1 Introduction

Fluorescent nanomaterials have greatly attracted attention because of their excellent fluorescent performance and special small size effect.\textsuperscript{1-4} In the development of fluorescent nanomaterials, semiconductor quantum dots (QDs), such as PbS QDs and CdTe QDs, usually have size-tunable and narrow emission spectra, high photostability, and resistance to metabolic degradation in bioapplications.\textsuperscript{5-7} Although great success has been achieved on semiconductor QDs and rare earth ion doped nanoparticles, the heavy metals of semiconductor QDs caused high toxicity to the organism. Additionally, low biocompatibility limited the application of semiconductor QDs in biological systems. Therefore, it is very necessary to develop non-toxic or low toxic fluorescent nanomaterials instead of semiconductor QDs.

Recently, graphitic carbon nitrides (CN), as a type of carbon-based nanomaterials, have secured considerable interest due to their unique properties, such as low toxicity, fascinating electronic band structure, unique structural characteristics and being environment friendly.\textsuperscript{6,7} Among these CN materials, g-C\textsubscript{3}N\textsubscript{4} is the most extensively investigated photocatalyst due to its chemical stability and a tunable electronic structure. Currently available g-C\textsubscript{3}N\textsubscript{4}-based materials including layered g-C\textsubscript{3}N\textsubscript{4} and composites based on g-C\textsubscript{3}N\textsubscript{4} generally have been applied in many fields such as photocatalysis,\textsuperscript{8-10} photo-degradation,\textsuperscript{11,12} antibacterial field,\textsuperscript{13-15} sensors\textsuperscript{16,17} and so on. However, the g-C\textsubscript{3}N\textsubscript{4} is generally limited to the C/N ratio higher than 0.75 \textit{i.e.} C\textsubscript{3}N\textsubscript{4}. The relatively low nitrogen content in the carbon framework suffer from low stability, further limiting their performance in various applications.\textsuperscript{18} Recently, Vinu \textit{et al.} reported a novel carbon nitride with the more nitrogen content (with g-C\textsubscript{3}N\textsubscript{4} stoichiometry ratio).\textsuperscript{19-22} It was demonstrated that the g-C\textsubscript{3}N\textsubscript{4} provided much better electronic properties than g-C\textsubscript{3}N\textsubscript{4} with less nitrogen content.\textsuperscript{21} And the novel g-C\textsubscript{3}N\textsubscript{4} extended its absorption in visible region. It implies that the g-C\textsubscript{3}N\textsubscript{4} has more excellent optical performances. On the other hand, the g-C\textsubscript{3}N\textsubscript{4} had more surface functional groups (such as –NH\textsubscript{2} groups) largely improving the interaction between g-C\textsubscript{3}N\textsubscript{4} and the guest species (\textit{e.g.} biomolecules, biomarker).\textsuperscript{22} It implies that the g-C\textsubscript{3}N\textsubscript{4} has great potential in the field of biochemical analysis. In addition, the triazole structure also endowed g-C\textsubscript{3}N\textsubscript{4} to be fluorescence, chemical stabilization and biocompatibility. From the above, the g-C\textsubscript{3}N\textsubscript{4} is expected to use as a novel and ideal fluorescent material.

Although the bulk g-C\textsubscript{3}N\textsubscript{4} exhibits great potential for optical application, there are still some problems need to be overcome before its practical application. Firstly, the strong interactions between g-C\textsubscript{3}N\textsubscript{3} layers make it insoluble in water. Secondly, the g-C\textsubscript{3}N\textsubscript{4} with the relatively low fluorescence quantum yields (FLQY) is sub-micrometer-sized. The large size of g-C\textsubscript{3}N\textsubscript{4} limits...
its wide application in the biological fields. Compared with the bulk materials, the quantum dots (such as graphene quantum dots, graphene oxide quantum dots) with sizes less than 10 nm have excellent optical properties, better hydrophilicity and more suitable for biological applications.21–23 Therefore, it will be interesting to develop effective routes for cutting bulk g-C3N4 into quantum dots-sized pieces i.e. g-C3N4 quantum dots (g-C3N4-dots), and the g-C3N4-dots will be promising candidate fluorescence materials for optical, biomedical, and cellular imaging areas.

