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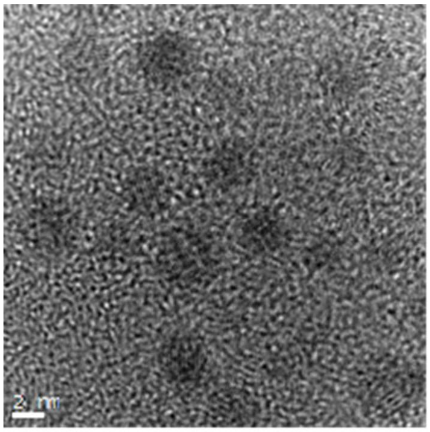

Synthesized grahene oxide quantum dots in small size by acid cutting.

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Facile Synthesis and Photoluminescence of Graphene Oxide Quantum dots and Its Reduction Products

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A simple chemical method of acid treatment has been developed for cutting graphene oxide to graphene oxide quantum dots with controllable size (~3.0 nm). The newly-produced graphene oxide quantum dots have high stability and could be well-dispersed in water for several months. The bright blue emission as well as an excitation-dependent photoluminescence activity is observed in GOQDs. In contrast, the photoluminescence emission of graphene quantum dots obtained by the reduction of graphene oxide quantum dots has distinctive blue shift when compared with that of graphene oxide quantum dots. The difference of PL properties between graphene oxide quantum dots and graphene quantum dots would be related to the change of the bandgap from the different size of the isolated sp^2 cluster in the sp^3 matrix of graphene.

Introduction

Graphene, one atom layer of carbon organized in honeycomb lattice, has attracted intense interest due to its unique properties and potential applications. As a zero bandgap semiconductor pristine graphene exhibits no optical luminescence, which limited its applications in the field of optoelectronics such as transparent conductive electrodes of solar cells and light emitting diodes.[1] Recently, the development of graphene quantum dots (GQDs) provides the opportunity for regulating and adjusting the bandgap of graphene.[2] Besides that, by controlling the size and surface functionalities, the optical properties of GQDs could be simply tailored in the visible light region. According to the previous reports, GQDs could exhibit strong blue or green luminescence and have excellent solubility, biocompatibility, high chemical stability and low toxicity with potential applications in bioimaging, biosensing, and photovoltaics.[3-7] Till now, many efforts were employed to synthesize GQDs, which could be classified as two aspects: (1) “Top-down” methods (Cutting various carbon resources into GQDs) included electrochemical routes,[2] chemical oxidation cutting carbon fiber or graphene sheets derived from graphene oxide (GO)[3,4,7,8] and carving graphite crystallites using high-resolution electron beam lithography;[9] (2) “Bottom-up” methods (Synthesis of GQDs from small molecules), such as transforming C60 molecules,[10] citric acid and other organic molecules into GQDs.[6,11,12] Among the “Top-down” methods, GO plays an important role and serves as an excellent precursor for producing GQDs. GO is a graphite that covalently decorated with oxygen-containing functional groups, which exhibit its unique characteristics: (1) GO features both conducting π states from sp^2 carbon sites and the σ states from sp^3 bonded carbons, so it is an electronically hybrid material. By controlling the ratio of the sp^2 and sp^3 fractions, the luminescence of GO could be tunable;[13,14] (2) Due to its abundant oxygen functional groups, GO is hydrophilic and could be well-dispersed in water to form stable colloidal suspensions.[15,16] However, the size controlled synthesis of “Nano GO” has not been extensively studied, partially because GO was always used as the intermediate product for GQDs and lack of interest for the size-dependant properties. Currently, Nano GO was synthesized by two main methods, synthesis from graphite nanofibers by the modified Hummer’s method and chemical exfoliation by oxidation procedure. The reports indicated that nano GO sheets were more hydrophilic and stable than GO and exhibited excellent photoluminescence (PL) properties.[15, 17, 18] Nano GO would be another promising new material in the family of graphene for biological and medical applications due to its aqueous solubility and biocompatibility. Till now, there is only one article reported the synthesized nano GO in the size of quantum dots (< 10 nm) by a one-step hydrothermal procedure in a microwave.[19] However, the differences (such as surface groups and the related PL behaviours) between GOQDs and GQDs are almost completely unknown. Herein, we report on a simple chemical acid treatment method for synthesizing uniform extremely small GOQDs (~3 nm). It is found that the different precursor (GO) concentration plays an important role for controlling the size of GOQDs. And the structure and PL properties have firstly been compared between GOQDs and its reduction products GQDs.

