



Multi sensing functions integrated into one carbon-dot based platform via different types of mechanisms



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ABSTRACT

Multi-mode sensing achieved by one sensor, which can be manufactured cost-effectively and facily, is considerably attractive for analysts. In this work, triple sensing modes for Fe³⁺, Cr(VI) and ascorbic acid (AA) were integrated into one carbon-dot-based platform via different types of mechanisms. Firstly, the highly luminescent carbon dots (CDs) which would act as the triple-mode platform was prepared by a simple hydrothermal pyrolysis of citric acid and acrylamide at 180 °C for 10 h, with a high quantum yield being 55.4%. In HAC-NaAc buffer solution, the CDs was selectively quenched by Fe³⁺ ascribed to specific binding affinity causing photo-induced electron transfer (PET). However, the interference of Fe³⁺ on the CDs was masked in PBS solution, and the fluorescence of the CDs was gradually turned off with the concentration of Cr(VI) increasing due to the inner filter effect (IFE). On the other hand, the fluorescence of the CDs/Cr(VI) system was increasingly recovered by AA owing to the elimination of IFE (EIFE) resulting from the reduction of Cr(VI). Under the optimized conditions, the linear ranges for the selective detection of Fe³⁺, Cr(VI) and AA were found to be 1–40, 2–180 and 8–160 μM, with the limits of detections as low as 0.87, 2.10 and 0.91 μM, respectively. Furthermore, the proposed methods were successfully applied to directly detect Fe³⁺, Cr(VI) and AA in real samples (Fe³⁺ in tap water and lake water, Cr(VI) in lake water and industrial water and AA in *Actinidia chinensis* Planch and human urine) with high accuracy. Interestingly, AA excreted in human urine after oral administration of AA tablets was fluorescently monitored in real-time by the CDs/Cr(VI) system.

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1. Introduction

Multi-mode sensing achieved by one chemosensor with high selectivity, sensitivity and accuracy, which might be manufactured cost-effectively and facily with easily obtained source, is considerably attractive for analysts. Recently, a new emerging carbon-based nanomaterial, carbon dots (CDs), might fulfill such requirement, because they have high optical performance [1], and can be prepared by easily available and cheap precursors via facile synthesis approaches. Bright photoluminescence [2], as well as excellent photostability [3], favorable biocompatibility and low toxicity [4], are widely believed to be the high performance of CDs. To date, more and more materials which are easily available and cheap, such as citric acid [2], amino acid [5], wide natural sources including orange juices [6] and apple juices [7], grape peels [8], watermelon peels [9] and vegetables [10], had been reported as

precursors to prepare CDs with high performance. Combined with facile preparation methods, commonly including electrochemical oxidation [11], combustion/thermal [12], microwave heating [13], chemical oxidation [14], hydrothermal carbonization [15], and pyrolysis [16], CDs can be obtained considerably cost-effectively. In addition, the response signals of CDs to analytes may originate from fluorescence quenching [17] and enhancement [18] via different mechanisms, as well as surface engineering will endow CDs more functions [19]. Multi sensing modes can be, therefore, integrated into one CD-based sensor manufactured cost-effectively and facily.

Most of the CD-based sensors had been reported for single-mode sensing, such as Hg²⁺ [3,15], Cu²⁺ [10,14], Fe³⁺ [2], Ag⁺ [12,18], H₂O₂ [17], HOCl [20], Methylene blue [21], NO₂ [22], O₂⁻ [23] and tetracycline [13]. Dual-mode sensing by one CD-based sensor had been reported by a few studies. For example, two types of metal ions, Fe³⁺ and Ag⁺, were selectively detected by one chemosensor based on fluorescent carbon dots [24]. Fe³⁺ and Cd²⁺ were individually measured by a CD-based sensor synthesized by reflux of cysteine in concentrated H₂SO₄ [25]. Qu's group [26] employed one CD-based

