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

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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.

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 nanoprobes, 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 pHS-25 meter (Leici Equipment Factory, Shanghai, China).

2.2. Reagents

2-(2-aminoethoxy)-ethanol ($OHCH_2CH_2OCH_2CH_2NH_2$) was purchased from Alfa-Aesar and used without further purification. Citric acid monohydrate, $CoCl_2 \cdot 6H_2O$, $BaCl_2$, $MgSO_4$, $CaCl_2$, $ZnSO_4 \cdot 7H_2O$, $MnSO_4 \cdot H_2O$, $CuSO_4 \cdot 6H_2O$, $Cd(Ac)_2$, $FeSO_4$, KCl, NaCl, $Al(NO_3)_3 \cdot 9H_2O$, 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 m mol) was dissolved in water (5 mL) and $OHCH_2CH_2OCH_2CH_2NH_2$ (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 and 250 °C, respectively. We supposed that relative low heating temperature

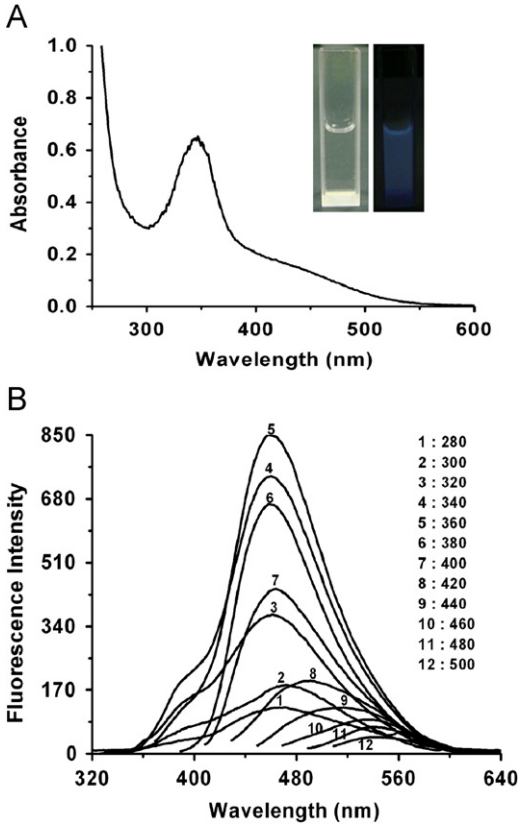

Fig. 1. Absorption (A) and emission spectra at different excitation wavelengths (B) of carbogenic NPs. The insets of (A) are images of carbogenic NPs solution under sunlight and 365 nm UV irradiation.