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Hydrothermal synthesis of fluorescent carbon dots from sodium citrate and polyacrylamide and their highly selective detection of lead and pyrophosphate

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ABSTRACT

Fluorescent carbon dots (CDs) have been a promising star in analytical and environmental fields. Present study designed a new bright-blue fluorescent carbon dots with sodium citrate and polyacrylamide by a hydrothermal method. The obtained CDs had an average diameter of 2.4 nm and exhibited excitation-independent property. The experimental results demonstrated that the bright-blue fluorescent CDs exhibited "off-on" property with Pb^{2+} and pyrophosphate (PPi), which proved that it was a good fluorescent probe for the determination of Pb^{2+} and PPi. The fluorescence intensity of CDs was significantly quenched by Pb^{2+} (turn-off) through forming CDs/Pb^{2+} complexes via an inner filter effect, and the fluorescence intensity of CDs/Pb^{2+} system was completely resumed by PPi (turn-on) owing to the release of CDs from the CDs/Pb^{2+} complexes due to higher binding force of PPi to Pb^{2+}. The detection limits were 4.6 nM for Pb^{2+} and 54 nM for PPi, respectively. The probe was successfully validated with real water samples and human urine. The results showed that this the probe was facile, rapid and exhibited high sensitivity, selectivity, repeatability and stability. This "off-on" fluorescent probe based on CDs provided a promising platform for environmental and biological sensing applications.

1. Introduction

Contamination of heavy metal ions has attracted serious concern due to their highly toxic and bio-accumulative properties [1,2]. Lead ion (Pb^{2+}), as a kind of common and widely used heavy metal ions, impacts the ecological environment and health of human even at a very low concentration. If the concentration of Pb^{2+} is more than 5 μM in blood, it will cause anemia, reproductive dysfunction, developmental disorders and nervous system dysfunction [3,4]. So far, a number of instrumental techniques, such as electrochemical impedance spectroscopy (IES), atomic absorption spectrometry (AAS) and inductive coupled plasma-mass spectrometry (ICP-MS), have been widely applied for the determination of Pb^{2+} [5–7]. However these methods usually need sophisticated operation, high costs and long analysis time. On the other hand, pyrophosphate ($P_2O_4^{7-}$ or PPi) is released upon hydrolysis of adenosine triphosphate to adenosine monophosphate under cellular conditions and it is also an inhibitor of several crystallization reactions. Detection and quantification of PPi have an important significance to help identifying diseases such as chondrocalcinosis or calcium pyrophosphate dihydrate (CPPD) crystal deposition disease [8–10]. Up to date, most of determination methods for PPi are on the base of organic small-molecule probes, which are complicated and time-consuming [11]. Thus, it is necessary to develop some relatively inexpensive, rapid, sensitive and selective methods for detecting Pb^{2+} and PPi at trace level.

As a new class of carbon nanomaterials, carbon dots (CDs) were firstly discovered in the purification procedure of single-walled carbon nanotubes in 2004 [12], which have absorbed enormous attention from the researchers. CDs have spherical structure with the size below 10 nm and display strong and stable fluorescence. Compared to other fluorescent materials such as organic dye molecules, metal nanoparticles and semiconductor quantum dots, CDs have a number of remarkable properties such as easy preparation, excellent aqueous solubility, fluorescent stability, low toxicity, outstanding biocompatibility and environmental friendliness, which make them widely used in sensing [13], bioimaging [14], photocatalysis [15], optoelectronic devices [16], and drug delivery [17]. Recently, many methods have been developed for the preparation of fluorescent CDs, such as arc discharge [18], laser ablation

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[19], electrochemical oxidation [20], acidic oxidation [21,22], combustion [23], hydrothermal treatment [24], ultrasonic treatment [25] and microwave-assisted methods [26], etc. Currently, many CDs have been developed as fluorescent probes for the determination of metal ions based on the fluorescence change in aqueous solutions. Gao et al. established a facile and green method to synthesize amino-functionalized fluorescent carbon dots (FCDs) with anhydrous citric acid as carbon precursors, sodium borohydride as reducing agent and ammonia as the passivation agent, which exhibited a good sensitivity with the detection limit of 20 nM for the determination of Hg^{2+} in water samples [27]. Gedda et al. prepared a kind of CDs from prawn shells, which was used as an excellently selective and sensitive sensor for the determination of Cu^{2+} with a low detection limit of 5 nM [28]. Jiang and co-workers synthesized high fluorescence Silicon-Carbon-Based Dots@Dopamine (Si-CDs@DA) for highly sensitive detection of Ag^{+} on the basis of fluorescence quenching mechanism, and the detection limit decreased to 2.5 nM [29]. As lead ion was concerned, a fluorescent probe based on CDs derived from chocolate was prepared and which exhibited highly sensitivity and selectivity for Pb^{2+}, and the detection limit was 12.7 nM [30].

