

Journal of Materials Chemistry C

Accepted Manuscript



This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this *Accepted Manuscript* with the edited and formatted *Advance Article* as soon as it is available.

You can find more information about *Accepted Manuscripts* in the [Information for Authors](#).

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard [Terms & Conditions](#) and the [Ethical guidelines](#) still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.

**Photoluminescence enhancement of Eu^{3+} ions by Ag species in SiO_2
three-dimensionally ordered macroporous materials**

Shenfeng Lai, Zhengwen Yang, Jun Li, Bo Shao, Jianzhi Yang, Yida Wang, Jianbei Qiu,
Zhiguo Song*

*College of Materials Science and Engineering, Kunming University of Science and
Technology, Kunming, 650093, China*

Corresponding Author: Zhengwen Yang E-mails: yangzw@kmust.edu.cn

Abstract: Existing states of silver depend on the sintering temperature in the SiO_2 three-dimensionally ordered macroporous (3DOM) materials. Several species related to the silver (Ag^+ ions, Ag^+-Ag^+ and Ag nanoparticles) were demonstrated in the SiO_2 3DOM materials prepared by 550 °C. Only Ag nanoparticles were observed in the SiO_2 3DOM materials prepared by 750 °C. The influence of silver species on photoluminescence properties of Eu^{3+} was investigated systematically in the SiO_2 3DOM materials. The results show that photoluminescence enhancement of Eu^{3+} ions was obtained by Ag species in the SiO_2 3DOM materials. For the SiO_2 3DOM materials prepared by 550 °C, the enhancement of Eu^{3+} luminescence is attributed to energy transfer from Ag^+-Ag^+ to Eu^{3+} under the excitation of 345 or 280 nm, while luminescence enhancement of Eu^{3+} is due to energy transfer from isolated Ag^+ to Eu^{3+} under the excitation of 245 nm. For the SiO_2 3DOM materials prepared by 750 °C, the luminescence of Eu^{3+} were enhanced due to plasmon resonance effect of Ag nanoparticles.

Keywords: Photoluminescence; energy transfer; plasmon resonance; three dimensionally ordered macroporous; silver species

Introduction

Three dimensionally ordered macroporous (3DOM) materials (inverse opal photonic crystals) consisted of metals, inorganic metals or polymer materials have been attracting much attention because of their potential applications in the separation and adsorbent media and so on.¹⁻⁶ In addition, the rare earth doped 3DOM materials were predicted to have unique optical properties, and the modification of linear or nonlinear optical properties from rare earth ions could be realized in such a material. Therefore, the rare earth doped 3DOM materials have wide interests in applications to the fields of optoelectronics and optical communications. For example, laser with lower threshold value and light emitting diodes with higher efficiency could be fabricated. Despite various advantages, there have many challenges for practical applications of the rare earth ions doped 3DOM materials. One obvious challenge is low emission efficiency of the rare earth ions doped 3DOM materials that caused by the small absorption cross section of rare earth ions due to its parity forbidden character of 4f–f transitions. At present, several methods such as Li⁺ doping and energy transfer were used to enhance the emission efficiencies of rare earth ions doped 3DOM materials.^{7,8}

As a valuable approach, surface plasmons (SPR) of noble metal nanoparticles have been proposed to modify the photoluminescence property of rare earth ions.⁹ The excitation field and the radiation rate of rare earth ions in the vicinity of metal nanoparticles could be enhanced, resulting in the luminescence enhancement of rare earth ions. Very recently, the photoluminescence enhancement of rare earth ions in colloids, glasses, or thin films was reported by the coupling of rare earth ions luminescence with the SPR of noble metal nanoparticles.^{10,11} Among various noble metals, noble silver was used extensively to enhance the luminescence of rare earth

ions. In contrast to other noble metals such as gold, noble silver has an obvious advantage to enhance luminescence of rare earth ions, that is existing states of silver is abundant in the glasses, or thin films including Ag^+ , Ag^+-Ag^+ , Ag^0 , Ag clusters ($\text{Ag}_2-\text{Ag}_{12}$) and nanoparticles.¹²⁻¹⁷ Moreover, various existing state silvers could be used to enhance the luminescence of rare earth ions. For example, the influence of silver species such as Ag^+ , Ag^+-Ag^+ , Ag^0 , Ag clusters and nanoparticles on the luminescence property of rare earth ions were reported in the glasses.¹⁶ However, as we know, there have been no experiment reports on the luminescence enhancement of rare earth ions doped 3DOM materials by various silver species. In addition, white light emitting diodes (WLED) has been an increasing interest owing to their potential applications in solid state lightings, displays and other photonic devices. One of the approaches to obtain WLED is the combination of yellow phosphors with blue diode chips (450–470 nm). However, this kind of WLED has poor color rendering index because of the lack of red light. In order to overcome this problem, another WLED is achieved by using a diode chip with shorter wavelength emission to excite three primary colors phosphors. Very recently, the diode chips from 325-350 nm (deep ultraviolet) to a shortest ultraviolet emission of 210 nm could be prepared. Correspondingly, the materials excited by different excitation wavelength were need for white LED. In the present work, we present preparation and photoluminescence properties of a new luminescent materials consisting of the SiO_2 : Eu 3DOM materials and including Ag species under the different excitation wavelength of 245, 280, 345nm. The influence of silver species on luminescence of Eu^{3+} was investigated in the SiO_2 3DOM materials under the different excitation wavelength. The luminescence enhancement of Eu^{3+} could be observed under the excitation of 245, 280, 345nm, and the enhancement mechanisms of Ag species on luminescence

of Eu^{3+} were discussed in the SiO_2 3DOM materials.

