Advanced Electrode Materials
Advanced Materials Series

The Advanced Materials Series provides recent advancements of the fascinating field of advanced materials science and technology, particularly in the area of structure, synthesis and processing, characterization, advanced-state properties, and applications. The volumes will cover theoretical and experimental approaches of molecular device materials, biomimetic materials, hybrid-type composite materials, functionalized polymers, supramolecular systems, information- and energy-transfer materials, biobased and biodegradable or environmental friendly materials. Each volume will be devoted to one broad subject and the multidisciplinary aspects will be drawn out in full.

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Among the hot topics concerning advanced materials are recent advances in electrode materials because of their importance not only in developing new biosensors but also in designing efficient batteries, fuel cells and, of course, energy storage and conversion systems. Therefore, we have tried to compile various valuable aspects of this hot topic as a part of the Advanced Materials Series.

In this book, a narrative is presented of recent advances in electrode materials and their novel applications, which are a cross section of advanced materials. Electrochemistry is a widely used branch of chemistry which combines chemical and electrical effects. It provides the advantages of high sensitivity, high performance and low cost. In electrochemistry, a well-designed electrode material is the key to many applications. Therefore, we have summarized different electrodes used in various fields for enhancing the quality of electrochemical systems. We begin with a chapter regarding advances in electrode materials, particularly those based on energy storage, since an electrode is one of the important parts of electrochemical capacitors as well as energy storage and conversion products. The major classes of suitable electrode materials used for capacitors are commonly activated nanoporous carbon, graphene, carbon nanotubes, conducting polymers, metal oxides and polymer composites, which have been extensively reported on in the literature.

Diamond-based electrodes have garnered great attention for use in electrochemical systems. Therefore, detailed techniques used in chemical vapor deposition (CVD) to generate polycrystalline and nanocrystalline diamond layers are also covered, along with methodologies employed to dope the diamond phase in order to obtain an electrically conductive material. Then, the use of diamond-based layers for the assembly of electrodes is summarized to inform readers in areas related to the environment and renewable energies, including food and pharmaceutical analysis, soil and water purification, supercapacitors, Li-ion cells and fuel cells. Recent advances in tungsten oxide/conducting polymer hybrid assemblies for electrochromic applications have taken place which emphasize the importance
of developing new technologies that can be used for electrochromic applications. Tungsten oxide (WO₃) has emerged as one of the key materials for electrochromic devices since it exhibits the best electrochromic activity among transition metal oxides. The introduction of WO₃/conducting polymer-based hybrid materials has prompted the development of nanocomposites with properties unmatched by conventional counterparts. The interdisciplinary research involving materials science, bioelectrochemistry and electrochemistry is still the hallmark of many technological and fundamental breakthroughs. The effectiveness of surfactant-free metal nanoparticles as “abiotic” catalysts in biotechnology are outlined, based on systems harvesting energy from biological sources for various sensing and wireless information-processing devices for biomedical, homeland and environmental monitoring applications. In another chapter, polyoxometalates (POMs) based on concepts of biosensors for renewable energy applications are summarized. POMs are a well-known class of discrete early transition metal-oxide clusters with a variety of sizes, shapes, compositions and physical and chemical properties, which undergo reversible multivalence reductions/oxidations. Electrochemical sensors based on ordered mesoporous carbons are also highlighted since they provide high sensitivity and selectivity.

