Progress in Materials Science 56 (2011) 1178–1271

Contents lists available at ScienceDirect

Progress in Materials Science

journal homepage: www.elsevier.com/locate/pmatsci

Graphene based materials: Past, present and future

Virendra Singh [a,b], Daeha Joung [a,c], Lei Zhai [a,d,*], Soumen Das [a,b], Saiful I. Khondaker [a,c,e,*], Sudipta Seal [a,b,*]

[a] Advanced Materials Processing Analysis Center and Nanoscience Technology Center, University of Central Florida, Orlando, FL, USA
[b] Department of Mechanical, Materials and Aerospace Engineering, University of Central Florida, Orlando FL, USA
[c] Department of Physics, University of Central Florida, Orlando, FL, USA
[d] Department of Chemistry, University of Central Florida, Orlando, FL, USA
[e] School of Electrical Engineering and Computer Science, University of Central Florida, Orlando, FL, USA

ARTICLE INFO

Article history:
Received 22 February 2011
Accepted 30 March 2011
Available online 3 April 2011

ABSTRACT

Graphene, a two dimensional monoatomic thick building block of a carbon allotrope, has emerged as an exotic material of the 21st century, and received world-wide attention due to its exceptional charge transport, thermal, optical, and mechanical properties. Graphene and its derivatives are being studied in nearly every field of science and engineering. Recent progress has shown that the graphene-based materials can have a profound impact on electronic and optoelectronic devices, chemical sensors, nanocomposites and energy storage. The aim of this review article is to provide a comprehensive scientific progress of graphene to date and evaluate its future perspective. Various synthesis processes of single layer graphene, graphene nanoribbons, chemically derived graphene, and graphene-based polymer and nano particle composites are reviewed. Their structural, thermal, optical, and electrical properties were also discussed along with their potential applications. The article concludes with a brief discussion on the impact of graphene and related materials on the environment, its toxicological effects and its future prospects in this rapidly emerging field.

Published by Elsevier Ltd.

Contents

1. Introduction 1181
2. History of graphene 1181

* Corresponding authors at: Advanced Materials Processing Analysis Center and Nanoscience Technology Center, University of Central Florida, Orlando, FL, USA.
E-mail addresses: Lei.Zhai@ucf.edu (L. Zhai), saiful@ucf.edu (S.I. Khondaker), Sudipta.Seal@ucf.edu (S. Seal).

0079-6425/$ - see front matter Published by Elsevier Ltd.
doi:10.1016/j.pmatsci.2011.03.003

