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N-doped carbon dots synthesized by rapid microwave irradiation as highly fluorescent probe for Pb^{2+} detection

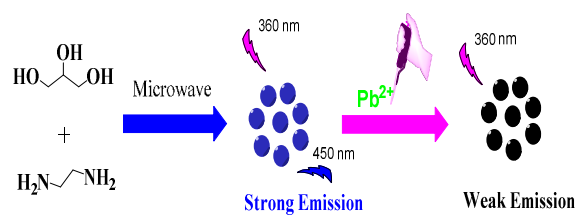
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A new NCDs were obtained and exhibit highly sensitive response toward Pb^{2+} which could be applied to real sample detection.



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N-doped carbon dots synthesized by rapid microwave irradiation as highly fluorescent probe for Pb²⁺ detection

Cite this: DOI: 10.1039/x0xx00000x

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Accepted 00th January 2012,

DOI: 10.1039/x0xx00000x

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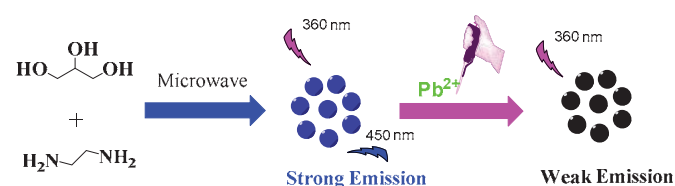
In this study, N-doped carbon dots (NCDs) could be prepared by using glycerol as carbon source and ethylenediamine as nitrogen doped molecules through one step microwave irradiation method. The resulting NCDs probe could exhibit a linear fluorescence response behaviour to Pb²⁺ as low as 15.0 nM detection limit, which could be applied for trace levels of direct pb²⁺ recognition.

In recent years heavy-metal pollution has received more and more attention due to their toxic effects on human health and the environment. Lead(II) ion as one of the toxic heavy metals is widespread in the environment such as air, water, soil and food that can easily enter human body through inhalation and ingestion. As reported, low-level lead can cause a number of serious diseases including high blood pressure, brain, central nervous system disorders and muscle paralysis.¹ Thus, the development of Pb²⁺ sensors with high sensitivity and selectivity is of great importance. So far, many reports have been devoted to detected Pb²⁺,² but most of these probes were based on organic molecules and its synthesis process requires large amounts of organic solvent which brought pollution to the environment. Therefore, many works have been focused on the green and friendly environment synthesis method for novel highly selective fluorescence Pb²⁺ probes.

Carbon quantum dots (CQDs) have been attracting much interest in the past few years because of their unique optical and biochemical properties. They are widely used in various fields,

including sensors, bioimaging, and photovoltaics.³ Compared with conventional organic dyes, CQDs have advantages on easy functionalization, low toxicity, and high resistance to photobleaching, and they can be used in place of traditional dyes.⁴ However, low quantum efficiencies, poor yields and complex processing still limit the practical application of CQDs.

Significant efforts have been made to synthesize novel CQDs by simple, fast methods.⁵ Zhang's group obtained new NCDs by direct pyrolysis of ethanalamine in air for 7 min.⁶ In this paper, a novel and large-scale strategy was developed for the preparation of fluorescence NCDs probe via rapid microwave irradiation of glycerol and ethylenediamine as showed in Scheme 1. During microwave irradiation, obvious blue colour change of the reactant mixtures could be clearly observed over time (Fig. S1) under ultraviolet (UV) irradiation at 365 nm. This kind NCDs probe could be obtained in high yield by using a simple process without any solvent or a catalyst, indicating that this type of one-step microwave irradiation method is economical for industrial-scale production of NCDs.



