Materials Letters 205 (2017) 145–149

Contents lists available at ScienceDirect

Materials Letters

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

Localized surface plasmon-enhanced emission from red phosphor with Au-SiO$_2$ nanoparticles

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ARTICLE INFO

Article history:
Received 12 April 2017
Received in revised form 15 June 2017
Accepted 16 June 2017
Available online 17 June 2017

Keywords:
Localized surface plasmon (LSP)
Phosphor
Nanoparticles
Light emitting diodes
Color rendering index

ABSTRACT

We investigated the effect of localized surface plasmon (LSP) on the efficiency of phosphors. Owing to the high densities of Au nanoparticles, we found that an additional absorption peak appeared at 650 nm, which can resonant couple with red phosphors. To avoid agglomeration caused by high-density Au nanoparticles, we suggest using Au-SiO$_2$ core-shell nanoparticles. The red phosphor efficiency was improved by achieving energy matching between the phosphor and LSP of the Au-SiO$_2$ core-shell nanoparticles. By optimizing the Au nanoparticle density and spacer layer thickness, the red phosphor efficiency was improved by 18% as compared to that of the isolated red phosphor. This study provides a solution for fabricating white light emitting diodes with high efficiency, high color-rendering index, and wide color gamut.

1. Introduction

Phosphor-converted white light emitting diodes (WLEDs) exhibiting advantages such as high efficiency, low energy consumption, and long lifetime have drawn much attention owing to their wide applications [1]. The most common approach for producing WLEDs is to combine a blue LED chip with yellow yttrium aluminum garnet:cerium (YAG:Ce^{3+}) phosphors, which provide a high efficiency. However, a poor color-rendering index and high color temperature are achieved owing to the relatively weak emission of the YAG:Ce^{3+} phosphor in the red spectral region. Furthermore, the "white" output light of such LEDs is limited owing to a high corrected color temperature (CCT) of 4500–11000 K, affording a cold white light output. To improve the color-rendering index and obtain a warm white light output, a complementary red light must be employed to compensate for the red color deficiency or to produce white light in blue-green-red mode. Hence, high efficiency red phosphors excitable by blue and UV LEDs are in great demand. $Y_2O_2S:Eu^{3+}$ and $CaAlSiN_3:Eu^{2+}$ are the commonly used commercial red-emitting phosphors. However, they exhibit disadvantages such as low efficiency, short working lifetime under UV irradiation, and air sensitivity [2,3]. In order to enhance the emission efficiency of currently available phosphors, many methods focusing on developing new materials and new production techniques have been proposed [4].

A promising alternative approach is to utilize localized surface plasmon (LSP), which is the collective oscillation of surface charges on metallic nanoparticles and nanostructures embedded in a dielectric matrix [5]. Overlapping of the local electromagnetic field with excitons in the phosphor results in a coupling effect, causing effective energy transfer from the excitons of phosphor into LSP for emission, thereby creating an alternative emission channel. Therefore, the phosphor efficiency can be significantly improved by increasing the spontaneous emission rate. The efficiency of rare-earth ions and phosphor has been reported to be improved by LSP [6–8]. However, reproducibility is a difficult issue since nanoparticles are easily agglomerated, resulting in a change in the resonance efficiency and energy. It is also important to control the size, density, shape, and surrounding material of the metal nanoparticles. Many methods of producing metal nanoparticles, nanotubes, and core-shell nanoparticles have been proposed [6–19].

Here, we focus on the feasibility of using plasmon-enhanced red phosphor in LEDs. To avoid Au nanoparticle agglomeration, we propose the use of multicore Au nanoparticles-SiO$_2$ core-shell nanoparticles, improving the efficiency by 18%.

