



Dual functional N- and S-co-doped carbon dots as the sensor for temperature and Fe³⁺ ions



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ABSTRACT

In this paper, we synthesized a new kind of dual functional nitrogen- and sulfur-co-doped carbon dots (C-dots) which could be applied as the fluorescent temperature sensor and the probe of trace amounts of Fe³⁺ ions via an one-pot facile hydrothermal approach from acrylic acid and methionine. The obtained C-dots with the average diameter of 2.3 nm manifested colorful fluorescence, good-solubility and attractive optical stability. The fluorescence lifetime is 7.92 ns. Although the quantum yield is 10.55%, the fluorescence can be fleetly and selectively quenched by Fe³⁺ ions. The detection limit was as low as 1.72 nM. In addition, high ionic strength, mild acids and alkaline only own a small impact on the fluorescence intensity of the C-dots. Furthermore, the C-dots could be deemed as a temperature sensor with significant reversibility, sensitivity and linearity. Meanwhile, the C-dots also possessed great recoverable and thermal stable fluorescence as expected.

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1. Introduction

It is universally acknowledged that how much paramount a role carbon element plays in nature. A multitude of excitement and effort has been captured to develop carbonaceous multi-functional nanomaterials such as graphene, carbon nanotubes, carbon quantum dots owing to their unique properties. Fluorescent carbon-based materials have attracted great attention in recent years, which mainly includes carbon quantum dots [1], graphene quantum dots [2,3], fluorescent graphene [4], nanodiamonds [5], and fullerene [6]. As one of them, carbon dots (C-dots) have generated enormous attention for a wide variety of promising applications in photocatalyst [7], sensor [8], printing ink [9], drug delivery [10] and bioimaging [11] because of their unique optical, electronic and chemical properties. Especially, distinguishing from metal-based quantum dots, C-dots possess high chemical inertness, low toxicity and good biocompatibility, which can be prepared with facile synthesis approaches. At present, a broad series of methods have been developed for their preparation since fluorescent C-dots were named since 2006 by Sun et al. [12], such as chemical oxida-

tion method [13], ultrasonic method [14], hydrothermal synthesis [15,16], solvothermal method [17], microwave method [18] and laser ablation method [19] which can be divided into two classes of methods, “top-down” and “bottom-up” [20]. Among them, thermal treatment synthesis is regarded as a simple, direct and efficient route for synthesis of C-dots with novel properties.

The facile access of C-dots makes heteroatom doping available and heteroatom doping of C-dots provides us an expedient route to tuning their surface, structure of electronic energy levels and local chemical properties [21]. Up to now, masses of efforts has been made to prepare nitrogen-doped, sulfur-doped or nitrogen- and sulfur-co-doped C-dots from natural biomass, peptide, amino acid and other small molecule, such as garlic [22], goose [23], grapefruit peel [24], hair fiber [25], cocoon silk [26] thioglycolic acid [27] and the mixture of glucose and glycine [28]. Compared to bare C-dots, nitrogen-doped C-dots might not only improve fluorescence properties but also allow to apply available functional groups for target sensing. The report about nitrogen and sulfur co-doped C-dots obtained by hydrothermal treatment of citric acid and L-cysteine indicated its excellent fluorescent property was ascribed to the doping changing surface state facilitating a high yield of radiative recombination [29]. Weng etc. demonstrated that hybrid carbon source employed for C-dots facilitated fluorescence enhancement

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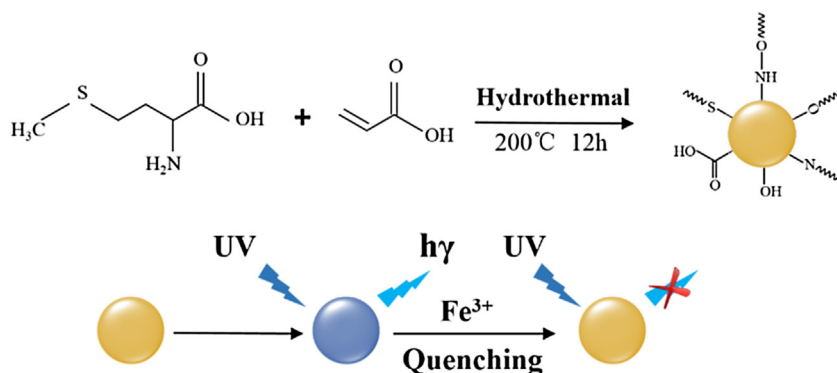


Fig. 1. Illustration of the formation process of the water-dispersible C-dots and its application for Fe^{3+} detection.

compared with that from a single source owing to the higher polymerization degree [28].

Fe^{3+} , one of the most essential metal ions in biological systems, plays crucial roles in clinic and environment. It is used in the physiological and pathological processes including cellular metabolism, enzyme catalysis and oxygen transport, as well as DNA and RNA synthesis. Abnormal Fe^{3+} fluctuations are the hallmarks of diseases, such as anemia, intelligence decline, heart failure, diabetes and so on. Thus, the determination of Fe^{3+} is of fundamental importance for the early identification and diagnosis of these diseases. In recent years, C-dots have been employed as platform for the development of Fe^{3+} sensor. The highly fluorescent nitrogen-doped C-dots obtained by solid-phase synthesis was used as sensitive probe for Fe^{3+} in living cells [30]. The S-doped C-dots were reported as probes toward Fe^{3+} detection [31]. Although these materials exhibited good performance in Fe^{3+} detection, the strategy which could improve the fluorescent Fe^{3+} sensing performance with high sensitivity and selectivity needs to be further studied.

