



Multifunctional nanoprobe based on upconversion nanoparticles for luminescent sensing and magnetic resonance imaging



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ABSTRACT

Copper ions (Cu^{2+}) play a key role in ecosystems and human health, however, the copper pollution caused by the excessive use of copper has become one of the main problems of modern world. In this paper, a facile method was developed to construct a multifunctional nanoprobe for Cu^{2+} detection by combining the mesoporous silica coated upconversion nanoparticles (UCNPs) with rhodamine B derivative. $\beta\text{-NaYF}_4\text{:Yb,Er@NaGdF}_4$, which could achieve upconversion luminescence (UCL)/magnetic resonance imaging (MRI) dual-mode imaging, was prepared first and then coated with mesoporous silica to form the hydrophilic nanospheres. Subsequently, a rhodamine B derivative DFPP-RhB (denoted as P) was grafted to the mesoporous silica to construct the final multifunctional nanoprobe (denoted as UCNPs@mSiO₂-P). In this nanoprobe, the mesoporous silica coated $\text{NaYF}_4\text{:Yb,Er@NaGdF}_4$ served as the energy donor, while the rhodamine B derivative P was used as the energy acceptor, resulting in an efficient luminescence resonance energy transfer (LRET) system. The UCNPs@mSiO₂-P nanoprobe shows high selectivity and sensitivity in detecting of Cu^{2+} . In addition, the T₁-weighted MRI measured in aqueous solutions reveals that the positive enhancement signals were obtained with increasing of Gd^{3+} concentrations. This method demonstrates a simple but fascinating strategy to combine the metal ion sensing and multimodal imaging.

1. Introduction

Metal ions play a vital role in ecosystems and human health [1–4]. Among them, copper, the essential trace element in biological systems, is of great importance since it is a cofactor of many metalloenzymes. Moreover, it is also pivotal in dioxygen transport and activation, energy generation, and signal transduction [5]. However, excessive Cu^{2+} ions in human body can result in serious diseases, including neurodegenerative diseases [6], organ failure, Wilson diseases [7], as well as Alzheimer's disease [8]. Furthermore, the widespread usage of Cu^{2+} can lead to serious environmental problems as well [9]. Hence, more and more attention has been devoted to the development of methods for Cu^{2+} detection in environmental and biological samples.

Up to now, the traditional techniques of detecting copper ions, for example, include atomic absorption spectrometry, voltammetric detection, and inductively coupled plasma mass spectroscopy (ICP-MS) [10–13], are often suffering from more or less drawbacks, such as time-consuming, complicated procedures and high cost, which limit their application in on-line monitoring. More recently, fluorescent detection of Cu^{2+} ions has increasingly drawn the interest of researchers, by which low cost, rapid, non-destructive, and naked-eye detection

could come true [14–16]. Compared with some traditional fluorophores, rhodamine B derivatives for detecting Cu^{2+} is fast, efficient and sensitive due to their unique features such as high photostability, wide wavelength range and high fluorescence quantum yield, which leads to their widespread applications in a lot of fields [17–21]. However, rhodamine B derivatives exhibit emission under excitation of UV or visible light, which may bring damage to healthy cells. What's more, most of the Cu^{2+} -selective probes are hydrophobic and not suitable for the imaging application because of their organic nature.

Different from traditional fluorophores with Stokes emission, rare-earth doped upconversion nanoparticles (UCNPs) with anti-Stokes emission resulting from sequential absorption of two or more low energy photons by ladder-like energy levels of the lanthanide dopants, are capable of converting near infrared (NIR) excitation light into UV or visible emission [22,23], resulting in a number of optical and chemical properties such as greater penetration depth, large Stokes shifts, low toxicity and no auto-fluorescence backgrounds [24,25]. In addition, the surface of the UCNPs is easy to be modified and further grafted with gold nanoparticles [26], proteins [27], DNA sequences [28], organic fluorescent molecules [15] to build the hybrid materials, which can be used for photothermal therapy, targeted diagnosis, DNA transport,

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fluorescence imaging and other applications [29–31]. In particular, when combined with fluorescent molecules (energy acceptor), UCNPs can serve as an excellent energy donor to construct a nanoprobe based on luminescent resonance energy transfer for detecting metal ions, anions, DNA sequences, etc.