3. Synthesis of graphene . . . 1182
3.1. Exfoliation and cleavage . . . 1182
3.1.1. Mechanical exfoliation in solutions . . . 1183
3.1.2. Intercalation of small molecules by mechanical exfoliation . . . 1184
3.2. Chemical vapor deposition (CVD) . . . 1186
3.2.1. Thermal CVD . . . 1186
3.2.2. Plasma enhanced CVD . . . 1188
3.2.3. Thermal decomposition on SiC and other substrates . . . 1188
3.3. Chemically derived graphene . . . 1188
3.3.1. Synthesis of graphene oxide and the reduction . . . 1188
3.3.2. Surface functionalization of graphene oxide (GO) . . . 1191
3.3.3. Structural and physical properties of reduced graphene oxide (RGO) . . . 1192
3.4. Other synthesis approaches . . . 1195
3.4.1. Total organic synthesis . . . 1195
3.4.2. Un-zipping carbon nanotubes (CNTs) . . . 1198
4. Graphene: characterization and properties . . . 1201
4.1. Characterization . . . 1201
4.1.1. Optical imaging of graphene layers . . . 1201
4.1.2. Fluorescence quenching technique . . . 1201
4.1.3. Atomic force microscopy (AFM) . . . 1203
4.1.4. Transmission electron microscopy (TEM) . . . 1204
4.1.5. Raman spectroscopy . . . 1206
4.2. Properties . . . 1207
4.2.1. Electrical transport property . . . 1207
4.2.2. Quantum Hall effect . . . 1211
4.2.3. Optical properties . . . 1212
4.2.4. Mechanical properties . . . 1214
4.2.5. Thermal properties . . . 1215
5. Chemically derived graphene: properties and applications . . . 1216
5.1. Assembly of GO/RGO for device applications . . . 1216
5.2. Electrical characterization of GO/RGO sheet . . . 1218
5.3. Defect density in chemically derived graphene . . . 1220
5.4. RGO as graphene quantum dot array: Coulomb blockade effect . . . 1221
5.5. Hopping conduction in RGO . . . 1222
5.5.1. Mott variable range hopping . . . 1222
5.5.2. Efros–Shklovskii (ES) VRH . . . 1224
5.6. Application of RGO for photodetector, phototransistor and emitter . . . 1224
5.7. Graphene thin film as transparent electrodes . . . 1226
5.8. Solar cell using GO/RGO . . . 1228
5.9. Electrochemical sensors and biosensors . . . 1230
6. Graphene based composites . . . 1232
6.1. Graphene–polymer composites . . . 1232
6.1.1. Synthesis of graphene reinforced polymer composite . . . 1234
6.1.2. Mechanical properties . . . 1236
6.1.3. Electrical properties . . . 1238
6.1.4. Thermal conductivity . . . 1239
6.1.5. Other properties . . . 1240
6.1.6. Applications . . . 1241
6.2. Graphene–nanoparticles composites . . . 1241
6.2.1. Synthesis . . . 1241
6.2.2. Applications . . . 1245
7. Toxicity of graphene/graphene oxide/reduced graphene oxide . . . 1254
8. Future prospects . . . 1258
Acknowledgements . . . 1259
References . . . 1259

1. Introduction

The 5th of October, 2010 was another beautiful day at Partin Elementary School in Oviedo. When Kaleb, a 6 year old kindergartener, took out his pencil and started writing letters on a piece of paper, he did not realize that he was using a material that caught the attention of all scientific community that same day. The Nobel Prize in Physics 2010 was awarded to Andre Geim and Konstantin Novoselov ''for ground breaking experiments regarding the two-dimensional material graphene'', a layer of graphite in the pencil. Graphene, one of the allotropes (carbon nanotube, fullerene, diamond) of elemental carbon, is a planar monolayer of carbon atoms arranged into a two-dimensional (2D) honeycomb lattice with a carbon–carbon bond length of 0.142 nm [1]. Electrons in graphene behave like massless relativistic particles, which contribute to very peculiar properties such as an anomalous quantum Hall effect and the absence of localization [2,3]. Graphene [2] has demonstrated a variety of intriguing properties including high electron mobility at room temperature (250,000 cm^2/Vs) [4,5] exceptional thermal conductivity (5000Wm^{-1} K^{-1}) [6] and superior mechanical properties with Young's modulus of 1 TPa [7]. Its potential applications include single molecule gas detection, transparent conducting electrodes, composites and energy storage devices such as supercapacitors and lithium ion batteries [7–20]. In addition, a distinct band gap can be generated as the dimension of graphene is reduced into narrow ribbons with a width of 1–2 nm, producing semiconductive graphene with potential applications in transistors [8–10]. There is no doubt that graphene has risen as a shining star in the horizon on the path of the scientists' searching for new materials for future electronic and composite industry. This review article narrates the brief history of graphene related research, and presents the synthesis of graphene and its derivatives and various characterization techniques pertaining to 2D structure. Many extraordinary properties of graphene such as electrical, mechanical, anomalous quantum Hall effect, thermal, and optical are discussed. These properties have generated tremendous interest among material researchers. The recent applications in various fields such as in large scale assembly and field effect devices, sensors, transparent electrodes, photodetectors, solar cells, energy storage devices, polymer composites, nanocomposites will be reviewed with a brief update on toxicology. The conclusion and outlook summarizes the research activities and presents the possible future research directions.