It is noted that CN is a graphite-like layered material linked to planar amino groups in each layer and weak van der Waals force between the layers.26–27 This special structure leads to the easy break of bonds between interlayers, while making it difficult to break the C-N bonds on the layers.28 Therefore, it is very necessary to develop a simple and efficient method to prepare g-C3N4-dots. Herein, we reported the synthesis of g-C3N4-dots through a facile alkaline assisted-hydrothermal strategy using bulk g-C3N4 as precursor firstly. Compared with other reported methods, the proposed synthesis method of CN quantum dots was low-cost, fast and simple (Table S1). And the entire synthetic process of g-C3N4-dots only required 60 min. The as-synthesized g-C3N4-dots exhibited high fluorescence (FL) with FLQY of 12%. Meanwhile, the g-C3N4-dots displayed peroxidase-like activity and well optical properties including acid resistance, alkaline resistance, salt stability, photo-stability, resistance to photo-bleaching. As satisfactory FL probes, the as-prepared g-C3N4-dots with good biocompatibility and low cytotoxicity were successfully applied in FL imaging of HeLa cells directly.

2 Experimental section

2.1 Materials

3-Amino-1,2,4-triazole, NaCl, HCl, NaOH, methylthiazolyl-diphenyltetrazolium bromide (MTT), quinine sulfate, ethyl acetate (EA), trichloromethane (CHCl3) and dimethylsulfoxide (DMSO), o-phenylenediamine (OPD), and 3’,3’,5,5’-tetramethylbenzidine dihydrochloride (TMB·2HCl) were obtained from Shanghai Reagent (Shanghai, China). All other chemicals used in this work were of analytical grade. FLQY was determined using a previously published procedure by using quinine sulfate as a reference standard (FLQY = 54%). Millipore Milli-Q ultrapure water (Millipore, ≥18 M cm⁻¹, U.S.A) was used throughout the experiments.

2.2 Apparatus

Transmission electron microscope (TEM) images were collected from a JEM-2100 transmission electronic microscope (JEM, Japan). The ultraviolet-visible (UV-vis) spectra were obtained by a UV-2450 UV-vis spectrophotometer (Shimadzu Co., Japan). An F-7000 fluorescence spectrophotometer (Hitachi Co., Japan) was applied for the fluorescence analysis. Fourier transform infrared spectra (FT-IR) were recorded on a Nicolet Nexus 670 FT-IR spectrope (Nicolet Instrument Co., USA). X-ray photoelectron spectroscopy (XPS) data was measured by a K-Alpha 1063 XPS (Thermo Fisher Co. U.K.) for analyzing structure information of g-C3N4-dots.

2.3 Preparation of bulk g-C3N4

The bulk g-C3N4 was prepared by direct thermal treatment of 3-aminio-1,2,4-triazole. Briefly, 4 g 3-aminio-1,2,4-triazole was put into an alumina crucible and then heated from the room temperature to 500 °C with a ramp rate of 13 °C min⁻¹ in air. Finally, the deep yellow bulk g-C3N4 was obtained after cooling to room temperature and then ground into fine powders in the agate mortar.

2.4 Preparation of g-C3N4-dots

The g-C3N4-dots were prepared by an alkali-assisted hydrothermal method. Typically, 0.03 g bulk g-C3N4 powder mixed with 0.3 g NaOH and 10 mL H2O under stirring. Then the solution was transferred into a 25 mL Teflon lined stainless steel autoclave. Afterward, the sealed autoclave was heated to 180 °C in an electric oven and kept for 60 min. After naturally cooled to room temperature, the product was centrifuged at 8000 rpm for 5 min to remove the large size particles and dialyzed against water through a dialysis bag (cut-off molecular weight 500 Da) for 2 days. The suspension of g-C3N4-dots was finally obtained and stored at 4 °C for further characterization and applications.

