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Two-Photon Fluorescence in N-Doped Graphene Quantum Dots

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***Abstract*—**Nitrogen-doped graphene quantum dots (N-GQDs) were fabricated by microwave-assisted hydrothermal technique. The optical properties of the N-GQDs were studied. The luminescence of the N-GQDs can be tuned by varying the excitation wavelength. Furthermore, two-photon luminescence of the N-GQDs excited by near-infrared laser can be obtained. It is shown that N-doping play a key role on two-photon luminescence. The N-GQDs are expected to find application in biological applications including bioimaging and sensing.

***Keywords*—**Graphene quantum dots, nitrogen doping, photoluminescence, two-photon fluorescence.

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I. INTRODUCTION

GRAPHENE has been well-studied in recent years because of its many unique and novel properties such as superior mechanical flexibility, excellent thermal stability, large surface area and environmentally friendly nature. Due to its zero band gap, graphene exhibits no optical luminescence. In principle, the band gap of graphene can be tuned by varying its size. Compared to two dimensional graphene nanosheets and one dimensional nanoribbons, zero-dimensional graphene quantum dots (GQDs) possess strong quantum confinement and edge effects when their sizes are down to 10 nm, which induce new physical properties [1]-[5]. Hence, GQDs have potential application in many fields, such as photovoltaics, bioimaging, light-emitting diodes, and sensors [6]-[9]. Doping carbon materials with heteroatoms can effectively tune their intrinsic properties including electronic characteristics and chemical features. [10], [11] Among those candidates, nitrogen (N) atom has been widely used for chemical doping of carbon nanomaterials. For instance, N doped carbon nanotubes (N-CNTs) showed highly effective electrocatalytic activities for the oxygen reduction reaction [12], [13]. Similarly, doping of GQDs with N atoms could effectively tune the band gap to introduce new properties for device applications. Nitrogen-doped graphene quantum dots (N-GQDs) can be prepared by various methods such as hydrothermal, electrochemical, organic synthesis and self-catalysis [14]-[17]. The electrocatalystic activity [14], [15], tunable luminescence [16] and biocompatible application [16] have been demonstrated. Here, we report a facile "one-pot" microwave-assisted technique to fabricate N-GQDs using glucose and aqueous ammonia as sources. The N-GQDs show good fluorescent properties. They also have strong tunable luminescence from excitation of ultraviolet to visible range. Most interestingly, our N-GQDs exhibited two-photon luminescence which may find potential application in bioimaging or energy collection.

II. EXPERIMENTAL DETAILS

The N-GQDs were prepared by mixing 3 wt% of glucose dissolved in aqueous ammonia (25%) at room temperature. After the solution became homogenous, it was heated in a microwave reactor (CEM Discover SP) for 5 minutes at 180°C. The microwave power used was 300 W. In the process of microwave radiation, the solution color changed from transparent to pale yellow as a result of N-GQDs formation. The solution was cooled down to room temperature under atmosphere condition. Transmission electron microscopy (TEM) and high resolution TEM were carried out on JEOL, JEM-2100F at the operating voltage of 200 kV. The UV-Vis spectra were conducted by a Shimadzu UV-2550 UV-Vis spectrophotometer at room temperature. Photoluminescence (PL) measurements on the N-GQDs were performed using FLS920P Edwinburgh Analytical Instrument apparatus. Xe lamp was used as excitation source. The absolute quantum yield measurement were carried out using integrating sphere (Edwinburgh Instruments, 150 nm in diameter coated with barium sulphate). During the quantum yield measurement, the sample was placed into the cuvettes inside the integrating sphere. The two-photon fluorescence was measured by femto second (fs) pulse tunable Ti:sapphire laser (Coherent, Chameleon). The wavelength and power of the laser can be tuned during the measurement.

III. RESULTS AND DISCUSSION

The TEM image of the N-GQDs is shown in Fig. 1 (a). The prepared N-GQDs show monodispersed distribution. The HRTEM image, as shown in Fig. 1 (b) reveals high crystallinity of the N-GQDs. The corresponding selected area Fourier transform (FFT) image is shown in the inset of Fig. 1 (b), revealing the lattice fringes of the [110] and [$1\bar{1}0$] planes of graphite. The line profile analyze of the diffraction fringe of the N-GQDs is shown in Fig. 1 (c). The distance between the lattice fringes is 0.23 nm which is close to that of bulk graphite. It is worth noting that the in-plane lattice spacing (0.23 nm) is slightly larger than that of bulk graphite (0.21 nm), probably due to the introduction of N atoms into the hexagonal carbon matrix [18]. The size distribution of the N-GQDs obeys Gaussian distribution (Fig. 1 (d)). The most probable size is 5.9 nm with a full width at half maximum (FWHM) of 1.64 nm. Electron energy loss spectroscopy (EELS) is used to characterize the chemical composition and structure of the