2. History of graphene

Although the usage of graphite started 6000 years ago, when Marican in Europe used it to decorate pottery, the research about graphene, essentially an isolated single-atom plane of graphite, dates back to the 1960s when surprisingly higher basal-plane conductivity of graphite intercalation compounds were discovered compared to that of the original graphite [11–13]. While the scientific community was excited about the discovery that might lead to a lighter, cheaper substitute for existing metal conductors, they were puzzled by the cause of the high conductivity of graphite intercalation compounds and cautious about the future applications. The research of graphene has grown slowly in late 20th century with the hope to observe superior electrical properties from thin graphite or graphene layers while obtaining graphene was considered to be a formidable task in both theoretical and experimental aspect. In the graphite intercalation systems, large molecules were inserted between atomic planes, generating isolated graphene layers in a three-dimensional matrix. The subsequent removal of the larger molecules produced a mixture of stacked or scrolled graphene layers without the control of the structure. It was generally believed that, based on both theoretical calculation and experimental observation, 2D materials did not exist without a 3D base. AB initio calculations showed that a graphene sheet was thermodynamically unstable with respect to other fullerene structures if its size was less than about 20 nm (‘‘graphene is the least stable structure until about 6000 atoms’’ and becomes the most stable one (as within graphite) only for sizes larger than 24,000 carbon atoms) [14]. Various attempts were made to synthesize graphene including using the same approach for the growth of carbon nanotubes (producing graphite with 100 layers of graphene) [15], chemical vapor deposition on metal surfaces (a few layers of graphene) [16,17], or the thermal decomposition of SiC [18]. Although these approaches did not produce perfect monolayer graphene, the studies showed high-charge mobility of a few layers of graphene and the CVD approach has been optimized and become a major technique to produce graphene nowadays [19–21]. It was until 2004 that Andre Geim and Konstantin Novoselov used a method to isolate graphene, a method similar to what young Kaleb did, drawing with a piece of graphite or peeling graphite with adhesive tape till the graphene is found. Such a ‘‘kindergartner’’ approach can provide high quality graphene with size in hundreds of microns [22]. These high quality graphene crystals realize the

investigation of their amazing properties. Since then, the research of graphene including the control of the graphene layers on substrates, functionalizing graphene and exploring the applications of graphene has grown exponentially. As shown in Fig. 2.1, the number of publications on graphene (according to ISI Web of KnowledgeSM) increases dramatically after 2004. The term of ‘‘graphene’’ was recommended by the relevant IUPAC commission to replace the older term ‘‘graphite layers’’ that was unsuitable in the research of single carbon layer structure, because a three-dimensionally (3D) stacking structure is identified as ‘‘graphite’’. The recent definition of graphene can be given as a two-dimensional monolayer of carbon atoms, which is the basic building block of graphitic materials (i.e. fullerene, nanotube, graphite).

8. Future prospects

It has become evident that the exceptional properties of graphene (including electrical, thermal, mechanical, optical, and long electron mean free paths) made it compelling for various engineering applications. Much effort has been devoted to exploring the fundamental physics and chemistry of graphene. Novel properties such as room temperature quantum Hall effect, highest charge transport and thermal conductivity originated from graphene’s 2-dimensional structures have not been observed earlier from most conventional three-dimensional materials. A large amount of research publications in the past 5 years signifies the importance of graphene that might surpass silicon research in the development of microelectronics. While silicon based research is at its mature stage to overcome the technological barrier, graphene is being extensively investigated as it holds the future for micro to nano scale electronics. The inherent semi-metal characteristic of graphene has been modified to realize the applications in transistors. Graphene nanoribbons and bilayer graphene are the results of such modification that leads to a suitable band gap and allows the applications in FET. However, graphene as a new material still faces many challenges ranging from synthesis and characterization to the final device fabrication. The exceptional properties were observed in the defect free pristine graphene prepared by graphite exfoliation using scotch tape method which is not appropriate for any large scale device manufacturing. The alternative methods have progressed to CVD and epitaxially grown single, bilayer and few-layer graphene. Recent reports demonstrated the scalability using CVD method to wafer scale on different substrates and facile transfer of graphene