In our previous work, we synthesized a rhodamine B derivative DFPP-RhB for Cu^{2+} detection with high sensitivity and selectivity. Noted that DFPP-RhB could be excited by visible light (520 nm), which matches well with the emission of Er doped UCNPs. Herein, we prepared a multifunctional nanoprobe by using mesoporous silica coated $\text{NaYF}_4:\text{Yb,Er}@/\text{NaGdF}_4$ UCNPs as the luminescence donor and Cu^{2+} -responsive rhodamine B derivatives DFPP-RhB as the acceptor for Cu^{2+} detection based on luminescence resonance energy transfer (LRET) process. In addition, the core-shell structured $\text{NaYF}_4:\text{Yb,Er}@/\text{NaGdF}_4$ could not only increase the upconversion emission intensity but also combine upconversion luminescence (UCL) with magnetic resonance imaging (MRI) for dual-mode imaging application.

2. Experimental

2.1. Chemicals and materials

$\text{YbCl}_3 \cdot 6\text{H}_2\text{O}$ (99.99%), $\text{YCl}_3 \cdot 6\text{H}_2\text{O}$ (99.99%), $\text{ErCl}_3 \cdot 6\text{H}_2\text{O}$ (99.99%), $\text{GdCl}_3 \cdot 6\text{H}_2\text{O}$ (99.99%), Cyclohexane (99.5%, analytical reagent), toluene (99.5%, analytical reagent), anhydrous ethanol (99.7%, analytical reagent), acetone (99.5%, analytical reagent) and ammonium nitrate (NH_4NO_3 , $\geq 99.0\%$) were obtained from Sinopharm Chemical Reagent Co., Ltd. Tetraethyl orthosilicate (TEOS, $> 99\%$) were purchased from Sigma-Aldrich Co. Ltd. Oleic acid (OA, 90%, technical grade), 1-octadecene (ODE, 90%, technical grade) was purchased from Alfa Aesar. Methanol (CH_3OH , 99.5%), sodium hydroxide (NaOH, $\geq 98\%$, reagent grade), ammonium fluoride (NH_4F , 98%), 3-(Triethoxysilyl)propyl isothiocyanate (95%, Guaranteed reagent) and cetyltrimethylammonium bromide (CTAB, $> 99\%$) were purchased from Aladin Company. Deionized water was used throughout. Solutions of Cu^{2+} , Hg^{2+} , Mn^{2+} , Na^+ , K^+ , Cr^{3+} , Mg^{2+} , Ni^{2+} , Fe^{3+} , Fe^{2+} , Ba^{2+} and Ca^{2+} were prepared from their chloride salts, solutions of Li^+ , Zn^{2+} and Co^{2+} were prepared from lithium fluoride, zinc acetate dihydrate, and cobaltous nitrate, respectively.

2.2. Synthesis of the mesoporous silica coated UCNPs (denoted as UCNPs@mSiO₂)

Monodispersed hexagonal $\text{NaYF}_4:\text{Yb,Er}$ and core-shell structured $\text{NaYF}_4:\text{Yb,Er}@/\text{NaGdF}_4$ were synthesized according to literature protocols with slight modifications [16]. 0.1g CTAB was dissolved in 20 mL deionized water, and then 2 mL UCNPs cyclohexane solution (5 mg mL^{-1}) was added. Then, the mixture was stirred at room temperature to evaporate the cyclohexane solvent until a transparent solution was obtained. After that, 10 mL CTAB stabilized nanoparticles solution was added into 20 mL deionized water, then 3.0 mL ethanol and 150 μL 2.0 M NaOH were added in above solution, the mixture was heated to 70 °C under vigorous stirring. 200 μL of tetraethyl orthosilicate (TEOS) was added dropwise and the mixture was maintained for another 2 h. The product was centrifuged and washed with anhydrous ethanol for three times. The template CTAB was removed by a fast and efficient ion exchange method: 90 mL ethanol solution containing 0.6g of NH_4NO_3 was mixed with the as-synthesized solution (10 mL) and the mixture kept at 60 °C for 2 h under stirring. The final product mesoporous silica coated UCNPs (UCNPs@mSiO₂) was washed with ethanol and redispersed in 10 mL of ethanol for further use.

