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Rapid detection of Cr(VI) ions based on cobalt(II)-doped carbon dots

Hong-Yu Zhang^{a,1}, Yu Wang^{b,1}, Shan Xiao^a, Han Wang^a, Ji-Hui Wang^{a,*}, Liang Feng^{b,*}^a School of Food Science & Technology, Dalian Polytechnic University, Dalian, Liaoning 116034, PR China^b Key Lab of Separation Science for Analytical Chemistry, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian, Liaoning 116023, PR China

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ABSTRACT

A new type of cobalt(II)-doped carbon dots (CCDs) have been fabricated and used successfully for sensing Cr(VI) ions on the basis of photoluminescence quenching. The structural characterization of as-obtained CCDs was thoroughly performed by transmission electron microscopy (TEM), Fourier transform infrared (FT-IR) and X-ray photoelectron (XPS) spectroscopy. The optical properties were also determined by absorption and fluorescence spectra. By recording 3D fluorescence spectrum, a unique intra-particle Förster resonance energy transfer (FRET) system was investigated. In addition, fluorescence quenching of CCDs was observed in the presence of Cr(VI) ions due to inner filter effect. A good linear relationship between the concentration of Cr(VI) ions and fluorescent intensity was obtained in the range from 5 μM to 125 μM ($R^2=0.99$), and the limit of detection was calculated as 1.17 μM (0.12 ppm for Cr(VI)). Importantly, this method was capable of rapidly detecting Cr(VI) ions in tap water and fish samples, which may be helpful in risk reduction of intake Cr(VI) contamination from water and seafood.

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1. Introduction

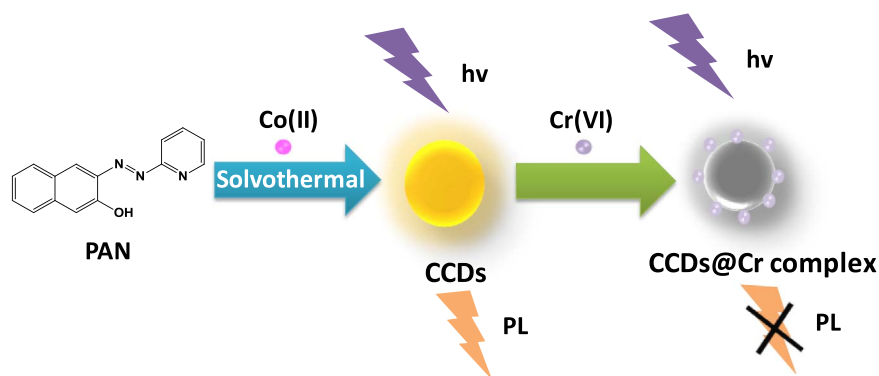
Chromium, as a fatal toxicant, has been paid numerous attention due to its wide usage in stainless steel, automobile parts, leather ware and other industrial products (Chiba et al., 1997; Thyssen et al., 2012). As the second most abundant inorganic groundwater contaminant at hazardous waste sites, the chromium involved in waste water may be taken directly by human through contaminated groundwater or indirectly through aquatic organisms such as fishes. In the year 2011, a serious chromium slag contamination accident occurred in Qujing in Yunnan province of China, and led to the Cr(VI) concentration largely above the Chinese Integrated wastewater discharge standard of the Cr(VI) (GB, 8978-1996). Most recently, a severe surface water pollution and concomitant drinking water contamination by Cr(VI) around smelters was also reported at South Africa, which holds the majority of the world's viable chromite resources (Loock-Hattingh et al., 2015). Meanwhile, a very recent investigation reported that the chromium concentrations in muscles of different wild marine fishes from Hainan coastal areas (South China Sea) (Liu et al., 2015) are ranged from 1.38 to 4.36 mg/kg (depending on species) which are in excess of the permitted maximum level of aquatic animals and their products (2 mg/kg) based on the Chinese National

Standard of Food Safety (GB, 2762-2012). These urge a rapid detection for the Cr(VI) concentration in discharge water as well as food to avoid excessive intake of Cr(VI). However, the current methods for Cr(VI) detection mainly rely on large equipment including atomic absorption spectrum (AAS), ion chromatography (IC), inductively coupled plasma mass spectrum (ICP-MS), and so on (Hagendorfer and Goessler, 2008; Michalski, 2005; Ueda et al., 1997). These methods generally require tedious sample pretreatments and rich expertise which strongly limit their usage in the rapid detection. Thus, a simple, sensitive and low-cost method for the detection of Cr(VI) ion in real samples is highly desirable.

During the last decade, the boom of nanomaterials science provided numbers of novel chemosensors for a variety of analytes. Recent literatures provide some chemosensors for Cr(VI) detection (Campos et al., 2015; Toal et al., 2005) Although these sensors offer splendid sensitivity to Cr(VI), they still suffer either from trivial fabrication (Punrat et al., 2016) or poor selectivity (Liu et al., 2016). Among various nanomaterials, carbon dots (CDs), the size of which is generally less than 10 nm, have drawn tremendous attentions on account of their unique properties such as small particle size, splendid chemical inertness, superior anti-photobleaching, easy functionalization and good biocompatibility (Hu et al., 2016; Li et al., 2015; Lim et al., 2015; Wang et al., 2015a; Wen et al., 2015; Yao et al., 2014; Yuan et al., 2016). Especially, in the development of less-toxic sensing platform which can avoid re-contaminating during the operation, carbon dots have already exhibited their splendid talents. As such, to find a green chemosensor that has a high sensitivity and selectivity toward Cr(VI) ions based on CDs is

* Corresponding authors.