layer for subsequent device fabrication.These breakthroughs offer novel and exciting opportunities for semiconductor industries. The chemical exfoliation of graphite into GO followed by thermal and chemical reduction, has offered a costeffective production route of reduced graphene oxide on a large scale. However, the chemical and thermal modification lowers the electrical and mechanical properties, along with its chemical reactivity leading to lack of control in functionalization by other groups. The controlled oxidation/reduction and functionalization are very important in tuning the material properties such as band gap, electrical conductivity, and mechanical properties. Therefore, controlled modification of graphite, GO, and RGO is crucial in expanding the applications of graphene-based materials. In addition, the large surface of low density GO and RGO in mass production may possess handling difficulty, which can lead to a health risk due to inhaling and handling toxic reducing chemicals. The health risk associated with graphene and their derivatives needs to be evaluated through the investigation of the toxicity and biocompatibility of these novel carbon structures and its derivatives.

The possible applications of graphene-based material include transparent flexible electrodes, graphene/polymer composites for mechanical parts, energy storage, sensors and organic electronics. Graphene/polymer composites have showed the lowest percolation threshold for electrical conductivity and improved mechanical, thermal, and gas barrier properties. However, the core issues such as the homogeneous distribution of individual graphene platelets, their orientation, connectivity, and interface bonding with matrix still require more investigation. The charge mobility of RGO is considerably higher than that of the amorphous silicon and existing semi-conducting conjugated polymers, enlightening the probable path for the application in electronics. The main hurdles with any device fabrication using RGO including defects at atomic level, the folding/wrinkling of RGO and the over lapping of RGO at macro-scale require continuous research endeavors.

The visibility of monolayer graphene under an optical microscope requires the suitable substrate to create contrast between different layers due to interference. Current detection of graphene using an optical microscope depends on the substrate thickness and incident light wavelength. More research is needed to develop a simple detection method of pristine graphene that is independent of support material. Aberration corrected high resolution TEM made it possible to reveal defect structures and graphene quantum dot at atomic

resolutions, providing opportunities to visually examine the doping and defects at atomic levels.

Although the advanced deposition technique of single layer and bilayer made it possible to fabricate large area devices, creating band gap in a controlled and practical manner is still challenging for the application in logic devices. Several methods aiming at tuning the substrates properties and nanoribbon dimension have been proposed to introduce tunable band gap essential for nanoelectronics. Particularly, this energy band gap can be achieved through quantum confinement, bilayer graphene, and chemical functionalization. The former, quasi-one-dimensional graphene nanoribbon has been considered with either edge localization or Coulomb blockade effects. Graphene nanoribbon with appropriate dimension (i.e. 10 nm) is expected to provide right band gap for efficient FET devices.

Cutting graphene into nanoribbon has shown great promise for FET logic applications, but associated with the electron scattering at the rough edges and disorder from the back substrate. On the other hand, FETs based on graphene bilayer still require large on/off ratio for logic applications. The new options such as tunnel FETs and bilayer pseudospin FETs have been suggested to tackle the challenge of the graphene devices problems based on the conventional FET principle. These concepts are supported by simulation studies but need to be experimented. The latter, oxides form of graphene (GO), has triggered significant research interest due to large scale integration. However, the electronic band structure is not clearly understood due to the nanoscale inhomogeneity. Recent atomic scale systematical investigation and geometrical microscopic studies provided the evidence of tunable band gap through varying oxidation level and reduction process. Therefore band gap opened graphene based through GNR and GO have been encouraged to become future practical nano electronic devices comparable to complementary metal oxide semiconductor circuits.