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One-pot electrochemical synthesis of functionalized fluorescent carbon dots and their selective sensing for mercury ion

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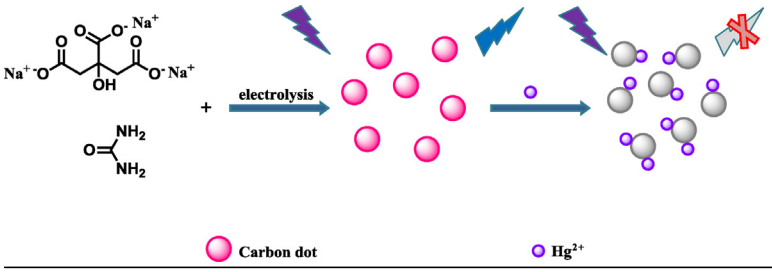
HIGHLIGHTS

- One-pot electrochemical synthesis of functionalized carbon dots (C-Dots).
- The C-Dots can serve as a fluorescent probe for sensitive detection of Hg^{2+}.
- The detection limit for Hg^{2+} is 3.3 nM.
- The sensor is successfully applied to Hg^{2+} determination in real samples.

GRAPHICAL ABSTRACT



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ABSTRACT

We propose a simple, economical, and one-pot method to synthesize water-soluble functionalized fluorescent carbon dots (C-Dots) through electrochemical carbonization of sodium citrate and urea. The as-prepared C-Dots have good photostability and exhibit a high quantum yield of 11.9%. The sizes of the C-Dots are mainly distributed in the range of 1.0–3.5 nm with an average size of 2.4 nm. It has been further used as a novel label-free sensing probe for selective detection of Hg^{2+} ions with detection limit as low as 3.3 nM. The detection linear range is 0.01–10 μM. The as-prepared C-Dots are also successfully applied for the determination of Hg^{2+} in real water samples.

1. Introduction

Fluorescent nanostructures are very attractive because of their promised applications in optoelectronic devices, biology labeling and biomedicine [1]. In the development of fluorescent nanomaterials, the discovery of semiconductor quantum dots (QDs) is considered as a major milestone. Semiconductor QDs usually have size-tunable and narrow emission spectra, high photostability, and resistance to metabolic degradation in bioapplications [2]. However, most of the high-performance QDs are composed of toxic heavy metal elements such as cadmium, which limit their use [3]. Thus, the development of non-toxic or low toxic fluorescent nanomaterials instead of semiconductor QDs is very necessary.

Carbon dots (C-Dots) have attracted tremendous attention, owing to their outstanding optical properties, low toxicity, good biocompatibility and robust chemical inertness [4]. A variety of methods have been developed to prepare fluorescent C-Dots, such as arc discharge [5], laser ablation [6], oxidative acid treatment [7], hydrothermal synthesis [8], electrochemical etching [9], pyrolysis [10], and microwave-assisted synthesis [11]. Sun et al. [6] reported a synthesis route toward fluorescent C-Dots via laser ablation of graphite powder in the presence of water vapor with argon as

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carrier gas. Liu et al. [7] reported a preparation method of C-Dots from the combustion soot of candles by treating with an oxidative acid and the subsequent purification using polyacrylamide gel electrophoresis (PAGE). Pan et al. [10] developed a one-step synthetic method for highly C-Dots by pyrolysis of ethylenediaminetetraacetic acid (EDTA) salts under a nitrogen atmosphere. Those methods mentioned above are available for the synthesis of C-Dots, however, most of prepared C-Dots have a low degree of functionality, which result in a poor interaction with analytes, consequently limit their application in the analytical chemistry. Recently, some efforts have been made on controlling the surface properties and functionalizing of C-Dots. Zhu et al. [12] integrated C-Dots coated with a specific organic molecule *N*-(2-aminoethyl)-*N*,*N*,*N*′tris(pyridin-2-ylmethyl)ethane-1,2-diamine (AE-TPEA) and CdSe/ZnS QDs to develop a ratiometric strategy for intracellular sensing of Cu^{2+} ions. Yu et al. [13] constructed a fluorescence resonance energy transfer system by integrating C-Dots with a NO recognition element phenylenediamine-containing naphthalimide for NO detection. Sun et al. [14] modified C-Dots with a cyanine dye which had a unique reactivity to bisulfite to develop a fluorescence (FL) nanoprobe for selective and quantitative detection of SO_2. These C-Dots-based materials are successful in constructing fluorescent nanosensors. However, their preparations usually require specific receptors and complicated surface modifications. Thus, developing simple and effective methods for rapid fabrication of specially functionalized C-Dots is highly desired.

Herein, we propose a simple, economical, and one-pot method to synthesize water-soluble functional fluorescent C-Dots through electrochemical carbonization of sodium citrate and urea. Compared with the previous work, the reaction time of proposed method is shorter and this method does not need expensive reagents, strong acid, high temperature, and further surface modification. Considering the mercury ion (Hg^{2+}) is a toxic heavy metal ion, and the Environmental Protection Agency (EPA) standard for the maximum allowable level of Hg^{2+} in drinking water is only 2 ppb [15]. The detection of Hg^{2+} concentration in the environmental monitoring system is important. Therefore, we design a fluorescence analysis method for high sensitive detection of Hg^{2+} based on as-prepared functionalized C-Dots. It is found that the as-prepared C-Dots can serve as a very effective fluorescent probe for label-free, sensitive, and selective detection of Hg^{2+}.

