



A luminescent lanthanide coordination polymer based on energy transfer from metal to metal for hydrogen peroxide detection

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ABSTRACT

A bimetal lanthanide coordination polymer nanoparticle (ATP-Ce/Tb-Tris CPNs) with good biocompatibility was synthesized in Tris–HCl buffer using adenosine triphosphate (ATP) molecules as the bridge ligands. The large absorption cross section and suitable emission energy of Ce³⁺ matching to the adsorption energy of Tb³⁺ (⁴f_n) results in the efficient energy transfer from Ce³⁺ to Tb³⁺, thus the synthesized ATP-Ce/Tb-Tris CPNs exhibit the characteristic green emission of Tb³⁺. Such energy transfer from metal to metal in fluorescent lanthanide coordination polymer nanoparticles (Ln-CPNs) has been demonstrated. It is found that the oxidation of Ce³⁺ in ATP-Ce/Tb-Tris CPNs to Ce⁴⁺ would interrupt the energy transfer from Ce³⁺ to Tb³⁺, leading to fluorescence quenching of Tb³⁺. On the basis of this quenching mechanism, ATP-Ce/Tb-Tris CPNs has been successfully used to detect reactive oxygen H₂O₂ with detection limit as low as 2 nM. If glucose oxidase is present in the system, glucose can be determined using the ATP-Ce/Tb-Tris CPNs nanosensor.

1. Introduction

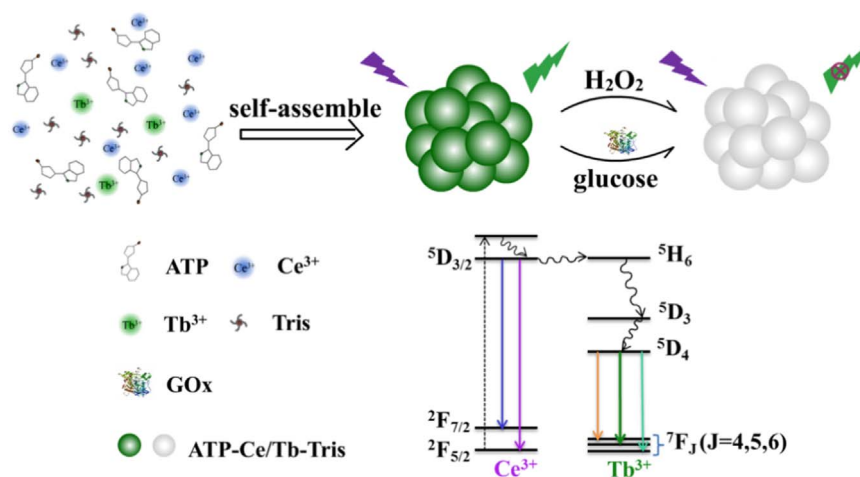
In the past decades, nanomaterial has drawn great attention from researchers for various biomolecules sensing (Huang et al., 2016; Shuai et al., 2016). Recently, lanthanide coordination polymer have been widely used as luminescent probes for their unique optical characteristics including large Stokes shifts, long luminescence lifetimes, and narrow emission bands (Dai et al., 2013; Wang et al., 2015). The terbium complexes with visible region emission and long luminescent lifetimes in the millisecond range have attracted growing interests, and have been used as luminescent probes in time-resolved luminescence bioassays (Hänninen and Härmä 2011; Heffern et al., 2013). However, direct excitation of Ln³⁺ is difficult because of the Laporte-forbidden f→f transitions (Cui et al., 2014). To address this problem, one general approach is to introduce an organic ligand (known as “antenna effect”) to absorb energy and transfer it to Ln³⁺ ions (Montgomery et al., 2009). In this case, the antenna ligands should have high molar absorptivity and well-matched triplet state energy levels for the resonance level of Ln³⁺ in order to efficiently populate the lanthanide ion emission (Li et al., 2015). Various organic ligands such as azaxanthone, phenanthridine, and tetracycline meet the requirements and have been applied to sensitize Tb³⁺ emission (Heffern et al., 2013). Nevertheless, these organic ligands have poor solubility in

aqueous solutions and poor biocompatibility, which limit the practical applications of these lanthanide-antenna complexes in biological systems (Dai et al., 2013; Smith et al., 2012).

