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Journal of Luminescence

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Study on fluorescence properties of carbogenic nanoparticles and their application for the determination of ferrous succinate

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ARTICLE INFO

Article history:

Received 19 April 2009

Received in revised form

9 February 2010

Accepted 11 March 2010

Available online 18 March 2010

Keywords:

Carbogenic nanoparticles

Fluorescence

Ferric ion

Ferrous succinate determination

ABSTRACT

A new type of fluorescent nanomaterial named carbogenic nanoparticles (NPs) has drawn considerable attention recently. In this study, we adopted a direct and simple synthetic method to produce the carbogenic NPs and investigated the fluorescence properties of the as-prepared carbogenic NPs in detail. It was found that the fluorescence of carbogenic NPs was stable with the variance of environmental conditions such as pH, temperature and UV irradiation. More interestingly, we found carbogenic NPs exhibited high selectivity and sensitivity towards ferric ions. Under optimum conditions, a good linear relationship could be obtained between the fluorescence intensity and concentration of ferric ions in the range of 5.0×10^{-5} – 5.0×10^{-4} mol L⁻¹, and the limit of detection is 11.2 μmol L⁻¹. Based on the fluorescence quenching of carbogenic NPs, a rapid and specific quantitative method was proposed for the determination of ferrous succinate. The content of ferrous succinate in commercial tablets determined by the present method was agreed with the spectrophotometric method results and the reproducibility and the recovery of the proposed method were satisfactory.

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1. Introduction

Fluorescent nanomaterials such as semiconductor quantum dots (QDs) [1], silicon nanoparticles (NPs) [2], and carbon nanotubes [3] have attracted much attention in the past decade for their unique optical properties. Recently, a new type of photoluminescent carbogenic NPs has generated a lot of interest and some research groups have worked on the synthesis and potential application of them. The particles were called “carbogenic” because they were not of pure carbon composition like carbon nanotubes or carbon nanodiamond but proved to be oxygen-containing carbon dots. Fluorescent carbogenic NPs can be obtained by various methods such as laser ablation of graphite [4,5] or carbon powders [6], proton-beam irradiation of nanodiamonds [7,8], carboxylation of carbon nanotubes [9–11], electrooxidation of graphite [12], hydrothermal decomposition of ammonium citrate salts [13,14] or separating from candle soot [15].

It is reported that fluorescent carbogenic NPs share similar optical virtues with metal-based quantum dots such as high quantum yield, tunable emission wavelength but show less physiological toxicity and environmental damage. Thus

carbogenic NPs are of great promise for a broad range of biological applications. For instance, carbogenic NPs have been used for labeling human breast cancer cells for multiphoton imaging [5] or further conjugated with biological and bioactive species for optical bioimaging of cancer cells and tissues [16]. However, as a new kind of fluorescent nanoprobe, the optical properties of carbogenic NPs are not thoroughly investigated, and their application for quantitative analysis is still rare.

In our study, we adopted a simple and inexpensive hydrothermal decomposition approach to synthesize the fluorescent carbogenic NPs and investigated their fluorescence properties in detail. It was found that the fluorescence of carbogenic NPs was stable with the variance of environmental conditions such as pH, temperature and UV irradiation. Interestingly, we also found out that the fluorescence of carbogenic NPs was selectively sensitive to the ferric ions. Accordingly, we proposed a new method for the determination of ferrous succinate in pharmaceutical tablets based on the fluorescence quenching of carbogenic NPs and the results were satisfactory.

2. Experimental

2.1. Apparatus

The absorption spectrum was acquired on a UV2100 UV–vis spectrometer (Shimadzu, Japan). Fluorescence spectra were recorded on an RF-5301 spectrofluorophotometer (Shimadzu,

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Japan) equipped with a 1 cm quartz cell. The transmission electron microscopy (TEM) image of the carbogenic NPs was acquired on a Philips FEI Tecnai 20 G2 S-TWIN transmission electron microscope (Philips, Netherlands). TGL-16 platform high-speed centrifuge (Hengfeng Equipment Factory, Jintan, China) was applied for centrifugation operation. All pH measurements were made with a Model pH-25 meter (Leici Equipment Factory, Shanghai, China).

2.2. Reagents

2-(2-aminoethoxy)-ethanol ($\text{OHCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{NH}_2$) was purchased from Alfa-Aesar and used without further purification. Citric acid monohydrate, $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, BaCl_2 , MgSO_4 , CaCl_2 , $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$, $\text{MnSO}_4 \cdot \text{H}_2\text{O}$, $\text{CuSO}_4 \cdot 6\text{H}_2\text{O}$, $\text{Cd}(\text{Ac})_2$, FeSO_4 , KCl , NaCl , $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, quinine sulfate and rhodamine B were acquired from Shanghai Chemical Reagents Company. Ferric chloride hexahydrate standard (labeled purity $\geq 99\%$) was purchased from Sigma-Aldrich Company. CdTe QDs were locally synthesized via the method described in our previous work [17]. Tris-HCl buffer solution (0.05 mol L^{-1}) containing 0.1 mol L^{-1} NaCl was freshly prepared. All water used in the experiment was double distilled.

