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Multifunctional water-soluble luminescent carbon dots for imaging and Hg^{2+} sensing†

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We propose an ingenious method for large-scale fabrication of water-soluble photoluminescent carbon dots (CDs) by a one-step microwave route in the presence of citric acid and ethylenediamine. In contrast to other CDs-based nanomaterials, the CDs prepared exhibit a highly fluorescent quantum yield (QY) and excellent stability in both organic and inorganic phases. After simple post-treatment, the CDs can be used as a new type of fluorescent ink for information storage and nanofiber electrospinning. It should be noted that the CDs are a superior fluorescent bioimaging agent in cells, plants and animals according to their excellent solubility and ultra-low toxicity. In addition, the CDs could be utilized as a modification-free biosensor reagent capable of detecting Hg^{2+} in complex environments. More significantly, environmental friendly "skillful pens" were fabricated that provided an effective platform for portable qualitative-detection of Hg^{2+}.

1. Introduction

Photoluminescent carbon dots (CDs), one of the new members of the carbon nanomaterial family, have drawn considerable attention owing to their promising advantages.[1–6] In comparison to conventional organic dyes and semiconductor quantum dots (QDs), which have raised significant health and environmental concerns, the CDs are remarkably advantageous in their green synthesis, high aqueous solubility, robust chemical inertness, easy functionalization, high resistance to photobleaching and low cytotoxicity.[3,7] CDs hold great promise in a wide range of technologies, such as bioimaging,[8–10] catalysis,[11,12] sensing,[13,14] and other different optoelectronic device applications.[15,16] However, with the exception of promising commercial applications, photoluminescence (PL) properties of CDs from solid states are still not satisfactory because of their low quantum yield (QY) or strong fluorescence quenching in their dry and aggregated states. Routes to synthesize CDs can be classified into two main categories: top-down and bottom-up methods. The former are based on post-treating nanocarbon broken from various larger carbon structures, while bottom-up methods include thermal decomposition, combustion and dehydration of suitable molecular precursors.[17] Generally, these methods involve intricate processes and severe reaction conditions, and the QY of the CDs obtained is very low with only a few exceptions. More recently, microwave pyrolysis of a solution of carbohydrates has become more and more popular because of its low cost and simple synthetic approach.[18–20] However, to achieve highly luminescent CDs, surface-passivation reagents are usually required.[15,21,22] Microwave pyrolysis of different carbohydrates either in the presence or absence of any surface passivating agent and the dehydration of carbohydrates with subsequent surface passivation have been reported to produce C-dots with sufficient QY. May be because of the high reaction temperature, and not increasing from low temperature to high temperature slowly, the polymer-like CDs could change to carbogenic CDs rapidly, which produce satisfactory CDs. Moreover, too much attention has been paid to their applications in biological labelling, bioimaging or drug delivery. In principle, of particular interest and significance are the findings that CDs in the solid state can exhibit strong PL emission and the PL from CDs can be quenched efficiently by either electron acceptor or electron donor molecules in solution. Therefore, exploring efficient strategies for the large-scale fabrication of CDs with high QY and further expanding their novel applications are still a challenge.

Herein, using citric acid and ethylenediamine as precursors, a one-step microwave synthesis of CDs with high QY on a large scale is reported. The morphology and chemical structures were investigated extensively. Compared to the currently available CDs-based nanomaterials, our strategies for the fabricating CDs holds great promise in their synthesis and applications. The benefits are as follows: (1) simple synthesis, only requiring

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microwave irradiation for 5 min; (2) low-cost and large-scale fabrication, thus the potential for industrial production; (3) strong fluorescence in dry and aggregated states, hence ensuring its innovative applications in patterning and information storage; (4) high QY (41.39%) without any modifier/surface passivated agent, excellent water-solubility and stability and good biocompatibility, and therefore they are utilized as fluorescent bioimaging agents in cells, plants and animals; (5) efficient PL quenching by Hg^{2+} ions, providing a particularly useful platform for portable detection of Hg^{2+} in complex environments.