Recent reports showed that the energy transfer between different Ln³⁺ ions (f→f) could be an alternative means to sensitize the luminescence of Ln³⁺ in mixed lanthanide coordination polymer although the idea can be dated to the last sixties (Blasse and Brill, 1967; Guo et al., 2010; Li et al., 2015; Ramya et al., 2012). In the case of Ce³⁺ ion, its 4f configuration has only one electron which can be easily excited into the 5d orbital upon UV irradiation due to the allowed electric dipole transitions (f-d transitions), resulting in occurrence of a strong absorption in UV region. Thus, Ce³⁺ ions are usually used as sensitizer to transfer excitation energy to other rare earth activator in inorganic crystals (Lai et al., 2008). The energy levels of Tb³⁺ (⁴f_n) matching to the excited state of Ce³⁺ generated via the allowed f-d transition upon UV irradiation enables efficient energy transfer from Ce³⁺ to Tb³⁺ (Jose and Lakshmanan, 2004; Li and Yam, 2007). The first studied inorganic material for Ce³⁺/Tb³⁺ co-doped was calcium phosphate glass, which possesses high transmission in the ultraviolet region and high quenching concentration of Tb³⁺ up to 10 mol% (Shionoya and Nakazawa, 1965). Other Ce³⁺/Tb³⁺ co-doped phosphates such as YPO₄ (Lai et al., 2008), LaPO₄ (Meyssamy et al., 1999), and GdPO₄ (Yi et al., 2014) with high quantum yields have also been

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Scheme 1. Schematic illustration of the synthesis of ATP-Ce/Tb-Tris CPNs, the detections of H₂O₂ and glucose, and the energy transfer from Ce³⁺→Tb³⁺.

synthesized. More recently, the inorganic nanoparticles such as LaF₃:Ce³⁺, Tb³⁺ (Wang and Li, 2007), NaYF₄:Ce³⁺, Tb³⁺ (Tu et al., 2011), and CaF₂:Ce³⁺, Tb³⁺ (Zheng et al., 2013) have been used as fluorescence probes for biomolecules detection. However, sensitization of Tb³⁺ by Ce³⁺ ions in lanthanide coordination polymer nanoparticles (Ln-CNPs) has not yet been reported.

Biomolecules such as nucleotides with nucleobases and phosphate groups have shown to be alternative ligands for synthesizing Ln-CNPs (Nishiyabu et al., 2009; Xu et al., 2014; Zeng et al., 2016). Herein, we used ATP as the bridge ligand to assemble with Ce³⁺ and Tb³⁺ in Tris-HCl buffer, forming a new kind of bimetallic ATP-Ce/Tb-Tris CNPs (Scheme 1). The synthesized ATP-Ce/Tb-Tris CNPs exhibit the characteristic green emission of Tb³⁺, which arises from the efficient energy transfer from Ce³⁺ to Tb³⁺. Compared with those Ce/Tb co-doped inorganic nanocrystal, the ATP-Ce/Tb-Tris CNPs possesses better biocompatibility, which is beneficial for its biological application. Meanwhile, such energy transfer method from metal to metal (i.e. Ce³⁺ to Tb³⁺) is different from those from organic ligand to Ln³⁺ of traditional lanthanide complex, providing an efficient means to construct novel luminescence Ln-CNPs.

