Small but strong: The influence of fluorine atoms on formation and performance of graphene quantum dots using a gradient F-sacrifice strategy

Peiwei Gong a, b, Jinqing Wang a, *, Kaiming Hou a, Zhigang Yang a, Zhaofeng Wang a, Zhe Liu b, Xiuxun Han a, **, Shengrong Yang a

a State Key Laboratory of Solid Lubrication, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou, 730000, PR China
b Key Laboratory of Life-Organic Analysis of Shandong Province, Qufu Normal University, Qufu, 273165, PR China

Abstract
Fluorinated graphene quantum dots (FGQDs) have distinctive charge distribution in structure and unique chemical bonds in composition, corresponding to novel performance different from common quantum dots. However, their synthesis is a challenge due to chemically inert C—F bonds and hydrophobic nature, and the fluorine influence on FGQDs remains scarce and to be studied. Herein, we first design a gradient fluorine-sacrificing strategy to synthesize FGQDs with controllable sizes and tunable fluorine contents from bulk fluorinated graphite. It is found that although fluorine atom is the second-smallest in periodic table, it not only greatly affects the size formation process, but also endows FGQDs with pH-independent luminescence without any additional surface passivation. And it is for the first time to experimentally observed that point defects in FGQDs induced by fluorine can greatly increase paramagnetism, which is 5 times higher than unfluorinated ones. Moreover, cytotoxicity experiments clearly reveal FGQDs show good biocompatibility, and it is the chemical surface rather than size that influences the cell viability. This work realizes fine control over both structure and chemistry of FGQDs, and thus allows a better insight into the fluorine effects on formation and performance of graphene quantum dots.

1. Introduction
Recent years have witnessed significant breakthroughs and prosperity of graphene quantum dots (GQDs) in both scientific and technological worlds due to its noble and novel properties [1–3]. With characteristic quantum-confinement and edge effects, the zero-dimensional (0D) GQDs have offered numerous possibilities and opportunities for researching the fundamental science in 0D layered structures [4,5], improving the performance via the integration of graphene into various electronic and optical applications [6,7], and promoting the revolution of traditional quantum dots in environmental and biological field [8,9]. And what makes it a more versatile and applicable material is decorating GQDs with functional groups or doping the structure with heteroatoms; chemical modification of GQDs with heteroatoms is of fundamental importance to tune their intrinsic structural properties [10], manipulate the electronic state [11], and adjust surface or local chemical environment [12], etc. Discovery or successful modification of GQDs with exotic atoms, can not only ignite tremendous fresh research interest and new insights into material science, but also induce fast explosion of novel applications of GQDs [13].

Fluorine, a small atom in periodic table, is powerful in modulating the chemical, structural and electronic features of carbon material owing to its high electronegativity. Decorating graphene with fluorine (namely fluorinated graphene, FG) has endowed graphene with unique electronic [14,15], luminescent [16,17], magnetic [18,19], electrochemical [20,21] and biological function [22,23], etc. And then it inspires us to deeply think what it will bring about as grafting fluorine onto GQDs. However, both the challenge of preparing FG and the dramatic inertia of C—F chemical bonds unmercifully make most of once available methods to prepare GQDs invalid. Accordingly, it remains a great challenge to prepare FGQDs, and the unique properties of FGQDs are almost completely unknown, not to mention its potential applications. Therefore, in view
of both science and technology, a reliable and effective method to prepare FGQDs with tunable morphology and chemistry is highly desirable.

In this study, a strategy to tackle this dilemma and bridge the gap between concept and research is developed. Low-cost and commercially available fluorinated graphite (FGi) was first employed to produce FGQDs by a gradient fluorine-sacrificing strategy, which fundamentally avoids the toxic process to prepare FG by fluorinating graphene and the long-time hydrothermal-cutting treatment. The designed technologies and skills in our method also make it easy to gain finer and wider control over the chemical composition and size, which further allows us to gain a better insight into the fluorine effects on formation, luminescence, magnetism and cytotoxicity of FGQDs. The practically applicable experiment method, interesting achievements and useful research results presented here are expected to ignite more research flame into GQDs and other carbon materials, and promote the newly born FGQDs to find wider applications in various fields.

2. Experimental section

2.1. Raw materials

Fluorinated graphite (FGi, Grade II) was purchased from Shanghai CarFluor Ltd. and used as provided. KOH (≥82.0%), NaOH (≥96.0%) and other chemical reagents were purchased from Sinopharm Chemical Reagent Co., Ltd. and used without further purification. Ultra-pure water (>18 MΩ cm) was used throughout for preparation and washing.