Experimental

Ordered opal templates were self-assembled on the quartz slides through the vertical deposition process of polystyrene (PS) microspheres with diameters of 380 nm. Typically, the PS microspheres were added to a small glass vessel. Clean quartz slides were placed vertically into the PS microsphere solution, which was placed in a 50 °C oven over a period of 5 to 6 days. After solvents volatilized spontaneously, the PS colloidal microspheres slowly self-assembled into highly ordered opal template on the quartz substrate driven by surface tension of the liquid.

The preparation of SiO_2 : x Ag (x=0 and 0.6 mol%), y Eu (y=0, 2 mol%) 3DOM materials were achieved by the template-assisted method, using tetraethyl orthosilicate [$\text{Si}(\text{CH}_3\text{CH}_2\text{O})_4$, TEOS], $\text{Eu}(\text{NO}_3)_3$ and AgNO_3 as raw materials. In the preparation of the SiO_2 : Ag, Eu sol, stoichiometric amounts of $\text{Eu}(\text{NO}_3)_3$, AgNO_3 and $\text{Si}(\text{CH}_3\text{CH}_2\text{O})_4$ were dissolved in ethanol, respectively, then the above three solutions were mixed together. The mixture was stirred for 3h, forming a homogeneous transparent SiO_2 : Ag, Eu solution. The prepared SiO_2 : Ag, Eu solutions were used to infiltrate into the voids of the opal template. After infiltration, the resulting samples were sintered in an air furnace at 550 or 750 °C to remove the PS microspheres, and the Ag species including SiO_2 : Eu 3DOM materials were obtained.

The morphology of SiO_2 : Ag, Eu 3DOM materials was recorded on the scanning electron microscope (QUANTA200) after sputtering the samples with a thin layer of gold and the chemical compositions of the SiO_2 : Ag, Eu 3DOM materials were analyzed by an energy dispersive x-ray spectroscopy (EDS) attached to a QUANTA200 scanning electron microscope (SEM). Specimen preparation for TEM observation was achieved by scrapping off SiO_2 : Ag, Eu 3DOM materials and

subsequent deposition on ultrathin holey carbon coated copper grids. Then transmission electron microscope (TEM) images of samples were taken using a JEOL 2100 transmission electron microscope. The optical absorption spectra of 3DOM materials were measured on a HITACHI U-4100 type spectrophotometer (Hitachi, Tokyo, Japan). The photoluminescence spectra were measured with a HITACHI F-7000 fluorescence spectrophotometer using a static 150 W Xe lamp as the excitation source. The excitation spectra were recorded at room temperature on the same Hitachi F-7000 spectrophotometer. Lifetime decay curves were measured on an Edinburgh FLS980 spectrofluorometer (UK). X-ray photoelectron spectroscopy (XPS) studies were carried out using an Mg-K α X-ray source (200 W) in an ultrahigh vacuum chamber ($\leq 2.0 \times 10^{-9}$ mbar).

Results and discussions

1、Enhanced photoluminescence of Eu³⁺ ions by energy transfer from Ag⁺-Ag⁺ to Eu³⁺ in the SiO₂ three-dimensionally ordered macroporous materials

The SiO₂: 0.6 mol% Ag without Eu³⁺ and SiO₂: 2 mol% Eu without Ag 3DOM materials sintered at 550 °C were denoted as the SiO₂-Ag and SiO₂-Eu, respectively. The SiO₂: 0.6 mol% Ag, 2 mol% Eu and pure SiO₂ without Eu³⁺ and Ag 3DOM materials sintered at 550 °C were denoted as the SiO₂-Eu-Ag and pure SiO₂ 3DOM materials, respectively. Figure 1 (a) and (b) show that the low- and high-magnified SEM images of SiO₂-Ag-Eu 3DOM material, respectively. From the SEM images, it is noted that a long-range ordered hexagonal arrangement was observed in the SiO₂-Ag-Eu sample, and the SiO₂-Ag-Eu 3DOM material was obtained. The microstructure characteristics of other SiO₂ 3DOM materials are similar with that of the SiO₂-Ag-Eu 3DOM material sintered at 550 °C. The EDS analyses of SiO₂-Ag-Eu 3DOM material sintered at 550 °C were performed, as shown in Figure 1(c). It

confirms that the main element peaks of Si, Eu, O and Ag were observed. Additionally, the Au peak in the EDS curve is also observed, which is attributed to an Au thin film coated on the sample surface to increase the sample's conductivity.

