

## Tailoring surface groups of carbon quantum dots to improve photoluminescence behaviors



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### ABSTRACT

A facile and green method to tailor surface groups of carbon quantum dots (CQDs) is developed by hydrothermal treatment in an autoclave. The photoluminescence (PL) behaviors of CQDs depend on the types of surface groups. Highly efficient photoluminescence is obtained through amino-hydrothermal treatment of the CQDs reduced by NaBH<sub>4</sub>. The effects of surface groups on PL behavior are attributed to the degrees of energy band bending induced by surface groups.

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## 1. Introduction

Recently, carbon quantum dots (CQDs) with the graphitic structure have received considerable attention as a new type of quantum dot because of their exceptional advantages such as large optical absorptivity, chemical stability, fine biocompatibility as well as low toxicity [1–4]. Unlike traditional quantum dots, their unique electronic and opto-electronic properties originate from structural defects since a perfect two-dimensional graphene lacks electronic bandgaps [1]. In fact, almost all of CQDs relevant to photoluminescence (PL) emissions can be observed structural defects though there are obviously many different ways to produce them [1–4]. It is totally confused that how the appropriate defects can be created in CQDs and why chemical functionalization can tune the bandgaps of CQDs. For example, PL emission from CQDs can be effectively improved and shifted by functionalizing them [5].

The defects in CQDs generally depend on the forming process (namely preparation method) and carbon source. For example, the amorphous structures are generally observed in CQDs from hydrothermal treatment of organic molecules while the structure of the products obtained from chemical oxidation and exfoliation

of carbon fibers have less defects [6–8]. Specially, both methods show the different PL behaviors, suggesting the effects of structural defects on PL properties. However, it is presently difficult to control structural defects in CQDs only through one method. By contrast, tuning the bandgaps of CQDs can be more readily realized through surface chemistry [1,9,10]. According to recent achievements [5,9–13], many elements (such as H, O, N, F, Cl) bonding with the surface of graphene and related materials give access to tunable electronic and optical properties. The progress for their underlying mechanism has been made so far. The suppression of the defect state emission was proposed to explain the role of surface functionalization in PL shift [10]. However, it is unclear now what the surface chemical structures are optimal for PL emission of CQDs and how they suppress non-radiative recombination of localized electron–hole pairs. To clearly understand the effects of surface chemical structures on PL behaviors, in this work, we carefully designed the surface groups of CQDs and proposed the dependence of PL behaviors of CQDs on the surface group-induced band bending. Furthermore, a method to enhance PL efficiency of CQDs was developed.

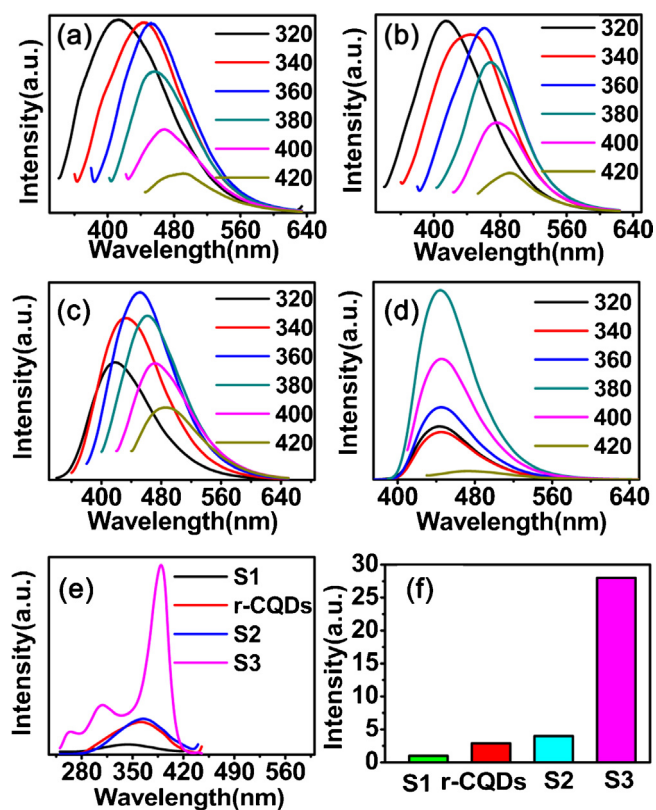
## 2. Experimental

### 2.1. Preparation of CQDs (S1)

The citric acid (1.05 g) was dissolved in DI water (25 mL). Then the solution was transferred to a poly(tetrafluoroethylene)

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**Fig. 1.** (a)–(d) PL behaviors of S1, r-GQDs, S2 and S3, respectively; (e and d) the comparisons of PLE and PL intensities of S1, r-CQDs, S2 and S3.

(Teflon)-lined autoclave (50 mL) and heated at 200 °C for 5 h. After the reaction, the reactor was cooled to room temperature naturally. Thus, the transparent solution containing CQDs were obtained and named as S1.

