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Notes

Tryptophan-based carbon dots as fluorescent probe for detection of Pb^{2+} and Fe^{3+} ions

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A Probe for metal ions based on carbon dots (CDs) has been prepared. A one-step method has been developed to synthesize the probe using tryptophan as the recognizing group. The synthesized probe has been evaluated for metal ions' detection. The results show increase in fluorescence in the presence of Pb^{2+}, over other 14 metal ions, illustrating the selective and sensitive detection of Pb^{2+}.

Keywords: Carbon dots, Fluorescence, Probes, Tryptophan, Metal ions, Sensors

Lead(II) ion (Pb^{2+}) is one of the heavy metal ion pollutants, which is found in a variety of commercial products and industrial materials[1-3]. High levels of lead in blood may cause renal disease, reproductive disorders, toxicity, irreversible neurological damage and cancer, particularly in children[4,5]. Thus, lots of efforts have been devoted to developing sensors for lead ions over the last few decades, including fluorescent chemosensor, nanosensor, biosensor, electrochemiluminescence sensor, etc[6-11]. For example, Ma *et al*. report a fluorescent sensor showing high sensitivity and specific selectivity for lead ion[12]. Zhao *et al*. developed a fluorescent lead ion probe using dithizone functionalized CdSe/CdS quantum dots[13]. He yao group developed a surface-enhanced Raman scattering silicon chip for high-performance Pb^{2+} detection using a DNA-cleaving reaction catalyzed by Pb^{2+} activated DNAzyme[14]. However, it is still relevant to develop a simple method for the determination of Pb^{2+} at ultratrace levels. Fluorescent chemosensors or nanosensors can be easily used in solution due to their having high sensitivity and selectivity, which make their application attractive.

As a new class of carbon nanomaterials with nearly spherical geometry, carbon dots (CDs) have attracted extensive interest in the past several years due to their chemical inertness, resistance to photobleaching, low cost, low cytotoxicity, favorable biocompatibility and easy functionalization[15-17]. Because of these attractive features, CDs have been widely used in biolabeling, bioimaging, sensing, photocatalysis, optoelectronic devices, etc[18-24]. Especially, the unique optic properties make it a promising alternative material to give the response signal. A lot of works have been reported in the field of CDs-based metal ions sensing[25-29]. However, a suitable group for recognizing ions is also important and necessary to construct a fluorescent probe.

Tryptophan is one of the amino acids often used as a probe for detection of ions due to the noncovalent binding forces between its indole ring and metal ion[12,30,31]. Introducing tryptophan onto CDs' surface is also a feasible way to construct metal ion probes. For example, Wan *et al*. synthesized L-tryptophan-capped carbon quantum dots to detect mercury ion in aqueous solution[32]. However, two steps are required to obtain the probe.

Herein we report a one-step method to synthesize tryptophan-contained CDs for the sensitive and selective fluorescence detection of lead ion, in which CDs show an increased fluorescence in the presence of lead ion.

Experimental

Carbon dots were prepared using a hydrothermal method. Briefly, 0.5 g tryptophan and 0.8 g citric acid were dissolved in 10 mL water and stirred for 2 h. The mixture was then kept in a Teflon equipped stainless steel autoclave, which was sealed and placed in a drying oven followed by hydrothermal treatment at 180 °C for 5 h. After the autoclave was cooled to room temperature, the product was subjected to dialysis for about 24 h using a dialysis tube (1000 Da, molecular weight cutoff). Finally, a yellowish powder (named cat-CDs) was obtained after freeze-drying. Tryptophan, citric acid, and tris(hydroxymethyl)aminomethane hydrochloride (Tris) were purchased from Aladdin Industrial Inc., Shanghai, China. The other reagents were purchased from Sinopharm Chemical Reagent Co. All the reagents were used as received.

UV-visible extinction spectra were measured on a Thermo Scientific Evolution 220 Spectrophotometer. Photoluminescence spectra were recorded in a microcell using a Perkin-Elmer LS55 luminescence spectrometer. High-resolution transmission electron microscopy (HRTEM) images were acquired on a FEI Tecnai G2 F20 microscope. The HRTEM samples were prepared by placing a drop of the colloidal solution onto a formvar-coated copper grid. Fourier transform infrared (FTIR) spectra were obtained on a Perkin-Elmer Spectrum GX FTIR Spectrometer.