2.3. Synthesis of carbogenic NPs

Carbogenic NPs based on citrate precursor were prepared via the procedure described by Bourlinos et al. [13] with some slight modifications. Briefly, citric acid monohydrate (1 g, 4.75 mmol) was dissolved in water (5 mL) and $\text{OHCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{NH}_2$ (0.65 g, 6.2 mmol) was added. The solution was evaporated until dry at 65°C for 3 days and the resulting thick syrup was heated hydrothermally in a Teflon equipped stainless steel autoclave at 250°C for 2 h using a muffle oven. The solid product was then directly dissolved in 5 mL water.

2.4. Drug sample treatment

Twenty ferrous succinate tablets were weighed and powdered in a mortar and the average weight of one tablet was calculated. 0.1436 g powder (equivalent to 48 mg ferrous succinate) was dissolved by 5 mL water in a 10 mL volumetric flask through sonication in an ultrasonic bath for 10 min. Then the pH of solution was adjusted to 3 with 1.5 mol L^{-1} sulfuric acid. Then, 0.16 mL hydrogen peroxide (30%) was dropped into the solution and stirred thoroughly for 10 min to ensure Fe^{2+} was oxidized to Fe^{3+} . Then the flask was kept in a water bath at 80°C to decompose excess hydrogen peroxide before diluting to volume with water. After transferring 2.00 mL of this solution to a 10 mL volumetric flask, it was adjusted to 7 with 0.05 mol L^{-1} Tris-HCl and insoluble excipients were removed with centrifugation at 15,000 rpm for 3 min.

2.5. Determination of ferrous succinate with carbogenic NPs

Two microlitres of carbogenic NPs solution (0.02 mg mL^{-1} according to citric acid monohydrate) was diluted with 20 mL, 0.05 mol L^{-1} pH 7.4 Tris-HCl buffer solution. 2.00 mL of the diluted solution was transferred into a quartz cell, and then titrated manually by successive addition of the treated drug sample solution with a microsyringe. The excitation wavelength was 360 nm and the emission spectra were recorded between 370 and 640 nm using 5 nm/5 nm slit widths.

3. Results and discussion

3.1. Characterization of the carbogenic NPs

The UV-vis absorption spectrum of carbogenic NPs aqueous solution in Fig. 1(A) revealed the absorption band was at 347 nm. Upon irradiation with a 365 nm UV lamp, it was found to emit blue luminescence. The fluorescence spectra of carbogenic NPs were measured with the excitation wavelength set from 280 to 500 nm by a 20 nm increment. The corresponding spectra are given in Fig. 1(B). As can be seen, when the excitation wavelength was between 280 and 400 nm, the fluorescence intensities firstly increase and then decrease while the emission wavelength remained stable, indicating that one fluorescent substance or structure dominates the fluorescence of the NPs in this excitation range. When the excitation wavelength varied from 400 to 500 nm, the fluorescence spectra red-shifted and decreased gradually. Despite the accurate emitting mechanism and chemical structure were still not quite clear, the fluorescence behavior observed clearly pointed towards the presence of different types of fluorophores within the particles, which had different double bond-conjugation extents and hence different maximum excitation and emission wavelengths [14].

The TEM image of the carbogenic NPs showed much less agglomerated particles with average size of 2.0 nm (Fig. 2). This size was much smaller than that reported in E.P. Giannelis' work (near 7 nm) [13]. Although in both works carbogenic NPs were prepared with the same materials and pyrolytic method, the reaction temperatures were different, which were 300°C and 250°C , respectively. We supposed that relative low heating temperature

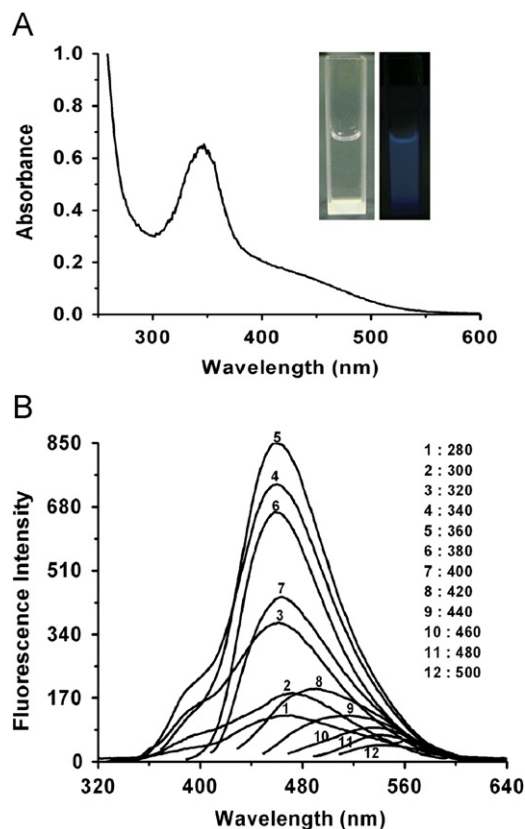


Fig. 1. Absorption (A) and emission spectra at different excitation wavelengths (B) of carbogenic NPs. The insets of (A) are images of carbogenic NPs solution under sunlight and 365 nm UV irradiation.