Temperature as the fundamental physical parameter performs important behavior of the effect on the chemical and biological systems. Accurate determination of temperature is of great importance due to the widespread applications [32]. Up to now, a number of promising materials have been developed on the detection, including scanning probe microscopy, Raman spectroscopy and fluorescence-based measurements [33–35]. Indeed, several nanomaterials with fluorescence have been reported for temperature determination, such as semiconductor quantum dots, organic dyes, fluorescent polymers [36–38].

Herein, a facile hydrothermal approach has been designed to obtain the fluorescent nitrogen- and sulfur-co-doped C-dots using acrylic acid and methionine as precursors (Fig. 1). Although methionine could be regarded as a good carbon source containing sulfur and nitrogen simultaneously, inspired by previous studies reported in literature [28], acrylic acid as one of the common unsaturated carboxylic acids with very fast polymerization rate was employed as the co-precursor with methionine for easy polymerization in the formation process of C-dots. The morphology, surface functional groups, chemical state and optical properties are investigated extensively. The C-dots exhibit narrow size distribution, excellent water-solubility, temperature-sensitivity and fluorescence thermal-recoverability. It showed commendable potential in traces Fe^{3+} ions detection and sensitive temperature sensor, which can broaden the applications of the carbon materials significantly. As an effective probe for Fe^{3+} , there was a good linear correlation between the quenching efficiency and the logarithm of Fe^{3+} concentration in two concentration ranges with lowest limit detection of 1.72 nM. As temperature sensor, the fluorescence intensity linearly decreased within the range from 25 °C to 75 °C with excellent sensitivity and significant reversibility/recoverability.

2. Experimental

2.1. Materials and apparatus

Methionine, acrylic acid, Na_3PO_4 , NaH_2PO_4 , FeCl_3 , FeCl_2 , PbCl_2 , CoCl_2 , BaCl_2 , CrCl_2 , NiCl_2 , MnCl_2 , LiCl , NH_4Cl , CaCl_2 , MgCl_2 , CuCl_2 and SnCl_4 were purchased from Sinopharm Chemical Reagent. AgNO_3 was purchased from Beijing Chemical Works. All reagents and chemicals were of analytical grade and used without further purification. Deionized water was used throughout all the experiments.

Transmission electron microscope (TEM) image of C-dots was carried out using a JEOL TEM-3010 instrument, operating at an acceleration voltage of 200 kV. The samples for TEM characterization were prepared by coating the given volume of C-dots dispersion on a carbon-coated copper grid, and then dried at room temperature for 12 h. The fluorescence and the absorption spectra were recorded by RF-5301PC (Shimadzu, Japan) fluorescence spectrophotometer and UV-2550 (Shimadzu, Japan) spectrophotometer, respectively. Fourier Transform infrared (FT-IR) spectrum was performed on a Nicolet iS10 FT-IR spectrometer (Thermo scientific, America) in the range of 400–4000 cm^{-1} . Analysis of the X-ray photoelectron spectroscopy (XPS) was recorded on Thermo ESCALAB 250 spectrometer and binding energies (± 0.1 eV) were determined with respect to the position C1s peak at 284.8 eV. The quantum yield was carried out with Edinburgh fluorescence spectrometer (FLS920) with an integrating sphere.

2.2. Synthesis process

This sort of C-dots was synthesized via one-pot hydrothermal method. In the quintessential synthesis, 1 mmol methionine and 335 μL acrylic acid were dissolved in 10 mL ultrapure water and stirred drastically until forming a clear solution. After that, the mixture was diverted into a 40 mL Teflon-lined autoclave and heated at 200 °C for 12 h in an oven. After the reaction, the solution which had cooled down to room temperature was dialyzed through a dialysis membrane (MWCO = 3000 Da) for 24 h to remove the redundant precursors and result small molecules. In the end, the product was collected and stored in the refrigerator for further research. For control experiment, the C-dots obtained only using individual precursor (methionine or acrylic acid) were both synthesized under the same condition.

2.3. Fe^{3+} ions detection

After a series of facile treatment, the C-dots solution was filled in a 10 mm optical path length quartz fluorescence cuvette which was placed in the RF-5301PC spectrometer and linked to a con-

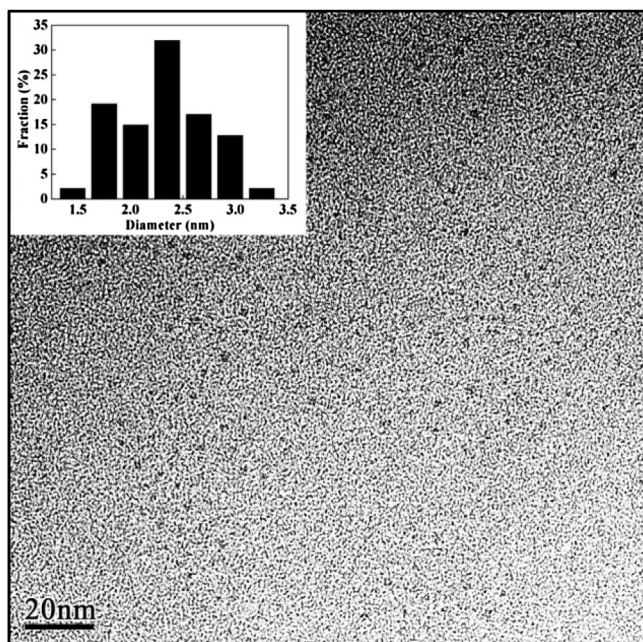


Fig. 2. TEM image and size distribution of C-dots.

