



Ratiometric fluorescence detection of Cd²⁺ and Pb²⁺ by inner filter-based upconversion nanoparticle-dithizone nanosystem

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ABSTRACT

This paper reports a fluorescence sensor based on inner filter effect (IFE) between upconversion nanoparticles (UCNPs) and dithizone for the highly selective and sensitive detection of cadmium ion (Cd²⁺) and lead ion (Pb²⁺) in black tea. The fluorescence at 546 nm, 657 nm, 758 nm and 812 nm were obtained and applied as signal indicator upon upconversion nanoparticles excitation at the single wavelength of 980 nm. With the formation of UCNPs-dithizone mixed system pH at 8, the dithizone-Cd²⁺ complex increases with increasing in concentration of Cd²⁺, which cause the bathochromic shifting in absorption bands and an upconversion fluorescence (UCF) quenching at 546 nm; at pH6, the absorption band of dithizone shows a blue shift with addition of Pb²⁺, leading an upconversion fluorescence recovering at 657 nm. However, in the presence/absence of Cd²⁺/Pb²⁺, the fluorescence at 758 nm and 812 nm were not influenced. This implies the Cd²⁺ and Pb²⁺ concentration could be monitored based on the fluorescence ratio I_{546}/I_{758} and I_{657}/I_{758} respectively. Under optimal condition, the fluorescence show a good linear within the ranges of 0.01 μM–1.0 μM for Cd²⁺; and 0.025 μM–1.0 μM for Pb²⁺, with a detection limit of 3.7 and 8.4 nM achieved. The method was applied for Cd²⁺ and Pb²⁺ in real sample (black tea and tap water) with recoveries of 99.6% to 108% and RSD value in the range of 0.96 to 1.23 for Cd²⁺, with recoveries of 96% to 103.2% and RSD value in the range of 0.98 to 1.27 for Pb²⁺.

1. Introduction

Tea is the most popular consumed beverage that contains several nutrients such as flavonoids, minerals and trace elements good for human health. However, the trace heavy elements in tea such as copper ion (Cu²⁺), mercury ion (Hg²⁺), lead ion (Pb²⁺), chromium ion (Cr²⁺), cadmium ion (Cd²⁺), manganese ion (Mn²⁺) raise grave issues about its safety [1]. According to the World Health Organization (WHO), levels of lead, cadmium, chromium, and other heavy metals must be controlled below defined limits. Among the heavy metals, cadmium ion (Cd²⁺) and lead ion (Pb²⁺) have been reported to pose a series of adverse health threats to humans such as nervous, cardiovascular, digestive, and reproductive systems disorders [2–6]. As a result, the World Health Organization and Environmental Protection Agency (EPA) have strictly defined the concentration limit of Pb²⁺ as low as 10 ppb [7]; and Cd²⁺ as low as 5 and 3 ppb [8]. Sequel, developing a sensitive, rapid and simple analytical method for precise monitoring of trace cadmium ions and lead ions in tea is becomes relevant to safeguarding its safety for consumes.

Currently, conventional analytical methods such as atomic absorption spectrometry (AAS), inductive coupled plasma emission

spectrometry (ICP-AES), inductively coupled plasma-mass spectrometry (ICP-MS) and anodic stripping voltammetry (ASV) are employed measure cadmium and lead ions [9,10]. However, these conventional analytical methods scope of usage are limited by cost, requirement of hired skilled labour for their operation, chemical dependent for sample pretreatment as well as their lack of real-time applicability. In order to address aforementioned limitations, many new sensors such as chemosensor [11–13], electrochemical sensors [14–16] and biosensors [17,18] have been utilized to detect trace Cd²⁺ and Pb²⁺. Varied deficiencies still exist in the new sensors despite their individual strengths. For instance, biosensors are easily influenced by detecting conditions whereas with electrochemical sensors have shorter service span. Chemosensor compared to biosensor and electrochemical sensor is stable and remained not influenced by with their detection conditions. However, fluorochrome containing chemosensors are disturbed by background fluorescence. As such, fabrication of a new chemosensor that can prevent background fluorescence interference becomes very relevant.

