Synthesis of High Fluorescence Graphene Quantum Dots and Their Selective Detection for Fe³⁺ in Aqueous Solution

Ting-Ting Xu, Jia-Xiang Yang, Ji-Ming Song,* Jing-Shuai Chen, He-Lin Niu, Chang-Jie Mao,

Sheng-Yi Zhang and Yu-Hua Shen

The Key Laboratory of Environment Friendly Polymer Materials of Anhui Province, School of Chemistry & Chemical Engineering, Anhui University, Hefei, Anhui, 230601, P. R. China.

Tel: +86 0551 63861279 : Fax: +86 0551 63861279

E-mail: jiming@ahu.edu.cn

Abstract

In recent years, carbon particles have gained numerous attentions because of their simple synthetic process, low toxicity and water solubility. The present work involves synthesis of two types of graphene quantum dots (GQDs) by treating sulfhydryl group (-SH) amino acid glutathione (GSH) in the presence and absence of AgNO_3 via one pot route, respectively. The Ag^+ ions from AgNO_3 can combine the -SH from GSH to form Ag_2S , thus surfaces of the obtained graphene quantum dots (N-GQDs) are mainly modified by some free hydroxyl groups (-OH), amino groups ($-\text{NH}_2$) and carboxyl groups ($-\text{COOH}$). In the absence of Ag^+ ions, the surfaces of as-prepared graphene quantum dots (SN-GQDs) not only include -OH, $-\text{NH}_2$ and $-\text{COOH}$, but also -SH. Interestingly, as-prepared two kinds of GQDs both have strong fluorescence with different emission wavelength. More importantly, these GQDs have special recognition ability for metal ions. The N-GQDs respond rapidly towards the presence of Fe^{3+} ions, and can be used as a probe to detect Fe^{3+} ions in waste water, while the SN-GQDs have a special recognition to Hg^{2+} ions.

Keywords: Graphene quantum dots; Glutathione; Silver nitrate; Fluorescence detection; Iron ion; Mercury ion

1. Introduction

In recent years, chemosensors have drawn tremendous attention of the scientific community because of their wide applications in various fields, such as environment [1], biological detection [2], and chemical industry [3]. There are many diverse types of chemosensors, such as, gas sensor [4], humidity sensor [5], biosensor [6] and ion sensor [7,8]. In the present century, fluorescent chemosensors are widely used to detect ions in solution, owing to their advantage of high sensitivity, simplicity and selectivity [9,10]. These advantages lead to the synthesis of many new fluorescent chemosensors. For instance, Gupta and his co-workers prepared two novel fluorescent rhodamine derivatives with a highly selective and sensitive fluorescent and colorimetric response to Cr^{3+} ions [11]. Batista et al. have synthesized a series of arylfuryl-bis(unduly)methane derivatives, which have a high selective recognition of Hg^{2+} ions in organic aqueous mixture [12].

Iron (Fe) is one of the most important trace elements in living organisms in order to enable oxygen-carrying capacity [13-15]. There approximately exists 4-5 g Fe in human body in different forms. Although Fe plays a vital role in the biological system, excess Fe will cause cell oxidation and annihilation of blood circulation in human body [16]. According to a recent study, Fe is another factor in the primary productivity of phytoplankton besides nitrate, phosphate and silicate [17]. Hence it becomes necessary to develop methods that allow rapid and simple detection of Fe element in solution. So far, there have some of the available approaches for Fe element determination, such as chemiluminescence [18], atomic absorption/emission

spectroscopy [19], colorimetric methods [20], spectrophotometry [21]. Among these, fluorescence spectrometry has attracted enormous attention, owing to its advantages of high sensitivity and rapid response [22,23].

Scheme 1. Schematic illustration of the preparation process for N-GQDs and SN-GQDs.

In this contribution, we successfully synthesized two kinds of graphene quantum dots (GQDs) with a simple synthetic strategy by hydrothermal treatment of glutathione (GSH). The synthesis process is displayed in Scheme 1. The results showed that N-GQDs were obtained in the presence of Ag⁺ ions, while SN-GQDs, obtained in the absence of Ag⁺ ions when other synthesis conditions were remained unchanged. Interestingly, both GQDs have good water solubility in spite of having different fluorescence. The fluorescence color of SN-GQDs is blue while the fluorescence color of N-GQDs, bluish green. Two kinds of GQDs have special the recognition and response ability for Fe³⁺ ions (N-GQDs) and Hg²⁺ ions (SN-GQDs), respectively. Meanwhile, the as-prepared N-GQDs respond rapidly towards the presence of Fe³⁺ ions, and can be used as a probe to detect Fe³⁺ ions in waste water.

2. Experimental

2.1. Reagents

Glutathione (GSH), silver nitrate (AgNO_3), and all other solvents used were of analytical grade. The analyte solutions of metal ions were prepared by dissolving CaCl_2 , KCl , $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, Na_2SO_4 , $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$, $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$, $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ and HgCl_2 .

