Facile Synthesis of Water-soluble Carbon Spheres for the Sensitive and Selective Determination of Fe$^{3+}$, Cr$^{3+}$ and Hg$^{2+}$ Ions.

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Abstract

Water-soluble carbon spheres (CS) were prepared by a facile one step hydrothermal synthetic method using glucose as carbon source and sodium hydroxide as additives. The morphology and chemical structure were characterized by transmission electron microscopy (TEM), Fourier transform infrared (FT-IR) spectrum, X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS). In addition, the ultraviolet-visible (UV-vis) absorption spectrum and the fluorescence spectrum of the prepared CS were also investigated. The emission spectrum of the obtained CS depends on the excitation wavelength which is similar to that of most carbon quantum dots. The fluorescence of the CS is quenched in the presence of Cr³⁺, Fe³⁺ and Hg²⁺. Based on this feature, the selective and sensitive detection of Cr³⁺, Fe³⁺ and Hg²⁺ was performed, and the detection limits are 6.72µM, 7.26µM and 9.51µM, respectively.

Key Words: Carbon spheres, fluorescence, determination
Introduction

Carbon nanomaterials have been well known for many years and play an important role in the application of nanomaterials. Different carbon nanostructures are prepared such as carbon nanotubes 1-3, porous carbon 4-6, graphene 7,8, carbon spheres (CS) 9-12. Among them, CS are attracting increasing attention because of the advantages of unique geometric characteristics such as good liquidity, adjustable porosity and controllable particle size distribution 13-16.

A various of methods were used to prepare CS, such as soft/hard template methods 17-18, hydrothermal method 19, Stöber method 20, chemical vapor deposition (CVD) method 21, 22, ultrasonic spray pyrolysis (USP) method 23, 24, etc. The soft template method has the advantages that the template is simple in construction and unnecessary to delete the template. However, it is not easy to control the morphology and the stability of the obtained CS is poor. The hard template method has good thermal stability and the morphology can be effectively controlled. The post-treatment of the hard template method is generally complicated and it is often necessary to remove the template with strong acid, strong base or organic solvent. The other methods have the disadvantages of low yields or high temperatures for the reaction. In contrast, the hydrothermal method is an economic, green and simple method to prepare size well controlled CS by controlling the reaction conditions such as temperature, time and ratio of ingredients 25. A great achievement has been made to prepare CS by hydrothermal method. Wang et al. 26 reported a kind of uniform micropores CS with pore size about 0.4 nm by hydrothermal method for the first time. Colloidal CS with diameter of 150~1500 nm was prepared by hydrothermal treatment with glucose as carbon source 27. The biomass carbon spheres (BCS) were prepared with glucose as a carbon source by hydrothermal method and the co-CdSe/BCS photocatalyst with excellent optical absorption property and electron transport ability were obtained 28.

Due to the high chemical stability, favorable temperature resistance, large specific surface area, excellent mechanical properties, low density and electrical conductivity has potential applications in many fields. Hollow mesoporous carbon sphere was used
to adsorb of bilirubin. Yang et al. synthesized activated mesopores and macropores CS for absorption of VB12. CS was also applied as supercapacitors in electrochemistry field. A hollow carbon spheres as anode catalyst carriers have been used for direct methanol fuel cells. Liu et al. studied the electrochemical properties of the obtained nano-sized cobalt oxide/mesoporous carbon sphere (Cox/MCS) as anode materials for lithium-ion batteries. In addition, palladium nanoparticle and a hollow carbon composite shell (Pd@hmC) prepared by Harada et al. have good catalytic activity for the oxidation of various primary benzylic and allylic alcohols. Besides, Zhang et al. developed a new type of fluorescent sensor for measuring L-tryptophan by using functionalized CS for the first time. Due to the excellent fluorescent performances, the applications of fluorescent CDs for heavy metal ions detection have intrigued great interest for the more seriously environmental pollution. A water-soluble carbon quantum dots were synthesized from lemon peel waste using a hydrothermal process and further used to design the economic, green and highly sensitive fluorescent probe for the detection of Cr6+ ions with detection limit of 73 nM. Zhang et al. developed the N-doped CDs for Hg2+ detection of which limit of detection was as low as 0.23 µM. Gupta et al. found that their synthesized CDs from biological media have ultrasensitive and highly selective for Pb2+ detection. However, the application of CS in fluorescence sensing is still limited and a CS-based sensing system with high specificity and sensitivity has not yet been explored. Few works have reported the detection of metal ions selectivity and sensitivity by CS using fluorescence spectroscopy.

