

Enhanced fluorescence and heat dissipation of calcium titanate red phosphor based on silver coating



Zhenhua Chen^a, Xinxin Qin^a, Qinghong Zhang^a, Yaogang Li^{b,*}, Hongzhi Wang^{a,*}

^aState Key Laboratory for Modification of Chemical Fibers and Polymer Materials, College of Materials Science and Engineering, Donghua University, Shanghai 201620, China

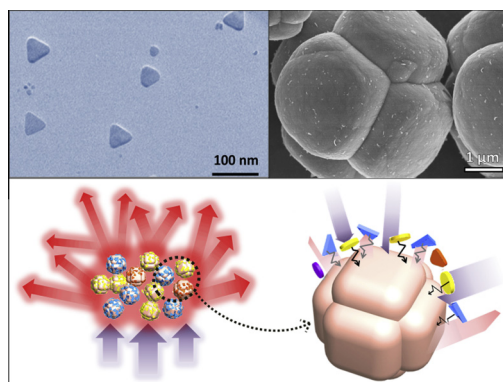
^bEngineering Research Centre of Advanced Glasses Manufacturing Technology, MOE, College of Materials Science and Engineering, Donghua University, Shanghai 201620, China

HIGHLIGHTS

- Silver colloid solutions with different extinction wavelengths were synthesised.
- Ag nanoparticles coated CaTiO₃:Eu³⁺ phosphor was obtained by opposites charge attracting.
- Both the PL intensity and heat dissipation of CTOE were enhanced by the Ag coating.
- Pc-LED made of Ag-coated CTOE had higher efficiency and more stable working status.

GRAPHICAL ABSTRACT

Ag nanoparticles coated CaTiO₃:Eu phosphor obtained from charge attracting process shows higher PL intensity and enhanced heat dissipation than the uncoated ones due to the LSPR effect and heat conduction of Ag nanoparticles, respectively.



ARTICLE INFO

Article history:

Received 8 May 2015

Revised 3 August 2015

Accepted 4 August 2015

Available online 4 August 2015

Keywords:

Calcium titanate phosphor

Heat dissipation

Localized surface plasmon resonance

Photoluminescence efficiency

Silver nanoparticles

ABSTRACT

Phosphor plays an important role in LEDs—the next generation of lighting source. However, many families of phosphor like titanate still face two severe problems: Low photoluminescence (PL) efficiency and poor thermal stability. Herein, the silver coating is applied to alleviate the above challenges. Ag nanoparticles with different morphology like disks or triangular plates are synthesised by a simple sol-reduction method, and then coated on the shape-regular CaTiO₃:Eu (CTOE) phosphor. When the localized surface plasmon resonance (LSPR) extinction spectrum of Ag nanoparticles matches well with excitation or emission wavelength, the PL intensity of CTOE phosphor would be efficiently enhanced. There is an optimum point of LSPR coating amount due to the balance of LSPR-enhancement and scattering/reflection–reduction of Ag nanoparticles. The coating of Ag also leads to an improvement in heat dissipation of CTOE phosphors; meanwhile an overmuch of Ag would also reduce the luminous efficiency. Thus the most suitable coating amount based on the overall consideration successfully enables the enhancement of both PL intensity and heat dissipation, and the pc-LED lamp packaged with Ag coated CTOE phosphor also shows a higher efficiency and more stable working status than the uncoated ones.

© 2015 Elsevier Inc. All rights reserved.

* Corresponding authors.

E-mail addresses: yaogang_li@dhu.edu.cn (Y. Li), wanghz@dhu.edu.cn (H. Wang).

1. Introduction

LEDs are emerging as the most promising solid-state light source for the next generation lighting and display fields due to their outstanding properties like energy savings, environment-friendliness and long lifetime [1–3]. The most widely used commercial pc-LEDs normally adopt a blue GaN LED chip covered by yellow-phosphor coating like $\text{Y}_3\text{Al}_5\text{O}_{12}:\text{Ce}$. However, this kind of white light has poor color rendering index and high color temperature due to the color deficiency in the red region [4–6]. The white LEDs based on red/yellow/green/blue phosphors and UV/blue chips have been widely studied for their high CRI and tuneable color temperature [7–9].

CaTiO_3 , which belongs to a representative perovskite family, possesses good physical–chemical resistance and stability even in some corrosive environments [10–12]. Thus lanthanide ions like Sm, Eu or Pr doped CaTiO_3 phosphors have been rapidly developed because of their chemical stability and environmental friendship [13,14]. Among these phosphors, $\text{CaTiO}_3:\text{Eu}^{3+}$ (CTOE) attracts most interests due to its high doping content and pure red emission [15]. CTOE has a much better chemical stability while a relatively lower PL intensity compare with the widely-used commercial red phosphor $\text{Y}_2\text{O}_2\text{S}:\text{Eu}^{3+}$ [16–18]. What is more, different from the rapidly developing wide-band red-emitting oxynitride/nitride phosphor, CTOE has a narrow-band emission beneficial to the light purity of LEDs used in display [19], meanwhile a worse thermal-stability [5]. Those weaknesses expedited deep research upon the promotion of CTOE's PL and thermal performance.