2.2. Instruments

The samples were characterized by different analytic techniques. Powder X-Ray diffraction (XRD) was obtained on a Rigaku D/max-RA X-ray diffractometer with $\text{CuK}\alpha 1$ radiation ($\lambda = 0.15406 \text{ nm}$). The transmission electron microscopy (TEM) images involving high resolution TEM (HRTEM) observation were carried out on a JEOL-2100 TEM with an acceleration voltage of 200 KV. Scanning electron microscopy (SEM) images were performed on a Hitachi S4800 microscopy operating at 5.0 KV. Atomic force microscope (AFM) images were recorded by using Micro Nano AFM-III. IR spectra were recorded on a Nicolet FT-IR (NEXUS-870) instrument by using KBr discs in the range of $4000\text{--}400 \text{ cm}^{-1}$. The Raman spectra were recorded with a Labram-HR spectrometer using the 532 nm line of the Ar ion for excitation. X-ray photoelectron spectroscopy (XPS) was performed by using a VG ESCA scientific theta probe spectrometer in constant analyzer energy mode with a pass energy of 28 eV and $\text{AlK}\alpha$ (1486.6 eV) radiation as the excitation source. UV-vis spectrometer (Shimadzu UV-3600 PC) was used to record diffuse reflectance spectra

of samples. The fluorescence spectra were recorded with PerkinElmer LS-55 Fluorescence spectrometer.

2.3. Synthesis of N-GQDs and SN-GQDs.

The N-GQDs and SN-GQDs were synthesized by a hydrothermal route. (1) Synthesis of N-GQDs: 0.034 g (0.2 mmol) AgNO_3 , 0.092 g (0.3 mmol) GSH were added into a teflon-lined stainless autoclave of 25 mL capacity in turn. Subsequently, 20 mL ethylene glycol was added into the autoclave. The solution was stirred vigorously for 20 min and then sealed and maintained at 200 °C for 12 h, after that, the autoclave was cooled to room temperature naturally. The product included upper clear liquid and lower sediment, that is to say, GQDs dispersed in the upper clear liquid (ethylene glycol), and the lower sediment was Ag_2S nanocrystals by subsequent characterization. They were collected them respectively. The upper clear liquid was centrifuged at 8000 rpm for 10 min, and the sediment was abandoned; then ethylene glycol was wiped off by rotary evaporation at 180 °C, and the solid state sample (GQDs) was obtained. The lower sediment of the product was washed by distilled water and ethanol absolute three times in turn. The sample was collected for further characterization. (2) Synthesis of SN-GQDs: the synthesis process was carried out similar to that of N-GQDs but in the absence of AgNO_3 in the origin reactants mixture, so the product didn't include Ag_2S nanocrystals.

2.4. Selectivity measurements of metal ions

As described in the previous literature [24], 15 μL of GQDs aqueous solution (10 mg/mL) was diluted to 3 mL by distilled water. Different ions solution of Ca^{2+} , K^{+} , Mg^{2+} , Al^{3+} , Na^{+} , Fe^{3+} , Co^{2+} , Mn^{2+} , Zn^{2+} , Ba^{2+} , Ni^{2+} , Cu^{2+} and Hg^{2+} were prepared under identical conditions. Because interaction between metal ions and the GQDs could quickly reach balance, there didn't need incubate after the metal ion solution was added to the GQDs solution. Then a fluorescence spectrum of the mixture solution was recorded.

2.5. Fluorescence detection of Fe^{3+} ions

In a typical experiment, 15 μL of GQDs aqueous solution (10 mg/mL) was put in a standard quartz cuvette. Then, the certain volume of Fe^{3+} ions solution was added into the cuvette. The mixed solution was diluted to 3 mL by distilled water at room temperature, followed by recording the fluorescence quenching spectra at the respective excitation wavelength.

2.6. Detection of Fe^{3+} ions in real sample

In order to evaluate the N-GQDs as a sensor for Fe^{3+} in real sample, the lake water were chosen as real sample. As described in the previous literature [25], the lake water, which were obtained from the artificial lake in our university, were centrifuged at 10,000 rpm for 20 min to remove solid impurities. Then, the water sample was prepared as different concentrations of Fe^{3+} ions solution. The water sample was added to the sensing system and the fluorescence spectra were recorded.

3. Results and discussion

3.1. Characterization of N-GQDs

Figure 1. (a) XRD patterns of the N-GQDs; (b) AFM pattern of the N-GQDs; (c,d) TEM images of N-GQDs, inset in (c) shows HRTEM image of an individual nanoparticle, inset in (d) shows size distribution of the N-GQDs.