Figure 2 (a) shows the TEM image of the SiO₂-Ag-Eu 3DOM material. The silver nanoparticles were observed in the SiO₂-Ag-Eu 3DOM material prepared at 550°C. In order to further demonstrate the formation of Ag nanoparticles in the SiO₂ 3DOM materials, the absorption spectra of pure SiO₂, SiO₂-Eu, SiO₂-Ag and SiO₂-Ag-Eu 3DOM materials were measured, as shown in the Figure 2(b). From the absorption spectra, it can be seen that the pure SiO₂, SiO₂-Eu, SiO₂-Ag and SiO₂-Ag-Eu 3DOM materials display an obvious absorption band centering at 510 nm, which is attributed to Bragg diffraction of the ordered periodic structure (photonic band gap). In contrast to the absorption spectra of the SiO₂ and SiO₂-Eu 3DOM materials without Ag, an absorption band about located at 410 nm was observed in the SiO₂-Ag and SiO₂-Ag-Eu 3DOM materials, which is contributed to the surface plasmon resonance absorption of silver nanoparticles.^{18,19} The results of absorption spectra demonstrated further that silver nanoparticles were formed indeed in the SiO₂-Ag-Eu 3DOM material. The intense absorption peaks ranging from 200-300 nm was attributed to the intrinsic oxygen deficient defects of the SiO₂ host.²⁰ The XPS spectra of SiO₂-Ag-Eu 3DOM material were measured, as shown in the Figure 2(c). From the XPS spectra, it can be seen the binding energy related to the Ag species were located at 367.9 and 368.4 eV, which reveals that the chemical state of silver in the SiO₂-Ag-Eu 3DOM material were Ag⁺ and Ag⁰.²¹

The excitation spectra of pure SiO₂, SiO₂-Ag and SiO₂-Eu 3DOM materials sintered at 550 °C were shown in Figure 3. The excitation spectrum monitored at 396 or 360 nm emissions in the pure SiO₂ 3DOM materials formed at 550 °C consists of a

excitation band located at 245 nm and a excitation band at 280 nm. The excitation band at 245 nm and a excitation band at 280 nm were corresponding to the intrinsic oxygen deficient and $\equiv\text{Si-O-O-Si}\equiv$ defects of the SiO_2 host,^{22, 23} respectively. Similar excitation bands related to the intrinsic oxygen deficient defects and $\equiv\text{Si-O-O-Si}\equiv$ defects were observed in the SiO_2 host.^{22, 23} For the excitation spectrum of $\text{SiO}_2\text{-Ag}$ 3DOM, a excitation band centered at 245 nm monitored at 396 nm emissions was observed. Various silver species such as simple ions Ag^+ , double ions $(\text{Ag}^+)_2$ and $(\text{Ag}_2)^+$ and more complex ions $(\text{Ag}_n)^{m+}$ can be formed in the SiO_2 matrices.¹⁶ The excitation band at about 245 nm from the Ag^+ was observed in the glass hosts, which is attributed to the transitions of $4d^{10}(^1\text{S}_0)\rightarrow 4d^95s(^1\text{D}_2)$ from Ag^+ .^{24, 25} Moreover, the emission band located at the 390 nm from $4d^95s(^3\text{D}_{1-3})$ to $4d^{10}(^1\text{S}_0)$ of the Ag^+ was also obtained in the glass excited at the 245 nm,^{24, 25} which is very similar with present results. Therefore, we think that the excitation band centered at the 245 nm may be related to both the Ag^+ and defects of SiO_2 host in the $\text{SiO}_2\text{-Ag}$ 3DOM materials, which was further demonstrated by the corresponding emission spectrum and the lifetime presented in the next section. For the excitation spectrum monitored at 614 nm emission in the $\text{SiO}_2\text{-Eu}$ 3DOM materials formed at the 550 °C, a excitation band around 245 nm and line excitation peak at 393 nm were observed, as shown in the inset pattern of Figure 3. The line excitation peak located at 393 nm results from the transitions of Eu^{3+} , while the origin of the excitation band located at 245 nm could be ascribed to the defects of SiO_2 host. The excited spectrum monitored at 540 nm emissions in the $\text{SiO}_2\text{-Ag}$ 3DOM sample was also present in the Figure 3. The 345 nm

broad excited bands in the region of 220-400 nm is attributed to the Ag^+-Ag^+ pairs in the $\text{SiO}_2\text{-Ag}$ 3DOM sample, which is very similar with previous result.¹⁷ The Ag^+ can aggregate to form the Ag^+-Ag^+ pairs when the distance between the Ag^+ ions is closed to 3 Å.^{25, 26} On the basis of previous structural investigations of various crystalline silver compounds, these Ag^+-Ag^+ pairs formation are attributed to homoatomic interactions between closed d^{10} shells.²⁵⁻²⁷ In order to demonstrate the presence of Ag^+-Ag^+ pairs, only Ag^+ including $\text{SiO}_2\text{-Ag}$ 3DOM sample were prepared at 400°C.¹² The XPS spectra of only Ag^+ including $\text{SiO}_2\text{-Ag}$ 3DOM sample were measured, as shown in the Fig. 2(c). The binding energy of Ag^+ is about 367.6 eV. The binding energy of the $\text{SiO}_2\text{-Ag}$ 3DOM sample prepared at 550°C is about 0.3 eV higher than the value of Ag^+ . The binding energy shift may be induced by the interaction between Ag^+ ions due to formation Ag^+-Ag^+ pairs. In the SiO_2 3DOM materials, the Eu^{3+} ions and Ag^+-Ag^+ were located at the amorphous network structure of SiO_2 and the Ag nanoparticles were embedded into the nanosized wall of SiO_2 3DOM materials, as shown in Scheme 1 in the supporting information.