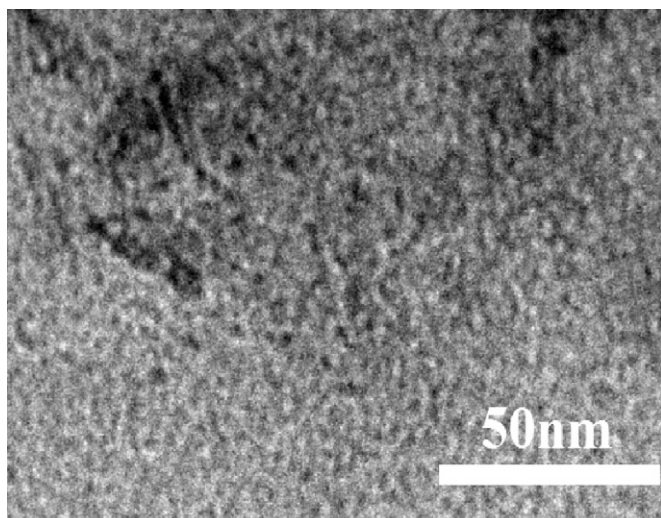


Fig. 2. TEM image of carbogenic NPs.

and rate would slow down hydrothermal decomposition process, which was a benefit for the formation of smaller particles.

3.2. Determination of quantum yield

The quantum yield (Φ) of carbogenic NPs was calculated according to the following equation [12]:

$$\Phi_x = \Phi_{ST}(m_x/m_{ST})(\eta_x^2/\eta_{ST}^2) \quad (1)$$

where Φ is the quantum yield, m is the slope obtained from the plot of the integrated fluorescence intensity versus absorbance of the diluted sample solution, η is the refractive index of the solvent, ST for the standard and X for the sample. The quantum yield of carbogenic NPs was calculated by comparing the integrated fluorescence intensities (excited at 360 nm) and the absorbance values at 360 nm of the carbogenic NPs with quinine sulfate as the standard (literature $\Phi=0.54$). The quinine sulfate was dissolved in $0.1 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$ ($\eta=1.33$) and the carbogenic NPs were dissolved in double distilled water ($\eta=1.33$). The data showed good linearity, and the slopes of carbogenic NPs and quinine sulfate were 6.4×10^5 and 1.8×10^6 , respectively. The quantum yield of carbogenic NPs was calculated as 19.2%. This result was much higher than that reported (i.e., quantum yield of 3%), which might be attributed to the fact that dots of smaller size had better photoluminescence efficiency [4].

3.3. Effect of pH on the fluorescence intensity of carbogenic NPs

The effect of pH on the fluorescence spectra of carbogenic NPs was investigated. Twenty microliters of carbogenic NPs colloid was diluted by 2.0 mL of 0.05 mol L^{-1} Tris-HCl buffer solutions adjusted to different pH. With the excitation wavelength of 360 nm, in the pH range from 5.0 to 10.0 with intervals of 1.0, the fluorescence emission peak at 461 nm did not shift and the intensity was also nearly stable. The stability of carbogenic NPs to pH could be an advantage for the application in biology and medicine.

3.4. Effect of temperatures on the fluorescence intensity of carbogenic NPs

Since temperature plays an important role in the optical performance of nanomaterials, studying the influence of temperature is of particular importance. By using rhodamine B

and CdTe QDs as references, the effect of different temperatures on the fluorescence intensity of carbogenic NPs in aqueous solution was tested (Fig. 3). As the temperature increased from 293 to 353 K, for carbogenic NPs, the fluorescence intensity at 461 nm decreased to 71.7% of its original value and the fluorescence emission peak did not show obvious shift. While for rhodamine B and CdTe QDs, the decreasing degree was much larger, with only 33.0 and 29.6% of their original fluorescence maintained. The results indicated that the fluorescence of carbogenic NPs was insensitive to temperature, as for biological labeling, it is desirable to have NPs with stable properties that are not affected by environmental factors, thus, it would provide carbogenic NPs with more opportunities for biolabeling [18].

3.5. Photostability of carbogenic NPs

The photostability of carbogenic NPs in aqueous solution was measured using CdTe QDs and quinine sulfate in 0.1 mol L^{-1} sulfuric acid as reference. It was found that the carbogenic NPs were more photostable than quinine sulfate as the fluorescence intensity decreased less after continuous irradiation for 7 h with a 360 nm 20 W UV lamp (Fig. 4). It was regarded that in the synthesis process of hydrophilic carbogenic NPs, the resulting amide linkages ($-\text{NHCO}-$) from the thermal dehydration of the ammonium carboxylate moieties ($-\text{NH}_3^+\text{OOC}-$) tethered the organic corona covalently to the surface of the citrate-derived

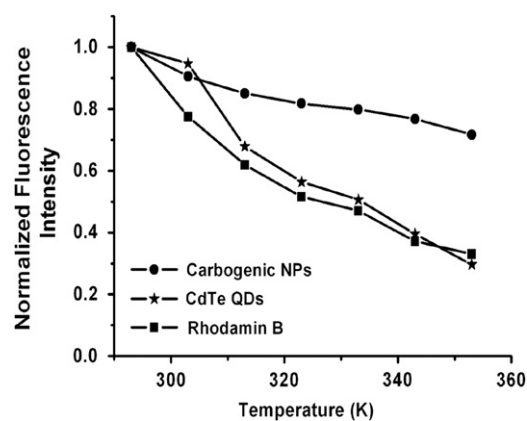


Fig. 3. Effect of temperature on the fluorescence intensity of carbogenic NPs, CdTe QDs and rhodamine B. The temperatures were 293, 303, 313, 323, 333, 343 and 353 K.

