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Graphene quantum dots in analytical science

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ABSTRACT

Graphene quantum dots (GQDs) are small fluorescent nanoparticles with unique properties that make them attractive tools for research in various fields. We review their state of the art in analytical chemistry and summarize their analytical applications. Also, we deal with GQDs as target analytes, a scarcely explored aspect in analytical nanoscience and nanotechnology, and suggest potential future directions for GQD-based analytical research.

Contents

1. Introduction 93
2. Synthesis 94
    2.1. Top down 94
    2.2. Bottom up 94
    2.3. Doped and functionalized GQDs 95
3. Analytical applications of GQDs 96
    3.1. Sensors and biosensors 97
        3.1.1. 3Photoluminiscence–based sensors 97
        3.1.2. Electrochemical sensors 106
    3.2. Immunosensing and aptasensing 107
        3.2.1. Immunosensors 107
        3.2.2. Aptasensors 107
    3.3. Other analytical applications 110
4. GQDs as analytes 110
5. Conclusions and future prospects 110
Acknowledgment 111
References 111

1. Introduction

Graphene has attracted increasing attention among the scientific community ever since it was isolated as a single layer of material from highly oriented pyrolytic graphite (HOPG) in 2004 by Novoselov and Geim using the "Scotch-tape method" [1]. Graphene, with its truly two-dimensional (2D) planar structure, and the thickness of a single atom, consists of carbon atoms arranged in a honeycomb lattice with sp^2 hybridization. Its unique properties include extremely high intrinsic mobility of charge carriers, zero band gap, large surface area and high chemical stability.

Graphene also exhibits superior mechanical, magnetic, optical and thermal properties [2]. However, it disperses poorly and tends to agglomerate in solvents. Research into this material has grown exponentially in recent years, particularly in material science, physics, chemistry, engineering, and analytical chemistry. Graphene quantum dots (GQDs), which constitute a zero-dimensional photoluminescence (PL) carbon-based nanomaterial consisting of very thin (typically 3–20 nm) graphene sheets that exhibit exciton

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confinement and quantum-size effect, recently aroused much scientific interest by virtue of their exceptional properties. Although graphene is a zero band-gap nanomaterial – and hence non-luminescent – it has an infinite exciton Bohr radius and affords quantum confinement in finite-sized specimens [3]. The band gap in GQDs is non-zero and can be tuned by altering the size and the surface chemistry of the dots [4].

These nanoparticles (NPs) can be obtained as single-layer, double-layer and multi-layer materials [5]. Quantum confinement and edge effects confer them with interesting properties, such as fluorescence (FL) activity, robust chemical inertness, excellent photostability, high biocompatibility and low toxicity. In addition, GQDs exhibit stable PL, resistance to photobleaching, tunable luminescence and high solubility in various solvents. GQDs provide an effective alternative to colloidal inorganic semi-conductive quantum dots (QDs), which have attracted much attention in the past two decades on account of their electronic and optical properties [6] but are highly toxic due to the release of heavy metals, such as cadmium, selenium, tellurium and zinc, from their core and their coating.

Although GQDs have been classified as carbon nanodots (C-dots), they differ from them in some respects. Thus, C-dots are quasi-spherical NPs less than 10 nm in diameter, possessing PL properties. However, GQDs are graphene nanosheets in the form of one, two or more layers all less than 10 nm thick and 100 nm in lateral size; also, they usually contain functional groups (carboxyl, hydroxyl, carbonyl, epoxide) at their edges that can act as reaction sites and alter PL emission from the dots by changing their electron density [7]. Quantum yield (QY), which is an important factor for FL materials, ranges from 2% [8] to 46% [9] in GQDs, depending on the particular method of synthesis and whether their surface is passivated [10], reduced [11] or further modified [12].

2. Synthesis

Progress in nanoscience and nanotechnology rests heavily on the development of effective methodologies of synthesis allowing new nanomaterials with specific properties shape, size, surface characteristics and inner structure to be obtained. Also, some chemicals allow the properties and the distribution of NPs to be adjusted as needed.

Approaches to synthesizing nanomaterials have traditionally been classified as “top-down” or “bottom-up”.

2.1. *Top down*

In top-down approaches, large macroscopic materials (bulk materials) are restructured and externally controlled in order to reduce their size and to obtain a specific shape. The resulting nanosized materials may exhibit very interesting, unique properties differing from those of the starting materials. Top-down syntheses of nanocomponents are usually expensive and slow, require special equipment and critical operating conditions – and toxic organic solvents or strong acids in some cases – and provide low yields, which make them unsuitable for large-scale production [10,13,14]. In addition, they introduce internal stress and faults in the crystallographic network that can lead to surface defects and structural damage – and ultimately to altered surface properties due to the typically large surface area per unit volume of these materials.