Compared to traditional fluorophores with Stokes emission, rare-earth doped upconversion (UCNPs) with anti-Stokes process can emit a higher energy photon through absorbing two or more low energy

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photons [19–24]. Upconversion nanosensors have many of unique demerits—allows deep penetration deep, have high chemical stability, large signal-to-noise ratio, shape absorption, and gives emission under 980 nm excitation [25–27]. Up till now, upconversion nanoparticle materials have successfully been applied to sensing [28,29], cell imaging [30] and laser cooling [31]. Additionally, many new sensors consist of upconversion nanoparticle materials for DNA-functionalized upconversion for detection of Hg^{2+} [32], and dual fluorescence resonance energy transfer (FRET) system for detection of Pb^{2+} and Hg^{2+} [33] have been reported. However, the fluorescence resonance energy transfer (FRET) detection mechanism utilized in the above sensors has a limitation as regard the requirement of distance between fluorescence donor and acceptor. Inner filter as detection mechanism, which is capable of surmounting this limitation of fluorescence resonance energy transfer (FRET), has successfully utilized in the detection of Sudan I-IV [34], F^- [35], chromium (VI) [36], uric acid [37] and H_2O_2 [38] based on more simple and effective reported method, giving import to the need for the development of a new chemosensor based on inner filter for Pb^{2+} and Cd^{2+} detection.

In this research, we propose an upconversion fluorescence chemosensor for rapid and ultrasensitive detection of cadmium ion and lead ion in black tea (Scheme 1). The detection of Cd^{2+} is attributed to the fluorescence quenching of UCNPs by dithizone through IFE and the formation of dithizone- Cd^{2+} complex, and whereas that for the detection of Pb^{2+} is linked to the fluorescence recovering of UCNPs in which case dithizone- Pb^{2+} complex is formed to render IFE ineffective. In the absence of Cd^{2+} , the upconversion fluorescence at 546 nm could hardly be influenced by dithizone. However, in the presence of Cd^{2+} , the absorption peak of dithizone shows a bathochromic shift, causing an upconversion fluorescence quenching at 546 nm through inner filter. On the other hand, the upconversion fluorescence at 657 nm was influenced by dithizone, however the absorption peak of dithizone shows a blue shift with the addition of Pb^{2+} , leading an upconversion fluorescence at 657 nm recovering. On the basis of these changes, a sensitive sensor for Cd^{2+} and Pb^{2+} in black tea was developed.

2. Experiments

2.1. Materials

Rare-earth chloride hexahydrate: $\text{GdCl}_3 \cdot 6\text{H}_2\text{O}$ (99.99%) $\text{YCl}_3 \cdot 6\text{H}_2\text{O}$ (99.99%), $\text{YbCl}_3 \cdot 6\text{H}_2\text{O}$ (99.99%), $\text{ErCl}_3 \cdot 6\text{H}_2\text{O}$ (99.99%), 1-octadecene (> 90%) and oleic acid (> 90%), 3-aminopropyltrimethoxysilane and tetraethyl orthosilicate (TEOS > 98%) were purchased from Macklin company (Shanghai, China). Dithizone and other reagents were purchased from Sinopharm Chemical Reagent (Shanghai, China).

2.2. Instrumentation

The synthesized upconversion nanoparticle was characterized before and after amino-modification by Nicolet Nexus 470 Fourier transform infrared spectrophotometer (Thermo Electron Co. U.S.A) using a KBr detector, JEM-2100HR transmission electron microscope (TEM, JEOL Ltd., Japan) operated at 120 KV, X-ray diffraction (XRD) measurements were carried out a Bruker D4 diffractometer at a scanning rate of $5^\circ/\text{min}$ in the 2θ ranged from 10 to 70° .

