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Facile synthesis of carbon dots with superior sensing ability

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Abstract: Carbon dots (CDs) have various applications in biomedical and environmental field, such as bio-imaging, bio-sensing and heavy metal detection. In this study, a novel class of CDs were synthesized using a one-step hydrothermal method. The fabricated CDs displayed stable photoluminescence, good water-solubility, and photo-stability. Moreover, the functional groups (carboxylic acid moieties and hydroxyls) on the surface of the obtained CDs enable it with superior sensing ability (e.g. very low detectable concentration for Pb^{2+} : 5nmol/L). With superior detection sensitivity, excellent fluorescent properties and facile fabrication method, the as-obtained CDs can find practical applications as cost-effective and sensitive chemo-sensors in water and food safety field.

Keywords: carbon dots, hydrothermal method, photoluminescence, detection, Pb

1. Introduction

Photoluminescent (PL) carbon-based materials with special nanoscale structures are attracting tremendous attention due to their excellent properties.¹⁻⁸ The strong tunable luminescence has tunability further to improve these carbon nanomaterials versatile properties, thus, make them display great potential application in various filed, such as biological labeling,⁹⁻¹⁰ drug delivery,¹¹ biological detection and imaging,¹²⁻¹⁶ optoelectronic devices,¹⁷⁻¹⁸ energy conversion.¹⁹⁻²⁰ Recent years, various methods have been used to synthesize novel carbon-based nanomaterials.²¹⁻²⁵ For example, CDs as one typical of the photoluminescent carbon-based nanomaterials have been developed due to its excellent optical absorptivity, chemical stability and water-soluble property.²⁰ Given its outstanding performance, a series of methods have

been developed to obtain CDs, such as laser ablation,²⁶ chemical oxidation,²⁷ electrochemical oxidation,²⁸ and hydrothermal synthesis.²⁹ However, the fabrication of the CDs with highly performance is still limited by the complexity of fabrication processes requiring specially designed equipment with expensive reagents/catalysts with severe and stringent synthesis conditions. Among these techniques, hydrothermal synthesis, a one-step method has attracted tremendous interest due to efficient yet facile process favorable for production of CDs in large quantities.³⁰ However, the efficient one-step method for preparation of CDs with functional groups still persist to pose several challenges reinstating the need for more efficient synthesis protocols. Current preparation methods fail to effectively control lateral dimensions and surface chemistry. Further these methods often fail to deliver optimal fluorescent properties with high quantum yields (QY). Hence, there is a growing need for eco-friendly synthesis of CDs which could be exploited for novel applications.

With the development of industrial processes, there has been a surge in environmental heavy metal contamination in water, air, soil, and foods, which poses a serious health concern. As a typical heavy metal ion, Pb^{2+} with a very high toxicity has been observed to induce a variety of permanent damages for human and animal health, even at a low concentration range. Hence, ultrasensitive detection of Pb^{2+} ions is very critical for environmental protection and food safety. In this study, we synthesized CDs with a high density of functional groups on its surface by a facile and green route using a class of carbon source (citric acid, CA) and passivating agent (ethylenediaminetetraacetic acid disodium salt, EDTA-2Na). Furthermore, the

synthesized fluorescent CDs could be designed as efficient C-based luminescent probes without the requirement of any complicated separation or further surface modification. Pb^{2+} was used as a candidate ion to evaluate the sensitivity of detection of the obtained CDs. Our results indicated that the obtained CDs have superior detection of Pb^{2+} even at a low concentration range. Equipped with outstanding fluorescent property and excellent water solubility, the developed CDs could be applied as a potential candidate in ultrasensitive detection field, such as heavy metal ions detection in the human body fluids, food safety and water environmental science.

2. Experimental section

2.1 Preparation of CDs

The CDs were synthesized by a hydrothermal method using novel carbon source (CA) and passivating agent (EDTA-2Na). Briefly, 0.02mM EDTA was dispersed in 100mL of 0.1mol/L citric acid solution then uniform mixed with absolute ethyl alcohol (V_{Et-OH} :V_{citric acid (aq)}=1:10). Then the mixture was transferred into a Teflon bottle, sealed and hydrothermally treated at 180°C for 7h. Then, the heated autoclave was cooled, and a light yellow solution was obtained. The solution was dialyzed by membrane based dialysis (MWCO=300) for 12h. Finally, CDs were recovered from the solution using concentrating the filtered solution treated by rotary evaporator.

