NUCL SCI TECH (2016) 27:35
DOI 10.1007/s41365-016-0038-1

Mercury (II) detection by water-soluble photoluminescent ultra-small carbon dots synthesized from cherry tomatoes

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Received: 22 July 2015 / Revised: 21 October 2015 / Accepted: 3 November 2015 / Published online: 7 April 2016

Abstract Mercury ions have been considered highly toxic to human health. What would be great is to develop the ionic probes without any toxicities themselves. Here, we report a friendly, highly sensitive mercury (II) ionic probe, water-soluble photoluminescence carbon dots which were synthesized by simply hydrothermal treatment of fresh cherry tomatoes without adding any other reagents. The ultra-small (<1 nm) carbon dots show robust excitation-depended photoluminescence under a wide pH range (4–10) or a strong ionic strength of up to 1 M, and the detection limit of mercury (II) has been determined as low as 18 nM. We envision such water-soluble, biocompatible carbon dots that could be applied to biolabeling, bio-imaging, and biosensing fields.

Keywords Carbon dots · Photoluminescence · Cherry tomato · Mercury · Detection

1 Introduction

Mercury is a neurotoxic and physiological toxic heavy metal, which severely affects human health. It mainly causes harm to the central nervous system, digestive system, and internal organs. More specifically, mercury vapors and organic mercury derivatives (e.g., methylmercury) can affect brain and its functions that result in personality changes, tremors, vision problems, deafness, and losses of muscle coordination, sensation, and memory [1]. Because mercury is non-biodegradable, it is a threat to human even at a very low concentration. The global mercury emission is about 7500 tons every year [2]. A number of fluorescent probes including organic dyes, nanoclusters, and quantum dots (QDs) have been developed for fluorescent detection of Hg^{2+} [3–6]. But these materials all suffer from the disadvantages such as complexed synthesis methods or significant toxicity even at relatively low concentrations. Therefore, simple, economical, green protocols are urgently needed.

Compared to QDs or organic dyes, carbon dots (C-dots) have attracted many attentions due to their extraordinary properties such as lower cost, bright photoluminescence (PL), biocompatibility, easy functionalization, low toxicity, and high photostability [7–9]. Almost all the carbon-containing materials, in particular many fruits and vegetables, also can be used as raw materials for C-dots synthesis [10–14]. C-dots are widely used in a plenty of applications such as imaging [15], sensing [16], labeling [17], fluorescent ink [18], lasers [19], and so on. C-dots represent that the researches on luminescent nanoparticles have reached a new stage. Cherry tomatoes are rounded, small-fruited tomatoes, which have been considered as an intermediate genetic admixture between wild currant-type tomatoes and domesticated garden tomatoes. Regarding to the chemistry components, cherry tomatoes rich in vitamin (about 1.7 times of common tomatoes), glutathione, and lycopene. In this paper, we synthesized C-dots through hydrothermal synthesis method [20–22] via cherry tomatoes. The as-

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Electronic supplementary material The online version of this article (doi:10.1007/s41365-016-0038-1) contains supplementary material, which is available to authorized users.

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prepared C-dots can be directly used as a probe for Hg^{2+} detection without any further modification, and the detection limit of Hg^{2+} is 18 nM.

2 Materials and methods

2.1 Materials and reagents

Cherry tomatoes was purchased from the localized (Hohhot, Inner Mongolia Autonomous Region, China) vegetable market. All other reagents such as H_2SO_4, $HgSO_4$, NaCl, NaH_2PO_4, and Na_2HPO_4 were of analytical reagent grade supplied by Sinopharm Reagent Co. Ltd (Shanghai, China) and used without further purification.

2.2 Preparation of CDs

C-dots were prepared by hydrothermal treatment of cherry tomatoes. The cherry tomatoes were smashed with a pestle and mortar. In a typical synthesis, 5 mL of the prepared cherry tomatoes liquid was transferred into a 50 mL steel-lined autoclave and heated at 200 °C for 5 h. The precipitate was discarded, and the supernatant was subjected to dialysis against Milli-Q water with a cellulose ester membrane bag (molecular-weight cutoff: 1 kDa) to remove small molecules and then to centrifugation at 10,000 rpm for 10 min. The pellet was dried under vacuum for 48 h and re-dispersed in Milli-Q water to reach a concentration of 0.4 mg/mL.