In this work, we prepared CS via a hydrothermal method with glucose as carbon and NaOH as additives. The addition of Cr3+, Fe3+, and Hg2+ lead to quench the fluorescence of the CS. Therefore, the prepared CS aqueous solution can be used to detect Cr3+, Fe3+ and Hg2+ selectively which are harmful to human and environment.

**Experimental**

*Reagents and chemicals*
Glucose, Cu(NO$_3$)$_3$·3H$_2$O (99.5%), Fe (NO$_3$)$_3$·9H$_2$O (98.5%), Pb(NO$_3$)$_2$ (99.0%), Mg(NO$_3$)$_2$·6H$_2$O (98.0%), Hg(NO$_3$)$_2$·H$_2$O (97.0%), Zn(NO$_3$)$_2$·6H$_2$O (99.0%), KNO$_3$ (99.0%), NaNO$_3$ (99.0%), Ba(NO$_3$)$_2$ (99.0%), Co(NO$_3$)$_2$·6H$_2$O (98.0%), AgNO$_3$ (99.8%), Ni(NO$_3$)$_2$·6H$_2$O (99.0%), Al(NO$_3$)$_3$·9H$_2$O (99.5%), Cr(NO$_3$)$_3$·9H$_2$O (99.0%), NaOH (96.0%), CH$_3$CH$_2$OH (99.7%), KH$_2$PO$_4$ (99.7%). All these reagents are from Tianjin Damao Chemical Reagent Co., Ltd. and used without further purification. Backup solutions (10.0 mmol·L$^{-1}$) of Cr$^{3+}$, Fe$^{3+}$, Hg$^{2+}$ and other common metal ions (10.0 mmol·L$^{-1}$) are prepared in the distilled water. Phosphate buffered solution (PBS) was fabricated to the required pH (7.0) value. The deionized water was used throughout the experiments.

**Apparatus**

Transmission electron microscopy (TEM) measurements was carried out with a TECNAI G$^2$ field-emission transmission electron microscope (FEI Company, USA).

X-ray photoelectron spectroscopy (XPS) measurements were carried with a PHI-5702 multifunctional spectrometer (Escalab 250Xi, ThermoFisher Scientific Company, USA).

The Fourier transform infrared (FT-IR) spectra of dried carbon spheres was obtained on a Model FTS-3000 spectrometer (Digilabgon, USA).

The X-ray diffraction (XRD) patterns were performed on a D8 advance X-ray diffractometer (Bruker, Germany).

The ultraviolet-visible (UV-Vis) absorption spectra were gained on a UV-vis 3000 spectrometer (Shimadzu Company, Japan).

The fluorescence spectra were recorded on a HORIBA Jobin Yvon FluoroMax-4 spectrofluorometer (HORIBA Instruments Inc Edison, NJ USA), both the silts of excitation and emission were fixed at 4 nm.

All pH measurements were made with a PHS-3C pH meter (Shanghai INESA & Scientific Instrument Co. Ltd, China).

**Preparation of CS**

According to the reference$^{39}$, CS were prepared directly by alkali carbonization of glucose. First, 1.0 g glucose and 0.1 g NaOH were dissolved in 15mL distilled water...
with stirring. Then, the solution was transferred into a 20mL Teflon-lined stainless-steel autoclave and treated at 180°C for 5 h. The resulted dark brown solution was cooled to room temperature and the liquid supernatant was obtained after centrifugation. To purify, the obtained solution was heated at 100°C to allow the residual NaOH to dissolve out. The solid was removed by filtration and leaving the solution was dried under vacuum. The obtained sample was finally dispersed into deionized water and stored at 4°C for further use.

Interaction of metal ions with the CS

The interaction of various metal ions (K⁺, Na⁺, Mg²⁺, Al³⁺, Cr³⁺, Fe³⁺, Co²⁺, Ni²⁺, Cu²⁺, Zn²⁺, Ba²⁺, Ag⁺, Pb²⁺ and Hg²⁺) with CS was investigated by their fluorescence spectra. 5.0 mL CS suspension (1.0 mg·mL⁻¹) was diluted to 100.0 mL with PBS (pH, 7.0). Different metal ion solution (100μL 10 mmol·L⁻¹) was mixed with the CS suspension (2 mL 0.05 mg·mL⁻¹). Then, the fluorescence spectra were recorded at excitation wavelength 360 nm.

Results and discussion

Morphology of the prepared CS

The morphology of resultant carbon spheres was characterized using TEM as shown in Fig.1. It can be seen that the average diameter of the isolated carbon spheres is about in the range of 300 nm as shown in Fig. 1b.

