ChemComm

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Facile preparation and upconversion luminescence of graphene quantum dots†

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A facile hydrazine hydrate reduction of graphene oxide (GO) with surface-passivated by a polyethylene glycol (PEG) method for the fabrication of graphene quantum dots (GQDs) with frequency upconverted emission is presented. And we speculate on the upconversion luminescence due to the anti-Stokes photoluminescence (ASPL), where the δE between the π and σ orbitals is near 1.1 eV.
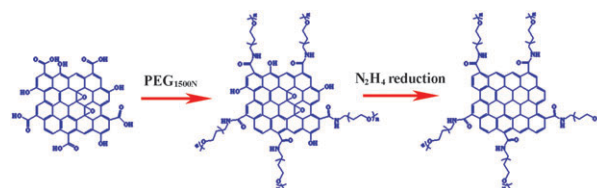
Recently, carbon quantum dots (CQDs) or carbon dots (C-Dots) have received much attention, as they may gradually replace traditional semiconductor quantum dots due to superiority in chemical inertness, biocompatibility and low toxicity.[1–9] CQDs are usually surface-passivated by polymers, such as PEG, and exhibit strong photoluminescence (PL).[2,10,11] The surface passivation is most effective following functionalization with biomolecules in bioimaging, disease detection and drug delivery. But the disadvantage is that CQDs possess size effects, the diameter of the CQDs with the visible light emission is less than 10 nm.[10,12,13] In addition, the CQDs were usually prepared by laser ablation of graphite, electrochemical oxidation of graphite, electrochemical soaking of carbon nanotubes, thermal oxidation of carbon precursors, vapor deposition of soot, proton-beam irradiation of nano-diamonds, microwave synthesis, and bottom-up methods.[14–21] We have reported a simple bottom-up synthesis method for the C-Dots by using a mesoporous silica microspheres template.[22] These complex processes are difficult for mass production.

Very recently, Pan and colleagues[23] have developed a simple hydrothermal route for cutting preoxidized micrometre-sized rippled graphene sheets into ultrafine GQDs with diameters mainly distributed in the 5–13 nm range. These GQDs were found to exhibit bright blue PL (quantum yield *ca.* 6.9%), which has never been previously observed among the CQDs because of their large lateral dimensions. However, the produced GQDs emit strongly under alkaline conditions but

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† Electronic Supplementary Information (ESI) available: Experimental details and instrumentation, quantum yield measurements. See DOI: 10.1039/c0cc04812g/

are almost completely quenched in acidic media. Herein, we present a new facile method to prepare GQDs surface-passivated by PEG. They exhibit bright PL in a water solution of neutral pH. Most interestingly, they also possess upconversion PL properties.

In this work, we report GQDs prepared by hydrazine hydrate reduction of GO with their surface passivated by PEG. Firstly, GO was further oxidised by HNO_3, and cut into small GO sheets. Then, the preparation of a GQDs precursor of treated GO with an oligomeric PEG diamine (PEG_{1500N}) as the surface passivation agent (Fig. 1) was based on the previously reported procedure.[2,3,10] The precursor was finally reduced by hydrazine hydration to fabricate GQDs. Strong blue PL was clearly shown under 365 nm and the green fluorescence was observed under a 980 nm laser. The PL quantum yield measured using rhodamine B as a reference is 7.4% (Table S1 in ESI†), comparable with those of reported luminescent carbon nanoparticles.[10] Interestingly, the fluorescence results of GQDs resembled those of band-gap transitions while the upconverted PL properties of GQDs were similar to the ASPL, and there is a constant energy difference between the excitation and emission light.[24]

Fig. 2 shows a transmission electron microscope (TEM) image of GQDs. Their diameters are mainly distributed in the range of 5–19 nm (13.3 nm average diameter, similar to that reported by Pan *et al.*),[23] suggesting that the as-prepared monodisperse GQDs are uniformly arranged. By the present method, GQDs consisted of a mixture of different sized graphene sheets. Fig. 2b shows a high-resolution TEM (HRTEM) image of an individual GQD. To further explore the optical properties of as-synthesized GQDs, a detailed PL study was carried out by using different excitation wavelengths. Fig. 3 shows the UV-vis absorption and normal PL spectra of GQDs. For the UV-vis absorption, there was no
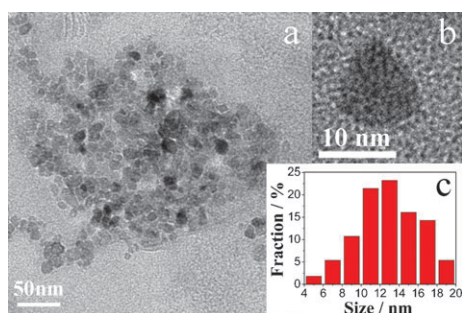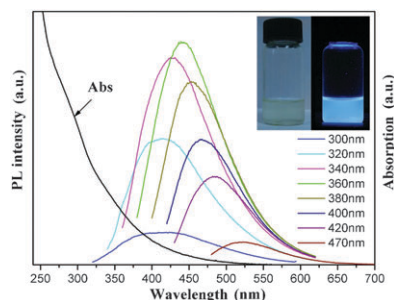

Fig. 1 Representation of GQDs containing an oligomeric PEG diamino surface passivating agent.

Fig. 2 (a) TEM image of the GQDs; (b) high-resolution image of an individual GQD; (c) diameter distribution of the GQDs.