The N-GQDs were synthesized via one step method under solvothermal condition. To determine the composition of the product, the samples were analyzed by the XRD. The XRD pattern of the product is displayed in Figure 1(a). There is a diffraction peak with the range of 20.30° - 24.30° , which corresponds to a graphitic structure [26,27]. And the reason of this broadening of the diffraction peak is the small size of N-GQDs [28]. AFM image was displayed in the Figure 1(b). It can be seen that well-dispersed quantum dots were produced in the process. The height profiles reveal that the typical topographic height difference of the N-GQDs is 1.514 nm. The literature has reported

that the theoretical thickness of a graphene monolayer is 0.34 nm [29], so the AFM results demonstrate that the obtained N-GQDs consist of 1-5 graphene layers. Figure 1(c) and (d) are TEM images of the synthesized N-GQDs. The TEM image indicates that N-GQDs have small spherical morphology with diameter of ca. 2.5 nanometer. In addition, HRTEM image (inset in Figure 1(c)) demonstrates that the d-spacing of 0.201 nm corresponds to (102) plane of graphitic carbon [30]. The inset in the Figure 1(d) shows that the diameters of N-GQDs are mainly distributed in the range of 2.0-3.0 nm with an average size of 2.5 nm. The lower sediment of product have also been collected and characterized. The XRD pattern shows that the collected precipitate is Ag₂S (JCPDS 14-0072) and TEM image displays that the Ag₂S have irregular morphology particles (see Supporting Information (SI), Figure S1). In order to determine the ratio of the reactant (GSH to AgNO₃) and explore the function of AgNO₃ in whole reaction system, the related experiments have also been finished (see SI, Figure S2-S3). Although the ratios of reactants is different, all of the GQDs have no IR vibrational absorption of the -SH at range of 2500-2600 cm⁻¹, indicating the -SH group fell out of GSH molecule in the presence of AgNO₃. However, in the absence of AgNO₃ and kept other experiment conditions same, the obtained sample (SN-GQDs) included -SH group from the IR characterization of the SN-GQDs (see SI, Figure S5). XRD pattern, AFM image and TEM images showed that SN-GQDs have similar diffraction peak and morphology to that of N-GQDs (see SI, Figure S4). This result revealed that AgNO₃ could induce -SH to drop from GSH molecules during solvothermal process.

Figure 2(a) is the IR spectrum of N-GQDs. There is a broad peak at around 3380 cm^{-1} which corresponds to the absorption features of stretching vibrations of N-H and O-H groups. It illustrates that a mass of amino and hydroxyl groups on the surface of N-GQDs impart good hydrophilicity to the products [31]. Moreover, the peaks at 1690 cm^{-1} analogous to the C=O bond and 1190 cm^{-1} corresponding to the C-O groups confirm the presence of the -COOH group. The peak at 2930 cm^{-1} corresponds to the C-H bond, and the band at 1420 cm^{-1} to the C-N bond [32].

Figure 2. (a, b) are IR spectrum and Raman spectrum of N-GQDs.

Raman spectrum was performed to support the composition of the product. As clearly shown in the Figure 2(b), there are two superimposed broad peaks of D-band and G-band at around 1600 and 1400 cm^{-1} , respectively, which were attributed to in-plane vibrations of crystalline graphite and disordered amorphous carbon [33,34]. G-band is higher than D-band, which indicates that the crystalline graphite is more in composition than amorphous carbon. These results are also consistent with the XRD and HRTEM analysis. The IR spectrum and Raman spectrum of SN-GQDs were tested too (see SI, Figure S5).

Figure 3. (a) XPS survey spectrum of N-GQDs, (b-d) high-resolution XPS spectra of C 1s, N 1s and O 1s, respectively.

XPS survey spectrum of the synthesized N-GQDs is shown in Figure 3(a), which displays the peaks of S 2p (163.8 eV), C 1s (285.4 eV), N 1s (399.0 eV) and O 1s (531.7 eV) [35,36]. To obtain more information about the samples, we performed high-resolution XPS spectra of C 1s, N 1s and O 1s. For the high-resolution C 1s region (Figure 3(b)), there are three peaks observed at 284.8, 286.0, and 287.5 eV, which are attributed to the C-C, C-O and C=O groups, respectively. In Figure 3(c), we can see that the binding energy of the N-(C)₃ and C-N-C characteristic absorption peak occur at 399.2 eV and 400.3 eV [37], respectively. The O 1s spectrum (Figure 3(d)) shows two peaks at 531.3 and 532.3 eV, which are assigned to the C=O and C-OH/C-O-C groups [38], respectively. The XPS spectra of SN-GQDs have been

tested too (see SI, Figure S6).

3.2. Absorption and emission spectra of sample

Figure 4. (a, b) the fluorescence excitation, emission and UV-vis absorption spectra of samples: (a) N-GQDs , (b) SN-GQDs; Inset in (a) and (b) shows the photographs under visible light (left) and UV light of 365 nm (right), respectively; (c) emission spectra of N-GQDs obtained by changing the excitation wavelength from 300 to 370 nm; (d) emission spectra of SN-GQDs obtained by changing the excitation wavelength from 347 to 420 nm.