2.2. Preparation of expanded FGi and hydroxyl-functionalized FG with gradient fluorine contents

To prepare expanded FGi (E-FGi), 100 mg dried FGi was blended uniformly with the mixed alkali (KOH–NaOH) powder in the following two designed recipes. For FG-1, the mass of the mixed alkali is about 318.7 mg; while for FG-2, the mass of the alkali is about 478.0 mg. Further increasing the mass ratio of alkali/FGi can also obtain similar products, yet the reaction ratio was set as above to obtain FG sheets uniformly with the mixed alkali (KOH for 2.5 h). After cooling down to room temperature, the product was finally obtained.

After cooling down to room temperature, the product was dispersed in ultra-pure water. After being sonicated for 2 h, single- or few-layered hydroxyl-functionalized FG sheets were finally obtained.

2.3. Preparation of FGQDs with tunable fluorine coverages and sizes

100 mg obtained FG samples was first dissolved into 10 mL concentrated H2SO4 and 3 mL ultra-pure water, and then the mixture was sonicated for 1.5 h to achieve a homogeneous dispersion. After another 10 mL concentrated H2SO4 and 60 mL HNO3 were added, the mixture was sonicated for 3 h, followed being heated at 70 °C for 24 h. After cooling down to room temperature, 200 mL ultra-pure water was added and the pH of the solution was tuned neutral. Upon vacuum filtration (0.22 μm filter), FGQDs were finally obtained and collected by dialysis (molecular weight: 500 Da). Compared with reported work of preparing FGQDs [24], our method by using FGi as the raw material completely avoids the complex process to prepare FG with toxic and violent gases (such as F2 or XeF2). And compared with our previous work [25], this newly developed method can not only be realized in low temperature (the highest temperature is 120 °C, while the lowest temperature is 70 °C), but also fundamentally avoids tedious long-time sonication and following high-temperature hydrothermal treatment, all of which make our method much more cost-effective and readily processible.

Samples FG-1 and FG-2 were treated under the same reaction conditions. To investigate the influence of temperature on FGQDs, sample FG-2 was reacted at 70 °C, 80 °C, 100 °C and 120 °C. And to evaluate the fluorine effects, GQDs was also prepared by using reduced graphene oxide under similar reaction conditions. Based on the reaction reagents and temperature, the products were abbreviated as FGQDs-1-70, FGQDs-2-70, FGQDs-2-80, FGQDs-2-100 and FGQDs-2-120.

2.4. Cellular viability

For 3-(4,5-dimethylthiazol-2-yl)-2,5-diphenyltetrazolium bromide (MTT) assay, Hela cells were employed to evaluate the biocompatibility of the as-prepared dried FGQDs powder. To calibrate the cellular survival rate, blank and control groups were set. In the blank group, only culture media was added; while in the control group, cells and culture media without samples were added. The measured optical density (OD) values of the blank, control, and experimental groups were coded as ODbla, ODcon, and ODexp, respectively. Finally, the cellular survival rate was calculated by the following equation:

\[
\text{Survival Rate} = \frac{\text{OD}_{\text{exp}} - \text{OD}_{\text{bla}}}{\text{OD}_{\text{con}} - \text{OD}_{\text{bla}}} \times 100\%
\]

The results were expressed as the mean ± SD (standard deviation).

2.5. Characterization and measurement

The chemical composition of the prepared samples was investigated by IFS 66 V/S Fourier transformation infrared (FTIR) spectrometer (Bruker, Germany), and X-ray photoelectron spectroscopy (XPS, EscaLab 250Xi) using a monochromated Al-Kα irradiation. The morphology of samples was observed by transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM, FEI Tecnai F30, operated at 300 kV), respectively. The photoluminescence excitation (PLE) and emission spectra were recorded on a FLS-920T fluorescence spectrophotometer equipped with a 450 W Xe light source and double excitation monochromators.

