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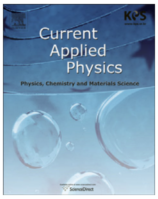

Graphene quantum dots and their possible energy applications: A review

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ABSTRACT

As new carbon-based materials, graphene quantum dots (GQDs) many advantages due to the additional unique properties that arise from their nanoscale small size. GQDs are expected to be suitable for various applications. For use of GQDs in various fields, mass production is critically required. To date, many methods for preparing GQDs with good properties and high yield have been introduced. The main synthesis strategies are known as bottom-up and top-down methods. Synthesis of GQDs from small organic molecules, known as the bottom-up approach, is appropriate for controlling the size of GQDs but requires multistep organic reactions and purification at each step. However, the top-down approach of breaking the carbon-carbon bonds of a large carbon source is easy and simple, and therefore suitable for mass production. Here, we briefly introduce the solution-process synthesis of GQDs using a top-down method and recent energy-related applications such as capacitors, lithium ion batteries, and solar cells.

1. Introduction

The discovery of graphene with sp^2–sp^2 carbon bonds and its subsequent development proved the way to a new generation of various devices due to its superior properties such as extremely high mechanical stiffness, strong elasticity, high thermal stability, and electrically high conductivity [1,2]. Intrinsically, graphene itself does not have a bandgap but can be opened by controlling the size, such as a nano-ribbon strip, and by introduction of other hetero atoms and defects into the graphene moiety.

On the other hand, graphene quantum dots (GQDs) that consist of nanometer-scaled graphene particles with sp^2-sp^2 carbon bonds are expected to show characteristic properties such as size-dependent general quantum dots (QDs) [41,42] or chemically modified quantum dots with sp^2-sp^2 carbon bonds. In contrast to graphene, most applications of GQDs have been focused on the photoluminescence (PL)-related fields since GQDs show a PL. In recent studies, additional excellent properties of GQDs such as high transparency and high surface area have been proposed for energy and display applications [44]. Because of the large surface area, electrodes using GQDs are applied for capacitors [44] and batteries [45,46], and the conductivity of GQDs is higher than that of graphene oxide (GO) [51]. In particular, their hole transporting ability is good, therefore GQDs can be applied for hole transport layers. In addition, due to their nm size, GQDs are well dispersed in various organic solvents to allow many organic reactions and solution processes. Therefore, with further modifications and with different synthesis conditions GQDs can be modified to show different PL colors, indicating changes in band gap. For commercially available products, the mass preparation of GQDs and simple device fabrication become important issues. For these purposes, the solution process with well-dispersed GQDs in various solvents is preferred.

Here, we introduce the solution-process synthesis of GQDs using a top-down method and energy-related applications such as capacitors, lithium ion batteries, and solar cells. Fig. 1 illustrates the unique properties of GQDs with energy related applications.

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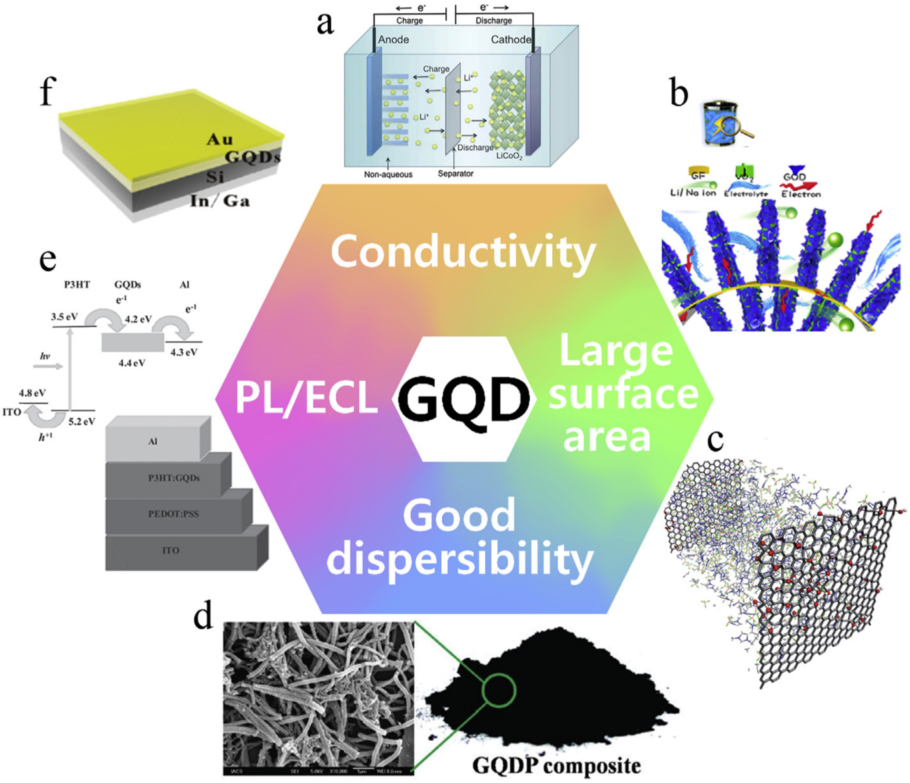

