Journal of Luminescence 154 (2014) 402–409

Contents lists available at ScienceDirect

Journal of Luminescence

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

Study on silicon oxide coated on silver nanocrystal to enhance fluorescence intensity of rare earth complexes

Yan-rong Qu, Xue-mei Lin, Ai-ling Wang, Zhong-xia Wang, Jie Kang, Hai-bin Chu *, Yong-liang Zhao **

College of Chemistry and Chemical Engineering, Inner Mongolia University, Hohhot 010021, China

ARTICLE INFO

Article history:
Received 11 July 2013
Received in revised form
15 April 2014
Accepted 7 May 2014
Available online 28 May 2014

Keywords:
Rare earth complexes
Halo-benzoic acid
$Ag@SiO_2$ core–shell nanoparticles
Metal-enhanced fluorescence

ABSTRACT

Twelve kinds of rare earth complexes were synthesized using halo-benzoic acid as anion ligand and Sm^{3+} and Dy^{3+} as central ions, respectively. The complexes were characterized by elemental analysis, rare earth coordination titration and electrospray ionization mass spectra, from which the compositions of the complexes were confirmed to be $RE(p\text{-}FBA)_3 \cdot H_2O$, $RE(p\text{-}ClBA)_3 \cdot 2H_2O$, $RE(p\text{-}BrBA)_3 \cdot H_2O$, $RE(o\text{-}FBA)_3 \cdot 2H_2O$, $RE(o\text{-}ClBA)_3 \cdot H_2O$, $RE(o\text{-}BrBA)_3 \cdot H_2O$ ($RE = Sm^{3+}$, Dy^{3+}). Besides, IR spectra and UV–visible absorption spectroscopy indicated that the carboxyl oxygen atoms of ligands coordinated to the rare earth ions. Moreover, $Ag@SiO_2$ core–shell nanoparticles (NPs) were prepared via a modified Stober method. The average diameters of silver cores were typically between 60 nm and 70 nm, and the thicknesses of the SiO_2 shells were around 10 nm, 15 nm and 25 nm, respectively. The influence of $Ag@SiO_2$ NPs on the luminescence properties of the rare earth complexes showed that the luminescence intensities of rare earth complexes were enhanced remarkably. As the thickness of SiO_2 shell increases in the range of 10–25 nm, the effect of metal-enhanced fluorescence become obvious. The mechanism of the changes of the fluorescence intensity is also discussed.

1. Introduction

Enhancing fluorescent properties of rare earth complexes including fluorescence intensity and the stability is very significant in the practical applications. Metal-enhanced fluorescence (MEF) is based on the utilization of plasmonic (noble metals) nanostructures with fluorescent species [1–3]. In recent years, it has been reported that noble metals have an effect of MEF. The interaction between surface plasmon resonance (SPR) and the fluorophores is important for the MEF [4–10]. Therefore, MEF is attracting attention of a number of researchers [11–15].

Nowadays, most studies on MEF are based on the two-dimensional surface of Ag, while less on the metal colloidal liquid phase system. Lakowicz et al. [16,17] has reported the preparation of $Ag@SiO_2$ core–shell structure, and this system can enhance the fluorescence intensity of Indole dye in solution for 3–5 times. Guo et al. [18] group also prepared $Ag@SiO_2$ core–shell structure with different shell thicknesses, and when the shell thickness reached about 75 nm, the fluorescence intensity of Rhodamine B isothiocyanate reached the best enhancement effect of 5-folds.

The effect of MEF is related to the distance from the fluorophore to the metal surface [19–24]. Moreover, the direct contact between rare earth complexes and Ag nanoparticles (NPs) could enhance the non-radiative energy transfer, which might lead to the quenching of fluorescence. Therefore, the main work of the experiment is to synthesize 12 kinds of rare earth complexes and 3 kinds of $Ag@SiO_2$ NPs with different shell thicknesses, then to study the influence of $Ag@SiO_2$ NPs with different shell thicknesses on the fluorescence intensity of Sm^{3+} and Dy^{3+}complexes with different halo-benzoic acids.

2. Experimental section

2.1. Reagents and instruments

Sm_2O_3 (99.99%), Dy_2O_3 (99.99%), trisodium citrate, p-fluorobenzoic acid, p-chlorobenzoic acid, p-bromobenzoic acid, o-fluorobenzoic acid, o-chlorobenzoic acid, o-bromobenzoic acid, ammonia, ethanol (95%), hydrochloric acid (37%), silver nitrate ($AgNO_3$), tetraethyl orthosilicate (TEOS) and other reagents are all analytical reagents. The elemental analysis (C and H) of the complexes was performed on a Vario EL Cube

* Corresponding author. Tel.: +86 13624849905.
** Corresponding author. Tel.: +86 13624849905; fax: +86 471 4992981.
E-mail addresses: binghai99@gmail.com (H.-b. Chu), hxzhaoyl@163.com (Y.-l. Zhao).