stant temperature water cycle (RA 8, LAUDA) for measurement. For the detection of Fe^{3+} ions, in a quintessential assay, we made it as followed: C-dots were diluted by phosphate buffer solution (PBS), then a given concentration of Fe^{3+} ions was added in sequence and mixed until forming the homogeneous solution. After 5 min, the fluorescence spectrum was recorded using an RF-5301PC spectrometer at 320 nm. For optimizing the test condition, the effects of temperature, pH and ionic strength on fluorescence of the C-dots were investigated. The temperature as being set surrounding the cuvette was regularly changed between 25 °C and 75 °C, and the time interval of each measurement was set as 5 min to guarantee the temperature stability of the solution. When came to the pH, PBS with different pH value (pH 3–10) were used to dilute C-dots for measurement. To study the ionic strength effect, different concentrations of NaCl (0–1 mol/L) were added into the C-dots solution. Some other common metal stock cations solutions (including Li^+ , Cr^{3+} , Fe^{2+} , Mn^{2+} , Ag^+ , Ba^{2+} , Ca^{2+} , Pb^{2+} , NH_4^+ , Mg^{2+} , Sn^{4+} , Ni^{2+} , Co^{2+} , Cu^{2+} and Hg^{2+} ions) were selected to detect the selectivity of the C-dots. Their chloride salts were used to avoid the influence of other different anions.

3. Results and discussion

3.1. Characterization

A battery of instruments had been used to characterize the composition and morphology of C-dots. TEM image (Fig. 2) clearly reveals the uniform morphology and narrow size distribution of the C-dots. The C-dots have an average particle size of 2.3 nm within the range 1.5–3.2 nm. It is obvious to capture the marvelous dispersivity and uniformity which agrees with the fact of actual dissolution.

The FTIR spectrum of the C-dots is given in Fig. 3. The band in the region of 2800–3440 cm^{-1} aroused from stretching vibrations of O–H and N–H [39]. The absorption peak at 1700 cm^{-1} could be assigned to the stretching vibration of C=O [40]. The absorption peak at 1548 cm^{-1} could be attributed to the stretching vibration of C=C, and the peak at 1400 cm^{-1} could be identified as C–N, N–H and –COO groups [25]. Respectively, the 1190 cm^{-1} could be ascribed to the C–O, C–N and C–S bonds [41] and 1036 cm^{-1} could be assigned to the –SO₃–, C–O–C, and C–O bonds [42].

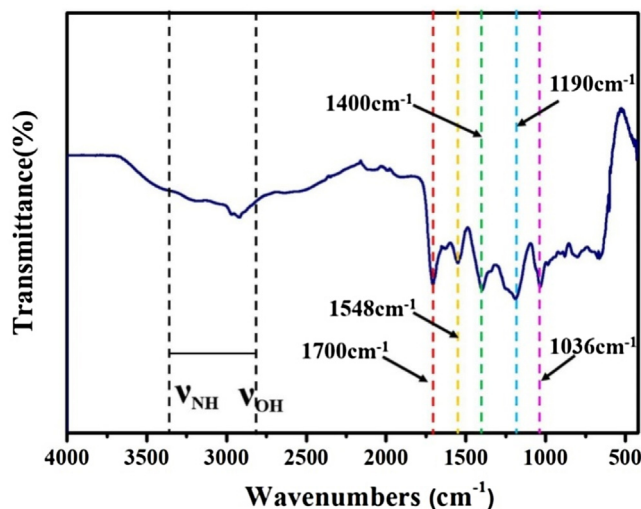


Fig. 3. FTIR spectrum of the C-dots.

The elemental composition and its chemical states of the C-dots were provided by XPS analysis (Fig. 4A). XPS survey spectrum revealed that the C-dots were mainly composed of oxygen (O1s, 532.6 eV), nitrogen (N1s, 400.1 eV), carbon (C1s, 284.7 eV) and sulfur (S2p, 162.9 eV) elements of C-dots. The corresponding relative contents were calculated to be around 69.9%(C), 4.02%(N), 24.45%(O) and 1.63%(S). In detail, the high resolution C1s spectrum (Fig. 4B) can be fitted into four component peaks, which are attributed to C–C(284.7 eV), C–N/C–S(285.9 eV), C–O(286.7 eV), C=O(288.5 eV). The relative contents of the above chemical states were calculated by their integral area ratio to the total area of C1s spectrum. The percentage of C–C, C–N/C–S, C–O and C=O are 68.8%, 10.9%, 7.0% and 13.3%, respectively. The binding energy peak at 284.7 eV was ascribed to the graphitic structure C–C bond [43], suggesting the presence of large numbers of graphitic structures in the obtained C-dots. Moreover, the peak of the high resolution spectrum of O1s (Fig. 4C) was asymmetry and can be fitted into two peaks at 531.3 eV and 532.3 eV, which could be assigned to C=O and C–O groups respectively [44]. As shown in the N1s spectrum (Fig. 4D), two peaks were observed at 399.4 eV and 401.2 eV respectively. It is the main peak at 399.4 eV that could be attributed to the pyridinic N accounted for 70%. The other small peak with binding energy of 401.2 eV originated from pyrrolic N [39]. As for the S2p XPS spectrum (Fig. 4E), the peaks centered at 162.6 eV, 163.6 eV and 166.0 eV indicated three forms of sulfur element. The main peaks (162.6 eV, 163.6 eV) agreed with the –C–S–(S_{2p,3/2} and S_{2p,1/2}) covalent bond of the thiophene-S due to the spin-orbit couplings [45]. Another one peak at 165.4 eV can be ascribed to the –C–SO₃– species like sulfate or sulfonate [25].

