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Structural evolution of graphene quantum dots during thermal decomposition of citric acid and the corresponding photoluminescence

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ABSTRACT

The thermally decomposed citric acid (TDCA) possesses either excitation-dependent or excitation-independent fluorescence as well as different quantum yields with varying synthesis conditions (i.e. temperature and reaction duration). These photoluminescent (PL) properties were found to be mainly determined by the quantitative competition between the graphene quantum dots (GQDs, average size in the range 0.7–1 nm) and the large-inhomogeneously-sized particles. Thermal induced reduction of oxygen containing functionalities leads to an enhancing effect to the PL of GQDs. The study reveals the structural evolution of the GQDs upon thermal treatment and attempts to establish their relationship to the PL property. The GQDs synthesized in this study are excellent sensing materials for trivalent iron cation with both notable selectivity and sensitivity.

1. Introduction

Graphene sheets smaller than 100 nm show quantum confinement behaviour which generates band gaps in their electronic band structures [1] in contrast to the well-known zero-gap feature of graphene sheets with much larger sizes [2]. This type of derivative of graphene is named graphene quantum dots (GQDs). Many theoretical and experimental studies have been carried out and revealed the excellent properties of GQDs including electronic properties [3–5], magnetic properties [6–8], and photoluminescent properties [9]. Due to these interesting properties, GQDs have great potential in a variety of advanced applications such as single-electron transistor [3], spintronics [10], energy conversion [5,11], memory [12], optoelectronics, sensing, and bio-imaging [13]. Moreover, compared with their counterparts semiconductor quantum dots, GQDs have competitive advantages with respect to their massless charge carriers [14], profound edge effects [15] and low cytotoxicity [16]. These characteristics can provide an environmental friendly and higher performance "dot" in applications where conventional semiconductor quantum dots are currently used.

Issues with the synthesis of GQDs are currently restricting the use of them. The current methods to prepare GQDs could be categorised into two groups, namely top-down and bottom up methods. The top-down methods include hydrothermal cutting [9,17,18], solvothermal cutting [19,20], microwave assisted cleaving [21], electrochemical method [22–24], oxidation of carbon fibre [25] or carbon nanotube [26], exfoliation of graphite nanoparticles [27], cage open of fullerenes [28] and

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improved Hummer's method [16]. All these methods involve cutting graphitic materials of large sizes into small fragments with sizes in the range of GQDs. In contrast to the relatively extensive research on top-down approaches, just a few researchers have investigated bottom-up synthesis routes despite their superiority in controllable size and uniform structures. The limited studies on bottom-up methods have used organic carbon precursors such as polyphenylene dendritic [11,29], hexa-peri-hexabenzocoronene [30], glucose [31]. Although different types of GQDs have been synthesized from these bottom-up methods, the routes of synthesis are quite complex.

Recently Dong et al. [32] have reported a GQDs preparation method by simply heating citric acid at 200 °C. However, this work simply regards the overall products of citric acid thermolysis as GQDs for short reaction durations (30 min) and as graphite oxide (GO) for longer duration (2 h). In this work, we provide detailed examination on the relationship between the synthesis conditions (temperature, duration) and product properties (physiochemical and optical), which is highly important for obtaining a good understanding of the reaction mechanism and device optimisation strategies. It also intends to provide a detailed account on the structural evolution of TDCAs during thermal decomposition, and an in-depth insight on the structure–property relationship of GQDs, which is a part of TDCAs. In addition to the new findings which could explain the evolution of PL behaviour of TDCAs versus temperature and reaction duration, this study also demonstrates the sensing potential of the as-synthesized GQDs to Fe^{3+} cation.

