Energy transfer and surface plasmon resonance in luminescent materials based on Tb(III) and Ag or Au nanoparticles in silica xerogel

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ABSTRACT

Two-component material consisting of terbium(III) ions doping silica xerogel prepared by sol–gel procedure shows enhanced Tb(III) photoluminescence. We postulate that in this material the enhancement is owing to energy transfer from one of the defect states in silica to emitting states $^3D_3$ and $^5D_4$ of Tb(III). Surface plasmon resonance effect causes two contrary phenomena. Thus, if in the vicinity of the Tb(III) emission centers are present nanoparticles of Ag, observed is additional improvement of the Tb(III) emission. While, presence of Au nanostructures in the silica doped with Tb(III) causes quenching of the luminescence. In general, both the three-component materials exhibit enhancement of the component silica emission band in the resultant 380 nm band and relatively high thermal stability, especially above 600 °C.

1. Introduction

Nanoscale materials are of great interests due to their unique, optical electrical and magnetic properties These properties are strongly dependent on the size and shape of the particles [1,2], and therefore it is very important to be able to control the morphology of the nanomaterials. Especially, the optical properties of metallic nanoparticles depend on the shape [3–5].

Common methods for size and shape control employ the capping agents, such as surfactants, ligands, polymers and dendrimers to confine the growth in the nanometer regime. These methods first of all produce spherical particles due to the low surface energy associated with such particles [6].

Nanostructured metal nanoparticles show a characteristic surface plasmon absorption with extinction coefficients exceeding those for organic laser dyes by several orders of magnitude, as previously reported Reisfeld et al. [7]. Collective plasmon oscillations lead to a strong field enhancement in the proximity of metal nanoparticles. All of these properties make metal nanoparticles very attractive for a wide range of optical and optoelectronic applications [8].

Much attention has been paid to the study of optical properties of nanometer-sized particles dispersed in glass or xerogel matrices from the viewpoint of scientific interest and their application [9]. The increase of luminescence due to surface and size quantization effects is a very promising route for the improvement of optical de-

vices. For instance, there is possibility to enhance by at least one order of magnitude the emission efficiency of a luminescent center in the vicinity of a metallic particle [10].

Recently, under observation are glasses doped with lanthanide(III) ions containing nanosized noble metal particles [11–13]. In these systems any significant influence of the metallic particles on the absorption and emission rates of the lanthanide ions is due to *surface plasmon resonance* (SPR) of metal nanoparticles. It is one of the elemental excitations in solid-state quantum physics that provides an increase in the local electromagnetic field strength around a nanometer-sized metal.

We are interested in use of the latter effect for intensity improvement of trivalent terbium luminescence in silica xerogel. Thus, the samples consists of Tb(III) ions as emission centers in the vicinity of Ag nanoparticles entrapped in silica xerogel.

2. Experimental

2.1. Chemicals

Silver nitrate, $AgNO_3$ (99.995%); tetrachloroauretic acid, $HAuCl_4 \cdot 3H_2O$; trisodium citrate dihydrate, $(OH)C_3H_4(COONa)_3 \cdot 2H_2O$ (99%); tetramethoxysilane, $(CH_3O)_4Si$ (TMOS, 98%) and terbium(III) chloride hexahydrate, $TbCl_3 \cdot 6H_2O$ (99.9%) were purchased from Aldrich. Ammonia solution and methanol (MeOH) were from POCh (Poland). For the preparation of all the samples deionized water was used.

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2.2. Preparation of silver nanoparticles

Preparation of Ag nanoparticles was based on reduction of $AgNO_3$ in the presence of trisodium citrate [14]. Thus, a 50 cm^3 aqueous solution containing $1.25 \cdot 10^{-5}$ mole $AgNO_3$ and $6.8 \cdot 10^{-5}$ mole sodium citrate was prepared. The solution was boiled 20 min. The sodium citrate serves only as a stabilizer, since it cannot reduce the silver salt at a room temperature.

Preparation of Au nanocrystals was realized by the similar method as above and with the same amount of tetrachlorauretic acid, water and trisodium citrate.

2.3. Synthesis of the material

The method used to prepare silica gels loaded with silver nanoparticles was a one-pot procedure. The Ag particles and Tb(III) ions were entrapped in silica xerogel by sol–gel method [15]. Thus, 2.46 cm^3 TMOS was dissolved in 4.0 cm^3 MeOH and 1.15 cm^3 water was added. Next, 2.0 cm^3 the aqueous sol of Ag (or Au) (concentration $c = 2.5 \cdot 10^{-4}$ M) and $5 \cdot 10^{-4}$ mole $Tb(NO_3)_3$ in MeOH were added to the mixture of TMOS and MeOH. The final molar ratio of TMOS:H_2O:MeOH was 1:4:8. After several hours a rigid wet gel with Ag nanoparticles was obtained. For comparison was prepared a sample consisting of Tb(III) ions immobilized in silica xerogel similar method. All the samples as were dried at 60 °C and then annealed at higher temperatures. Finally the materials were crushed and sieved (0.25–0.50 mm).

2.4. Apparatus

UV–vis absorption spectra were measured using a Perkin–Elmer Lambda 25 spectrophotometer equipped with 1 cm path length cuvettes.

The photoluminescence excitation and emission spectra were recorded using a Perkin–Elmer LS 50B spectrofluorimeter with a reflection attachment.