Fig. 3 UV-vis absorption (Abs) and PL spectra of the GQDs at different excitation wavelengths. Inset: photograph of the GQD aqueous solution taken under visible light and 365 nm UV light, from left to right, respectively.

clear absorption peak, but a long absorption edge. The PL spectra are generally broad and dependent on excitation wavelength, the PL peaks shifted to longer wavelengths with a maximum intensity as the excitation wavelength was changed from 300 to 470 nm, and the strongest peak excited at 360 nm, consistent with previous fluorescence analyses.[12,23] The pH-dependent PL spectra (Fig. S1 in ESI†) shows that the GQDs with their surface passivated by PEG_{1500N} exhibited bright PL in a water solution of neutral pH. And the intensity of PL peaks decreased by about 25% under both acidic and alkaline conditions, which was more stable than that reported under acidic conditions.[23]

The synthesized GQDs were shown to possess the upconversion PL properties. Fig. 4a shows the PL spectrum of GQDs excited by a 980 nm laser with the upconverted emissions located at about 525 nm, which is consistent with our observation. These results reveal that the GQDs have the upconversion property, so we conducted further studies on the upconversion performance. As shown in Fig. 4b, the excitation wavelength changed from 600 to 800 nm, the upconverted emissions peaks shifted from 390 to 468 nm, respectively. Remarkably, the shifting between the energy of upconverted emission light (E_m) and excitation light (E_x) was almost unchanged, about 1.1 eV. The inset shows the linear relationship between E_m and E_x, and the function of the fit line is $E_m = 1.00E_x + \delta E$ ($R^2 = 0.9983$) with $\delta E = 1.1$ eV. Many reports indicated that the upconverted PL property of CQDs should be attributed to the multiphoton active process.[2,12] However, we believe that this explanation is not sufficient.
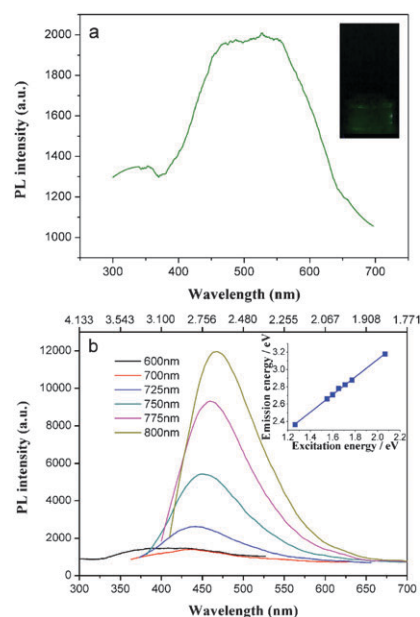
Fig. 4 (a) PL spectrum excited at 980 nm laser. Inset: photograph of the GQD aqueous solution taken under a 980 nm laser; (b) Upconverted PL properties of GQDs, inset is the energy of the excitation light as a function of the emission, and the function of the fit line is $E_m = 1.00E_x + \delta E$ ($R^2 = 0.9983$) with $\delta E = 1.1$ eV.

All these changes show that the surface passivation by PEG_{1500N} exerts a strong influence on the formation, microstructure, and optical properties of the GQDs. To further confirm and explain how these changes come from the quantum-sized GQDs, we established an energy level structural model of the GQDs to investigate the fluorescence properties (Fig. 3) and the upconversion PL properties (Fig. 4). Fig. 5 shows a schematic illustration of various typical electronic transitions processes of GQDs. The PL spectrum can be considered as a transition from the lowest unoccupied molecular orbital (LUMO) to the highest occupied molecular orbital (HOMO), as demonstrated in Fig. 5(a) and (b). The energy gap depends on the size of the graphene and the biggest gap was 4.9 eV.[25] Since the gap decreases gradually as the size of GQDs increases, the sample mixture of different particle-sized GQDs have different excitation and emission spectra, which is in agreement with previous reports.[12,25,26] The upconverted PL spectrum can be regarded as an anti-Stokes
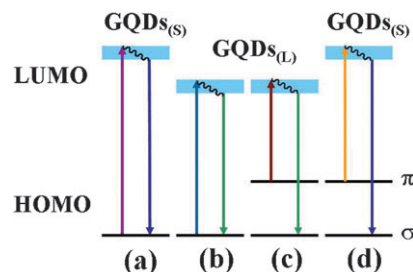
Fig. 5 A schematic illustration of various typical electronic transitions processes of GQDs. Normal PL mechanisms in GQDs for small size (a) and large size (b); Upconverted PL mechanisms in GQDs for large size (c) and small size (d).

transition as demonstrated in Fig. 5(c) and (d). The energy levels of π and σ orbitals were provided by the carbene ground-state multiplicity.[23,27–29] The carbene ground-state multiplicity is related to the energy difference (δE) between the π and σ orbitals. Hoffmann determined δE should be below 1.5 eV.[30,31] In the work here, the energy between the excitation light and the emission light in the upconversion process was close to 1.1 eV (<1.5 eV). Most scholars indicated the upconverted PL property of CQDs should be attributed to the multiphoton active process.[2,12] But we speculate that the GQDs were more like the ASPL.[24,32] When a bunch of low-energy photons excite the electrons of the π orbital, the π electrons would transition to a high-energy state such as the LUMO, and then the electrons transition back to a low-energy state. Thus, an upconverted PL is emitted when the electrons transition back to the σ orbital. Although the electrons of the σ orbital can also be transitioned, it only can emit normal PL (Fig. 5). This also explains why the upconversion excitation and emission light is a constant energy difference.[24,32,33]

In conclusion, we have developed hydrazine hydrate reduction GO with surface passivation by PEG$_{1500N}$ into ultrafine GQDs with strong blue emission and high upconverted PL. The surface passivation can produce GQDs with higher fluorescence performance and upconversion properties. The energy level structural models of GQDs explained the process of the formation of fluorescence and upconverted. GQDs may provide a new type of fluorescence and upconversion material for applications in bioscience and energy technology, and they may expand the application of graphene-based materials to other fields.

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