2. Results and discussion

Our strategy for the fabrication of CDs is described in the ESI† in detail. The transmission electron microscopy (TEM) images show that the CDs synthesized were highly monodisperse (Fig. S1†) and narrowly distributed with diameters in the range of 2.5 ± 0.5 nm (Fig. 1A and inset). A typical X-ray diffraction (XRD) pattern of the CDs displays a broad diffraction peak located around 18.5° (Fig. S2†), suggesting their amorphous nature, which is consistent with the discernible lattice structures from the HRTEM image (data not shown). To probe the chemical composition and content of the as-produced CDs, X-ray photoelectron spectroscopic (XPS) measurements were implemented. As shown in Fig. 1B, the survey spectra of the samples of CDs revealed the presence of C, N and O, as well as limited H (4%, calculated) without any other impurities. In detail, the C1s spectrum (inset) were deconvoluted into three peaks at 284.75, 286.15, and 287.7 eV, which are attributed to C–C/C=C, C–O, and C–N, respectively.[23] Moreover, sp^2-and sp^3-hybridized carbon atoms were distinguished using ^{13}C NMR spectroscopy (Fig. 1C) and ^1H NMR spectroscopy (Fig. S3†).[24] In addition, Fourier transform infrared spectroscopy (FT-IR) spectra were recorded to identify the functional groups on the CDs. As shown in Fig. 1D, the strong peaks at 1650 cm^{-1}, 1570 cm^{-1}, 1435 cm^{-1} and 1291 cm^{-1} are attributed to C=O, N–H, CH_2 and C–N, respectively. The broad band centered at 3276 cm^{-1} suggested the existence of –OH and N–H, which improve the hydrophilicity and stability of the CDs in an aqueous system.[23] The UV-Vis absorption and PL emission spectra of the as-prepared CDs were also investigated as shown in Fig. 1E. The absorption spectrum showed a narrow peak at 349 nm and the optimal excitation and emission wavelengths were located at 360 nm and 455 nm, indicating the narrow size distribution of CDs as well. The image of the CDs dispersion under UV light (365 nm) exhibited a blue color (inset), further revealing that the resultant CDs exhibit blue fluorescence.

To further explore the optical properties of the as-prepared CDs, the excitation-dependent PL behavior was investigated. Unlike most other luminescent CDs,[25,26] as shown in Fig. 1F, the PL peak of the resultant CDs remained unchanged while exhibiting an excitation-dependent PL behavior for the excitation wavelength exceeding 400 nm. Furthermore, the effects of reaction conditions on the QY of CDs were investigated. The microwave irradiation time was critical to PL of the synthesized CDs. In fact, as the reaction time progressed from 4 min to 15 min (Table S1†), the PL QYs could reach up to 41.39% under the optimized reaction conditions (5 min), which is much higher than those of most recorded fluorescent carbon-based materials.[19] In addition to high QY, the CDs prepared exhibited excellent stability, which is essential for their practical applications. The PL intensity of the CDs remained constant over a wide pH (3–11) aqueous solution (Fig. S4†) and also in DMF. In addition, these nanoparticles could be well-dispersed in many kinds of solvents without any detectable agglomeration, and there were no changes in color and PL intensities after exposure to room light for more than one month (Fig. S5†). The preeminent PL of CDs is a feature of their potential applications, which will be discussed in the next section.

To make full use of the high QY, the CDs were utilized to prepare carbon nanofibers (CNFs) by electrospinning a solution of CDs with the aid of polymers. As observed from the SEM images (Fig. 2A and B), the CNFs prepared lengthed up to tens of micrometers, showing high aspect ratios and an average diameter of 300 nm (Fig. S6†). Under ultraviolet (365 nm) and blue (488 nm) light excitation, the CNFs exhibited blue (Fig. 2C) and green (Fig. 2D) luminescence, respectively, and they overlapped very well (Fig. 2E). In addition, the water-soluble CDs were also available as a fluorescent agent for daily work. After simple post-treatment, the CDs have been employed as a new type of biocompatible fluorescent ink. Multiple words and images were printed on a filter paper marked with "CDs" letters