3. Results and discussion

It is suggested that two prerequisites guarantee the successful realization of exfoliating and modifying FGi in one step: one is that the high electronegativity gap between carbon and fluorine (4.0 for fluorine and 2.55 for carbon on the Pauling scale [26]) makes the carbon atom on FGi more positive, providing the possibility for nucleophilic hydroxyl to attack carbon and then substitute fluorine; the other is that the pre-designed nucleophilic reagents can provide mobile hydroxyl ions at a temperature much lower than the decomposition temperature of C–O and C–F, ensuring both the functionalization of oxygen and reservation of fluorine. Besides functionalization of FGi with hydroxyl to improve its solubility in water, after cooling down to room temperature the molten salts that have intercalated between FGi layers recrystallize and their volume expand, which further increases the interlayer space and finally facilitates the exfoliation. TEM images in Fig. 1 a, b clearly reflect the effective exfoliation and modification processes, both of which reveal that large, transparent and corrugated FG sheets with
few layers are readily obtained. Then chemical composition analysis was carried out to investigate whether fluorine retains and hydroxyl invades as our initial design. FTIR spectra in Fig. 1c show that C–F bonds in the forms of covalent C–F (located at 1215 cm\(^{-1}\)) and –CF\(_2\) (located at 1342 cm\(^{-1}\)) bonds robustly maintain on FG, and oxygen-containing groups in the forms of C–O (1047 cm\(^{-1}\)) and C–OH (1384, 3430 cm\(^{-1}\)) are successfully introduced onto FG\(^{-}\). This is also supported by XPS survey spectra imparted in Fig. 1d, in which both oxygen and fluorine elements are detected on the two prepared FG sheets.

Meanwhile, XPS investigation also gives the element composition of the two kinds of FG sheets (for FG-1, the fluorine content is about 29.7%; while for FG-2, the fluorine content is about 20.2%), confirming the fact that fluorine coverage on FG sheets can be pre-designed by adjusting the ratio of alkali to FG\(_i\). These above data and discussions suggest that our method is more than a pretreatment of bulk FG\(_i\) to prepare 0D FGQDs, it is also an effective method that realizes simultaneously modifying and exfoliating FG\(_i\) to prepare 2D FG sheets. The successful introduction of hydroxyl into FG not only contributes to the exfoliation of FG\(_i\) in water, but also greatly improves the solubility of FG, which can be dispersed in water and keep stable for days (Fig. S1 a-b). And it is just this dispersibility conversion from insoluble to soluble in water for FG that greatly facilitates the oxidation and cutting of FG in acid solution. Meanwhile, it is also observed that although following the way to prepare GQDs by adding mixed acid directly\(^{[27,29]}\) can also obtain FGQDs, yet the yield is low. It is considered that even some fluorine atoms are removed from the structure, the FG sheets are still chemically inert to some degree. To improve this, a sonication-assisted pre-oxidized in acid before heating was developed (see the Experimental Section to prepare FGQDs) and it turns out working well.

A definitive quality identification of the prepared FGQDs was performed by TEM characterization to investigate their morphology. As depicted in Fig. 2a, FGQDs-1-70 with highly uniform size is successfully obtained, and a much closer look at the quantum dots in the magnified TEM image indicates the average lateral dimension of the sample is about 2.5 nm. Meanwhile, statistic size distribution in Fig. 2c indicates that the size of the FGQDs-1-70 mostly (about 80%) falls within the scope of 2 nm–3 nm. The crystallinity of the FGQDs-1-70 was investigated and revealed by HRTEM observation (the inset in Fig. 2b); the marked inter-planar distance of 0.21 nm agrees well with the (100) lattice spacing of graphene\(^{[30,31]}\). In contrast, FGQDs-2-70 prepared from FG with lower fluorine coverage obtained under the same conditions (heated at 70 °C) exhibits smaller sizes (Fig. 2d–f), and about 76% of the quantum dots are in the size range of 2 nm–3 nm, and about half are 2 nm. This interesting experimental discovery indicates that FG sheets with lower fluorine coverage might be softer to be oxidized and cut into quantum dots; under this assumption, the oxidizing acids will typically go after low-hanging fruit if they must choose one to cut, leading to the result of FG-2 to be more easily cut into smaller ones. Another amusing experimental phenomenon is that for FG-2, when the reaction temperature rises up to 120 °C, the average size of FGQDs-2-120 reaches up to 3.5 nm (See TEM images and statistic size distribution shown in Fig. 2g–i). Meanwhile, a
more detailed inspection of the influence of temperature on the size of FGQDs (See TEM images and statistic size distribution in Figs. S2a–d) indicates that when the reaction temperature rises from 70, 80, 100–120 °C, the average lateral dimension of FGQDs-2 increases from about 2.0 nm (obtained at 70 and 80 °C), 3.0 nm (obtained at 100 °C) to 3.5 nm (obtained at 120 °C). If the heating process is compared to a sharp scissor in cutting FG into FGQDs, it is then concluded that when the scissor is hot-blooded, larger FGQDs can be tailored; if it is cold-blooded, smaller ones can be obtained. According to above experimental data and discussion, it is found this method is experimentally effective to synthesize FGQDs from commercially available bulk FG, and more importantly, the sizes of FGQDs can be pre-designed by modulating the fluorine content or just by adjusting the heating temperature.