Results and discussion

The Fourier transform infrared (FTIR) spectra of tryptophan, citric acid and cat-CDs, and some groups changed after hydrothermal treatment (Fig. 1a). The main peak of citric acid around 1720 cm^{-1}, corresponding to the carboxyl group, disappears in the cat-CDs, which means that the carboxyl group reacted during synthesis. For tryptophan, no obvious movement was observed on these bands around 3404 cm^{-1}, 3040 cm^{-1}, 1660 cm^{-1}, 1593 cm^{-1}, 1411 cm^{-1} and 742 cm^{-1} after hydrothermal treatment, but two weak peaks appear around 1610 cm^{-1} and 1500 cm^{-1}, which can be attributed to amide I band and amide II band, respectively. Thus, citric acid and tryptophan combine to give an amide in cat-CDs. Similar results were obtained from the UV-vis spectra and photoluminescence (PL) spectra. The cat-CDs has an obvious absorption peak around 280 nm, which is consistent with the absorption peak of tryptophan, and a weak broad absorption band around 350 nm, which

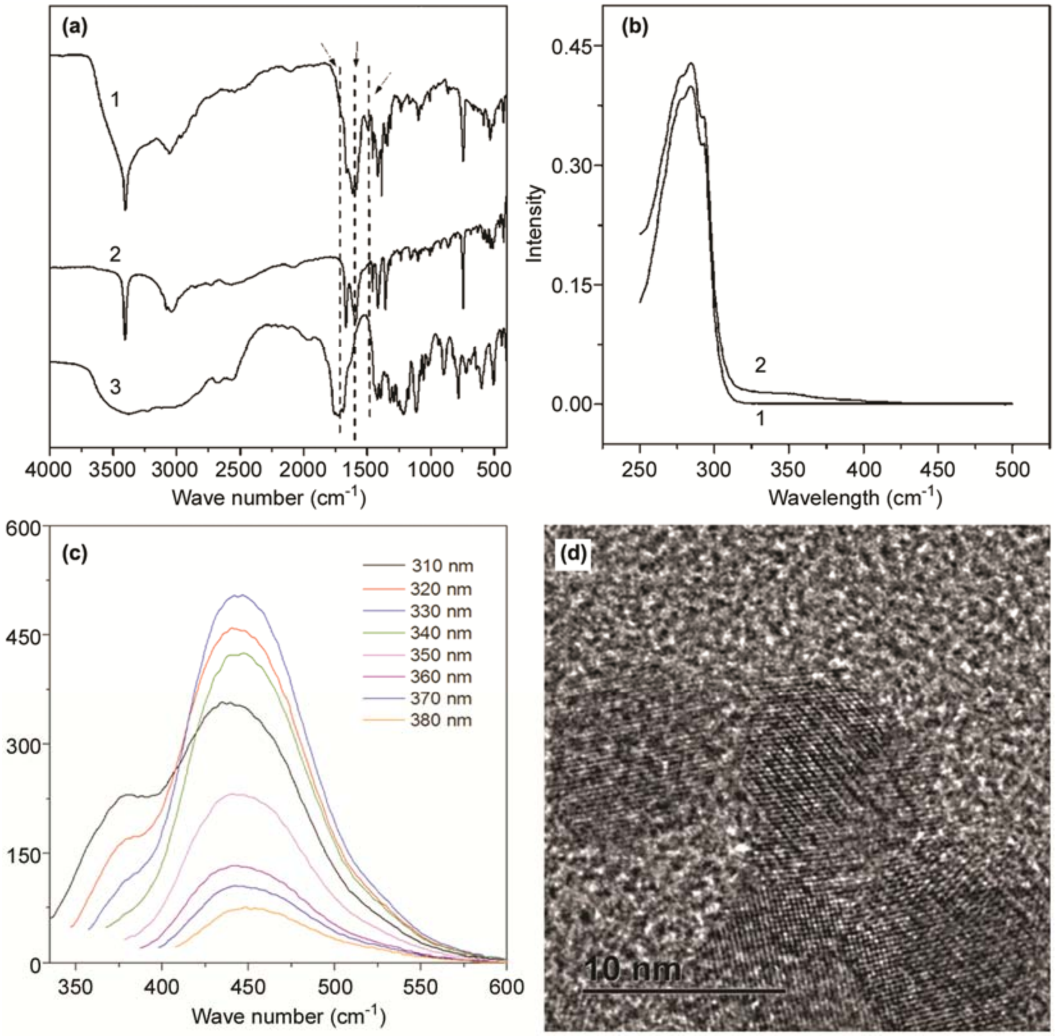

Fig. 1 — (a) FTIR spectra of cat-CDs (1), tryptophan (2) and citric acid (3). (b) UV-vis spectrum of tryptophan (1) and cat-CDs (2). (c) photoluminescence spectrum of cat-CDs under different excitation wavelengths, and, (d) TEM images of cat-CDs.

is ascribed to the nanocarbon π–π* transition[33] (Fig. 1b). The PL spectrum of cat-CDs under different excitation wavelengths shows that the cat-CDs have an emission peak at 353 nm (λ_{ex} = 275 nm), similar to the emission peak of tryptophan. The cat-CDs also have an emission peak around 444 nm, which is ascribed to the CDs, this peak was red-shifted to ca. 450 nm when the excitation wavelength changed from 310 nm to 380 nm (Fig. 1c). This result reveals that the cat-CDs had a weak excitation-dependent PL behavior, which may be due to the surface state affecting the band gap[34]. Combining the results obtained from FTIR and UV-vis, we can conclude that the cat-CDs were synthesized successfully, and there appear to be indole rings or similar structures in CDs due to the UV-vis absorption peak and PL peak ascribed to indole rings. During the hydrothermal treatment, citric acid reacts with amine group to form fluorescent derivatives of citrazinic acid, which contribute to