http://dx.doi.org/10.1016/j.jlumin.2014.05.013
0022-2313/

elemental analyzer; the contents of rare-earth ions were analyzed by the EDTA complexometric titration method with xylenol orange as indicator. Electrospray ionization mass spectra (ESI-MS) were recorded on a LCQ Advantage MAX mass spectrophotometer with DMSO as solvent. The molar conductivity was measured by DDSJ-308A conductive meter in the solution of DMF. The infrared spectra were determined by a Nicolet Nexus 670 FT-IR spectrometer. The TU-1901 double beam spectrophotometer was used to obtain UV–visible spectra. The fluorescence spectra were determined by an Edinburgh Analytical Instruments FLS-920 fluorescence spectra-photometer, both excitation and emission slit widths were 5 nm. The size and morphology of the $Ag@SiO_2$ NPs were observed by a JEM-2100 transmission electron microscope (TEM).

2.2. Synthesis of rare earth complexes

2.2.1. Preparation of rare earth chloride

1.744 g of white solid Sm_2O_3 was weighed, a certain amount of hydrochloric acid was added to dissolve the solid, and made the solution pH 1. The liquid was evaporated by heating the mixture until crystallized film appeared above the solution, then cooled the liquid to room temperature, white powdered solid appeared. The powder was dissolved in anhydrous ethanol, then transferred the solution into 100 mL of volumetric flask; from above, 0.1 mol L^{-1} $SmCl_3$ ethanol solution was obtained.

Preparation of 0.1 mol L^{-1} $DyCl_3$ ethanol solution is similar to samarium chloride.

2.2.2. Synthesis of rare earth complexes

P-fluorobenzoic acid (3 mmol) was dissolved in the mixture solvent (10 mL anhydrous ethyl alcohol and 2 mL distilled water) with vigorously stirring. The pH value of the solution was adjusted to be 6.2 with $NH_3 \cdot H_2O$. $SmCl_3$ (1 mmol) was added into the above solution with the pH readjusted to 6. After stirring at 60 °C for 3 h, the solution was placed at room temperature overnight. The precipitate was filtrated, washed with ethanol for three times, and dried at 50 °C, after which the powder of samarium complexes was obtained. The synthesis procedures of other complexes are similar to that of $Sm(p\text{-}FBA)_3 \cdot H_2O$.

2.3. Preparation of Ag colloids

2 mL of 0.250 mol $L^{-1}AgNO_3$, 2 mL of 0.200 mol L^{-1} sodium citrate aqueous and 500 mL of secondary water were added to the 1000 mL of round-bottomed flask under vigorous stirring. After boiling for 15 min, the reaction solution was cooled to room temperature. The as-prepared silver colloid solution was centrifuged at 500 rpm for 1 h to remove the larger colloids, and the remaining silver nanoparticles were diluted to 500 mL.

2.4. Preparation of $Ag@SiO_2$ NPs

Three 500 mL of round-bottomed flasks were prepared, which contains 150 mL of anhydrous ethyl alcohol, 1 mL of 0.200 mol L^{-1} sodium citrate aqueous and 50 mL of silver colloids, then adjusted pH with ammonia to about 9. 5 mL, 15 mL and 35 mL TEOS were added dropwise to the system. The reaction was stirred at room temperature for 24 h. Finally, the solutions were centrifuged at 8000 rpm for 1 h, and then three kinds of $Ag@SiO_2$ NPs with different shell thicknesses were obtained. The concentration of the $Ag@SiO_2$ NPs is about 1.0×10^{-4} mol L^{-1}.

3. Results and discussion

3.1. Characterization of rare earth complexes

3.1.1. Composition analysis and molar conductivities of the complexes

The composition analysis and molar conductivities are shown in Table 1. It can be calculated from the data that their composition is consistent with the complexes described above. Their molar conductive values are between 11.4 S cm^2 mol^{-1} and 21.5 S cm^2 mol^{-1}, which means that only a small section of the complexes ionizes in DMF, and these complexes are all non-electrolyte [25].