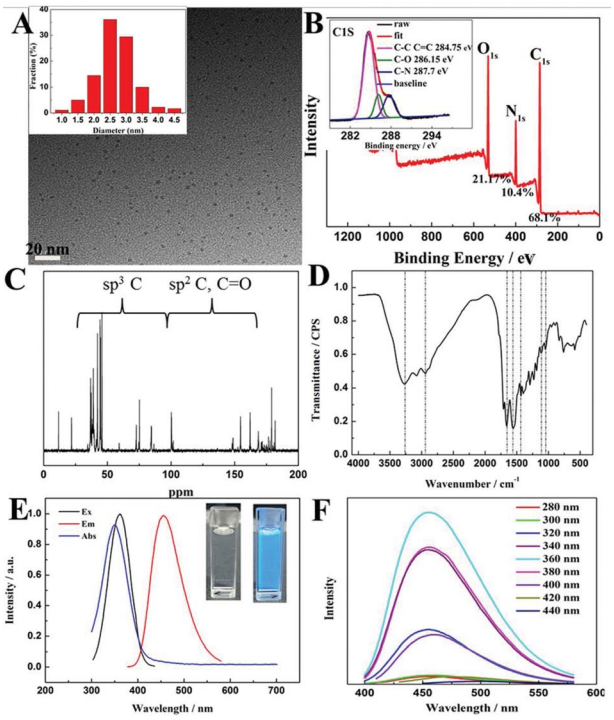

Fig. 1 (A) HRTEM image and size distribution (inset) of the CDs synthesized; scale bar: 20 nm. (B) XPS of the CDs (inset: C1s spectra). (C) ^{13}C-NMR and (D) FTIR spectra of the CDs. (E) UV-Vis absorption, PL excitation and emission spectra, and (inset) images of the CDs under room light (left) and UV light (right) in an aqueous solution. (F) Excitation-dependent PL spectra of the CDs in an aqueous solution.

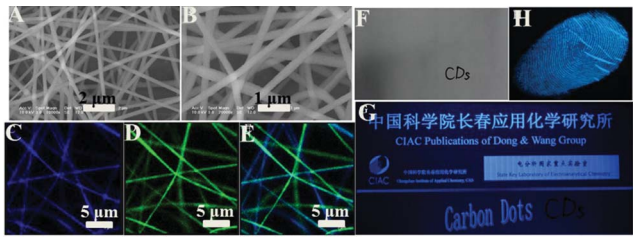

Fig. 2 SEM (A and B) and fluorescent images (C–E) of the CNFs captured in exciter filter wavelengths of (C) 365 nm, (D) 488 nm and (E) an overlay of C and D. Digital images of the filter paper printed with CDs ink under (F) room light and (G) a UV hand lamp (365 nm). The marked letters "CDs" were written with an ordinary pen. (H) A CDs-formed fluorescent fingerprint on filter paper captured under a UV hand lamp.

written with an ordinary pen, which were invisible under ambient light (Fig. 2F). However, these patterns could be clearly revealed under UV light (Fig. 2G). Notably, being exposed under ambient light for two months, the fluorescent properties of the products exhibited no significant changes (Fig. S7†). Furthermore, the CDs could be used as inkpad. As shown in Fig. 2H, a fluorescent CDs fingerprint was printed on filter paper, which could reflect human's fingerprint discriminately and clearly. Compared with traditional inks, the water-soluble CDs inks are clear, permanent, allelomorphic, pollution-free, and easy to clean with water, which provides a new way to feed their potential requirement on a commercial scale.

