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A new dual fluorescent probe preparation and its biodiagnose function *in vitro*

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ABSTRACT

A new dual fluorescent probe was prepared by encapsulating the complex of cerium (III) and quinizarin into silica nanoparticles. Cerium (III) and quinizarin can form a stable dual fluorescent complex in ethanol, but this complex would dissociate in the aqueous medium, which limited its application in biosystem. So, such complex was encapsulated inside the silica nanoparticles to solve this problem. The results indicated that the stability and water solubility of the complex were greatly improved after been encapsulated into the silica nanoparticles. In addition, its dual fluorescent probe function was studied *in vitro*.

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1. Introduction

Dually fluorescent probes have attracted increasing interest in the fields of optical sensors, optoelectronic devices and biodiagnostics because of the improved detection sensitivity and their tunable detection range. There are a wide variety of dually fluorescent probes preparation ways, varying from different fluorescent reagents co-encapsulation inside nanoparticles to different fluorescent reagents combination approaches [1,2], such as double rare earth ions co-doped nanomaterials [3], rare earth ion and fluorescent dye co-doped solid matrixes [4,5] and rare earth ion and fluorescent dyes complexes [6]. At the present, two-color species have used in laser devices, molecules for non-linear optics and probes to study biological systems [7–9]. However, some complexes of rare earth ion and fluorescent dyes can only stable in organic solvents but dissociate in aqueous medium, which would limit their application for biological detection. So, how to improve the stability and solubility of these complexes in aqueous solution has aroused great concern in the field of fluorescent-based biodiagnose.

Silica particles are very versatile materials can be used in many applications fields, such as drug delivery systems, chemical and biochemical sensors and advanced laser devices [10–13]. Encapsulating the hydrophobic fluorescent regents into silica nanoparticles can improve their hydrophily, stability and biological adaptability. A lot of single-color dyes are already used for visualizing nuclei [14], membrane [15] and cytoplasm [16]. Recently, two-color species have aroused great public concern because they can increase laser efficiency and enlarge tunable spectral range by altering the molar ratios of the different components [17]. So, we suppose that encapsulating the dual emission complexes of rare earth ion and fluorescent dyes inside the silica nanoparticles can greatly improve their dispersibility in aqueous solution. Furthermore, in the complex-nanoparticle system, the complex can be envisaged as discretely embedded in the particle matrix, and therefore protected from exposure to the aqueous environment, preventing the dissociation of complex caused by water. According to the assumption, we prepared complex of rare earth ion and fluorescent dyes in organic solvent, and then encapsulated such complexes in silica nanoparticles.

To demonstrate this concept, we prepared the complex of cerium (III) and quinizarin (QNZ) in ethanol. The complex has dually fluorescent peaks ascribed to cerium (III) [18–23] and quinizarin, separately [24,25]. However, such complex was dissociated in aqueous solution. So we encapsulated the cerium (III)/quinizarin complexes into the silica nanopaticles to solve this problem. The results indicated that after been encapsulated into the silica nanoparticles, the stability and water solubility of the complex was greatly improved. Furthermore, strong blue and green fluorescence signal can be detected after such particles were taken up THP-1 cells. Above results implied that the dually fluorescent silica nanoparticles embedded with cerium (III)/quinizarin complexes have potential as fluorescent nanoprobes for biological imaging systems.

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2. Experimental sections

2.1. Materials

$CeCl_3 \cdot 7H_2O$ and quinizarin (1,4-dihydroxyanthraquinone, QNZ) were purchased from Acros Organics. 3-Aminopropylmethyldiethoxysilane (APMES; 99%) was purchased from Sigma. Dulbecco's minimum essential medium (DMEM) was from Gibico. Anhydrous ethanol and other chemicals were all analytical grade. 1.25×10^{-3} mol L^{-1} stock standard solution of QNZ was prepared by dissolving an accurately weighed amount of guaranteed reagent in anhydrous ethanol and protected from exposure to the light. 1.0×10^{-2} mol L^{-1} stock standard solution of cerium (III) chloride was prepared using analytical grade product in anhydrous ethanol.

2.2. Preparation and encapsulation of Ce (III)/QNZ complex

The Ce (III)/QNZ complex was prepared by mixing different volume of stock standard solution of QNZ with cerium (III) chloride in ethanol. Silica nanoparticles entrapped with Ce (III)/QNZ complex were synthesized by an improved sol–gel technique, and the process referred to the literature [26]. Stock standard solutions of Ce (III) (7.5 μL) and QNZ (60 μL) were mixed with an electromagnetic stirrer in ethanol (99.9%, 20 mL) for 30 min at room temperature in the dark. APMES (99%, 50 μL) was slowly added, and ammonia (27%, 50 μL) was added dropwise with controlled stirring to initiate the hydrolysis reaction, then stirred continuously for 24 h to complete the hydrolysis process. Lastly the solution was dried under high vacuum to remove the ethanol and ammonia using rotary evaporators to get the silica nanoparticles embedded Ce (III)/QNZ complex (SiO_2–Ce (III)/QNZ). The result colloid was dissolved in anhydrous ethanol for the contrast experiments or deionized water for the later cells research. All measurements were performed at room temperature.

