Abstract:
The invention relates to a method for forming graphene quantum dots, and in particular, to doped graphene quantum dots. The graphene quantum dots are co-doped with nitrogen and sulfur. The co-doped elements introduce a new type and high density of surface state of graphene quantum dots, leading to high yield and excitation-independent emission.
METHOD FOR FORMING NITROGEN AND SULFUR CO-DOPED GRAPHENE
QUANTUM DOTS

Cross-Reference to Related Application

[0001] This application claims the benefit of priority of United States of America Provisional Patent Application No. 61/731,274, filed November 29, 2012, the contents of which being hereby incorporated by reference in its entirety for all purposes.

Technical Field

[0002] The invention relates to a method for forming graphene quantum dots, and in particular, to doped graphene quantum dots. The graphene quantum dots are co-doped with nitrogen and sulfur. The co-doped elements introduce a new type and high density of surface state of graphene quantum dots, leading to high yield and excitation-independent emission.

Background

[0003] Quantum dots (QDs) are nanoparticles with size-dependent optical and electronic properties that have been proposed for various applications such as energy-efficient displays and lighting, photovoltaic devices and biological markers. Compared with other fluorescent (FL) materials (conventional dyes or polymers), QDs offer many promising advantages, such as bright fluorescence, high photo stability, and resistance to metabolic degradation in bioapplications.

[0004] However, most of high-performance QDs are limited by toxicity from their heavy metal elements like cadmium. Extensive efforts have been made on the development of non- or low-toxic FL nanomaterials as alternatives to the semiconductor based QDs. Carbon-based QDs including carbon nanoparticles of less than 10 nm in size, known as carbon quantum dots (CQDs) and graphene nanosheets of less than 100 nm in size, known as graphene quantum dots (GQDs),
respectively, are particularly encouraging due to their outstanding optical properties, low toxicity, good biocompatibility and robust chemical inertness.

[0005] Various methods have been demonstrated in preparation of FL carbon-based QDs such as electrochemical oxidation processes, chemical oxidation methods, hydrothermal cutting strategies and carbonizing organics routes. Nevertheless, most of the developed methods are unsatisfactory due to expensive equipment required, low yield, or complicated procedure. In particular, most of the obtained carbon-based QDs possess relatively low FL quantum yield (FLQY, usually less than 50%) in comparison to the conventional semiconductor QDs. Most recently, doped CQDs were proposed for highly FL dots. For example, ZnS-doped QCDs with the passivation of oligomeric poly(ethylenelycol) diamine (PEG1500N) molecules show a 78% FLQY after a gel column fractionation. However, the preparation of highly FL ZnS-doped CQDs is complicated. Moreover, the poor chemical inertness of the ZnS would be a severe limitation to broad applications of the CQDs.

[0006] Thus, there remains need to develop a facile, low cost and high yield method for preparation of GQDs with strong FL emission.

Summary

[0007] Present inventors have found a simple method of doping graphene quantum dots with nitrogen and sulfur. The resultant nitrogen and sulfur co-doped graphene quantum dots (N,S-GQDs) exhibit very high fluorescent quantum yield of 73% (rather strong blue luminescence) and excitation-independent emission, resulting from the synergistic effect of the dopants nitrogen and sulfur atoms. Advantageously, the preparation method involves the use of common carbon source and nitrogen and sulfur source, low costs, high yield and a one-step facile process, and is therefore of significance in large-scale production for broad applications of graphene quantum dots.
In one aspect, a method for forming nitrogen and sulfur co-doped graphene quantum dots is disclosed herein. The method includes heating a mixture of a carbon source and a compound containing nitrogen and sulfur in an autoclave. The compound containing nitrogen and sulfur may include at least one of L-cysteine, thiourea, mercaptoethylamine, glutathione, and methionine. The carbon source may include at least one of citric acid and malic acid.

**Brief Description of the Drawings**

In the drawings, like reference characters generally refer to the same parts throughout the different views. The drawings are not necessarily drawn to scale, emphasis instead generally being placed upon illustrating the principles of various embodiments. In the following description, various embodiments of the invention are described with reference to the following drawings.