These encouraging results prompted us to evaluate the feasibility of CDs as a new fluorescent marker for living cell imaging.[27] For effective bioimaging, it is required that the selected fluorescent marker has not only optical merits but also low cytotoxicity.[28] To evaluate the cytotoxicity of CDs, the viability of HeLa cells treated with CDs was measured by the methyl thiazolyl tetrazolium (MTT) method. As shown in Fig. 3A, HeLa cells were incubated with different doses of CDs for 24 and 48 h, respectively. Subsequently, the viability remained greater than 90% even when incubated with an ultrahigh concentration (800 μg mL^{-1}) of CDs for 48 h, demonstrating the intrinsically low toxicity of the CDs (without any further functionalization).[29] Fig. 3B shows photographs of the HeLa cells captured by a laser scanning confocal microscope. It is obvious that the transfected HeLa cells became quite bright owing to the strong fluorescence from the CDs, indicating a large amount of CDs have been internalized into the cells (Fig. S8†). Consistent with fluorescence microscopy assay results, bright blue (Fig. 3C) and green (Fig. 3D) fluorescence could be observed under ultraviolet and blue light excitation, respectively and the two-channel luminescence images for the same scanning area overlapped well (Fig. 3E). This multicolor emission shows a great advantage of the CDs over other labelling agents, because it gives us much space to choose the wavelength for observation *in vitro*.

Given their low cytotoxicity, we further tested the toxicity and feasibility of the CDs as bioimaging agents in both plants and animals. Firstly, some selected mung beans were raised in an aqueous solution of CDs (4 mg mL^{-1}) using a constant-temperature bath (23 °C). Similar to bean sprouts grown in water (Fig. S9†), no abnormal sprouts were found after three days grown in an aqueous solution of CDs (Fig. 4A). Under a UV hand lamp, the sprouts exhibited a strong characteristic blue luminescence from CDs, which illustrated that the CDs could permeate throughout the plant cells, and had no perceptible effect on plant growth (Fig. 4B). The potential value of CDs as luminescent probes for *in vivo* imaging was then carried out in mice. The dorsum was shaved for fluorescence detection of the CDs trapped in organs. An aliquot (100 μL) of CDs dispersed in water was subcutaneously injected into a mouse (Fig. 4C). From Fig. 4D, a bright emission was clearly visible at the injection site, which has also been detected from HeLa cells and sprouts treated with CDs, thereby revealing that the application of CDs could be extended to *in vitro* fluorescence imaging. For intravenous injection, 100 μL of the CDs solution was injected into mice. During whole-body circulation, no obvious emission was

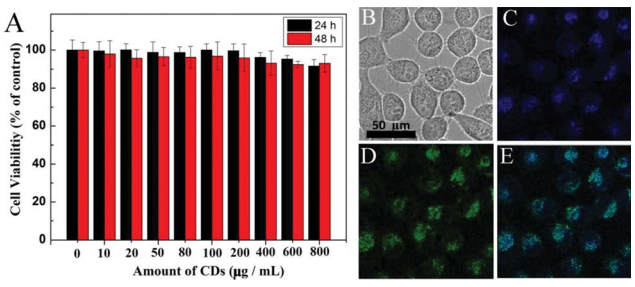

Fig. 3 (A) Cytotoxicity testing results of CDs on HeLa cells viability. The values represent percentage cell viability (means% ± SD, n = 6). (B–E) Laser scanning confocal microscopy images of CDs to HeLa cells. The samples were observed under (B) bright field and excited at (C) 405 nm, (D) 488 nm and (E) overlay of C and D.

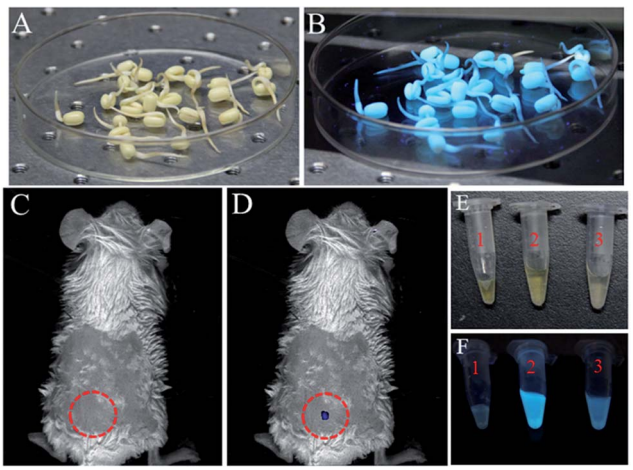

Fig. 4 Optical and fluorescent images of bean sprouts grown in an aqueous solution of CDs (4 mg mL^{-1}) under (A) daylight and (B) 365 nm excitation. (C) Bright field and (D) as-detected fluorescence of mice through subcutaneous injection of the CDs. PL spectra of the urine of mice under (E) daylight and (F) 365 nm excitation: (1) without injection of an aqueous solution of CDs; (2, 3) after injection of an aqueous solution of CDs for (2) 2 h and (3) 4 h.