Figure 4 shows the emission spectra of pure SiO_2 , $\text{SiO}_2\text{-Ag}$, $\text{SiO}_2\text{-Eu}$ and $\text{SiO}_2\text{-Ag-Eu}$ 3DOM materials under the excitation of 280 nm. An emission band located at 360 nm and shoulder at 460 nm were observed in the all 3DOM materials. It is well known that various luminescent defects including $\equiv\text{Si-O-O-Si}\equiv$, $\equiv\text{Si-Si}\equiv$ and oxygen deficient defects can be formed in the SiO_2 host.^{22, 28, 29} The emission band located at 360 nm and shoulder at 460 nm may be attributed to the $\equiv\text{Si-O-O-Si}\equiv$ and $\equiv\text{Si-Si}\equiv$ defects of SiO_2 host in the all 3DOM materials, respectively, and the similar

results were reported in the previous works.^{22, 28, 29} In the SiO₂-Ag 3DOM material, it is obvious that the shape of emission spectrum is different in comparison with that of pure SiO₂ 3DOM material without Ag under the excitation of 280 nm. Besides the 360 nm broad emission band from ≡Si-O-O-Si≡ defects, another broad emission band at 540 nm was observed in the emission spectrum of the SiO₂-Ag 3DOM material, which indicated that the 540 nm broad emission band must be from Ag active centers. According to previous reports, silver species with various existed states were formed in the SiO₂ hosts, and they exhibited interesting luminescent properties ranging from UV to red emissions.^{17, 30} The 550 nm green emission attributed to the Ag⁺-Ag⁺ was obtained under the excitation of 350 nm,¹⁷ and the emission band from 340 to 410 nm of Ag⁺ was also observed excited at 275 nm.²⁹ The broad band at 540 nm may be attributed to Ag⁺-Ag⁺ in the present work. To further investigate the origin of emission bands located at the 360 and 540 nm, decay curves of the 360 and 540 nm luminescence in the pure SiO₂, SiO₂-Eu, SiO₂-Ag and SiO₂-Ag-Eu 3DOM samples were measured under the 280 nm excitation, respectively, as shown in Figure 5. The luminescence decay times can be fitted by the second-order exponential technique based on the following equation:³¹

$$I = A_1 \exp\left(\frac{-t}{\tau_1}\right) + A_2 \exp\left(\frac{-t}{\tau_2}\right) \quad (1)$$

where I is the luminescence intensity; A_1 and A_2 are fitting parameters; t is the time, τ_1 and τ_2 are luminescence lifetimes. The second-order exponential fitting suggested that there are two luminescent mechanisms to contribute the emission band 360 or 540 nm. The total luminescence intensity of the SiO₂ 3DOM materials comes from the active

luminescent ions at the surface and the interior active luminescent ions of 3DOM materials. The wall of the 3DOM materials is nanosized, and the many active luminescent ions may be located at surface. The photoluminescence of active luminescent ions located at surface of nanomaterials were quenched by the surface defects and impurities.³² The luminescence decay from active luminescent ions at the surface may be different from that of interior active luminescent ions due to surface defects and impurities. Therefore, the decay curve exhibits double exponential nature due to the different sites of active luminescent ions. The fitting curves were provided in the Fig.1 in the supporting information. Based on the τ_1 and τ_2 values fitted by equation (1), the average lifetime (τ) can be calculated by the following equation.³³

$$\tau = \frac{A_1\tau_1^2 + A_2\tau_2^2}{A_1\tau_1 + A_2\tau_2} \quad (2)$$

The corresponding lifetimes (τ) were given in the Table I. It can be seen that the lifetime of monitoring maximum 360 nm and long tail 540 nm emission from the $\equiv\text{Si-O-O-Si}\equiv$ defects is almost same (6.5 μs) in the pure SiO_2 3DOM materials. The decay lifetime of 540 nm emission in the $\text{SiO}_2\text{-Ag}$ 3DOM material is 63 μs . The notable change of lifetime from 6.5 to 63 μs is attributed to the difference of active luminescent centers in the pure SiO_2 and $\text{SiO}_2\text{-Ag}$ 3DOM materials. The 6.5 μs lifetime is attributed to the SiO_2 defects in the pure SiO_2 3DOM materials, while the 63 μs lifetime is the combination of lifetime from SiO_2 defects and $\text{Ag}^+\text{-Ag}^+$ pairs in $\text{SiO}_2\text{-Ag}$ 3DOM materials. The luminescence lifetime of $\text{Ag}^+\text{-Ag}^+$ pairs is related to the hosts. The luminescence lifetime of $\text{Ag}^+\text{-Ag}^+$ pairs is related to the hosts. The 60 μs lifetime of $\text{Ag}^+\text{-Ag}^+$ pairs was reported in the $\text{Na}_{2-x}\text{Ag}_x\text{ZnP}_2\text{O}_7$ ²⁵, which is shorter

