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Ratiometric fluorescence sensing of mercuric ion based on dye-doped lanthanide coordination polymer particles

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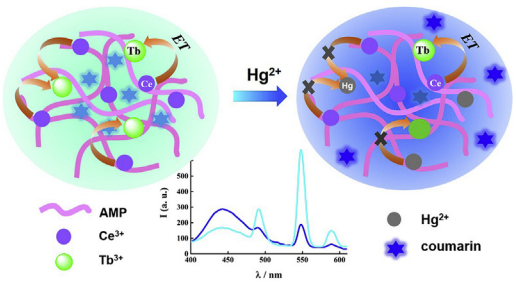
HIGHLIGHTS

- The dye-doped lanthanide infinite coordination polymer was synthesized by a simple self-assemble process.
- The obtained coumarin@Ce/Tb-AMP showed dual response towards Hg^{2+}.
- The ratiometric sensor exhibited a wide linear range, low detection limit, good selectivity, and anti-interference ability.
- It was successfully applied in detecting Hg^{2+} in drinking water and human blood serum with satisfactory results.

GRAPHICAL ABSTRACT



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ABSTRACT

This work focused on the development of a novel ratiometric fluorescence sensor for detection of Hg^{2+} by using dye-doped lanthanide infinite coordination polymer (Ln-ICP) particles. The dye-doped Ln-ICP used herein was prepared by self-assemble of adenosine monophosphate (AMP) with Ce^{3+} and Tb^{3+} (Ce/Tb-AMP) through self-adaptive chemistry, in which the fluorescent dye coumarin was encapsulated during the assembly process as a guest molecule. Under 310 nm irradiation, the obtained coumarin@Ce/Tb-AMP itself emitted characteristic green luminescence of Tb^{3+}, accompanied with a weak fluorescence at 445 nm originated from coumarin encapsulated in the Ce/Tb-AMP networks. The fluorescence emission of coumarin became strong when it was released to the solution. In the presence of Hg^{2+}, the coumarin@Ce/Tb-AMP was destroyed due to the specific coordination interaction between AMP and Hg^{2+}, which leaded to the release of coumarin to the solution meanwhile. Consequently, the fluorescence of Ce/Tb-AMP was quenched, while that of coumarin enhanced. On the basis of this strategy, we developed a novel ratiometric fluorescent sensor for the detection of Hg^{2+} by measuring the ratio of fluorescent intensity of the coumarin@Ce/Tb-AMP suspension, which showed a wide linear range from 0.08 to 1000 nM and detection limit of 0.03 nM with high selectivity and sensitivity. Furthermore, the constructed ratiometric fluorescent sensor was successfully applied in detecting Hg^{2+} in drinking water and human blood serum (HBS) with satisfactory results.

1. Introduction

As one kind of most toxic heavy metal, mercury pollution is greatly hazardous and widespread to environmental and biological

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systems especially in nowadays with the rapid development of modern industry. Owing to the non-biodegradable property, it became a kind of persistent contaminant once it was released into the environment, and thus bio-accumulated in the food chain [1,2]. Moreover, Hg^{2+} can break S-S or S-H bonds in protein or enzymes because of its strong affinity to S-containing ligands, and then causes serious damage to human health by leading to a wide variety of diseases in brain, central nervous system and kidney even at very low level [3–6]. Therefore, it is urgent and significantly necessary to exploit the highly selective and sensitive method for the rapid recognition and detection of Hg^{2+} in the area of life security and environmental protection.

Amongst the various detection techniques, fluorescent analytical method has drawn a great deal of attention due to its appealing advantages, including rapid response, facile operation, versatility, high sensitivity and selectivity, wide spread availability of equipment [2,5,7–10]. To date, a variety of fluorescent probes have been synthesized by generally functionalizing a fluorophore with the recognition group for specific targeted to Hg^{2+} [6,11–13]. However, the practical applications have been limited by several factors, such as the complicated and time-consuming synthesis of probes, toxic organic reagents, poor water-solubility [5,14]. In addition, most of these sensors displayed fluorescence "turn-on" or "turn-off" response upon specific binding with Hg^{2+}. Such a single change in fluorescence intensity could be easily influenced by various factors associated with instrument and environment, and thus prevented their further practical applications. Ratiometric fluorescent methods can overcome the inherent problems by simultaneously recording ratio signals for two emission intensities at different wavelengths, which largely eliminates the fluctuations both arising from instrument and environment, and thus makes it more suitable for the practical applications [15–20].

