Nano-Structures & Nano-Objects 13 (2018) 1–20

Contents lists available at ScienceDirect

Nano-Structures & Nano-Objects

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

Naturally occurring green multifunctional agents: Exploration of their roles in the world of graphene and related systems

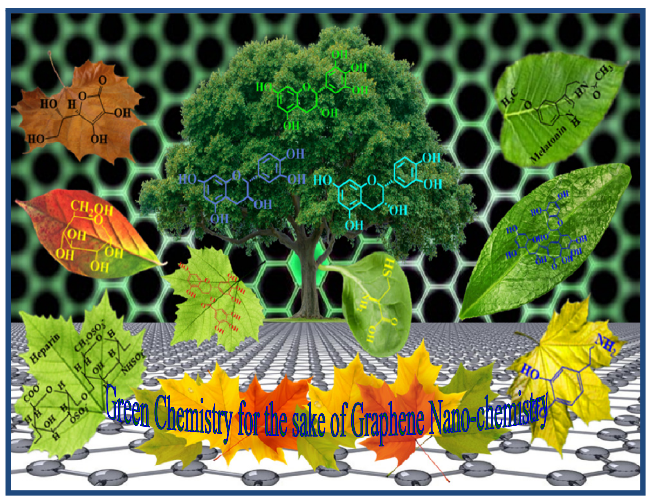
Abhijit Karmakar, Tamanna Mallick, Sreeparna Das, Naznin Ara Begum *

Department of Chemistry, Visva-Bharati (Central University), Santiniketan 731235, West Bengal, India

HIGHLIGHTS

- Use of naturally occurring and green multifunctional agents of bio-origin.
- Green synthesis of graphene-based materials.
- Review deals with the research activities going on in this field.
- Green synthesized graphene products have potential technological applications.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 1 September 2017
Received in revised form 6 October 2017
Accepted 12 October 2017

Keywords:
Graphene
Reduced graphene oxide (rGO)
Green chemistry
Green multifunctional agents
Naturally occurring biomolecules
Plants

ABSTRACT

There is an overwhelming demand for the eco-friendly and cost-efficient synthetic protocols for graphene, reduced graphene oxide and other graphene based products with tailor-made structural properties. In the recent times, various green chemical synthetic methods attracted the interest of the researchers working in the field of graphene-nanochemistry. The main objective of this review is to make the readers acquainted with the plethora of research activities going on in the field of green synthesis of wide range of graphene-based materials using naturally occurring green multifunctional agents of biological origin. These green synthesized graphene based materials are being hugely explored nowadays for their potential technological applications.

Our aim in this review was to provoke the readers' interest to discover these promising green chemical alternative synthesis protocols of graphene-based products and to understand the mechanistic pathways of these synthetic methods which is highly significant in the further development, standardization and commercialization of these promising synthetic strategies of graphene and graphene related systems.

Contents

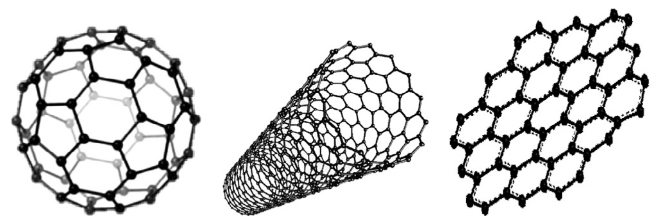
* Corresponding author.
E-mail address: naznin.begum@visva-bharati.ac.in (N.A. Begum).

https://doi.org/10.1016/j.nanoso.2017.10.005
2352-507X/

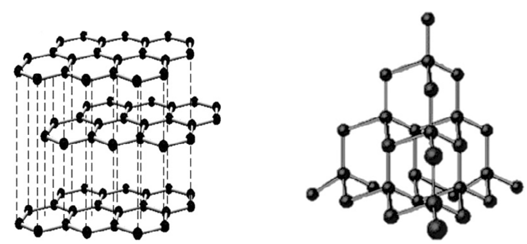
1. Graphene, the new generation smart material-Why is it unique?

