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Review Article

Enhancement of graphene quantum dots based applications via optimum physical chemistry: A review

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ABSTRACT

Graphene quantum dots (GQDs) is a promising new substance from the carbon material family that has been attracting researchers of many fields, such as biomedical sensors, medical imaging, polymer science, solar cells, light emitting diodes, and photoelectrons. Its unique electrical and mechanical properties could encourage its usage due to its low cost, high surface area, safety, stable luminescence, excellent biocompatibility, suitable conductivity, and low toxicity. The dispersibility of GQDs in common solvents depends on hydrophobicity/hydrophilicity, which is particularly important toward its homogeneous incorporation into various polymer layers. This review discusses the global demand for GQDs and explore the main factors encouraging its utilization in various devices. Moreover, different synthesis methods of GQDs were compared, and recent investigation on GQDs based composite applications are analyzed. Finally, the future of GQDs is detailed, focusing on the gaps in its role in future technology.

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1. Introduction

The need to improve the quality and performance of materials in various applications have always been the main concern of researchers. There are many developed materials utilized in different devices, such as nanomaterials [1,2], polymers [3],

microbes [4], and silica [5]. Nanomaterials are challenging to produce in a large scale [6]. However, it is known to be important element in devices due to its high sensitivity and limit of detection [7,8]. Choosing a right material in the development of any application is an utmost matter [8].

Graphene compared to various dimensional (fullerenes in 0D, nanotubes in 1D & graphite in 3D) [9,10] is carbon sheet of

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single atoms in 2D configuration. It has fascinated researchers due to its high surface area and high flexibility in the context of moving carrier [11], excellent flexibility of mechanical, superior chemical/thermal solidity, as well as its higher performance in field-effect mobility [12]. However, its application is limited due to the simple mixture and low scattering of 2D graphene sheets in common solvents [13]. To circumvent these problems, a favorable method used to modify the graphene in 2D sheets to graphene quantum dots of 0D [14]. Graphene quantum dots (GQD) are actually sheets of graphene smaller than 100 nm [15]. It is exceptional due to its several unique properties, such as its stability in luminescence, biocompatibility, perfect dispersibility in polymers, conductive appropriately, and low toxicity. GQD has been extensively studied for applications such as electrochemical biosensor [16], bio-imaging [17], nanocomposites [18] light emitting diodes [19], and photovoltaics [20]. The magnitude of bandgaps can be adjusted using the size of the GQDs [21], the form of the shape, level of thickness, and the segment of the sp^2 domain, exhibiting the different spectacles due to its quantum confinement and edge effects [22,23]. GQDs are garnering attention due to it being a viable replacement for conventional quantum dots (QDs), based on its inertness, environmentally friendliness, high fluorescent activity, and stability in photoluminescence. Improved grafting of the surface is excellent in various applications, specifically nanocomposites and medical applications [24]. Moreover, GQDs has better crystallinity than carbon dots (CDs), and usually consist of graphene due to its graphene matrices, similar to the crystalline structure in single or few layers of graphene, rendering it excellent toward improving the capability of supercapacitors and lithium-types batteries [25,26]. Brothie [27] reviewed that GQDs will enhance the phenomena of physical and chemical related to properties in optical and electronic for chiral nanostructures. Their biocompatibility enable it as vehicle in drug delivery application.

Generally, GQDs measures 3–20 nm. It is made up of less than 5 layers of graphene sheets. The graphene sheets in the GQDs has dimension and heights from 1.5 to 100 nm and 0.5 to 5 nm, respectively [28,29]. Their shape is mostly circular and elliptical, however, there are quadrates [30] and hexagonal dots [31]. Basically, the characteristics of GQDs are similar to graphene, made up of C, O & H and carbonyl, carboxyl, hydroxyl, and epoxy as its surface groups and crystalline nature [32].

This review aims to provide a fundamental knowledge on GQDs as applicable in many applications. The subjects discussed include the need of GQDs in various applications and comparison of methods in fabricating GQDs. The priority of GQDs in sensory applications has been described as well. Finally, the limitations in GQDs in multiple applications are detailed and addressed.

2. World demand of GQDs

Besides all the promising carbon materials, GQDs has exceptional properties, making it unique in the context of electronic devices [33]. It is usually classified by its dimensions and chemical compositions [13]. The small dimension gives

inimitable quantum confinements and edge effects. This ensuing excellent fluorescence characteristics and adjustable photoluminescence makes it great for bioimaging optical sensing, drug delivery, electrochemical, biosensors, and photovoltaics [25,34,35].

According to Arvand et al. [15], GQDs has a bigger of carboxyl, is small in volume, and conductive, making it excellent for making nano-sized, sensitive, stable and low cost electrochemical sensor [36]. The application of GQDs reduces costs, and Li et al. [1] pointed out that GQDs are expected to overtake solar cells in reduced cost and light-emitting diode (LEDs). It could also enhance the capability of supercapacitors and batteries lithium type (LIBs). They also stressed that GQDs can be functionalized with complex surface groups, especially for oxygen-related functional groups such as carboxyl [37] and hydroxyl [38]. These surface groups improve the optical properties GQDs [38] and make it dispersible in aqueous medium. Also, heteroatoms, such as nitrogen [39], sulfur [40] and other elements enhance the luminescence and electrical conductivity of GQDs significantly by tuning its electronic structures [41]. Zheng et al. [42] highlighted that GQDs is effective in drug delivery due to its small size and its provision of immediate visual monitoring of kinetic release. The exceptional catalytic and physicochemical properties render it excellent in numerous bio-medical applications. According to Vinoth et al. [43], GQDs is outstanding in biocompatibility, chemical inertness, toxicity, and conductivity, making it excellent in bio-sensing, cell imaging and a potential class of solar cells and bio-imaging probes. Also, the GQDs possess rich functional groups at its edges, due to the presence of carbonyls and carboxylic acid groups, which are easily soluble in water and susceptible to functionalization [44].

Zhou et al. [45] outlined that GQDs can be used as a fluorescent probe for detecting ions and as biomaterial due to its higher photostability. It guarantees stable signal in fluorescence, which will in turn result in accurate detections. They also revealed that the qualitative detection of the analyte can be obtained by monitoring the varying intensity of fluorescence. There is no need for expensive instruments, time consuming operations, and complicated pre-treatments. GQDs are also low in toxicity and environmentally friendly.

3. Synthesis methods of GQD

There are two methods for synthesizing GQDs; top-down and bottom-up [46]. Choi [47] claims the two-down method is popularly used compared to bottom up method in synthesizing GQDs. It starts from allotropes of carbon, such graphene, graphene oxide, reduced graphene, and graphite. However, both methods have their respective advantages and disadvantages.

3.1. Top down approaches

The top-down method involves cutting graphene sheets into GQDs by chemical ablation [48], mechanical grinding [49], and electrochemical synthesis [50]. Approaches include lithography in nanoscale [51], oxidation [52], hydrothermally or solvothermal [53], aided with microwave [54], aided with

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