Analytica Chimica Acta xxx (2018) 1–8

Contents lists available at ScienceDirect

Analytica Chimica Acta

journal homepage: www.elsevier.com/locate/aca

Functional preserving carbon dots-based fluorescent probe for mercury (II) ions sensing in herbal medicines via coordination and electron transfer

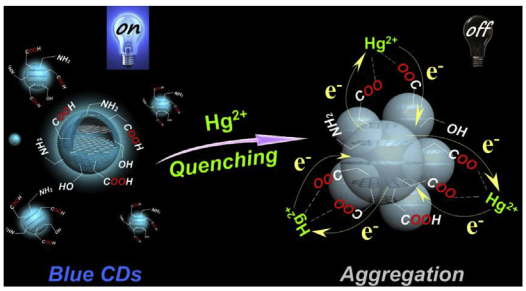
Jia Hui He [a], Yun Ying Cheng [b], Tong Yang [a], Hong Yan Zou [a, *], Cheng Zhi Huang [a, b, **]

[a] Key Laboratory of Luminescence and Real-Time Analytical Chemistry (Southwest University), Ministry of Education, College of Pharmaceutical Sciences, Southwest University, Chongqing, 400715, China
[b] Chongqing Key Laboratory of Biomedical Analysis, Chongqing Science & Technology Commission, College of Chemistry and Chemical Engineering, Southwest University, Chongqing, 400715, China

HIGHLIGHTS

- The CDs of abundant carboxyl functional groups could respond specially to the Hg^{2+}.
- The binding mechanism of Hg^{2+} with CDs is well studied.
- The visual detection of Hg^{2+} in the complex herbal medicines samples has been successfully realized.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 11 April 2018
Received in revised form
11 June 2018
Accepted 15 June 2018
Available online xxx

Keywords:
Carbon dots
Hg^{2+}
Herbal medicines
Fluorescent probe
Electron transfer

ABSTRACT

Mercury ions (Hg^{2+}) are one of the compulsory items in the quality control of herbal medicines for its serious toxicity to human health. Highly selective and sensitive Hg^{2+} detection, especially in complex real samples, is still challenging. In this work, Fluorescent (FL) carbon dots (CDs) with a core-shell structures composed of the crystalline core of stacked sp2-hybridized carbon layers and the shell of functional groups on the periphery of carbon layers are facilely prepared through a one-step hydrothermal synthetic route. They can specifically interact with Hg^{2+} in aqueous medium to form aggregates, during which coordination of carboxyl functional groups on the surface of CDs with Hg^{2+} occurred, which facilitated electron transfer from the CDs to Hg^{2+}. As a result, fluorescence of the CDs was quenched with a high efficiency, making the detection of Hg^{2+} highly sensitive with the limit of determination (LOD) of 2.2 nM (3σ). With that, detection of Hg^{2+} in the complex compound herbal medicines samples with highly reproducible results has been successfully realized by using the as-prepared CDs, showing that fluorescent CDs-based probe may have great potential in the quality controls of heavy metals for pharmaceutical analysis.

* Corresponding author.
** Corresponding author. Key Laboratory of Luminescence and Real-Time Analytical Chemistry (Southwest University), Ministry of Education, College of Pharmaceutical Sciences, Southwest University, Chongqing, 400715, China.
E-mail addresses: zhy2013@swu.edu.cn (H.Y. Zou), chengzhi@swu.edu.cn (C.Z. Huang).

https://doi.org/10.1016/j.aca.2018.06.053
0003-2670/

1. Introduction

Herbal medicines, particularly compound herbal medicines owing to synergistic effect-enhanced curative effects, are widely used by large sections of the population [1–4]. In addition, these herbal medicines have been reported to contain significant levels of heavy metals [5,6]. Therefore, quality controls of toxic heavy metals in herbal medicines, including compound herbal medicines, of course, are critical since their contents are much strictly controlled by the Good Agriculture Practice (GAP) during the planting and General Manufacturing Practice (GMP) during drugs production [7]. For example, mercury is considered to be one of the most hazardous heavy metal pollutants because of its toxicity to kidney, brain, endocrine system and central nervous system of both humans and animals through enzyme inhibition and induction of oxidative stress [8–10], and thus mercury ions (Hg^{2+}) is one of the compulsory items in the quality control of compound herbal medicines [7,11,12].

At present, cold-vapour atomic absorption spectroscopy (CV-AAS) and inductively coupled plasma mass spectrometry (ICP-MS) have been widely adopted to detect Hg^{2+} [5,13,14], which can satisfy the requirements on sensitivity and accuracy. However, these methods need sophisticated analytical instrumentation, well-trained personnel and complex sample pre-treatment processes, limiting their applications [15]. Although organic small molecules (OSMs) probe can achieve a high sensitivity and selectivity, it has to be prepared through complicate procedures, and most of the reported fluorescent OSMs have poor water-solubility and their photostability is not ideal, which greatly limited their applications in reality [16]. In addressing these difficulties, developing a simple, rapid, low-cost analytical approach with high sensitivity and selectivity for Hg^{2+} detection in complex matrixes is quite meaningful.

