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Enhanced fluorescence from Dy^{3+} owing to surface plasmon resonance of Au colloid nanoparticles

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Abstract

Gold colloidal containing rare earth ions Dy^{3+} were prepared at room temperature. Fluorescence spectra of Dy^{3+} ions and Au colloid containing Dy^{3+} were measured. For solution containing Dy^{3+}, fluorescence emission occurs at visible light wavelength region. Two emission peaks are observed at 480 nm and 570 nm respectively when the corresponding excitation wavelength is at 350 nm. When Au colloids were added to the solution containing Dy^{3+}, both these two fluorescence peaks were enhanced. Furthermore, with the increasing Au content, the fluorescence increases first and then decreases. We believe that this increased fluorescence are due to the local field enhancement around Dy^{3+} ions owing to the induced higher orders of surface plasmon resonance.

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Keywords: Fluorescence; Au colloid; Dysprosium ions; Surface plasmon resonance; Local field

1. Introduction

Rare earth ions in nanometer-size semiconductors or metallic low dimensional structures have received much attention in recent years due to their special electronic and optical properties [1–4]. Hussain et al. [1] have reported the fluorescence characteristics of the measured emission transitions of Eu^{3+} and Dy^{3+} doped laser liquids, by the application of the Judd-Ofelt intensity factors obtained from their absorption spectral profiles. Ishizaka and Kurokawa [2] have highly incorporated the rare earth ions into alumina by sol–gel method derived from aqueous $AlCl_3$ solution. The absorption, emission and lifetime have been examined for each doped film at room temperature. In the letter of Brik et al. [3], optical spectra of Dy^{3+}:$LiYF_4$ (Dy^{3+}:YLF) single crystal were analyzed using Judd-Ofelt theory and discrete variational multielectron method. Oscillator strengths of transitions up to 39,000 cm^{-1} in the absorption spectrum, branching ratios and nonradiative transition rates were calculated; assignment of the absorption transitions was given. In the paper of Gu et al. [4], Dy^{3+} doped ZnO nanocrystals have been synthesized via a simple combustion method. The as-prepared cuboid-like ZnO nanocrystals appear to be single hexagonal crystalline phase with an average diameter of 20 nm. The characteristic luminescence of doped Dy^{3+} ions has been evaluated, and the highly enhanced photoluminescence of Dy^{3+} ions can be obtained by Li^+ doping.

In nanometer-size metallic particles, there are several classes of electromagnetic modes such as surface modes and local field. Surface plasmons are collective electromagnetic oscillations at metallic surfaces. It is widely accepted that for optical processes the primary role of the roughness in metals or the small size of noble metal particles is to enhance the local optical fields via localized plasmon resonance, and thus improve the efficiency of light absorption and emission [5–7]. Hayakawa et al. [8 9] have described the increase of europium ion fluorescence owing to resonant plasma oscillation of silver particles in silica glass, which were precipitated by annealing in a reducing

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atmosphere sol–gel derived SiO_2 glass containing Ag^+ and Eu^{3+} ions. They have come to the conclusion that the most probable mechanism for the fluorescence increase is a local field enhancement around Eu^{3+} ions, due to the induced surface plasmon resonance of Ag particles. Recently, they have also reported the enhanced photoluminescence of trivalent europium ions in the vicinity of nanometer-sized Au particles in glasses. They believed that Eu^{3+} ions were strongly excited by the energy transfer from C=O groups, which were placed in enhanced local fields near Au nanoparticles due to higher orders of surface plasmon resonances [10].

In this paper, we report on the fluorescence excitation and emission spectra properties of gold colloidal containing Dy^{3+}. The relation between the fluorescence enhancement and the Au content has also been studied. Furthermore we discuss in detail the mechanisms of the enhanced fluorescence from Dy^{3+}.

2. Experimental

Dysprosium oxide Dy_2O_3 (0.03 g) was dissolved in H_2O (25 ml, including 20% HNO_3). This synthesis was conducted under an ultrasonication at room temperature. The resultant solution was transparent and has no color. Gold colloid nanoparticles were prepared via electrochemical method [11 12]. The transmission electron microscopic (TEM) images are obtained by using a JEOL JEM-200CX TEM, the Au nanoparticles with mean diameter 15 nm have been observed, as shown in Fig. 1. The color of the resultant solution was red. At last, various amounts of gold colloid were added to the solution containing Dy^{3+} with gentle mixing. Then the resultant solution turns to light pink.