**Fig. 1** shows (a) TEM image of the N,S-GQDs. (b) AFM image of the N,S-GQDs. (c) Height profile along the line in (b). Insets in (a) and (b) show the size and height distributions of the N,S-GQDs.

**Fig. 2** shows (a) XPS spectra of the N,S-GQDs. High-resolution C\textsubscript{s} (b), N\textsubscript{s} (c) and S\textsubscript{2p} (d) peaks of the N,S-GQDs.

**Fig. 3** shows fluorescent spectra (solid lines) of the obtained N,S-CQDs and UV-Vis absorption spectra (dotted lines) of CA (a), L-cysteine (b) and the thus-obtained N,S-CQDs (c). Inset: Photograph of the obtained N,S-CQDs under illumination of white-light (left) and UV (365 nm) light (right).

**Fig. 4** shows fluorescent decays (345 nm laser excitation, and monitored through 415 nm bandpass filter) of the N,S-GQDs, N-GQDs and O-GQDs.

**Fig. 5** shows a schematic representation for the fluorescent mechanism of OGQDs, N-GQDs and N,S-GQDs.
Fig. 6 shows FTIR spectra of CA, L-cysteine and the obtained N,S-GQDs.

Fig. 7 shows XRD pattern of the as-prepared N,S-GQDs.

Fig. 8 shows Raman spectra of the obtained N,S-GQDs.

Fig. 9 shows fluorescent spectra of the aqueous solution of the obtained N,S-CQDs with excitation of different wavelength.

Fig. 10 shows pH effect on the FL intensity of the obtained N,S-GQDs. Inset: FL spectra of the obtained N,S-GQDs in solutions of different pH (recorded for progressively increasing pH values from 2 to 5 in 0.5 increments).

Fig. 11 shows UV-Vis absorption and FL spectra (recorded from 285 to 480 nm with 15 nm increment) the obtained O-CQDs (a) and N-CQDs (b).

Fig. 12 shows UV-Vis absorption of N,S-GQDs obtained from precursors containing different mass of L-cysteine (the mass of citric acid monohydrate was 2 g in all samples).

Fig. 13 shows fluorescent spectra of the aqueous solution of the obtained N,S-GQDs (citric acid monohydrate/L-cysteine: 2/0.125). (a) Recorded from 285 to 360 nm with 15 nm increment; (b) Recorded from 375 to 480 nm with 15 nm increment. In the inset, the emission spectral intensities are normalized.

Description

The following detailed description refers to the accompanying drawings that show, by way of illustration, specific details and embodiments in which the invention may be practised. These embodiments are described in sufficient detail to enable those skilled in the art to practise the invention. Other embodiments may be utilized and structural, logical, and electrical changes may be made without departing from the scope of the invention. The various embodiments are not
necessarily mutually exclusive, as some embodiments can be combined with one or more other embodiments to form new embodiments.

[0024] Present disclosure relates to the development of a one-step and high yield preparation of nitrogen and sulfur co-doped graphene quantum dots (N,S-GQDs), which exhibit excellent fluorescence properties.

[0025] In one aspect, the method for forming the nitrogen and sulfur co-doped graphene quantum dots includes heating a mixture of a carbon source and a compound containing nitrogen and sulfur in an autoclave.

[0026] Graphene is a substance made of pure carbon, with atoms arranged in a regular hexagonal pattern similar to graphite, but in a one-atom thick sheet. It is an allotrope of carbon whose structure is a single planar sheet of sp2-bonded carbon atoms that are densely packed in a honeycomb crystal lattice.

[0027] A nanostructure is a structure or object that can have any form and has dimensions typically ranging from 1 to 100 nm (nanometre). More specifically, a nanostructure has at least one dimension being less than 100 nm. In present disclosure, graphene nanosheets of less than 100 nm in size, i.e. graphene quantum dots (GQDs), are of particular interest.