Conducting polymer-based electrochemical DNA biosensing is also detailed in the book. Electrode materials for fuel cells lead to important reactions such as oxygen evolution reactions (OER), hydrogen evolution reactions (HER), and oxygen reduction reactions (ORR). In metal-air batteries and fuel cells, the most sluggish reaction is the ORR reaction, which is the bottleneck of numerous electrochemical reactions. Key electrocatalytic reactions occur at the cathode of a proton exchange membrane fuel cell (PEMFC). Therefore, inexpensive materials that have high activity, stability, and resistance to methanol crossover effects for ORR-HOR and OER reactions have been summarized in one of the chapters. In another chapter, a study of phosphate polyanion electrodes and their performance with glassy electrodes for potential application in lithium-ion solid-state batteries is presented in order to stress the importance of new generation solid-state batteries. Then, in a related area, conducting polymer-based hybrid nanocomposites for lithium batteries are given. In this chapter, host-guest and core-shell hybrid nanocomposites based on conducting conjugated polymers and inorganic compounds, which are considered active components of the lithium batteries, are reported. Later on, electrode materials for fuel cell applications are categorized and evaluated in two separate parts as catalyst supports and anode/cathode catalysts. Platinum (Pt)-based catalysts make fuel cell technology less cost-effective due to the limited supply
and high cost of Pt. Thus, research on the cost reduction of fuel cells is dealt with either by optimization of existing Pt catalysts or development of Pt or non-Pt alloy catalysts with new and improved electronic structures. Novel photoelectrocatalytic electrode materials for fuel cell reactions are also summarized, with the main focus of the chapter being the recent progress of novel photoresponsive electrodes as anode catalysts for improving the photoelectrocatalytic activity of low molecular weight alcohols oxidation under light irradiation. Finally, advanced nanomaterials for the design and construction of anode materials for microbial cells are detailed at the end of the book.

The invaluable efforts of distinguished researchers from ten different countries with seventeen different affiliations have helped build a comprehensive book from the perspective of advanced materials. By including information presented by such a wide range of authors we hope to contribute to the understanding of students and researchers as well as industrial partners from different fields.

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September 2016
Part 1

STATE-OF-THE-ART ELECTRODE MATERIALS
Advances in Electrode Materials

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Abstract
Electrode is the key part of the electrochemical capacitors (also known as supercapacitors) as well as energy storage and conversion products or other electrochemical devices, so the electrode materials are the most important factors to determine the properties of these tools. The major classes of suitable electrode materials used for the capacitors as well as an energy storage and conversion materials or other electrochemical devices are activated nanoporous carbon, graphene, carbon nanotubes, conducting polymers, metal oxides, and polymer composites, which have been extensively reported in the literature. In addition, the well-known applications of advanced electrodes in metals production, energy storage in batteries and supercapacitors, and catalyst supports have appeared in the literature on both carbon materials and their interactions with electrolytes and redox systems. Since the significant application of graphite electrodes for electrochemical production of alkali metals, carbon materials have been broadly used in both analytical and industrial electrochemistry. The often-cited benefits of carbon electrodes contain reasonable cost, wide potential window, relatively inert electrochemistry, and electrocatalytic activity for a variety of redox reactions. Energy storage techniques appear as one of the most promising options in harvesting renewably generated energy during the optimum manufacture period for future use. Of the available electrical energy storage devices, fuel cells, batteries, and capacitors have been the technology of choice for most applications. Herein, the storage principles and characteristics of electrode materials, including carbon-based materials, transition metal oxides, and conductive polymers for advanced electrodes are depicted briefly.

Keywords: Electrode material, semiconductors, carbon materials, electrochemistry, conducting polymers

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1.1 Advanced Electrode Materials for Molecular Electrochemistry

Regardless of extensive developments of carbon materials for electrochemistry, recent years have brought essential novelties that impart the significance to the utility of the material in organic and biological electrochemistry. Fullerenes, vapor-deposited carbon films, and microfabricated carbon structures tender features compared with the graphitic carbon electrodes in universal use in the early 1990s and also enable modern adoptions in electronics, sensing, as well as electrocatalysis [1].

Due to the facts, nanocarbon is believed to play a crucial role. Carbon nanoscience brings promise for an evolution in electronics in the future. Three important elements make \( sp^2 \) carbon particular for facing the nanochallenges. First is the strong covalent \( sp^3 \) bonding between atoms, next are the enlarged \( \pi \)-electron clouds coming from the \( pz \) orbitals, and third is the simplicity of the \( sp^2 \) carbon system [2].

1.1.1 Graphite and Related \( sp^2 \)-Hybridized Carbon Materials

The energy difference between the \( 2s \) and \( 2p \) orbitals is less than the energy gain, through C–C bond. Due to the fact, when carbon atoms bind to each other, their \( 2s \) and \( 2p \) orbitals can mix. To generate the diamond structure, the orbitals for one \( 2s \) and three \( 2p \) electrons mix, creating four \( sp^3 \) orbitals (regular tetrahedron). In comparison, in the \( sp^2 \) configuration, the \( 2s \) and two \( 2p \) orbitals mix to generate three in-plane covalent bonds. In this situation, each C atom has three nearest neighbors, creating the hexagonal planar network of graphene. At last, the \( sp \) hybridization, mixing the orbitals of only one \( 2s \) and one \( 2p \) electron is also possible, and it gives rise to linear chains of carbon atoms, the basis for polyene, the filling of the stem of certain nanotubes [3], and providing a step in the coalescence of adjacent nanotubes [4].