Fig. 1. a) Illustration of general Li ion battery [55]. b) Schematic illustration of the GVG electrode with bicontinuous electron and Li/Na ion transfer channels for Li/Na battery [45]. c) Illustration of supercapacitor electrode [54]. d) Solution processed GQDs with conducting polymer composite [43]. e) Illustration of general mechanism of solar cell [21]. f) Schematic illustration of Si/GQDs hetero junction solar cell [52]. Reprinted with permission from refs. [21,43,45,52,54,55]. Copyright 2011, 2014 and 2015.

2. Synthesis

There are many methods for synthesizing various quantum dots (QDs). Among them, top-down and bottom-up strategies are well categorized [3]. For general metal QDs, the bottom-up method is preferred over the top-down approach because it is much easier to uniformly control the size, which is directly related to the band gap of QDs.

In the case of GQDs, the size also can be controlled through a cage-opening of fullerene [4] and by organic synthesis using the bottom-up method [5,6]. However, preparation of GQDs using the bottom-up method requires very stringent conditions with specific organic materials after complicated reaction steps [5,6].

On the other hand, preparation of GQDs using the top-down method that involves cutting down bulk carbonaceous materials into small pieces is preferred, as described below. The starting materials are abundant raw carbon materials that can be cheaply and easily prepared. In addition, due to the simple preparation steps, researchers are trying to develop top-down methods for mass production. For starting materials, GO is a good candidate because it contains an abundance of oxygen-containing functional groups that can be easily broken down into nanometer sized and single-layered GQDs (Fig. 2a) [8]. However, since the preparation of GO itself involves several processes [7], the direct use of a natural resource without specific production processes, such as graphite, as a starting material has recently been introduced. The yield of GQDs from graphite is not high since natural graphite does not have enough functional groups. To enhance the yield of GQDs various methods have been investigated, including the use of strong acidic conditions like a modified Hummers method and the use of microwaves as an external power source [29,30]. In general, for controlling the size of QDs, sorting the size of quantum dots using top-down strategies has been tried [11,33,34]. Until now, however, generating uniform diameter GQDs at the synthesis step by applying the top-down method has not been greatly successful, although separation of GQDs according to the diameter size have shown marginal success.

In this review paper we focus on the various synthetic methods to prepare GQD, in particular with the top-down solution process, for a high product yield from GO, graphite, or other carbon materials as starting materials.

2.1. Starting materials and methods for making GQDs

2.1.1. Graphene and graphene oxide

The functional groups on graphite play an important role in breaking down the carbon-carbon bonds of graphite, so single or few layered GO is one of the best starting materials [8]. The GO nanosheets are functionalized enough with oxygen-containing groups that can be easily broken down into small parts and also well dispersed in various solvents, especially in water. Due to these advantages, there are numerous reports of the use of GO as the starting material for the synthesis of GQDs in solution phases.

2.1.1.1. Hydro- and solvo-thermal methods. Pan et al. suggested a solution process for GQDs from oxidized graphene sheets (GS) involving a hydrothermal method at 200 °C [8]. To increase the product yield, they oxidized the graphene sheets to introduce more oxygen-containing groups such as ketone, carboxyl, hydroxyl, and ether groups. The size of GS is reduced during the oxidation and reduction processes. As a result, GS becomes GQDs with 9.6 nm average diameter after hydrothermal de-oxidation with