In the presence of oxidizing agents such as H₂O₂, the Ce³⁺ in ATP-Ce/Tb-Tris CNPs can be oxidized into Ce⁴⁺, which gives rise to the interrupt of energy transfer from Ce³⁺ to Tb³⁺, resulting in the fluorescence quenching of ATP-Ce/Tb-Tris CNPs. Based on this quenching mechanism, a ATP-Ce/Tb-Tris CNPs fluorescent probe for H₂O₂ detection has been developed, which exhibits a much more sensitive response towards H₂O₂ than those cerium oxide sensors (Artiglia et al., 2014; Liu et al., 2015). In addition, this ATP-Ce/Tb-Tris CNPs sensor can be extended to detect glucose if glucose oxidase is present in the detection system.

2. Experimental section

2.1. Reagents

Adenosine triphosphate (ATP) and glucose oxidase (GOx) were bought from Sigma-Aldrich (USA). Glucose, Tb(NO₃)₃·6H₂O (> 99.99%), Ce(NO₃)₃·6H₂O (> 99.99%), Tris(hydroxymethyl)aminomethane, 30 wt% H₂O₂ solution, and other metallic salts were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). All the chemicals were used without further purification. Human serum samples were provided by Jiangxi Provincial People's Hospital, and diluted one hundred fold with ultrapure water after centrifugation at 1000 rpm for 5 min

2.2. Apparatus

The fluorescence spectra and UV-Vis absorption spectra were performed with a Hitachi F-7000 fluorescence spectrophotometer (Tokyo, Japan) and a UV-2450 spectrophotometer (Shimadzu, Japan), respectively. A Hitachi SU-8010 scan electron microscope (FE-SEM, Japan) and JEOL2010 transmission electron microscope (TEM, Japan) were used to characterize the size and morphology of ATP-Ce/Tb-Tris CNPs. The Fourier transform infrared (FT-IR) spectra were taken on a Nicolet 5700 FT-IR spectrometer (Waltham, MA, USA). X-ray photoelectron spectroscopy (XPS) data were measured by a VG Multilab 2000X instrument (Thermal Electron, USA).

2.3. Preparation of ATP-Ce/Tb-Tris CNPs

ATP-Ce/Tb-Tris CNPs were prepared through assembling ATP with Ce³⁺ and Tb³⁺ in Tris-HCl buffer. Typically, ATP (2 mM, 1 mL) was first added into pH 7.4 Tris-HCl buffer (50 mM, 1.6 mL), then a mixture solution of Ce(NO₃)₃ (4 mM, 1.6 mL) and Tb(NO₃)₃ (4 mM, 0.4 mL) was added gradually into the above buffer system under stirring (500 rpm) at room temperature, generating a white flocculent suspension within 1 min. After purification through centrifugation (16000 rpm, 15 min), and washed by ultrapure water for several times, these flocculent suspension were re-dispersed in 2 mL water to form ATP-Ce/Tb-Tris CNPs (1 mM) suspension and stored at 4 °C prior to use.

2.4. Biocompatibility test of ATP-Ce/Tb-Tris CNPs

To investigate the cytotoxicity of ATP-Ce/Tb-Tris CNPs, the standard MTT assay on A549 cells was conducted to assess the cell viability. Briefly, A549 cells (4×10⁴ cells per well) were seeded in 24-well plates, after being incubated 24 h in a humidified atmosphere containing 5% CO₂ at 37 °C, different concentrations of ATP-Ce/Tb-Tris CNPs (0–3.0 mM) were added, and cells were incubated for another 24 h under the same culture condition. Then, the A549 cells were washed with PBS buffer (pH 7.4), and incubated with MTT assay solution for 2 h, the absorbance at 490 nm was measured.

2.5. H₂O₂ sensing

The H₂O₂ assay was performed under the following procedure. ATP-Ce/Tb-Tris CNPs stock solution (1 mM, 10 μL) and H₂O₂ with different concentrations were added to 20 μL Tris-HCl buffer (50 mM, pH 7.4) in turn, keeping the total volume of 200 μL. After incubated for 25 min at room temperature, the fluorescence spectra were recorded

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