2. Experimental

A sapphire substrate was used to fabricate samples for performing photoluminescence (PL) measurements. A paste mixture,

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http://dx.doi.org/10.1016/j.matlet.2017.06.082
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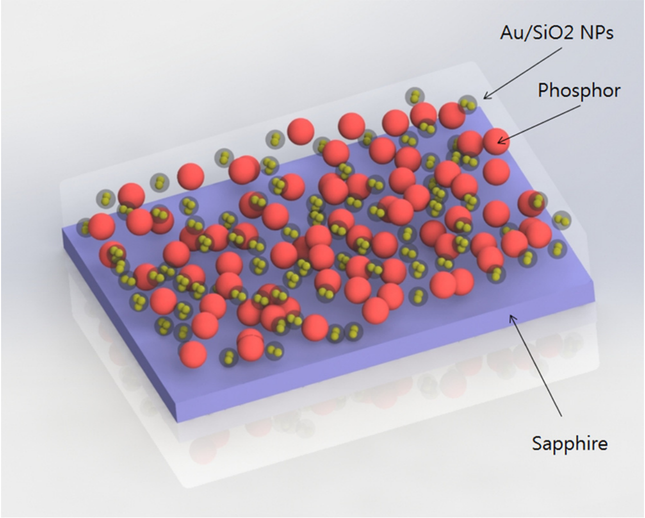

Fig. 1. Schematic diagram of the control samples with red phosphor and Au-SiO_2 core-shell nanoparticles on a sapphire substrate.

consisting of silicon resin, red phosphor, and metal nanoparticles, was spin coated on the sapphire substrate at 2000 rpm. Fig. 1 shows the schematic of the control samples with red phosphor and Au-SiO_2 core-shell nanoparticles on sapphire substrate.

Citrate-capped Au nanoparticles were prepared via a modified Frens method [17]. All reagents used to fabricate the Au and Au-SiO_2 core-shell nanoparticles were purchased from Sigma-Aldrich. To a boiling solution of 20 mL 0.1 wt% chloroauric acid ($HAuCl_4 \cdot 3H_2O$) in a 100-mL beaker under stirring, 1 mL of 1 wt% trisodium citrate dihydrate ($Na_3C_6H_5O_7 \cdot 2H_2O$) was quickly added. The color of the solution changed within several minutes from yellow to black and subsequently to red depending on the nanoparticle size. We could directly coat the surfaces of these gold nanoparticles with conformal shells of amorphous silica using a sol-gel process reported previously [18,19]. To fabricate Au-SiO_2 core-shell nanoparticles, 10 mL of the Au nanoparticle solution was centrifuged for 1 h at 3500 rpm to separate Au nanoparticles. The nanoparticles were then diluted with 20 mL isopropyl alcohol. The Stöber system was formed by mixing the 20-mL solution and 500 μL ammonium hydroxide. Then, 0.6 mL TEOS was added four times for 24 h at 25 °C under stirring to produce Au-SiO_2 core-shell nanoparticles. $CalSiN_3:Eu^{2+}$ was used as the red phosphor material.

The surface morphology of the evaporated Ag nanoparticles was determined using scanning electron microscopy (SEM; Hitachi S-4800). The LSP resonance can lead to extinction of the incident electromagnetic wave. Thus, the extinction spectra enabled us to study the plasmonic resonance caused by metallic nanoparticles [5]. The extinction (absorption) spectrum of the Ag particles was obtained using a (Agilent 8453 UV–Visible).