[0028] The carbon source can be any substance that decomposes or breaks down to form graphene upon heating. The present method is particularly attractive since a large variety of low cost and abundance of such carbon sources are available. In various embodiments, the carbon source may include at least one of citric acid and malic acid. In one embodiment, the carbon source may include citric acid.

[0029] Advantageously, the dopants nitrogen atoms and sulfur atoms are provided by a single compound. Such compounds are preferably conveniently available and are low costs. In various
embodiments, the compound containing nitrogen and sulfur may include at least one of L-cysteine, thiourea, mercaptoethylamine, glutathione, and methionine. In one embodiment, the compound containing nitrogen and sulfur may include L-cysteine.

[0030] In various embodiments, the mixture of the carbon source and the compound containing nitrogen and sulfur is hydrothermally heated in a Teflon equipped stainless steel autoclave.

[0031] Hydrothermal heating is a generic description of a process that involves heating a mixture in an aqueous system and under pressure (with steam), to a temperature of above 100°C. Thus, the process involves high temperature processing. For example, the mixture of the carbon source and the compound containing nitrogen and sulfur may be heated at between 150°C and 300°C, such as about 150°C, 160°C, 170°C, 180°C, 190°C, 200°C, 210°C, 220°C, 230°C, 240°C, 250°C, 260°C, 270°C, 280°C, 290°C, or 300°C.

[0032] In certain embodiments, the mixture of the carbon source and the compound containing nitrogen and sulfur may be heated at 200°C.

[0033] In various embodiments, prior to the heating in an autoclave, the mixture of the carbon source and the compound containing nitrogen and sulfur may be dissolved in water first, followed by evaporation. For example, the dissolved mixture may be evaporated at above 50°C, such as about 50°C, 55°C, 60°C, 65°C, or 70°C, for about 6 h, 7 h, 8 h, 9 h, 10 h, 11 h, or 12 h, until the product is dry.

[0034] The mixture of the carbon source and the compound containing nitrogen and sulfur is heated for a sufficient amount of time for the formation of graphene quantum dots and doping of the thus-formed graphene quantum dots by nitrogen and sulfur. In various embodiments, the mixture of the carbon source and the compound containing nitrogen and sulfur may be heated for 1 to 10 h.
For example, the mixture of the carbon source and the compound containing nitrogen and sulfur may be heated for about 1 h, 2 h, 3 h, 4 h, 5 h, 6 h, 7 h, 8 h, 9 h, or 10 h.

[0035] In certain embodiments, the mixture of the carbon source and the compound containing nitrogen and sulfur may be heated for 3 h.

[0036] In yet further embodiments, the mixture of the carbon source and the compound containing nitrogen and sulfur may be heated at 200 °C for 3 h.

[0037] In various embodiments, the mixture of the carbon source and the compound containing nitrogen and sulfur may be heated at a heating rate of 5 °C min⁻¹ to 30 °C min⁻¹, such as about 5 °C min⁻¹, 6 °C min⁻¹, 7 °C min⁻¹, 8 °C min⁻¹, 9 °C min⁻¹, 10 °C min⁻¹, 11 °C min⁻¹, 12 °C min⁻¹, 13 °C min⁻¹, 14 °C min⁻¹, 15 °C min⁻¹, 16 °C min⁻¹, 17 °C min⁻¹, 18 °C min⁻¹, 19 °C min⁻¹, 20 °C min⁻¹, 21 °C min⁻¹, 22 °C min⁻¹, 23 °C min⁻¹, 24 °C min⁻¹, 25 °C min⁻¹, 26 °C min⁻¹, 27 °C min⁻¹, 28 °C min⁻¹, 29 °C min⁻¹, or 30 °C min⁻¹.

[0038] In certain embodiments, the mixture of the carbon source and the compound containing nitrogen and sulfur may be heated at a heating rate of 10 °C min⁻¹.

[0039] In yet further embodiments, the mixture of the carbon source and the compound containing nitrogen and sulfur may be heated at 200 °C for 3 h and a heating rate of 10 °C min⁻¹.