2.3 Hydrodynamic diameter and zeta potential measurements

Both the hydrodynamic diameter (D_h) and the zeta potential measurements were conducted on a dynamic light scattering (DLS) instrument (Malvern Zetasizer Nano ZS90, Malvern Instruments Ltd, Worcestershire, UK) equipped with quartz or disposable cuvette (DTS0012, minimum sample volume is 1 mL) fitted with a 633 nm He–Ne laser beam. Measurements were taken at 25 °C and 90° scattering angle. D_h and PDI were obtained by cumulant analysis (software of Zetasizer Nano-ZS90, Malvern Instruments Ltd).

2.4 Spectroscopy measurement

The absorbance and the photoluminescence (PL) spectra were recorded on a UV–Vis spectrometer (U-2900, Hitachi) and a fluorescence spectrometer (Fluorolog®-MAX 4, Horiba), respectively. Both equipped with a 1.0 cm quartz cell. For PL measurement, both excitation and emission slits were set up to 5 nm.

2.5 Hg^{2+} sensing

The Hg^{2+} solution with different concentration was prepared by dissolving $HgSO_4$ in phosphate-buffered saline (PBS). 1 mL C-dots (0.4 mg/mL) was dissolved in 39 mL PBS (pH 6.0) to detect Hg^{2+}. For the sensing assay, 10 μg/mL C-dots mixed with Hg^{2+} solution of varied concentrations of 0.018, 0.039, 0.0781, 0.1562, 0.3125, 0.625, and 1.25 μM to a final volume of 2 mL was used for recording the PL spectra by a fluorescence spectroscopy, respectively.

3 Results and discussion

The C-dots dissolved in pure water showed a characteristic absorption spectrum with a peak at 281 nm and a relatively narrow and symmetric emission spectrum with a peak at 439 nm upon the excitation at 360 nm (Fig. 1a). The insert picture of Fig. 1a shows the symbolic blue photoluminescent property of C-dots under illumination of UV light (right). It is similar to most of the reported photoluminescent C-dots [23] and G-dots [24], and the PL of our C-dots is also excitation dependent (Fig. 1b), which is generally attributed to the optical selection of size-depended quantum effect and emissive traps on the C-dots surface [25, 26]. The water-soluble C-dots were firstly evaluated by DLS. The average hydrodynamic size of C-dots evaluated by DLS is 0.64 ± 0.2 nm with a polydispersity index (PDI) of 0.622 (Fig. 1c), which is consistent with the size analysis results by AFM (Fig. S1). The zeta potential measurement proved that the surface of the as-prepared C-dots is positively charged (Fig. 1d).

The photostability of fluorophores is a very important property which determines the feasibility toward successful bio-applications. From Fig. 2, it is clear that the PL intensity of C-dots remains relatively constant with varying ionic strengths up to 1.0 M (Fig. 2a) and under long time up to 12 h illumination of white light (Fig. 2c), which indicates the robust photostability of the as-prepared C-dots in aqueous solution. However, the pH tests show that the PL intensities of C-dots decrease in the solutions of high or low pH, but remain relatively constant in the pH range of 5–8 (Fig. 2b). Moreover, obvious photobleaching can be also found after 5 h of continuous UV excitation (Fig. 2d). Because the emission control of the surface state/molecule state can be strongly affected by surrounding factors, such as solvent pH [27], which could account for the decrease of our C-dots' PL intensity at a pH that was too low/high or under exposure to high-power UV radiation.

From the previous publications [10, 22, 28], we know that Hg^{2+} can efficiently quench the fluorescence of C-dots

