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Microwave bottom-up route for size-tunable and switchable photoluminescent graphene quantum dots using acetylacetone: New platform for enzyme-free detection of hydrogen peroxide

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ABSTRACT

We report a microwave sequential bottom-up route to produce green and blue luminescent graphene quantum dots (g-GQDs and b-GQDs) with size-tunable and switchable functionalities by tailoring the diameter size and functional groups via microwave carbonization and aromatization processes from acetylacetone as a starting organic solvent. The b-GQDs as the final product show only one emission peak at 433 nm and pH-independent blue luminescence, because two-step microwave irradiation could reduce the size and the oxygen-functional groups of the g-GQDs as an intermediate product. Also, the b-GQDs provide an exemplar enzyme-free platform for hydrogen peroxide detection through the electrochemical sensing due to much higher electron density and electron donating properties. In contrast, the g-GQDs show two different switchable photoluminescent emissions at ~460 nm (P1) and ~500 nm (P2): the P1 emission with sky-blue fluorescence originates from randomly conjugated oxygen-functional groups on the basal plane and/or edge of the g-GQDs and the P2 emission with green fluorescence results from quasi-molecular fluorophores formed by the electronic coupling of carboxylic acid groups.

1. Introduction

Graphene quantum dots (GQDs) have been newly recognized as one of the essential nano-materials due to their unique and startling properties such as quantum confinement, tunable band gap, stable fluorescence, high surface area, and high electrical conductivity [1–10]. By modulating their size, surfaces and edges, the band gap and photoluminescences of GQDs can be also tailored for a specified target application. Additionally, GQDs are empowered with low cytotoxicity,

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excellent solubility, chemical inertia, and good surface grafting, thus making them exemplar in the fields of optoelectronics, sensors and bio-imaging [2,11–14].

The most fascinating feature of GQDs is their photoluminescence (PL). The PL phenomena of GQDs have been qualitatively explained with exciton of carbon, emissive traps, quantum confinement, aromatic structures, oxygen-containing functional groups, free zigzag sites and edge defects [1,15]. However, a meticulous quantitative explanation is beyond the ken of present knowledge and the exact mechanism of GQDs remains unsettled. Until now, various synthetic routes of fabricating GQDs have been intensively investigated including top-down [11–21] and bottom-up [22–26] approaches. Methods of cutting carbon fibers [17], graphene sheet and graphene oxide [4,16,20] are classified into the top-down method. The bottom-up strategy involves the formation of GQDs via stepwise solution chemistry of oxidative condensation reactions, *via* molecular precursor with cage-opening of fullerene [25], *via* carbonizing of some special organic precursor like glucose or citric acid using hydrothermal treatment [22,24], and *via* reduction of a pre-synthesized polycyclic aromatic hydrocarbon hexa-peri-hexabenzocoronene precursor [23]. However, some bottom-up routes reported before release toxic and harmful gases and waste, requiring tedious and additional process steps to resolve much concerned negative ecological aspects [23–25,27].

For the practical engineering applications, the PL of GQDs should be controlled by tailoring the size [16,17], zigzag and/or armchair distribution [12], and residual defects of GQDs [3,18,19]. However, some previous methods are not suitable for the precise control of these parameters because of a non-selective chemical cutting, a random reduction process, and complicated multistep processes. Therefore, there is a need for a better prototype of the synthetic route, which not only aids easy, economical, ecological and reproducible production of the GQDs, but also allows for a precise control over the size and emission-color of the GQDs. Until now, fluorescence has been extensively applied to various sensors including biosensors. Recent reports manifest GQDs as a potential material for efficient and selective electrochemical sensing, by utilizing better electron accepter and transporter of GQDs [29]. Most GQD biosensors require enzymes or cross-linkers to detect specified chemicals and biomolecules. But, the cross-link binders can critically degrade the durability and life of biosensors by the contamination of the GQD sensor and uncontrolled desorption mechanism [5,29]. Carbon quantum dots also was used to develop a sensitive fluorescent sensor for H_2O_2 detection in aqueous media by quenching in fluorescent intensity [30]. The graphene and glassy carbon electrode can exhibit fast electron transfer for $Fe(CN)_6^{3-/4-}$ redox couple and can be used for a sensitive detection of the enzyme-free detection of H_2O_2. So, the enzyme-free detection of some chemicals and biomolecules can be a challenging topic for reliable and repeatable GQD biosensors.

Herein, we report a novel microwave assisted bottom-up method to produce functionally switchable and size-tunable GQDs by microwave carbonization and aromatization processes of a simple and economical organic solvent, acetylacetone (AcAc). Due to the weak acidic nature of AcAc, the dehydration and decomposition reactions proceed in a controlled manner under microwave irradiation and subsequently the formation of aromatic clusters take place *via* aldol condensation in the presence of H^+ as a catalyst and cycloaddition as described in Supplementary information. Our two-step sequential route to produce a green PL emitting GQD (g-GQD) and a blue PL emitting GQD (b-GQD) provides a succinct control over the size and functional groups by modulating microwave power and irradiation time as shown in Fig. 1. However, the AcAc starting material does not have a distinct PL emission from 350 nm to 500 nm, as shown in Fig. S1. The g-GQDs having carbonyl and carboxyl groups exhibit quasi-molecular fluorophores as an intermediate product with narrow green emission band width, while b-GQDs having specific hydroxyl functional groups exalt the blue luminescence with splendid functionalities of pH-independence and enzyme-free detection of H_2O_2.

2. Experimental section

2.1. Materials

Acetylacetone (99% purity), Sodium phosphate monobasic (NaH_2PO_4, 98%), sodium phosphate dibasic (Na_2HPO_4, 99%), sodium hydroxide (NaOH, 97%), and Phosphoric acid (H_3PO_4,

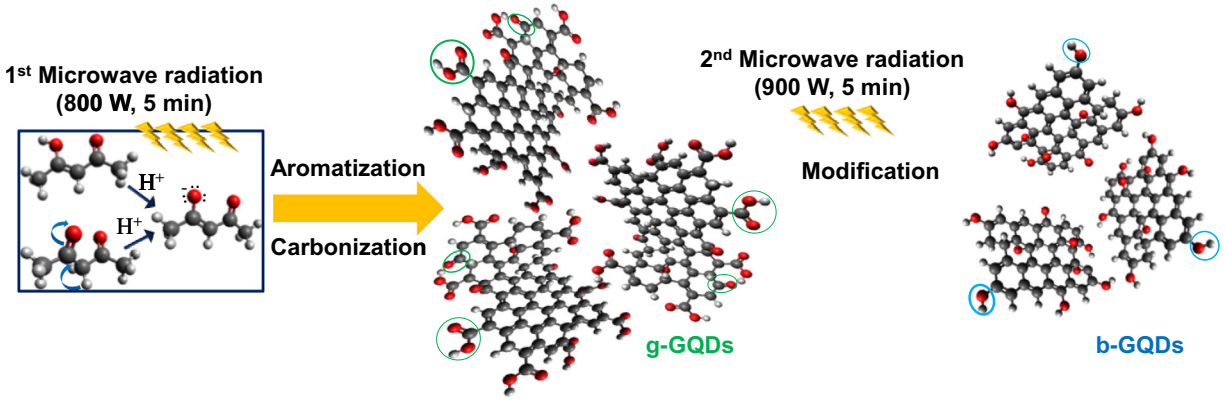

Fig. 1 – Schematic illustration of microwave bottom-up route for g-GQDs and b-GQDs: green circles mean carboxyl and carbonyl groups and blue circles indicate hydroxyl groups. (A color version of this figure can be viewed online.)

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