2.5 Calculation of FLQY

The FLQY of g-C3N4-dots was calculated using quinine sulfate as a reference. Quinine sulfate (literature Φ = 0.54) was dissolved in 0.1 M H2SO4, and the g-C3N4-dots were dispersed in ultrapure water. The QYs was determined by comparing the integrated FL intensity and the absorbance value of the g-C3N4-dots samples with that of the references. The absorbance less than 0.05 (at the excitation wavelength) at 335 nm and 360 nm for quinine sulfate and g-C3N4-dots was obtained, respectively. The slope method was used to calculate the QYs of g-C3N4-dots using the equation:

\[
QY_{u} = \frac{QY_{s}(m_{s}/m_{u})(n_{u}/n_{s})}{QY_{u}/QY_{s}} \tag{1}
\]

where QY is the quantum yield, \(m\) is the slope determined by the curves and \(n\) is the refractive index (1.33 for water and 1.80 mol L⁻¹ H2SO4 aqueous solution). The subscript “s” refers to the standards and “u” refers to the unknown samples. For these aqueous solution, \(n_{u}/n_{s} = 1\). Series of concentrations of the references and the g-C3N4-dots samples were measured to obtain the slopes.

2.6 Cell imaging and toxicity assay

The cytotoxicity of the g-C3N4-dots to human epithelial carcinoma (Hela) cells was evaluated by a standard methylthiazolyl-diphenyltetrazolium bromide (MTT) assay. Hela cells were seeded in 96-well U-bottom plates at a density of approx. \(5 \times 10^4\) to \(1 \times 10^5\) cells per mL (90 mL per well) that were initially cultured for 12 h in an incubator (37 °C, 5% CO2), followed by the addition of the g-C3N4-dots suspension with different

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concentrations. After another 24 h of being cultured with the g-C₃N₅-dots, 20 mL of the MTT solution (normal saline or 1 mg mL⁻¹ phosphate buffer solution) was added to each sample and incubated at 37 °C for 4 h. The culture media were discarded, followed by the addition of 150 mL of dimethyl sulfoxide (DMSO) to dissolve the formazan under shaking for more than 15 min. The cell viability rate (VR) was calculated based on the following equation:

\[
VR (\%) = \frac{A}{A_0} \times 100\%
\]

where \(A\) is the absorbance of the experimental group (the cells that were treated with the g-C₃N₅-dots suspensions) and \(A_0\) is the absorbance of the control group.

3 Results and discussion

3.1 Characterization of the g-C₃N₅-dots

To obtain g-C₃N₅-dots with high FLQY, the effect of the mass ratio of g-C₃N₅ powder and NaOH, hydrothermal temperature, and hydrothermal time were optimized. As shown in Fig. S1,† the precursors (the mass ratio of g-C₃N₅ powder and NaOH was 0.03 : 0.3) were heated to 180 °C in an electric oven and kept for 60 min. The FL intensity of the prepared g-C₃N₅-dots reaches the highest value. Furthermore, the FLQY of as-prepared g-C₃N₅-dots was investigated at different synthesis conditions and the results are listed in (Table S2†). And the quinine sulfate solution (quantum yield 54%) was acted as reference. The highest FLQY of as-prepared g-C₃N₅-dots is 12.0%. From the above, the excellent g-C₃N₅-dots with the highest FLQY can be obtained from hydrothermal reaction of 0.03 : 0.3 g-C₃N₅/NaOH at 180 °C for 60 min and be chosen as fluorescent probes for further application.

To explore the morphology of the as-prepared g-C₃N₅-dots, we investigated their transmission electron microscopy (TEM) image, high-resolution transmission electron microscopy (HRTEM) image, X-ray diffraction (XRD) spectra. As shown in Fig. 1A, the TEM image of the g-C₃N₅-dots reveals that the as-prepared g-C₃N₅-dots are well-dispersed in water (Fig. 1A). A well-resolved crystal lattice noted in the high-resolution TEM (HRTEM) image (inset in Fig. 1A) confirms the crystalline structure of the g-C₃N₅-dots. The labeled interplanar distance is 0.24 nm, which is consistent with the (100) lattice spacing of graphene.29,30 To further investigate the crystal structure of g-C₃N₅-dots, X-ray diffraction (XRD) patterns of bulk g-C₃N₅ and g-C₃N₅-dots were analyzed. As shown in Fig. S2,† the prepared g-C₃N₅-dots still have high crystallinity and stable crystal structure. For the bulk g-C₃N₅, the XRD patterns presents two diffraction peaks at 27.1° and 12.1°, which are attributed to the interplanar stacking of CN layers and are characteristic peaks of polymeric carbon nitride. For the g-C₃N₅-dots, the absence of the small peak at 12.1° reveals that the products display the decreased planar size of the CN layers. Meanwhile, the (002) peak shifts from 27.1° for bulk carbon nitride to 27.1°, which indicates the gallery distances are tuned during the formation process of g-C₃N₅-dots.