E-mail addresses: wangjh@dipu.edu.cn (J.-H. Wang), fengl@dicp.ac.cn (L. Feng).¹ These authors contribute equally to this work.



Scheme 1. Schematic of Co(II)-doped CDs for Cr(VI) ions detection. PL: photoluminescence; CCDs: Co(II)-doped CDs.

very expected.

Recently, we introduced a methodology for fabricating manganese doped CDs which possessed distinctive optical properties and extra sensing capability in virtue of their metal-coordination scaffold (Wang et al., 2015b). In this work, by doping a different metal impurity, we herein report a novel cobalt(II)-doped CDs (CCDs) which exhibit a good selectivity and sensitivity for Cr(VI) ions through a facile one-step solvothermal method by using 1-(2-Pyridylazo)-2-naphthol (PAN) and cobalt chloride as precursors (Scheme 1). By experiments, we found that the surface groups of CCDs can interact with Cr(VI) by forming non-radiative complex which consequentially weakens the surface-trap-related emission of CCDs. Owing to the unique intra-particle Förster resonance energy transfer (FRET) from surface-trap-emission to Co-related emission, the whole emission band of CCDs exhibits a simultaneous decrease. The limit of detection (LOD) is 1.17 μM (0.12 ppm for Cr(VI)) with a linear quantitation range of 5 μM to 125 μM ($R^2=0.99$). In addition, the detection of Cr(VI) in spiked tap water and fish samples were also performed and satisfactory recoveries were obtained. Importantly, the results were in good agreement with those obtained from inductively coupled plasma optical emission spectroscopy (ICP-OES).

2. Experimental

2.1. Chemicals and materials

1-(2-Pyridylazo)-2-naphthol and all the anions ($\text{Cr}_2\text{O}_7^{2-}$, SO_4^{2-} , $\text{H}_2\text{PO}_4^{2-}$, CO_3^{2-} , NO_2^- , NO_3^- , F^- , Br^- , I^- , S^{2-}) were purchased from Alfa Aesar (Shanghai, China). The metal ions (K^+ , Ca^{2+} , Na^+ , Mg^{2+} , Zn^{2+} , Fe^{3+} , Cu^{2+} , Cr^{3+} , Fe^{2+}) were bought from Shanghai Jingchun Reagent Co., Ltd. (Shanghai, China). Ethanol, ethyl acetate, nitric acid and hydrogen peroxide were obtained from Tianjin Kemiou Chemical Reagent Co., Ltd. (Tianjin, China). Dialysis kits, Pure-A-Lyzer 3500 kDa, was purchased from Sigma Aldrich. All commercial chemicals were used as received without further purification. Deionized water was used for the dilution throughout the experiment.

2.2. Instrument for characterization of CCDs

The UV–Vis absorption spectra were recorded by a Persee TU-1901 UV–Vis spectrophotometer, and all fluorescence spectra of the CCDs were measured by F-4600 fluorescence spectrophotometer. The surface morphology of CCDs was determined using JEM-2100 transmission electron microscopy (TEM) operating at 200 kV. The Thermo Nicolet IS50 Fourier transform infrared (FT-IR) spectrometer was used to analyze the chemical bonding information of as-prepared Co(II)-doped CDs. The X-ray

photoelectron spectroscopy (XPS) was employed to investigate the content of elements and the conformation of the CCDs by Thermo Scientific K-Alpha instrument. The fish sample was digested by a MDS-6 G Microwave Digestion System.

2.3. Synthesis of Co(II)-doped CDs

The synthesis of Co(II)-doped CDs was based on our previous method with a slight change. Specifically, 49.85 mg (0.2 mmol) PAN and 95.17 mg (0.4 mmol) cobalt chloride were dissolved into 10 mL ethanol with assistance of ultrasonic treatment for about 20 min. The homogeneous mixture was then transferred into a 25 mL Teflon-lined stainless autoclave, and was heated to 180 °C. The reaction was kept for 4 h and then cooled down to room temperature. The product was dried to remove solvent. The as-obtained powder was dissolved in 50 mL ethyl acetate (EA) and extracted with 50 mL deionized water, and the organic phase was collected and dried to give crude CCDs. The fluorescent CCDs was finally obtained by dialysis against ethanol with a dialysis kit (3500 kDa MWCO) for 48 h. The CCDs powder were acquired by nitrogen-blow method and re-dispersed in ethanol at a concentration of 0.64 mg/mL for further use. For comparison with CCDs, PAN carbon dots (PCDs) share the same synthetic route as that of CCDs but without the addition of cobalt chloride salts.

2.4. Detection of Cr(VI) ions

In the standard experiment, the CCDs powder was dispersed in ethanol with a concentration of 40 $\mu\text{g/mL}$. $\text{Cr}_2\text{O}_7^{2-}$ solution with different concentrations was added to the CCDs ethanol solution. The mixture was shaken up and incubated for five minutes at room temperature to ensure the complete reaction. The fluorescence spectrum of homogeneous solution was measured by F-4600 fluorescence spectrophotometer at the excitation wavelength of 370 nm. Moreover, the comparative experiments were also conducted with other nine anions and nine metal ions under the same condition.

2.5. Calculation of the quantum yield

The quantum yield of CCDs was determined basing on an established procedure. Fluorescein (QY=0.925 at 496 nm) dissolved in 0.1 M NaOH (refractive index, 1.33) was used as reference (Magde et al., 2002), while the CCDs was dispersed in ethanol (refractive index, 1.36). The absorbance of the two solution at 496 nm was kept below 0.1 to prevent the reabsorption phenomenon. Moreover, both solutions were measured in the same instrumental condition. The quantum yield was calculated as follows:

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