The absorption spectrum of N-GQDs in water solution is shown in Figure 4(a). There is a small absorption peak located at 320 nm in the UV-vis spectrum. The maximum absorption wavelength of SN-GQDs in water emerged at about 300 nm in the UV-vis spectrum (Figure 4(b)). The fluorescent excitation and emission spectra of N-GQDs and SN-GQDs are shown in Figure 4(a) and Figure 4(b), respectively. When N-GQDs are excited by the UV light at 330 nm, a maximum fluorescence peak of N-GQDs is located at 425 nm and a shoulder peak at about 475 nm (Figure 4(a)). The

inset in Figure 4(a) exhibits the color change of N-GQDs solution from pale yellow to bluish green under excitation by UV light at 365 nm. When SN-GQDs are excited by the UV light at 347 nm, a maximum fluorescence peak of SN-GQDs is located at 430 nm (Figure 4(b)). The inset in Figure 4(b) exhibits the color change of SN-GQDs solution from pale yellow to blue under excitation by UV light at 365 nm. The emission range of N-GQDs was integrated between 300 nm and 370 nm and the wavelength of maximum emission was always located at about 425 nm (Figure 4(c)). From the above results, it is revealed that the fluorescence emission of N-GQDs is not excitation-dependent. Figure 4(d) demonstrates that the fluorescence emission of SN-GQDs is excitation-dependent. The fluorescence peak has a clear red shift and fluorescence intensity decreases with the change of excitation wavelength. This phenomenon may due to the distribution of different emissive trap sites, the difference in particle size and multi fluorescence components in SN-GQDs [39,40].

3.3. Selectivity and specificity of N-GQDs and SN-GQDs

Figure 5. (a) The fluorescence response of N-GQDs (Ex = 330 nm, $[M^{n+}] = 2.0 \times 10^{-3}$ M, $[N-GQDs] = 10$ mg/mL); (b) The corresponding relative fluorescence intensities before (black) and after (red) the Fe^{3+} (2.0×10^{-3} M) was added to the N-GQDs solution in the same condition; (c) The fluorescence response of SN-GQDs (Ex = 347 nm; $[M^{n+}] = 2.0 \times 10^{-3}$ M, $[SN-GQDs] = 10$ mg/mL); (d) The corresponding relative fluorescence intensities before (black) and after (red) the Hg^{2+} (2.0×10^{-3} M) was added to the SN-GQDs solution in the same condition.

In order to estimate the special recognition ability of N-GQDs and SN-GQDs, different ions solution of Ca^{2+} , K^+ , Mg^{2+} , Al^{3+} , Na^+ , Ba^{2+} , Co^{2+} , Fe^{3+} , Cu^{2+} , Mn^{2+} , Zn^{2+} , Ni^{2+} and Hg^{2+} were prepared under the identical conditions. All of these prepared metal ions were added in the N-GQDs and SN-GQDs under the same conditions for testing fluorescence response. Figure 5(a) and (c) show the fluorescence response of N-GQDs and SN-GQDs. The relative fluorescence intensity (F_0/F) was used to test whether the quenching behavior of N-GQDs and SN-GQDs by specific ion was selective. The F and F_0 in the Figure 5(a) are the fluorescence intensity of N-GQDs at 425 nm in the presence and absence of metal ions, respectively. While for Figure 5(c), The F and F_0 are the fluorescence intensity of SN-GQDs at 430 nm in the presence and absence of metal ions. Figure 5(a) and Figure 5(c) intuitively shows that there are no obvious variation after the addition of Ca^{2+} , K^+ , Mg^{2+} , Al^{3+} , Na^+ , Ba^{2+} , Co^{2+} , Cu^{2+} , Mn^{2+} , Zn^{2+} and Ni^{2+} . However, when the equal amounts of Fe^{3+} were added to the N-GQDs solution, the value of F_0/F have a obviously enhanced because the

fluorescence intensity of N-GQDs have a significant drop-off (Figure 5(a)), while that of SN-GQDs have same phenomenon in the presence of Hg^{2+} (Figure 5(c)). This results shows that N-GQDs have a good recognition to Fe^{3+} ions, while SN-GQDs to Hg^{2+} ions. To explore the competition of the ions, we added Fe^{3+} ions into other metal ions solution with same concentration to inspect the change of relative fluorescence intensities. In the Figure 5(b) and Figure 5(d)), black vertical bar indicates original fluorescent response of metal ions, while red vertical bar, fluorescent response after Fe^{3+} ions (or Hg^{2+} ions) being added. We could find that the relative fluorescent intensity were steeply increased by further treatment with equivalent Fe^{3+} ions (Figure 5(b)) and Hg^{2+} ions (Figure 5(d)) under the same condition.

3.4. Response mechanism

Figure 6. The mechanism of selectivity and specificity of (a) N-GQDs and (b) SN-GQDs.

