Journal of Luminescence 175 (2016) 88–93

Contents lists available at ScienceDirect

Journal of Luminescence

journal homepage: www.elsevier.com/locate/jlumin

Full Length Article

# Tuning surface properties of graphene oxide quantum dots by gamma-ray irradiation

Shunkai Lu, Fan Liao*, Tao Wang, Lili Zhu, Mingwang Shao*

*Jiangsu Key Laboratory for Carbon-Based Functional Materials & Devices, Institute of Functional Nano & Soft Materials (FUNSOM), Soochow University, Suzhou, Jiangsu 215123, China*

ARTICLE INFO

*Article history:*
Received 10 December 2015
Received in revised form
4 February 2016
Accepted 18 February 2016
Available online 27 February 2016

*Keywords:*
Graphene oxide quantum dots
γ-ray irradiation
Fluorescence quenching
Rhodamine 6G

ABSTRACT

Gamma-ray irradiation was employed to tune surface properties of graphene oxide quantum dots (GOQDs), such as functional groups and defect density. The GOQDs were first oxidized under γ-ray irradiation with doses ranging from 0 to 200 kGy, and then reduced under larger irradiation doses from 200 to 400 kGy. In other words, both the defect density and the number of surface functional groups increased first and then decreased along with the increasing irradiation dose. This process was confirmed with UV–visible absorption, X-ray photoelectron spectroscopy, Raman spectra and Fourier transform infrared spectra. In order to estimate their π-conjugated content, the GOQDs were served to quench the fluorescence of Rhodamine 6 G. The results showed that there existed a positive relationship between the π-conjugated content and the static quenching coefficient $V_qNa$, which might have a potential value.


## 1. Introduction

Graphene oxide quantum dots (GOQDs), single atom thick nanomaterials with abundant functional groups [1], have sparked considerable interest over the past few years. They can be regarded simply as composition of individual nanosheets of graphene decorated with various oxygen functional groups on both the basal planes and edges [2]. It is convenient and practical to prepare GOQDs by chemical or physical methods [3,4]. Owing to their specific structure and the existence of various oxygenated functional groups, GOQDs exhibit various kinds of excellent properties, which make them valuable in many potential applications [5,6]. Amongst them, quantitative analysis built on graphene oxide (GO)-based fluorescence quenching has been of increasing interest [7].

The convertible oxygenous functional groups of GOQDs promote the modification on the surface and make them promising materials for compositing with other materials [8]. Gamma-ray (γ-ray) irradiation is an eco-friendly and energy-saving method, which has been applied extensively as an attractive tool for the fabrication, modification and manipulation of carbon materials [9–11]. It is reported that defects and crystal lattice deformation of monolayer graphene could be produced after γ-ray irradiation [12]. The effect of γ-ray on GO would be different in various gaseous phase [13]. In addition, GO could be reduced after irradiation [14–16] owing to the decomposition of water after the γ-ray irradiation [17,18]. Although there are a number of recent studies on the effects of γ-ray irradiation on graphene [18–21], similar reports linked to GOQDs remain sparse.

In this work, the pristine GOQDs were irradiated by γ-ray with different irradiation doses. The results showed that the surface properties of GOQDs, such as functional groups and defect density, could be tuned with controlling the doses of γ-ray irradiation, which was characterized with UV–visible absorption, X-ray photoelectron spectroscopy (XPS), Raman spectra and Fourier transform infrared (FT-IR) spectra.

To further confirm the mutative surface properties, fluorescence quenching was conducted, which may supply a fundamental and valuable source of surface information [22–26]. It is considered that electron or energy transfer between them is responsible for the phenomenon [24]. Here, Rhodamine 6 G (R6G), a well-known organic dye with high photostability and quantum yield [27], was chosen as the fluorescent agent in the investigation of the fluorescence quenching process caused by GOQDs. With the help of various spectroscopic techniques, the γ-ray irradiation effects on GOQDs in suspension and the interaction between fluorophore and GOQDs with different irradiation doses were investigated. It was found that there existed the positive relationship between the static quenching coefficient $V_qNa$ and the π-conjugated content of GOQDs, which might find practical applications in the quantitative measurement.

* Corresponding authors. Tel.: +86 512 65880953; fax: +86 512 65882846.
*E-mail addresses:* fliao@suda.edu.cn (F. Liao), mwshao@suda.edu.cn (M. Shao).

http://dx.doi.org/10.1016/j.jlumin.2016.02.024
0022-2313/

## 2. Material and methods

### 2.1. Materials and chemicals

The pristine GOQDs were purchased from Shanghai Simbatt Energy Technology Company and diluted to 0.2 mg/mL. The R6G was obtained from Shanghai Chemical Company. A $1.0\times10^{-5}$ M stock solution of R6G was prepared. All chemicals were used as received without further purification.

### 2.2. Preparation of irradiated GOQDs

The GOQDs dispersion (0.2 mg/mL) was irradiated with a predefined absorbed dose and dose rate (2.5 kGy/h) by gamma ray in sealed tubes under room temperature. The irradiation process was carried out by the Radiation Technology Research Institute of Soochow University, using a Co-60 source. The total dose received by the samples was recorded by a dose meter.

### 2.3. Preparation of R6G-GOQDs complex

In fluorescence measurements, a 3.0 mL aliquot of stock solution ($1.0\times10^{-5}$ M) of R6G was transferred into a 4 mL colorimetric tube, and an appropriate amount (0–1.0 mL) of GOQDs with various irradiation doses (0–400 kGy) was added. The fluorescence spectra were recorded with an excitation wavelength of 365 nm.