2.2 Detection of Pb^{2+}

For Pb^{2+} detection, 30 mg prepared CDs were dissolved in distilled water (100 mL). 5mL CDs aqueous solution was added in a reagent bottle subsequently added the Pb^{2+} ion solution with various concentrations. The Pb^{2+} concentration was ranging from 5

to 55 nmol/L. The PL emission spectra ($\lambda_{\text{ex}}=355$ nm) were recorded after reaction between Pb^{2+} and the CDs (10 min).

2.3 Chemical and Structure Characterization

The morphology of the prepared CDs was characterized using transmission electron microscopy (TEM, JEM-2010). The groups on the prepared CDs were examined by the Fourier transform infrared (FT-IR) spectrum (Bruker Co. Germany) was obtained in a KBr pellet, scanning from 4000 to 500 cm^{-1} wavelength range. Photoluminescence (PL) spectra and lifetime of the prepared CDs were recorded by an FLS920P Edinburgh Analytical Instrument apparatus, which equipped with a 450 W xenon lamp and the excitation sources was a F900H high-energy microsecond flash lamp.

3. Results and discussion

3.1 Synthesis and Characterization of CDs

The CDs were prepared by a hydrothermal method (as shown in Figure 1) using novel carbon source (CA) and passivating agent (EDTA-2Na), and have excellent optical absorptivity, chemical stability, and low toxicity. These unique properties make the prepared CDs be promising candidates for numerous practical applications, such as sensor, bio-imaging, medical diagnosis. In this study, the CDs were successfully prepared using the citric acid as the carbon source and the EDTA-2Na as the passivation agent.

The TEM image of the prepared CDs was shown in Figure 2a and 2b, which indicated that the prepared CDs showed a uniform dispersion. Moreover, diameters of

these prepared CDs were the range of 2 to 4 nm, and the average size was 3.0 nm. The high resolution TEM image (Figure 2c) displayed that the prepared CDs have good crystallinity. The results of the TEM images were clearly indicated that the prepared CDs can be well dispersed, and diameter has a narrow size distribution. Furthermore, the selected area electron diffraction pattern (inset in Figure 2c) obtained from the upper single CDs can be indexed to the (101), (112) and (011) planes. In addition, the prepared CDs showed excellent water-soluble and PL performance, as shown in the Figure 2 (d) and (e), respectively. The PL of the prepared CDs is much strong enough and could be seen by the naked eye.

The chemical characterization of the prepared CDs was tested by FT-IR and X-ray photoelectron spectroscopy (XPS). The functional groups of the prepared CDs were employed by FT-IR spectra (Figure 3a). The results indicate that numerous oxygen containing groups were clearly detected, the absorption peak of -OH was about 3432 cm^{-1} , the peaks of 2912 cm^{-1} and 2834 cm^{-1} was corresponded to -CH₂- asymmetric and symmetric vibration respectively, and the vibrational absorption peak of C=O was 1630 cm^{-1} . In addition, the asymmetric stretching vibrations of C-NH-C were observed (1114 cm^{-1}) and the bending vibrations of N-H could also be observed (1250 cm^{-1}). These results demonstrated that the prepared CDs were successfully modified by EDTA-Na, and abundant -OH, epoxy, -C=O, -NH and -CH groups were on the prepared CDs surface.³¹⁻³² The XPS spectra of prepared CDs are showed in Figure 3b, reveals the main characteristic peaks located at 532 eV and 284 eV, which are assigned to O1s and C1s signals, respectively. Moreover, three main peaks of C

atoms (Figure 3b insert) of high-resolution C1s spectra displays the signal located at 284.6 eV (C-C and C-H),³³ 286.2 eV (C-O-C, epoxide group) and 288.3 eV (-COOH, carboxyl group), respectively.³⁴ The results of XPS and FT-IR indicated a successful fabrication of CDs, and many functional groups on these CDs surface, such as the hydroxyl and carboxyl groups. These functional groups make the prepared CDs have an excellent stability in water or organic solvent, thus making them to have enhanced capacity to detect of heavy metal ions in aqueous mediums.³⁵⁻³⁶ Optimal fluorescence is an important feature for the prepared CDs, which plays an important role for wide range of practical applications. The PL excitation and emission spectra were carried for further exploring the optical properties of the prepared CDs. The excitation and emission spectra of the prepared CDs (Figure 4a) showed a broad and symmetrical band with the maximum at 355nm and 432nm, respectively, which was a typical luminescent feature of CDs. In addition, the PL decay profile of the prepared CDs displayed in Figure 4b, and the results indicated that PL decay curve could be well fitted into a single exponential function as:

$$I(t) = A_0 \exp(-t / \tau_1).$$

Thus, the corresponding lifetime was calculated by fitting to single exponential functions using iterative reconvolution, and the lifetime for CDs was determined to be 2.36ns.