than that obtained in the present work. The 89 μs lifetime of Ag^+-Ag^+ was obtained in the aluminophosphate glass matrix,²⁴ while the lifetimes of Ag^+-Ag^+ pairs is from 125 to 175 μs in the $\text{Ag}_2\text{O}-\text{ZnO}-\text{P}_2\text{O}_5$ glass.¹⁷ In the present work, the short lifetime of 540 nm from SiO_2 host may result in decreasing of the final lifetime of 540 nm in the SiO_2-Ag 3DOM material in comparison with that of Ag^+-Ag^+ pairs. Therefore, the true lifetime from the Ag^+-Ag^+ should be longer than 63 μs in the SiO_2-Ag 3DOM material. Here the lifetime from the Ag^+-Ag^+ is different from these reported by the previous works, which may be attributed to crystal field difference around the Ag^+-Ag^+ in the SiO_2 host in contrast to the previous hosts.²⁵ In addition, the lifetime of the 360 nm emission is almost same in the pure SiO_2 , SiO_2-Eu , SiO_2-Ag and $\text{SiO}_2-\text{Ag}-\text{Eu}$ 3DOM samples, indicated that the 360 nm emission is from the same active defect centers, and no energy transfer from SiO_2 to Ag^+-Ag^+ pairs occurs under the excitation of 280 nm. As seen from table I, the value of A_1 is less than that of A_2 for the lifetimes of the Ag^+-Ag^+ pairs, suggested that the interior Ag^+-Ag^+ pairs is the main luminescent centers for the 540 nm emissions in the 3DOM materials. However, the value of A_1 is much larger than that of A_2 for the lifetimes of 360 nm from the $\equiv\text{Si}-\text{O}-\text{O}-\text{Si}\equiv$ defects. It indicates that the more $\equiv\text{Si}-\text{O}-\text{O}-\text{Si}\equiv$ defects may be located at the surfaces of 3DOM samples in contrast to the Ag^+-Ag^+ pairs. It is well known that the $\equiv\text{Si}-\text{O}-\text{O}-\text{Si}\equiv$ defect in the SiO_2 host is kind of oxygen-surplus defects.^{22,23} The $\equiv\text{Si}-\text{O}-\text{O}-\text{Si}\equiv$ defects were formed by the reaction between $\equiv\text{Si}-\text{Si}\equiv$ defects and O_2 .²² At the surfaces of 3DOM materials, more O_2 may get in touch with the $\equiv\text{Si}-\text{Si}\equiv$ defects, which may result in the formation of more $\equiv\text{Si}-\text{O}-\text{O}-\text{Si}\equiv$ defects. Thus, the

values of A_1/A_2 for the lifetimes of the $\equiv\text{Si-O-O-Si}\equiv$ defects are larger than these of Ag^+-Ag^+ pairs. On the other hand, considering the influence of surface defects and impurities, the responding lifetime from surface Ag^+-Ag^+ should shorter than that of interior. However, the τ_1 is larger than τ_2 in the present works. The influence factors of lifetime are complicated. The crystal field difference around the surface and interior Ag^+-Ag^+ pairs in the SiO_2 3DOM materials may be considered besides the influence of surface defects and impurities. The specific reasons may be investigated in future.

In addition, the line emissions of Eu^{3+} were observed in the emission spectra of the SiO_2 -Eu and SiO_2 -Ag-Eu 3DOM materials, as shown in Figure 4. Obviously, the sharp peaks at 590 and 614 nm are related to ${}^5\text{D}_0 \rightarrow {}^7\text{F}_1$ and ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$ transitions of Eu^{3+} , respectively. Luminescence enhancement of Eu^{3+} was observed in the SiO_2 -Ag-Eu 3DOM sample under the excitation of 280 nm in comparison with that of SiO_2 -Eu 3DOM sample. The emissions of Eu^{3+} increase by 11 fold after the addition of Ag. There are two reasons for the enhancement. One is the energy transfer from the Ag^+-Ag^+ to Eu^{3+} . Based on the decay lifetime (Table I and Figure 5) of the 540 nm emission in the SiO_2 -Ag and SiO_2 -Ag-Eu 3DOM samples under the 280 nm excitation, the lifetime from the Ag^+-Ag^+ was found to decrease in the SiO_2 -Ag-Eu sample in contrast to the SiO_2 -Ag sample without Eu^{3+} , indicating the presence of energy transfer from Ag^+-Ag^+ to Eu^{3+} . Another reason may be associated with the surface plasmons effect of Ag nanoparticles. According to the TEM image and absorption spectrum of SiO_2 -Ag-Eu sample, part Ag^+ transform to Ag nanoparticles in the SiO_2 -Ag 3DOM material sintered at the 550 °C. Hence, for the SiO_2 -Ag-Eu 3DOM

material, another origin of the luminescence enhancement of Eu^{3+} is contributed to the increasing of radiative decays rate and population of excited level of Eu^{3+} caused by the surface plasmons effect of Ag nanoparticles. Influence of surface plasmons effect of Ag nanoparticles on luminescence property of the $\text{SiO}_2\text{-Ag-Eu}$ 3DOM material was investigated in the 3th section.