It was indicated via the spectrum of FTIR and XPS that the as-prepared C-dots consisted of functional groups with oxygen, nitrogen and sulfur elements, that was the reason why the as-prepared C-dots owned the excellent water solubility, marvelous dispersivity and significant optical properties for the potential applications.

3.2. Optical properties

As shown as the UV–vis spectrum (Fig. 5A), the C-dots solution exhibits a broad peak at 315 nm, which indicated the presence of the carbonyl or conjugated carbonyl groups [46]. It could be attributed to the n–π* transition of C=O band [47]. Accordingly, the C-dots solution appears yellowish color under visible light, which illustrated by the inset in Fig. 5A.

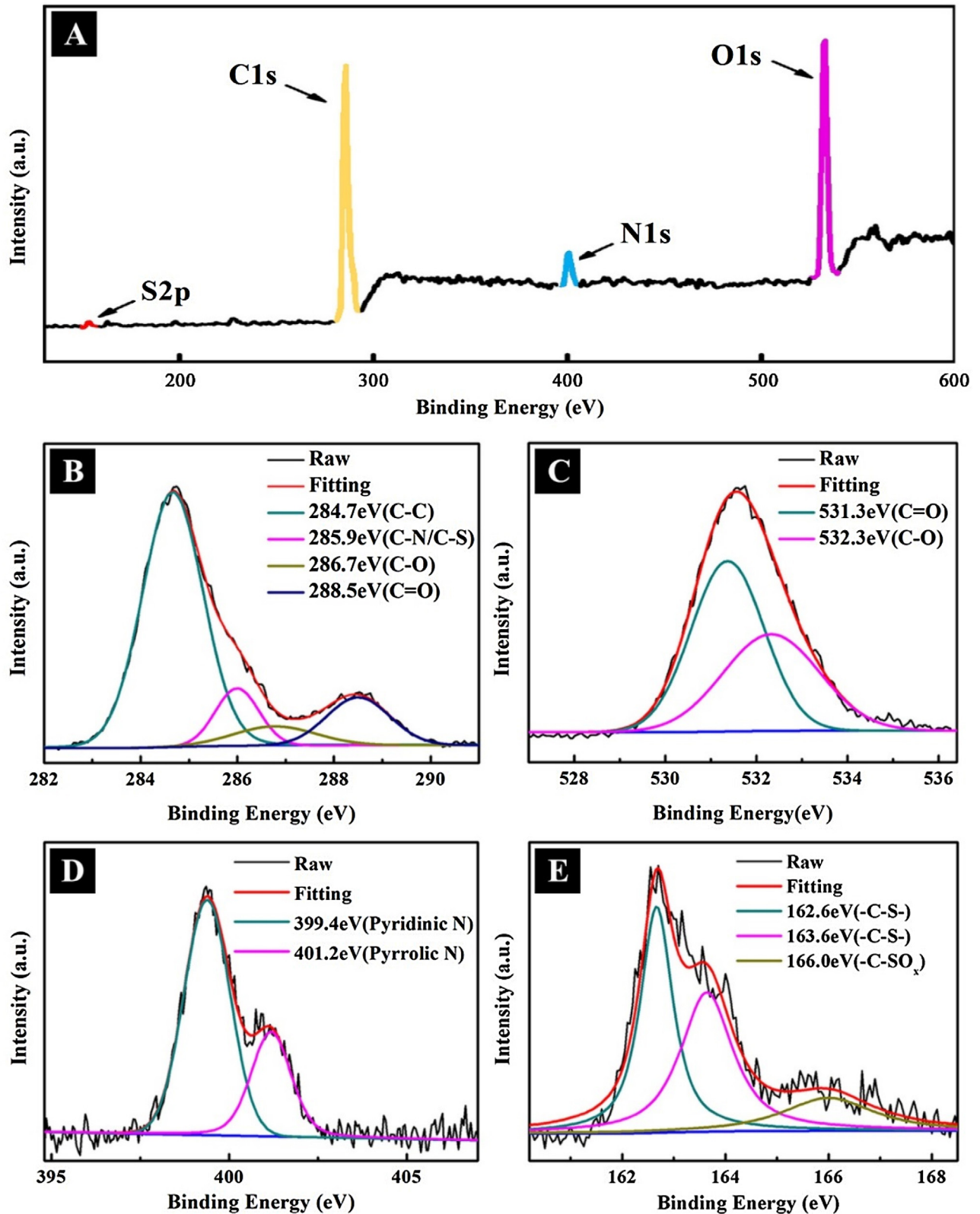


Fig. 4. (A) XPS survey spectrum of the C-dots; (B-E) High-resolution C1s, O1s, N1s and S2p peaks of the C-dots, respectively.

PL spectra of the as-prepared C-dots solution were measured at room temperature. When excited by different wavelength from 360 nm to 540 nm with the increment of 20 nm, as shown as Fig. 5B, the corresponding PL emission peak shifted from 440 nm to 555 nm across 115 nm, meanwhile, the PL intensity of emission

peaks firstly increased and then decreased. The results demonstrated the optimal emission was at 485 nm when excited by 420 nm. The fluorescence photographs of the C-dots in accordance with its PL spectra are shown in Fig. 5C. The C-dots solution manifested gorgeous colors resembling the colors of a rainbow when

