Nano Today (2014) **9**, 668—683

Available online at www.sciencedirect.com

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

REVIEW

Graphene and its composites with nanoparticles for electrochemical energy applications

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Received 28 June 2014; received in revised form 18 August 2014; accepted 1 September 2014
Available online 26 September 2014

KEYWORDS
Graphene;
Doped-graphene;
Liquid phase exfoliation;
Graphene—nanoparticle composites;
Energy storage;
Energy conversion

Abstract Graphene is a two dimensional (2D) planar and hexagonal array of carbon atoms and has been studied extensively as advanced nanomaterials for important technological applications. This review summarizes the recent developments in chemistry, materials and energy applications of graphene, doped graphene and their composites with nanoparticles (NPs). It first highlights the new chemistry used to synthesize high quality graphene. It then outlines the methodologies developed to dope graphene with heteroatoms to modify and control graphene properties. It further describes the general approaches to graphene—NP composites via either direct NP growth onto graphene or self-assembly of the pre-formed NPs on graphene surface. These graphene—NP composites provide some ideal systems for studying synergistic effects between graphene and NPs on catalysis. The review focuses on applications of graphene—NP composites in increasing electrochemical energy storage density and in catalyzing chemical reactions with much desired electrochemical efficiencies.

Introduction

Graphene is a two dimensional (2D) planar and hexagonal array of carbon atoms. Each of these carbons is sp^2-hybridized and is linked together by three strong C—C—σ bonds of 120° apart. The unhybridized p-orbital is perpendicular to the sp^2-hybridization plane, conjugating with the same p-orbitals on other carbon atoms via π interaction

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http://dx.doi.org/10.1016/j.nantod.2014.09.002
1748-0132/

across the entire 2D plane surface [1]. With σ bond of 1.46 Å and lattice parameter of 2.46 Å [2], graphene possesses very unique electronic and mechanical properties [3]: its valence band mirrors its conduction one with two bands intersecting at its Fermi level [4,5], giving graphene the unique zero-gap semiconductor properties with charge carrier mobility $>2 \times 10^5\ \mathrm{cm^2/Vs}$ at an electron density of $2 \times 10^{11}\ \mathrm{cm^{-2}}$ [6—8] and thermal conductivity >3000 W/mK [9]; the strong σ—π bonds make graphene mechanically robust with its Young's modulus >0.5—1 TPa [10]. The complete planar exposure of the carbon atoms renders graphene a theoretical surface area $>2500\ \mathrm{m^2/g}$ [11,12]. The delocalized π electrons are also responsible for various interactions between any two graphene layers and between graphene and a substrate [4]. Thus, graphene has been coupled with metals [13,14], alloys [15], oxides [16,17] and other polymeric compounds to form composites [18—22]. The properties of graphene can be further modified by the introduction of heteroatoms in the graphitic plane [23]. The replacement of a carbon atom with another atom breaks the electro-neutrality of the σ—π network within graphene, making the 2D network more susceptible to chemical reactions [24]. The new properties evolved from graphene and its hybrid structures have been explored extensively for advanced technological applications in electronics, optics, catalysis and energy storage/conversion [2,25—33].

This review intends to summarize the recent developments in chemistry, materials and energy applications of graphene, doped graphene and their composites with nanoparticles (NPs). It includes both the work from the author's groups and the representative examples from others to highlight the important aspects on graphene chemistry and applications. It will first summarize new chemistry used to synthesize high quality graphene. It will also outline the methodologies developed to dope graphene with heteroatoms to modify and control graphene properties. The more controlled synthesis leading to high quality graphene and its solutions in various solvents allows for rational assembly of NPs on graphene surface, providing an ideal system to study synergistic effect between graphene and NPs on the enhanced catalytic properties. The review will focus on applications of graphene-based nanomaterials in electrochemical energy storage (lithium based batteries and supercapacitors) and conversion devices (fuel cells and electrolyzers).