Fluorescent carbon dots (CDs) have attracted much attention in the fields of either optical metrology or bioimaging owing to their unique optical properties such as excellent photostability and broadband light-absorbing abilities [17–21]. Furthermore, fluorescent CDs have been widely used to detect or image metal ions in environmental or biological samples [22–24]. However, to serve as a more promising quantification method of Hg^{2+}, there are challenges in terms of practical applications that impede their further applications. Firstly, the specificity of fluorescent CDs for recognitions of metal ions such as Hg^{2+} was not good enough due to the interference of coexisting metal irons such as Fe^{3+} and Cu^{2+} which are easy to exchange electron with CDs as well [25,26]. That is to say, the quantitation of Hg^{2+} is unsatisfactory in complex matrix. Secondly, the low content of Hg^{2+} in complex real samples makes the detection facing up difficulties. Therefore, it is meaningful to develop a special probe by designing fluorescent CDs with functional groups for selective and sensitive Hg^{2+} detection.

Herein, a new method for Hg^{2+} detection has been developed utilizing fluorescent CDs prepared by an easy hydrothermal synthetic route using spermine and citric acid (CA) as precursors. The as-prepared functional preserving CDs can specifically bind with Hg^{2+} through coordinative interaction with carboxyl functional groups facilitating electron transfer from CDs to Hg^{2+}, quenching the fluorescence of the CDs with a high efficiency. Thereby, the sensitive and selective detecting Hg^{2+} can be achieved. The principle is illustrated in Scheme 1.

2. Material and methods

2.1. Materials

The spermine is obtained from Sigma-Aldrich (Steinheim, Germany), while citric acid (CA) is commercially available from Aladdin Chemistry Co. Ltd (Shanghai, China). Mercury dichloride is obtained from Xiya Reagent Research Centre (Shandong, China). Britton-Robinson (BR) buffer is adopted to control the acidity. All solutions are prepared with deionized water from a Millipore Milli-Q Ultrapure Water System.

2.2. Apparatus

The fluorescence (FL) and UV–vis absorption spectra are recorded with an F-2500 FL spectrophotometer (Hitachi, Tokyo, Japan) and a UV-3600 spectrophotometer (Hitachi, Tokyo, Japan), respectively. Transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) are obtained from a Tecnai G2 F20 S-TWIN microscopy (FEI, USA). Atomic force microscopy (AFM) images are captured on a Dimension Icon Scan Asyst atomic force microscope (Bruker Co.). Elemental and functional groups analysis is performed on an ESCALAB 250 X-ray photoelectron spectrometer (XPS, Thermo Fisher Scientific Inc.) and FTIR-8400 S Fourier transform infrared spectrometer (Shimadzu, Kyoto, Japan), respectively. The Raman spectrum of the as-obtained sample on an Ag substrate is recorded on a LabRAM HR800 Laser confocal Raman spectrometer (Horiba Jobin Yvon Inc., France) at ambient temperature (about 25 °C). Zeta potentials are measured by dynamic laser light scattering (ZEN3600, Malvern). The fluorescence lifetime is measured with an FL-TCSPC spectrophotometer (Horiba Jobin Yvon Inc., France).

2.3. Preparation of carbon dots

0.05 g spermine and 0.10 g citric acid are dissolved into 5.0 mL water, and then the solution is transferred into a 25 mL Teflon-lined stainless-steel autoclave and heated at 160 °C for 3 h. After the reaction completed, the autoclave is naturally cooled down to room temperature. Then, the aqueous solution is subjected to dialysis (MW = 1000 Da) for 48 h to eliminate the overreacted residue and the solution of CDs is available. The CDs solution is dried by freeze-drying under vacuum (−80 °C) to obtain solid powder. 0.0134 g CDs solid powder dissolved into 10.0 mL water as stock solution and stored at 4 °C for further application.

2.4. Standard procedure for detecting Hg^{2+}

The detection of Hg^{2+} is performed at room temperature. In a typical assay, 0.10 mL BR buffer and 0.1 mL CDs (13.4 μg mL^{-1}) are added in a 2.0 mL tube, followed by the addition of different concentrations of the Hg^{2+} and then diluted to 1.00 mL with water and mixed well. Then it is transferred to scan the fluorescence spectra on an F-2500 fluorescence spectrophotometer. The selectivity for the Hg^{2+} is investigated by adding other metal ion solutions instead of Hg^{2+} ions in a similar way.

2.5. Detection Hg^{2+} in real samples

Compound herbal medicines samples including Fufang-Shuanghua pill (Sample 1) and Changyanning pill (Sample 2) are collected from local drugstore in Chongqing. Fufang-Shuanghua pill is mainly composed by four kinds of medicinal herbs, which is a prescription often used for treating patients with cold and sore throat. And Changyanning pill, which consists of five kinds of medicinal herbs, is a prescription often used for treating patients with dyspepsia and abdominal pain. The two samples are grinded fully. 0.5 g samples from grinded powder dissolved into 10 mL water, and then filtered with a 0.22 μm membrane, respectively. The compound herbal medicines samples are spiked with standard

Please cite this article in press as: J.H. He, et al., Functional preserving carbon dots-based fluorescent probe for mercury (II) ions sensing in herbal medicines via coordination and electron transfer, Analytica Chimica Acta (2018), https://doi.org/10.1016/j.aca.2018.06.053