Figure 6 (a) shows the luminescent spectra of pure SiO_2 , $\text{SiO}_2\text{-Eu}$, $\text{SiO}_2\text{-Ag}$ and $\text{SiO}_2\text{-Ag-Eu}$ 3DOM samples under excitation at the 345 nm. Broad emission band located at about 400 nm ranging from 360 to 700 nm can be seen in all the SiO_2 3DOM samples, which is the characteristic emission of defect of SiO_2 host. A 540 nm broad emission band from $\text{Ag}^+\text{-Ag}^+$ was also observed in the $\text{SiO}_2\text{-Ag}$ 3DOM material. For the emission spectra of the $\text{SiO}_2\text{-Eu}$ and $\text{SiO}_2\text{-Ag-Eu}$ 3DOM materials, typical line emissions of Eu^{3+} were observed in the $\text{SiO}_2\text{-Eu}$ and $\text{SiO}_2\text{-Ag-Eu}$ 3DOM samples. The emission intensity of Eu^{3+} in the $\text{SiO}_2\text{-Eu}$ 3DOM material is very weak, while emission intensity in $\text{SiO}_2\text{-Ag-Eu}$ 3DOM material increases and an enhanced Eu^{3+} emission by 12.8 times were obtained. Enhanced emission of Eu^{3+} in the $\text{SiO}_2\text{-Ag-Eu}$ 3DOM material was attributed to the plasmons effect of Ag nanoparticles and energy transfer from $\text{Ag}^+\text{-Ag}^+$ to Eu^{3+} . To further testify the presence of energy transfer from $\text{Ag}^+\text{-Ag}^+$ to Eu^{3+} , decay curves of 540 nm luminescence of $\text{SiO}_2\text{-Ag}$ and $\text{SiO}_2\text{-Ag-Eu}$ 3DOM samples were measured under the 345 nm excitation, as shown in Figure 6(b). The luminescence lifetime at the 540 nm for $\text{SiO}_2\text{-Ag}$ 3DOM sample is about 48 μs under the excitation of 345 nm. After the Eu^{3+} addition, the luminescence lifetime at 540 nm from $\text{Ag}^+\text{-Ag}^+$ decreased to 23 μs in the $\text{SiO}_2\text{-Ag-Eu}$ 3DOM sample. The

decreasing of decay lifetime from Ag^+-Ag^+ is strong evidence for the energy transfer from Ag^+-Ag^+ to Eu^{3+} .

2、Enhanced photoluminescence of Eu^{3+} ions by energy transfer from Ag^+ to Eu^{3+} in the SiO_2 three-dimensional ordered macroporous materials

Figure 7(a) shows emission spectra of pure SiO_2 , $\text{SiO}_2\text{-Ag}$, $\text{SiO}_2\text{-Eu}$ and $\text{SiO}_2\text{-Ag-Eu}$ 3DOM samples prepared at 550 °C under the excitation of 245 nm. An emission band located at 396 nm was observed in the pure SiO_2 and $\text{SiO}_2\text{-Eu}$ sample, which may be attributed to the defect of pure SiO_2 host. As the excitation was 250 nm, the 395 nm emission band attributed to SiO_2 defects was reported in the pure SiO_2 host.²³ The evolution of this emission band after the Ag addition is presented. In the $\text{SiO}_2\text{-Ag}$ and $\text{SiO}_2\text{-Ag-Eu}$ samples, an emission band at about 396 nm was obtained. However, the shape of emission spectrum of pure SiO_2 3DOM materials without Ag is obviously different in comparison with that of $\text{SiO}_2\text{-Ag}$ 3DOM material under the excitation of the 245 nm. Therefore, the origin of the 396 nm emission may be not attributed to the same active centers under a 245 nm excitation in the pure SiO_2 and $\text{SiO}_2\text{-Ag}$ 3DOM material. Previously, the broad emission band at about 400 nm from $4d^95s(3D_{1-3})$ to $4d^{10}(1S_0)$ of the Ag^+ was observed in the glass hosts under the excitation of 245 nm,^{24,25} which is very similar with present results. Therefore, we think that the 396 nm broad emission band is related to both Ag^+ ions and SiO_2 defects in the $\text{SiO}_2\text{-Ag}$ 3DOM material prepared at 550 °C. Figure 7 (b) shows the luminescence lifetime at the 396 nm for the pure SiO_2 , $\text{SiO}_2\text{-Ag}$, $\text{SiO}_2\text{-Eu}$ and $\text{SiO}_2\text{-Ag-Eu}$ 3DOM materials under the excitation of 245 nm. It can be seen that lifetimes are different in the all 3DOM materials. The Ag addition in the SiO_2 3DOM can increase the luminescence lifetime at the 396 nm. It can be concluded that the origin of 396 nm emission band in the $\text{SiO}_2\text{-Ag}$ 3DOM materials may be not only

attributed to the defects of SiO₂ under a 245 nm excitation. The reported decay time of Ag⁺ ions is about 12 μs,³⁰ which is the same with the present work. Therefore, lifetime measurement had further proved that the Ag⁺ ions occurred indeed in the SiO₂-Ag 3DOM material prepared by 550 °C. A very weak line emission from Eu³⁺ was observed in the SiO₂-Eu 3DOM material under the 245 nm excitation, which is attributed to the energy transfers from silica matrix to the Eu³⁺. The emission intensity and lifetime (τ) at 396 nm (As shown in table II) from the SiO₂ defects in the SiO₂-Eu 3DOM material was decreased in contrast to the pure SiO₂ 3DOM material excited at the 245 nm, suggested that the energy transfers from silica matrix to the Eu³⁺ occurred. In addition, luminescence of Eu³⁺ was significantly enhanced in the SiO₂-Ag-Eu 3DOM samples after addition of Ag, and about 8 fold enhancement was obtained, which is attributed to energy transfer from Ag⁺ to Eu³⁺. The energy transfers from Ag⁺ to Eu³⁺ can be demonstrated by comparing the variety of emission intensity and lifetimes in the SiO₂-Ag and SiO₂-Ag-Eu 3DOM materials.