The Fourier transform infrared (FT-IR) spectra of g-C₃N₅-dots were obtained. We explored the FTIR spectrum of bulk g-C₃N₅ firstly. As shown in Fig. 2A, the FTIR spectrum for bulk g-C₃N₅ shows a peak at 3136 cm⁻¹ which corresponds to the stretching vibrations of –OH, –COOH, and –NH₂ on the surface of g-C₃N₅-dots and endow g-C₃N₅-dots with good polarity and dispersity in water and DMSO.31

To investigate the functional information of g-C₃N₅-dots, the

![Fig. 1](image-url) (A) Typical TEM and HRTEM (inset) images of g-C₃N₅-dots. (B) Size distribution histograms of g-C₃N₅-dots.
peaks of products are almost no change after alkaline assisted-hydrothermal process. The result indicates that g-C₃N₅-dots preserve the same functional structure as bulk g-C₃N₅. However, the FT-IR spectrum of g-C₃N₅-dots shows a new and strong peak at 3380 cm⁻¹, which is attributed to the bending vibrations of –OH. We infer that –OH is generated by breaking the structure of bulk g-C₃N₅ in the process of alkaline assisted-hydrothermal treatment. These above results confirm that the as-synthesized nanoparticles are functionalized by –OH and –COOH.

On the other hand, we further investigated functional information of g-C₃N₅-dots via X-ray photoelectron spectra (XPS). The XPS survey spectrum (Fig. 2B) of g-C₃N₅-dots further confirms that the material is mainly composed of 36.44% C and 61.8% N with 1.76% O. The small amount of O can be related to CO₂ adsorption on the surface of g-C₃N₅-dots. The C₁s spectra (Fig. 2C) suggest that the presence of C–NH₂ (289.1 eV), N₂–C=N (287.7 eV) and adventitious C (285.7 eV). The N₁s spectra (Fig. 2D) show three peaks at 399.9 eV, 398.2 eV, which are attributed to the π–π*, –C–NH₂, and –C–N=C, respectively. The π–π* and –C–N=C reveal the presence of graphitic sp² network. And –C–NH₂ further confirm that the presence of tris-triazine ring in the CN framework.

### 3.2 The synthetic mechanism of g-C₃N₅-dots

Additionally, the possible synthetic mechanism of g-C₃N₅-dots was proposed. Under alkaline-assisted-hydrothermal condition, the hydroxyl groups can be transferred to produce free radicals (e.g. ‘OH and ‘O⁻). These free radicals are the key for the cleavage of bulk g-C₃N₅ into small g-C₃N₅-dots in the hydrothermal process under alkaline solution. To demonstrate our inference, g-C₃N₅ powder was treated by hydrothermal strategy under neutral (pure water) solution, acid solution (1.5 M HCl) and alkaline solution (1.5 M NaOH) for 60 min, respectively. And the morphology features, optical properties and functional information of these obtained products were characterized. Firstly, the TEM images of the synthesized products were obtained to study the effect of different solution conditions on the morphology of the prepared products, respectively. As shown in Fig. S4† the products prepared by hydrothermal method with the treatment of neutral solution and HCl solution display bulk structure with large size, respectively. However, the product prepared by alkaline assisted-hydrothermal method uniformly distribute in water and the diameters of g-C₃N₅-dots mainly distribute in the range of 2–4 nm. The result is due to the fact that the free radicals obtained from alkaline assisted-hydrothermal condition can break C–N bonds on the g-C₃N₅.
These free radicals acting as "scissors" cut large-sized g-C3N5 fragments into g-C3N5-dots. Furthermore, the alkaline assisted-hydrothermal process for synthesis of g-C3N5-dots was investigated by TEM. From Fig. S5,† it is noted that the product obtained from alkaline assisted-hydrothermal process at 30 min has a larger size (12 nm) compared with the product obtained at 60 min (3 nm). Based on above discussion, the larger-sized g-C3N5 is cut into smaller-sized g-C3N5, and then is converted into g-C3N5-dots finally. And the alkali environment facilitates the formation of g-C3N5-dots.