The goal of present study is to carry out an attempt to prepare a new CD with sodium citrate and polyacrylamide, and further develop an effective fluorescent probe for highly sensitive determination of Pb^{2+} and PPi. Pb^{2+} can chelate with the prepared CDs to form the CDs/Pb^{2+} complexes, due to the strong interaction between Pb^{2+} and the specific groups on the surface of CDs, which will lead to the fluorescence quenching, as termed "turn-off" effect. The fluorescence of CDs/Pb^{2+} system will be restored by the addition of PPi due to the stronger binding preference between Pb^{2+} and PPi, as termed "turn-on" effect. Hence the CDs was used to design an "off-on" fluorescence probe for highly sensitive and selective detection of Pb^{2+} and PPi. The determination process was demonstrated in Fig. 1. Besides, some critical parameters related to the detection such as the concentration of CDs, the incubation time, pH of CDs solutions had been investigated and optimized to obtain good sensing performance for the determination of Pb^{2+} and PPi.

2. Experimental

2.1. Materials

Acrylamide, quinine sulfate (98%, suitable for fluorescence), triethylamine hydrochloride, ammonium molybdate were purchased from Aladdin Industrial Co. Ltd. (Shanghai, China). Sodium citrate was purchased from J&K Scientific Co. Ltd. (Beijing, China). Multi-walled carbon nanotubes were purchased from Shenzhen Nanotech Port (Shenzhen, China). All other reagents were of analytical reagent grade and purchased from Beijing Chemical Reagent Company (Beijing, China) without further purification. Purified water was used throughout all the experiments.

2.2. Synthesis of CDs

Before synthesis of CDs, the polyacrylamide was prepared. In the procedure, 5.0 g acrylamide and 80 mL purified water were added into a 250 mL three flask, and heated for 15 min at 30 °C under stirring. Further, 0.025 g potassium persulfate dissolved in 10 mL purified water was added, and heated at 90 °C for 2 h with stirring. After cooling to room temperature, the solution was concentrated by rotary evaporation and the product was dried in an oven for 2 h. For the synthesis of CDs, 1.0 g sodium citrate and 0.52 g polyacrylamide were dissolved in 20 mL purified water. After vigorous stirring, the mixture was added into a 50 mL PTFE reaction kettle and reacted in an electroheat baking oven at 200 °C for 3 h. After the kettle was cooled to ambient temperature naturally, a blue-green solution was obtained. And then, the solution containing the CDs was collected after dialyzing against purified water for 3 h and dried in an oven. Finally, the CDs were dispersed in purified water at a concentration of 1.0 mg mL^{-1} for subsequent experiments.

2.3. Characterization

UV–vis absorption spectra were recorded by a TU-1810 UV–vis spectrophotometer (PGeneral, Beijing, China). Fluorescence measurements were measured on an F-7000 fluorescence spectrophotometer (Hitachi, Tokyo, Japan). The morphologies were achieved by a JEM-2100 transmission electron microscope (JEOL, Akishima-shi, Japan) using an acceleration voltage of 200 kV. Fourier transform infrared spectroscopy (FTIR) measurements were carried out on a Nicolet Magna-IR 750 spectrometer (Thermo Fisher, New York, USA). X-ray photoelectron spectra (XPS) were performed on a Thermo Fisher K-Alpha spectrometer (Thermo Fisher, New York, USA). X-ray diffraction (XRD) was obtained on a Philips D/Max-2500 multipurpose X-ray diffractometer with Cu Kα radiation at 40 kV and 200 mA. (Philips, Amsterdam, Holland). Raman spectra were measured with an inVia Raman microscope with a laser at an excitation wavelength of 633 nm (Renishaw, London, England). Zeta potential measurements were performed on a Zetasizer Nano ZS zeta potential analyzer (Malvern, Malvern, England).

2.4. Quantum yield measurements

Relative fluorescence quantum yield of the CDs was determined using quinine sulfate dissolved in 0.1 M H_2SO_4 (literature QY: 0.54 at 340 nm) as a reference by the following equation [31],

Here the subscripts "s" and "r" denote sample and reference, respectively. Q refers to Quantum yield. I is the integrated emission intensity (Excitation wavelength, 360 nm). A represents the UV–vis absorbance which is kept below 0.05 to minimize reabsorption effects, and n is the refractive index with 1.33 as the default for both quinine sulfate and CDs solvent.

2.5. Fluorescence detection for Pb^{2+} and PPi

For the detection of Pb^{2+}, 15 μL of CDs solution and different amounts of Pb^{2+} were added into a 2.0 mL centrifuge tube, and the mixture was diluted to 1.5 mL with purified water and mixed

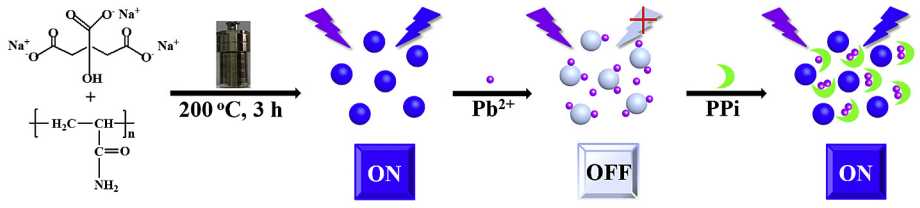

Fig. 1. Schematic diagram of the preparation for CDs and their application for Pb^{2+} and PPi determination. (A colour version of this figure can be viewed online.)