel cells employing dehydrogenase enzymes.42–45 The adsorption of NAD⁺ on most carbon materials (including carbon nanotubes and graphite) is a serious problem, which has not been well understood. We demonstrated that the adsorption of NAD⁺ at sp² carbon materials is caused by the presence of oxygen-containing groups, namely carboxylic groups, formed at the edges and edge-like defects of graphene sheets. These oxygen-containing moieties are naturally present in graphene sheets owing to their spontaneous oxidation in air. With the aid of X-ray photoelectron spectroscopy (XPS), cyclic voltammetry, and amperometry,
we demonstrated that the adsorption of NAD\(^+\) and passivation of electrodes occurs at the edges and edge-like defects of graphene. XPS and Car-Parrinello molecular dynamics proved that only when a positive NAD\(^+\) is positioned close to a graphene sheet edge that contains a -COO\(^-\) group, is there significant interaction, which agrees with what was found experimentally. No relevant interactions could be observed when NAD\(^+\) is located close to the basal plane of graphene or near hydrogen-only substituted edges of graphene sheets (Figure 8).

Applications

Sensors and Biosensors

Graphene and graphene nanoplatelets are ideal materials for electrochemical sensing and biosensing. They possess most of the advantageous properties of carbon nanotubes (such as homogeneous distribution of electrochemically active sites on a nanometer scale) without carrying the most challenging element of carbon nanotube materials – that is, residual metallic impurities. Papakonstantinou and co-workers\(^4\) demonstrated that graphene nanoplatelets with a thickness of 5–40 graphene sheets (grown without any catalyst) show properties similar to that of edge plane HOPG (EPPG) and superior to that of glassy carbon electrodes. Unlike HOPG, nanoplatelets can easily be incorporated into composite materials with a high degree of uniformity. The fast heterogeneous electron transfer kinetics and sensitive sensing properties towards the detection of dopamine in the presence of typical interferences, such as ascorbic and uric acid, arises from the high density of edge plane sites at the ends of the graphene nanoplatelets and their ability to act as nano connectors for electrical connection with electrode substrates (Figure 9). Lu et al.\(^4\) fabricated a sensitive
The authors suggested that the resulting highly sensitive and selective glucose biosensor results based on graphene nanoplatelets could be an inexpensive alternative to carbon nanotubes for the fabrication of affordable high-performance biosensors. Again, we should emphasize that not only the high cost of CNTs but primarily the difficult-to-control amount of metallic impurities present in them, make graphene nanoplatelets ideal replacements for CNTs in many electrochemical applications.

Niwa and co-workers\(^{45}\) employed nanocarbon materials containing sp\(^2\) and sp\(^3\) hybridized carbon for the detection of DNA methylation. The authors observed that the clear oxidation peaks of thymidine and cytidine observed on their sp\(^2\)/sp\(^3\) nanocarbon electrodes could not be observed on the glassy carbon electrodes because of a large background current and small potential window which results to overlapped the thymidine and cytidine oxidation peaks. This work proved the superior electrochemical properties of nanocarbon films over those of glassy carbon and EPPG electrode surfaces. It should be noted, however, that the oxidation of guanosine, adenosine, and 5-methylcytidine at the nanocarbon film electrode occurs at very similar potentials to those on EPPG and glassy carbon electrodes (Figure 10). Niu and co-workers\(^{46}\) explored graphene/ionic liquid-based composites for the biosensing of glucose. The graphene sheets were stabilized by polyvinylpyrrolidone and the ionic liquid was based on polyethylenimine-functionalized ionic liquid. The positively charged ionic liquid is capable of the electrostatic incorporation of a negatively charged glucose oxidase enzyme and results in an attractive glucose-sensing device. The resulting biosensor achieved direct electron transfer from glucose oxidase using such nanocarbon/ionic liquid electrodes with the dispersed enzyme.\(^{46}\)