3.2 Detection of Pb²⁺ by Fluorescence Quenching of CDs

As shown in FT-IR and XPS spectra, the as-prepared CDs contain a high density of carboxylic acid moieties and hydroxyls on their surface. Thus, these oxygen

containing groups enhance the potential applicability for the heavy metal ions detection. In this study, we focused on the detection of Pb^{2+} by our as-prepared CDs. The detection based two factors: one is that $\text{Pb}(\text{OH})_2$ has a very low solubility product constant ($K_{\text{sp}}=1.2\times 10^{-15}$), which could make Pb^{2+} be easy to combine with hydroxyls on the prepared CDs surface of. Another is the combination between Pb^{2+} and EDTA^{2-} groups caused the CDs aggregated and induced fluorescence quenching of CDs. The possible fluorescence quenching mechanism of the as-prepared CDs solution after addition of Pb^{2+} is shown in Figure 5. This demonstrated that the synergistic effects of these oxygen containing groups and EDTA^{2-} could make CDs to effectively aggregate and achieve the optimal degree of fluorescence quenching, thereby exhibiting excellent detection sensitivity.

We use aqueous solution (pH=5) of the prepared CDs to detect various concentration of Pb^{2+} , and evaluate the effect of Pb^{2+} concentration on the PL emission of prepared CDs solution. The results were shown in Figure 6, indicate that the PL performance of the prepared CDs with obvious quenching when at a Pb^{2+} concentration higher than 5nmol/L . However, the PL performance was not evidently obviously with decreasing the Pb^{2+} concentrations. This phenomenon could be attributed to two mainly possible factors regarding Pb^{2+} aggregation at low concentrations. Firstly, the carboxylic acid moieties on its surface of as-prepared CDs posed a limitation on the Pb^{2+} aggregation on CD surface. Secondly, EDTA^{2-} groups introduced into the CDs also play a very important role in Pb^{2+} aggregation. However, the Pb^{2+} could not have effective interaction with EDTA^{2-} groups due to the cross

interference with other groups at the Pb^{2+} concentration lower than 5nmol/L . These results strongly suggested that the determined concentration of CDs ($\text{CCDs}=140\mu\text{g/mL}$) could be only used in detecting Pb^{2+} within a certain acceptable range of concentration ($>5\text{nmol/L}$). Furthermore, the fluorescence lifetime of prepared CDs solution after interaction with different concentration of Pb^{2+} has hardly any variation (Figure 7), which indicated that the quenching phenomenon followed a static progression.³⁷⁻⁴⁰

To further investigate the effect of Pb^{2+} concentration on the fluorescence properties of CDs solution, we studied the mutual influence between different concentrations of Pb^{2+} and CDs. When the Pb^{2+} was added into the prepared CDs solution, the fluorescence of prepared CDs solution was subjected to quenching, which could be attributed to the interaction between Pb^{2+} and carboxylic groups. The results indicated that Pb^{2+} could potentially undermine the stability of the functional groups luminescence and reduce the aggregation of CDs in the solution. Figure 8a shows the fluorescence emission spectra of the prepared CDs aqueous solution with different concentration of Pb^{2+} . These results indicated that the PL emission intensity of the prepared CDs solution was decreased with the Pb^{2+} concentration increasing.

The quenching of the fluorescence intensity by the Pb^{2+} could be calculated using the Stern-Volmer equation:

$$F_0/F = 1 + K_{sv} [\text{Pb}^{2+}]$$

Where F_0 is the fluorescence intensity without Pb^{2+} , F is the fluorescence intensity obtained with the presence of the Pb^{2+} and K_{sv} is the Stern-Volmer (conductional

stability) constant. The typical Stern-Volmer plot is shown in Figure 8b, which demonstrated that a calibration curve of $F_0/F=0.99+1.5\times10^6 [Pb^{2+}]$ was obtained, and the concentration of Pb^{2+} was observed (the range of concentration was 5 to 55 nmol/L). The minimum detection concentration of Pb^{2+} was measured, which was much lower compared to the maximum level of detection mentioned by the National Standard of China (24 nmol/L), and also belows the permitted maximum level of the US Environmental Protection Agency (EPA).