The idea of \( sp^2 \) nanocarbons begins with the single graphene sheet (Figure 1.1), the planar lattice of \( sp^2 \)-hybridized carbon atoms. The system can be large in the plane, and it is only one atom thick, thus representing a two-dimensional \( sp^2 \) nanocarbon [2].

Three-dimensional (3D) graphite is one of the best-known/investigated forms of pure carbon, being found as a natural source (mineral). Of all materials, graphite possesses the highest melting point (4200 K), the highest thermal conductivity (3000 W/mK), and a high-room-temperature electron mobility (30 000 cm²/Vs) [5]. Synthetic graphite was developed in 1960 by Arthur Moore [2] and was named highly oriented pyrolytic
Figure 1.1 Structures of $sp^2$ carbon materials, including (a) single-layer, (b) a single-wall carbon nanotube (SWCNT), and (c) a C60 fullerene.

Table 1.1 Applications of traditional graphite-based materials including carbon fibers [6].

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<th>Commercial applications</th>
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<tr>
<td>Graphite and graphite-based products</td>
<td>Materials-processing applications such as furnaces/crucibles, large electrodes in metallurgical processes, electrical, and electronic devices such as electric brushes, membrane switches, variable resistors, etc.</td>
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<td></td>
<td>Electrochemical applications for electrode materials in primary and secondary batteries, separators for fuel cells, nuclear fission reactors, bearings and seals (mechanical), and dispersions such as inks.</td>
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<tr>
<td>Carbon-fiber-based products</td>
<td>Carbon-fiber composites aerospace (70%), sporting goods (18%), industrial equipment (7%), marine (2%), and miscellaneous (3%).</td>
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<tr>
<td>Carbon–carbon composites</td>
<td>High-temperature structural materials, aerospace applications, such as missile nose tips, re-entry heat shields, etc. brake-disc applications (lightweight, high thermal conductivity, stability), rotating shafts, pistons, bearings (low coefficient of friction), biomedical implants such as bone plates (biocompatibility).</td>
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graphite. Graphite and its related carbon fibers [2] have been utilized commercially for decades [6]. Their utility ranges from a conductive fillers and mechanical structural reinforcements in composites to electrode materials exploiting their resiliency (Table 1.1) [6].
1.1.2 Graphene

Graphene is an encouraging new-generation conducting material with the potential to displace customary electrode (i.e. indium tin oxide) in electrical and optical devices. It combines several advantageous features containing low sheet resistance, high optical transparency, and splendid mechanical properties. Recent study has concurred with growing interest in the application of graphene as an electrode material in transistors, light-emitting diodes, solar cells, and flexible devices.

Since discovered, graphene has attracted interest due to its benefits such as high charge mobility, transparency, mechanical strength, and flexibility [7]. Due to the fact, graphene is supposed to play a vital role as a transparent electrode in electronic and optoelectronic devices [7]. Transparent electrodes are a significant element of a number of devices, such as displays (liquid crystal displays, cellular phones, e-paper), light-emitting diodes, and photovoltaic devices. Among these, graphene is significantly interesting because it has been successfully synthesized on a large scale as a good conducting and transferable film [7].

1.1.2.1 Graphene Preparation

Graphene has been produced by several methods (which were well reviewed by Jo et al. [7]), including:

- a. precipitation on a silicon carbide surface [8],
- b. mechanical exfoliation from graphite [9],
- c. chemically converted graphene from solution-phase graphene oxide [10],
- d. growth by chemical vapor deposition (CVD) on catalytic metal surfaces [11].