[0040] After heating the mixture of the carbon source and the compound containing nitrogen and sulfur, the final product may be diluted and neutralized. Thus, in various embodiments, the method may further include adding a basic solution, such as sodium hydroxide or potassium hydroxide, after heating.

[0041] In summary, the nitrogen and sulfur co-doped graphene quantum dot formed by present method exhibits a long term (i.e. stable) homogeneous phase without any noticeable precipitation at room temperature. The resultant nitrogen and sulfur co-doped graphene quantum dots shows
very high fluorescent quantum yield of 73% (rather strong blue luminescence) and excitation-independent emission, resulting from the synergistic effect of the dopants nitrogen and sulfur atoms.

[0042] In order that the invention may be readily understood and put into practical effect, particular embodiments will now be described by way of the following non-limiting examples.

Examples

[0043] Citric acid (CA) and L-cysteine were used to produce nitrogen and sulfur co-doped graphene quantum dots (N,S-GQDs) through a one-step hydrothermal treatment. The CA serves as a carbon source, while L-cysteine provides the dopants nitrogen and sulfur. Compared with the reported GQDs, the as-prepared N,S-GQDs exhibit very high fluorescent quantum yield (FLQY) (73%) and excitation-independent emission, resulting from the synergistic effect of the doped nitrogen and sulfur atoms.

[0044] Preparation of Nitrogen and Sulfur Co-doped Graphene Quantum Dots With Citric Acid and L-Cysteine (N,S-GQDs). The N,S-GQDs were prepared by thermal treatment of molecular organic salts with the mixed carbon source and the surface modifier in the single precursor. In preparation, CA monohydrate (2 g, 9.5 mmol) and L-cysteine (1 g, 8.3 mmol) were dissolved in 5 mL water, followed by evaporating at 70 °C until dry within 12 hours. The resulted thick syrup was heated hydrothermally in a Teflon equipped stainless steel autoclave at 200 °C for 3 h and a heating rate of 10 °C min⁻¹. Next, the black syrup product was diluted to 100 mL after neutralized with 1 mol/L NaOH solution.

[0045] Preparation of Graphene Quantum Dots With Citric Acid (O-GQDs). The O-GQDs were prepared from citric acid monohydrate. 2 g CA monohydrate was heated hydrothermally in a Teflon equipped stainless steel autoclave at 200 °C for 3 h and a heating rate of 10 °C min⁻¹.
Finally, the orange syrup product was diluted to 100 mL after neutralized with 1 mol/L NaOH solution.

[0046] Preparation of Graphene Quantum Dots With Citric Acid and Glycine (N-GQDs). The N-GQDs were prepared from citric acid monohydrate and glycine. 2 g CA monohydrate and 0.62 g (8.3 mmol) L-cysteine were dissolved in 5 mL water. Then the solution was evaporated until dry at 70 °C for 12 hours. The resulting thick syrup was heated hydrothermally in a Teflon equipped stainless steel autoclave at 200 °C for 3 h and a heating rate of 10 °C min⁻¹. Finally, the black syrup product was diluted to 100 mL after neutralized with 1 mol/L NaOH solution.

[0047] Characterization. The height distribution of the obtained GQDs was characterized by atomic force microscopy (Nanoman, Veeco, Santa Barbara, CA) by using tapping mode. The crystal structure of the GQDs was characterized by X-ray diffraction (Bruker AXS, λ = 0.15418 nm). Fourier transform infrared spectra were obtained on a FTIR spectrophotometer (Thermo Nicolet 360). UV/vis spectra were obtained by a UV/Vis spectrophotometer (UV 2450). Raman spectra were measured using a Renishaw 1000 microspectrometer (excitation wavelength of 514.5 nm), All fluorescence spectra were obtained by a spectrofluorometer (Fluoromax-4). X-Ray photoelectron spectroscopy data for the GQD solutions deposited on glass substrates were measured by a Kratos AXIS Ultra spectrometer with a monochromatized Al Kα X-ray source (1486.71 eV) for determining the composition and chemical bonding configurations. High resolution transmission electron microscopy images were recorded on a HRTEM JEOL 2100 system operating at 200 kV.