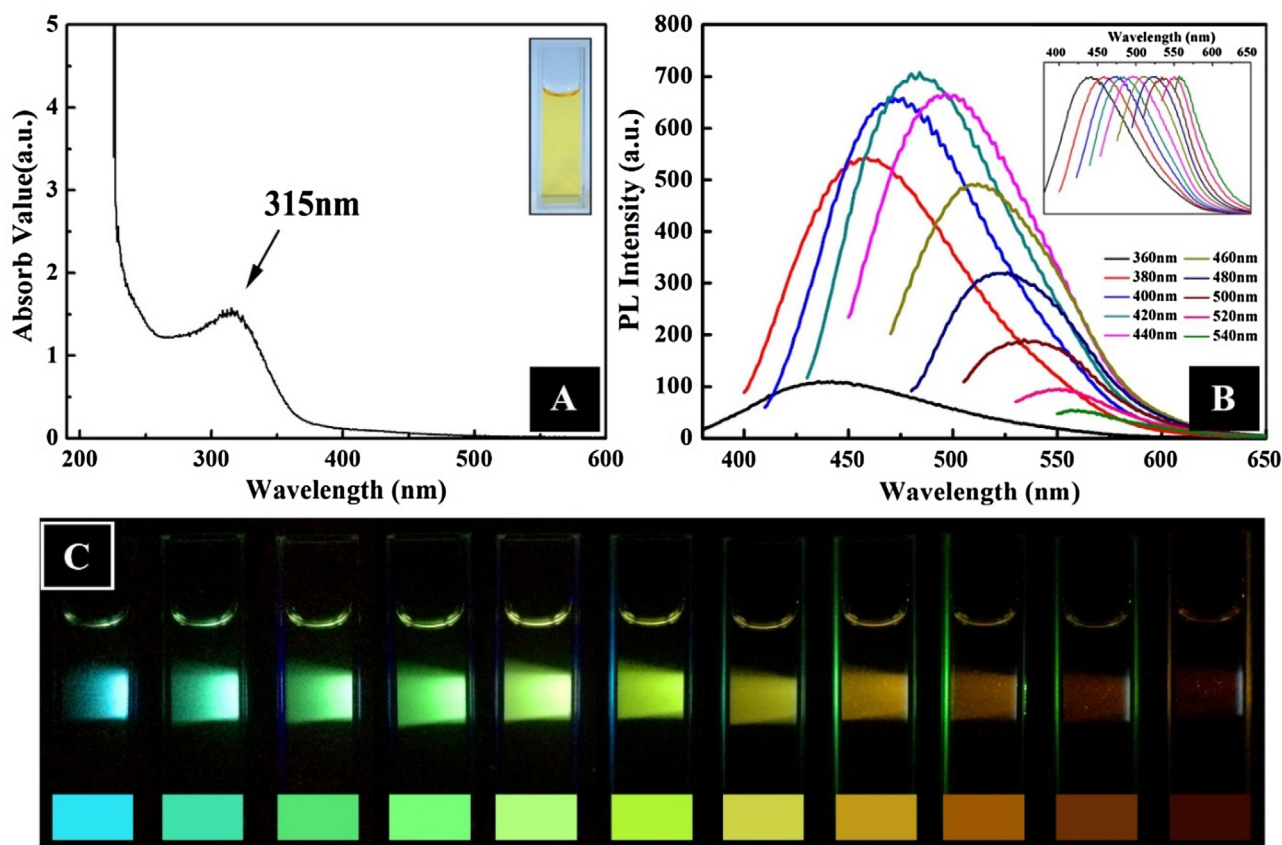


Fig. 5. (A) UV-vis absorption spectra of C-dots; (B) Emission spectra recorded for progressively longer excitation wavelengths in 20 nm increments from 360 nm to 540 nm. Inset: the normalized PL emission spectra; (C) The C-dots solution (16.65 mg/mL) exhibited gorgeous colors when excited at the different wavelengths range from 360 nm to 560 nm with the increments of 20 nm.

excited at different wavelengths. It is the direct observation that the emission alteration and the fluorescence variation trend (weak-strong-weak) under different excitation. The excitation-dependent PL behaviors, which are similar to the previous reports, are contributed to the surface state affecting the band structure of C-dots resulted by the quantum dimensions of the size and complex chemical groups of C-dots [39]. Meanwhile, fluorescence lifetime measurements and the quantum yield of the as-prepared C-dots were also carried out. As shown in Fig. S1, the decay curve can be fitted by a double-exponential function with lifetime of 3.95 ns (57.69%) and 13.35 ns (42.31%) at 320 nm excitation with an intensity-weighted average time of 7.92 ns. It is acknowledged that in the solution the present of diverse fluorophores or energy levels is responsible for the multiple lifetimes [43]. Its quantum yield was measured as 10.55% using Edinburgh fluorescence spectrometer (FLS920) with an integrating sphere. In addition, we have investigated the up-conversion PL spectra of the as-prepared C-dots solution (Supporting information, Fig. S2). In the spectrum, the excitation wavelength ranged from 740 nm to 880 nm with the increments of 20 nm. It was weaker when compared with the PL intensity of down-conversion. However, it was still meaningful when considered the applications in the field of bio-imaging to ensure the cells alive being detected.

For comparison, the C-dots obtained only using individual precursor (methionine or acrylic acid) were both synthesized under the same condition. Their PL spectra were measured and the results were given in Figs. S3 and S6. These two C-dots also exhibited excitation wavelength-dependent emission behaviors. However, the QY of both samples were 2.05% and 3.36% respectively, which were much lower than that of sample obtained by methionine-acrylic

acid hybrid precursors (10.55%). The results were similar to the literature reported that the PL could be elevated by hybrid carbon source compared with individual precursor [28].