Selectivity measurements of metal ions showed that N-GQDs had a better

recognition to Fe^{3+} ions than Hg^{2+} ions whereas SN-GQDs exhibited just the opposite. In addition, both of them displayed no clear response to other metal ions. We thought the above phenomenon could be explained as follows. IR spectra indicated that these two kinds of the GQDs were modified by -OH, -NH₂ and -COOH. The previous literatures have reported that these organic groups have an affinity with Fe^{3+} ions and Hg^{2+} ions [41-43]. Thus, they have more response to Fe^{3+} ions and Hg^{2+} ions compared with other ions. Figure 6(a) is the diagrammatic representation of action mechanisms of the N-GQDs. Due to the three positive charges of Fe^{3+} ions, there occurs a strong interaction with these organic groups than Hg^{2+} ions and other metal ions. Meanwhile, three positive charges had resulted in more electrons transferred to the d orbital of Fe^{3+} ions [44,45]. Figure 6(b) is the illustration of action mechanisms of the SN-GQDs. Unlike N-GQDs, there have an excess -SH on the surface of SN-GQDs. As we all know, there is a strong affinity between Hg^{2+} ions and -SH. The formation of Hg-S bands is a process of effective electron transfer, which facilitates the non-radiative recombination of the excitations [46]. Therefore, N-GQDs have a better response to Fe^{3+} , while SN-GQDs have a better response to Hg^{2+} .

3.5. Effect of acidity and alkalinity on the fluorescence property

Figure 7. (a) The fluorescence intensity at 425 nm of N-GQDs solutions at different pH value; (b) the fluorescence intensity at 425 nm of sample after the same amount of Fe^{3+} ions were added to the N-GQDs solution with different pH ($[\text{Fe}^{3+}] = 2.0 \times 10^{-3} \text{ M}$, $[\text{N-GQDs}] = 10 \text{ mg/mL}$), respectively.

To explore the stability of the fluorescence for N-GQDs, we have tested the fluorescence intensity N-GQDs solution by varying the pH values from 1.5 to 12.5. Figure 7(a) shows that the fluorescence intensity of N-GQDs aqueous solution has subtle changes at the different pH conditions. After the same amount of Fe^{3+} ions was added to the above solution, the fluorescence intensity remained essentially stable in the pH range of 3.5-9.5, but a little decreased in pH range of 1.5-2.5 and increased in pH range of 10.5-11.5 (Figure 7(b)). It demonstrates that fluorescence quenching was weakened at intense alkaline environment, while the quenching was enhanced at intense acidic condition. Because at alkaline environment, Fe^{3+} ions easily reacted with OH^- to generated $\text{Fe}(\text{OH})_3$. The results illustrates that the N-GQDs have a better stability under the pH range of 3.5-9.5, and this range can be selected as the optimum pH for the fluorescence quenching.

Figure 8. Time-dependent fluorescence response.

We also studied the incubation time of the sensing system, as shown in Figure 8. Three different concentrations of Fe^{3+} ions were added to the N-GQDs solution, sequentially, and the fluorescence intensity at 425 nm declined rapidly and almost no change was detected after 30 s, which indicates that the N-GQDs have a rapid response time for Fe^{3+} ions. So there is no need for extra incubation time for detection of Fe^{3+} ions.

3.6. Standard curve for the determination of Fe^{3+} ions.

Figure 9. (a) The fluorescence spectra of N-GQDs (10.0 g/mL) by treating with different concentrations of Fe^{3+} ions, inset shows the fluorescence quenching photographs of N-GQDs with different Fe^{3+} ions concentrations (from left to right: 0, 5.0×10^{-4} M, 1.0×10^{-3} M, 1.5×10^{-3} M and

2.0*10⁻³ M); (b) The relationship between the F/F₀ and the Fe³⁺ ions concentrations.

Figure 9(a) displays the fluorescence spectra of N-GQDs aqueous solution with the different concentrations of Fe³⁺ ions. The fluorescence intensity at 425 nm gradually decreased with increasing Fe³⁺ ions concentrations. There is hardly any fluorescence until the Fe³⁺ ions concentrations reach 2.0*10⁻³ M. The inset in the Figure 9(a) displays the gradual color change of the solution from bluish green to colorless with increasing concentrations of Fe³⁺ ions, which is consistent with the fluorescence spectra. And the standard curves for the determination of Fe³⁺ ions have been displayed in Figure 9(b). The above result reveals that there is a good linear relationship between the relative fluorescence intensity, where the F and F₀ are the fluorescence intensity at 425 nm before and after the addition of Fe³⁺ ions and the concentrations of Fe³⁺ ions from 5.0*10⁻⁵ to 2.0*10⁻³ M with a correlation coefficient (R) of -0.9953. **The detection limit is estimated to be 70 nM at a signal-to-noise ratio of 3 (S/N=3).** It also demonstrates that N-GQDs can potentially be used as a probe for detecting Fe³⁺ ions in wastewater.

Table 1

Comparison of the fluorescent probe for detecting Fe³⁺ ions between this work and the reported literatures.

Fluorescent probe	Linear range (μM)	Detection limit (μM)	Correlation coefficient (R ²)	Ref.
1,8-naphthalimide-based fluorescence chemosensor	5-50	2	0.9948	13
NA-GQDs	0.5-500	0.1	0.98	14

Fluorescent graphene oxide	5-50	0.64	/	47
N-GQDs	50 - 2000	0.07	0.9906	This work

Compared with current reports (Table 1), the prepared N-GQDs have a wider linear range and good linear relation, which demonstrates that it is a promising material for monitoring Fe^{3+} ions in water samples.