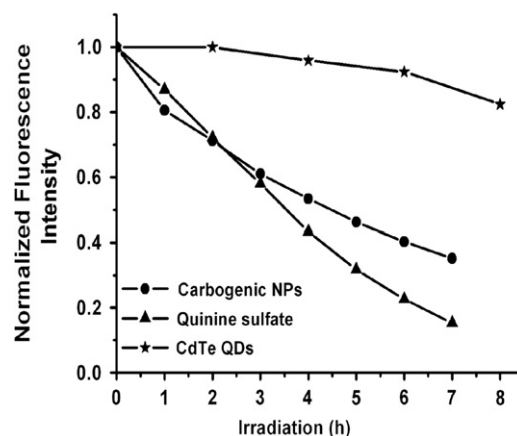


Fig. 4. Photostability test on carbogenic NPs, CdTe QDs and quinine sulfate excited at 360 nm.

carbogenic core [14]. Thus, carbogenic NPs were composed of complex structure with intense organic shell surrounding the inner fluorescent emitting core. We deduced that the corona on the surface could prevent the inner core fluorescent species from UV light degradation, hence they exhibited more anti-bleaching feature than normal dyes. However, it was still apparent that their organic composition determined that their photostability was still not qualified to compare with that of the semiconductor quantum dots.

3.6. Long-term fluorescence stability of carbogenic NPs

The fluorescence intensity of carbogenic NPs in aqueous solution was investigated for several days at room temperature. In a period of 22 days, the fluorescence intensity changed little, indicating that the carbogenic NPs aqueous solution showed long-term stability.

3.7. Effect of the metal ions on the fluorescence intensity of carbogenic NPs

The effects of K^+ , Na^+ , Zn^{2+} , Fe^{3+} , Co^{2+} , Ba^{2+} , Mg^{2+} , Fe^{2+} , Cu^{2+} , Cd^{2+} , Al^{3+} , Mn^{2+} and Ca^{2+} on the fluorescence spectra in 0.05 mol L^{-1} pH 7.4 Tris-HCl buffer solution were investigated. Fig. 5 showed that the fluorescence of carbogenic NPs was insensitive to most physiologically important cations at a level of $1.0 \times 10^{-3} \text{ mol L}^{-1}$, and only Fe^{3+} could effectively quench their fluorescence. This interesting phenomenon impelled us to further investigate the effect factors on the quenching and the possibility to apply carbogenic NPs for ferric ion sensing.

3.8. Optimization of experimental conditions

Initial experiments showed that the ferric ions quench the fluorescence intensity of carbogenic NPs in a concentration dependent manner that is best described by the Stern-Volmer-type equation [19]:

$$F_0/F = 1 + K_{SV}[Q] \quad (2)$$

where F and F_0 are the fluorescence intensities of carbogenic NPs at a given ferric ion concentration and in a ferric ion-free solution, respectively. K_{SV} is the quenching constant and $[Q]$ is the ferric ion concentration. Hence, we studied the effects of pH, buffer solution and ionic strength on the fluorescence quenching caused by ferric ions with a criterion of quenching constant K_{SV} .

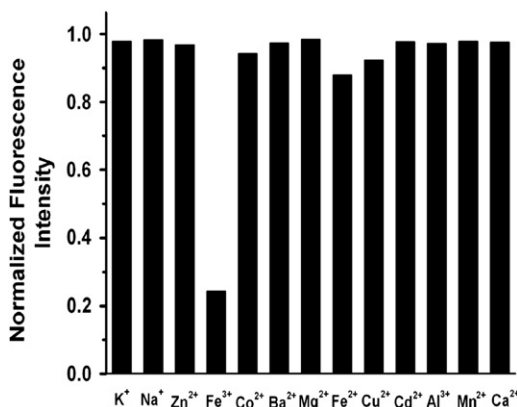


Fig. 5. Effect of biologically relevant cations on the fluorescence of carbogenic NPs in 0.05 mol L^{-1} pH 7.4 Tris-HCl buffer solution. The concentration of the ions was $1.0 \times 10^{-3} \text{ mol L}^{-1}$.