observed in the dorsum. As shown in Fig. 4E, after 2 h post-injection, a bright fluorescence in the urine was visible, while the observed fluorescence got generally weaker at 4 h post-intravenous injection, suggesting a low accumulation level of the CDs (Fig. 4F, corresponding spectrum given in Fig. S10†). These results suggest that the injected CDs without a modifier/surface passivated agent can be easily excreted *via* urine and have no obvious toxicity as bioimaging materials *in vivo*. The mechanism for rapid and efficient urinary excretion and elimination of QDs (hydrodynamic diameter <5.5 nm) from the body have been investigated in detail by Frangioni's group.[30]

Heavy-metal ions, such as mercury and lead, can cause serious and permanent damage to human organs due to their accumulative characters in the environment and biota.[31,32] Therefore, detection of these heavy-metal ions is central to environmental monitoring of water or soil.[33]

Of particular interest and significance is the finding that the CDs prepared can be utilized as a highly efficient nanoprobe for Hg^{2+} detection. Fig. 5A shows the fluorescent quenching value of CDs with increased Hg^{2+} concentration, and the inset shows the linear relationship between PL intensity and Hg^{2+} concentration. The detection limit was calculated to be 20 nmol L^{-1}, which is lower than the acceptable Hg^{2+} concentration in drinking water (0.006 mg mL^{-1}) according to the World Health Organization (WHO).[34] Besides sensitivity, selectivity is another important parameter to evaluate the performance of the sensing system. We then investigated the effect of representative metal ions (Cd^{2+}, Fe^{2+}, Ag^{+}, Pb^{2+}, Fe^{3+}, Cr^{2+}, Mg^{2+}, Ca^{2+}, Na^{+}, K^{+}, Co^{2+}, Zn^{2+}, Mn^{2+}, Cu^{2+} and Hg^{2+}) on the CDs fluorescence quenching under the same conditions. As shown in Fig. 5B, most of those metal ions at ultrahigh concentrations (0.2 mmol L^{-1}), can not induce obvious fluorescence decreases of the CDs except for Fe^{3+} ions. Fortunately, in the valid range for Hg^{2+} detection from 0 to 3 μM (Fig. S12 A†), no obvious fluorescence quenching took place in the present of Fe^{3+} ions (Fig. S11†). These results validate the high efficiency of our nanoprobe to detect Hg^{2+} in water. However, a much more challenging goal is to detect Hg^{2+} in real samples, since many of the current nanoprobes are not stable enough when used in a complicated environment.

