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Historical perspective

Nitrogen-doped graphene and graphene quantum dots: A review onsynthesis and applications in energy, sensors and environment

Manpreet Kaur [a], Manmeet Kaur [a], Virender K. Sharma [b,*]

[a] Department of Chemistry, Punjab Agricultural University, Ludhiana 141 004, India
[b] Program for the Environment and Sustainability, Department of Environmental and Occupational Health, School of Public Health, Texas A&M University, 212 Adriance Lab Rd, 1266 TAMU, College Station, TX 77843, USA

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ABSTRACT

Doping of nitrogen is a promising strategy to modulate chemical, electronic, and structural functionalities of graphene (G)and graphene quantum dots (GQDs) for their outstanding properties in energy and environmental applications.This paper reviews various synthesis approaches of nitrogen-doped graphene (N-G) and nitrogen-doped graphene quantum dots (N-GQDs).;Thermal, ultrasonic, solvothermal, hydrothermal, and electron-beam methods have been applied to synthesize N-G and N-GQDs.These nitrogen-doped carbon materials are characterized to obtain their structural configurations in order to achieve better performance in their applications compared to only either graphene or graphene quantum dots.Both N-G and N-GQDs may be converted into functional materials by integrating with other compounds such as metal oxides/nitrides, polymers, and semiconductors.These functional materials demonstrate superior performance over N-G and N-GQDs materials.Examples of applications of N-G and N-GQDs include supercapacitors, batteries, sensors, fuel cells, solar cells, and photocatalyst.

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* Corresponding author.
E-mail address: vsharma@sph.tamhsc.edu (V.K. Sharma).

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1. Introduction

One of the most important issues of the 21st century is to secure sustainability of energy that meets the global energy demand.Consumption of energy keeps increasing, for example 30% increase in the period of 1987 to 2012 [1]. Technological solution to meet the energy need of the society must not only be clean and efficient but also affordable [1,2]. Among the various catalysts applied to produce and transport energy, carbon-based nanomaterials (i.e.,metal free catalysts) have received profound attention in advanced oxidation processes to remove organic pollutants [3–7]. These nanomaterials have shown remarkable performance in reactions relevance to energy generation and storage such as hydration of allynes, fuel cells, oxidative dehydrogenation, and oxidation of numerous alcohols [8–10].

Another emerging issue of the century is to provide clean water to human population.According to a report of the United Nations and World Health Organization (WHO), more than 2 billion people lack safe drinking water at home [11]. More than 360,000 children die every year under 5 years of age due to water related diseases.With an increase in pollution of drinking water resources (e.g.,groundwater and surface water), meeting the demand of purified water to population is a challenge of great magnitude [12, 13].Water has also strong effect on energy production, thus affecting the economy of both developed and developing countries.Carbon-based nanomaterials may play important role in this century because of their potential applications in energy production and water remediation [14].

Carbon has different forms that contain changeable micro-textures (or various morphologies).Carbon has many allotropic forms, which include diamond, black carbon, carbon nanotubes, fullerenes, and graphene [15, 16].Among these different forms, graphene is one of the most researched nanomaterials in the last few years due to its various energy and environmental applications [17–20].

2. Graphene and graphene quantum dots

Graphene is a flat monolayer of sp^2 hybridized carbon atoms arranged in a hexagonal lattice with a distance of 0.142 nm between two carbon atoms [21]. It is a two-dimensional honeycomb lattice that forms the building blocks of some important allotropes. Graphene can be converted into three-dimensional (3-D) graphite by stacking or to one dimensional (1-D) nanotubes by rolling [22]. Graphene can also transform to zero-dimensional (0-D) fullerenes through wrapping. Graphene involves the π-conjugation, which results in its extraordinary electrical, mechanical and thermal properties [23]. Graphene is found to be impermeable to liquids and gases [24]. In comparison to the most effective materials, graphene has higher current density and higher thermal conductivity. Graphene possesses specific surface area of 2630 m^2/g, which is similar to the activated carbon but much higher than specific surface area of the carbon black (smaller than 900 m^2/g) or carbon nanotubes (from 100 to 1000m^2/g). Because of its extraordinary properties, applications of graphene are in nano-systems and nanodevices [25].Graphene is the only form of carbon in which atoms are available from both sides for carrying out chemical reactions [26].

Graphene oxide (GO), a functionalized form of graphene, is obtained by exfoliating graphite. Graphene oxide has attracted renewal interests due to its superior properties like mechanical stability, large surface area, and tunable electrical and optical properties [27–29]. GO is a good candidate for coordinating to other molecules or materials because of important functional groups present on its surface *i.e.* hydroxyl, carboxyl and epoxy groups. Due to its great structural diversity, GO and its composites can be used for energy storage and environmental protection including photocatalyst for water splitting, water purification, and removal of air pollutants [30–33].

Graphene quantum dots (GQDs) are a few atoms thick graphene and their size is less than 30 nm. GQDs possess excellent features such as large diameter, high surface area, and good surface grafting using conjugated π-π network and other physical properties [34]. These properties include highly tunable photoluminescence, remarkable UV-blocking property, good biocompatibility, unique spin property, and high photo stability. It possesses a wide range of applications in ion detection, bio-imaging, photo catalysts, photo detectors, electrochemical luminescence, optical sensors and photovoltaic devices [35–39].Doping of graphene and GQDs with heteroatoms has led to improve their catalytic activities towards oxidation-reduction reactions which are a prerequisite for energy storage/conversion.

Introduction of heteroatom (e.g.,boron, nitrogen, oxygen, phosphorous, and sulfur) into carbon lattice can adequately disorientate the electron network, which is homogeneously conjugated.This network regulates the surface properties by adjusting the charge distribution and spinning culture of doped domains [40]. Nitrogen is adjacent to carbon in periodic table thus possess similarity in atomic radius (0.70 Å) with carbon (0.77 Å) and greater electronegativity ($\chi_N = 3.04$) than C ($\chi_c = 2.55$), makes it easier to incorporate nitrogen into carbon network via substitution doping. For example, metallic N-doped graphene sheets [41].Electron states of graphene can be intrinsically altered by N-doping and subsequently it endows pristine graphene with improved activity towards specific reactions and catalysis [42–44].

The general structure of nitrogen-doped graphene (N-G) is given in Fig.1 [45].N-G has three major types of bonding configurations: (i)

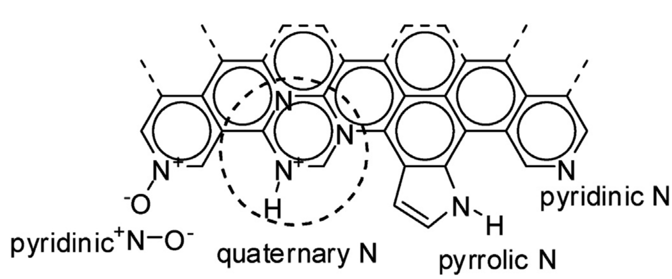

Fig.1. Bonding configurations of nitrogen atoms in N-graphene (Reproduced from [45] with the permission of American Chemical Society).

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