3. Results and discussion

The UV–visible spectra are recorded on a Hitachi U-2001 spectrophotometer. To a solution containing only Dy^{3+}, a strong absorption peak was noted at around 350 nm, as shown in Fig. 2. When amount of Au colloid were added to the solution containing Dy^{3+}, this absorption peaks fixed at 350 nm increase. Furthermore, a new absorption peak fixed at 530 nm was observed, which is due to the surface plasmon resonance of Au nanoparticles.

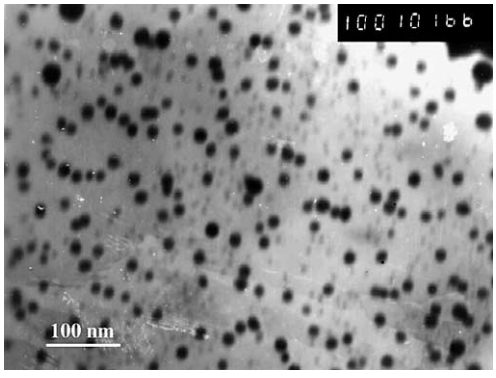

Fig. 1. TEM image of gold colloidal nanospheres.

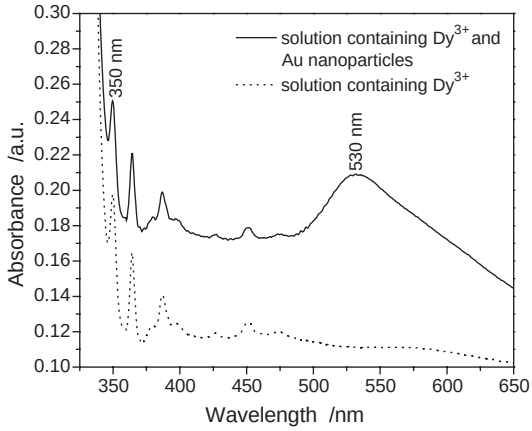

Fig. 2. Absorption spectra of solution containing Dy^{3+} and solution containing both Au nanoparticles and Dy^{3+}.

Both fluorescence excitation and emission spectra are recorded on a Perkin Elmer LS 55 spectrophotofluorometer. It is known that, to a solution containing Dy^{3+}, two fluorescence emission peaks will take place at 483 and 576 nm respectively corresponding to $^4F_{9/2}\rightarrow{}^6H_{15/2}$ and $^4F_{9/2}\rightarrow{}^6H_{13/2}$ transitions of the Dy^{3+} ion [1]. So the fluorescence excitation spectra are studied in order to find the sensitive excitation frequency. The excitation spectrum in Fig. 3 is the scanning excited wavelength from 200 to 450 nm when the detection wavelength was located at 483 nm. The excitation spectrum in Fig. 4 is the scanning excited wavelength from 200 to 550 nm when the detection wavelength was located at 576 nm. The experimental results in Figs. 3 and 4 show that both the fluorescence at 483 nm and 576 nm are sensitive to the excitation at 350 nm. It is

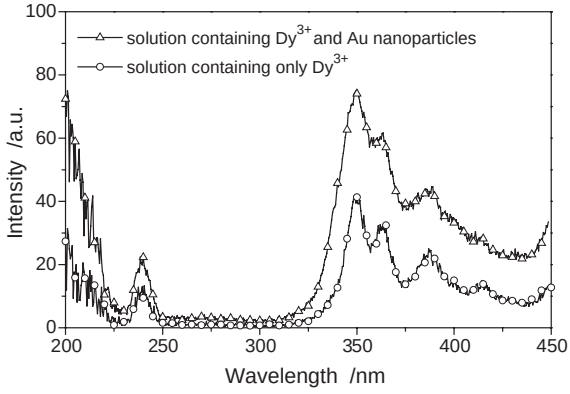

Fig. 3. Excitation spectra of solution containing only Dy^{3+} and solution containing both Au nanoparticles and Dy^{3+} (detection wavelength is 483 nm).