Electronic and optoelectronic materials and devices inspired by nature

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Abstract

Inorganic semiconductors permeate virtually every sphere of modern human existence. Micro-fabricated memory elements, processors, sensors, circuit elements, lasers, displays, detectors, etc are ubiquitous. However, the dawn of the 21st century has brought with it immense new challenges, and indeed opportunities—some of which require a paradigm shift in the way we think about resource use and disposal, which in turn directly impacts our ongoing relationship with inorganic semiconductors such as silicon and gallium arsenide. Furthermore, advances in fields such as nano-medicine and bioelectronics, and the impending revolution of the ‘ubiquitous sensor network’, all require new functional materials which are bio-compatible, cheap, have minimal embedded manufacturing energy plus extremely low power consumption, and are mechanically robust and flexible for integration with tissues, building structures, fabrics and all manner of hosts. In this short review article we summarize current progress in creating materials with such properties. We focus primarily on organic and bio-organic electronic and optoelectronic systems derived from or inspired by nature, and outline the complex charge transport and photo-physics which control their behaviour. We also introduce the concept of electrical devices based upon ion or proton flow (‘ionics and protonics’) and focus particularly on their role as a signal interface with biological systems. Finally, we highlight recent advances in creating working devices, some of which have bio-inspired architectures, and summarize the current issues, challenges and potential solutions. This is a rich new playground for the modern materials physicist.

Introduction

In the last three decades, zero-dimensional, one-dimensional, and two-dimensional carbon nanomaterials (i.e., fullerenes, carbon nanotubes, and graphene, respectively) have attracted significant attention from the scientific community due to their unique electronic, optical, thermal, mechanical, and chemical properties. While early work showed that these properties could enable high performance in selected applications, issues surrounding structural inhomogeneity and imprecise assembly have impeded robust and reliable implementation of carbon nanomaterials in widespread technologies. However, with recent advances in synthesis, sorting, and assembly techniques, carbon nanomaterials are experiencing renewed interest as the basis of numerous scalable technologies. Here, we present an extensive review of carbon nanomaterials in electronic, optoelectronic, photovoltaic, and sensing devices with a particular focus on the latest examples based on the highest purity samples. Specific attention is devoted to each class of carbon nanomaterial, thereby allowing comparative analysis of the suitability of fullerenes, carbon nanotubes, and graphene for each application area. In this manner, this article will provide guidance to future application developers and also articulate the remaining research challenges confronting this field.
Recently, the emerging need for high-speed electronics and renewable energy has motivated researchers to discover, develop, and assemble new classes of nanomaterials in unconventional device architectures. Among these materials, carbon-based nanomaterials have attracted particular attention due to their unique structural and physical properties. Carbon nanomaterials, composed entirely of sp2 bonded graphitic carbon, are found in all reduced dimensionalities including zero-dimensional fullerenes, one-dimensional carbon nanotubes (CNTs), and two-dimensional graphene. With nanometer-scale dimensions, the properties of carbon nanomaterials are strongly dependent on their atomic structures and interactions with other materials. Consequently, significant recent effort has been devoted to the mass production of structurally homogeneous samples and their large-scale assembly into device architectures with well-controlled surfaces and interfaces. Although developments in the growth and post-synthetic purification of monodisperse carbon nanomaterials have been reviewed elsewhere, this topic is briefly summarized below in Section

Advances in producing highly monodisperse carbon nanotube and graphene samples have renewed interest in employing them as the basis of electronic, optoelectronic, photovoltaic, and sensing applications, thus forming the central theme of this review. In Section 2, we discuss digital electronics, analog electronics, and optoelectronic devices based on CNTs (individual CNTs as well as CNT thin films) and graphene. Section 3 explores photovoltaic applications of fullerenes, CNTs, and graphene, while Section 4 focuses on chemical and biological sensing enabled by carbon nanomaterials. The review concludes with a summary of the most salient points and a perspective on the future prospects and challenges for this field.