Secondly, UV-vis spectra and fluorescence spectra of their products were explored to investigate the effect of solution condition on optical properties of the obtained products. As shown in Fig. 3A, the day light photographs of synthesized products under neutral solution and acid solution show colorless clear, respectively. However, the day light photograph of synthesized product under alkaline solution shows light yellow and the product show two obvious absorbance peaks at 225 nm and 280 nm (Fig. 3B). And the control experiments (Fig. 3C and D) show that products in neutral and acid environments have no FL, whereas the product obtained from alkaline assisted-hydrothermal process shows distinct FL under excitation. And the alkali environment facilitates the formation of g-C3N5-dots.

Thirdly, XPS spectra of three prepared products in different conditions were explored to further investigate the effects of synthetic conditions on the functional information of products. As shown in Fig. 4A and B, high-resolution XPS of the C1s and N1s of three prepared products have little change. And the peak area of –NH2, –C–N–C, C–NH2, N2–C=–N and Adv. C almost remain unchanged (Table 1). However, the peak area of both C=O and C–O of the product obtained from alkaline assisted-hydrothermal condition is larger than that of the products in neutral and acid environments (Fig. 4A and Table 1). The result is consistent with UV-vis spectra (Fig. 3B). Based on the above discussion, we infer that alkaline condition makes for the production of –OH and C=O. And the abundant electron donor groups (–OH and –NH2) on the surface of g-C3N5-dots obtained from alkaline assisted-hydrothermal process are beneficial to fluorescence emission.

It is noted that optical property is an important parameter to their future application in biosensors and bioimaging. Therefore, the optical properties of g-C3N5-dots were characterized by ultraviolet-visible (UV-vis) spectrophotometer and FL spectrophotometer. As shown in Fig. 5A, the characteristic absorption peaks around 225 nm and 280 nm found in the UV-vis spectra are ascribed to the n-π* transition of C=O and π-π* transition of C=C, respectively. The as-synthesized g-C3N5-dots have a maximum emission at 440 nm under an excitation at 360 nm (Fig. 5A). FL emission spectra of g-C3N5-dots display excitation-
dependent FL behavior at different excitation wavelengths that change from 320 nm to 460 nm. This behavior is attributed to surface defect and size distribution of g-C₃N₅-dots. The FLQY of the prepared g-C₃N₅-dots is calculated with quinine sulfate solution (quantum yield of 54%) as reference (Fig. S6†). The fluorescence quantum yield (FLQY) of the prepared g-C₃N₅-dots is calculated to be about 12%. And we choose the optimum g-C₃N₅-dots with a high FLQY for further application.

3.3 The optical stability of g-C₃N₅-dots

To explore the optical stability of g-C₃N₅-dots, a detailed FL study was obtained. The FL intensities of g-C₃N₅-dots have little change even under high salt concentration (Fig. S7A). And the FL intensities of g-C₃N₅-dots are pH independent under acidic or basic conditions (Fig. S7B). As mentioned above, as-synthesized g-C₃N₅-dots are functionalized by abundant oxygen-containing functional groups (such as –OH and –COOH), which improve the hydrophilicity and stability of them in aqueous. What is more, the FL intensity does not change even after continuous excitation with a 150 W Xe lamp (Fig. S7C). Otherwise, the FL intensities of g-C₃N₅-dots are stable for more than a month without any distinct reduction (Fig. S7D). The results demonstrate that the as-synthesized g-C₃N₅-dots have excellent photostability. According to these unique optical properties of g-C₃N₅-dots, g-C₃N₅-dots have tremendous practical application potential in the field of biosensors and bioimaging.