3. Results & discussion

LSP of Au nanoparticle causes green emission; however, it changes with nanoparticle agglomeration [20–22]. To estimate the change in the resonance energy of LSP that matches with the energy of red phosphor, we measured the absorption spectrum of Au nanoparticles with various densities. SEM images revealing the surface morphology of the Au nanoparticles are shown in Fig. 2. The average size of the Au nanoparticles is 40 ± 10 nm. The Au nanoparticle density was significantly improved by increasing the absorption time before washing with deionized (DI) water during drop coating. Au nanoparticles with densities of $6.4 \times 10^{-8}\,cm^{-2}$, $20 \times 10^{-8}\,cm^{-2}$, $43 \times 10^{-8}\,cm^{-2}$, and $55 \times 10^{-8}\,cm^{-2}$ are shown in Fig. 2(a), (b), (c), and (d), respectively. Fig. 2(e) shows the UV–visible spectra of Au nanoparticles with different densities. At densities lower than $20 \times 10^{-8}\,cm^{-2}$, nanoparticles exhibit a single plasmon peak at 520 nm. On increasing the density, the absorption at 520 nm increased. At $43 \times 10^{-8}\,cm^{-2}$, an additional peak appears at 650 nm, which could be attributed to the interaction of Au nanoparticles owing to a decrease in the distance between nanoparticles [23]. This result indicates that the high density of Au nanoparticles (or distance between nanoparticles) is important for achieving resonant energy coupling between red phosphor and nanoparticles. However, increasing the density of Au nanoparticle without aggregation is difficult while mixing with phosphor. It is also reported that the nanoparticle aggregation cannot be avoided and aggregation results in changes in the SP resonance peak [21].

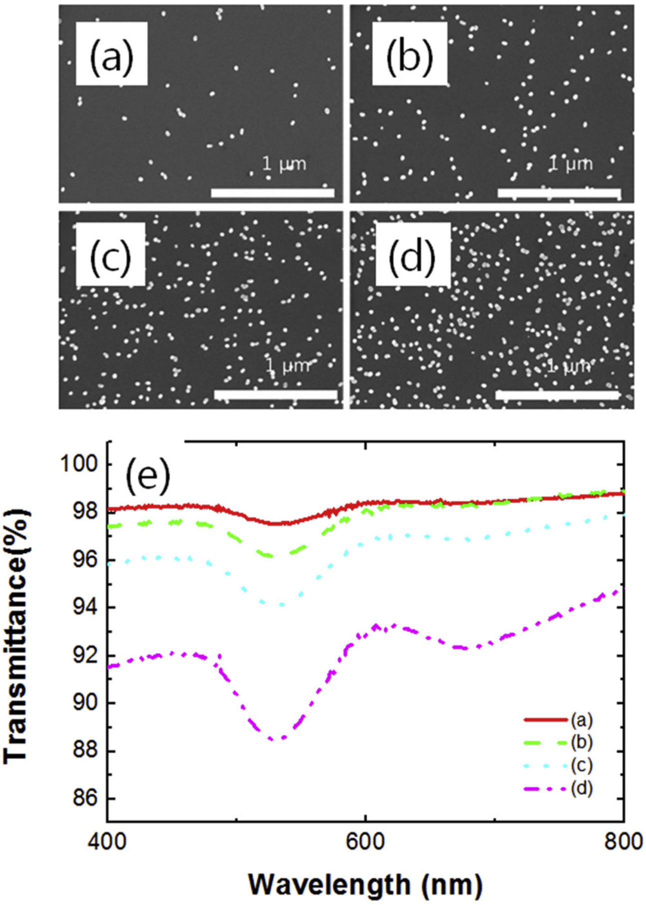

Fig. 2. FE-SEM images of Au nanoparticles depending on absorption times of (a) 2, (b) 5, (c) 10, and (d) 20 min, and (e) transmittance of Au nanoparticles with various densities.

To solve these problems, we prepared multicore Au-SiO_2 core-shell nanoparticles by inducing high surface charges in Au nanoparticles by controlling the citrate concentration [22]. As shown in Fig. 3, the particle size is increased to 150 ± 40 nm with silica coating. The number of Au nanoparticles in the SiO_2 shell is not uniform (1–5) as shown in Fig. 3(c) and (d). However, no agglomeration of Au nanoparticles is observed in the SiO_2 shell. The distance between the Au nanoparticles in SiO_2 is below 20 nm, which might result in achieving resonance between Au nanoparticles and the red phosphor. The crystal structure of Au nanoparticles from an assembly of Au-SiO_2 core-shell nanoparticles was also obtained from both X-ray diffraction (XRD) and selected area electron diffraction as shown in Fig. 3(e) and (f),