2.3. Characteristics

Transmission electron microscopy (TEM) was employed to determine the morphology and size of the aqueous dispersion of nanoparticles, using a FEI-Tevnai G220 S-TWIN electron microscope, operating at an accelerating voltage of 200 kV. UV–vis absorption spectra were obtained on a Varian Cary 5000 spectrophotometer. Fluorescence spectra were performed using a Perkin-Elmer LS-50B fluorometer. FTIR spectra were recorded using a Nicolet Nexus 670 FT-IR infrared spectrometer. The fluorescence decays were measured with the technique of time correlated single photon counting (TCSPC) in a JOBIN-YBON IBH-FluoroMax-4 apparatus. Quantum-yield values were calculated using quinine sulfate and rhodamine B as references. Zeta potential measurements of void SiO_2, complex before and after encapsulation were carried out using a Malvern Zetasizer Nano 90 light scattering.

2.4. In vitro diagnose

For studying the *in vitro* diagnose function of SiO_2–Ce (III)/QNZ. THP-1 cells were seeded in a DMEM supplemented with 10% fetal bovine serum (FBS) at a concentration of around 1×10^5 mL^{-1} in a 6 well cell culture plate, following the established protocol. The plates were then placed overnight in an incubator at 37 °C with 5% CO_2. The next day, serum free medium was replaced on the plates, at this stage; SiO_2–Ce (III)/QNZ (5uM) was added to the cell culture plate and the plate was placed in incubator for another 4 h. The cells were then rinsed briefly with phosphate-buffered saline (PBS) and examined immediately by fluorescence microscopy.

3. Results and discussion

3.1. The formation of Ce (III)/QNZ complex

The complexation processes of Ce (III) and QNZ can be monitored clearly by the UV–vis spectra. Fig. 1 showed the UV–vis spectra for QNZ and for QNZ/Ce (III) at different molar ratios. The absorption spectrum of QNZ was obviously changed after chelating with Ce (III). QNZ owned characteristic absorption bands with maximum intensities at 480 nm and 515 nm. With increasing concentration of Ce (III), the broad band at 480 nm was slowly disappearance and changed into a shoulder peak centered at 490 nm, while the peak at 515 nm was stronger and red-shifted accordingly. In addition, a new absorption peak occurred at 565 nm, which was due to the metal-to-ligand charge transfer (MLCT) of the Ce (III)/QNZ complex. Above results indicated the formation of Ce (III)/QNZ complex.

Continuous variation method was used to determine the composition of the complex (Fig. S1), the experiment result manifested that Ce (III)/QNZ molar ratios were 1/1 and the calculated association constant of the complex was 5.403×10^4.

The fourier transform infrared (FTIR) spectra of free QNZ and Ce (III)/QNZ complex revealed that quinizarin coordinated to cerium (III) ion through the ionized hydroxyl groups and neighboring carbonyl moieties (Fig. S2). The proposed structure of Ce (III)/QNZ polymeric species was showed in Scheme 1. Zeta potential measurements showed the potential was −47.2 mV for void SiO_2 and +9.09 mV for Ce (III)/QNZ complex; when the complex was encapsulated inside silica nanoparticles, the potential was −38.5 mV in our experiment condition, which suggested electrostatic effect possibly played major roles in the formation of Ce (III)/QNZ doped silica nanoparticles. However, Ce (III)/QNZ complex would dissociate quickly in the aqueous medium (Fig. S3). In order to enhance the stability and water-solubility of Ce (III)/QNZ complexes, we encapsulated them into the silica nanoparticles.

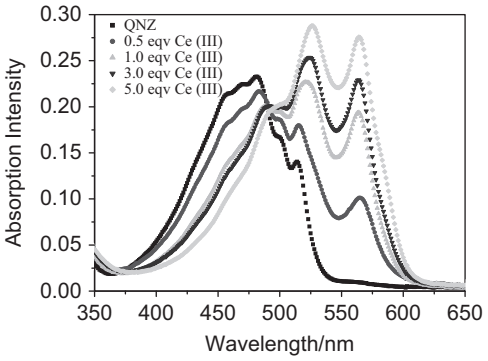
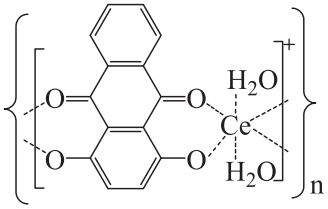


Fig. 1. UV–vis spectra of quinizarin and QNZ/Ce (III) at different molar ratios in ethanol.



Scheme 1. Proposed structure of 1:1 Ce (III)/QNZ polymeric species.

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