CDs emission in the blue spectral range[34-36]. There is an amino group and a carboxyl group in tryptophan, which participate in the formation of CDs. However, the indole ring has fewer functional group, some indole rings may retain their skeleton which results in the UV-vis absorption peak around 280 nm and PL peak at 353 nm. The morphology of cat-CDs is also characterized by HRTEM, which shows that the cat-CDs are nearly spherical nanoparticles with a size of about 9 nm (Fig. 1d).

The stability of the carbon dots-based probe, cat-CDs, against photobleaching is investigated by 30 min continuous illumination under 340 nm (the emission wavelength is 444 nm). There is only slight decrease in the emission intensity of cat-CDs (Supplementary data, Fig. S1). Such result reveals that cat-CDs exhibit excellent fluorescence stability under exciting light.

The pH stability was also investigated in pH range from 2 to 12 (Supplementary data, Fig. S2). The results show that the probe is sensitive to pH, its intensity is higher in alkaline environment than in acidic environment. Since many metal ions are not stable in alkaline solution, pH 7.5 (maintained using 10.0 mM Tris-HCl buffer solution) was used in subsequent experiments to study the detection of metal ions.

Then, the application of cat-CDs in metal ions detection was studied systemically. The photoluminescence spectra of the cat-CDs solution in the absence and presence of various metal ions at pH 7.5 separately show that most of the ions (with a final concentration of 200 μM) induced PL intensity decrease, with Fe^{3+} causing the most significant decrease, whereas the presence of Pb^{2+} resulted in the increase of PL intensity (Fig. 2a). To describe the PL changes quantitatively, the PL intensity ratio of I/I_0 at 444 nm was used to analyze the selectivity of cat-CDs towards metal ions, where I denotes the PL intensity of cat-CDs in the presence of ions and I_0 denotes that in the absence of ions. The I/I_0 value for Pb^{2+} is obviously higher than that for other ions, and the value is the lowest for Fe^{3+} (Fig. 2b). That is, cat-CDs probe has selective response to Fe^{3+} and Pb^{2+}. Many groups have reported CDs-based Fe^{3+} probe[37-40], because of the coordination between Fe^{3+} and