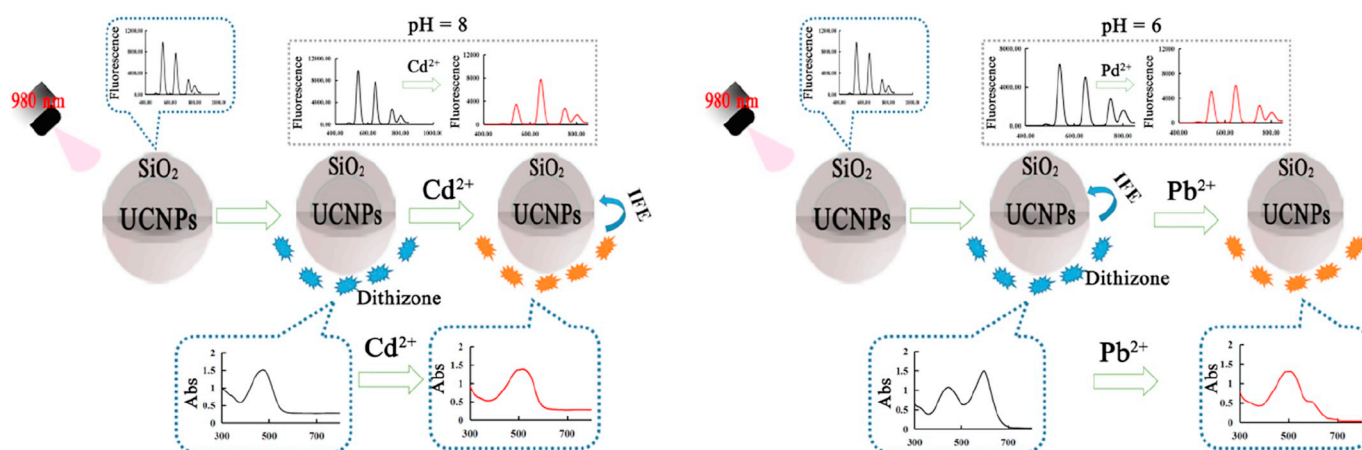
2.3. Fabrication and modification of UCNPs

Oleic acid-capped $\text{NaYF}_4:\text{Yb}$, Ho UCNPs were prepared by a modified method described in previous research [39]. 3 mL of oleic acid and 7 mL of 1-octadecene were added into a 250 mL three necked flask containing 2 mL of RECl_3 (0.2 M, RE = Y/Gd (78%), Yb (20%), Ho (2%)) in methanol, and the solution was heated to 160°C for 40 min and then cooled down to 25°C . Thereafter, 10 mL ethanol of NH_4F (1.5 mmol) and NaOH (1 mmol) was added dropwise under vigorous stirring conditions and the resultant solution heated to 70°C for 30 min to allowed the ethanol to evaporate. Finally, the solution was heated to 300°C under argon for 1 h and cooled down to room temperature. The resulting nanoparticles were precipitated by the addition of ethanol, centrifuged at 8000 rpm for 10 min, washed with ethanol and cyclohexane three times, and then dried at 60°C for 8 h.

To acquire water-solution upconversion nanoparticle, the detailed amino-modification procedure was done as follows: 0.2 g UCNPs was mixed in 20 mL of ethanol under ultrasound; thereafter 20 mL of distilled water and 1.25 mL of ammonia (25%) were added to flask containing mixture. After the flask was heated to $60\text{--}70^\circ\text{C}$, 200 μL of tetraethoxysilane (TEOS) was added dropwisely and maintained for 10 h; and followed by the dropwise addition of 200 μL of 3-aminopropyltriethoxysilane maintained for 3 h at $60\text{--}70^\circ\text{C}$. Finally the product of reaction was washed three times with distilled water-ethanol (1:1) and dried in oven at 50°C for 8 h.

2.4. Spectroscopy assays of Cd^{2+} and Pb^{2+} using UCNPs-dithizone mixed nanosystem

Cadmium and lead ions in the form of chloride were prepared using deionized water as solvent. 0.1 M of HCl and/or NaOH solution was prepared to adjust pH. 2 mL of dithizone solution at an optimal concentration (0.1 mg/mL for Cd^{2+} , 0.15 mg/mL for Pb^{2+}) was added to a 5 mL centrifuge tube containing equal amounts of 0.5 mg/mL UCNPs. Then Cd^{2+} solution ($\text{cp} = 0.01, 0.025, 0.05, 0.1, 0.25, 0.5, 0.75, 1.0 \mu\text{M}$) and Pb^{2+} solution ($\text{cp} = 0.025, 0.05, 0.1, 0.25, 0.5, 0.75, 1.0 \mu\text{M}$) were respectively added to content of a set of glass bottles to



Scheme 1. Schematic illustration of the process developing UCNPs-dithizone mixed system to detect Cd^{2+} and Pb^{2+} .

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