Fig.1 TEM image(a) and the size distribution(b) of the prepared CS.
Chemical structure of the prepared CS

The FT-IR spectrum of the prepared CS is shown in Fig. 2a. The peak at 3411 cm⁻¹ corresponds to the stretching vibration of -OH group. The peak at 2927 cm⁻¹ attributes to the stretching vibration absorption of C-H group. The peaks at 1703 and 1610 cm⁻¹ indicate the existence of C=O and C=C groups. The peak at 1400 cm⁻¹ corresponds to the bending vibration of C-C group. The stretching vibration absorption peaks of C-O-C and C-O groups appear at 1264 and 1069 cm⁻¹, respectively. These observations clearly indicate that the surface of the resulted CS contains hydrophilic carboxyl and hydroxyl groups which lead to a good water dispersibility.

Fig.2b. shows the XRD pattern of the CS. The board peak near 22° attributes to the existing of highly disordered carbon atoms 40. The elemental analysis of CS has been carried out using XPS analysis as shown in Fig.2c. It indicates the CS contains mainly carbon and oxygen elements and the ratio of atomic contents are 69.11% and 30.89%, respectively. The peak at 500.4eV attributes the Auger electron of residual sodium. Fig.2d is the high resolution XPS spectrum of C1s. It indicates that there are four different chemical surroundings for C1s. The peaks at 284.6eV, 284.0eV, 286.0eV and 287.9eV correspond to C-C, C=C, C-O and C=O bonds, respectively. The results also reveal that the surface of the CS contains a large number of hydrophilic functional groups 36.
Fig. 2 (a) FT-IR spectrum, (b) XRD pattern, (c) XPS of the CS, (d) XPS of C1s for the CS.

UV-visible absorption spectrum of CS

Fig. 3 depicts the UV-vis absorption spectrum of the CS in aqueous solution. There is a strong peak around 250 nm. The peak attributes to the $\pi-\pi^*$ transition of the aromatic sp$^2$ domains which results in nearly no observed fluorescence signal.$^{41}$
The origin of fluorescence in CS is not yet entirely understood, there is mounting evidence that emission arises both from the confined sp$^2$ conjugation in the core of CS and the surface state. Fig. 4a clearly illustrates the fluorescence intensity of the CS depends on excitation wavelength. The fluorescence intensity gradually increases when the excitation wavelengths are changed from 300 to 360nm as shown in Fig.4a. And then, the fluorescence intensity decreases gradually and the emission wavelength shifts to long-wavelength with the excitation wavelength increasing. The phenomenon is mainly due to the influence of the CS particles with different sizes and the distribution of different emission sites on the surface of the CS $^{42-44}$. Fig.4b depicts the performance of up-conversion fluorescence of the CS. Up-conversion luminescence refers to the emission of short-wavelength light under the excitation of long-wavelength light. The up-conversion fluorescence characteristic of CS can be attributed to the anti-Stokes type emission which absorbances two or more photons simultaneously and produces a shorter wavelength than the excitation wavelength $^{45}$. The fluorescence intensity is the maximum and the emission wavelength is 442nm at the excitation wavelength of 360nm (Fig.4a). In short, the emission wavelength of the CS changes with the excitation wavelength.

Fig.3 UV-visible absorption spectrum of CS.
Fig. 4 Fluorescence emission spectra of the CS at different excitation wavelength. The range of excitation wavelength (a) 300-500 and (b) 800-900.

*The effect pH on the FL emission intensity of the prepared CS*

Fig. 5 shows the effect of pH on the FL intensity of CS. When pH increases in the range of 3 to 7, the FL intensity of the CS increases gradually and the FL intensity reaches the maximum at pH = 7. Then, the FL intensity gradually decreases with the pH increasing from 7 to 11. The carboxyl groups of the CS get protonated which leads to deactivation of the emission site and quenches the FL intensity in the acidic condition. On the contrary, the FL intensity can be restored to some extent in the alkaline due to the deprotonation of carboxyl groups which changes the distribution of electron cloud between the functional groups and the carbon backbone $^{46,47}$. In a word, pH has a significant effect on the FL intensity of carbon spheres when studied between pH 3 and 11 and pH = 7 is used for a further research.