3.7. Detection of N-CQDs as a sensor to Fe^{3+} in real sample.

Figure 10. (a) The fluorescence spectra of N-GQDs (10.0 g/mL) by treating with different concentrations of Fe^{3+} ions (from top to bottom: 0, 5.0×10^{-5} M, 2.0×10^{-4} M, 5.0×10^{-4} M, 1.0×10^{-3} M and 2.5×10^{-3} M) in lake water. (b) The relationship between the F/F_0 and the Fe^{3+} ions concentrations.

To evaluate the N-GQDs as a sensor to Fe^{3+} in real sample, the performance of the N-GQDs for real sample analysis was investigated by lake water samples obtained from the artificial lake in our university. Figure 10(a) displays that the fluorescence spectra of N-GQDs by treating with different concentrations of Fe^{3+} ions in lake water. It can be seen that the fluorescence intensity at 425 nm gradually decreased with increasing Fe^{3+} ions concentrations. The standard curves for determining Fe^{3+} in the lake water were shown in the Figure 10(b). There is a good linear correlation in the

range of $0-2.5 \times 10^{-3}$ M with a correlation coefficient (R) of -0.9938. Although there are different kinds of organics and minerals in the lake water, the sensing system have a good detection for Fe^{3+} . It demonstrated that the prepared N-GQDs can be used as a sensor in real environmental samples.

4. Conclusion

In this work, we have successfully synthesized two kind of water soluble GQDs with different specific recognition ability for metal ions by an effective and facile solvothermal method using GSH as carbon source. Ag^+ ions play a key role for synthesis of two kinds of GQDs. In the presence of Ag^+ ions, thiol-free N-GQDs were obtained, and this quantum dots had a bright bluish green fluorescence and a good linear relationship between fluorescence intensity and concentration of Fe^{3+} ions within a wide concentration range between 1.0×10^{-5} and 2.0×10^{-3} M and the detection limit is estimated to be 70 nM at a signal-to-noise ratio of 3 (S/N=3). There is no need for incubation period because of quick response. Therefore, the N-GQDs can be potentially used as probe to detect Fe^{3+} ions in wastewater. However, in the absence of Ag^+ ions during synthesis process, SN-GQDs with thiol were prepared, this quantum dots had a bright blue fluorescence, and showed rapid response to the existence of Hg^{2+} ions. In addition, the present synthetic scheme provides a simple and convenient route for fluorescent quantum dot.

Acknowledgements

The authors are thankful for the support rendered by the National Science Foundation of China (NSFC) (Grants 21641007, 21471001), Natural Science Foundation of Anhui Province (Grant no.1508085MB22), Major Project of Education Department of Anhui Province (KJ2016SD63) and the Innovation Experimental Fund of Anhui University (yqh100041). We also thank The Key Laboratory of Functional Inorganic Materials Chemistry of Anhui Province for the financial support.

References

- [1] A. Bencinic, V. Lippolis, Probing biologically and environmentally important metal ions with fluorescent chemosensors: Thermodynamic versus optical response selectivity in some study case, *Coord. Chem. Rev.* 256 (2012) 149-169.
- [2] M. Dabrowski, P. S. Sharma, Z. Iskierko, et al., Early diagnosis of fungal infections using piezomicrogravimetric and electric chemosensors based on polymers molecularly imprinted with D-arabitol, *Biosens. Bioelectron.* 79 (2016) 627-635.
- [3] L. J. Fan, Y. Zhang, C. B. Murphy, et al., Fluorescent conjugated polymer molecular wire chemosensors for transition metal ion recognition and signaling, *Coord. Chem. Rev.* 253 (2009) 410-422.
- [4] S. Z. Deng, V. Tjoa, H. M. Fan, et al., Reduced graphene oxide conjugated Cu₂O nanowire mesocrystals for high-performance NO₂ gas sensor, *J. Amer. Chem. Soc.* 134 (2012) 4905-4917.
- [5] V. K. Tomer, S. Duhan, Nano titania loaded mesoporous silica: Preparation and application as high performance humidity sensor, *Sens. Actuators, B* 220 (2015) 192-200.
- [6] A. N. Sekretaryova, A. V. Volkov, L. V. Zozoulenko, et al., Total phenol analysis of weakly supported water using a laccase-based microband biosensor, *Anal. Chim. Acta* 907 (2016) 45-53.
- [7] T. Y. Han, X. Feng, B. Tong, et al., A novel “turn-on” fluorescent chemosensor for the selective detection of Al³⁺ based on aggregation-induced emission, *Chem. Commun.* 48 (2012) 416-418.
- [8] H. G. Lee, K. B. Kim, G. J. Park, et al., An anthracene-based fluorescent sensor for sequential detection of zinc and copper ions, *Inorg. Chem. Commun.* 39 (2014) 61-65.
- [9] X. Chen, T. Pradhan, F. Wang, et al., Fluorescent chemosensors based on spiro ring-opening of xanthenes and related derivatives, *Chem. Rev.* 112 (2012) 1910-1956.
- [10] H. N. Kim, W. X. Ren, J. S. Kim, et al., Fluorescent and colorimetric sensors for detection of lead, cadmium, and mercury ions, *Chem. Soc. Rev.* 41 (2012) 3210-3244.
- [11] V. K. Gupta, N. Mergu, A. K. Singh, Rhodamine-derived highly sensitive and selective colorimetric and off-on optical chemosensors for Cr³⁺, *Sens. Actuators, B* 220 (2015) 420-432.
- [12] R. M. F. Batista, S. P. G. Costa, R. M. P. Silva, et al., Synthesis and evaluation of arylfuryl-bis(indolyl)methanes as selective chromogenic and fluorogenic ratiometric receptors for mercury ion in aqueous solution, *Dyes and Pigments.* 102 (2014) 293-300.
- [13] H. M. Jia, X. Gao, Y. Shi, et al., Fluorescence detection of Fe³⁺ ions in aqueous solution and living cells based on a high selectivity and sensitivity chemosensor, *Spectrochim. Acta, Part*

