

A solvent-free gaseous detonation approach for converting benzoic acid into graphene quantum dots within milliseconds

Honghao Yan, Chuang He, Xiaojie Li*, Tiejun Zhao

State Key Laboratory of Structural Analysis for Industrial Equipment, Dalian University of Technology, Dalian, Liaoning 116024, China

ARTICLE INFO

Keywords:

Graphene quantum dots
Gaseous detonation
Formation mechanism
Photoluminescence mechanism

ABSTRACT

Graphene quantum dots (GQDs) in high reproducibility are synthesized by a gaseous detonation method which converts untreated benzoic acid (BA) precursor into powdered GODs without complicated post-treatment in 3–5 ms. The as-prepared GQDs resulting in an absolute photoluminescence quantum yield (PLQY) of 21.5% exhibit dual-wavelength-independent emission with the maximum PL emission at 431 nm and 460 nm under excitation maximum at 300 nm dispersed in ethyl alcohol. Based on surface structure, photoluminescence (PL) behaviors of GQDs and the characteristics of gaseous detonation, the formation mechanism of GQDs is speculated. Moreover, further study regarding the optical properties of reducing GQDs (R-GQDs) and thermal annealing GQDs (A-GQDs), it is possible to reveal PL mechanism of GQDs. This research not only provides a one-pot solvent-free route to rapid and large-scale preparation of GQDs, but also accounts for the hypothetical formation and PL mechanism of the obtained GQDs.

1. Introduction

Graphene quantum dots (GQDs), being a dazzling star in the nanocarbon family, are graphene nanosheets of less than 100 nm size [1]. The superior properties, such as resistance to photo-bleaching [2], good biocompatibility [3–6], and tunable luminescence [6–8] make them popular in fluorescent probes [9, 10], bio-imaging [6, 11–13], and optoelectronic devices [14, 15]. Generally, the synthetic approaches of GQDs fall into top-down and bottom-up [16, 17]. The top-down approaches involve cutting bulk graphene sources into GQDs via hydrothermal [8] or solvothermal method [13], electrochemical approach [18], microwave-assisted route [12], ultrasonic shearing [19], and acid oxidation [20], while bottom-up approaches are achieved using organic molecules to synthesize graphene moieties with a conjugated structure through microwave synthesis [2, 15] or solution chemistry [21, 22]. So far, the microwave synthesis is popular by virtue of simple synthetic scheme, time-saving process and cheap precursors without acid-free treatment [2, 15]. However, the limitations of microwave synthesis are not to be sneezed at, such as a little production and complicated post-treatment to obtain powdered GODs. Recently, some new synthetic approaches such as high-energy ball milling [23] and chemical vapor deposition [24] have been reported. Compared with the microwave synthesis, new synthetic approaches have some successes in production or post-treatment, but the disadvantages are evident such as time-consuming process and low yield. Therefore, a facile, rapid and efficient

synthetic approach of GQDs is still highly desirable.

Gaseous detonation, which uses combustible gas and oxygen as explosion sources to generate detonation wave that gives rise to a complex and fast series of chemical reactions in the precursors after ignition, has been successfully applied in materials synthesis, such as carbon nanostructure materials [25, 26] and metal oxides [27, 28]. The gaseous detonation approach can directly produce powdered nanomaterials on a large scale within milliseconds using untreated precursors [26]. As far as we know, the synthesis of GQDs by gaseous detonation has not been reported.

Herein, we report a one-pot gaseous detonation approach to prepare GQDs with untreated BA as the carbon source and hydrogen and oxygen as the explosion source. It is effortless to synthesize powdery GQDs directly within milliseconds by the gaseous detonation approach which is much faster than that of the hitherto reported synthetic method of GQDs. More importantly, through controlling detonation parameters, the results about GQDs are in high reproducibility. The obtained GQDs resulting in an absolute PLQY of 21.5% exhibit dual-wavelength-independent emission with maximum PL emission at 431 nm and 460 nm under excitation maximum at 300 nm. Moreover, stable PL behaviors within pH 3.0–14.0 and high resistance to photo-bleaching are observed. Based on surface structure, PL behaviors of GQDs and the characteristics of gaseous detonation, the formation mechanism of GQDs is speculated. Furthermore, further study regarding the optical properties of R-GQDs and A-GQDs, we try to reveal the possible PL

* Corresponding author.

E-mail address: 923309973@qq.com (X. Li).

mechanism of GQDs.

2. Experimental

2.1. Materials

BA, absolute ethyl alcohol and NaBH_4 were purchased from Sinopharm Chemical Reagent Co. (Shanghai, China). Hydrogen and oxygen with the purity of 99.999% were purchased from Dalian Special Gases Co. (Dalian, China). All chemicals were used as received without further purification.

2.2. Synthesis of GQDs

A self-made detonation titanium tube, which could achieve thermoregulation by an oil heater around the tube, was used to carry out the experiment. The tube, being a cylinder container with inner diameter of 100 mm, length of 1100 mm and volume of 8.6 L, which could be sealed by flange plates with rubber ring, possessed vacuum-pumping system, temperature-controlling system, pressure-monitoring system and high-energy-igniting system. A vacuum pump, which connected the detonation tube via an exhaust pipe, was the main part of the vacuum-pumping system. The temperature-controlling system could adjust the heating temperature up to 473.15 K while the pressure-monitoring system was able to monitor the internal pressure in real time. The high-energy-igniting system contained a high-energy igniter located the end of the detonation tube which could generate over 40 J ignition energy to detonate the combustible gas mixture. Fig. 1 exhibits the schematic of the detonation tube.