The size and character of a graphene film depend on the technique used for its fabrication. Berger et al. reported the heat treatment of SiC in a vacuum or in an inert environment to generate a graphene layer on the SiC surface [12], which is a result of the evaporation of silicon atoms from the SiC surface and the resultant segregation of carbon atoms on the surface. It was expected that this procedure would be appropriate for the fabrication of high-quality graphene; but, the size of a single domain of the layer thickness has not overstepped a few micrometers. There was also reported the successful isolation of graphene by mechanical exfoliation with Scotch tape [9]. This exfoliation method will remain the method of choice for fabricating proof-of-concept devices [13].
In 2006, Stankovich et al. reported a solution-based process for producing single-layer graphene [14]. After oxidation by Hummers’ method, graphene oxide becomes a layered stack of puckered sheets with AB stacking [15]. Graphene oxide itself is not conducting, but the graphitic network can be substantially restored by thermal annealing or through treatment with chemical reducing agents. Moreover, electrical enhancement of reduced graphene oxide layer may be achieved by doping process and/or a hybrid approach with other conducting elements such as carbon nanotubes (CNTs) [16] and metal grids [17].

Precipitation on a silicon carbide surface and mechanical exfoliation techniques are not suitable for large-scale fabrication of devices. In comparison, chemically converted graphene from solution-phase graphene oxide and CVD-grown graphene layers permit large-scale graphene integration with other materials [18, 19].

1.1.2.2 Engineering of Graphene

High conductivity and low optical absorption execute graphene an extremely inviting material for a transparent conducting electrode. Graphene layers that have high conductivity and low optical loss can be modified to achieve i.e. doped graphene films and/or graphene electrodes.

The usefulness of graphene in applications such as electrodes is widely directed by two crucial factors: (1) sheet resistance and (2) visible-light transmission. The sheet resistance is lowered as the graphene layer becomes thicker, but the transmission is also decreased as the thickness grows up. An appropriate transparent conductor should be characterized with high electrical conductivity connected with low absorption of visible light [7].

To improve the conducting properties of graphene, the charge concentration of the carbon film has to be adjusted by shifting the Fermi level of graphene’s zero-gap band structure away from the Dirac point, where the density of states is zero [20]. The required stiff band shift may be prompted by chemical doping [20], electrostatic gating [21], a metal contact [22], or dipole formation [23]. In example, hole (p) or electron (n) doping can be observed by utilization of elements as B or N [24], which can be immediately substituted into the carbon grate [25]. The nitrogen species in N-doped graphene are pyridinic N and pyrrolic N, which are generated predominately by substituting a carbon atom with nitrogen along in-plane edge or defect sites because such carbon atoms are more chemically active than those within the lattice of perfect graphene. Alike, in a B-doped graphene grate are met by a B–C bond and B–O bond.
Graphene may also be doped through the adsorption of chemical species on its surface, i.e. by immersing graphene layers in AuCl₃ solution [26]. HNO₃ is another example of an adsorbate that can be utilized to p-dope graphene lattices [27]. In fact, the modification of sheet resistance and work function by doping process is valid in enhancing the performance and efficiency of different electrical and optical devices based on graphene electrodes.

1.1.3 Carbon Nanotubes

A SWCNT (Figure 1.1) can be imagined as a cylinder generated by rolling up a graphene sheet along a vector \( C_n = n\mathbf{a}_1 + m\mathbf{a}_2 \), where \( \mathbf{a}_1 \) and \( \mathbf{a}_2 \) are the basis vectors of the hexagonal crystal lattice of graphene. The indexes \((n, m)\) state the two integral parameters (diameter and chirality) of the nanotube.

The unusual structure–property attitude creates SWCNTs as a candidate for molecular electronic tools such as channel material for field-effect transistors (FETs) [28]. Moreover, a number of researches have already reported that SWCNTs exhibit interesting electronic properties, which are well outside their standard material counterparts, i.e. the charge transport capability of metallic SWCNTs can attain \( 10^9 \) A/cm² (better than aluminum or copper), while semiconducting SWCNTs can achieve field-effect mobilities up to \( 10^4 \) cm² V⁻¹s⁻¹ [29]. However, tools based on separate SWCNTs suffer from weak uniformity and reproducibility, mostly in order to hardness in solid synthesis of nanotubes with homogeneous structural advantages, as well as governable setup of SWCNTs over a large area [30]. Due to the fact, macroscale setups of SWCNTs, particularly random networks and thin layers, are deemed to enable the most truthful adoptions of nanotubes in molecular electronics in the short time since they tender not only convenient technology but also unitary and reproducible output [30]. Moreover, SWCNT networks are in particular adequate for flexible and stretchable electronic devices since the lateral deformation of the curvy and entangled SWCNTs may accommodate really large strains [31]. Truly, there have already been a number of reports demonstrating the valid promise of nanotube networks as the channel materials and/or electrodes in various types of flexible/stretchable electronic tools, such as integrated circuits [32], sensors [31], organic light-emitting diodes [33], supercapacitors [34], touch panels [35], and other.