Results and discussion

Nano GO materials have normally been synthesized through tuning the degree of oxidation of GO sheets by chemical exfoliation. And it has been reported that the oxidation time and the amount of oxidants would control the sizes of the final nano GO sheets.[17, 18] In our experiment, the as-prepared GO by chemical exfoliation was further treated by the strong acid mixture (concentrated HNO_3 and H_2SO_4), which could introduce more defects and functional groups and then cut GO effectively. The diagram of the synthesis of GOQDs and their reduced products GQDs is shown in Figure 1a. The colour of the product was changed from colourless (GOQDs 1) to pale yellow (GOQDs 2) and then yellow (GOQDs 3), and the as-prepared GOQDs solution was found to exhibit a long-term homogeneous phase without any noticeable precipitation at room temperature (figure 1b). The high concentration of GO enhanced the colour of the final product, which is mostly dependent on the size of the GOQDs. The phenomena will be discussed by the following analysis of the TEM. Figure 2a, b and c show the TEM image, EDX composition analysis and the size distribution of GOQDs 1. Fairly uniform GOQDs with the average diameter of ca. 3.0 nm are observed in TEM image (Figure 2a), which are much smaller than those of reported Nano GO sheets [17, 18]. As shown in figure 2d and 2f, the average diameter of the reduced product (GQDs1) decreased to ca. 2 nm with the similar morphology to that of GOQDs 1, suggesting that the reduction process does not largely change the average size of the graphene quantum dots. And this would provide a new pass for controllable synthesis of GQDs. The analysis of EDX indicates that GQDs 1 has less oxygen content than that of GOQDs 1, implying the recovery of the π-π conjugation as normally observed in the reduced graphene oxide (RGO) (figure 2e and 2b). In addition to that, the sizes of GOQDs strongly depend on the concentration of the GO precursor. As shown in Figure 2g and 2h, the average diameter of GOQDs 2 increases to 4.5 nm and some of the quantum dots overlap to each other and form the elliptical quantum dots. For GOQDs 3, the GOQDs aggregated in much larger size (10~30 nm) without distinctive observed quantum dots (figure S1). Therefore, under the same acid treatment condition, the concentration of the precursor has great effect to control the size of the GOQDs. Higher concentration of GO would increase the viscosity of the reaction system, provide more opportunities for interaction between the GOQDs and then enlarge the size of quantum dots. HRTEM observation confirms the high crystallization with a lattice parameter of 0.26 nm in GOQDs 2 (figure 2i), constructing with different ordination quantum dots Interestingly, the GOQDs 2 edges seem to be mainly parallel to the zigzag edges more than armchair ones, which is also observed in graphene quantum dots fabricated by carbon fibers in previous report.[4]

The corresponding AFM (figure 3) image of GOQDs 1 reveals a typical topographic height of 1.45 nm. Consequently, it can be concluded that most of the GOQDs 1 are few layers graphene oxide (less than 5 layers).[3, 5]