Scheme.1 Cartoon illustrations of the procedures NCDs

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† Electronic supplementary information (ESI) available: quantum yield calculate, FT-IR and XPS spectroscopy; reaction time effect, pH effect, stability and water samples analysis. See DOI: 10.1039/c4nj02367f

As evident from TEM (Fig. 1a), it could be clearly observed that the NCDs are highly dispersed in aqueous solution and their diameters are not of uniform size distributed in the range of 2.1-14.6 nm with an average diameter of 5.4 nm (Fig. 1b). The FT-IR spectrum of the NCDs described some main absorption peaks (Fig. S2), such as the O-H stretching vibrations at 3470 cm⁻¹, C-H stretching vibrations at 2950 and 2890 cm⁻¹, strong C=O stretching vibrations at 1643 cm⁻¹ C=C, the characteristic stretch band of the

amine C=N bond is situated at 1470 cm^{-1} , which shows that the NCDs are rich in carboxylic groups on their surface and have excellent water-solubility. Elemental analysis and the surface composition were performed by XPS technique (Fig. S3). Elemental analysis data showed NCDs (C 72.65%, N 6.570%, O 20.78%) which further proved this nanomaterial containing carbon, nitrogen and oxygen elements as FT-IR spectrum described.

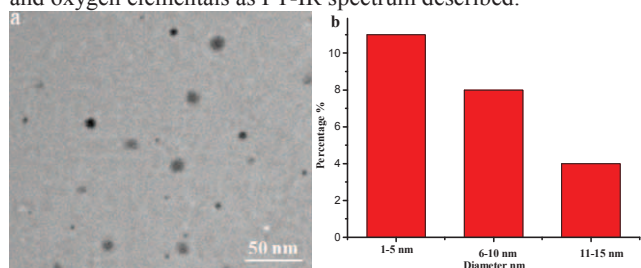


Fig.1 (a) TEM image of NCDs; (b) Particle size distribution of NCDs

The UV-visible absorption spectrum of the NCDs was performed in water, fig. 2a showed two typical absorption peaks at 275 and 340 nm, ascribed to $\pi-\pi^*$ transitions of the C=C bond and $n-\pi^*$ transitions of the C=O bond, respectively.⁷ The maximum emission wavelength of the NCDs was centered at 429 nm by using 360 nm excitation wavelength. The fluorescence quantum yield of the NCDs in water at an excitation wavelength of 360 nm was found to be 7.5% by using quinine sulfate as a reference (see the ESI for details) suggesting that microwave irradiation is a critical step in the synthesis of fluorescent NCDs. Herein, we also found that the fluorescence emission intensities showed gradual decrease with obvious red shift from 429 to 465 nm by changing the excitation wavelength from 360 to 400 nm (Fig. 2b), which indicated that the NCDs depend closely on the chosen excitation wavelength.

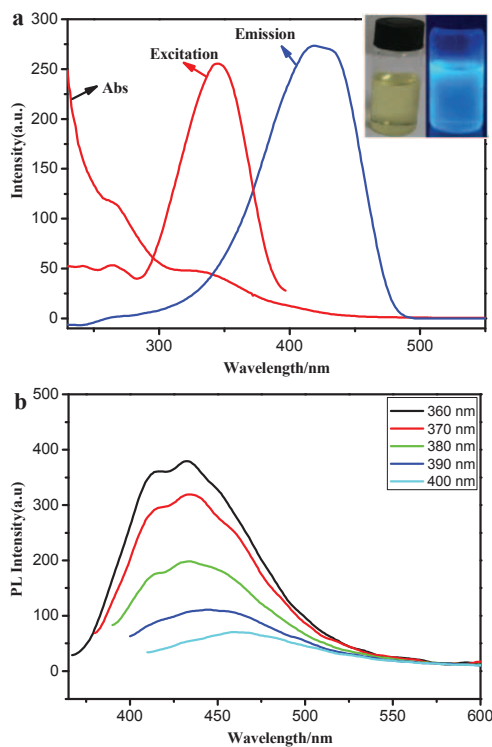


Fig. 2 (a) UV-vis absorption, excitation and emission spectrum of the NCDs at 360 nm excitation wavelength and excitation spectrum of NCDs at 429 nm emission wavelength (inset: Photographs of NCDs taken under visible light and 365 nm UV light). (b) Fluorescence spectrum of the NCDs at different excitation wavelength form 360 nm to 400 nm.