Various experiments had been taken to realize the above goals in the past years, such as composition adjustment, morphology control and surface modification. Wu et al. gained enhanced photoluminescence of CTOE phosphor by the doping of Li ions [20]. In our previous work, regular CTOE rectangular prisms had a better thermal stability than common ones [21], and controllable synthesis of CTOE phosphors with magic-column spherical, magic-cube spherical or polyhedral shapes led to an enhancement of quantum yield [22]. However, there was little study on the surface modification for CTOE phosphor, especially in the promotion of both PL intensity and thermal stability.

Metal nanoparticles like Ag and Au have been exploited in a variety of applications based on their unique optical and electronic properties [23–25]. These properties are obtained mainly due to the LSPR absorption [26–28]. The LSPR is a collective oscillation of the nanoparticle's conduction electrons in nanoparticles when they are excited by incident electromagnetic radiation at a specific wavelength [29]. Recently, researchers have tried to employ LSPR in lighting and display devices, such as OLEDs and LEDs [30]. Lee et al. found that the photo luminescence intensity of phosphors was improved by LSPR effect owing to the Ag nanoparticles [31], and later they successfully promoted the luminescence intensity of phosphor-converted LEDs by simply mixing phosphors and metal nanoparticles in the silicone resin [32]. Therefore it is foreseeable that LSPR may also play a positive role in the enhancement of CTOE phosphor, nonetheless similar work was seldom reported.

In this work, we have focused on enhancement of fluorescence and heat dissipation for CTOE phosphor coated with Ag nanoparticles. The influence of Ag nanoparticles' size and morphology upon the LSPR effect was discussed. The most suitable concentration for fluorescence and heat dissipation was also determined.

2. Experimental section

2.1. Preparation of Ag nanoparticles

In a typical experiment, an aqueous solution of AgNO_3 (50 mM, 50 mL), $\text{C}_6\text{H}_5\text{Na}_3\text{O}_7 \cdot 2\text{H}_2\text{O}$ (Trisodium citrate, 75 mM, 500 mL),

H_2O_2 (30 wt%, 60 mL), and PVP (polyvinylpyrrolidone, Mw ~29,000, 1.75 mM, 1000 mL) were mixed and vigorously stirred at room temperature. To this mixture, NaBH_4 (100 mM, 50–125 mL) was rapidly injected in dark environment, kept on fast stirring until the color did not change any more.

2.2. Coating of CTOE phosphor with Ag nanoparticles

The “magic-column spherical” CTOE phosphor was synthesised by the method reported in our initial work [21]. In a typical experiment, 3 g CTOE phosphor was dispersed in 1 L acetic acid solution (pH = 4) by vigorous stirring. 60 mL Ag colloid solution was injected into the dispersed suspension at the speed of 5 mL/h by a syringe pump. The isoelectric points of CTOE phosphor and Ag nanoparticles were about 5.8 and 2.2 respectively as characterized. It was found that the most suitable coating pH was about 4, making the two particles carry opposite electrical charge.

2.3. Characterization

The morphology of the samples was inspected using scanning electron microscope (Hitachi SEM S-3000) and transmission electron microscope (Hitachi TEM H-800). The extinction spectra were recorded on a spectrophotometer (PerkinElmer LAMBDA 950). The isoelectric point of samples was characterized by a zetasizer (Malvern Nano ZS). The steady-state PL properties of phosphor were measured using a fluorescent spectrophotometer (JASCO FP-6600). The transient state fluorescence spectroscopy was measured on a fluorescence lifetime spectrometers (PTI's QuantaMaster 3). The temperatures and infrared thermal images were recorded using an infrared thermometer (FLIR Thermo-Vision A40 M). The properties of the pc-LED lamps were evaluated by an intensified multichannel spectrophotometer (Hongpu Optoelectronics HSP-3000) under a drive current of 70 mA.

3. Results and discussion

3.1. Morphology and extinction of Ag

As the reducing agent and morphology control components, NaBH_4 plays an important role on the synthesis of Ag nanoparticles. Thus starting solutions are prepared with constant amount of AgNO_3 , Trisodium citrate, H_2O_2 and PVP, but varying amounts of NaBH_4 in the experiment.

The different Ag colloid solutions made from different amounts of NaBH_4 (I: 125 mL, II: 100 mL, III: 75 mL and IV: 50 mL) are simply synthesised by the reduction reaction. In general, larger red-shifts are observed as the NaBH_4 concentration decreased, as shown in Fig. 1A. It could also be clearly observed by the naked eye from the digital photos in Fig. 1B.

Red-shifts in the inplane dipole surface plasmon might be correlated with shape and increasing section area of the silver nanoparticles. Transmission electron microscopy (TEM) analysis (Fig. 2A–D) of the resulting nanoparticles shows that not only the varying shapes from disks to triangular plates but also the increases in edge lengths had formed over the reducing of NaBH_4 amounts. This could be easily explained by a simple crystal rule, showed in Fig. 2E: a higher reactant concentration would spur a large-scale nucleation, leading to abundant of small particles; while a relatively lower concentration promoted the growth of triangular.

In order to investigate the relationship between morphology and extinction of Ag nanoparticles, the extinction peak wavelength (λ_{max}) and geometrical parameters like section shape, edge length, section area (SA), sqrt section area (SSA) and thickness (T) of samples I–IV have been listed in Table 1. When the λ_{max} increases

Download English Version:

<https://daneshyari.com/en/article/606596>

Download Persian Version:

<https://daneshyari.com/article/606596>

[Daneshyari.com](https://daneshyari.com)