FTIR reveals the existence of -OH (3464 cm^{-1}), C=O (1792 cm^{-1}), C=C (1625 cm^{-1}), C-H (1374 cm^{-1}) and C-OH (1118 cm^{-1}) groups in GOQDs.[4] The FTIR intensity of oxygen-containing groups decreases after the reduction in GQDs (figure 4a). Additionally, the GQDs exhibit very weak absorption of C=O, implying that the GOQDs were reduced inadequately to GQDs. The strong absorption of stretching vibration of C-H at ca. 1374 cm^{-1} observed in GOQDs suggests that acid treatment would cut the GO sheets into small pieces and remain some incompletely carbonized parts both at the edge and on the plane of the sheets.[6] XPS is a powerful tool to identify the elements' states and composition in bulk materials. As can be seen in Figure 4b, the XPS survey spectra of GOQDs 1 and the resultant GQDs 1 show predominant C1s peak at ca. 284.8 eV, O1s at ca. 532.3 eV and small amount of N at ca. 400.0 eV, the source of N is nitric acid. The O/C ratio for the GOQDs is ca. 1.53, higher than that of GQDs (ca. 0.99), and the results are consist with the above analysis of EDX. The high resolution spectra of O1s for GOQDs 1 and GQDs 1 have been compared in Figure 4c and 4d. Generally, there are several different O groups in GOQDs, which are characterized by the appearance of several spectral peaks: HO-C=O at 531.2 eV, C=O at 532.8 eV and C-OH at 535.4 eV.[22] After the reduction, the intensity of the high resolution of O 1s peaks has significantly decreased in GQDs, this confirmed the most of the oxygen groups were removed after the reduction. Under the irritation of 365 nm lamp, GOQDs exhibit an intensive blue luminescent emission at the center of ca. 460 nm (Figure 5a). It is believed that the blue PL emission should be related to the bandgap induced by the ordered sp^2 clusters isolated within the sp^3 C-O matrix. GOQDs 2 exhibit the higher PL intensity than that of GOQDs 1 and GOQDs 3. So the optimizing GO concentration should be 2 mg/ ml to produce the strongest emission for GOQDs. The PL excitation (PLE) spectra (Figure 5b) recorded with the strongest luminescence shows broad peak centered around 350 nm, related to the transition from the lowest unoccupied molecular orbital (LUMO) to π orbital transition of graphene sheets.[14] The previous research believed that GQDs and GO share the same luminescence origin, however, there are some significant differences in PL properties between the GOQDs and GQDs, even when they possess similar sizes. The differences are as follows, (1) The observed PL emission peak of GQDs has a blue shift (~ 20 nm) as well as the narrower full width at half maximum (FWHM) compared with that of GOQDs. As mentioned above, GQDs has less oxygen-containing groups than that of GOQDs. It has been reported that decreasing the degree of oxidation in GQDs have similar phenomena compared to our results.[23] The O-rich groups, in addition to the size, surface traps and zig-zag sites, greatly contribute to the observed blue-shift and narrow FWHM in the PL emission.[3, 23, 24, 25] (2) The maximum PL emission wavelength of GOQDs is substantially dependent on the excitation wavelength (seen in figure 5d). When the excitation wavelength increases gradually from 355 to 385 nm, the maximum PL emission wavelength shifts from 460 to 500 nm and remain the almost same shape. However, GQDs is nearly excitation-independent. And with the increasing of excitation wavelength, another emission peak emerges at ca. 545 nm, which would be related to the surface defects.[2]

Synthetic procedures

All chemicals used in this experiment were of analytical grade and used as received without further purification. Deionized water was used for all experiments. GO was prepared from flake graphite powder in modified Hummers method reported in previous article.[20] The as-prepared different concentration of GO aqueous solution (0.5 mg/ml, 2 mg/ml and 5 mg/ml) in 60 ml were treated with the mixed concentrated nitric acid (16 ml) and sulphuric acid (4 ml) at 80℃ for 24 h. After cooling to room temperature, the suspension was subjected to mild ultrasonication for 30 min, and then neutralized to pH 7.0 with NaOH. The aqueous solution of GOQDs was obtained and then filtered through a 44 um microporous membrane to remove the large tracts. For convenience, GOQDs with different precursor (GO) concentration are named as GOQDs 1 (0.5 mg/ml), GOQDs 2 (2 mg/ml) and GOQDs 3 (5 mg/ml). For comparison, the reduction products, GQDs (named as GQDs 1, GQDs 2 and GQDs 3 corresponding to the above names of GOQDs), were prepared by the normal reduction method of GOQDs using hydrazine as the reducing agent.[21]

All PL spectra were obtained by a Fluorescence (FL) spectrophotometer (Analytic Jena AG, Specord 50). The Fourier transform infrared (FTIR) spectra was obtained on a FTIR spectrophotometer (Nicolet NEXUS 670 FTIR spectrometer). X-ray photoelectron spectroscopy (XPS, PHI-5702, Physical Electronics) was performed using a monochromated Al Kα irradiation. The morphologies and element analysis of different samples were observed by transmission electron microscopy (TEM), high-resolution transmission electron microscopy and energy dispersive X-Ray spectroscopy (EDX) (FEI Tecnai F30, operated at 300 kV). Atomic force microscopy (AFM) images were obtained on Asylum Research MFP-3D-SA. Size distributions were measured by Nano Measurer 1.2.

Conclusions

In summary, we have demonstrated an efficient top-down method to synthesis the graphene oxide quantum dots and graphene quantum dots in controllable size. Size distribution depend much on the concentration of the precursor and a optimize concentration of graphene oxide has been found to prepare extremely small size graphene oxide quantum dots (~3nm). The prepared graphene oxide quantum dots exhibit blue emission and the emission peak shift from 460 nm to 500 nm with the photoluminescence emission wavelength changing from 355 nm to 385 nm. Differently, the blue emission (450 nm) and green emission (545 nm) were both obtained in graphene quantum dots. And the differences of photoluminescence properties between GOQDs and graphene quantum dots are ascribed to the different degree of oxidization as well as the surface defects.

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Notes and references

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† Footnotes should appear here. These might include comments relevant to but not central to the matter under discussion, limited experimental and spectral data, and crystallographic data.

Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/b000000x/

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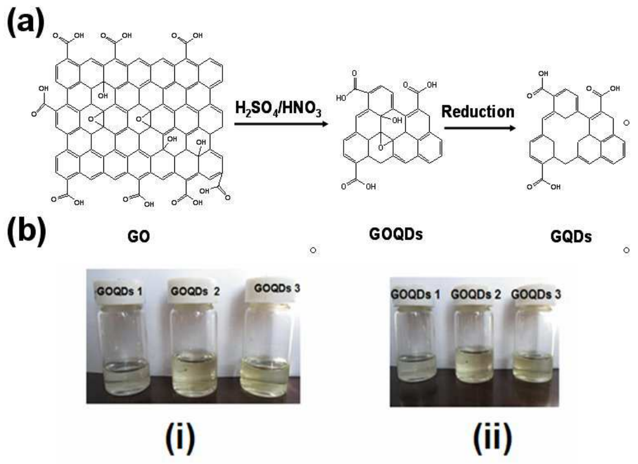

Figure 1. (a) Diagram for the synthesis of GOQDs and GQDs. (b) Photos of the GOQDs taken when synthesized (i) and after 3 months (ii).

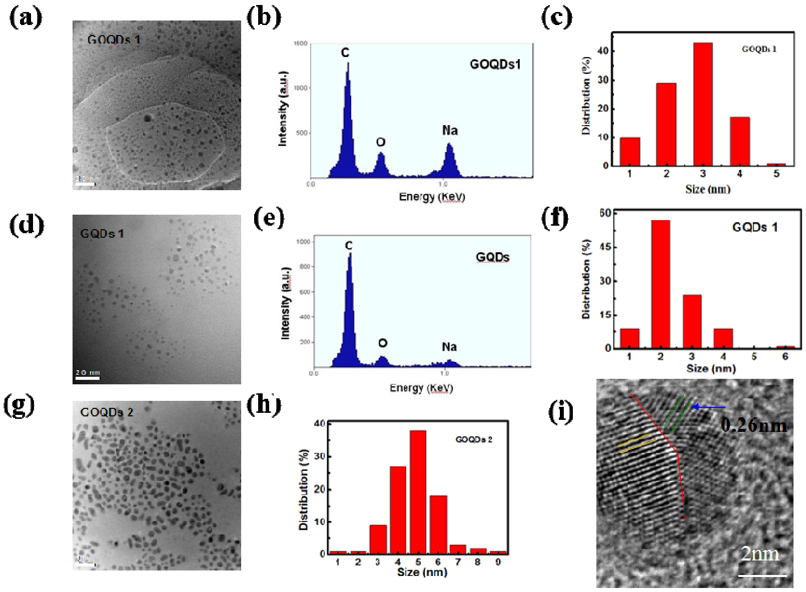

Figure 2. TEM images GOQDs 1 (a), GQDs 1 (d)and GOQDs 2 (g); EDS of GOQDs 1 (b) and GQDs 1 (e); Size distribution of GOQDs 1 (c), GQDs 1 (f) and GOQDs 2 (h); An enlarge view of HRTEM image of GOQDs 2 (i).

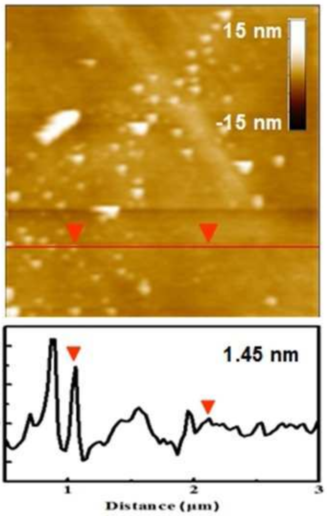

Figure 3. AFM images of GOQDs1

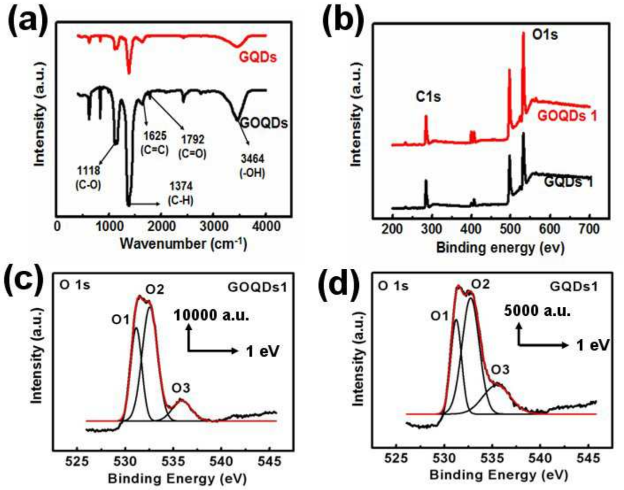

Figure 4. (a) FTIR spectra of GOQDs and GQDs. (b) XPS survey spectrum of GOQDs and GQDs. (c) High-resolution XPS of O1s spectra of GOQDs (c) and GQDs (d).