In any case, top-down approaches to synthesis are the more commonly used in nanoscience and nanotechnology. The main precursors used in top-down syntheses of GQDs include graphene oxide (GO) [15], coal [16], carbon fibers [17], graphite powder [18] or rods [19], single-walled carbon nanotubes (SWCNTs) [20] or multi-walled CNTs (MWCNTs) [21], carbon black [5], graphene [22] and, recently, metal-organic framework (MOF)-derived porous carbon [23]. The precursors are usually subjected to acid, hydrothermal, solvothermal or electrochemical treatment, laser ablation or exfoliation.

Acid-based chemical procedures of synthesis use one of several possible acids to cut bulk materials into GQDs. The treatment involves using a concentrated strong acid (e.g., as nitric acid [5,24], mixtures of nitric and sulfuric acids in variable proportions of 3:1–1:3 [15,17] – and sonication in some cases [20,25] – or nitric acid in combination with amidative cutting [18], in addition to temperatures up to 80°C and solution stirring.

Hydrothermal routes for GQD synthesis involve dissolving or dispersing an appropriate carbon-based raw material in water and heating at 180–200°C at high pressure in a closed container (usually an autoclave) for 2–12 h [19,26–28]. Solvothermal syntheses of GQDs use organic solvents {e.g., dimethylformamide (DMF) [29]}, and heating temperatures and times similar to those of hydrothermal routes. Fig. 1 depicts the hydrothermal treatment of SWCNTs for the production of GQDs.

The electrochemical preparation of GQDs requires applying an anodic potential of 1 V for 7 h, 11 h or 15 h to a MWCNT-coated working electrode in order to fracture the micromaterial [30]. Alternatively, GDQs can be obtained by electrolyzing a graphite rod immersed in a 0.1 M NaOH solution with a current intensity of 80–200 mA cm^{-2} [19] or by cyclic voltammetry (CV) (viz. by electrochemical reaction of a GO film working electrode immersed in a 0.1M PBS solution subjected to a potential of ±3 V [31]).

Recently, GQDs were synthesized by laser ablation with a femtosecond laser (800 nm, 35 s pulses for 20 min) of HOPG in aqueous media [32] and by irradiating graphite powder with an Nd:Yag laser in the presence of benzene (1064 nm, 10 ns pulses for 30 min) [33].

Ultrasound-assisted exfoliation of graphite nanofibers [34], electrochemical exfoliation of graphene [22], organic solvent-assisted exfoliation of graphite NPs [35], and exfoliation and disintegration of graphite flakes and MWCNTs by intercalation of highly reactive potassium between layers and walls, respectively [36], are among the most widely used top-down methods of synthesis for GQDs. A method involving a one-step sonication–redox treatment of GO with $KMnO_4$ and providing GQDs in a high QY in a short time without the need for an acid was recently reported [37].

2.2. *Bottom up*

Bottom-up routes of synthesis for GQDs assemble basic building blocks with suitable properties, including elemental precursors, such as atoms, molecules or nanoclusters, by controlling their interactions in order to facilitate environment-friendly large-scale production of these nanomaterials [38,39]. Bottom-up approaches to synthesis introduce fewer defects than top-down approaches; also, they afford more uniform chemical composition, and precise control over the shape and size distribution of the product. However, they have been less widely explored than top-down routes.

In one bottom-up route, ethylene gas was continuously injected into argon plasma to generate a carbon-atom beam that flowed through a carbon tube for dispersal in a chamber to obtain size-controllable GQDs [40]. Haloaromatic compounds, such as chlorobenzene and dichlorobenzene, have been used as carbon sources for laser-induced photochemical stitching [41]. Thus, the oxidation of polyphenylene dendritic precursors by solution chemistry produces GQDs [3]. These nanomaterials can also be obtained by hydrothermal treatment combined with (*a*) prior charring of polycyclic aromatic hydrocarbons (PAHs) with a strong acid, such as H_2SO_4 [42]; or, (*b*) microwave heating of glucose, sucrose or fructose aqueous solutions [43]. Pyrolysis of L–glutamic acid [44] or citric acid [45] (Fig. 2) above 200°C provides an easy, fast bottom-up method for the synthesis of highly-fluorescent NPs. Also, a combined top-down/bottom-up approach was used to obtain alginate