[0048] The obtained N,S-GQD solution exhibits a long-term homogeneous phase without any noticeable precipitation at room temperature. High-resolution transmission electron microscopy (HRTEM) images (Fig. 1a) show that the prepared GQDs are mono-dispersive nanosheets with an
average size of 10 nm. The atomic force microscopy (AFM) image (Fig. 1b) shows the
topographic height of the obtained GQDs, which is mostly distributed in the range from 0.5 to 3.5
nm, with an average value of 2 nm.

X-ray photoelectron spectroscopy (XPS) results (Fig. 2a) display that the N,S-GQDs are
mainly composed of carbon (42.9 atom%), nitrogen (5.10 atom%), sulfur (2.30 atom%) and
oxygen (41.66 atom%). The high-resolution spectrum of C\textsubscript{i\_s} exhibits three main peaks (Fig. 2b).
The binding energy peak at 284.5 eV evidences the graphitic structure (sp\textsuperscript{2} C-C) of the N,S-GQDs.
The peak around 285.5 eV suggests the presence of C-O, C-S and C-N, and the peak around 288.0
eV could be assigned to C=0 and C=S. The high-resolution spectra of N\textsubscript{i\_s} (Fig. 2c) and S\textsubscript{2p} (Fig.
2d) reveal that nitrogen and sulfur are present in forms of C-N and S-C, and C=S, respectively.
These results suggest that the nitrogen and sulfur atoms are surface-doped in the N,S-GQDs.

Fourier Transform Infrared (FTIR) spectra (Fig. 6) further confirm the presence of oxygen-
containing groups (-OH, -COO\textsubscript{-}, -C=0), -C=SH, -C=S, C-N. X-Ray powder diffraction (XRD)
was used to characterize the obtained N,S-GQDs (Fig. 7). Like most reported GQDs, the N,S-
GQDs show a broader (002) peak centered at around 25.5°, which further proves the graphene
structure of the N,S-GQDs. Raman spectroscopy was used to confirm the quality of the N,S-GQDs
(Fig. 8). Two major features of D band and G band were observed at around 1485 cm\textsuperscript{-1} and 1585
cm\textsuperscript{-1}, respectively. The relative intensity of the "disorder" D-band and the crystalline G-band
(I\textsubscript{D}/I\textsubscript{G}) for the obtained GQDs is about 0.5, indicating its high quality.

Fig. 3 shows that the N,S-GQDs in aqueous solution has two typical UV-Vis absorption
peaks at 242 and 345 nm, respectively, while the absorption of CA is below 230 nm and the
absorption of L-cysteine is very weak above 230 nm. The peak at 242 nm, corresponding to the \( \pi \)
\rightarrow \( \pi^{\ast} \) transition of the aromatic sp\textsuperscript{2} domains leads to nearly no observed FL signal. The other
transition centered about 345 nm due to the trapping of excited-state energy by the surface states results in strong emission. Supreme bright violet-blue luminescence under the illumination of UV (365 nm) light even at a very low concentration (10 μg/mL) of the N,S-GQDs aqueous solution can be clearly seen in the inset of Fig. 3. Unlike most carbon-based QDs, the emission wavelength of the S-GQDs is independent on the excitation wavelength (when the excitation wavelength is changed from 285 nm to 380 nm, the emission wavelength showed nearly no shift, Fig. 9). The maximum excitation wavelength and emission wavelength of the N,S-GQD aqueous solution are 345 and 415 nm, respectively. The FLQY of the N,S-GQDs excited with 345 nm UV light can be as high as 73.0% by selecting the quinine sulfite as standard. The FL of the N,S-GQDs is strong and stable in a wide range of pH values (2-5) (Fig. 10). However, as the pH value is lower than 5, both excitation and emission spectra red shift with the decrease of the pH values. Meanwhile, the FL intensities decrease gradually. The effect of the pH values can be understood in terms of the change in surface charge due to protonation-deprotonation. The N,S-GQDs can also be well dispersed in most welcome organic solvents, such as acetonitrile and chlorobenzene, N,N-dimethylformamide, which is advantageous in non-aqueous and organic phase to fabricate photovoltaic cells.