Possible energy transfer process from the Ag⁺-Ag⁺ or Ag⁺ to Eu³⁺ were investigated based on their energy level diagram, as shown in Figure 8. Upon 280 or 345 nm excitation, the Ag⁺-Ag⁺ pairs are excited from the ground state to the excited state. An excited the Ag⁺-Ag⁺ pairs transfers the excitation energy to neighboring Eu³⁺ ions, leading to the population of ⁵D₃ excited level of Eu³⁺ ions. Then Eu³⁺ ions in the ⁵D₃ excited level relaxed nonradiative to luminescent ⁵D₀ level. The radiative transition from ⁵D₀ level to ⁷F₀₋₃ level results in the characteristic emissions of Eu³⁺ ions. For the energy donor from Ag⁺ to Eu³⁺ ions, the excitation level of Ag⁺ was populated under the excitation of 245 nm. An excited Ag⁺ ions transfer their energy to a neighboring Eu³⁺ ions, promoting transition of Eu³⁺ ions from ground state to the ⁵D₃ excited state. The luminescent excitation ⁵D₀ level of Eu³⁺ was populated by

nonradiative relaxation from 5D_3 level, resulting in characteristic emissions of Eu^{3+} ions.

Color tunability of the photoluminescence emission is required for the application of lighting and display devices. Many approaches have already been proposed for this purpose, including co-doping of various active centers, using of different excitation wavelength and variety of doping concentration of active centers. Among these methods, using of different excitation wavelength has been demonstrated to be a convenient and versatile technique for generating color tunable emission. The above results show that the color tunable emission of the $\text{SiO}_2\text{-Ag}$ and $\text{SiO}_2\text{-Ag-Eu}$ 3DOM materials can be obtained by changing the excitation wavelength. In order to obtain the true color of $\text{SiO}_2\text{-Ag}$ and $\text{SiO}_2\text{-Ag-Eu}$ 3DOM materials, the chromaticity coordinates (CIE) of the $\text{SiO}_2\text{-Ag}$ and $\text{SiO}_2\text{-Ag-Eu}$ 3DOM materials under the excitation of 245, 280, 345 nm are calculated based on the photoluminescence spectra, as shown in Figure 9. It is obvious that the photoluminescence color tunability can be obtained by changing the excitation wavelength. It is interesting that the white emission was observed under the excitation of 280 nm in the $\text{SiO}_2\text{-Ag}$ 3DOM materials, indicated that it can potentially be used as a new efficient white luminescent material.

3、Photoluminescence enhancement of Eu^{3+} by SPR of Ag nanoparticles in SiO_2 three dimensional ordered macroporous material

The influence of Ag nanoparticles on Eu^{3+} luminescence in $\text{SiO}_2\text{: Ag, Eu}$ 3DOM material was investigated. Figure 10 (a) shows the TEM image of the $\text{SiO}_2\text{: 2mol\% Eu, 0.6mol\% Ag}$ 3DOM material prepared by 750 °C. The larger silver nanoparticles in the $\text{SiO}_2\text{: 2mol\% Eu, 0.6mol\% Ag}$ 3DOM material prepared at 750°C were obtained in comparison with that of $\text{SiO}_2\text{: 2mol\% Eu, 0.6mol\% Ag}$ 3DOM material

prepared at 550°C. The high resolution TEM image of Ag nanoparticles in the SiO₂: 2mol% Eu, 0.6mol% Ag 3DOM material was shown in Figure 10 (b). It is noted that the lattice fringes of the individual Ag nanoparticle are clearly observed, and the distance between the lattice fringes was about 0.144 nm, which match with the spacing of the (220) lattice planes of the Ag.

Figure 10(c) shows the absorption spectra of SiO₂: 2mol%Eu with and without 0.6 mol% Ag 3DOM materials prepared by 750 °C. It can be seen that an obvious intense plasmon resonance absorption band from silver nanoparticles was observed in contrast to that of SiO₂: 2mol%Eu, 0.6mol% Ag 3DOM material sintered at 550 °C, which is attributed to the formation of more and larger Ag nanoparticles in the 3DOM material prepared by 750 °C. Figure 10(d) shows the excitation spectrum of SiO₂: 2mol%Eu, 0.6mol%Ag 3DOM materials prepared by 550 and 750 °C by monitoring the 614 nm emission. It shows that a main excitation peak was located at 235 nm in the SiO₂: 2mol%Eu, 0.6mol%Ag 3DOM materials prepared by 750 °C, which was attributed to the defects of SiO₂ host. In addition, several very weak sharp excitation peaks originated from the Eu³⁺ were observed in the range of 300-400 nm. In the SiO₂: 2mol%Eu, 0.6mol% Ag 3DOM material prepared by 550 °C, the main excitation band located at 345 nm is attributed to the Ag⁺-Ag⁺ by monitoring the 614 nm emission, indicating the presence of the energy transfer from Ag⁺-Ag⁺ to Eu³⁺. In contrast to the SiO₂: 2mol%Eu, 0.6mol% Ag 3DOM material prepared by 550 °C, no the excitation peak from Ag⁺-Ag⁺ was observed in the SiO₂-Ag-Eu 3DOM materials prepared by 750 °C, which suggested that Ag⁺-Ag⁺ transfer to Ag nanoparticles at the higher sintering temperature. Only Ag nanoparticles were formed in the SiO₂-Ag-Eu 3DOM materials prepared by 750 °C, which was further demonstrated by the emission spectra (not shown herein).