In this paper, the fluorescence response of the NCDs on pH effects were carried out in different phosphate buffers (pH=1–13). Almost no fluorescence change was observed for NCDs over a wide range of pH values from 4 to 10 as showed in Fig. S4. Therefore, we further investigated the fluorescence response behaviors towards various metal ions (Cu^{2+} , Ni^{2+} , Mn^{2+} , K^+ , Co^{2+} , Cd^{2+} , Ca^{2+} , Na^+ , Fe^{3+} , Ag^+ , Fe^{2+} , Zn^{2+} , Mg^{2+} , Hg^{2+} and Pb^{2+}) in aqueous solution (pH= 6.8 phosphate buffer). As is evident from Fig. 3, almost no fluorescence emission intensity change of the NCDs could be observed except Pb^{2+} indicating that this kind NCDs could be used as a highly selective and sensitive probe for Pb^{2+} detection.

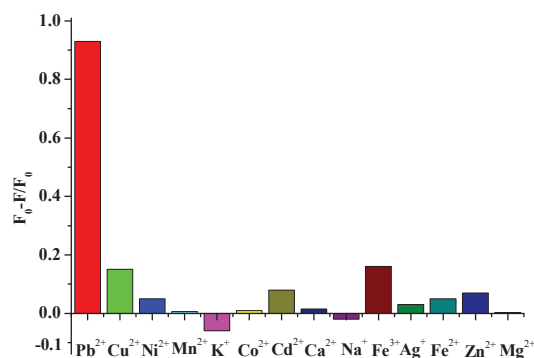


Fig.3 The various fluorescence intensity ratio (F_0/F) of the NCDs solution in the absence and presence of various individual metal ions. F_0 and F are the fluorescence intensity at 360 nm in the absence and presence of ions, respectively.

The relationship between Pb^{2+} concentration and fluorescence intensity was further investigated. As showed in Fig. 4a, the Pb^{2+} ions efficiently quenched the NCDs fluorescence emission when the concentration of Pb^{2+} ions reached $6.0\ \mu\text{M}$, the fluorescence intensity gradually decreased to about 95% of its initial value, which proved that Pb^{2+} can interact with NCDs effectively. From 0.1 to $6.0\ \mu\text{M}$, the relationship between the fluorescence intensity (F/F_0) of the NCDs and the Pb^{2+} ion concentration is linear (Fig. 4b). The equation is $F/F_0 - 1 = 2.492[\text{Pb}^{2+}] + 1.121$, $R^2 = 0.999$. Under the same experimental conditions, the limit of detection of Pb^{2+} ions was estimated to be $0.015\ \mu\text{M}$, based on $3SD/k$ (where SD is the standard deviation of the corrected blank signal of the NCD and k is the slope of the calibration curve). A large number of studies showed that different type of NCDs can interact with different metal ions through oxygen or amino functional groups on the NCDs surface and leads to fluorescence quenching or enhancement, unfortunately the mechanism of action is still not clear.⁸ In this study, the d orbital of Pb^{2+} received electron in the excited state of NCDs through nonradiative electron-transfer more easily compared to the other metal ions. In this paper, the fluorescence decays of NCDs in the absence and presence of Pb^{2+} showed that the fluorescence decay lifetime of NCDs is $\sim 4.57\text{ ns}$, but decreases to $\sim 4.53\text{ ns}$ for Pb^{2+} as shown in Fig.5, demonstrating that the mechanism of the quenching process involves complexation interaction and the static quenching

dominates over dynamic quenching. The NCDs stability in solution was also studied, as shown in Fig. S5, the fluorescence spectrum were almost unchanged after one day and one month, which demonstrates that the resulting NCDs fluorescent emission is quite stable.