GQDs were prepared as follows: BA (4 g) as carbon source was tiled in the detonation tube. Secondly, the flange plates and vacuum-pumping system were used to seal and vacuumize the tube, respectively. Then, the temperature control system was taken advantage of to heat the gaseous detonation tube to 393.15 K. The amount of sublimation of BA could be determined by observing the variation of the pressure-monitoring system. Hydrogen and oxygen were pumped into the tube, respectively. The molar ratio of BA, hydrogen and oxygen was 3:8:8. It took 2–3 min to blend the gases spontaneously. The pressure was controlled below 0.75 atm. Finally, the high-energy igniter was made use of to detonate the gas mixture. Consequently, the BA was transformed into powdery GQDs within 3–5 ms under the effect of detonation of gas mixture. After cooling down to 333.15 K, black powdered GQDs (0.21 g) in the detonation tube were collected. The as-obtained GQDs didn't conduct any kind of purification. The time spanning the whole experiment could be controlled within 60 min.

2.3. Preparation of reducing GQDs (R-GQDs) and thermal annealing GQDs (A-GQDs)

The as-obtained GQDs (0.01 g) were dissolved in the ethanol solution (10 mL). Then the distilled water (10 mL) and Sodium borohydride (NaBH_4 , 0.05 g) were added to GQDs ethanol solution under vigorous stirring at room temperature for overnight. The R-GQDs were obtained by drying.

The A-GQDs were obtained using a tube furnace to heat the as-obtained GQDs (0.01 g) put in a quartz boat at 723.15 K for 15 min under nitrogen atmosphere.

2.4. Instrumentation

High resolution transmission electron microscopy (HRTEM) images were recorded on a Tecnai F30 field-emission electron microscope operating at 300 kV (FEI, USA). The test sample for TEM was prepared as follows: GQDs were diluted in absolute ethyl alcohol and the suspension dropped on carbon-coated copper grid by evaporation in the air. Atomic force microscopy (AFM) images were measured in the tapping mode on a MultiMode3D atomic force microscopy with a tip type of RTESP (Veeco, USA). The test sample for AFM was prepared as follows: GQDs ethanol solution was spotted onto a fresh silicon slice and dried in air. X-ray diffraction (XRD) patterns were confirmed by an X-ray diffractometer (Rigaku D/MAX 2400, Japan) using $\text{Cu K}\alpha$ as excitation source ($\lambda = 0.15406 \text{ nm}$) with $6^\circ/\text{min}$ scanning speed. Raman spectra were performed using an excitation wavelength at 532 nm by XploRA Raman spectrometer (Horiba Co., France). The as-prepared powdery GQDs without any treatment were used for Raman test. X-ray photoelectron spectroscopy (XPS) was carried out using X-ray photoelectron spectrometer (Thermo ESCALAB 250, USA) with an $\text{Al K}\alpha$ 280 eV radiation source and the C1s peak at 284.8 eV as a binding energy calibration. UV–vis absorption spectra were obtained using a UV–vis-NIR spectrophotometer (Perkin-Elmer Lambda 750, USA) with a 1.0 cm quartz cell. Fourier transform infrared (FTIR) spectra were characterized by a Nicolet-6700 FTIR spectrophotometer (Thermo, USA) from 500 to 4000 cm^{-1} using KBr pressed disks. PL spectra were recorded by a F-7000 fluorescence spectrophotometer (Hitachi High Technologies, Japan) employing a 1 cm quartz cell at room temperature. The absolute PLQY of the GQDs was obtained using the Quantaury-QY Instrument (Hamamatsu Photonics CO. Ltd., Japan). GQDs ethanol solution diluted to the absorbance of 0.1 was prepared for absolute PLQY test. The pH values were acquired employing a PB-10 pH-meter (Beijing Sartorius Instruments Co. Ltd., China). The thermal annealing operation was achieved by a tube furnace (Hefei Kejing Materials Technology Co. Ltd., China).

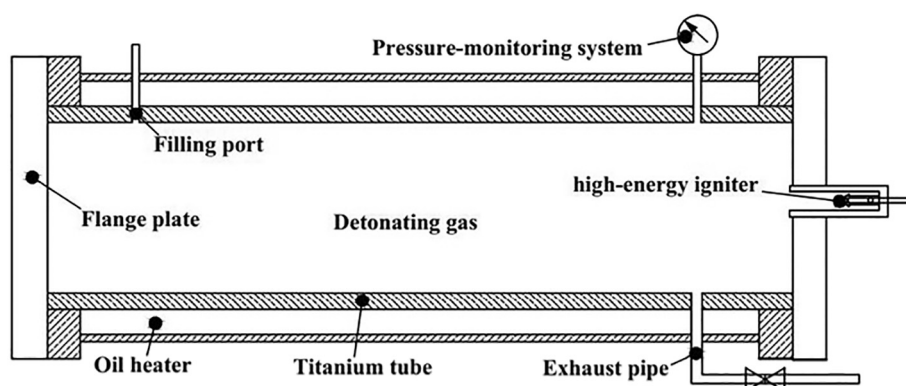


Fig. 1. Schematic of detonation tube.

Download English Version:

<https://daneshyari.com/en/article/7110794>

Download Persian Version:

<https://daneshyari.com/article/7110794>

[Daneshyari.com](https://daneshyari.com)