3.1.2. Electrospray ionization mass spectra (ESI-MS)

ESI-MS for $Sm(p\text{-}FBA)_3 \cdot H_2O$: 475.79, 506.10, 586.02, 663.79.
ESI-MS for $Sm(o\text{-}FBA)_3 \cdot 2H_2O$: 476.55, 506.08, 586.37, 663.70.
ESI-MS for $Sm(p\text{-}ClBA)_3 \cdot 2H_2O$: 274.56, 429.04, 506.12,601.77.
ESI-MS for $Sm(o\text{-}ClBA)_3 \cdot H_2O$: 274.48, 428.91, 505.66, 599.74.
ESI-MS for $Sm(p\text{-}BrBA)_3 \cdot H_2O$: 474.96, 567.88, 645.75, 785.39.
ESI-MS for $Sm(o\text{-}BrBA)_3 \cdot H_2O$: 474.96, 568.00, 645.69, 785.47.
ESI-MS for $Dy(p\text{-}FBA)_3 \cdot H_2O$: 437.99, 516.09, 595.79, 675.73.
ESI-MS for $Dy(o\text{-}FBA)_3 \cdot 2H_2O$: 438.07, 516.05, 595.87, 675.63.
ESI-MS for $Dy(p\text{-}ClBA)_3 \cdot 2H_2O$: 318.44, 610.61, 665.63, 708.15.
ESI-MS for $Dy(o\text{-}ClBA)_3 \cdot H_2O$: 318.51, 610.76, 665.61, 707.55.
ESI-MS for $Dy(p\text{-}BrBA)_3 \cdot H_2O$: 474.92, 577.75, 655.83, 709.74.
ESI-MS for $Dy(o\text{-}BrBA)_3 \cdot H_2O$: 474.87, 577.90, 655.75, 709.68.

3.1.3. Infrared spectroscopy

The IR spectra of the ligands and the complexes were tested in the range of 4000–400 cm^{-1} and some of them are given in Fig. 1. The IR data are given in Table 2. Spectra analysis of o-HBrBA, $Sm(o\text{-}BrBA)_3 \cdot H_2O$ and $Dy(o\text{-}BrBA)_3 \cdot H_2O$ are shown as follows: IR spectrum of ligand shows $\upsilon_{(OH)}$ at 3433–2547 cm^{-1}, which occurs red-shift in the complexes. $\upsilon_{(C=O)}$ at 1685.32 cm^{-1} and the $\delta_{OH(COOH)}$ at 1117.86 cm^{-1} in the ligand disappear in the complexes. New absorption peaks of $\upsilon_{as(COO}^{-}$ and $\upsilon_{s(COO}^{-}$ appear at around 1543 cm^{-1} and 1407 cm^{-1} in the complexes. Another new absorption peak of $\upsilon_{(O-M)}$ appears at 569.1 cm^{-1} and 570.2 cm^{-1} in the complexes, respectively. All the changes indicate that the rare earth ions have coordinated to the ligands. The $\Delta\nu$ ($\Delta\nu = \nu_{(COO)as} - \nu_{(COO)s}$) value is used to determine the nature of the bonding of carboxylate to metal ions. It is generally believed that $\Delta\nu$ is below 200 cm^{-1} for the bidentate carboxylate moiety, but greater than 200 cm^{-1} for the unidentate carboxylate moiety [26]. As shown in Table 2, all the values of $\Delta\nu$ are between 113.5 cm^{-1} and 139.6 cm^{-1}, and indicate that the title complexes are

Table 1
Composition analysis (%) and molar conductivities λm (S cm^2 mol^{-1}) of the rare earth complexes.

Complexes	C (%)	H (%)	RE (%)	λm (S cm^2 mol^{-1})
$Sm(p\text{-}FBA)_3 \cdot H_2O$	42.87(43.07)	2.12(2.39)	26.01(25.64)	11.4
$Dy(p\text{-}FBA)_3 \cdot H_2O$	42.56(42.18)	2.52(2.34)	26.83(27.20)	12.0
$Sm(p\text{-}ClBA)_3 \cdot 2H_2O$	39.04(38.62)	2.56(2.45)	23.45(22.99)	12.2
$Dy(p\text{-}ClBA)_3 \cdot 2H_2O$	38.15(37.89)	2.75(2.41)	24.82(24.44)	11.8
$Sm(p\text{-}BrBA)_3 \cdot H_2O$	32.74(32.83)	2.26(1.82)	19.37(19.54)	13.8
$Dy(p\text{-}BrBA)_3 \cdot H_2O$	32.77(32.30)	1.92(1.79)	20.35(20.83)	14.3
$Sm(o\text{-}FBA)_3 \cdot 2H_2O$	41.61(41.79)	2.54(2.65)	25.21(24.88)	18.2
$Dy(o\text{-}FBA)_3 \cdot 2H_2O$	40.55(40.94)	2.36(2.60)	26.54(26.40)	18.6
$Sm(o\text{-}ClBA)_3 \cdot H_2O$	39.88(39.72)	2.17(2.21)	23.55(23.64)	20.3
$Dy(o\text{-}ClBA)_3 \cdot H_2O$	39.32(38.95)	2.07(2.16)	24.83(25.12)	21.5
$Sm(o\text{-}BrBA)_3 \cdot H_2O$	32.59(32.83)	2.05(1.82)	19.63(19.54)	19.0
$Dy(o\text{-}BrBA)_3 \cdot H_2O$	32.58(32.30)	1.94(1.79)	20.41(20.83)	18.2

Remark: the values in brackets are theoretical values.