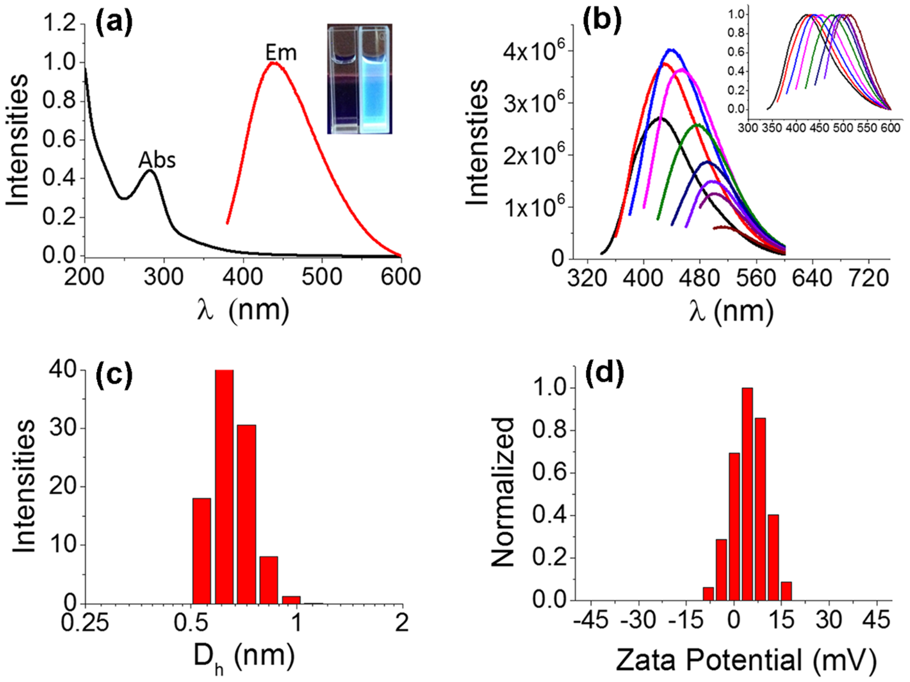

Fig. 1 **a** UV–Vis absorption (*black line*) peaks at 281 nm and PL (*red line*) peaks at 439 nm of the C-dots upon the excitation with a wavelength of 360 nm. The *inset* is a digital photograph of C-dots dispersed in pure water under illumination of daylight (*left*) and 365 nm UV light (*right*), respectively. **b** PL spectra of the C-dots with various excitation wavelengths from 320 to 500 nm (slit = 5 nm). The *inset* is the normalized PL spectra. **c** Hydrodynamic diameter (D_h) distribution histogram of C-dots by DLS, the histogram statistics shows the average D_h is 0.64 ± 0.2 nm with a PDI of 0.622. **d** The zeta potential result of C-dots is 5.2 mV

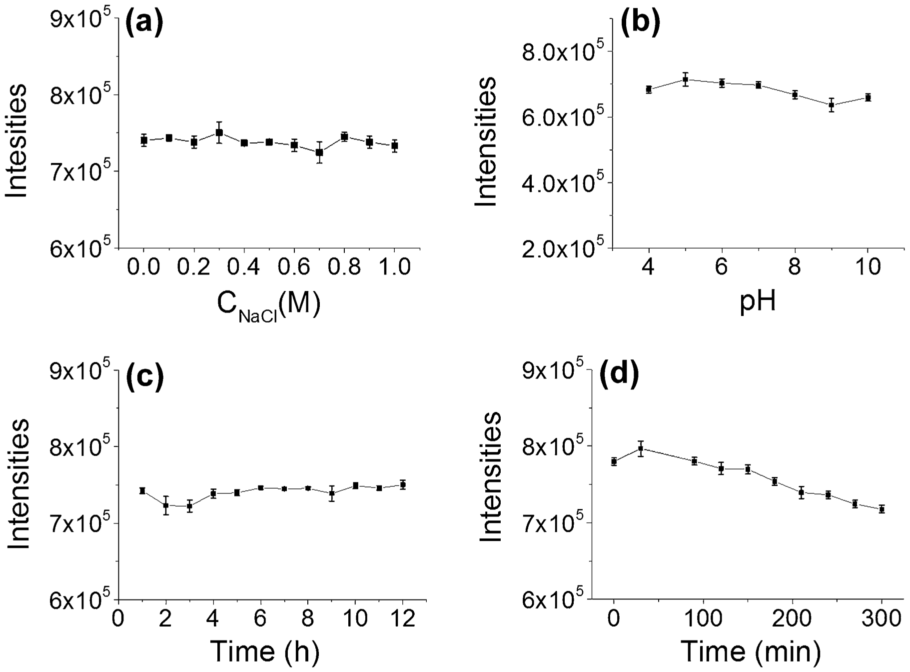

Fig. 2 Effect of **a** ionic strength and **b** pH on the PL intensity of C-dots (10 µg/mL) at 439 nm when excited at 360 nm. The 10 mM phosphate buffer was used for pH 4–10 solutions. All the values are the average of triplicate measurements. The stability of the fluorescence intensity of C-dots for different time under **c** white light and **d** UV

presumably via electron or energy transfer. Therefore, C-dots can be used as a very good tool for the Hg^{2+} sensing. Since the as-prepared C-dots are stable at a pH range from 5 to 9 and resistant to a higher ionic strength, both of which are suitable for a biosensor, so we chose PBS buffer for the Hg^{2+} detection experiments. As shown in Fig. 3a, when different concentrated Hg^{2+} was added into the 10 µg/mL C-dots solution, respectively, the PL intensity of C-dots was gradually quenched. This may be attributed to the fact that the interaction between Hg^{2+} and the carboxylate and thiol groups makes C-dots close to each other, which accelerates the non-radiative recombination of the excitons through an effective electron transfer process, leading to a substantial decrease of the PL of C-dots. The sensing assay of different metal ions by the as-prepared C-dots showed a high selectivity for Hg^{2+}