Morphology characterization and investigation clearly indicates that FGQDs with highly uniform size and tunable sizes can be readily realized, and then another key question that remains unexplored is whether fluorine atoms are still reserved after the cutting process and then how many of them are remaining on FGQDs. To address these issues, detailed chemical analyses of the samples are displayed in Fig. 3a–f. FTIR spectra in Fig. 3a clearly show that for the three samples, robust C–F bonds in the forms of covalent C–F (located at 1215 cm⁻¹) and –CF₂ (located at 1342 cm⁻¹) stably remain on the small scaffold of FGQDs [23]. Moreover, it is also observed that different from FG-1 and FG-2 that only contain C–O single bonds on FG sheets, a new absorption peak characteristic of C=O bonds (located at 1727 cm⁻¹) [27] appears in the three FGQDs, implying that during the oxidation and cutting processes, the FGQDs are further oxidized. Meanwhile, the chemical changes of the samples are also reflected and confirmed by XPS investigation in Fig. 3b–f.

To present clearer element information of the samples, XPS measurements were carried out on these FGQDs. XPS survey spectra in Fig. 3b reveal that only carbon, oxygen and fluorine elements can be detected, indicating the high purity of the samples. The investigation on element content shows that for samples of FGQDs-2-70 and FGQDs-2-120, their fluorine contents (18.2% for the former and 17.8% for the latter, respectively) are lower than that of FGQDs-1-70 (24.0%) obtained from FG-1 with higher fluorine coverage; it is also observed that the oxygen contents of FGQDs obtained from FG2 increase with the elevation of the heating temperature, suggesting that under the same conditions higher temperature can induce further oxidation of FGQDs. The detailed elemental composition of the samples obtained from XPS analyses are supplied in Fig. S3. Meanwhile, the F1s spectra of FGQDs (Fig. 3c) located at about 689.0 eV, agree well with the three peaks in the XPS survey spectra (located at 689.0, 832.7 and 861.8 eV), both of which can be ascribed to a reflection of covalent C–F bonds on a carbon structure [32]. A more visualized composition and nature of the chemical bonds of the samples were investigated by

Fig. 2. TEM images of the obtained FGQDs samples: (a) A wide-field image of the obtained FGQDs-1-70; (b) A closer look at the size and shape of FGQDs-1-70; (c) Size distribution of FGQDs-1-70. Images of (d–f) and (g–i) show the corresponding experimental results of FGQDs-2-70 and FGQDs-2-120. (A colour version of this figure can be viewed online.)
high resolution XPS spectra in Fig. 3d–f. Three fitted peaks characteristic of weak covalent C–F bond (wC–F, 289.3 eV), covalent C–F bond (290.0 eV) and –CF2 bond (291.4 eV) can be readily found on the three samples; besides these, C–O groups in the forms of C–O (287.3 eV) and C=O (289.3 eV) also exist on the three FGQDs [31]. These above elemental analyses again demonstrate that C–F bonds remained on the structure of FGQDs and hydrophilic C–O groups are also successfully grafted onto the small scaffold of FGQDs. And these data further prove that our method is effective to synthesize FGQDs, making it possible for FGQDs with tunable fluorine coverage to be obtained from commercially available bulk FG in mild experimental conditions.

According to above data and discussions based on both morphological and elemental investigations, it is suggested that our method endows time-honored FG with new glory; it is more morphological and elemental investigations, it is suggested that our method endows time-honored FG with new glory; it is more time-honored FG with new glory; it is more functional and destructive, and this slowly gnawing process that when the heating temperature is lower after high-temperature processing and nearly complete removal of fluorine occurs after 500 °C, some stable C–F bonds of FGQDs can survive after high temperature (see XPS survey spectra of FGQDs–2–120 in Fig. S4). And among many of the exotic properties of FGQDs, the optical performance is most alluring and it is also the fundamental one that determines its potential integration into optoelectronic, photo-catalyst, solar cells, light-emitting diodes and biological applications. Thus a systematic investigation on the PL performance is carried out on the obtained FGQDs and the corresponding reaction processes to prepare FG and FGQDs are schematically summarized in Fig. 4.