Although the intrinsic luminescence mechanism of C-dots has not been entirely understood. Several mechanisms have been proposed according to previous researches [48,31], such as excitons of carbon core [49], emissive traps [12] and electronic conjugated structure [50]. For heteroatom doped C-dots, it has been reported that the abundant functional groups containing heteroatom would be able to introduce new formed excitation energy traps [51] or passivate surface defects [31], leading to the impact on the photoluminescence of C-dots. According to the above experimental results, synergistic effects of these mechanisms were probably responsible for N/S co-doped C-dots with tunable emission. Unfortunately, with a lack of definitive experimental evidence, the relative contribution of these mechanisms to N/S co-doped C-dots is still an open question. However, it is certain that mix precursors of acrylic acid and methionine play key roles in elevating the PL intensity of C-dots. The result is similar to the literature reported by Weng etc [28]. The higher fluorescence intensity of C-dots obtained by methionine-acrylic acid mixture precursor can be attributed to sufficient condensation polymerization and abundant functional groups, which act as excitation energy traps and lead to the brighter photoluminescence.

3.3. Temperature, pH and ionic strength effect on fluorescence emission

In temperature range from 25 °C to 75 °C, the fluorescence of C-dots were also investigated to study the influence of tem-

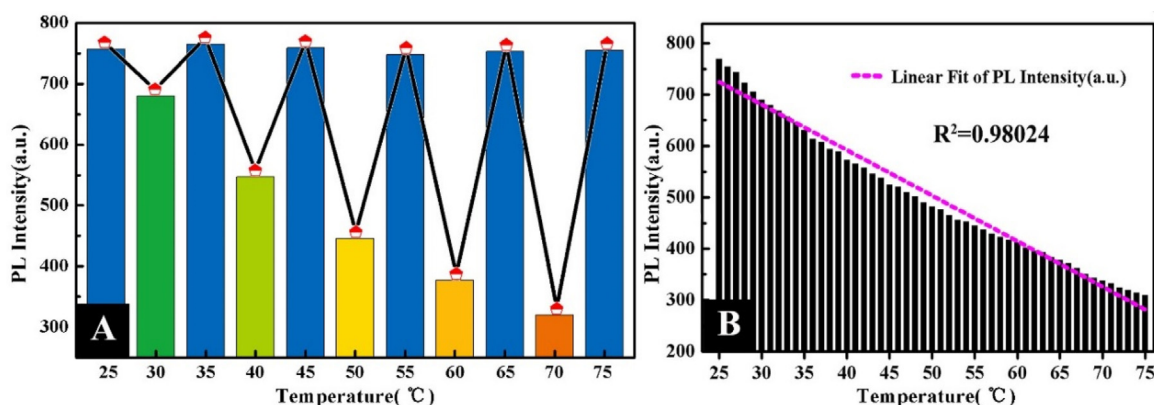


Fig. 6. Temperature effect on the fluorescence emission of C-dots: (A) Cyclic test; (B) Linear temperature increase.

perature (Fig. 6A). Herein, we employed a constant temperature water cycle (RA 8, LAUDA) to link to RF-5301PC spectrometer for the sample temperature control. To verify the reversibility and restorability of the C-dots fluorescence, we designed an experiment with a pendular value of temperature to observe the fluorescence variation. According to the illustration Fig. 6A, it was obvious that the fluorescence intensity decreased at higher temperature and the fluorescence was recovered when temperature back to 25 °C. The result demonstrated that the C-dots exhibited marvellous reversibility and restorability whenever the temperature changed. In other words, the temperature (25–75 °C) cannot cause permanent destruction on the surface fluorescent structure of the as-prepared C-dots. There is a good linear correlation between the fluorescence intensity and the temperature within the range of 25–75 °C (Fig. 6B).

$$F = 973.56109 - 8.85593T (R^2 = 0.98024, T: 25^\circ\text{C} - 75^\circ\text{C})$$

Where F is the fluorescence intensity and T represents the temperature. The C-dots fluorescence intensity performed the decrease performance with the rise of temperature linearly. It possess great potential in temperature sensing to promote temperature sensor used the fluorescent nano-materials. The work here may broaden the application of fluorescent materials. The decrease phenomenon may attributed to that the aggregation of C-dots occurred which caused the obvious fluorescence quenching [15]. Meanwhile we tried to apply the undoped C-dots synthesized using only acrylic acid as precursor in temperature sensors (Fig. S7). Unfortunately, undoped C-dots possessed weaker quenching effect under same temperature elevation than N, S/C-dots.

The effect of pH on the fluorescence of the C-dots was also evaluated from pH = 3 to pH = 10. As seen in Fig. 7A, the fluorescence intensity was recorded under different pH conditions. The intensity was not almost unaltered expect the small decrease under strong alkaline or acidic condition. The pH owned a small impact on the fluorescence of C-dots, which differed from most of others recorded in the reports [20,31,40]. It was demonstrated that the structure of C-dots was relatively stable and not simply ruined with environmental pH variation. We also have investigated the effect of ionic strength on the fluorescence of the C-dots. As seen in Fig. 7B, different concentrations of NaCl solutions range from 0 mmol/L to 1 mol/L were formulated as the solvents for the C-dots. The fluorescence intensity remained almost unchanged with the NaCl concentrations. The stability of the effective fluorescence benefits the application of the C-dots (Table 1).

Table 1

Comparison of different recently published optical methods for the determination of Fe^{3+} used C-dots with different precursors.