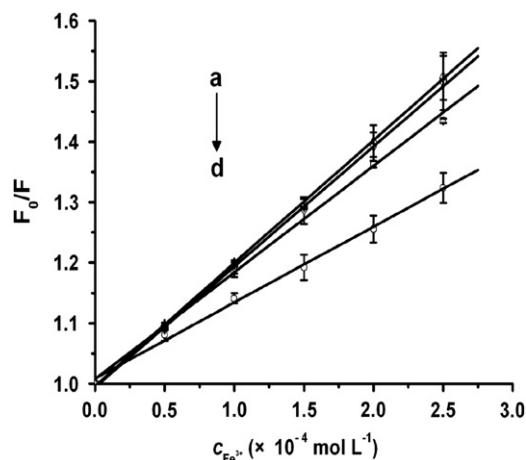


Fig. 6. Fluorescence response of carbogenic NPs to addition of Fe^{3+} in different pH of 0.05 mol L^{-1} Tris-HCl buffer solution, (a) pH=8, (b) pH=7, (c) pH=6 and (d) pH=5 ($n=3$).

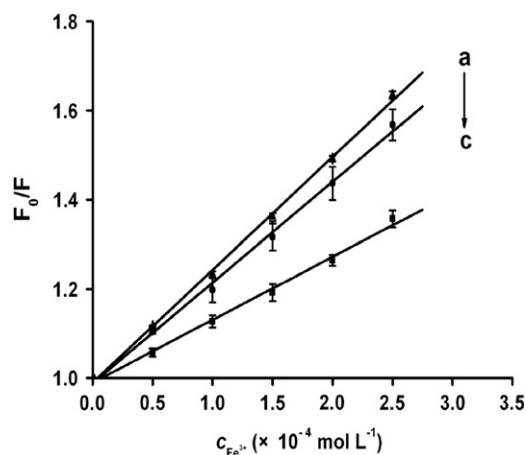


Fig. 7. Fluorescence response of carbogenic NPs to addition of Fe^{3+} in different buffer systems. (a) Tris-HCl, (b) NaAc-HAc and (c) $Na_2B_4O_7-H_3BO_3$ solution with pH 7.4 ($n=3$).

The influence of pH on the fluorescence intensity of carbogenic NPs with successive addition of ferric ions was shown in Fig. 6. Maximum K_{SV} was obtained from the slope at pH 7 and 8 ($0.20 \times 10^4 \text{ L mol}^{-1}$). Therefore, at pH 7.4, a neutral physiological environment was employed in our study for Fe^{3+} sensing. Various buffer solutions such as Tris-HCl, NaAc-HAc and $Na_2B_4O_7-H_3BO_3$ were tested with the adjusted concentration and pH. As shown in Fig. 7, the greatest K_{SV} was obtained with a 0.05 mol L^{-1} pH 7.4 Tris-HCl buffer solution ($0.25 \times 10^4 \text{ L mol}^{-1}$). Relative fluorescence intensities of carbogenic NPs in 0.05 mol L^{-1} pH 7.4 Tris-HCl buffer solution against different ionic strengths were also measured. The concentration of sodium chloride was fixed at 0, 0.05, 0.1, 0.5 and 1.0 mol L^{-1} . It was found that the quenching efficiency was not influenced by ionic strength. Therefore, a pH 7.4, 0.05 mol L^{-1} Tris-HCl buffer solution containing 0.1 mol L^{-1} NaCl was selected for the present study.

3.9. Effect of reaction time

During the experiments, we found that the reaction between carbogenic NPs and the ferric ion solution finished very soon and the fluorescence intensity changed little for more than 60 min

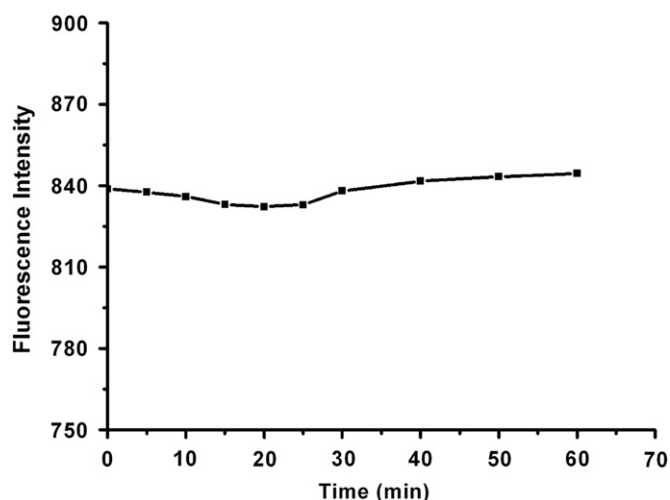


Fig. 8. Effect of reaction time on the fluorescence intensity of carbogenic NPs-ferric ion solution system ($c_{\text{Fe}^{3+}} = 0.5 \times 10^{-4} \text{ mol L}^{-1}$).