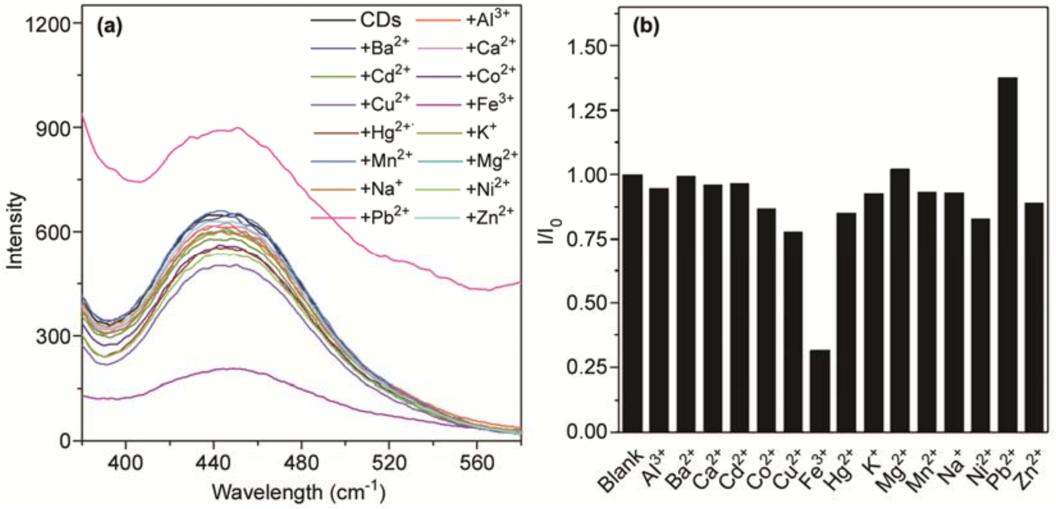

Fig. 2 — (a) Fluorescence spectra of cat-CDs (5.0 μg/mL) in 10.0 mM Tris-HCl solution (pH 7.5) in the presence of 200 μM of metal ions (λ_{ex} = 340 nm), and (b) The intensity ratio of the fluorescence emission bands at 440 nm in the presence of each indicated ion.

functional groups such as carboxylic and phenolic hydroxyl groups. These probes also exhibit fluorescence quenching in the presence of Fe^{3+}, which is ascribed to ultrafast electron-transfer processes. For cat-CDs, it can also be concluded that the Fe^{3+}-induced fluorescence quenching is due to nonradiative electron transfer because of the interaction between the carboxyl group and Fe^{3+}. Ma *et al*., have synthesized a fluorophore by combining pyrene and L-tryptophan, in which the entire indole ring of tryptophan binds to the Pb^{2+} through a noncovalent interaction[12]. Therefore, we think that it will result in interaction between Pb^{2+} and indole rings on CDs surface, which may decrease the distance from indole ring to CDs, and result in enhanced fluorescence due to the strong energy-transfer interactions between the tryptophan and CDs[41].

For sensitivity study, the PL spectra of cat-CDs against Pb^{2+} concentration were measured in the range of 20–200 μM. The whole PL spectrum increases with the addition of Pb^{2+} (Fig. 3a). The values of I/I_0 at 444 nm against Pb^{2+} concentration were plotted (Fig. 3b) and exhibit good linearity against the concentration of Pb^{2+} in the range of 20–200 μM, with a correlation coefficient R^2 = 0.98349. The sensitivity of cat-CDs to Fe^{3+} was also studied in detail. The values of I/I_0 decrease gradually with Fe^{3+} concentration, exhibiting a good linearity against Fe^{3+} concentration in the range of 40–200 μM, with a correlation coefficient R^2 = 0.98134 (Fig. 4).