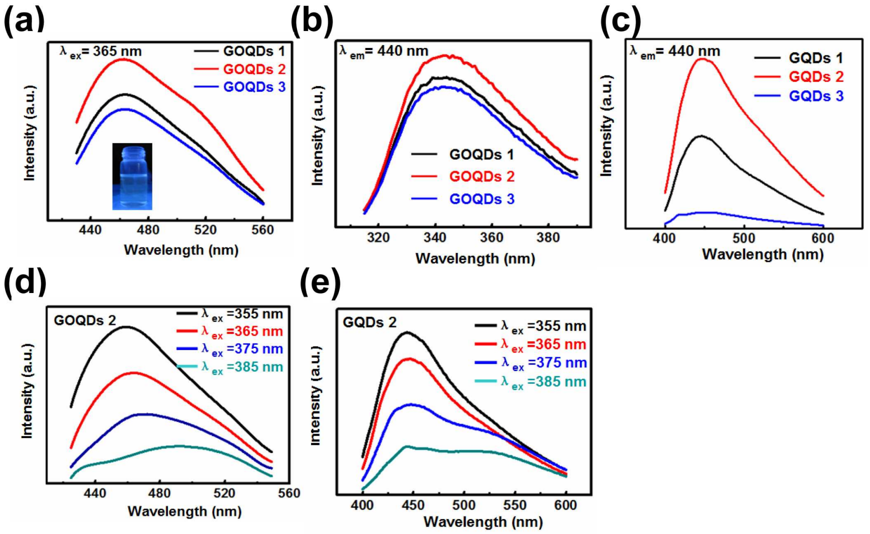

Figure 5. PL properties of GOQDs and GQDs. (a) Emission spectra of the GOQDs 1, GOQDs 2 and GOQDs 3 with excitation at 365 nm. Inset: Photograph of the solution of the GOQDs 2 under 365 nm UV light. (b)Excitation spectra of the GOQDs 1, GOQDs 2 and GOQDs 3 with emission at 460 nm. (c) Emission spectra of the GQDs 1, GQDs 2 and GQDs 3 under 365 nm excitation. (d) Emission spectra of the GOQDs 2 (e) and GQDs 2 (f) with excitation at different wavelength.

Supplementary Figures

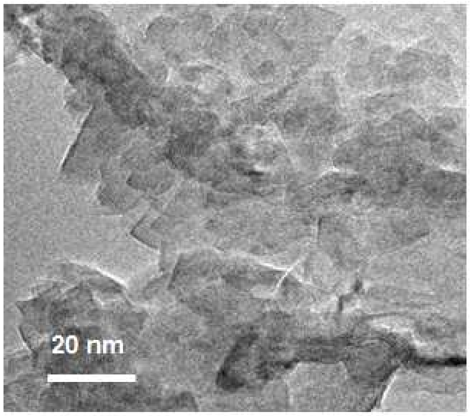

Figure S1. SEM image of GOQDs 3

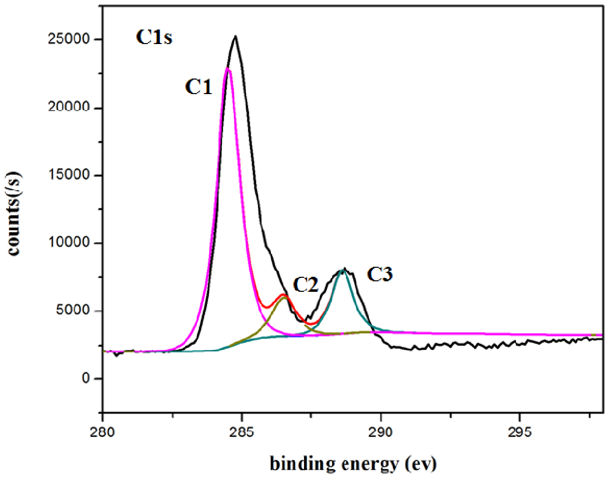

Figure S2. C1s XPS spectra of graphene oxide quantum dots.