2.3. Synthesis of DFPP-RhB

Rhodamine B hydrazide DFPP-RhB was provided by our group [32].

2.4. Synthesis of the multifunctional nanoprobe (denoted as UCNPs@mSiO₂-P)

20 mg of UCNPs@mSiO₂ were dissolved in 10 mL of toluene. When the mixture was heated to 110 °C, 10 μL of 3-(Triethoxysilyl) propyl isothiocyanate was added. The mixture was refluxed under argon for 24 h. After cooling to room temperature, DFPP-RhB (50 mg) was added and the mixture was refluxed for another 24 h. The nanoparticles were washed several times with anhydrous ethanol. The obtained nanoprobe (UCNPs@mSiO₂-P) was dispersed in 10 mL of anhydrous ethanol for characterization.

2.5. Detection of Cu^{2+} ions

Stock solutions of metal ions (0.1 M) were prepared in deionized water and diluted to the appropriate concentration when used. The solution of UCNPs@mSiO₂-P nanoparticles (2.0 mg/mL) was prepared in 50% (v/v) water/ethanol solution. For titration experiments, the Cu^{2+} solution was added to 2.0 mL of UCNPs@mSiO₂-P solution incrementally by the aid of a micropipette. Selectivity experiments were performed by adding appropriate amounts of metal ions solution to 2.0 mL of the nanoprobe UCNPs@mSiO₂-P, and then UV-vis absorption and fluorescence spectra were recorded. For competition experiments, Cu^{2+} was added to the test solutions containing UCNPs@mSiO₂-P and other metal ions of interest. All solutions were stirred for 1 min before the spectroscopic tests. For upconversion luminescence measurements, excitation was fixed at 980 nm, and emission was collected from 400 to 670 nm, and for downconversion fluorescence measurements, excitation was fixed at 520 nm, and emission was collected from 540 to 700 nm.

2.6. Characterization

The morphologies of nanoparticles were characterized on a JEM-200CX transmission electron microscope (TEM) operated at 120 kV and a JEM-2010F high-resolution transmission electron microscope (HR-TEM) operated at 200 kV. Powder X-ray diffraction (XRD) measurement was performed on a 18 kW D/MAX2500 V diffractometer using $\text{Cu K}\alpha$ radiation at a step width of 8° min^{-1} . Fourier transform infrared spectroscopy (FT-IR) spectra were carried out on an Avatar 370 in the spectral range from 4000 to 400 cm^{-1} . Nitrogen (N_2) adsorption/desorption isotherms were performed using a QuadraSorb Station 2 with nitrogen. The samples were outgassed for 3.0 h at 130 °C prior to the measurements. Surface areas were obtained by Brunauer-Emmett-Teller (BET) method, and pore sizes were obtained by Barrett-Joyner-Halenda (BJH) method. Thermogravimetric analysis (TGA) was carried out on a Perkin-Elmer Pyris Diamond thermal analyzer up to 800 °C at a heating rate of $10^\circ \text{ C min}^{-1}$ under N_2 . UV-vis absorption spectra were recorded on a 760CRT dual beam spectrophotometer. Fluorescence spectra were determined on an Edinburgh Instruments FS920 fluorescence spectrometer ($\lambda_{\text{ex}} = 520 \text{ nm}$, excitation slit: 3 nm, and emission slit: 5 nm), the upconversion luminescent emission spectra were obtained with the excitation of an external 0–800 mW 980 nm adjustable CW laser ($\lambda_{\text{ex}} = 980 \text{ nm}$, excitation slit: 5 nm, and emission slit: 1.5 nm). The longitudinal relaxation time T_1 and relaxivity r_1 of the UCNPs@mSiO₂-P was measured with a magnetic resonance imaging (MRI) instrument with 3.0 T magnetic fields. The T_1 values were recorded at different concentrations of Gd^{3+} (0–0.4 mM Gd^{3+}) and the longitudinal relaxivity r_1 ($1/T_1$) was deduced by the slope of the fitted regression line.

3. Results and discussion

3.1. Synthesis and characterization of UCNPs@mSiO₂-P

As shown in Scheme 1, the oleic acid stabilized $\text{NaYF}_4:\text{Yb,Er}$ were

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