[0051] Although the FL mechanism of carbon-based QDs is still not clear, two popular hypotheses, namely emissive traps and electronic conjugate structures have been proposed. As our described experimental results above, at the absorption around 245 nm corresponding to the $\pi \rightarrow \pi^*$ transition of the aromatic sp$^2$ domains the N,S-GQDs produces nearly no observed FL signal. It has been well reported that the surface states should have more prominent impact on the photophysical properties of carbon based QDs. It is reasonable that the FL of the GQDs should be attributed to the radiative recombination of electrons and holes trapped on the GQD surface. Therefore, we
argue that the strong FL emission of the N,S-GQDs are mainly resulted from the surface-doped nitrogen and/or sulfur atoms.

[0052] To further confirm this possible explanation, two additional GQDs were prepared using the same method, of which one was prepared using CA alone as the precursor, labeled as O-GQDs due to their abundant oxygen-containing groups, while another was prepared using CA and a sulfur-free amino acid (glycine) as the precursor, labeled as N-GQDs for the existence of nitrogen-containing groups.

[0053] The optical properties of O-GQDs are much different from the N,S-GQDs: (1) the O-GQD solution shows a broad UV-Vis absorption below 500 nm without any obvious peak (Fig. 11a); (2) the emission spectra of the O-GQDs are broad and excitation-dependent, and the maximum emission wavelength (excited with 345 nm UV light) is 435 nm, which is about 20 nm red-shift than that of the N,S-GQDs; (3) The FLQY of the O-GQDs excited with 345 nm is calculated to be 5.3%, which is much lower than that of the N,S-GQDs; (4) Although both the FL decay of the O-GQDs and the N,S-GQDs could be fitted by a single-exponential function, the FL decay curve of the O-GQDs is much different from that of the N,S-GQDs (Fig. 4). The lifetime of the O-GQDs (7.45 ns) is much shorter than that of the N,S-GQDs (12.11 ns). On the contrary, the N-GQDs show a number of optical properties similar to the N,S-GQDs: (1) although the N-GQD solution shows a broad UV-Vis absorption below 500 nm, two peaks could also be observed around 245 and 345 nm, respectively; (2) Although the FL spectra is broad and excitation-dependent, the maximum emission wavelength (excited with 345 nm UV light) is 415 nm, which is identical to the N,S-GQDs; (3) the FLQY excited with 345 nm UV light is calculated to be 16.9%, which is much higher than that of the O-GQDs; (4) the FL decay curve of the N-GQDs is similar to that of the N,S-GQDs. The lifetime of the N-GQDs is 11.78 ns, which is also quite close to that of the N,S-
GQDs. These results clearly indicate that the N,S-GQDs and the N-GQDs should have the same FL origin, which is different from that of the O-GQDs.

[0054] Thus, a mechanism model is proposed to explain the FL processes of the three GQDs (Fig. 5). The O-GQDs have different kinds of surface states (labeled as O-states) corresponding to a relatively wide distribution of different energy levels to generate a broad UV-Vis absorption band, broad and excitation-dependent emission spectra. The nitrogen-doping introduces a new kind of surface state (labeled as N-state). Electrons trapped by the new formed surface states are able to facilitate a high yield of radiative recombination. Since the density of the N-state is comparable with that of those O-states in the N-GQDs, the FL spectra are still broad and excitation-dependent although the FLQY of the N-GQDs is higher than that of the O-GQDs. For the N,S-GQDs, the introduced sulfur atoms can enhance dramatically the density of the N-state, leading to that the original surface states nearly neglected in the N,S-GQDs. Therefore, the N,S-GQDs show a high FLQY and excitation-independent emission.