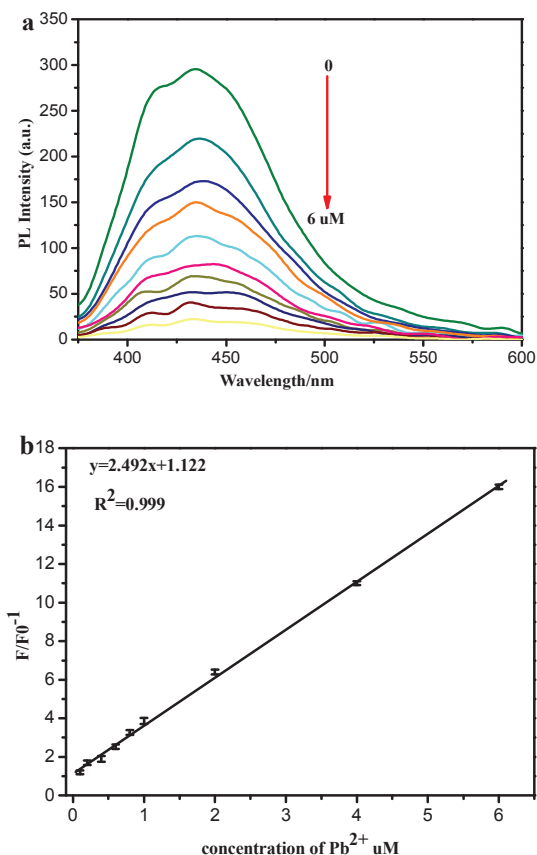


Fig. 4 (a) Fluorescence Emission spectra of NCDs in the presence of Pb^{2+} (from up to down, the concentration of Pb^{2+} is 0, 0.1, 0.2, 0.4, 0.6, 0.8, 1.0, 2.0, 4.0, 6.0 μM , respectively). (b) Fluorescence intensity response of NCDs to the concentration Pb^{2+} (Inset: the fluorescence intensity of NCDs as a function of Pb^{2+} concentration from 0.1 to 6 μM . $\lambda_{ex}=360$ nm).

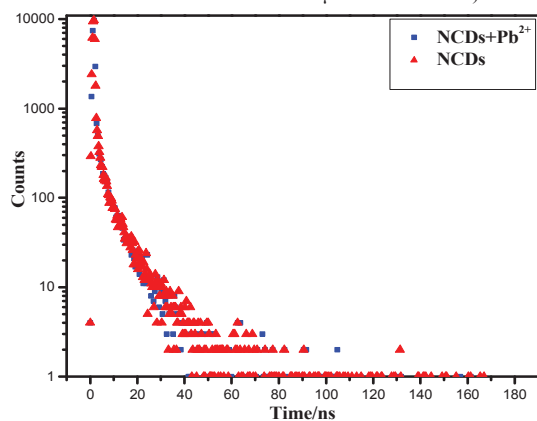


Fig. 5 Fluorescence decay of NCDs in the absence and presence of Pb^{2+} .

To investigate the applicability and reliability of the proposed probe, NCDs was applied to real ultrapure water sample, 1-100 nM Pb^{2+} was spiked before the sample was detected using a standard

addition method. The analytical results are showed in table S1, the recovery values ranged from 88.0% to 102.0%. These results show that the established sensing system can be effectively used for the direct detection of real samples that may contain trace levels of Pb^{2+} .

In summary, we developed a fast, green, and economic route for NCDs preparation from glycerol and ethylenediamine via one-step microwave irradiation. The obtained NCDs can exhibit high sensitivity and selectivity for Pb^{2+} relative to other competitive metal ions. This kind of the NCDs was used as a fluorescence probe to analyze real water samples with good reproducibility.

Experimental

All the reagents were of analytical grade and used without further purification. In a typical synthesis procedure, glycerol 5 mL and ethanolamine 20 μL were mixed and placed in glass ampoule, and then the ampoule was placed inside the microwave reactor and irradiated for 2, 5, 10, 15, 20 min (1 kW, 2.45 GHz). After cooling to room temperature, the NCDs were obtained and stored in the refrigerator (4°C) before use.

The particle size distributions of NCDs were observed using a transmission electron microscopy (JEOL JEM-2100). The IR spectra of the product were measured by a Nicolet Nexus 670 Fourier transform infrared (FT-IR) spectroscope with a resolution of 4 cm^{-1} and scan times of 64. Ultraviolet-Visible (UV-Vis) absorption spectra were measured with a Varian Cary 50 spectrophotometer at 1 cm of the light path length. Fluorescence spectra were recorded on Varian cary Eclipse fluorescence spectrophotometer with an excitation wavelength of 365 nm. X-ray photoelectron spectroscopy (XPS) analysis was carried out on a PHI 5000 Versa probe electron spectrometer from ULVAC-PHI.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (No. 51173078, 21172106, 21474048), open project of Beijing National Laboratory for Molecular Sciences and a Project Funded by the Priority Academic Program Development of Jiangsu Higher Education Institutions (PAPD).

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