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.

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 electrocatalytic 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 Edinburgh Analytical Instrument apparatus. Xe lamp was used as excitation source. The absolute quantum yield measurement were carried out using integrating sphere (Edinburgh 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 [110] 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
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 $\pi$ (or $\pi$) to $\pi^*$ 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).

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 ($\Delta E$) between excitation and emission wavelengths. As proposed by Hoffmann [26], the value of $\Delta E$ 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 $\Delta E$ 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].
The strong orbital interaction between NH\textsubscript{3} bonding and graphene-based materials to other fields. N-GQDs may provide a new type of fluorescence and upconversion material and two-photon induced luminescence. The N-GQDs may exhibit excellent optical properties with tunable 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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REFERENCES