A 149 (2015) 674-681.

- [14] L. B. Li, L. Li, C. Wang, et al., Synthesis of nitrogen-doped and amino acid-functionalized graphene quantum dots from glycine, and their application to the fluorometric determination of ferric ion, *Mikrochim. Acta* 182 (2015) 763-770.
- [15] H. L. Van, E. Engstrom, I. Rodushkin, et al., Isotopic analysis of the metabolically relevant transition metals Cu, Fe and Zn in human blood from vegetarians and omnivores using mutil-collector ICP-mass spectrometry, *J. Anal. At. Spectrom.* 27 (2012) 1327-1334.
- [16] W. Y. Lin, L. L. Long, L. Yuan, et al., A novel ratiometric fluorescent Fe^{3+} sensor based on a phenanthroimidazole chromophore, *Anal. Chim. Acta* 634 (2009) 262-266.
- [17] C. H. Ma, L. P. Lin, Y. Y. Du, et al., Fluorescence quenching determination of iron(III) using rhodamine 6G hydrazide derivative, *Anal. Methods* 5 (2013) 1843-1847.
- [18] P. J. Zhang, Z. J. Xue, D. Luo, et al., Dual-peak electrogenerated chemiluminescence of carbon dots for iron ions detection, *Anal. Chem.* 86 (2014) 5620-5623.
- [19] W. Li, P. Simmons, D. Shrader, et al., Microwave plasma-atomic emission spectroscopy as a tool for the determination of copper, iron, manganese and zinc in animal feed and fertilizer, *Talanta* 112 (2013) 43-48.
- [20] X. H. Gao, Y. Z. Lu, S. J. He, et al., Colorimetric detection of iron ions (III) based on the highly sensitive plasmonic response of the N-acetyl-L-cysteine-stabilized silver nanoparticles, *Anal. Chim. Acta* 879 (2015) 118-125.
- [21] M. T. Stauffer, L. J. Hunter, S. K. Troncone, Determination of iron in abandoned mine drainage by UV-Vis spectrophotometry and flame atomic absorption spectrophotometry, *Spectrosc. Lett.* 40 (2007) 429-437.
- [22] S. H. Li, Y. C. Li, J. Cao, et al., Sulfur-doped graphene quantum dots as a novel fluorescent probe for highly selective and sensitive detection of Fe^{3+} , *Anal. Chem.* 86 (2014) 10201-10207.
- [23] S. Sarkar, M. Chatti, N. K. B. Adusumalli, et al., Highly selective and sensitive detection of Cu^{2+} ions using Ce(III)/Tb(III)-Doped SrF_2 nanocrystals as fluorescent probe, *ACS Appl. Mater. Interfaces* 7 (2015) 25702-25708.
- [24] L. Shang, S. J. Dong, Silver nanocluster-based fluorescent sensors for sensitive detection of Cu(II), *J. Mater. Chem.*, 18 (2008) 4636-4640.
- [25] R. Z. Zhang, W. Chen, Nitrogen-doped carbon quantum dots: Facile synthesis and application as a "turn-off" fluorescent probe for detection of Hg^{2+} ions, *Biosens. Bioelectron.* 55 (2014) 83-90.
- [26] C. F. Zhang, Y. Y. Cui, L. Song, et al., Microwave assisted one-pot synthesis of graphene quantum dots as highly sensitive fluorescent probes for detection of iron and pH value, *Talanta* 150 (2016) 54-60.
- [27] D. Y. Pan, J. C. Zhang, Z. Li, et al., Hydrothermal route for cutting graphene sheets into blue-luminescent graphene quantum dots, *Adv. Mater.* 22 (2010) 734-738.
- [28] L. B. Tang, R. B. Ji, X. K. Cao, et al., Deep ultraviolet photoluminescence of water-soluble self-passivated graphene quantum dots, *ACS Nano* 6 (2012) 5102-5110.
- [29] J. Ju, W. Chen, Synthesis of highly fluorescent nitrogen-doped graphene quantum dots for sensitive, label-free detection of Fe (III) in aqueous media, *Biosens. Bioelectron.* 58 (2014) 219-225.
- [30] W. Lu, X. Qin, S. Liu, et al., Economical, green synthesis of fluorescent carbon nanoparticles

