Journal of Luminescence 204 (2018) 104–109

Contents lists available at ScienceDirect

Journal of Luminescence

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

Regulation of gold nanoparticles for the rare earth luminescence enhancement based on nanoporous silica glass

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ARTICLE INFO

Keywords:
Nanoporous silica glass
Rare earth ions
Nanoparticles
Luminescence intensity

ABSTRACT

A silica composite system with rare earth ions and gold nanoparticles was fabricated based on nanoporous silica glass. The formation and optical properties of the systems were controlled by the nanoparticles doping concentration and heat treatment. The luminescence intensity dependence on the $HAuCl_4$ doping concentration and heat-treated temperature were investigated. At the optimized concentration of $HAuCl_4$ and heat-treated temperature, the maximal luminescence intensity can be enhanced up to 14.33-fold for Yb^{2+} and 10.52-fold for Eu^{2+}. It is indicated that the rare earth ions luminescence can be regulated by interactions distance between different types of RE ions and metal NPs as well as the state of nanopores.

1. Introduction

The unique electron shell structure of rare earth (RE) ions allows them to be widely utilized in illumination, displaying, data storage and fiber devices [1–3]. In the electron shell structure of RE ions, the 4f electron shell is affected slightly by external atmosphere under the shielding of outer 5s and 5p electrons. There are two transitions of RE ions, one is the forbidden transition in the 4f configuration while the other is the 4f-5d transition usually occurring in the two valence RE ions. The forbidden transition between 4f configuration is less affected by the external crystal field and express sharp emission. The lifetime of the excited state is generally from microseconds to milliseconds. The 4f-5d transition occurs between the 4f shell and outer 5d shell. The electrons located at 5d shells do not get shelter from the outer shell and the emission peak of the RE ions can be easily affected by the external matrix environment. The luminescence of these transitions is abundant with broadband emission and the lifetime is at microsecond scale. Recently, metal nanoparticles (NPs) have promoted infinite potential in RE ions luminescence enhancement because of their distinctive properties in maneuvering the interactions between NPs and local electromagnetic field [3–7]. This characteristic has made it possible to be utilized in illumination display, fluorescent probe and optical fiber amplification. The luminescence emission of RE ions, such as Er^{3+} [8,9], Yb^{3+} [10,11], Pr^{3+} [12], Sm^{3+} [13], Eu^{2+}, and Eu^{3+} [1,14], has been demonstrated to be greatly enhanced by metallic NPs. The enhancement mechanism can be partly attributed to the energy transfer from NPs to RE ions and the enhanced local optical field induced by Surface Plasmon Resonance (SPR) from NPs, especially when the wavelength of incident light is close to the SPR absorption peak [15,16]. When the excitation wavelength matches well with the specific incidence conditions, the free electrons of the metal will be excited and the intense resonance is occurred, which is well known as SPR. SPR exhibits great ability in altering the luminescence intensity of RE ions by enhancing surrounding electromagnetic field. The SPR effect is closely related to the NPs characters, which refers to the composite, shape, size and surrounding environment of the nanostructures as well as the interaction distance with RE ions [17].

Some approaches have been reported in preparing NPs with great performance, such as sol-gel method [18,19], thermal annealing [20], ion implantation [21], electron beam lithography [22], template method [23,24], photochemical reducing technics [25]. Among these methods, thermal annealing method is competitive to prepare NPs in a more efficient and convenient way. In terms of the characteristics of NPs, they can be defined and controlled by changing the heat-treated temperature and atmosphere in thermal annealing method. The application aspect strongly depends on the prescribed properties of NPs embedded in glass matrix. Considering the great optical performance, it's of great significance to achieve a balance between the physical parameters and other competing factors. Regulating the size and geometrical shape of NPs is the simplest way to engineer the optical function of them. Nanoporous silica glass (NPSG) [26], which possesses plentiful non-bridging oxygen as well as network broken bond and

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https://doi.org/10.1016/j.jlumin.2018.07.041
Received 26 February 2018; Received in revised form 24 July 2018; Accepted 25 July 2018
Available online 26 July 2018

destroys the glass network continuity in physical way, shows a great promising in adsorbing more ions. Moreover, NPSG is equivalent to a kind of molecular sieve, that is, RE ions and NPs can be confined in the nanopores and nanochannels of the glasses. Such flexible interconnected nanostructures have certain effects on the size, shape, distribution as well as the interaction distance with RE ions, which can regulate the growth of NPs in a more accurate way. Accordingly, the emission intensity of RE ions can be adjusted in this way.

The trivalent Ytterbium ions are widely used as gain ions in high power fiber laser, which has been deeply investigated. While the divalent Ytterbium ions are rarely studied. Yb^{2+} is the potential factors contributing to the photodarking in Yb^{3+} doped fiber laser [27]. As a sensitizer, Yb^{2+} can enhance the luminescent properties and chromogenic properties of Eu^{2+}, which has widely application prospects in UV-LED [28]. Europium is a kind of rare earth element which is widely ultilized in visible luminescent materials. The divalent charge state of Eu^{2+} shows broad-band emission in the blue and green spectral range [29]. Such materials express great potential in preparing scintillators, white light source, X-ray storage, and etc [30,31]. However, the emission band of divalent charge state of rare earth ions are usually associated with 4f-5d transition which is sensitive to the glass host. Yb^{2+} radiation shows a very broad band emission nearly covers the whole visible range with ultra-violet or blue laser excitation in the different glass matrix while the Eu^{2+} shows blue emission under ultra-violet excitation. Thus, it is of great significance to study on the Yb^{2+} and Eu^{2+} radiation in NPSG.