### 2.4. Characterization

All the measurements were carried out at ambient conditions. UV–vis absorption spectra were obtained using a Lambda 750 UV–vis spectrophotometer. Raman spectra were collected with an HR 800 Raman spectroscope (J Y, France) equipped with a synapse CCD detector and a confocal Olympus microscope. A 514 nm laser was employed in all the Raman detections. The XPS measurements were obtained in a KRATOS AXIS Ultra DLD system using monochromatic Al Kα radiation (1486.6 eV). The full-width at half-maximum of the peak height (FWHM) of the $Ag3d_{5/2}$ for the high-resolution spectra was 0.48 eV. Transmission electron microscopy (TEM) and High resolution transmission electron microscopy (HRTEM) of GOQDs was performed on a Hitachi H-800. The zeta potential was measured by a dynamic light scattering instrument (Zetasizer Nano ZS, Malvern). FT-IR spectra were recorded on a Nicolet 5700 spectrometer (USA) in transmission mode. All fluorescence measurements were performed using a Horiba JobinYvon Fluoromax-4 spectrofluorimeter, while the fluorescence lifetime was measured with a Horiba JobinYvon FL-1057 spectrofluorimeter. A Supercontinuum Light Source System (Fianium SC400-4-PP) was used to provide excitation at 370 nm for the fluorescence lifetime measurements. Emission was monitored and kept at 556 nm by means of time-correlated single photon counting. Fluorescence lifetimes were obtained using a least-square fit of the experimental data with the instrument response function deconvoluted.

## 3. Results and discussion

### 3.1. The irradiation of GOQDs

High-resolution C1s spectra of GOQDs irradiated by 0, 50, 100, 200, 300, 400 kGy, respectively, are shown in Fig. 1. The spectra can be deconvoluted into 3–4 peaks, including binding energy at about 284.6 eV ($sp^2$ C–C), 285.4 eV (C–H), 286.1 eV (C–O), and 288.1 eV (C=O) [28,29]. As shown in Fig. 1, among the irradiation dose ranging from 0 to 200 kGy, gradually increased component

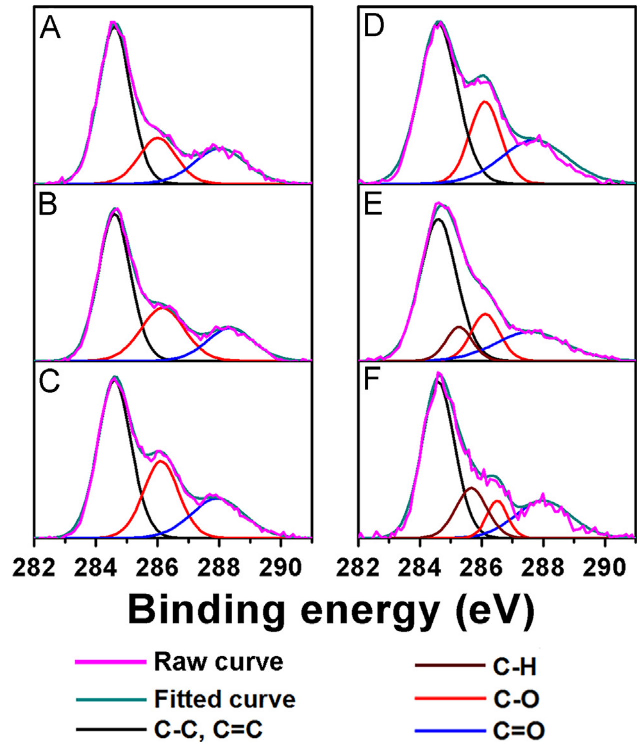


**Fig. 1.** XPS C1s spectra of GOQDs irradiated with different doses (A to F represent 0, 50, 100, 200, 300, 400 kGy, respectively).

for C–O and C=O could be observed, demonstrating the oxidation of GOQDs.

The γ-ray irradiation derived from Co-60 can decompose the water molecules to both oxidative (·OH) and reductive (·H and $e^-_{aq}$ ) species [17], and the generated $e^-_{aq}$ has the strongest reducibility [30]. In addition, the γ-ray is powerful enough to damage the bonds between atoms, leading to vacancies and defects [31]. During low-dose radiation, ring-opening carbon-bear free radicals would bond with oxygen came from the residual air in the suspension, which made dramatic increase of C–O and C=O. However, a new characteristic peak appeared corresponding to the C–H group at 285.4 eV. And the peak at 286.1 eV (C–O) decreased dramatically when the irradiation dose was increased to 300 and 400 kGy, indicating the reduction of GOQDs. The exhaustion of the residual oxygen in the suspension finally was conducive for the $e^-_{aq}$ to play the dominant role at large-dose irradiation. The C–O–C bonds would react with carbon free radicals linked with the irradiation induced H to form C–H, which would decrease the hydrophily of GOQDs. As shown in Fig. S1 (Supporting information), the zeta potential of GOQDs increased dramatically when the irradiation dose increased to 300 kGy, which is consistent with the reduction of oxygenous functional groups and the decreased hydrophility [32]. In addition, the carbon free radicals may bond with each other as well to form C=C bond [33]. Above all, the numbers of C–O and C=O groups increased first and then decreased, while the number of C–H increased monotonously in the irradiation dose of 0–400 kGy.

The morphological evolution of GOQDs under 0, 200, 400 kGy γ-ray irradiation is shown in Fig. 2(A)–(C). The diameter distributions of both raw and irradiated GOQDs calculated from the TEM images were generated as histogram plots in Fig. 2(D)–(F). As shown, the average lateral size of the raw and irradiated GOQDs with the dosage of 200 and 400 kGy is about 4.4, 5.6, and 3.5 nm, respectively. The TEM images of 100, 300 kGy GOQDs and the corresponding distributions of their average lateral size are shown in Fig. S2 (Supporting information). With irradiation dosage of