Precursors	LR ^a (nM)	LOD ^b (nM)	References
Citric acid and Tris	2000–50000	1300	[20]
Prunus avium fruit	0–1000000	960	[53]
Rice straw and AMIM-Cl	0–7000	200	[54]
Sodium citrate and $\text{Na}_2\text{S}_2\text{O}_3$	1000–500000	100	[31]
Garlic	2–3000	0.22	[29]
Acrylic and methionine	1560–200000	1025	This study
Acrylic and methionine	12.5–1000	1.72	This study

^a Linear range.

^b Limit of detection.

3.4. Fluorescence response of the as-prepared C-dots to Fe^{3+} ions as nanoprobe

We investigated the fluorescence quenching effect of various metal ions on the as-prepared C-dots. As shown in Fig. 8A, the concentration of cations was 1.25 mmol/L and it was obviously observed that the vast majority of the fluorescence strongly decreased because of the added Fe^{3+} , which exhibited remarkably selectivity toward Fe^{3+} ions over other competitive cations with the same concentration. Furthermore, different concentrations of Fe^{3+} ions were added into the C-dots solution (8.8×10^{-2} mg/mL) to investigate the dependence of the quenching (Fig. 8B). The fluorescence intensity of the C-dots decreased upon the increasing concentration of Fe^{3+} ions, the insets in Fig. 8B (Fe^{3+} concentration: 1.56–200 μM) intuitively showed the gradual decrease of fluorescence intensity with the progressively increasing Fe^{3+} ions. To further obtain lower detection limit, diluted C-dots (8.8×10^{-4} mg/mL) were chosen to implement Fe^{3+} quenching test (Fig. 8C). As expected, the diluted C-dots could response to as low as 12.5 nM Fe^{3+} . There is a good linear correlation between the quenching efficiency (F/F_0) and the logarithm of Fe^{3+} concentration within the range of 1.56–200 μM (Eq. (1)) and 12.5–1000 nM (Eq. (2)).

$$F/F_0 = 1.039 - 0.3682 \log C (\mu\text{mol/L}) (R^2 = 0.9873, C: 1.56 - 200 \mu\text{M}) \quad (1)$$

$$F/F_0 = 1.09292 - 0.11208 \log C (\text{nmol/L}) (R^2 = 0.9637, C: 12.5 - 1000 \text{ nM}) \quad (2)$$

Where F_0 and F are the fluorescence intensities of the C-dots before and after the addition of Fe^{3+} , and C represents the concentration of Fe^{3+} . The calculated detection limit was 1.72 nM based on three times the standard deviation rule. It is demonstrated that the method was able to be overwhelmingly feasible for the detection of trace Fe^{3+} . In addition, the sensing properties of C-dots obtained using methionine only also have been investigated. The fluorescence quenching effect of various metal ions on the C-dots sample (synthesized with methionine only) was investigated shown in

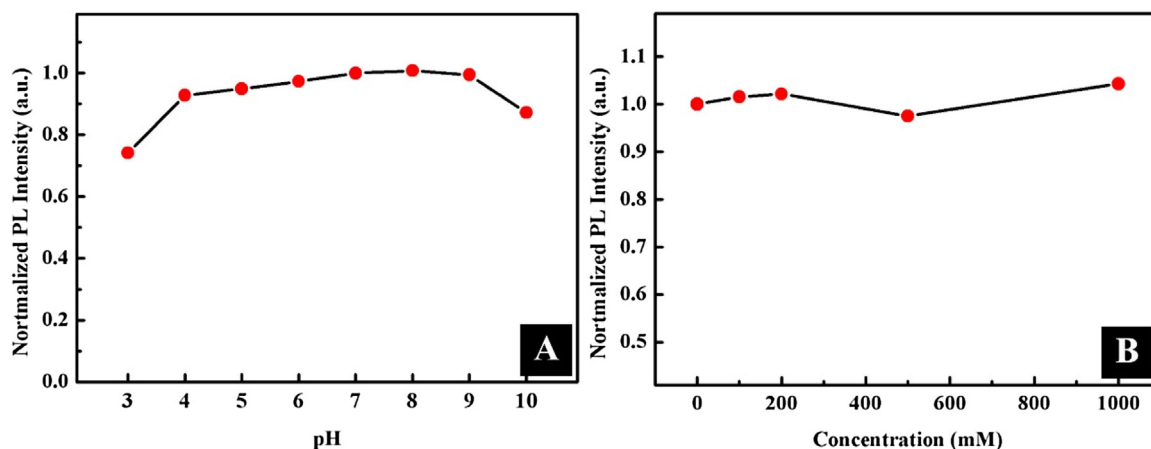


Fig. 7. pH (A) and ionic strength (B) effect on the fluorescence of C-dots.