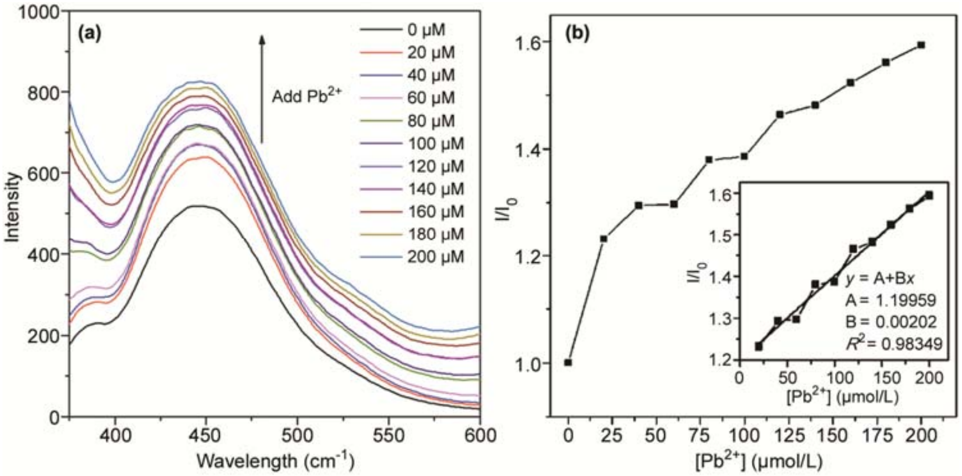

Fig. 3 — (a) Fluorescence spectra of cat-CDs (5.0 μg/mL) in the absence and presence of Pb^{2+} in 10.0 mM Tris-HCl solution (pH 7.5), and, (b) responses of I/I_0 as a function of the Pb^{2+} concentration, λ_{ex} = 340 nm, λ_{em} = 444 nm. [Inset: linear fitting plot of I/I_0 versus Pb^{2+} concentration].

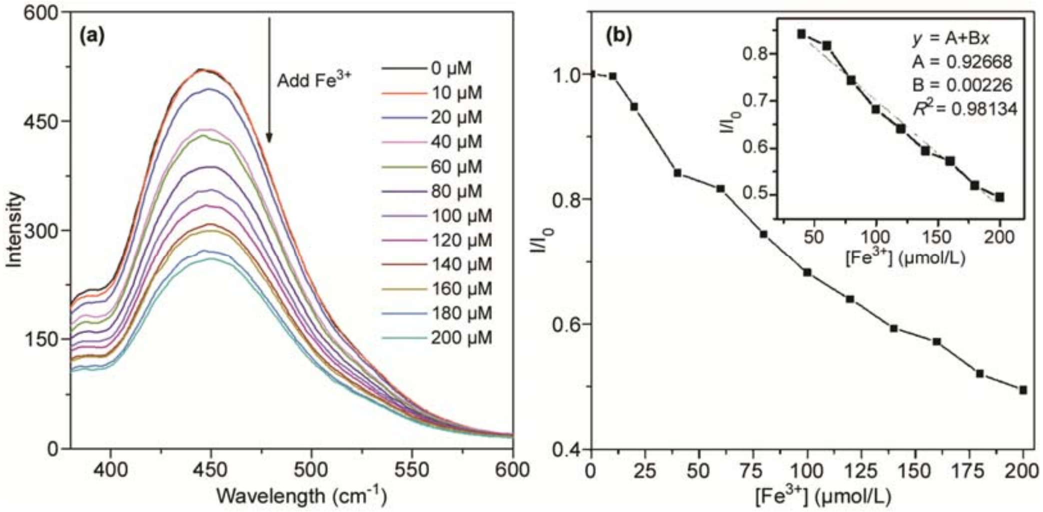

Fig. 4 — (a) Fluorescence spectra of cat-CDs (5.0 μg/mL) in the absence and presence of Fe^{3+} in 10.0 mM Tris-HCl solution (pH 7.5), and, (b) responses of I/I_0 as a function of the Fe^{3+} concentration, λ_{ex} = 340 nm, λ_{em} = 444 nm. [Inset: linear fitting plot of I/I_0 verse Fe^{3+} concentration].

Comparing cat-CDs to tryptophan-containing fluoroionophore sensor reported by Ma *et al.*[12] it is CDs observed that instead of pyrene give signal change in the detection of Pb^{2+}. This result may imply that introducing the part combining with ions in a commercial probe is a possible route to construct a new probe at a low cost with low cytotoxicity. Also, only one single step i.e., the addition of recognizing group in the synthesizing process is required to synthesize such CDs-based probe.

In summary, tryptophan was used to fabricate carbon dots for the purpose of introducing indole on the surface of CDs through a one step process. UV-visible spectra and FTIR imply that indole rings or similar structures exist in the synthesized cat-CDs after hydrothermal process. The cat-CDs have a selective and sensitive fluorescent increase response to lead ion over 14 other metal ions, and a fluorescent quenching response to Fe^{3+}. Further study reveals that the increase of cat-CDs verse Pb^{2+} has a good linearity in the range of 20–200 μM. This approach provides a new insight for preparing ions probe.

Supplementary data

Supplementary data associated with this article are available in the electronic form at http://www.niscair.res.in/jinfo/ijca/IJCA_57A(10)1270-1274_SupplData.pdf.

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