Besides the aim of developing a practically applicable method to produce FGQDs with tunable size and controllable surface density, the fact that both deficient knowledge of FGQDs and the curiosity to uncover their mystery prompt us to explore the properties of FGQDs and find their potential applications. For FGQDs, one distinct property that other graphene or carbon quantum dots can’t surpass is the stability due to strong C–F bond, which is stable up to 500 °C and thus they are more reliable in practical applications [28]. It is also found in our work that although the fluorine contents become lower after high-temperature processing and nearly complete removal of fluorine occurs after 500 °C, some stable C–F bonds of FGQDs can survive after high temperature (see XPS survey spectra of FGQDs–1–70 after being treated under 200 °C, 300 °C, 400 °C and 500 °C shown in Fig. 5). And among many of the exotic properties of GQDs, the optical performance is most alluring and it is also the fundamental one that determines its potential integration into optoelectronic, photo-catalyst, solar cells, light-emitting diodes and biological applications. Thus a systematic investigation on the PL performance is carried out on the obtained FGQDs and their potential applications. For FGQDs, one distinct property that other graphene or carbon quantum dots can’t surpass is the stability due to strong C–F bond, which is stable up to 500 °C and thus they are more reliable in practical applications [28]. It is also found in our work that although the fluorine contents become lower after high-temperature processing and nearly complete removal of fluorine occurs after 500 °C, some stable C–F bonds of FGQDs can survive after high temperature (see XPS survey spectra of FGQDs–1–70 after being treated under 200 °C, 300 °C, 400 °C and 500 °C shown in Fig. 5). And among many of the exotic properties of GQDs, the optical performance is most alluring and it is also the fundamental one that determines its potential integration into optoelectronic, photo-catalyst, solar cells, light-emitting diodes and biological applications. Thus a systematic investigation on the PL performance is carried out on the obtained FGQDs and the corresponding results are displayed in Fig. 5 and Fig. S6. It is observed although FGQDs–1–70 and FGQDs–2–120 possess different sizes and element densities, they exhibit similar PL behavior; namely, both of them present a strong emission peak at about 430 nm when excited under 320 nm wavelength, and the PLE spectra of the two samples under the monitors of 431 nm and 430 nm show strong peaks around 320 nm, indicating that the small difference in size

Fig. 3. Chemical composition analyses of the three samples. (a) FTIR spectra and (b) XPS survey spectra for FGQDs–1–70, FGQDs–2–70 and FGQDs–2–120. The chemical components and functional groups of the three FGQDs samples are labeled; (c) High resolution XPS spectra of F 1s for the three samples; High resolution XPS spectra of C 1s for (d) FGQDs–1–70, (e) FGQDs–2–70 and (f) FGQDs–2–120. (A colour version of this figure can be viewed online.)
distribution and surface state between the two samples don’t cast profound consequence on their PL behavior. On the other hand, a detailed comparison made between FGQDs-2 samples (Fig. 5 d, g and Fig. S6 a, d) clearly reveals that, with increasing the size the PL emission peak red-shifts from 430 nm (for FGQDs-2-70), 527 nm (for FGQDs-2-80), 545 nm (for FGQDs-2-100) to 550 nm (for FGQDs-2-120), indicating size effects gradually gain weight on the PL emission behavior of the samples. Also, it is noticed that...
compared to FGQDs-1-70 and FGQDs-2-70, from sample of FGQDs-2-80, the PLE peaks of FGQDs-2 split into a predominant one at around 350 nm and a shoulder at around 400 nm. The PL performance of GQDs can be affected by the surface chemistry of foreign atoms or groups that induce electron transition from antibonding to nonbonding orbitals, and can also be influenced by size changes in the sp² domains [35–38]. For FGQDs, oxygen and fluorine atoms are co-doped in the structure, resulting in sp³ hybrid carbon; besides, HRTEM investigation (Fig. 2) reveals that sp² domains also exist on the carbon structure of FGQDs. These data suggest that for FGQDs besides the intrinsic state emission (electron-hole recombination or quantum size effect/zigzag effect), defect state emission (surface defects) could also find a place in the luminescence behavior [8], which accounts for the split peak and the broadening peak width. This hypothesis well explains the PL performance of the samples, and is supported by the experimental data (see TEM and size distribution research in Fig. 2 and Fig. S2 as well as the chemical analyses of the samples in Fig. 3 and Fig. S5).