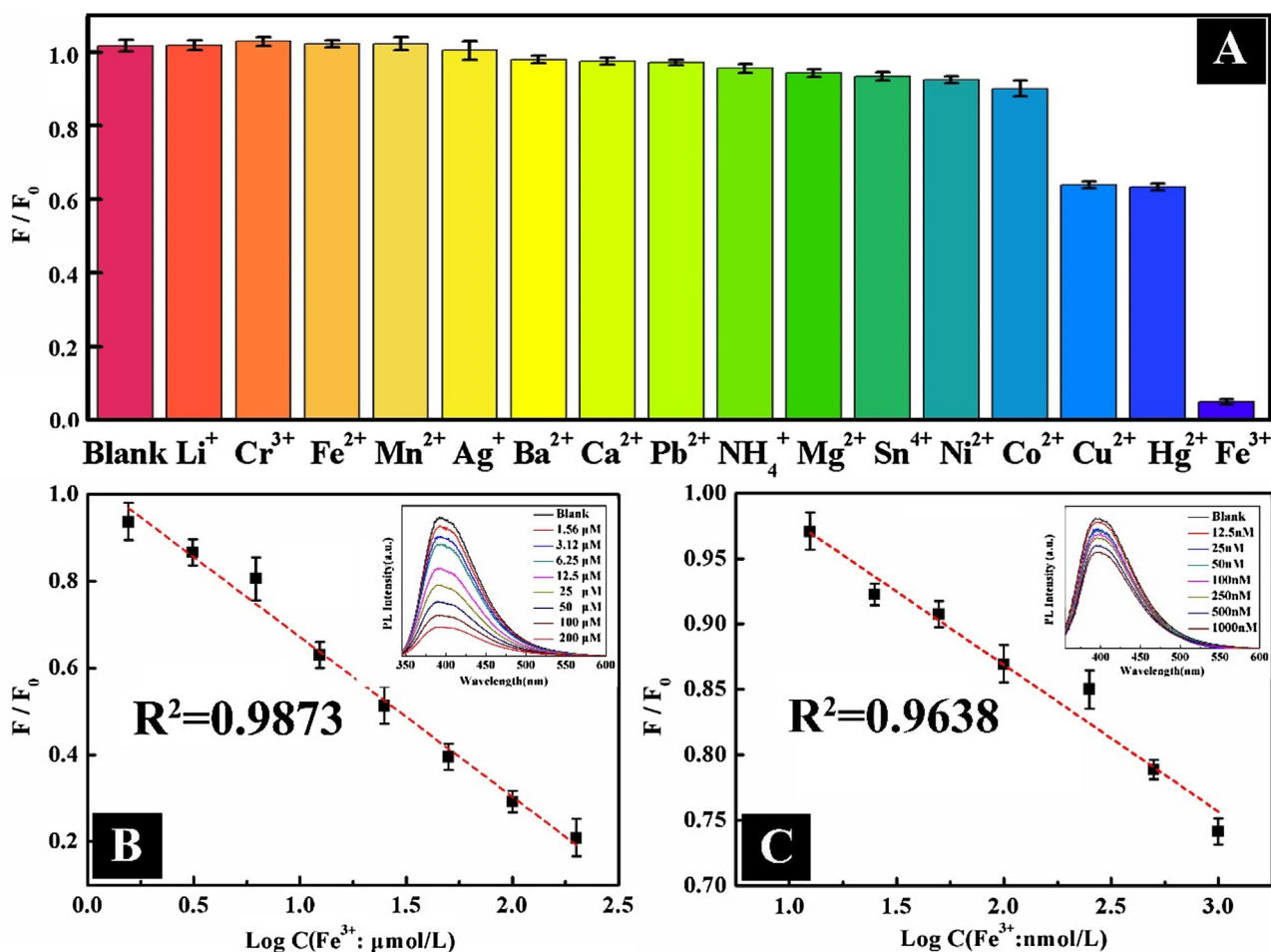


Fig. 8. (A) The selectivity of C-dots to various metal ions (1.25 mmol/L); The dependence of F/F_0 on the concentration of Fe^{3+} ions within (B) the range of 200 μM – 1.56 μM (C-dots concentration: 8.8×10^{-2} mg/mL) and (C) 1000 nM – 12.5 nM (C-dots concentration: 8.8×10^{-4} mg/mL). Inset: Emission spectra recorded with different concentrations of Fe^{3+} ions respectively.

Fig. S4. The C-dots also performed similar quenching properties to Fe^{3+} with good selectivity. However, as seen in Fig. S5, the C-dots solution obtained using methionine only manifested worse sensitivity towards Fe^{3+} . Compared with recently published fluorimetry method based on C-dots with different precursors, our N- and S-co-doped C-dots obtained by methionine-acrylic acid hybrid precursors exhibited superiority in wider detection range and lower limit detection.

There are several reasons behind the strong quenching of fluorescence intensity by Fe^{3+} . Previous researches [28,51] reported that Fe^{3+} ions exhibit a higher affinity for N and O on the surface of C-dots. Accordingly, the photoluminescence quenching could be believed to be related to the nonradiative electron transfer process between the C-dots and Fe^{3+} . It is well acknowledged that Fe^{3+} could absorb [52] and react with the large numbers of $-OH$, $-COOH$ and $-NH_2$ groups distributing on the surface of C-dots, which led to

the chelation or coordination and caused the formation of nonradiative electron/hole recombination, resulting in the consequently quenching of fluorescence [9]. Probably due to the chelating process of Fe^{3+} ions with C-dots in comparison with other metal ions, the marvelous selectivity of these C-dots was able to be manifested [23]. Compared with the C-dots using only methionine as precursor, the C-dots synthesized by methionine-acrylic acid hybrid precursors possessed higher sensitivity with better limit of detection to Fe^{3+} , which could be ascribed to acrylic acid-induced modulation of the chemical and electronic characteristics and its more oxygen-containing coordination groups.

4. Conclusion

In summary, we developed a facile and one-pot hydrothermal approach to fabricate nitrogen- and sulfur-co-doped C-dots by using acrylic and methionine as precursor. The obtained C-dots with an average diameter of 2.3 nm manifested colorful luminescence, good-solubility and attractive optical-stability. Meanwhile, mild acids, alkaline and high ionic strength own a small impact on the fluorescence. Hence the obtained C-dots can be deemed as fluorescent probe for Fe^{3+} ions in aqueous solution with high sensitivity and selectivity. The detection limit was as low as 1.72 nM. Otherwise, the temperature effect on the fluorescence intensity made the C-dots could be applied as the temperature sensor with significant reversibility, sensitivity and linearity.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.snb.2016.09.032>.

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