Alwarappan et al.\(^{47}\) probed utility of graphene nanosheets for utilization for electrochemical sensing of dopamine and serotonin in the presence of ascorbic acids. They compared graphene nanosheets to SWCNTs and they found superior electrochemical performance of graphene sheets when comparing to that of the SWCNTs. Using a four-point probe technique, they found the conductivity of graphene particles to be approximately 60 times better than that of SWCNTs. They
reasoned that a higher heterogeneous electron transfer rate at graphene electrodes (when compared to SWCNTs) results from the higher conductivity of graphene nanoparticles film (vs SWCNTs). However, in principle there is no direct correlation between conductivity of a film of particles and heterogeneous electron transfer. In addition, it should be noted that even though the paper by Alwarappan et al. uses the term “graphene” for their electrodes, it is clear from TEM/ED characterization that the particles are crystalline, thus perhaps the term “graphene nanoplatelets” would be more accurate. In addition, reasoning that the conductivity of SWCNTs is sluggish and this results in a sluggish heterogeneous transfer rate goes against most of the research done on CNTs in the past two decades, showing SWCNTs demonstrate ballistic conductivity and excellent electrochemical properties. We wish to conclude that very careful characterization of graphene used for electrochemical purposes is needed to avoid misleading claims. We wish to suggest that the electrochemistry of graphene related materials should be compared to that of graphite, not CNTs.

Energy storage
Graphene sheets are extremely attractive for energy storage applications because of their very high theoretical surface area of 2630 m² g⁻¹. The advantages of graphene sheet-based electrodes were demonstrated for applications as fuel cells, rechargeable Li⁺ ion batteries, and ultracapacitors.

Graphene-based ultracapacitors were developed by Ruoff and co-workers. Ultracapacitors store energy in a double layer at the surface of the material; graphene is the ideal candidate for their construction. The work by Ruoff et al. was based on chemically modified graphene as an electrode material (for schematics of graphene based electrodes for ultracapacitors and for the ultracapacitor design, see Figure 11, A). The main innovative idea of the chemically modified graphene electrodes is that the ultracapacitor does not depend on the rigid porous structure of activated carbon to deliver its large surface area but on the flexible graphene sheets, which adjust their position depending on the electrolyte used. The weight-specific capacitance of chemically modified graphene was found to be up to 1352 F g⁻¹.

Lithium-based rechargeable batteries are another class of energy storage devices where graphene was employed with several advantages. Standard graphite-based electrodes intercalate Li⁺ into the graphite lattice (theoretical capacity of graphite Li⁺ battery is 372 mA h g⁻¹). To increase the specific capacity of Li⁺-based batteries, graphene sheet-based electrodes were used and achieved superior capacity (540 mA h g⁻¹). When CNTs or C₆₀ molecules were used as spacers to prevent restacking of the graphene sheets, the capacity of the Li⁺ battery was increased even further, to 730 or 784 mA h g⁻¹, respec-
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Fig. 11. Graphene for energy storage. (A) Ultracapacitors: a) SEM image of CMG particle surface, b) TEM image showing individual graphene sheets extending from chemically modified graphene surface, c) low and high (inset) magnification SEM images of chemically modified graphene electrode surface, and d) schematic of test cell assembly. (B) Lithium batteries: Cross-sectional TEM images of graphene nanoplatelets with almost the same numbers (5–6) of graphene stacking layers for a) graphene nanosheets, b) graphene nanosheets separated by CNT, and c) graphene nanosheets separated by C₆₀. Reprinted with permission from Refs [7] and [48], respectively.

Conclusions

Graphene is a material that would have been predicted as impossible to exist 70 years ago.50,51 It is remarkable how such an “impossible” material makes an impact in a wide variety of areas, including electrochemistry. Graphene sheets and graphene nanoplatelets exhibit large surface areas and excellent...
conductivity, and they are typically impurity-free. In comparison to carbon nanotubes, this is their major advantage together with a much lower cost. Their fundamental electrochemical properties are similar to those of edge-plane pyrolytic graphite but significantly better than those of other electrodes, such as glassy carbon or activated carbon. In addition, they can be used in the nanoarchitectonic designs of nanodevices. Given the promising properties of graphene, the work summarized in this paper is just the beginning of a fantastic topic. The best is yet to come!

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