- and their use as probes for sensitive and selective detection of mercury(II) ions, *Anal. Chem.* 84 (2012) 5351-5357.
- [31] D. Qu, M. Zheng, P. Du, et al., Highly luminescent S, N co-doped graphene quantum dots with broad visible absorption bands for visible light photocatalyst, *Nanoscale* 5 (2013) 12272-12277.
- [32] D. Sun, R. Ban, P.-H. Zhang, et al., Hair fiber as a precursor for synthesizing of sulfur- and nitrogen-co-doped carbon dots with tunable luminescence properties, *Carbon* 64 (2013) 424-434.
- [33] R. Purbia, S. Paria, A simple turn on fluorescent sensor for the selective detection of thiamine using coconut water derived luminescent carbon dots, *Biosens. Bioelectron.* 79 (2016) 467-475.
- [34] X. M. Sun, Y. D. Li, Colloidal carbon spheres and their core/shell structures with noble-metal nanoparticles, *Angew. Chem. Int. Ed.* 43 (2004) 597-601.
- [35] J. Ju, R. Z. Zhang, W. Chen, et al., Photochemical deposition of surface-clean silver nanoparticles on nitrogen-doped graphene quantum dots for sensitive colorimetric detection of glutathione, *Sens. Actuators, B* 228 (2016) 66-73.
- [36] W. P. Wang, Y. C. Lu, H. Huang, et al., Solvent-free synthesis of sulfur- and nitrogen-co-doped fluorescent carbon nanoparticles from glutathione for highly selective and sensitive detection of mercury(II) ions, *Sens. Actuators, B* 202 (2014) 741-747.
- [37] X. H. Gao, Y. Z. Lu, R.Z. Zhang, et al., One-pot synthesis of carbon nanodots for fluorescence turn-on detection of Ag^+ based on the Ag^+ -induced enhancement of fluorescence, *J. Mater. Chem. C* 3 (2015) 2302-2309.
- [38] R. Z. Zhang, W. Chen, Nitrogen-doped carbon quantum dots: Facile synthesis and application as a "turn-off" fluorescent probe for detection of Hg^{2+} ions, *Sens. Actuators, B* 55 (2014) 83-90.
- [39] B. Chen, F. Li, S. Li, et al., Large scale synthesis of photoluminescent carbon nanodots and their application for bioimaging, *Nanoscale* 5 (2013) 1967-1971.
- [40] S. Liu, J. Tian, L. Wang, et al., Preparation of photoluminescent carbon nitride dots from CCl_4 and 1,2-ethylenediamine: a heat-treatment based strategy, *J. Mater. Chem.* 21 (2011) 11726-11729.
- [41] A. D. Zhao, C. Q. Zhao, M. Li, et al., Ionic liquids as precursors for highly luminescent, surface-different nitrogen-doped carbon dots used for label-free detection of $\text{Cu}^{2+}/\text{Fe}^{3+}$ and cell imaging, *Anal. Chim. Acta* 809 (2014) 128-133.
- [42] S. N. A. M. Yazid, S. F. Chin, S. C. Pang, et al., Detection of Sn (II) ions via quenching of the fluorescence of carbon nanodots, *Mikrochim. Acta* 180 (2013) 137-143.
- [43] S. J. Zhu, Q. N. Meng, L. Wang, et al., Highly photoluminescent carbon dots for multicolor patterning, sensors, and bioimaging, *Angew. Chem. Int. Ed.* 52 (2013) 3952-3957.
- [44] Y. Liu, N. Xiao, N. Q. Gong, et al., one-step microwave-assisted polyol synthesis of green luminescent carbon dots as optical nanoprobe, *Carbon* 68 (2014) 258-264.
- [45] X. Y. Teng, C. G. Ma, C. J. Ge, et al., Green synthesis of nitrogen-doped carbon dots from konjac flour with "off-on" fluorescence by Fe^{3+} and L-lysine for bioimaging, *J. Mater. Chem. B* 2 (2014) 4631-4639.
- [46] Y. Guo, Z. Wang, H. Shao, et al., Hydrothermal synthesis of highly fluorescent carbon nanoparticles from sodium citrate and their use for the detection of mercury ions, *Carbon* 52 (2013) 583-589.

- [47] Q. S. Mei, C. L. Jiang, G. J. Guan, et al., Fluorescent graphene oxide logic gates for discrimination of iron (3+) and iron (2+) in living cells by imaging, Chem. Commun. 48 (2012) 7468-7470.

Graphical Abstract

Two types of graphene quantum dots (GQDs) with different fluorescence emission wavelength were obtained by treating sulfhydryl group (-SH) amino acid glutathione (GSH) in the presence and absence of AgNO_3 via one pot route, respectively. These GQDs have special recognition ability for metal ions. The one respond rapidly towards the presence of Fe^{3+} ions, and can be used as a probe to detect Fe^{3+} ions in waste water, while the other have a special recognition to Hg^{2+} ions.