Several methods are accessible to create CNT networks and thin films as presented in Figure 1.2. In general, they may be grouped into two classes: dry processes and solution ones [36]. Dry techniques are mostly direct
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CVD growth and dry drawing from vertically aligned nanotube orders [37]. Direct CVD-grown SWCNT layers comprise extremely long nanotubes bonded by strong interbundle connections [38] and thereby have excellent conductivity, making them appropriate for the electrode material of many functional devices like super-fast actuators [39], stretchable supercapacitors [34], and strain sensors [40]. Nevertheless, the size of CVD furnaces reduces the area of this kind of SWCNT films to standard below 100 cm² [38].

Since there is now no effective technique to grow structurally or electrically homogeneous SWCNTs, the biggest limit of CVD-grown SWCNT films is that the as-grown samples typically contain a mixture of nanotubes with all types of chirality and metallicity. Therefore, these structures cannot be used as channel materials for transistors until the metallic conduction is eliminated by special process such as electrical breakdown, stripe patterning, or dry filtration [41].

1.1.3.1 Carbon Nanotube Networks for Applications in Flexible Electronics

As is well-known from the literature, semiconductor-enriched single-wall carbon nanotubes (sSWCNTs) are perfect expectants for the channel
material of flexible thin-film transistors (TFTs) due to the unexampled mixture of low-temperature technology, mechanical facility, optical transparency, and unusual electrical character. By using high-purity sSWCNT solutions, Wang et al. fabricated wafer-scale nanotube networks with high density and uniformity [42], which in consequence provided the fabrication of TFTs and logical circuits on both rigid and flexible solids [43]. Due to the trade-off between on/off ratio and transconductance, TFTs with wide channel lengths (high $I_{on}/I_{off}$) are adequate for logical circuits, while the tools with short channel lengths (large $g_m$) are appropriate for analog and radio frequency application. In addition, capacitance–voltage (C–V) measurements are performed to precisely determine the gate capacitance which in turn leads to an accurate assessment of the field-effect mobility ($\mu$), with a typical value of ~50 cm$^2$ V$^{-1}$ s$^{-1}$ [43], similar to that of low-temperature polysilicon and much higher than those of amorphous silicon and organic semiconductors. Moreover, the use of ultrathin polyimide solids results in highly flexible TFTs and integrated logical circuits, including inverter, NOR, and NAND gates. Such tools and circuits reveal sufficient stability after thousands of bending cycles. TFTs have also been incorporated into different functional systems, including sensors [44], displays [45], and electronic skins [46]. Substituting different type of sensors, such as chemical sensor, light sensor, and temperature sensor, for the pressure sensor could allow various functionalities of e-skin or superior to natural skins and find a wide range of applications in smart robotics and security/health-monitoring tools.

Huge progress has been observed recently in SWCNT-based flexible and stretchable electronics. Nevertheless, almost no SWCNT-based flexible product is commercially available at this moment [47]. A number of challenges remain to be conquered before SWCNT-based electronic tools and setups can be fabricated ready for the commercial applications.

In the material feature, while semiconductor-enriched SWCNTs are already commercially available, there is still wide inhomogeneity in terms of chirality and nanotube length. It is clear that purity and sufficient homogeneity of the starting material is advantageous for steady tool performance. Moreover, long nanotubes are required to low the number of tube-to-tube junctions, which could lead to subsequent improvement in tool mobility. However, the dissolution and separation of long nanotubes (>10 μm) are not facile. Moreover, the effects of surfactants on tool electrical behaviors require more precise development. The surfactants used to disperse SWCNTs are hard to eliminate and can behave as obstacles for electronic conduction. Consequently, new surfactant-free procedures need to be investigated to effectively dissolve SWCNTs. Recent reports of