In this work, we demonstrated a ratiometric fluorescent method for Hg^{2+} assay based on dye-doped lanthanide infinite coordination polymer (Ln-ICP) particle, which combined the unique optical properties of Lanthanide-based luminescence including long fluorescence lifetime, large Stokes and/or anti-Stokes shifts and sharply spiked emission bands [21–24], as well as the adaptive inclusion ability of nucleotide/lanthanide particles [25]. Herein, the dye-doped Ln-ICP was prepared by self-assemble of adenosine monophosphate (AMP) with Ce^{3+} and Tb^{3+} to construct the supramolecular networks, in which fluorescent dye coumarin was encapsulated as a guest molecule through adaptive inclusion ability. The obtained coumarin@Ce/Tb-AMP displayed greenish-blue fluorescence under excitation, composing both the strong characteristic green emissions of Tb^{3+} due to the efficient energy transfer from Ce^{3+} as well as the growing supramolecular networks bind with AMP, and weak luminescence of coumarin. Upon the presence of Hg^{2+}, on the one hand, the proper coordination environment of Tb^{3+} was destroyed owing to the high affinity of Hg^{2+} to AMP [26], and thus its luminescence decreased accordingly. On the other hand, the release of encapsulated coumarin to the solution occurred meanwhile, resulting in the increase of its fluorescence. Therefore, the strategy of dual signal response of coumarin@Ce/Tb-AMP provided a straightforward method for the ratiometric assay for Hg^{2+}, and high sensitivity could be expected by the amplified signal readout through readings of two channels simultaneously. To the best of our knowledge, the ratiometric fluorescent method for the detection of Hg^{2+} based on the dye-doped Ln-ICP has not been mentioned so far.

2. Materials and methods

2.1. Chemicals

Adenosine monophosphate (AMP) and 7-amino-4-methyl coumarin (coumarin) were purchased from Sangon Biotech Co., Ltd. (Shanghai, China). Terbium nitrate pentahydrate ($Tb(NO_3)_3 \cdot 5H_2O$, >99.9%), cerium nitrate hexahydrate ($Ce(NO_3)_3 \cdot 6H_2O$, >99.9%), 2-[4-(Hydroxyethyl)-1-piperazinyl] ethanesulfonic acid (HEPES), mercury nitrate ($Hg(NO_3)_2$) standard solution, metallic salts (e. g., NaOH, KCl, $AgNO_3$, $MgCl_2$, $MnCl_2$, $Pb(NO_3)_2$, $CaCl_2$, $ZnCl_2$, $CdCl_2$, $FeCl_3$, $FeCl_2$, $FeCl_3$, $AlCl_3$, $Ni(NO_3)_2$, $CoCl_2$, $Cu(NO_3)_2$, CuCl) and other chemicals, such as amino acids, uric acid (UA), ascorbic acid (AA), dopamine (DA) and glucose were obtained from Aladin Co. Ltd. (Shanghai, China). HEPES buffer solution (100 mM) was prepared by dissolving HEPES in ultrapure water, and the pH was adjusted to 7.4 through NaOH solution (1.0 M). All the chemicals involved were of analytical grade and used without further purification. Ultrapure water used in the experiments was purified by a Thermo Scientific Barnstead GenPure water purification system (Thermo Fisher Scientific Co. Ltd., Shanghai, China).

The drinking water samples were obtained from a local supermarket. The health human blood serum (HBS) samples were obtained from healthy volunteers and stored at 4 °C until required for analysis. Unless stated otherwise, the experiments were carried out at room temperature.

2.2. Instruments

Fluorescence spectra were recorded using a 970CRT fluorescence spectrometer (Shanghai, China) equipped with a xenon lamp source. The excitation wavelength was set at 310 nm and both slit width were of 5 nm for excitation and emission. The morphologies of synthesized Ln-ICP were investigated using scanning electron microscopy (SEM, Sigma 500, Gemini, Japan) equipped with an energy dispersive X-ray spectrometer (EDS) detector. UV–vis absorption spectra were conducted on a Lambda 35 UV–vis spectrometer (Pgeneral Instrument, Beijing, China).

2.3. Preparation of Ce/Tb-AMP and coumarin@Ce/Tb-AMP particles

Ce/Tb-AMP was synthesized using an adapted version of the procedure reported in our previous study [24]. In this regard, 3.6 mL of $Ce(NO_3)_3$ (10 mM) and 0.9 mL of $Tb(NO_3)_3$ aqueous solution (10 mM) were added into 4.5 mL of HEPES buffer (0.1 M, pH 7.4) containing AMP (10 mM), and this mixture was gently stirred for 3 h at room temperature. Then, the white precipitate was obtained by centrifugation at 9000 rpm for 3 min, and washed with ultrapure water for three times. Subsequently, the pellet containing Ce/Tb-AMP particles was re-suspended in 9.0 mL HEPES buffer solution (0.1 M, pH 7.4), and the Ce/Tb-AMP suspension was stored at 4 °C before use.

To introduce coumarin in the Ce/Tb-AMP, coumarin was added to HEPES buffer solution containing AMP prior to the addition of $Ce(NO_3)_3$ and $Tb(NO_3)_3$ aqueous solution [25]. The subsequent procedure was same to that of Ce/Tb-AMP as described above. The obtained precipitate was washed with ultrapure water for several times until no obvious fluorescence of coumarin was detected in the supernatant. Finally, the pellet was redispersed in 9.0 mL HEPES buffer (0.1 M, pH 7.4) to form coumarin@Ce/Tb-AMP suspension, which was stored at 4 °C for use.

2.4. Fluorescent response of Coumarin@Ce/Tb-AMP toward Hg^{2+}

The ratiometric fluorescent assay for Hg^{2+} was performed by mixing coumarin@Ce/Tb-AMP suspension with different concentrations of Hg^{2+} in a quartz cuvette. The resulting mixture was shaken well and the kinetic luminescence was monitored, which can be completed within 5 min. So, the mixture was allowed to

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