3.4 The bioimaging and peroxidase-like activity of g-C₃N₅-dots

Compared with bulk g-C₃N₅ materials, their quantum dots exhibit distinct physicochemical properties due to their quantum confinement effect. Therefore, it is possible to expand the potential application in bioimaging of g-C₃N₅-dots. Firstly, the cytotoxicity of the g-C₃N₅-dots was investigated by the 3-(4,5-

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Table 1  Peak area of binding energy of high-resolution XPS data of O₁s, N₁s and C₁s of synthesized products under different conditions (H₂O, 1.5 M HCl and 1.5 M NaOH), respectively

| Different conditions | Peak area (O₁s) | Peak area (N₁s) | Peak area (C₁s) |
|---------------------|----------------|----------------|----------------|
|                     | C–OH           | C==O           | –NH₂           | –C–N=C         | C–NH₂       | N₂–C==N       | Adv. C        |
| H₂O                 | 2816.32        | 1210.31        | 7587.91        | 3970.94        | 6779.36     | 4459.06       | 9715.36       |
| HCl                 | 3034.85        | 4802.70        | 7360.12        | 4101.93        | 6230.16     | 4906.48       | 12 099.17     |
| NaOH                | 10 124.06      | 8953.22        | 7360.12        | 3875.86        | 6267.98     | 4481          | 11 591.41     |

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Fig. 4  High-resolution XPS of (A) C₁s, (B) N₁s and (C) O₁s of synthesized products under different conditions (H₂O, 1.5 M HCl and 1.5 M NaOH), respectively.

Fig. 5  (A) UV-vis spectra and fluorescence spectra of g-C₃N₅-dots. (B) Fluorescence emission spectra of g-C₃N₅-dots at different excitation wavelengths that change from 320 nm to 460 nm.
dimethylthiazol-2-yl)-2,5-diphenyltetrazolium bromide (MTT) assay. From Fig. 6A, the result shows that the cell viability remains greater than 86% with the increasing concentration of g-C₃N₅-dots in the range of 0.05–0.3 mg mL⁻¹. The result indicates that the g-C₃N₅-dots have low cytotoxicity and excellent biocompatibility. Then, the g-C₃N₅-dots were introduced into HeLa cells for in vitro bioimaging. As shown in Fig. 6B, the HeLa cells display good morphology. And a significant blue emission from the intracellular region could be observed in dark field. From Fig. 6C and D, the cell morphology displays no significant changes. All these results indicate that the as-synthesized g-C₃N₅-dots exhibit low cytotoxicity and excellent biocompatibility and have the application potentials as FL probe for bioimaging and related biological applications.

Additionally, we investigated the peroxidase-like activity of g-C₃N₅-dots in the catalysis for oxidation of peroxidase substrates TMB (or OPD) in presence of H₂O₂. As shown in Fig. S8,† TMB–H₂O₂, TMB–g-C₃N₅-dots, OPD–H₂O₂, OPD–g-C₃N₅-dots systems have no absorbance peak and their solutions exhibit colorless. However, there are two obvious absorbance peaks at 652 nm and 444 nm in TMB–g-C₃N₅-dots–H₂O₂ system and OPD–g-C₃N₅-dots–H₂O₂ system, respectively. Up to now, there are few reports about g-C₃N₅-dots as enzymatic mimetics. The peroxidase-like activity of g-C₃N₅-dots is similar to the reported other quantum dots.³¹ These results suggest that the as-prepared g-C₃N₅-dots possess excellent peroxidase-like activity, further indicating the tremendous practical application potential in the field of biosensors.

4 Conclusion

In summary, the novel g-C₃N₅-dots were fabricated by a facile alkaline-assisted hydrothermal strategy for the first time. The synthetic mechanism of g-C₃N₅-dots was discussed. Under the alkaline-assisted hydrothermal process, the high temperature and high pressure conditions make hydroxyl groups transfer to produce free radicals. These free radicals acting as “scissors” cut large-sized g-C₃N₅ fragments into g-C₃N₅-dots. The proposed method has many advantages of low-cost, easy operation and time-saving. The entire synthetic process of high fluorescence g-C₃N₅-dots requires only 60 min. The as-prepared g-C₃N₅-dots with triazole ring display superior salt tolerance, pH-stability, anti-photobleaching and excitation-dependent behavior. In addition, g-C₃N₅-dots with low toxicity and excellent biocompatibility were successfully used for cell imaging. The study provides a simple and effective strategy for synthesis of g-C₃N₅-dots and prompts the novel g-C₃N₅-dots for some potential application in the field of biosensors and bioimaging.

Conflicts of interest

There are no conflicts to declare.
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