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Review

Molecularly engineered graphene surfaces for sensing applications: A review

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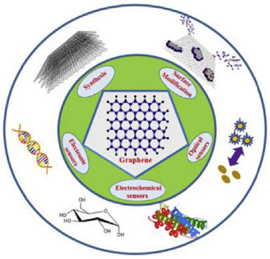
HIGHLIGHTS

- The importance of surface chemistry of graphene materials is clearly described.
- We discuss molecularly engineered graphene surfaces for sensing applications.
- We describe the latest developments of these materials for sensing technology.

GRAPHICAL ABSTRACT



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ABSTRACT

Graphene is scientifically and commercially important because of its unique molecular structure which is monoatomic in thickness, rigorously two-dimensional and highly conjugated. Consequently, graphene exhibits exceptional electrical, optical, thermal and mechanical properties. Herein, we critically discuss the surface modification of graphene, the specific advantages that graphene-based materials can provide over other materials in sensor research and their related chemical and electrochemical properties. Furthermore, we describe the latest developments in the use of these materials for sensing technology, including chemical sensors and biosensors and their applications in security, environmental safety and diseases detection and diagnosis.

Contents

Abbreviations: 2D, two-dimensional; CVD, chemical vapor deposition; CNT, carbon nanotube; GO, graphene oxide; RGO, reduced graphene oxide; GOD, glucose oxidase; FRET, fluorescence resonance energy transfer; GSs, graphene sheets; SiC, silicon carbon; GNR, graphene nanoribbon; AChE, acetylcholinesterase; MGF, mesocellular graphene foam; DPV, differential pulse voltammetry; HA, Hypocrellin A; TMB, 3,3′,5,5′-tetramethylbenzidine; GH, graphene oxide–hemin; TRAP, telomerase repeat amplification protocol; PCR, polymerase chain reaction; IEP, isoelectric point; 1D, one-dimensional; GQD, graphene quantum dot; EDC, 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide; DCC, *N*,*N*′-dicyclohexylcarbodiimide; NHS, *N*-hydroxysuccinimide; ssDNA, single stranded DNA; PVA, polyvinyl alcohol; PDDA, poly(diallyldimethylammonium chloride); PEI, polyetherimide; PVP, polyvinylpyrrolidone; GCE, glassy carbon electrode; AuNps, Au nanoparticles; H_2O_2, hydrogen peroxide; TBHP, *tert*-butylhydroperoxide; IL-graphene, liquid-functionalized graphene; SLG, single-layer graphene; SiNW, silicon nanowires; 3D, three-dimensional; SEM, scanning electron microscope; FET, field-effect transistors.

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Prof. Jingquan Liu received his bachelor from Shandong University in 1989. His master and Ph. D. were obtained from the University of New South Wales (UNSW) in 1999 and 2004, respectively, where his Ph.D. was undertaken under the guidance of Prof. Justin Gooding. In 2004, he worked as a CSIRO-UTS post-doctoral fellow prior to returning to UNSW with Prof. Tom Davis as a Vice-Chancellor's Research Fellow in 2006. In 2010, he took up a professorship at Qingdao University. He has co-authored over 80 peer-reviewed research papers and 2 book chapters. His research interests focus on the synthesis of various bio- and nano-hybrids of versatile polymeric architectures.

Zhen Liu received his master degree of materials processing and engineering under the supervision of Prof. Jingquan Liu from Qingdao University in 2013 and has co-authored 5 papers. He is currently a Ph.D. candidate at Deakin University under the supervision of Dr. Wenrong Yang. His project focuses on the preparation of graphene and furthering the application of graphene-based materials in energy devices.

Prof. Colin Barrow is Chair of Biotechnology at Deakin University. He is also Director of the Centre for Chemistry and Biotechnology (CCB). Professor Barrow's research is primarily focused on food biotechnology and the application of nanomaterials for industrial purposes. Professor Barrow has a Ph.D. in chemistry from the University of Canterbury in New Zealand and an MBA from Penn State in the USA. Prof. Barrow has approximately 180 peer-reviewed publications, several patents, and has presented at numerous conferences and workshops. He has served as a member of the Expert Advisory Committee for Canadian Natural Health Product Directorate (NHPD), is on the Executive and is a founding member of International Society for Nutraceuticals and Functional Foods (ISNFF).

Dr. Wenrong Yang received his Ph.D. degree in Chemistry from the University of New South Wales (UNSW) in Australia in 2002. After several years as a Research Fellow at CSIRO, UNSW, and University of Sydney, he joined Deakin University as a Lecturer in 2010. His current research interests are centered on the synthesis and surface functionalization of Carbon-based soft materials and their applications in biosensor and green energy, bionics, and environmental protection.

1. Surprising carbon: an introduction to graphene

Graphene is a relatively new member of the nanocarbon family, composed of well separated two-dimensional (2D) layers composed of aromatic carbon atoms, first reported in 2004 by Novoselov et al. [1]. Graphene's unique structure and properties has made it an attractive candidate for sensor applications and like other nanomaterials possessing desirable bulk properties, does not have the required surface characteristics necessary for particular applications. Functionalization of the surface is thus essential for sensor applications [2–4] and various covalent and non-covalent chemistries have been reported affording graphene-based materials the surface properties needed for such devices [5–9].

Although relatively new, graphene has already been extensively utilized in various fields because of its distinctive physical and chemical properties, which include superior electrical conductivity, excellent mechanical flexibility, large surface area plus high thermal and chemical stability [10]. For instance, graphene has been exploited for energy applications, due to its high conductivity, transparency and ultra-thin sheets [4,11–13]. Because of graphene's high surface area ($2630\,m^2\,g^{-1}$) [14], excellent mechanical strength and aromatic-rich structure, it has been employed as a pollutant adsorbent due to the attraction of small molecules to its surface. These properties also contribute to its use as a catalyst or catalytic support for fuels and photo degradation of organics [15–19]. Moreover, graphene plays a crucial role in sensing applications which utilize its exceptional electrical properties (*e.g.*, extremely high carrier mobility and capacitance), electrochemical properties (*e.g.*, high electron transfer rate), optical properties (*e.g.*, excellent ability to quench fluorescence) and structural characteristics. In this review, we place an emphasis on surface chemistry and functionalization of graphene used as electrochemical, electrical and optical sensors. The methods for the preparation of graphene and their relative advantages and disadvantages are also discussed.

Graphene's properties can be controlled by chemical derivatization, with important parameters being the synthetic conditions, dimensions, number of layers and doping, which provide chemical flexibility for various sensing purposes [20]. Therefore, graphene preparation methods should be carefully selected according to the specific sensing target and mechanism to be utilized, with a balanced consideration on performances (*e.g.*, detection limit and dynamic range), reproducibility, cost and manufacturability [21]. Generally speaking, these methods can be classified as exfoliation, thermal decomposition, chemical vapor deposition (CVD), opening carbon nanotubes (CNTs), thermal reduction and oxidation–reduction, plus others [22,23]. Each of these preparation methods has advantages and drawbacks over the other methods. For example, the oxidation–reduction method for producing graphene from graphite can be used for mass production, whereas the as-