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N-GQDs, as shown in Fig. 1 (e). There are four obvious peaks located at 285 eV, 296 eV, 401 eV and 408 eV. The first two peaks (285 and 296 eV) are attributed to the K-edges of C, corresponding to $1s \rightarrow \pi^*$ and $1s \rightarrow \sigma^*$ respectively. The latter peaks (401 and 408 eV) correspond to K-edges of N which associate with $1s \rightarrow \pi^*$ and $1s \rightarrow \sigma^*$ of C=N respectively [19]. The N/C atomic ratio of the N-GQDs is found to be 6.28%.

The UV-Vis absorbance spectrum of the N-GQDs is shown in Fig. 2 (a). There are three UV absorption peaks located at 215 nm, 272 nm and 302 nm. These peaks are associated with the electron transitions from π (or n) to π* of C=C, C=N and C=O respectively [18]. Comparing with the UV-Vis absorption of undoped GQDs (Fig 2 (b)), the GQDs exhibit two absorption peaks at 228 nm ($\pi \rightarrow \pi^*$ of C=C) and 283 nm ($n \rightarrow \pi^*$ of C=O).

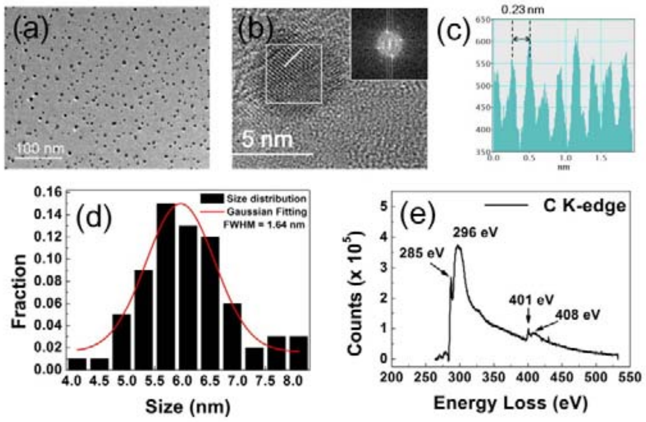

Fig. 1 (a) TEM image of the N-GQDs assembled on Cu grid coated with ultrathin amorphous carbon film. (b) HRTEM image of the N-GQDs. Inset: The fast Fourier transform (FFT) image of a selected area (white square). (c) The line profile analyses of the diffraction fringes. The lattice parameter is 0.23 nm. (d) Size distribution of the N-GQDs. (e) EELS spectrum of the N-GQDs

The excitation-dependent photoluminescence (PL) for the N-GQDs is shown in Fig. 2 (c). Similar to conventional carbon-based quantum dots [20], [21], the emission wavelength is dependent on the excitation wavelength. An emission peak at 520 nm is observed when the sample is excited by 350 nm. When the excitation wavelength changed from 350 to 520 nm, the PL peak shifted from 520 to 593 nm. As shown in Fig. 2 (d), the emission wavelength increases with the excitation in a linear relationship. The tunable PL can be explained in terms of surface states formed by the functional groups [22] at the surface of the N-GQDs. Briefly, the functional groups have different energy levels which results in a series of emissive traps. The surface state emissive trap dominates the emission at a certain wavelength. By comparing with the PL spectra of the undoped GQDs excited by various wavelengths, the emission peak of the N-GQDs shift to longer wavelength [6]. It is believed that N doping dominates the shift of the emission. The quantum yield (QY) of the N-GQDs was determined to be 8.4%, which is comparable to undoped GQDs prepared by other methods [19]-[21], [23].

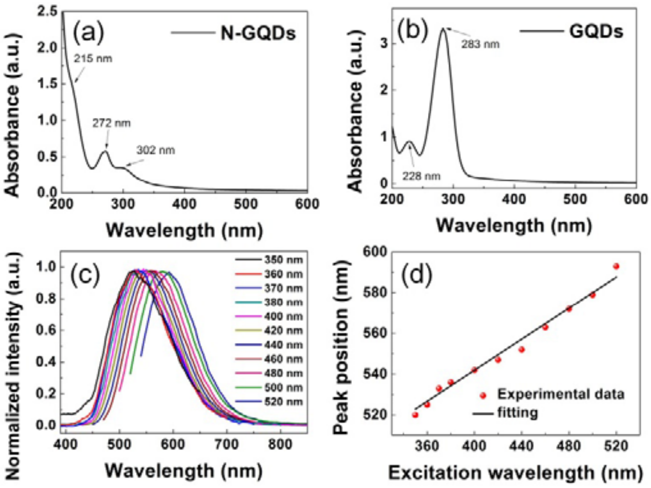

Fig. 2 UV-Vis absorbance of the (a) N-GQDs and (b) undoped GQDs. (c) PL spectra of the N-GQDs excited by various wavelengths. (d). The linear relationship between the emission and excitation wavelength of the N-GQDs