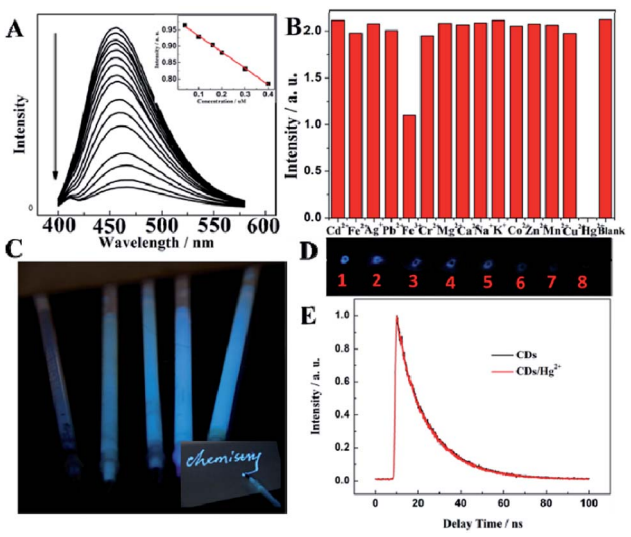

Fig. 5 (A) Fluorescence quenching of the CDs in the presence of Hg^{2+} ions (0–60 μM). (B) Comparison of the fluorescence intensities of the CDs after the addition of Hg^{2+} ions (20 μM) and other metal ions (200 μM), respectively. (C) Optical images of colorful rollerball pens loaded with different concentrations of the CDs inks. (Inset: the fluorescent text written on a filter paper under a UV hand lamp). (D) The photograph of a ring on filter paper written with different amounts of Hg^{2+} (from 1 to 8 : 0, 30 nM, 100 nM, 300 nM, 500 nM, 1 μM, 30 μM, and 50 μM, respectively) under a UV hand lamp. (E) Fluorescence decay of the CDs without and with Hg^{2+} (0.02 mM) as a function of time (375 nm excitation, delay time at 455 nm emission).

To evaluate the practicality of this sensor, we applied a standard addition method to detect Hg^{2+} in lake water obtained from the South Lake of Changchun. On the basis of ICP-OES, after addition of 40, 60, 100, 160 nM Hg^{2+} to the lake water, the recoveries were 102.5%, 98.2%, 96.1% and 99.2%, respectively (Table S2†), which indicated the accuracy and reliability of our nanoprobe for Hg^{2+} determination in environmental samples. To realize a facile use of this nanoprobe, portable Hg^{2+}-responsive rollerball pens were developed. It was noteworthy that the rollerball pens loaded with different concentrations of CDs inks prepared exhibited multicolor luminescence (Fig. 5C) and could readily flow during writing without leakage or coagulation within the pen (inset), therefore these might replace commercial colored pens, which possess high toxicity. As observed in Fig. 5D, eight homology rings were written on a common filter paper (or any other substrates without autofluorescence) with one of the pens, and the color of the rings changed to light blue gradually, and then to colorless upon the addition of Hg^{2+}. Compared with other test papers reported, our fabricated "skillful pen" had great superiority in Hg^{2+} determination—they are environmental friendly, affordable, portable and easy-to-operate for real-time monitoring. Finally, the decay dynamics was measured to investigate the PL quenching mechanism of this system. As shown in Fig. 5E, the lifetime contains two lifetime components, 3.4 ns and 15.5 ns for CDs, and 3.6 ns and 15.4 ns for CDs/Hg^{2+}, meaning the same average lifetime for the CDs before and after coordination with Hg^{2+} ions, which demonstrated no non-radiative electron-transfer happening during the PL quenching progress.[35] The energy state of the Hg^{2+} complex in the coordinated ions may be influenced by the nature of the CDs, and the fluorescent quenching of the CDs would be due to the selective absorption of light by the Hg^{2+} atom. At the same time, we found that the maximum emission peaks of the CDs located at 455 nm gradually red-shifted to 466 nm with varying concentrations of Hg^{2+} (Fig. S11B†). These results indicate the special coordination interaction between Hg^{2+} ions and the phenolic hydroxyl groups of the CDs contribute to the quenching progress, which has been used for the detection of metal ions or colored reactions in traditional organic chemistry.[36]

3. Conclusions

In summary, we developed a one-step microwave route for large-scale fabrication of water-soluble CDs. The morphology and

chemical structures have been investigated extensively. In comparison with reported CDs-based nanomaterials, the CDs prepared exhibit highly fluorescent QY and excellent stability in both organic and inorganic phases, and therefore can be used as a new type of fluorescent ink for information storage and nanofiber electrospinning. A particularly attractive feature of the CDs prepared is their excellent solubility and ultra-low toxicity, empowering the CDs promising use *in vitro*, plants and *in vivo* imaging. It should be noted that the CDs could be utilized as a modification-free biosensor reagent capable of detecting Hg^{2+} in complex environments, and has a remarkable selectivity over other representative metal ions. More significantly, environmental friendly "skillful pens" were fabricated, and provided an effective platform for the portable qualitative-detection of Hg^{2+}. Investigations on the distinct PL properties and luminescent quenching mechanisms of the CDs in the presence of Hg^{2+} ions are still underway.

Acknowledgements

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