A single element, carbon offers cornucopia of its allotropic forms with almost all the dimensionalities e.g. from zero dimensional fullerene to one dimensional carbon nanotubes and three dimensional graphite and diamond (Fig. 1). However, it is surprising that the two dimensional allotropic form of carbon was missing till 2004 when André Geim and Konstantin Novoselov isolated and characterized graphene (Fig. 1) at the University of Manchester [1]. This ground-breaking discovery brought them Nobel Prize in the year 2010 and this uniquely smart nanomaterial became known outside their Physics laboratory.

Years back, scientists have hypothesized about graphene but only after this discovery, the scientific world came to know that the two dimensional nanostructure could exist in reality. The term "graphene" was derived from the word "graphite" and a *suffix* "ene" [2]. Actually graphene, the crystalline two dimensional allotrope of carbon is a single layer originated or isolated from graphite. In graphite, one graphene layer is separated from another layer by a distance of 3.35 Å. According to the IUPAC definition, "graphene is a single carbon layer of graphite structure, describing its nature by analogy of a polycyclic aromatic hydrocarbon of quasi-infinite size". The two-dimensional planar sheet of graphene consists of sp^2-hybridized carbon atoms which are densely packed with each other (one carbon atom is apart from another one by approximately 1.42 Å) through covalent linking and thus, a honeycomb (hexagonal) like crystal lattice structure is generated (Fig. 1). The three sp^2-hybridized orbitals of each carbon atom form three σ bonds with its three neighbors while remaining one p-orbital on each of these carbon atoms overlaps with that of its nearest neighbor to form π-bond which is oriented in the perpendicular direction with respect to the plane of the graphene. This phenomenon gives rise to the unique crystal lattice structure of graphene with long range delocalization of π-electron clouds and unusual stability of graphene [3,4]. This is also the cause of the origin of several interesting structure-dependent properties of graphene, like unique optical and electronic properties, unusual quantum Hall effect, high thermal conductivity, exceptional mechanical strength of graphene (it is 200 times stronger than even the strongest steel) etc. [5,6]. Due to all these diverse properties, the graphene is greatly explored by the scientists in numerous ways and it finds its potential applications in the development of electrode systems, solar cell components, sensors, composite materials, opto-electronic devices, biomedical tools and supercapacitors etc. [7–13] but these types of advanced applications of graphene in the industrial scale demand its large scale production. Not only that, such production methods must have tailor-made control over the structural properties of the synthesized graphene and other graphene-based products. This is really a challenge for the scientists working in the field of graphene-nanochemistry.



(a) Fullerene 0D. (b) Carbon nanotube 1D. (c) Graphene.



(d) Graphite 3D. (e) Diamond 3D.

Fig. 1. Various allotropes of carbon.

2. Synthesis of graphene-How far is it challenging?

Around the globe, researchers are engaged in the development of cost-effective as well as large scale synthetic methods of high quality graphene sheets with tailored structure and task-specific properties. In the recent times, plethora of graphene synthesis methodologies are being developed which may be broadly classified as the top-down and bottom-up methods. In the following section, we have given a brief overview of these methods.

However, it is quite evident that the development of an absolute method which is free from all types of sort-comings of graphene synthesis is still missing.

One of the widely used top-down methods of graphene synthesis is micro-mechanical exfoliation [14–16] which is effective in the production of single or few layer graphene [14–16]. In fact, the first successful production (and isolation) of single and few layer of graphene, done by André Geim and Konstantin Novoselov is an example of mechanical exfoliation method (which is known to us as their pioneering adhesive tape technique).

Mechanical exfoliation method is useful for the synthesis of monolayer to few-layers graphene but the reproducibility of this method is uncertain and at the same time, this method is not useful for the large scale production of high quality graphene. Moreover, in mechanical exfoliation, there is always a chance of the collapse of each of the separate atomic layers of the graphene or the damage of the spatial structure of the synthesized graphene [9]. On the other hand, among the bottom-up approaches of graphene synthesis, the two most popularly used methods are chemical vapor deposition (CVD) and epitaxial growth techniques [14]. Each of these