Besides the difference among them, all of the FGQDs also share a common yet extraordinary PL behavior: all FGQDs exhibit excitation-independent PL behavior. As can be observed in Fig. 5 b, c, h and Fig. S6 b, e, only the PL intensity while not the central peak position varies with excitation wavelength, and a much clearer impression of this experiment results are collected in Fig. 5c, f and i. This is a characteristic that can rarely be found in carbon-based fluorescent materials without surface-passivation, whose PL peaks often shift to longer wavelengths as the bathochromic shift of excitation wavelength is applied. Through literature research, it was found that this excitation-independent PL behavior has been reported in GQDs whose surfaces or edges are passivated by high concentration of polymers [39–41]. And in our case, it is observed in FTIR and XPS (see Fig. 3) investigations that abundant oxygen groups exist on the structure of FGQDs besides fluorine atoms, and contents of the functional groups are different in our samples, yet they share the similar excitation-independent behavior. So the surface passivation effect is not the predominant reason for the excitation-independent behavior of our samples. On the other hand, previous work pointed out that electronic properties and mechanisms involved in quantum-confined PL can induce excitation-independent behavior [37], and polydispersity of GQDs could also affect the PL spectra and cause excitation-dependent PL behavior [18], indicating that by carefully synthesizing GQDs with good size uniformity one can obtain GQDs exhibiting excitation-independent PL behavior. As have been studied in TEM investigation, every kind of FGQDs obtained by our method possesses relatively high uniform size and the majority of them exhibit similar sizes and structure. It is reasonable to speculate that the good size uniformity of FGQDs guarantees the extraordinary PL performance.

Another special property that makes FGQDs outstanding from other common graphene or carbon based quantum dots is their unique power to easily handle the provocation of pH on their own without any passivation, which previously could only be obtained in GQDs after being passivated by polymers [42]. PL emission intensity of GQDs without passivation often depends mostly on the pH of the solutions, which often quenches under acidic conditions. However, once powerful changes of pH can no longer greatly affect the PL emission intensity of FGQDs (Fig. 6), and robust luminescence can be readily obtained under different acid or base conditions without any after-treatment. Meanwhile, it is also observed that for these three samples, the more fluorine atoms they contain the less they are affected by change of pH. A close comparison between FGQDs-1 and FGQDs-2 reveals that a much smaller PL intensity deviation to the average value (the dash dot line in Fig. 6) occurs for FGQDs with higher fluorine coverage under different pH. It is no wonder that for FGQDs, this property does exist and fluorine atoms play the key role in the effective resistance of pH changes. Yet then the question is how fluorine atoms play the role?

The mechanism previously developed to explain the effects of pH mostly considers that a protonation and de-protonation process between the zigzag sites and hydrogen ion can affect the PL behavior of GQDs by changing the pH conditions [27], and that passivation of GQDs by removal of functional groups or decoration with polymers can also degrade the influence of pH changes [12]. On the other hand, according to classical Linus Carl Pauling theory on the electronegativity of element, fluorine atom enjoys the highest electronegativity value (4.0 on the Pauling scale) [26]. Thus the high electronegativity difference between fluorine and carbon (2.55 on the Pauling scale) makes it easy for the charge of carbon atoms on FGQDs to transfer onto fluorine atoms, and accordingly fluorine atoms on the scaffold exhibit more positive charge. These positive carbon atoms on the small FGQDs not only greatly influence the charge distribution of FGQDs, but also effectively avoid or degrade the protonation process in acid condition due to electrostatic repulsion. And this further prevents the transition of carbene state on GQDs, which in turn and finally leads to stable emission regardless of pH change [27]. On the other hand, it is also noticed that fluorine atoms can also dramatically affect the surface energy of GQDs like other fluorine-contained carbon materials [43,44], and this effect also makes it possible for fluorine atoms on FGQDs play the role of passivation like polymers. Either the changes of charge distribution or surface energy of FGQDs, or both of them could cooperatively guarantee the stable emission of FGQDs regardless of the varying environmental conditions. It is believed that this pH-independent behavior of FGQDs could promote FGQDs to find applications that require stable emission under rigorous conditions while no other modification or passivation is involved.