In addition, we also evaluated the interactive effects at a higher concentration range between high concentrations of both CDs Pb^{2+} ions in aqueous solutions. The quenched response between of the prepared CDs solution and Pb^{2+} (Figure 9) indicated that the CDs have excellent detection sensitivity of Pb^{2+} at high concentration range. These results indicated that the prepared CDs could be potentially applied a sensor to detect Pb^{2+} in the body liquid or applied in other area, where detection of high concentration of Pb^{2+} is critical.⁴¹⁻⁵⁰

4. Conclusions

In summary, we have developed a facile one-step and environmentally-friendly method to prepare CDs using novel carbon source (CA) and passivation agent (EDTA-2Na). The obtained CDs demonstrated good water-solubility, photo-stability and most importantly an ultrasensitive detection property for the detection of Pb^{2+} ions. It was found that the surface passivation agent EDTA-2Na plays a key role for the enhanced PL performance of carbon dots for metal ion detection. Moreover, the detailed study on interaction of CDs solution against Pb^{2+} at various concentration

ranges indicate that the solution of Pb^{2+} quenched CDs could be used to detect Pb^{2+} at both very sparsely and highly concentrated solutions (5 to 55 nmol/L). These results indicate that our CDs could hold a great potential to be suitably engineered for a wide range of heavy metal detection applications. We expect that this strategy can provide a new approach for developing a great variety of low cost and sensitive sensors for water detection and food safety applications.

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Notes

The authors declare no competing financial interest.

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Figure 1. Schematic diagram of synthesis of CDs. First, EDTA-2Na was dispersed in citric acid solution then uniform mixed with absolute ethyl alcohol. Then the mixture was transferred into a Teflon bottle, treated at 180°C. Finally, the CDs were obtained by rotary evaporator after the solution dialyzed by membrane based dialysis.

Figure 2. TEM images (a, b) and HRTEM image (c) of CDs, photographs of CDs dispersions in water with sunlight (d) and UV-light (365 nm, center) illumination (e).

Figure 3. FT-IR spectrum (a) and XPS spectra (b) of the obtained CDs.

Figure 4. PL excitation (black line) and emission (red line) spectra (a) and the luminescent decay curve (b) of CDs in aqueous solution.

Figure 5. The fluorescence quenching mechanism of CDs was caused by Pb^{2+} by CDs aggregate.

Figure 6. PL emission spectra of CDs aqueous solution ($C_{\text{CDs}}=140\mu\text{g/mL}$) with different concentrations of Pb^{2+} . $C_{\text{Pb}^{2+}}$: 5, 10, 15, 20, 25, 30, 35, 45, 50, 70, 1E4, 2E4, 3E4 nmol/L ($\lambda_{\text{ex}}=310$ nm, solution pH=5).

Figure 7. Fluorescence decay curves of pure CDs and CDs after their interaction with 200 μmol/L, 350 μmol/L Pb^{2+} solution (a), the lifetime of CDs and CDs after their interaction with Pb^{2+} (b).

Figure 8. Fluorescence emission spectra of CDs aqueous solution after interaction with different concentrations of Pb^{2+} (a). $C_{Pb^{2+}}$: 5, 15, 20, 25, 30, 35, 40, 45, 55 nM (C_{CDs} 30 μ g/mL, solution pH=5, λ_{ex} =310 nm). Stern-Volmer plots of the fluorescence quenching of CDs in aqueous solution by Pb^{2+} (b).

Figure 9. PL emission spectra of CDs (140 mg/mL) solution with various concentration of Pb^{2+} interaction. $C_{\text{Pb}^{2+}}$: 0, 50, 100, 150, 200, 250, 300, 350 μM (λ_{ex} =355 nm, solution pH=6).

Supplementary Information

Facile synthesis of carbon dots with superior sensing ability

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Fig. S1 The fluorescence quenching mechanism of EDTA²⁻ groups of the CDs was caused by Pb²⁺ aggregation on single CDs.