Although this review summarizes much of the historically significant work on carbon nanomaterials, the most recent developments are emphasized. Moreover, no comprehensive literature review exits on the impact created by sorted carbon nanomaterials in device applications. Consequently, readers who are interested in more thorough coverage of the early literature are referred to previously published review articles since this review highlights major breakthroughs following the advent of sorting techniques. For example, the fundamental properties of carbon nanotubes relevant to electronic and optoelectronic applications have been reviewed extensively in Ref.6-9, while large-area electronics based on carbon nanotube thin films are discussed in Ref.10, 11. Electronic applications of graphene with a particular emphasis on fundamental physics are covered in Ref.,12-15 while research on graphene-based optoelectronic and photovoltaic applications is covered in Ref16. Fullerene-based photovoltaics are summarized in Ref.,17, 18 and sensing applications using carbon nanotubes and graphene are overviewed in Ref.19-22. In addition to these review articles, several pedagogical books have been written on carbon nanotubes,23-25 and similar treatises on the fundamental properties and applications of graphene are currently in press

Carbon allotropes

Carbon is well known to form distinct solid state allotropes with diverse structures and properties ranging from sp3 hybridized
diamond to sp2 hybridized graphite. Mixed states are also possible and form the basis of amorphous carbon, diamond-like carbon, and nanocrystalline diamond. Diamond is a metastable form of carbon that possesses a three-dimensional cubic lattice with a lattice constant of 3.57 Å and C-C bond length of 1.54 Å. In contrast, graphite is the most thermodynamically stable form of carbon at room temperature and consists of a layered two-dimensional structure where each layer possesses a hexagonal honeycomb structure of sp2 bonded carbon atoms with a C-C bond length of 1.42 Å. These single atom thick layers (i.e., graphene layers) interact via noncovalent van der Waals forces with an interlayer spacing of 3.35 Å. The weak interlayer bonding in graphite implies that single graphene layers can be exfoliated via mechanical or chemical methods as will be outlined in detail below. Graphene is often viewed as the two-dimensional building block of other sp2 hybridized carbon nanomaterials in that it can be conceptually rolled or distorted to form carbon nanotubes and fullerenes.

Fullerenes are the zero-dimensional form of graphitic carbon that can be visualized as an irregular sheet of graphene being curled up into a sphere by incorporating pentagons in its structure. Fullerenes come in various forms and sizes ranging from 30 to 3000 carbon atoms. As a fullerene is elongated in one dimension, it approaches the structure of a carbon nanotube (CNT). Conceptually, CNTs are seamless cylinders of single or few layered graphene with a high aspect ratio (i.e., length to diameter ratio) that ranges from 102 to 107. The structure, diameter, and electronic type of a single-walled carbon nanotube (SWCNT) are determined by the chiral vector (i.e., roll-up vector) that defines the circumference of the SWCNT with respect to the graphene lattice (Fig. 1a). Multi-walled carbon nanotubes (MWCNTs) consist of nested, concentric shells of SWCNTs with a spacing between individual walls of 3.4 Å.

Synthesis and growth of carbon nanomaterials

The first carbon nanomaterial to be successfully isolated was C60 (i.e., buckminsterfullerene) using laser ablation of graphite in a high flow of helium by Kroto, et al.27 Although reports of even numbered carbon clusters28 existed prior to the landmark C60 paper, these clusters were produced in large size distributions and thus were unsuitable for characterization. Fullerenes have since been synthesized by a large number of groups using a variety of processes which include electric arc discharge, electron beam ablation, and sputtering.29, 30 Most of these processes use graphite electrodes or targets as the carbon source. In some cases, composites of graphite and metal oxides are employed as targets to generate endohedral fullerenes where a metal atom is encapsulated inside the fullerene carbon cage.31, 32 Fullerenes have been detected in common combustion flame soot33-35 and have also been synthesized using bottom-up chemical methods.