The fine control over the chemical and structure of FGQDs also allows us to experimentally investigate the paramagnetism properties. As shown in Fig. 7, Mn⁺ can be obtained by fitting the corresponding M(H/T) curves and clearly, fluorine atoms at a relatively low concentration can produce surprising enhancement of paramagnetism, which is about 5 times higher than GQDs without fluorine. Moreover, it is observed that FGQDs with different sizes and similar fluorine contents (for FGQDs-2-70 and FGQDs-2-120) possess close Mn value, and for FGQDs that possess similar size and different fluorine contents (for FGQDs-1-70 and FGQDs-2-70), the higher fluorine contents the higher paramagnetism can be obtained. These data obviously reflect that it is the fluorine coverage rather than the size or oxygen that influences the paramagnetism improvement. And according to magnetism studies on graphene [18,45], it can be concluded that point defects induced by fluorine adatoms dominate the generation of localized spin magnetic moments on defective FGQDs. And from the aspect of structure, not all the fluorine atoms can contribute to the magnetism. The magnetic contribution can come only from cluster edges and would be determined by a particular configuration of fluorine atoms near the edges. These experimental findings firstly indicate that FGQDs not only enjoy highly fluorescent properties, but also exhibit noteworthy paramagnetism, which can be applied as a novel contrast agent for magnetic resonance imaging (MRI). And it is worthy noticing that compared to other MRI contrast agents, fluorinated (19F) contrast agents are highly desirable due to the scarce distribution of fluorine in the human body, and thus the observed signals are robust and exhibit an excellent degree of specificity [46]. Therefore, our method provides a new and potentially valuable application of FGQDs in bio-imaging field, a single material possessing both fluorescence imaging and MRI.

The prerequisite for conducting bio-related research and exploring the potential bio-applications of FGQDs is to know their
toxicity effects on cells, so cell viability of Hela cells after being exposed to the three obtained FGQDs was evaluated and the corresponding results were summarized in Fig. 8. It is observed that all FGQDs with different size and fluorine content exhibit low toxicity to cells even at a high concentration of 200 µg/mL. For FGQDs possessing similar size and different fluorine contents (FGQDs-1-70 and FGQDs-2-70), the one with less fluorine coverage exhibits less inhibition of cells; for FGQDs possessing similar fluorine contents and different sizes (FGQDs-2-70 and FGQDs-2-120), they exhibit nearly the same cell viability. This indicates that surface states have more influence than size on the cell activity. Furthermore, it is also concluded from these experiment data that for all the FGQDs, the cell viability obviously degrades with increasing the concentration of FGQDs. This unconventional behavior indicates that fluorination of GQDs can greatly modify the chemical and superficial environment of FGQDs, and finally lead to more sensitive response of the cells to the concentration changes.

4. Conclusions

In conclusion, our investigations on FGQDs concerning morphology, chemistry, PL performance, magnetism and cytotoxicity indicate that high-quality FGQDs with tunable size and fluorine coverage can be readily obtained from commercialized FGi, and fluorine atoms have great influence on their performance. By an effective control over the pre-treatment of FGi, once chemically inert bulk FGi becomes active and can be readily exfoliated into few-layered FG sheets, and further tailored into FGQDs. Fluorine atoms make FGQDs containly resist pH effects, display stable luminescence in both acid and alkali conditions. Moreover, noteworthy paramagnetism induced by fluorine atoms endows FGQDs with potential MRI properties, which fundamentally distinguishes themselves from GQDs. And cytotoxicity experiment reveals that FGQDs possess good biocompatibility, and it is the surface state rather than the size of the FGQDs that have more influence on the cell viability. In a word, considering the mild reaction conditions, operational simplicity, effective tunability of the method, and the outstanding and novel properties of the FGQDs samples, this work will provide enlightening insights into chemical functionalization and preparation of GQDs, and promote the practical applications of FGQDs in novel fields.

Acknowledgements

The authors thank Prof. Yuhua Wang, Prof. Desheng Xue and Daqing Gao in Lanzhou University for PL and magnetism analyses. We also thank the financial support from the National Natural Science Foundation of China (Grant Nos. 51375474 and 51675514), the promotive research fund for young and middle-aged scientists of Shandong Province (ZR2016EM004), Project of Shandong Province Higher Educational Science and Technology Program (J16LA03) and Doctoral Start-Up Scientific Research Foundation.