*Determination of metal ions*

Fig. 6 shows the selectivity of the CS to metal ions at the same concentration (0.5 mmol·L$^{-1}$). It is observed that the fluorescence can be quenched toward Cr$^{3+}$, Fe$^{3+}$, Hg$^{2+}$. The three metal ions can be identified for two main reasons: (1) the inner filter effect of Cr$^{3+}$, Fe$^{3+}$, Hg$^{2+}$; (2) the transfer of electron from the CS to Cr$^{3+}$, Fe$^{3+}$, Hg$^{2+}$ $^{48-52}$. The former is caused by the absorption of excited or emitted light by the absorbent in the detection system; the latter may be due to the binding of Cr$^{3+}$, Fe$^{3+}$, Hg$^{2+}$ to the hydroxyl groups on the surface of the CS causing the transfer of non-radiative electrons from the excited state of the CS to Cr$^{3+}$, Fe$^{3+}$, Hg$^{2+}$ $^{53-55}$. 
Fig. 5 FL intensity of CS at different pH.

Fig. 6 Fluorescence responses of CS aqueous solutions in the presence of 0.1 mmol·L⁻¹ of different metal ions. (Ex = 360 nm).
Fig. 7 (a, c, e) Emission spectra of 0.05mg·mL$^{-1}$ CS aqueous solution upon addition of various concentrations of Cr$^{3+}$/Fe$^{3+}$/Hg$^{2+}$ (from 10 to 2500μM). Inset a, c, e: the linear of the expression of $F_0/F$ as a function of Cr$^{3+}$/Fe$^{3+}$/Hg$^{2+}$ concentration (10-700μM, 10-700μM, 10-300μM), respectively (Ex=360nm). (b, d, f) Interference in the presence of 0.15μM Cr$^{3+}$/Fe$^{3+}$/Hg$^{2+}$ and with the addition of 1.5μM different metal ions respectively. Blank group: without any metal ions (Ex=360 nm).

In order to study interaction between Cr$^{3+}$, Fe$^{3+}$, Hg$^{2+}$ and CS in aqueous solution, the FL intensity of CS with Cr$^{3+}$, Fe$^{3+}$, Hg$^{2+}$ is investigated. The FL intensity gradually
decreased with the increasing Cr$^{3+}$, Fe$^{3+}$, Hg$^{2+}$ concentration (0-2500μM) as shown in Fig. 7. The relative fluorescence intensity (F$_0$ and F are the FL intensity of the CS in the absence and presence of metal ions) of the CS have good linear relationship in the range of 10-700μM, 10-700μM and 10-300μM for Cr$^{3+}$, Fe$^{3+}$ and Hg$^{2+}$, respectively as following by a Stern-Volmer plot. The detection limits of Cr$^{3+}$, Fe$^{3+}$ and Hg$^{2+}$ reach to 6.72μM, 7.26μM and 9.51μM, respectively. The results were compared with the previously reported ones. Although the detection limits of Cr$^{3+}$, Fe$^{3+}$ and Hg$^{2+}$ in the present work weren’t as low as which in previously reported references by using CDs as chemical sensors, it demonstrates that CS can also be applied in detection heavy metal ions in environmental pollutants.

Cr$^{3+}$: F$_0$/F=0.0010[Cr$^{3+}$] +1.0193(R$^2$=0.9951)  
Fe$^{3+}$: F$_0$/F=0.00093[Fe$^{3+}$] +1.0113(R$^2$=0.9918)  
Hg$^{2+}$: F$_0$/F=0.00071[Hg$^{2+}$] +1.0967(R$^2$=0.9515)

The FL intensity of CS was quenched by addition of 0.15μM Cr$^{3+}$/ Fe$^{3+}$/ Hg$^{2+}$ in the presence of the other metal ions of 1.50μM as shown Fig.7. The results suggest that the addition of other metal ions doesn’t interference the FL intensity of the CS. Therefore, the CS can be used to detect of Fe$^{3+}$, Cr$^{3+}$ and Hg$^{2+}$ ions sensitively and selectively in water samples.

Conclusions

We have successfully gained the fluorescence CS via one-step hydrothermal way what is both economical and green. The CS have not only drown-conversion but also up-conversion fluorescence properties what are similar to carbon quantum dots characteristic. The prepared CS can be applied for the simultaneous detection of Cr$^{3+}$, Fe$^{3+}$, Hg$^{2+}$ that can quench fluorescence of CS based on fluorescence inner filter effect or the transfer of electron. The CS is likely to be used for the determination of Cr$^{3+}$, Fe$^{3+}$, Hg$^{2+}$ in water samples, and the tested metal ions are heavy metal ions that are harmful to humans. So, the paper provides a way for detection heavy metal ions in water samples.

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