Contents lists available at ScienceDirect

Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy

journal homepage: www.elsevier.com/locate/saa

Fluorescence enhancement of europium complexes by core–shell Ag@SiO$_2$ nanoparticles

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HIGHLIGHTS

- Three kinds of Ag@SiO$_2$ with shell thickness of around 10, 15 and 25 nm were prepared.
- Six complexes of europium with halo-benzoic acid were synthesized.
- Ag@SiO$_2$ nanoparticles can significantly enhance the fluorescence of the complexes.
- When the thickness of SiO$_2$ shell is 25 nm, enhancement of fluorescence is the biggest.
- The order of enhancement for the complexes with different halogen atom is F < Cl < Br.

GRAPHICAL ABSTRACT
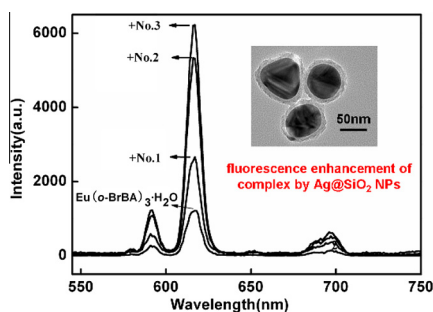
ABSTRACT

Three kinds of core–shell Ag@SiO$_2$ nanoparticles with shell thickness of around 10, 15, and 25 nm, respectively, have been prepared by modified Stöber method and used for fluorescence enhancement. Six kinds of europium complexes with halobenzoic acid have been synthesized. Elemental analysis and lanthanide coordination titration show that the complexes have the compositions of Eu(p-XBA)$_3$·H$_2$O and Eu(o-XBA)$_3$·2H$_2$O (X = F, Cl, Br). The fluorescence spectra investigation indicates that the introduction of Ag@SiO$_2$ nanoparticles into the europium complexes' solution can significantly enhance the fluorescence intensities of the complexes. The sequence of enhancement factors for halobenzoic acid complexes with different halogen atoms is F < Cl < Br, and the fluorescence enhancement factors increase as the excitation wavelength of complexes increase. When the thickness of the SiO$_2$ shell is 25 nm, the fluorescence intensity of the europium complexes can reach a maximum enhancement factor of 5.1. The fluorescence enhancement mechanism may be the metal-enhanced fluorescence resulting from surface plasmon resonance of nanoparticles. And the nanoparticles near the complexes can effectively prevent complexes from the interaction with the solvent molecules, leading to a decrease of nonradiative energy transfer and the suppression of luminescence quench.

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1. Introduction

Lanthanide complexes have important applications in fluorescence materials, electroluminescence devices and fluorescence probes for biological systems [1,2]. However, there exist some restrictions for the practical application of the lanthanide complexes, essentially owing to their weak luminescence intensities, short lifetimes and low quantum efficiencies [3]. Substantial research efforts have shown that noble-metal (Au, Ag) nanoparticles can enhance the fluorescence intensities, radiative decay rates and fluorescence quantum yields of lanthanide complexes [4]. The

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effect of metal-enhanced fluorescence is related to the distance between the fluorophore and the metal surface [5]. The direct contact between lanthanide complexes and metal nanoparticles could enhance the non-radiative energy transfer, which might lead to the quench of fluorescence, but far distance between them may result in no fluorescence enhancement. Therefore, an appropriate distance can optimize the metal-enhanced fluorescence of lanthanide complexes. Since the silica surface chemistry can covalently introduce versatile surface functionalities (e.g., COOH, CHO, NH_2, or NCO) with readily available coupling agents [6,7], it is desirable to coat the metal nanoparticles with a shell of silica to permanently preserve their optical properties for effective functionalization [8–10]. Zhang et al. have reported $Ag@SiO_2$ nanoparticles can enhance the fluorescence intensity of Rose Bengal [11–13], but the effect of $Ag@SiO_2$ nanoparticles on the fluorescence of lanthanide complexes are few reported [14,15].

Aromatic carboxylate ligands have been widely used in lanthanide complexes for their diverse coordination modes, strong bonding ability and efficient energy transfer to the lanthanide ions [16–18]. Especially, the halogen atoms (F, Cl, Br) in halogenated benzoic acids are electron withdrawing groups, which may have an important influence on the luminescence excitation and emission of center lanthanide ions. Therefore, six kinds of europium complexes with different halogenated benzoic acids ($Eu(p\text{-}XBA)_3 \cdot H_2O$ and $Eu(o\text{-}XBA)_3 \cdot 2H_2O$, X = F, Cl, Br) are synthesized to investigate the effect of halogenation on the metal-enhanced fluorescence of lanthanide complexes.

In order to study the effect of distance between lanthanide complexes and metal nanoparticles on the metal-enhanced fluorescence, we develop core–shell $Ag@SiO_2$ nanoparticles with various shell thickness of around 10, 15 and 25 nm [19–22]. Results demonstrate that the introduction of $Ag@SiO_2$ nanoparticles into the europium complexes' solution can significantly enhance the fluorescence intensity of the complexes and the fluorescence enhancement is the strongest when the shell thickness of $Ag@SiO_2$ nanoparticle is 25 nm. The enhancement factors for halo-benzoic acid complexes vary with different halogen atoms. And the fluorescence enhancement mechanisms are also discussed.

