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Review

Trends in green reduction of graphene oxides, issues and challenges: A review

Mahesh Agharkar [a], Sachin Kochrekar [a], Slah Hidouri [a,b], Musibau A. Azeez [a,c,*]

[a] Department of Chemistry, University of Pune, Pune, Maharashtra 411007, India
[b] Laboratory of Physics of Layered Materials and Hybrid Nanomaterials (PMLNMH), Faculty of Science of Bizerta, Jarzouna 7021, Tunisia
[c] Department of Pure and Applied Biology, Ladoke Akintola University of Technology, PMB 4000, Ogbomoso, Nigeria

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ABSTRACT

Graphene has occupied the central stage in material science research all over the world. Various techniques and methods have emerged, the most common being top down approach, where graphene is synthesized from graphite. In this approach, reduction of graphene oxide is considered as the most important step and it is generally achieved by strong chemical reducing agents such as $NaBH_4$ and hydrazine hydrate. But now, new generation of researchers have developed various natural and eco-friendly methods of reducing graphene oxide. This review summarizes the green methods employed in natural reduction of graphene oxide, which includes use of biomolecules, microorganisms and plant extracts. Issues and challenges are raised to provide pathways for future endeavors that will translate into service delivery for the benefit of human.

Contents

1. Introduction

Graphene research has expanded quickly since the substance was first isolated in 2004. Graphene is the only form of carbon (and generally all solid materials) in which each single atom is in exposure for chemical reaction from two sides (due to the 2D structure) [1]. It is known that carbon atoms at the edge of graphene sheets have special chemical reactivity, and graphene has the highest ratio of edgy carbons (in comparison with similar materials such as carbon nanotubes). In addition, various types of defects within the sheet, which are very common, increase the chemical reactivity [2].

As of 2014, graphene is not used in commercial applications, however, many areas of applications have been proposed and/or are under active development including; electronics, biological engineering, filtration, lightweight/strong composite materials, photovoltaic and energy storage [3–7]. Potential graphene applications include lightweight, thin, flexible, yet durable display screens, electric circuits, and solar cells, as well as various medical, chemical and industrial processes enhanced or enabled by the use of new graphene materials [8–12].

Researchers are taking into consideration two primary methods for the fabrication of graphene-: a top-down (TD) and a bottom-up

* Corresponding author at: Ladoke Akintola University of Technology, Department of Pure & Applied Biology, Ogbomoso, Nigeria. Tel.: +234 8034236886.
E-mail address: maazeez@lautech.edu.ng (M.A. Azeez).

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(BU) approach. BU constructions is done by starting with smaller entities and build them up to larger functional constructs such as manufacturing a paper from wood pulp or chopped bamboo. TD fabrication is analogous to skillfully removing few fully intact papers from a hard bound book.

Obtaining single graphene layers from graphite is a major difficulty. In TD approach, there are reported methods on the production of graphene such as micromechanical cleavage [13], graphitization of SiC [14] and solution exfoliation of graphite in organic solvents [15]. However, these methods turn out a poor yield of graphene layers. Chemical reduction of graphite oxide colloidal suspensions has been considered as an effective route to synthesize graphene sheets due to its simplicity, reliability, ability for large-scale production and exceptionally low price [16].

A number of reducing agents such as dimethylhydrazine [17], hydroquinone [18], aluminum powder [19], sodium borohydride [20], sulfur containing compounds [21], hexamethylenetetramine [22], polyelectrolyte [23], Ethylenediamine (EDA) [24], sodium citrate [25], carbon monoxide [26] and norepinephrine [27] have been experimented on and were found to have performed under various conditions i.e., acid/alkali [28], thermal treatment [29] and others treatments such as laser [30], plasmas [31], microwave [32], sonochemical [33], electrochemical [34], two-step reduction [35] and so on. These different reduction methods result in graphene with different properties.

Despite the distinct advantages of chemical route for reduction of GO, the reduced GO (RGO) tends to form irreversible aggregation (resulting from strong van der Waals attractive forces among the graphene planes) which creates bottle neck and confines its processability. However, this can be eliminated by chemical modification of graphene using small organic molecules, biomolecules etc [36–39].