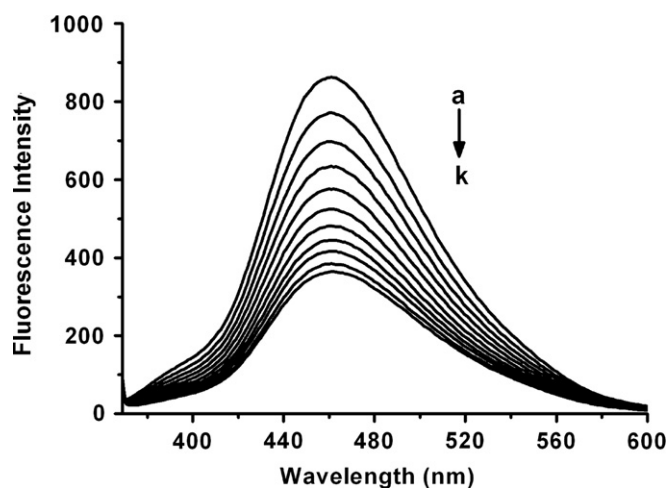


Fig. 9. Fluorescence quenching of carbogenic NPs caused by Fe^{3+} . The concentration of Fe^{3+} from the top to the bottom was 0, 0.5, 1.0, 1.5, 2.0, 2.5, 3.0, 3.5, 4.0, 4.5, and $5.0 \times 10^{-4} \text{ mol L}^{-1}$. The solvent was 0.05 mol L^{-1} pH 7.4 Tris-HCl buffer solution containing 0.1 mol L^{-1} NaCl.

(Fig. 8). Accordingly, we recorded the fluorescence intensity in 30 s after the ferric ion solution was added.

3.10. Calibration curve

Under the optimal condition, the emission spectra of carbogenic NPs with different amounts of ferric ions were recorded (Fig. 9). The Stern–Volmer quenching curve describing F_0/F as a function of ferric ion concentration in the range of 5.0×10^{-5} – $5.0 \times 10^{-4} \text{ mol L}^{-1}$ was shown in Fig. 10, and the K_{SV} was found to be $1.4 \times 10^3 \text{ L mol}^{-1}$. The limit of detection (LOD) is defined by the equation $\text{LOD} = 3\sigma/k$, where σ is the standard deviation of blank measurements ($n=10$) and k is the slope of calibration graph. Here LOD was $11.2 \mu\text{mol L}^{-1}$.

3.11. Precision and accuracy

To assess the precision and accuracy of the method, determinations were carried out for a set of 10 measurements of a $5.0 \times 10^{-5} \text{ mol L}^{-1}$ standard ferric ion solution under the optimal

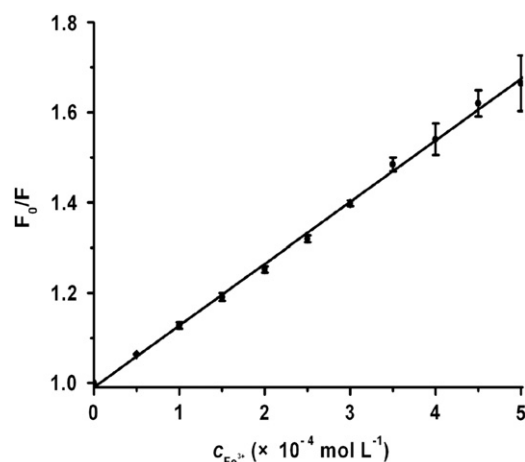


Fig. 10. Stern–Volmer plot of Fe^{3+} concentration dependence of the fluorescence intensity of carbogenic NPs ($n=3$).

Table 1

Effects of several excipients on the fluorescence of carbogenic NPs.

Excipients	Coexisting concentration ($\mu\text{g mL}^{-1}$)	Change of F (%)
Magnesium stearate	Saturated solution	2.14
L-HPC	Saturated solution	1.95
Starch	Saturated solution	0.87
MCC	Saturated solution	1.73
D-Glucose	200	2.57
Sucrose	200	2.43
β -CD	200	2.57

condition. The average result for 10 determinations was $4.8 \times 10^{-5} \text{ mol L}^{-1}$ with the relative standard deviation of 0.6%. These values indicated that this method had a good accuracy and precision.

3.12. Effect of interferences

In order to investigate the possibility of practical application in determination of pharmaceutical preparation, the interference from some excipients often contained in tablets, such as microcrystalline cellulose (MCC), low-substituted hydroxypropyl cellulose (L-HPC), starch, D-glucose, sucrose, magnesium stearate and β -cyclodextrin (β -CD), were tested in the chosen condition. Because MCC, L-HPC, starch and magnesium stearate are barely soluble in water, their saturated solutions were selected to study the effects. The results in Table 1 indicated that the substances exhibited little influence on the fluorescence of carbogenic NPs, so no special separation treatment was taken before sample determination.

3.13. Application

Three synthetic samples of ferric ions with ions and excipients were determined under the optimal condition. As presented in Table 2, the results were satisfactory. The proposed method was then applied to determine ferrous succinate in commercial tablets. The recovery was made using the standard addition method, by adding a known amount of standard ferric ion solution to the pre-analyzed tablet sample in three different levels. Results are given in Table 3. The recoveries were in the range of 97.2–100.4%. The spectrophotometric analysis was also performed as a reference method [20]. As shown in Table 4, the

Table 2
Results for the determination of the ferric ions in synthetic samples ($n=3$). The concentration of all metal ions was 0.05 mol L^{-1} . The concentration of β -CD and D-glucose was 10 mg mL^{-1} . L-HPC, magnesium stearate, MCC were saturated in mixture solution.