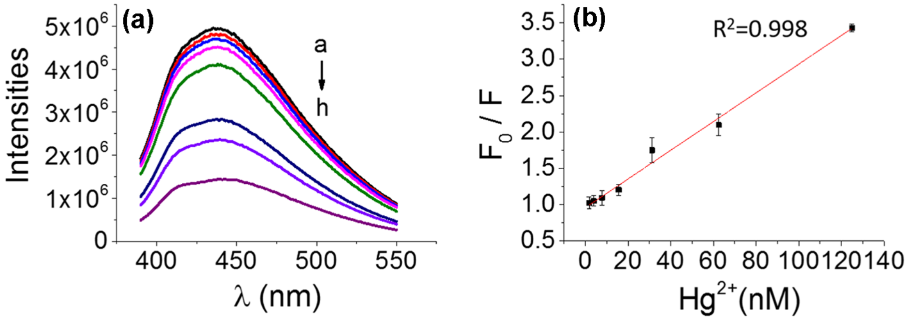

Fig. 3 **a** PL spectra of C-dots in the presence of various concentrations of Hg^{2+}. The final concentrations of Hg^{2+} as indicated from a to h as are 1.25 µM, 0.625 µM, 312.5 nM, 156.2 nM, 78.1 nM, 39 nM, and 18 nM, respectively. **b** The Stern–Volmer plot of C-dots PL intensity against the concentration of the quencher Hg^{2+}. The correlation coefficient (R^2) of the fitting line is 0.998

(Fig. S2). This interaction would undermine the stability of the C-dot's PL properties and cause the quenching of PL, which can be described using the Stern–Volmer equation [29–31].

$$\frac{F_0}{F} = 1 + K_{SV}\left[Hg^{2+}\right] \quad (1)$$

where F_0, F are the PL intensity in the absence and presence of Hg^{2+}, and K_{SV} is the Stern–Volmer quenching constant. A typical Stern–Volmer plot is shown in Fig. 3b, and a good linear fitting function of $F_0/F = 0.96 + 0.0197 \times [Hg^{2+}]$ can be obtained over the concentration ranging from 1.8×10^{-8} to 1.25×10^{-6} M. The binding constant of Hg^{2+} with C-dots is determined to be 1.97 μM^{-1}, with a detection limit of 18 nM. With this calibration equation, we also detected the real water samples from city tap water and two lakes' water; however, compared with the manually prepared mercury ions-containing solutions, these water samples showed very low PL signals (Fig. S3), which did not only indicate the good quality of our drink water and the lakes' water, but also proved our as-prepared C-dots can be really applied to the mercury ions detection.

4 Conclusion

In this article, we have successfully synthesized C-dots with cherry tomatoes through a facile hydrothermal synthesis method. The resulting C-dots have been thoroughly characterized from hydrodynamic diameter to optical properties under different solution gradients and have been further applied to detect mercury ions with a detection limit up to 18 nM, which could be attributed to the glutathione abundant in cherry tomatoes, in that both carboxyl and thiol groups of glutathione can form a strong bond with Hg^{2+}, which might be critical for selective detection of mercury ions. Due to the resources derived from, the C-dots can be more biocompatible in principle than others derived from chemicals, and their ultra-small diameter combined with the robust photoluminescent properties could make them find more applications in biolabeling, bio-imaging, and biosensing fields beyond the industrial field.

Acknowledgments This work was supported by Grants from the National Natural Science Foundation of China (Nos. 21171086 and 81160213), and Inner Mongolia Grassland Talent (No. 108-108038), Natural Science Foundation of Inner Mongolia Autonomous Region of China (Nos. 2013MS1121 and 2015MS0806), Inner Mongolia Department of Science and Technology (No. 211-202077), and the Inner Mongolia Agricultural University (Nos. 109-108040, 211-109003, and 211-206038).

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