An additional negative aspect of the chemical reduction method is the high toxic nature of the reducing agents (hydrazine, dimethylhydrazine, sodium borohydride, hydroquinone, etc). The existence of trace amounts of such toxic agents could have harmful effect, particularly in cases of bio-related applications such as catalysis and drug delivery. Even in the case of metal/hydrochloric acid reduction of GO, particles/traces of metals may stay behind as impurities. In this context, employment of green nanotechnology which reports on the reduction of GO to overcome the above problem by using reducing agents such as biomolecules, microbes and phytoextracts reduction has become extremely crucial.

2. Green technology

Green nanotechnology in which biomolecules, microbes and plant extracts are used as both reducing and capping agent has been widely explored in the synthesis of metal nanoparticles. Here, the chemical components that are implicated in the bio-reduction process, formation and stabilization of nanoparticles have been found to include biomolecules such as proteins, amino acids, polysaccharides, alkaloids, alcoholic derivatives, polyphenolic compounds, enzymes, chelating agents and vitamins [40,41]. This same principle has been extended to bio-reduction of GO to graphene. Biological approach to synthesis of graphene has been adjudged to be environmental friendly, cheap with resultant high product yield, devoid of harsh and toxic chemicals, and easy to handle [42].

3. Bacteria intervention for GO reduction

Bacteria have various capacities to manipulate atoms and chemical molecules in order to survive. There are natural paths used by bacteria depending on which kind of final form of a molecule is required for its life. Bacteria also use uncommon organic and inorganic molecules around her to substitute an essential molecule urgently needed as respiratory substrate through an adaptive oxidation and/or reduction mechanisms to serve as possible sources of energy. This power of electronic manipulation of various compounds opened avenues for scientist to inspire from a biological process various methodologies for synthesis a new materials at different scales.

There have been various reports on synthesis of nanoparticles through exploitation of the capacity of bacteria cells to reduce metallic salts. GO is one of such nanomaterials that bacteria have enduring capacity and mechanism for its reduction (Table 1). The mechanism of reaction involved depend on bacterial cells that have such capacity directly or indirectly for hydrolyzing acid groups associated with nanosheets of carbon especially oxygen atoms. Like a final acceptor of electron in respiration process of bacteria, GO oxide can capture the electron coming from the respiration process [43]. For instance, Wang et al. used *Shewanella* for reducing GO via external electron transfer mediated by the outer membrane c-type cytochromes included heme group, and by self-secreted electron mediators (Fig. 1) [44].

Bacillus subtilis was also used for reduction of GO and development of an advanced supercapacitor in this same way, while Zhang et al. showed that GO reducing bacteria participate not only in the reduction step but also in the final composite by being entrapped inside the reduced graphene. This work show that a chosen methodology for reduction of GO can define the application of a final nanomaterial [45]. It seems that different types of bacteria can participate in the reduction and in the orientation of a final material obtained with micro-organism assistance. Raveendran et al. used extremophiles bacteria for reducing GO to get a highly conductive graphene that can be used in microelectronics [46]. Here, the reduction of GO comes from the potential of extremophiles with adequate mechanisms for degradation of a toxic element in order to survive under harsh environmental condition. *Escherichia coli* in mixed-acid fermentation with an anaerobic condition were used to reduce chemically exfoliated graphene oxide (GO) nanosheets with attendant bactericidal property attributed to the surfaces of rGO nanosheets formed [47], while this same bacteria biomass have been employed in the reduction of GO to graphene sheets that are dispensable in water [48].

Wang et al. [49] opined on the possibility of bacterial reduction of GO being associated with a catalytic reaction assisted by enzymes like glycose oxidase. Huge amount of various enzymes are produced inside bacterial cells. In the case of using a whole cell of bacteria for reduction of GO, these enzymes are not readily available unless they are localized in the membrane. In addition, such reaction require some part of the external group in the nanosheets and/or a final product of a catalytic reaction that can react with GO and achieve its reduction.Nevertheless, reducing GO by bacteria has made in situ manipulation of GO possible and bacteria has become a natural factory capable of recycling and synthesizing a desired graphene from the pre-existent precursor. However, in another investigation by Avinav et al. GO was obtained from a cellulose precursor and reduced in situ using *Gluconacetobacter xylinus* [50].

Table 1
Representative list of bacteria used for reduction of graphene oxide.

Sr. No.	Bacteria	Reference
1	*Shewanella*	[44]
2	*Bacillus sibtilus*	[45]
3	Extremophiles bacteria	[46]
4	*Escherichia coli*	[47,48]
5	*Gluconacetobacter xylinus*	[50]