In this work, NPSG was used as the matrix material to regulate metallic NPs and their interaction with RE ions. The different doping concentration and heat treatments were carried out to control physical features of NPs. The spectroscopic properties were systematically investigated to understand the regulation of RE ions luminescence. The results showed that the luminescence intensity of RE ions could be greatly enhanced by SPR effect induced by metallic NPs in NPSG.

2. Experimental

Firstly, SiO_2, Na_2CO_3 and H_3BO_3 were used as the raw materials to fabricate the sodium borosilicate glass with the composition (in mol%) of $66SiO_2$–$26H_3BO_3$–$8Na_2CO_3$. All reagents were purchased from Alladin reagent with the purity of 99.99%. The melted bulk glass to the size of 10 mm*10 mm*1 mm could be obtained by mechanically processing. The phase separation and acid treatment were carried out to create interconnected nanopores in NPSG [32]. Secondly, the phase separation of borosilicate glass was carried out at 590 °C for 24 h. After such heat treatment, the glass was separated into two different phases: one phase rich in sodium and boron and the other phase rich in silica. Different phase showed distinct tolerance ability to inorganic acid. The phase rich in sodium and boron could be easily dissolved in hot acid like nitric acid, hydrochloric acid and sulphuric acid, while the other phase, rich in silica, could not be dissolved. Hence, immersed in hot diluted hydrochloric acid for 10 h at 90 °C, the soluble phase rich in sodium and boron of the glass sample could be washed out and left the interconnected SiO_2 skeleton. The nanopore size of the NPSG can be adjusted by the host composite and subsequent treatment in a wide range, which determines the absorption degree and homogeneity of doping ions. Then the noble metal ions were introduced into the NPSG by the solution doping method. After soaking the NPSG samples into the mixture solution of × mol% $Eu(NO_3)_3{\cdot}6H_2O$ or $Yb(NO_3)_3{\cdot}5H_2O$ and y mol% $HAuCl_4$ for 2 days, the glass samples were heat-treated under different temperatures (600 °C,700 °C, 800 °C, 900 °C, 1000 °C) in 95%Ar/5%H_2 reducing atmosphere, respectively.

The pore structure of the NPSG was measured by field emission scanning electron microscope (FESEM) Sirion 200 (FEI, NL). The morphology of Au NPs was taken by transmission electron microscope (TEM). Powder X-ray diffraction (XRD) spectrum was recorded by a powder diffractometer with Cu Kα radiation (40 kV × 25 mA) and a graphite monochromator with 2θ from 10° to 80°. The absorption spectrum of glass sample in the wavelength range of 400–1100 nm was measured with a Perkin-Elmer-Lambda 950 UV/Vis/NIR spectrophotometer. The luminescence spectrum was measured by Jasco FP6500 Spectrofluorometer. All measurements were taken at room temperature.

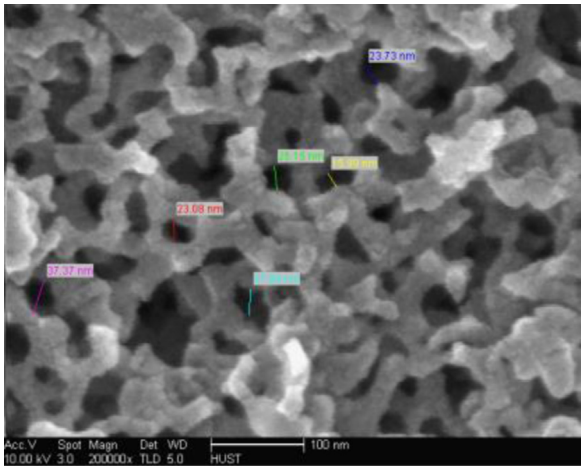

Fig. 1. The SEM image of the nanopores of NPSG.

3. Results and discussion

3.1. Shape, size and SPR peak

Fig. 1 displays the SEM images of the prepared NPSG. The micropore structure labeled shows that the size of nanopores are centrally distributed from 20 nm to 30 nm. The size of the nanopores can be adjusted in a certain range by changing the matrix composite and phase separation technology.

To analyze the crystal structure of the Au NPs in NPSG, the X-ray diffraction (XRD) patterns of the sample containing nanoscale Au is measured (Fig. 2).

Four different diffraction peaks located at 33.86°, 44.65°, 64.6°, 76.6° can be seen in the Fig. 2, which correspond to (111), (200), (220), (311) crystal face in the gold crystals respectively (JCPDS Card File No. 04-0784). With the increasing of the $HAuCl_4$ concentration, more of Au NPs can be formed, that is, more crystal faces can be exposed in this case. Thus, the diffraction peaks become sharper with higher doping concentration.

The size of formed Au NPs can be estimated by the Scherrer equation [33],

$$D = K\lambda/\beta \cos\theta \quad (1)$$

K- a constant, value is 0.89; λ-X ray wavelength, value is 0.15405 nm; β- the diffraction peak half width; θ- diffraction angle.

From the XRD patterns, we can get different diffraction angle θ_i (i = 1, 2, 3, 4). The size of metallic NPs can be calculated by the Eq. (1). The average particle diameters of Au NPs is around 21.21 nm, which corroborates the regulation function of nanopores on the size of metallic NPs. Fig. 2(b) shows the XRD pattern of the composite system with rare earth element Yb and gold nanoparticles. It can be seen that just four peaks related to the gold nanoparticles exist in the XRD pattern. There is no crystal of rare earth element in the glass.

Fig. 3 shows the morphology of the Au NPs in the composite system with NPs and rare earth ions. Fig. 3(a) shows composite system with Au NPs and element Yb with heat-treated temperature of 800 °C while Fig. 3(b) presents the dimension distribution of Au NPs with 1000 °C. It can be seen that more small size Au NPs around 5 nm exist in the visual field of Fig. 3(a). High temperature accelerates the decomposing of