Synthesis of graphene via liquid phase exfoliation

Synthesis of high quality graphene is key to understanding and controlling its physical and chemical properties [34,35]. Figure 1 summarizes the methods (as well as the costs associated with the methods) used to prepare graphene. Graphite is the natural choice as a starting precursor to produce graphene as the graphitic layers are already present within the graphite structure and graphene can be obtained by simply ''peeling off'' these graphitic layers via mechanical and/or chemical means [36—39]. Alternatively, graphene can be prepared by chemical vapor deposition (CVD) [33,40—46], which requires high vacuum (to avoid contaminants from environment) and high temperature (to facilitate precursor decomposition).

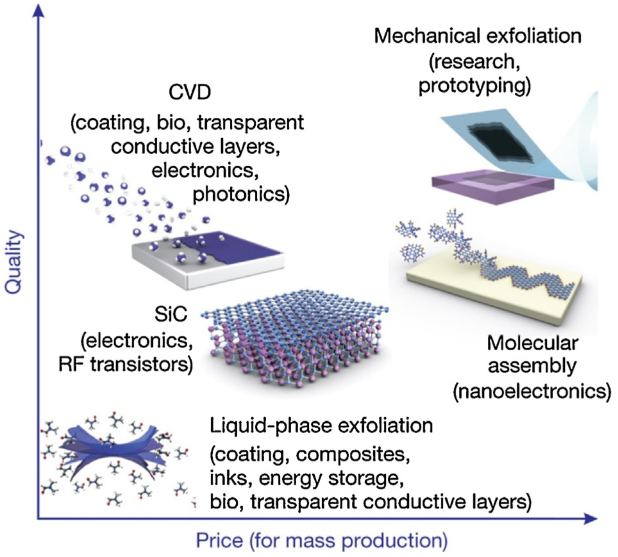

Figure 1 Common methods used for graphene production. Reprinted with permission from [34]. Copyrights 2012 Nature Publishing Group.

The liquid phase exfoliation (LPE) is a process in which graphite is exposed to liquid medium and single layer of graphitic plane is peeled off [34]. In graphite, graphitic planes are held together by interlayer attractions with the interaction area energy density at $\sim 40\ \mathrm{mJ/m^2}$ (Figure 2a) [35,47]. The potential energy associated with these interactions is inversely proportional to the distance between the adjacent layers. Therefore, mechanical, thermal and/or chemical means are often applied to counter these attractions in the exfoliation process and proper molecules (either as a solvent or as a surfactant) can be explored to stabilize graphene against its re-stacking [37,48]. Alternatively, exfoliation can be achieved electrochemically in solution via injecting negative charge to the graphitic layers for layer separation [47,49,50]. Recent experiments have demonstrated that LPE is a much easier process to produce the stabilized graphene than any of the other strategies demonstrated [37,48].

To overcome the interfacial forces of pristine graphite, a proper organic solvent with ''strong'' binding power to the graphitic plane needs to be selected to counter the interfacial interaction among the graphite layers and to stabilize the graphene once the single sheet is peeled off (Figure 2a) [35]. N-methylpyrrolidone (NMP), N,N-dimethyl formamide (DMF), *ortho*-dichlorobenzene (*o*-DCB) are the common solvents used for graphene formation and stabilization [37,51]. Ionic liquid, such as 1-hexyl-3-methylimidazolium hexafluorophosphate (HMIH), is also used to exfoliate graphite with graphene concentration reaching up to 5.33 mg/mL [52]. Recently, graphene is synthesized in 10—12 wt% in acetonitrile, CH_3CN, by first pre-heating the graphite precursor to cause graphite layers to expand and by reacting the expanded layers with CH_3CN in the common solvothermal and sonication condition (Figure 3) [53]. When the graphite swells, the small CH_3CN can be inserted into the graphitic interlayers, facilitating graphene separation and