Apart from the strong downconversion PL features, the N-GQDs also exhibit upconversion PL properties. As shown in Fig. 3 (a), when the excitation wavelength changes from 700 to 950 nm, the upconverted emission peak shifts from 472 to 596 nm. In addition, it is found that the emission peak is generally broad and dependent on excitation wavelength. The strongest PL emission (FWHM ~ 150 nm) is located at 517 nm when the excitation wavelength is 800 nm. The upconversion properties of N-GQDs may be beneficial to energy transfer component in photocatalyst design [24] and bioimaging [25]. The upconversion PL can be generally explained by two mechanisms, the multiphoton active process and anti-Stokes PL. The former is associated with the relationship between the emission intensity and input pump power, while the latter is related to the energy difference (ΔE) between excitation and emission wavelengths. As proposed by Hoffmann [26], the value of ΔE should be kept constant and less than 1.5 eV. To explore the upconversion mechanism of our N-GQDs, the shifting between the energy of upconverted emission (E_m) and excitation (E_x) is plotted in Fig. 3 (b). The linear relationship between E_m and E_x appears at the plot with a fitting function. The value of ΔE in N-GQDs is ranged from 0.7 to 0.9 eV, which does not remain constant. In addition, the power-dependent emission of the N-GQDs is studied by tuning the laser pump power (Fig. 3 (c)). The N-GQDs was excited by the wavelength of 900 nm with the laser power changed from 835 to 1670 mW. As the power increases, the upconverted emission intensity of the N-GQDs increases without any peak shift. The inset shows the quadratic relationship obviously between the intensity and laser power. These results suggest the two-photon excitation is responsible for the upconversion luminescence [27].

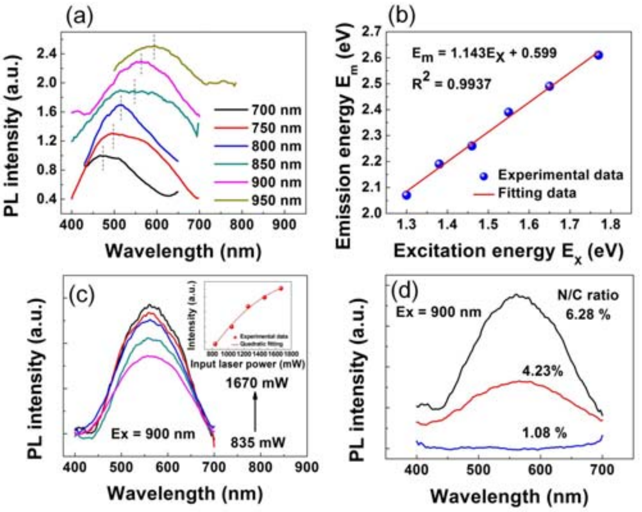

Fig. 3 (a) Upconversion PL spectra of the N-GQDs. (b) The energy of the emission light as a function of the excitation light. (c) The upconverted emission intensity with various input pump power. The excitation wavelength is 900 nm. Inset: The quadratic relationship of the obtained PL intensity of the N-GQDs with the excitation power. (d) The PL spectra with various N/C atomic ratios at the excitation of 900 nm

The emission with various N/C atomic ratios of the N-GQDs excited by 900 nm is shown in Fig. 3 (d). The N/C ratio of the N-GQDs is determined by EELS. At low ratio, the emission is almost disappeared. When the N/C ratio increases, the emission intensity also increases. The result shows that N doping play an important role on two-photon luminescence.

The luminescence of the N-GQDs may originate from the π –π electron transition since the N-GQDs has large π conjugated system. Furthermore, the lone pair electrons from the strong electron donating group NH_3 which is doped to the aromatic ring of N-GQD can be excited to the aromatic rings to form the p−π conjugation, further enlarging the π-conjugated system. [28] .The strong orbital interaction between NH_3 bonding and π-conjugated system of the N-GQDs elevates the primary HOMO to a higher orbit [29]. This results in facilitating the charge transfer and enhancing the two-photon excitation. Hence, strong two-photon induced luminescence can be observed.

In conclusion, we have demonstrated a “one-pot” microwave-assisted hydrothermal synthesis of N-GQDs. The N-GQDs exhibited excellent optical properties with tunable and two-photon induced luminescence. The N-GQDs may provide a new type of fluorescence and upconversion material for applications in bioscience and energy technology. They may also open an opportunity for application of graphene-based materials to other fields.

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