2. Experimental

2.1. Chemicals and characterization

Sodium citrate, urea, sodium dihydrogen phosphate, disodium hydrogen phosphate, were obtained from Sinopharm Chem. Reagent Co., Ltd. (Shanghai, China). All chemicals were used as received without any further purification. Ultrapure water (18.2 mΩ; Millpore Co., USA) was used throughout the experiment.

Transmission electron microscopy images of C-Dots were obtained using a JEOL-1230 transmission electron microscope (JEOL, Japan). Fourier transform infrared (FT-IR) spectrum in the 4000–400 cm^{-1} region was recorded on a Nicolet Nexus 670 FT-IR spectroscope (Nicolet Instrument Co., USA). Ultraviolet–visible (UV–vis) spectra were collected using a UV-2450 UV–vis spectrophotometer (Shimadzu Co., Japan). Fluorescence spectra were obtained using a F-4500 fluorescence spectrophotometer (Hitachi Ltd., Japan).

2.2. Synthesis of fluorescent C-Dots

C-Dots were synthesized through a simple, convenient and one-step electrochemical method. Sodium citrate and urea with appropriate proportion were added to ultrapure water (10 mL) to form a transparent solution under stirring. Two platinum sheets ($1.5 \times 2\ cm^2$) were employed as the positive and negative electrodes, respectively, and the distance between the two platinum sheets was about 1 cm. The reaction proceeded for about 1 h at 5 V potential (DC) until the transparent solution turned brown. The product solution was dialyzed against ultrapure water through a dialysis membrane (with 1000 Da MWCO) for about 6 h to obtain the fluorescent C-Dots.

2.3. Fluorescence assay of Hg^{2+}

The detection of Hg^{2+} was performed at room temperature in pH 6.0, 10 mM phosphate buffer solution (PBS). 20 μL of C-Dots solution was added into 880 μL of PBS buffer, followed by the addition of 100 μL different concentrations of Hg^{2+}. The FL emission spectra were recorded after reaction for 15 min at room temperature.

3. Results and discussion

3.1. Characterization of C-Dots

In order to obtain C-Dots with excellent fluorescence properties, we investigated the effect of the ratio of sodium citrate and urea. Different C-Dots were synthesized at the ratio of sodium citrate and urea 1:3, 3:1 and 2:2, respectively. The FL quantum yield was detected with quinine sulfate solution (quantum yield 54%) as reference. The FL quantum yield of the C-Dots synthesized by the ratio of sodium citrate and urea at 1:3, 3:1 and 2:2 are 11.9%, 2.6% and 3.0%, respectively. The maximum excitation wavelength and emission wavelength of these C-Dots are nearly unchanged, and they both have the excitation-wavelength-dependent FL properties (Figs. S1 and S2). Among these different C-Dots, we had chosen the optimum C-Dots with a high quantum yield of 11.9% which were synthesized at the ratio of sodium citrate and urea 1:3 as fluorescent probe for further application.

The morphology of the as-prepared C-Dots was characterized using transmission electron microscopy (TEM). As shown in Fig. 1A, the TEM image of the C-Dots reveals that the as-prepared C-Dots are well-dispersed. The sizes of C-Dots are mainly distributed in the range of 1.0–3.5 nm with an average size of 2.4 nm (inset in Fig. 1A). The functional groups on surface of C-Dots were then investigated using FT-IR spectroscopy. As shown in Fig. 1B, the FT-IR spectrum of C-Dots exhibits distinct absorption bands at 3261, 3336, 3425 cm^{-1}, which can be attributed to stretching vibrations of O—H and N—H. The absorption band at 1668 cm^{-1} is assigned to the vibration of C=O. The high-intensity peaks at 1596 and 1398 cm^{-1} correspond to the asymmetric and symmetric stretching vibrations of COO^-, respectively [16]. The above observations confirm that the as-synthesized nanoparticles functionalized by hydroxyl, carboxyl and amino groups can improve the stability and hydrophilicity of the C-Dots in an aqueous system.

The optical properties of the as-prepared C-Dots were investigated by the UV–vis absorption and the FL spectroscopy. As shown in Fig. 2A, C-Dots aqueous solution has a broad absorption spectrum (dotted line). The maximum excitation wavelength and emission wavelength of the C-Dots aqueous solution are 351 and 433 nm, respectively (solid lines). Very bright blue luminescence under the illumination of UV (365 nm) light of the C-Dots solution can be clearly seen in the inset of Fig. 2A. The C-Dots solution exhibits excitation-wavelength-dependent FL properties with emission peaks ranging from 410 nm to 517 nm at excitation from 300 nm to 460 nm (Fig. 2B). The behavior is considered to be related to different sizes and a distribution of