[0055] To further prove this hypothesis, N,S-GQDs with lower density of N-state were prepared by tuning the ratio of CA and L-cysteine in the precursor. When L-cysteine in the precursor is decreased gradually from 1 g to 0.125 g while fixing CA of 2 g, the absorption peak around 345 nm decreases compared with the background absorption (Fig. 12), thus suggesting decreased N-state's density. Meanwhile, the FLQY of the obtained S-GQDs decreases from 73% to 37% (Table 1). Furthermore, the N,S- GQDs prepared with low density of N-state also exhibit broad and excitation-dependent emission spectra. Taking the N,S-GQDs obtained from the precursor of 2 g CA and 0.125 g L-cysteine for example (Fig. 13), the emission wavelength is excitation-independent when the excitation wavelength is lower than 375 nm, but exhibits a red-shift from 415 to 540 nm when the excitation wavelength is increased gradually from 375 to 480 nm.
Table 1. Effect of the mass of L-cysteine in the precursor (the mass of citric acid nxmohydrate was 2 g in all samples) on the FLQY of the obtained N,S-GQDs.

<table>
<thead>
<tr>
<th>Mass of L-cysteine (g)</th>
<th>0.125</th>
<th>0.25</th>
<th>0.5</th>
<th>1</th>
</tr>
</thead>
<tbody>
<tr>
<td>FLQY</td>
<td>37%</td>
<td>56%</td>
<td>65%</td>
<td>73%</td>
</tr>
</tbody>
</table>

[0056] In conclusion, nitrogen and sulfur co-doped GQDs have been synthesized from a precursor comprising L-cysteine and citric acid. The obtained N,S-GQDs are nanosheets with an average height of 2 ran and an average width of 10 ran. The N,S-GQDs show high yield and excitation-independent emission. The N,S-GQDs exhibit excellent FL activity coupled with the low-toxicity of carbon based materials could provide important broad applications in bioimaging and beyond. Even though the exact mechanism is still unclear, it is reasonable to believe that the doping of nitrogen can introduce the GQDs a new kind of surface state, whose density can be increased dramatically by the co-doped sulfur atoms, which offers great scientific insights to FL enhancement mechanism of GQDs.

[0057] By "comprising" it is meant including, but not limited to, whatever follows the word "comprising". Thus, use of the term "comprising" indicates that the listed elements are required or mandatory, but that other elements are optional and may or may not be present.

[0058] By "consisting of" is meant including, and limited to, whatever follows the phrase "consisting of. Thus, the phrase "consisting of" indicates that the listed elements are required or mandatory, and that no other elements may be present.

[0059] The inventions illustratively described herein may suitably be practiced in the absence of any element or elements, limitation or limitations, not specifically disclosed herein. Thus, for example, the terms "comprising", "including", "containing", etc. shall be read expansively and without limitation. Additionally, the terms and expressions employed herein have been used as
terms of description and not of limitation, and there is no intention in the use of such terms and
expressions of excluding any equivalents of the features shown and described or portions thereof,
but it is recognized that various modifications are possible within the scope of the invention
claimed. Thus, it should be understood that although the present invention has been specifically
disclosed by preferred embodiments and optional features, modification and variation of the
inventions embodied herein herein disclosed may be resorted to by those skilled in the art, and that
such modifications and variations are considered to be within the scope of this invention.

[0060] By "about" in relation to a given numerical value, such as for temperature and period of
time, it is meant to include numerical values within 10% of the specified value.

[0061] The invention has been described broadly and generically herein. Each of the narrower
species and sub-generic groupings falling within the generic disclosure also form part of the
invention. This includes the generic description of the invention with a proviso or negative
limitation removing any subject matter from the genus, regardless of whether or not the excised
material is specifically recited herein.

[0062] Other embodiments are within the following claims and non-limiting examples. In
addition, where features or aspects of the invention are described in terms of Markush groups,
those skilled in the art will recognize that the invention is also thereby described in terms of any
individual member or subgroup of members of the Markush group.
Claims

1. A method for forming nitrogen and sulfur co-doped graphene quantum dots, the method comprising heating a mixture of a carbon source and a compound containing nitrogen and sulfur in an autoclave.