CNTs were subsequently isolated as an offshoot of fullerene synthesis since the initial techniques that resulted in CNT synthesis were either intended to produce fullerenes37 or derived from existing fullerene production techniques such as the Kratschmer-Huffman method.38, 39 The first observations of CNTs and their subsequent large-scale synthesis using arc discharge techniques were reported by Iijima and coworkers.38, 40, 41 Laser ablation
was later demonstrated as an alternative method for growing CNTs by Smalley et al.42-44. Since it was observed that transition metals embedded in graphite electrodes/targets produced carbon nanotubes with higher yield and reproducibility, chemical vapor deposition (CVD) using transition metal nanoparticle catalysts was then developed to produce high quality single-walled and multiwalled CNTs in vertically aligned arrays. Vertically aligned arrays can also be grown on metallic and quasicrystalline substrates. Extending the metal nanoparticle catalyst concept, CNTs were later synthesized by pyrolysing metal carbonyls in the presence of other hydrocarbons. When optimized in a high pressure carbon monoxide (HiPco) environment, the carbonyl pyrolysis process led to high yield production of SWCNTs. The synthesis of both SWCNTs and MWCNTs have since been thoroughly studied and reviewed by many.1, 52-55 CNTs synthesized by arc discharge, HiPco, and CVD (using Co-Mo catalysts) are now commercially available in kilogram quantities.

Graphene, although often referred to as the mother of all graphitic carbon, was the final carbon nanomaterial to be isolated on an insulating substrate and electrically characterized by Geim and coworkers in 2004. Similar methods were employed by the Ruoff group in 2006 to create graphene oxide (GO) that was mostly single layered. All of these methods result in an aqueous dispersion/colloid of thin GO flakes by subjecting graphite to highly oxidizing conditions that functionalizes the basal plane of graphene with hydrophilic functional groups. The resulting GO can be partially reduced to form reduced graphene oxide (r-GO) via chemical methods, annealing in reducing environments, or laser irradiation. Several variants of these oxidation and reduction processes have been developed and are necessary to address this issue, epitaxial graphene has been realized by graphitization of both doped and undoped silicon carbide (SiC) single crystal wafers at high temperatures. Although this recent work has triggered substantial interest in epitaxial graphene, it should be noted that reports of SiC graphitization date back several decades. Furthermore, claims of epitaxial monolayer graphite (MG) on metal carbides at high temperatures using hydrocarbon precursors also exist from the early 1990’s as have been comprehensively reviewed elsewhere. However, only the recent work on SiC has demonstrated graphene growth with sufficient quality for electronic applications. While this approach to epitaxial graphene offers wafer-scale growth, it is difficult to achieve uniform monolayer graphene coverage, and the product suffers from inferior electronic properties compared to mechanically exfoliated graphene.

Solution-processing is another important technique to synthesize graphene at low cost in a scalable manner. The earliest reports of 'graphite oxide' synthesis trace back to the work of Hummers, Brodie, and Staudenmeier. Similar methods were employed by the Ruoff group in 2006 to create graphene oxide (GO) that was mostly single layered. All of these methods result in an aqueous dispersion/colloid of thin GO flakes by subjecting graphite to highly oxidizing conditions that functionalizes the basal plane of graphene with hydrophilic functional groups. The resulting GO can be partially reduced to form reduced graphene oxide (r-GO) via chemical methods, annealing in reducing environments, or laser irradiation. Several variants of these oxidation and reduction processes have been developed and are
summarized in recent reviews. Although this method is promising for large-scale solution processing of graphene-based materials, the harsh oxidizing conditions irreversibly damage the basal plane of graphene, leading to deterioration of its properties. This problem can be partially circumvented by directly exfoliating graphene from graphite using ultrasonication with suitable choice of surfactants and solvents. In all cases, solution-based methods for preparing single-layer graphene result in relatively small flakes that are sub-optimal for wafer-scale applications.

Conclusions

In this Report on Progress in Physics we have reviewed in brief the status of bio-inspired and bio-compatible electronic and optoelectronic materials and devices. The focus has been largely on organic and bio-organic conductors and photoactive systems, although the subjects of natural dielectrics and substrates have also been addressed. Research efforts in this emerging field are motivated by a number of factors: the need for more sustainable high tech materials; the requirements of interfacing with biological systems in bionanomedicine and bioelectronics; and the drive towards cleaner energy solutions. Traditional organic electronics and optoelectronics provide much of the chemical and physical ‘foundation elements’ for the field which is highly multi-disciplinary. The physics of organic and bio-organic semiconductors is dominated by a number of intrinsic features: high degrees of energetic and structural disorder; the molecular nature of organic solids; strong electronic correlations; electrical conduction within extended π-conjugated networks; hybrid electronic–ionic (protonic) transport; and the excitonic nature of photoexcitations.

References