2. Experimental

2.1. Synthesis of thermally decomposed citric acid (TDCA)

A 50 ml round flask was placed into a silicone oil bath. After the oil bath was heated to desired temperatures (i.e. 180, 200, 230 and 270 °C), 500 mg of citric acid (CA, Chem-Supply) was added into the flask. Upon the completion of reaction for desired duration, 15 ml of sodium hydroxide solution (Chem-Supply) (0.5 mol/L) was added to the flask. After the sample was completely dispersed into the solution, the dispersion was transferred to a 100 ml beaker and magnetic stirred for 15 min. The pH of the final dispersion was then adjusted to 7.

2.2. Dialysis of TDCA

10 ml of as prepared dispersion was added to a 3.5 kDa dialysis tube membrane (Spectrum Labs). The tube was then immersed into a 20 ml of DI water in a 50 ml beaker for 24 h. The remaining solution (GQDs solution) in the beaker was collected after the tube was removed. The removed 3.5 kDa tube membrane along with the remaining solutions inside was then subject to further dialysis for another 24 h for purification. The solution collected from the beaker was added into a 1 kDa dialysis tube membrane then allowed for 24 h of dialysis to purify the GQDs.

2.3. Preparation of GQDs dispersions with different cations loading

GQDs dispersions with an absorbance of 0.15 at 370 nm under UV/Vis were prepared by diluting the parent solution which was obtained by dialysis of TDCA synthesized at 200 °C for 30 min. The PH of all the GQDs solutions, for both test of selectivity with different cations and construction of calibration curve for detectable cation (Fe^{3+}), were fixed at 6.9 by applying a buffer composed of mixed phosphate salts (Rex, INESA Scientific Instrument). $FeCL_3{\cdot}6H_2O$, $CaCl_2$, $ZnSO_4{\cdot}7H_2O$, $CuSO_4{\cdot}5H_2O$, $MgSO_4$ (Chem-Supply) were added into the GQDs dispersions to form dispersions with the same cations concentration at 0.25 mM for the test of selectivity. Since the amount of added cations in the solutions is very small, the influence to the concentration of GQDs is negligible. For acquisition of the calibration curve of detectable cation (Fe^{3+}), a series of loading of Fe^{3+} from 1 μM to 1 mM were adopted.

2.4. Characterisation

Fluorescence spectra were collected through a Fluorescence spectrometer (Thermo Scientific Lumina). An UV/Vis spectrometer (Agilent 8453) was applied for acquisition of the absorption spectra. Quantum yields (QY) were measured by using quinine sulphite standard solution (quinine sulphite dissolved in 0.05 M H_2SO_4, Quantum yield 54%) as the reference. All samples for quantum yields measurement were prepared by diluting the original samples to the extent that the solution absorbance at 370 nm is below 0.05. Elemental compositions were analysed by X-ray photoelectron spectroscopy (XPS, Kratos Axis Ultra). Particle size measurement was conducted via dynamic light scattering (DLS, Malvern Zetasizer-Nano ZS). Transmission electron microscopy (TEM) of both low (JEM-1010) and high (Philips Tecnai F20) resolutions, along with AFM (NT-MDT NTEGRA Spectra) were employed for the morphology analysis of the as-prepared samples.

3. Results and discussion

3.1. PL properties of TDCAs

Excitation independent fluorescence spectra were obtained for TDCAs synthesized at lower temperatures (i.e. 180 and 200 °C) and for relatively shorter durations (<40 min), however, at lower temperatures for longer durations and at higher temperatures (i.e. 230 and 270 °C) even with duration as short as 5 min (Fig. S1), samples with excitation-dependent fluorescence spectra were obtained as shown in Fig. 1. Fig. 2 shows the quantum yields (QYs) for TDCAs synthesized at fixed temperature 200 °C with varied reaction time (red round dots)) and for fixed duration of 20 min but at varied temperature (black square). For the fixed temperature at 200 °C, the QYs show a trend of gradual increase till peaking at 30 min followed by a decrease with the extension of reaction time. On the other hand, for the fixed duration of 20 min, QY drops when temperature increases. It is worth noting that for all the excitation-independent samples there is a distinctive