## 2.2. Preparation of the reduced CQDs (r-CQDs)

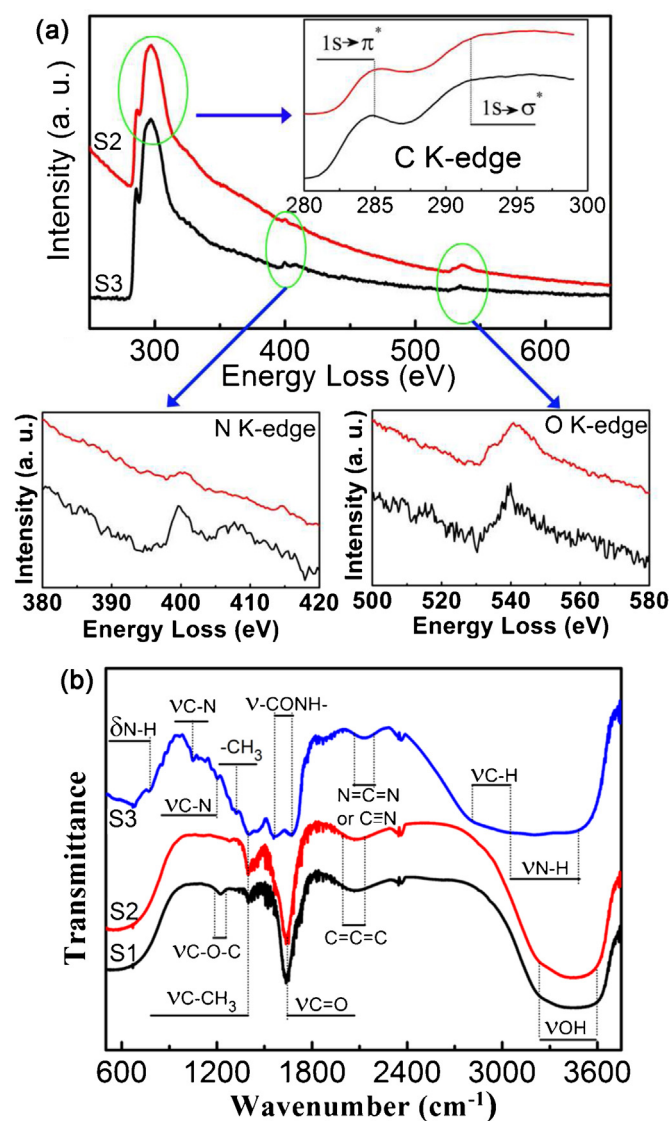
The r-CQDs were prepared by reported methods [2,16]. Briefly, as-prepared S1 (10 mL) solution was neutralized by  $\text{Na}_2\text{CO}_3$  or NaOH. Then 50 mg  $\text{NaBH}_4$  was dispersed in the neutralized S1 solution, and stirred gently overnight at room temperature.

## 2.3. Amino-hydrothermal treatment of S1

The S1 solution (10 mL) was mixed with 536  $\mu\text{L}$  of ammonia solution (28 wt%) in a glass vial and subjected to ultrasonication (500 W, 60 kHz) for 15 min, then the mixture solution was transferred to a poly(tetrafluoroethylene) (Teflon)-lined autoclave (50 mL) and heated at 70 and 200 °C for 5 h, respectively. Cooling to room temperature, the light yellow solution (named as S2) was obtained at 70 °C treatment while the dark brown solution (named as S3) was obtained at 200 °C treatment.

## 2.4. Preparation of S2-m and S3-m

The citric acid (0.42 g) was readily re-dispersed in DI water (10 mL) and then mixed with ammonia solution (28 wt%, 536  $\mu\text{L}$ ). After ultrasonic dispersion for 15 min, the mixture solution was transferred to the poly(tetrafluoroethylene) (Teflon)-lined autoclaves and heated at 70 °C and 200 °C, respectively, for 5 h. Finally, the white transparent at 70 °C (named as S2-m) and dark green solution at 200 °C (named as S3-m) containing CQDs was obtained after cooling to room temperature.



**Fig. 2.** (a) EELS spectra of S2 and S3; the insets show the EELS spectra of C K-edge, N K-edge and O K-edge of S2 and S3. (b) FTIR spectra of S1, S2 and S3.

## 2.5. Preparation of S4 and S5

The r-CQDs solution (10 mL) was mixed with 536  $\mu\text{L}$  of ammonia solution (28 wt%) in a glass vial. After ultrasonic dispersion for 15 min, the mixture solution was transferred to a poly(tetrafluoroethylene) (Teflon)-lined autoclave and heated at 200 °C for 5 h. Cooling to room temperature, S4 was obtained. The prepared S3 (10 mL) solution was neutralized by  $\text{Na}_2\text{CO}_3$  or NaOH and then adding 50 mg  $\text{NaBH}_4$  to the neutralized S3 solution. After gently stirring overnight at room temperature, one obtains S5.

## 2.6. Instrumentation and characterization

Fluorescence and absorption spectra were recorded at room temperature on a Hitachi F4500 fluorescence spectrophotometer and a Shimadzu UV-2550 UV/Vis spectrometer, respectively. Diluted supernatants containing CQDs were dropped onto copper grids covered with amorphous carbon film to prepare specimens for transmission electron microscopy (TEM) observation, which was performed in a FEI Tecnai G2F20 microscope with a field-emission gun operating at 200 kV, and electron energy loss spectroscopy

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