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sensor prepared by hydrothermal treatment of dopamine to successfully detect Fe^{3+} and dopamine in aqueous solution. The CDs from pyrolysis of Assam tea was also reported as a dual-mode sensor to detect dopamine and ascorbic acid [27]. Triple-mode sensing for metal ions by one CD-based sensor had been reported by our group, in which the selectivity of the CDs capped with COO^- can be switched by different buffer solutions, and the CD-based sensor was successfully applied to the individual detection of Fe^{3+} , Hg^{2+} and Pb^{2+} ions in mineral water and tap water samples via PET mechanism [28]. A new type of dual-emission CDs prepared via one-step thermal decomposition of AA and alcohol had been performed as a highly efficient and sensitive triple-mode sensor for the selective detection of Fe^{3+} , Bi^{3+} and Al^{3+} [29].

In this work, another new triple-mode sensing for Fe^{3+} , Cr(VI) and AA in aqueous solution using one CD-based sensor via different mechanisms was described. Iron is the most essential trace metal element in all living organisms, which plays important roles in many chemical and biological processes in living organism, such as the transport of oxygen, storage metabolism, electron transfer in enzymatic reaction and in mitochondrial respiratory chain. Its deficiency or overloading in human body can disturb cellular homeostasis and metabolism, probably resulting in hepatitis, cancer, neurodegeneration, Alzheimer's disease and Parkinson's disease [30,31]. Cr(VI) is known to be seriously hazardous because it has acutely carcinogenic, mutagenic, teratogenic effects on human beings [32]. AA is an important vitamin (Vitamin C) and a natural antioxidant in the human body. It plays crucial roles in biological activities, such as iron uptake in human intestinal cells, collagen synthesis, immune responses, and organism formation such as ligaments, blood vessels, cartilage, bones, and tendons, and treatments for scurvy and cancer [33,34].

It is of great interest to establish cheap and facile methods to detect Fe^{3+} , Cr(VI) and AA with high selectivity and sensitivity. Common approaches for the detection of Fe^{3+} and Cr(VI) are UV-vis spectroscopy, atomic absorption spectrometry (AAS), electrochemistry, inductively coupled plasma atomic emission (ICP-AES) [35–37]. And analytical methods for AA generally include capillary electrophoresis, electrochemistry, liquid chromatography, fluorescence, spectrophotometry and chemiluminescence (CL) [38–40]. To integrate different approaches that might need expensive devices and complicated processes for the detection of Fe^{3+} , Cr(VI) and AA into one CD-based sensor is considerably significant.

In this work, highly luminescent carbon dots (CDs) with a high quantum yield of 55.4% was facilely prepared by a hydrothermal method using citric acid and acrylamide as precursors. Notably, the fluorescence of the CDs can be selectively quenched by Fe^{3+} ions in HAC-NaAc solution at pH = 5.0, attributed to photo-induced electron transfer (PET) caused by the specific interactions between Fe^{3+} and functional groups on the surface of the CDs. And its excitation peak at 340 and emission peak centered at 420 nm can be overlapped by the absorption bands centered at 350 and 440 nm of Cr(VI) , resulting in the inner filter effect (IFE) of Cr(VI) on the fluorescence of the CDs in a highly efficient way. However, Cr(VI) can be reduced by AA, and the IFE of Cr(VI) on the CDs will be eliminated upon the addition of AA, resulting in an increase in fluorescence of the CDs/ Cr(VI) system. Accordingly, it inspired us to develop a method to detect Fe^{3+} , Cr(VI) and AA using one CD-based platform via different types of mechanisms including PET, IFE and elimination of IFE (EIFE), as shown in Scheme 1. The proposed method was successfully applied to directly detect Fe^{3+} , Cr(VI) and AA in real samples (Fe^{3+} in tap water and lake water, Cr(VI) in lake water and industrial water and AA in *Actinidia chinensis* Planch and human urine). Although the components of the real samples are very complicated, the spiked Fe^{3+} , Cr(VI) and AA can be recovered from these samples with high accuracy. It sug-

gests that the proposed method is highly selective. Interestingly, AA excreted in human urine after oral administration of AA tablets was fluorescently monitored in real-time by the CDs/ Cr(VI) system.