Number	Amount ($10^{-4} \text{ mol L}^{-1}$)	Main interferences	Amount found ($10^{-4} \text{ mol L}^{-1}$)	R.S.D. (%)
1	2.5	Mg^{2+} , Cu^{2+} , magnesium stearate, β -CD	2.43 ± 0.03	1.6
2	2.5	K^+ , Ba^{2+} , L-HPC, D-glucose	2.51 ± 0.02	1.0
3	2.5	Mn^{2+} , Co^{2+} , MCC, L-HPC	2.41 ± 0.02	1.2

Table 3
Results of recovery studies by standard addition method ($n=3$).

Background ($\times 10^{-4} \text{ mol L}^{-1}$)	Added ($\times 10^{-4} \text{ mol L}^{-1}$)	Found ($\times 10^{-4} \text{ mol L}^{-1}$, $n=3$)			Average ($\times 10^{-4} \text{ mol L}^{-1}$)	Recovery (%)	R.S.D. (%)
0.50	0.25	0.743	0.745	0.742	0.743	97.2	0.6
	0.50	1.001	0.997	0.985	0.994	98.8	1.7
	1.00	1.518	1.460	1.533	1.504	100.4	3.8

Table 4
Assay results for the determination of ferric ions in commercial tablets.

Ferrous succinate tablets	Repeated determination ($n=6$) (%)						Average (%)	R.S.D. (%)
Spectrophotometric method	42.1	41.8	41.9	41.2	41.3	41.8	41.7	0.85
This method	38.5	40.3	39.6	41.4	40.8	41.4	40.3	2.8

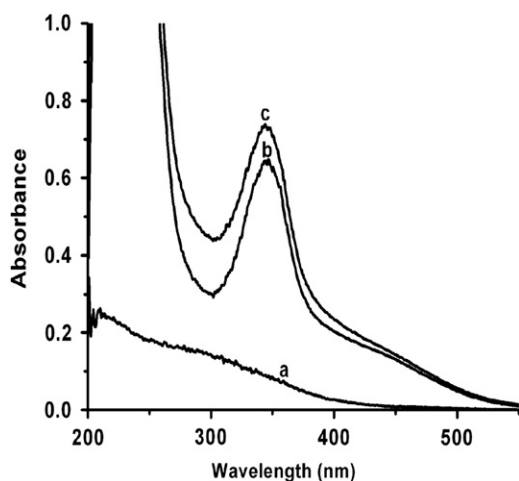


Fig. 11. The absorption spectra of carbogenic NPs in the absence and presence of Fe^{3+} . (a) $5.0 \times 10^{-5} \text{ mol L}^{-1} \text{ Fe}^{3+}$, (b) carbogenic NPs, and (c) carbogenic NPs with $5.0 \times 10^{-5} \text{ mol L}^{-1} \text{ Fe}^{3+}$.

content of ferrous succinate in tablets assayed by the present method agreed with the spectrophotometric method result.

3.14. Possible mechanism

Possible mechanism of fluorescence quenching of carbogenic NPs by ferric ions was analyzed from the point of view of their ion selective chemical structure and inner filter effect. Despite the accurate structure of the carbogenic NPs being still unclear, the phenomenon that the emission band maximum shifted to longer wavelengths as the excitation wavelength increases across the whole visible range suggests a superposition of different types of fluorescent species (e.g., condensed polyaromatic systems) in carbogenic NPs [14]. In addition, their multi-element composition (C, O, H and N) of synthesis materials offered the possibility of

formation of complicated heterocyclic compounds such as certain fluorescent recognition groups like quinoline [21,22], acridine [23], and cyanostyryl [24], which played an important role in the selectivity of ferric ions.

Additionally, the inner filter effect (IFE) of ferric ions was also taken into consideration. It is regarded that absorption of excitation and/or emission radiation by a sample reduces fluorescence intensity and results in a nonlinear relationship between the observed fluorescence intensity and the concentration of the fluorophore [25]. Because the value of Fe^{3+} absorbance at 360 nm was a little larger than 0.05 at the experimental condition (Fig. 11), we deduced that the IEF could also be responsible for the quenching of carbogenic NPs. However, linear Stern–Volmer plots were obtained in the present work, which indicated that the quenching contribution of IFE was much smaller than that of ferric ion sensitive structures.

4. Conclusion

In summary, water-soluble carbogenic NPs were prepared by a facile hydrothermal decomposition approach in this paper. It was found that the fluorescence of carbogenic NPs was stable with the variance of environmental conditions such as pH, temperature and UV irradiation. In addition, carbogenic NPs were found to be a kind of satisfactory selective Fe^{3+} probe in physiological buffer solution. Based on this feature, a new fluorometric method for quantitative analysis of ferrous succinate in commercial tablets was developed. Under optimum conditions, a good linear relationship between the fluorescence intensity ratio of system and concentration of ferric ions even at $5.0 \times 10^{-4} \text{ mol L}^{-1}$, and the limit of detection is $11.2 \mu\text{mol L}^{-1}$. The content of ferrous succinate in commercial tablets determined by the present method agreed with the spectrophotometric method result and the reproducibility and the recovery of the proposed method were satisfactory. Clearly, the potential of carbogenic NPs as fluorescence probes has just begun to be realized and the application in analytical chemistry is still in its infancy. The works such as the chemical structure of the NPs, the fundamental quenching

mechanism as well as the surface modification strategy are needed to be investigated. Therefore, we believe there will be more work in this area in the coming years.