The annealing of the luminescent samples was carried out in an air atmosphere in a programmable oven equipped in a temperature controller of type SM-946.

3. Results

Luminescence spectra of silica xerogel obtained by sol–gel procedure are demonstrated in Fig. 1. Significant bands in the excitation spectra are placed at 221, 232 and 250 nm (Fig. 1(A)). While the emission spectra consist of a broad band peaked at 363 nm and its longer wavelength side is structured in each spectrum with peaks placed at 391, 457, 481 and 526 nm.

In Fig. 2 are present luminescence spectra of the material with Tb(III) incorporated into SiO_2 xerogel. The excitation spectrum (λ_{em} = 542 nm) recorded after drying at 60 °C consists of three characteristic bands at 224, 270 and 350 nm. The first band is characteristic for exciton in the silica, while the second band corresponds to the $4f^n \rightarrow 4f^{n-1} 5d^1$ transition in Tb(III) and third one is of the type of f–f transition attributed to $^7F_6 \rightarrow {}^5D_2$ transition in this ion [16].

Applied excitation wavelength equal to 224 nm causes a great enhancement of the typical Tb(III) emission spectrum [(curve (a)] in comparison with the used normal for Tb(III) λ_{exc} = 350 nm [curve (b)]. The enhanced Tb(III) spectrum consists first of all of strong and sharp bands at 488, 542, 585 and 620 nm, corresponding to $^5D_4 \rightarrow {}^7F_J$ transitions, where J = 6, 5, 4 and 3, respectively [17]. There is also a broad band (λ_{max} = 380 nm) present. The inset in Fig. 2 shows that the luminescent material achieves the highest emission intensity after drying at 200 °C but the material treated
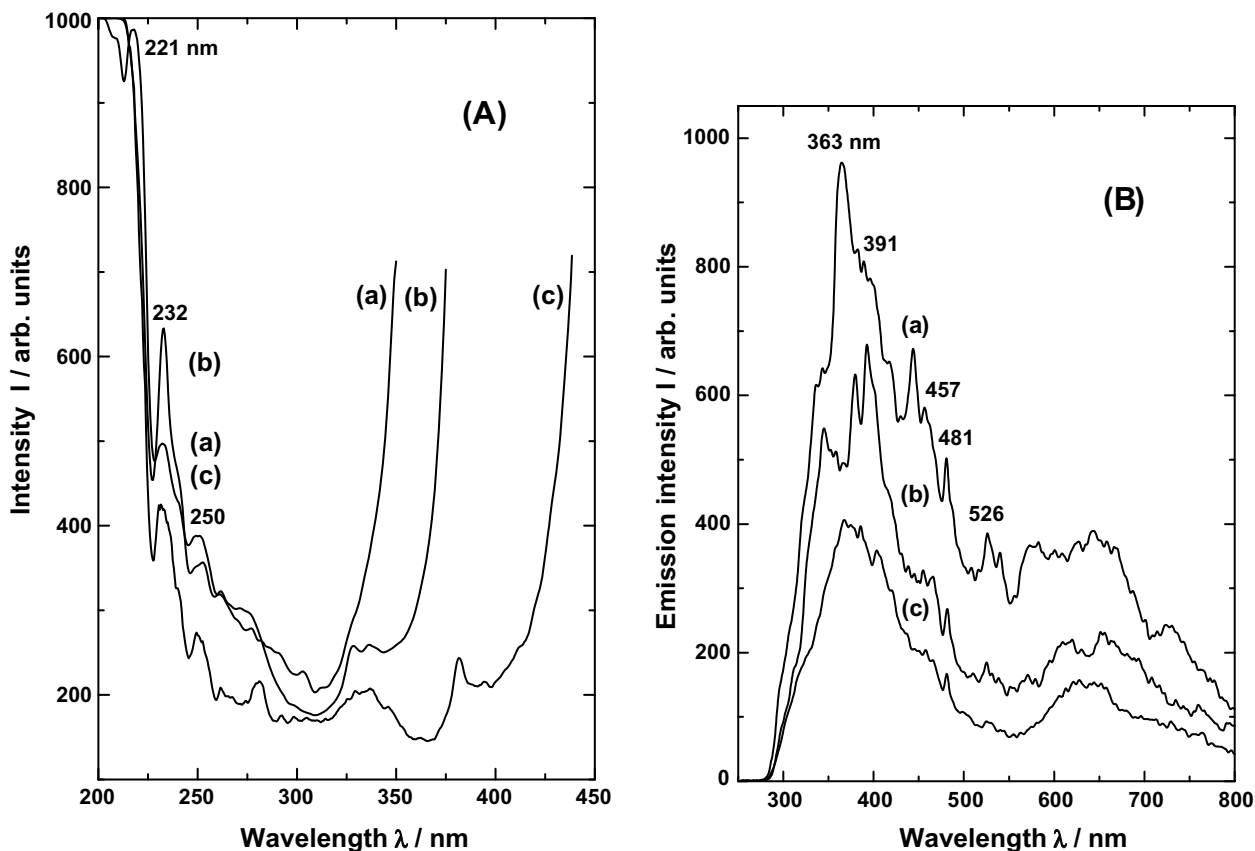

Fig. 1. Luminescence spectra: (A) excitation [λ_{em} = (a) 363, (b) 391 and (c) 457 nm], and (B) emission [λ_{exc} = (a) 221, (b) 232 and (c) 250 nm] of silica xerogel.