2. Experimental section

2.1. Chemical reagents

Eu_2O_3 (99.99%), HCl, $AgNO_3$, ammonia, anhydrous ethanol, p-fluorobenzoic acid (p-FBA), p-chlorobenzoic acid (p-ClBA), p-bromobenzoic acid (p-BrBA), o-fluorobenzoic acid (o-FBA), o-chlorobenzoic acid (o-ClBA), o-bromobenzoic acid (o-BrBA), N,N-dimethyl formamide (DMF), tetraethoxysilane (TEOS), sodium citrate and other agents are all of analytical grade and used as recieved.

2.2. Preparation of $Ag@SiO_2$ nanoparticles

2 mL 0.20 mol L^{-1} sodium citrate aqueous solution was added into 500 ml of boiling aqueous solution containing 2 mL 0.25 M $AgNO_3$ under vigorous stirring [23–26]. After boiled for 15 min, the solution was cooled to room temperature [1]. The as-prepared silver colloid was centrifuged at 500 rpm for 1 h to remove large nanoparticles, and the remaining silver nanoparticles was diluted to 500 mL with water.

The core–shell $Ag@SiO_2$ nanoparticles were synthesized as follows. 10 mL as-obtained silver colloids were transferred respectively to three 500 mL round bottom flasks containing 150 mL ethanol and 1 mL 0.20 mol L^{-1} sodium citrate. And the pH values of the solutions were adjusted to ∼9 via the addition of ∼30 wt.% ammonia. Subsequently, 5 mL, 15 mL and 35 mL 10 mmol/L TEOS ethanol solutions were added into each flask within 4 h under vigorous stirring, respectively. And the resulting solutions were allowed to further react for 24 h at room temperature. Three kinds of $Ag@SiO_2$ nanoparticles (No.1, No.2 and No.3) were collected by centrifugation at 8000 rpm for 30 min and washed with ethanol for three times.

2.3. Synthesis of europium complexes

3 mmol p-FBA (or p-ClBA, p-BrBA, o-FBA, o-ClBA and o-BrBA) was first dissolved in the mixed solvent of 10 mL ethanol and 2 mL distilled water with vigorously stirring. The pH value of the reaction mixture was adjusted to about 6 with ammonia. And 1 mmol $EuCl_3$ was dropwise added to the solution. The pH value of the mixture was readjusted to 6, after which the mixture was heated to 60 °C and stayed at 60 °C for 3 h. Then the mixture was left still at room temperature overnight. After filtered, washed with ethanol for several times, and dried to constant weight, the white precipitates $Eu(p\text{-}FBA)_3 \cdot H_2O$, $Eu(p\text{-}ClBA)_3 \cdot 2H_2O$, $Eu(p\text{-}BrBA)_3 \cdot H_2O$, $Eu(o\text{-}FBA)_3 \cdot H_2O$, $Eu(o\text{-}ClBA)_3 \cdot H_2O$ and $Eu(o\text{-}BrBA)_3 \cdot 2H_2O$ were obtained, respectively.

2.4. Characterization

Silver and $Ag@SiO_2$ nanoparticles were characterized by JEM-2100 Transmission Electron Microscope (TEM). The composition of C, H was determined by Vario EL Cube elemental analyzer. The contents of europium were determined by EDTA titration method with xylenol orange as the indicator. The UV spectra were recorded on a Shimadzu UV-265 spectrophotometer. Infrared spectra were obtained on a Nicolet Nexus 670 FT-IR spectrometer. Fluorescence spectra were obtained on an Edinburgh FLS-920 fluorescence spectra-photometer. 2.00 mL 1.0×10^{-3} mol L^{-1} of the complex solution was transferred into quartz cell, after which 30 μL $Ag@SiO_2$ solution was added. The volume effect was so small that could be ignored. The solution was allowed to stand for 3 min to equilibrium, after which the fluorescence spectra were detected.

3. Results and discussion

3.1. Morphology analysis of core–shell structure $Ag@SiO_2$ nanoparticles

TEM images of silver nanoparticles are shown in Fig. 1A. Most of the silver nanoparticles are nearly spherical and their average diameter is 60–70 nm. Fig. 1B–D showed almost all the Ag nanoparticles were coated with SiO_2 shell. And the three kinds of $Ag@SiO_2$ core–shell nanoparticles (No.1, No.2 and No.3) possess a shell thickness of 10, 15 and 25 nm, respectively.

UV–vis absorption spectra are an efficient measurement for tracking metallic colloid formation process [27]. The surface plasmon absorption in the visible region is very sensitive to particle size, shape and the properties of the surrounding medium [13]. According to the Mie's theory, the maximum absorption peak of silver nanoparticles would move to longer wavelength with the increasement of the coating thickness [28,29]. Fig. 1E shows the UV–vis spectra of citrate-protected silver nanoparticles and $Ag@SiO_2$ nanoparticles with different shell thickness. The surface plasmon bands of $Ag@SiO_2$ nanoparticles red-shift about 8–20 nm compared with the uncoated silver nanoparticles, which may result from the increase of the local refractive index around the particles [30,31].