References

- [1] J. Sun, L.W. Wang, W.E. Buhro, *J. Am. Chem. Soc.* 130 (2008) 7997.
- [2] F. Erogbogbo, K.T. Yong, I. Roy, G.X. Xu, P.N. Prasad, M.T. Swihart, *ACS Nano* 2 (2008) 873.
- [3] C. Lu, A. Akey, W. Wang, I.P. Herman, *J. Am. Chem. Soc.* 131 (2009) 3446.
- [4] Y.P. Sun, B. Zhou, Y. Lin, W. Wang, K.A.S. Fernando, P. Pathak, M.J. Meziani, B.A. Harruff, X. Wang, H. Wang, P.G. Luo, H. Yang, M.E. Kose, B. Chen, L.M. Veca, S.Y. Xie, *J. Am. Chem. Soc.* 128 (2006) 7756.
- [5] L. Cao, X. Wang, M.J. Meziani, F. Lu, H. Wang, P.G. Luo, Y. Lin, B.A. Harruff, L.M. Veca, D. Murray, S.Y. Xie, Y.P. Sun, *J. Am. Chem. Soc.* 129 (2007) 11318.
- [6] S.L. Hu, K.Y. Niu, J. Sun, J. Yang, N.Q. Zhao, X.W. Du, *J. Mater. Chem.* 19 (2009) 484.
- [7] S.J. Yu, M.W. Kang, H.C. Chang, K.M. Chen, Y.C. Yu, *J. Am. Chem. Soc.* 127 (2005) 17604.
- [8] C.C. Fu, H.Y. Lee, K. Chen, T.S. Lim, H.Y. Wu, P.K. Lin, P.K. Wei, P.H. Tsao, H.C. Chang, W. Fann, *Proc. Natl. Acad. Sci. USA* 104 (2007) 727.
- [9] J. Zhou, C. Booker, R. Li, X. Zhou, T.K. Sham, X. Sun, Z. Ding, *J. Am. Chem. Soc.* 129 (2007) 744.
- [10] M. Bottini, C. Balasubramanian, M.I. Dawson, A. Bergamaschi, S. Bellucci, T. Mustelin, *J. Phys. Chem. B* 110 (2006) 831.
- [11] X. Xu, R. Ray, Y. Gu, H.J. Ploehn, L. Gearheart, K. Raker, W. Scrivens, *J. Am. Chem. Soc.* 126 (2004) 12736.
- [12] Q.L. Zhao, Z.L. Zhang, B.H. Huang, J. Peng, M. Zhang, D.W. Pang, *Chem. Commun.* 41 (2008) 5116.
- [13] A.B. Bourlinos, A. Stassinopoulos, D. Anglos, R. Zboril, M. Karakassides, E.P. Giannelis, *Small* 4 (2008) 455.
- [14] A.B. Bourlinos, A. Stassinopoulos, D. Anglos, R. Zboril, V. Georgakilas, E.P. Giannelis, *Chem. Mater.* 20 (2008) 4539.
- [15] H. Liu, T. Ye, C. Mao, *Angew. Chem. Int. Ed.* 46 (2007) 6473.
- [16] P. Juzenas, W. Chen, Y.P. Sun, M.A.N. Coelho, R. Generalov, N. Generalova, I.L. Christensen, *Adv. Drug Delivery Rev.* 60 (2008) 1600.
- [17] Y.Q. Wang, C. Ye, Z.H. Zhu, Y.Z. Hu, *Anal. Chim. Acta* 610 (2008) 50.
- [18] J.H. Wang, H.Q. Wang, Y.Q. Li, H.L. Zhang, X.Q. Li, X.F. Hua, Y.C. Cao, Z.L. Huang, Y.D. Zhao, *Talanta* 74 (2008) 724.
- [19] M.R. Eftink, in: *Fluorescence Quenching Reactions: Probing Biological Macromolecular Structures, Biophysical and Biochemical Aspects of Fluorescence Spectroscopy*, Plenum Press, New York, 1991.
- [20] W.B. Fortune, M.G. Mellon, *Ind. Eng. Chem. Anal. Ed.* 10 (1938) 60.
- [21] T.S. Lee, C. Yang, J.L. Kim, J.K. Lee, W.H. Park, Y. Won, *J. Polym. Sci. Pol. Chem.* 40 (2002) 1831.
- [22] N.J. Li, Q.F. Xu, X.W. Xia, L.H. Wang, J.M. Lu, X.W. Wen, *Mater. Chem. Phys.* 114 (2009) 339.
- [23] T.S. Lee, C. Yang, W.H. Park, *Macromol. Rapid Commun.* 21 (2000) 951.
- [24] J. Na, W.H. Park, T.S. Lee, *React. Funct. Polym.* 59 (2004) 225.
- [25] Q. Gu, J.E. Kenny, *Anal. Chem.* 81 (2009) 420.