Progress in Materials Science 86 (2017) 1–24

Contents lists available at ScienceDirect

Progress in Materials Science

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

Graphene-encapsulated materials: Synthesis, applications and trends

Eden Morales-Narváez [a], Lívia Florio Sgobbi [a,b], Sergio Antonio Spinola Machado [b], Arben Merkoçi [a,c,*]

[a] Catalan Institute of Nanoscience and Nanotechnology (ICN2), CSIC and The Barcelona Institute of Science and Technology, Campus UAB, Bellaterra, Barcelona 08193, Spain
[b] Group of Electrochemical Materials and Electroanalytical Methods, São Carlos Institute of Chemistry, University of São Paulo, São Carlos, SP CP 780, Brazil
[c] ICREA, Pg. Lluís Companys 23, 08010 Barcelona, Spain

ARTICLE INFO

Article history:
Received 7 June 2016
Received in revised form 28 September 2016
Accepted 2 January 2017
Available online 3 January 2017

Keywords:
Composite materials
Biomedicine
Imaging
Energy
Environment
Nanomaterials

ABSTRACT

Graphene-based materials (GBM) are an exceptional type of materials that offer unprecedented application capabilities to the scientific and technologic community. The encapsulation of different materials such as drugs, nanoparticles, polymers, oxides and cells by GBM is leading to outstanding hybrid materials with unprecedented behaviours promising a myriad of advantageous applications, including micro/nanomotors, biosensing platforms, bio/imaging agents, drug delivery systems, potential tumour treatment alternatives, environmental remediation platforms, advanced batteries and novel supercapacitors. We present an overview on graphene-encapsulated materials and their most important synthesis pathways. In addition, we explore the synergistic functionalities provided by these composites and highlight the state-of-the-art related to energy, environmental and bio-applications, among others. Finally, we discuss their challenges and future outlooks.

Contents

Abbreviations: APTES, 3-aminopropyltrimethoxysilane; AuNPs, gold nanoparticles; CA-graphene/LFP, activated graphene-encapsulated $LiFePO_4$; CTAB, hexadecyltrimethylammonium bromide; CVD, chemical vapour deposition; DCC, (*N,N′*-dicyclohexylcarbodiimide); DMF, dimethylformamide; EDC, 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide; Fe@GNS, Fe encapsulated in graphene sheets; Fe_3O_4@G, graphene wrapped in Fe_3O_4 nanoparticles; Fe_3O_4@SiO_2-rGO, magnetic microsphere-confined graphene adsorbent; GHMCSs, graphene-coated hollow mesoporous carbon spheres; GM, graphene-encapsulated mesoporous; GNs, graphene nanosheets; GO, graphene oxide; GBMs, graphene-based materials; GQDs, graphene quantum dots; HATU, (1-[bis(dimethylamino)methylene]-1H-1,2,3-triazolo[4,5-b]pyridinium 3-oxid hexafluorophosphate); HGSs, hollow graphene spheres; LBL, layer-by-layer self-assembly; LFP, $LiFePO_4$; LIBs, Li-ions batteries; LTO, $Li_4Ti_5O_{12}$; NHS, N-hydroxysuccinimide; NPs, nanoparticles; PAH, poly(allylamine); PFO, poly(9,9-di-n-octylfluorenyl-2,7-diyl); PS, polystyrene; rGO, reduced graphene oxide; Rubpy, tris(2,2′-bipyridyl)ruthenium(II) chloride; SDS, sodium dodecyl sulphate; SERS, surface-enhanced Raman scattering; SnO_2-HNS/G, hollow SnO_2 nanospheres wrapped by graphene; Sulfo-NHS, N-hydroxysulfo-succinimide; Sulphur@rGO, reduced graphene oxide encapsulated sulphur; TEG, tetraethylene glycol.

* Corresponding author at: Catalan Institute of Nanoscience and Nanotechnology (ICN2), CSIC and The Barcelona Institute of Science and Technology, Campus UAB, Bellaterra, Barcelona 08193, Spain.
E-mail address: arben.merkoci@icn2.cat (A. Merkoçi).

http://dx.doi.org/10.1016/j.pmatsci.2017.01.001
0079-6425/

1. Introduction

Graphene-based materials (GBM) are typically composed of one-atom thick sheets containing sp^2 bonded carbon atoms patterned in a two dimensional honeycomb lattice [1]. GBM are generally classified according to three crucial parameters (i) lateral size, (ii) number of layers and (iii) C/O ratio [2]. Depending on these three key parameters, GBM offer a broad family of materials with a myriad of different and unique thermal, optical, mechanical and electrical properties [3]. Regarding the aforementioned parameters, GBM may behave as conductors [4], semimetals [5,6], semiconductors [7], insulators [8], hydrophobic or hydrophilic materials, stronger or weaker acceptors of fluorescence resonance energy transfer [9,10] or may interact with biological components in a diverse way [11]. As a consequence, these extraordinary properties make GBM appealing for all fields of science and technology.

Pristine graphene, polycrystalline graphene, graphene oxide, reduced graphene oxide and graphene quantum dots are the most common GBM. Pristine graphene is a perfect lattice of sp^2-bonded carbon atoms with no defects found throughout its honeycomb-like pattern and it is a single crystalline grain [12]. Polycrystalline graphene possesses a large area and is composed of single-crystalline graphene grains of various orientations organized like a jigsaw puzzle by grain boundaries, which leads to topological defects such as dislocations [13]. Graphene oxide (GO) is a lattice of sp^2-bonded carbon atoms incorporating defects as it is disrupted by sp^3 carbon bonds and exhibits oxygen-containing moieties such as carboxyl groups exposed on the edges and hydroxyl and epoxy groups on the basal plane [14]. Hence, GO often exhibits some hydrophilic islands onto its basal plane according to its C/O ratio [15]. Reduced graphene oxide (rGO) is composed of GO after being reduced *via* either a chemical or physical method and as a consequence its final C/O ratio is greater than that of the starting GO [16,17]. Graphene quantum dots (GQDs) are nanoscaled crystals of graphene that are tiny enough to yield exciton confinement and quantum size effect (generally GQDs have diameters of less than 20 nm). As a result, GQDs show photoluminescent properties that can be tailored depending on their size and surface chemistry [18]. The most important pathways for GBM fabrication are chemical vapour deposition, epitaxial growth, mechanical cleavage, wet chemical synthesis, and exfoliation of graphite [15,19], which have been broadly covered in the literature [20,21]. These methods allow for the generation of several GBM revealing different features in terms of oxidation grade, number of layers, edge and basal defects and lateral size [22].

GBM exhibit an interesting portfolio of properties that are appealing for technologists and scientists to complement or enhance the properties of other materials by designing novel composites [23]. These properties range from chemical to physical properties, included but not limited to high electrical conductivity, photothermal response, photoluminescence, optical absorption, fluorescence quenching abilities, high specific surface area, broad chemical modification capabilities and high adsorption of biomolecules. On the one hand, being two-dimensional materials, GBM are likely to wrap particulate materials smoothly. On the other hand, GO and rGO platelets are amenable to being processed in suspension. Hence, they are excellent encapsulating agents which can be exploited in cutting-edge hybrid materials. Herein we introduce an overview on graphene-encapsulated materials and their most important methods of synthesis. We also describe the synergistic physicochemical properties offered by these hybrid materials and discuss the state-of-the-art related to energy, biomedicine, bioanalytical and environmental applications exploiting these composites mainly over the last four years.