2. Experimental section

2.1. Materials

AgNO_3 , CaCl_2 , NiCl_2 , CoCl_2 , CuCl_2 , $\text{Fe(NO}_3)_3$, Hg(Ac)_2 , MgCl_2 , MnSO_4 , $\text{Pb(NO}_3)_2$, AlCl_3 , BaCl_2 , CrCl_3 , NaCl , LiNO_3 , KCl and $\text{Zn(NO}_3)_2$ were purchased from Damao Chemical Corp (Tianjin, China). Citric acid, Acetic Acid, Sodium acetate trihydrate, Glycine (Gly), Glutamic acid (Glu), Histidine (His), H_2O_2 , Urea, Glucose (Glc), Fructose (Fru), Lactose (Lac), Ethylene glycol (EG), NaH_2PO_4 , Na_2HPO_4 and Acrylamide were obtained from Aladin Ltd. (Shanghai, China). All chemicals were used without any further purification. The ultrapure water used throughout all the experiments was purified through Water Purifier Nanopure water system (18.3 M Ω cm). Tap water, lake water, urine and *Actinidia chinensis* Planch were used as the real samples. Generally, tap water contains a lot of cations and anions [41]. Besides cations and anions, there are many organic matters present in lake water [42]. The components of urine include nitrogen-containing products of protein decay, and also inorganic salts [43]. *Actinidia chinensis* Planch has plenty of AA, and its components are much more complex.

2.2. Characterizations

The morphology and size of CDs were analyzed by transmission electron microscopy (TEM, Hitachi HT-7700, operated at 80 kV). Fluorescent spectra were performed by a fluorescence spectrometer F-4600 (Hitachi, Japan). The X-ray diffraction (XRD) of the carbon dots was collected using a D8 ADVANCE X-ray diffractometer (Bruker AXS, German) with $\text{Cu-K}\alpha$ radiation (40 kV, 40 mA, $\lambda = 1.5418 \text{ \AA}$) at a scanning rate of 1° min^{-1} in the range from 10° to 80° . The Fourier transform infrared spectroscopy (FTIR) spectrum of the CDs was recorded using a FT-IR200 spectrometer (Thermo, America) using KBr pellets technique, over the ranging from 400 to 4000 cm^{-1} . The quantum yields (QYs) of the prepared carbon dots were determined using quinine sulfate in 0.1 M H_2SO_4 (literature QY: 54.6%) as the standard sample by comparing the integrated fluorescence intensities (excitation at 360 nm) and absorbance values at 360 nm of the carbon dots aqueous solutions with those of quinine sulfate [15,44].

2.3. Synthesis of the CDs

The CDs was synthesized by a facile hydrothermal method. Briefly, 200 mg citric acid and 400 mg acrylamide were dissolved with 25 mL ultrapure water in a 50 mL Teflon-lined stainless steel autoclave, and then heated at 180°C for 10 h. The resultant solution was purified by gel column (G-25) with ultrapure water as the eluent, and the wavelength of 365 nm was used to monitor the fraction eluted from the column. The solid powder of the CDs was collected from the fractions by lyophilization.

2.4. Detection of Fe^{3+} , Cr(VI) and AA in aqueous solution

For the detection of Fe^{3+} and Cr(VI) , Fe^{3+} was added into HAC-NaAc buffer solution, and Cr(VI) into PBS solution of the CDs (0.03 mg mL^{-1} , pH 5.0) at various concentrations, then their fluorescence spectra were recorded after reaction for 20 min. For the detection of AA, CDs/ Cr(VI) system was established by mixing CDs (0.03 mg mL^{-1}) and Cr(VI) ($10 \mu\text{M}$) in PBS solution, thereafter, AA was added into CDs/ Cr(VI) system at different concentrations,

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