2. The method of claim 1, wherein the compound containing nitrogen and sulfur comprises at least one of L-cysteine, thiourea, mercaptoethylamine, glutathione, and methionine.

3. The method of claim 1 or 2, wherein the carbon source comprises at least one of citric acid and malic acid.

4. The method of any one of claims 1 to 3, wherein the mixture is heated at between 150 °C and 300 °C.

5. The method of claim 4, wherein the mixture is heated at 200 °C.

6. The method of any one of claims 1 to 5, wherein the mixture is heated for 1 to 10 h.

7. The method of claim 6, wherein the mixture is heated for 3 h.

8. The method of any one of claims 1 to 7, wherein the mixture is heated at a heating rate of 5 °C min⁻¹ to 30 °C min⁻¹.

9. The method of claim 8, wherein the mixture is heated at a heating rate of 10 °C min⁻¹.

10. The method of any one of claims 1 to 9, wherein prior to the heating, the mixture is first dissolved in water, followed by evaporation.

11. The method of any one of claims 1 to 10, further comprising adding a basic solution after heating the mixture.

12. A nitrogen and sulfur co-doped graphene quantum dot formed by a method of any one of claims 1 to 11.
FIG. 2

(a) Binding energy vs. counts/s for elements O(1s), N(1s), C(1s), S(2s), S(2p), Si(2s), Si(O).

(b) Binding energy vs. counts/s for C(1s) with peaks at 284.5 (sp² C-C), 285.5 (C-N, C-O, C-S), and 288.9 (C-O, C=S).

(c) Binding energy vs. counts/s for N(1s) with peaks at 400.6 (C-N) and 399.7 (C-N).

(d) Binding energy vs. counts/s for S(2p) with peaks at 163.4 (S₂, S=S-C), 163.9 (S₂, S=S), and 164.8 (S₂, S=S-C).
FIG. 4

Normalized Intensity

Time / nm

N,S-GQDs
N-GQDs
O-GQDs

FIG. 5

Density

Energy

O-GQDs  N-GQDs  N,S-GQDs

1. Electrons were excited from ground state and trapped by the surface states.
2. Excited electrons come back to the ground state via a Non-radiative route.
3. Excited electrons come back to the ground state via a radiative route.

Ground state
A. CLASSIFICATION OF SUBJECT MATTER

B82Y 40/00 (2011.01)  C01B 31/04 (2006.01)  C09K 11/06 (2006.01)

According to International Patent Classification (IPC) or to both national classification and IPC.

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

Database: ESPACENET and Keywords: graphene, carbon, quantum, dot, doped, nitrogen, sulphur and the like

Database: GOOGLE, and GOOGLE SCHOLAR with keywords: graphene, carbon, quantum, dot, doped, nitrogen, sulphur and the like

Database: WPI, EPDOC and IPC/CPC marks: HOIL, Y10S997/00, B82, and keywords: quantum _dot, QD, CQD, GQD, carbon+, gra[ph,f]+, doped, nitrogen, sulfur, sulphur and like terms

Database: IN SPEC and keywords: carbon, gra[ph,f]+, quantum _dot, CQD, GQD, doped, nitrogen, sulfur, sulphur and like terms

C. DOCUMENTS CONSIDERED TO BE RELEVANT

<table>
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<th>Category*</th>
<th>Citation of document, with indication, where appropriate, of the relevant passages</th>
<th>Relevant to claim No.</th>
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<td>Special categories of cited documents:</td>
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<td>document defining the general state of the art which is not considered to be of particular relevance</td>
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<td>document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</td>
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<td>document referring to an oral disclosure, use, exhibition or other means</td>
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<td>&quot;&amp;&quot;</td>
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Documents are listed in the continuation of Box C

Further documents are listed in the continuation of Box C

See patent family annex

Date of the actual completion of the international search: 10 February 2014

Date of mailing of the international search report: 10 February 2014

Name and mailing address of the ISA/All

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Due to data integration issues this family listing may not include 10 digit Australian applications filed since May 2001.