Figure 11 shows the emission spectra of the SiO₂: 2 mol% Eu and SiO₂:2 mol% Eu, 0.6 mol% Ag 3DOM materials under the excitation of 235 nm. Typical emission of Eu³⁺ was observed in both 3DOM materials. The emission intensity of Eu³⁺ increases by 4 fold in the SiO₂:2 mol% Eu, 0.6 mol% Ag 3DOM materials in comparison with the SiO₂:2mol% Eu 3DOM materials without Ag nanoparticles, which is attributed to the SPR effect of Ag nanoparticles. In the previous works,³⁴ two luminescence enhancement mechanisms from the SPR effect of Ag nanoparticles have been reported. One is the surface plasmon induced excitation enhancement of active centers attributed to the local electric field enhancement around the metal nanoparticles. Another is the increasing of radiative decay rate of active centers. In order to demonstrate the origin of enhancement of Eu³⁺ luminescence, luminescence lifetime values of the SiO₂: 2 mol% Eu and SiO₂:2 mol% Eu, 0.6 mol% Ag 3DOM materials were measured. The lifetime values were determined to be 2.11 ms and 0.69 ms for SiO₂: 2mol % Eu and SiO₂:2mol% Eu, 0.6mol % Ag 3DOM materials, respectively. The decay lifetime for Eu³⁺ decreased after formation of Ag nanoparticles, which suggested the increasing of radiative decay rate of Eu³⁺ is one of the enhancement reasons of Eu³⁺ luminescence. In addition, the population of the excited level of Eu³⁺ was influenced due to the presence of Ag nanoparticles based on the three energy level diagram shown in Figure 12. The population of the excited level of Eu³⁺ can be expressed by the following steady state rate equation:

$$\frac{dN_{S_1}}{dt} = IA_1N_{S_0} - N_{S_1}W_{S_n} - N_{S_1}W_{S_r_1} = 0 \quad (3)$$

$$\frac{dN_{S_2}}{dt} = W_{S_n}N_{S_1} - N_{S_2}W_{S_r_2} - N_{S_2}W_{ET}n_0 = 0 \quad (4)$$

$$\frac{dn_2}{dt} = N_{S_2}W_{ET}n_0 - n_2W_1 - n_2W_{r_1} = 0 \quad (5)$$

$$\frac{dn_1}{dt} = n_2W_1 - n_1W_{r_2} = 0 \quad (6)$$

$$Wsr_1 = 0 \quad (7)$$

$$Wr_1 = 0 \quad (8)$$

Where N_{S_0} , N_{S_1} , and N_{S_2} denote ground and excitation level population number of donor ($\text{Ag}^+ - \text{Ag}^+$, Ag^+ or SiO_2 host), respectively. n_0 , n_1 and n_2 are the ground and excitation level population number of Eu^{3+} ions, respectively. W_{S_n} and W_I are the nonradiative transition rate. The Wsr_1 , Wsr_2 , Wr_1 and Wr_2 denote the radiative transition rate. W_{ET} is the energy transfer rate from donor to acceptor. IA_I is the product of excitation field and transition possibility from ground state to excitation state.

By resolving the above rate equation, the solution for the population of the excited level of Eu^{3+} ions is:

$$n_1 = \frac{IA_1 N_{S_0} W_{ET} n_0}{Wr_2 (Wsr_2 + W_{ET} n_0)} \propto I \quad (9)$$

It can be seen from the equation (9) that the population of the excited level of Eu^{3+} ions is related to the intensity of excitation light. It is well known that surface plasmons from the collective oscillations of the free electrons occur around Ag nanoparticles, which give rise to giant and high localized electric field around the Ag nanoparticles, resulting in the enhancement of the excitation field. Thus, the population of the excited level of Eu^{3+} ions increased, leading to the luminescence enhancement of Eu^{3+} .

Influence of Ag contents on photoluminescence property of Eu^{3+} was investigated in the SiO_2 3DOM materials prepared by 750°C . The absorption spectra of the SiO_2 : 2mol%Eu, x mol% Ag (x=0, 0.2, 0.4, 0.6, and 0.8) 3DOM materials prepared by 750°C were shown in the inset of Figure 10(c). It can be seen that the 410nm absorption intensity is related to Ag concentration. The 410nm absorption

intensity increased with increasing of Ag concentration, suggesting more Ag nanoparticles were formed in the SiO₂: Eu, Ag 3DOM materials. The emission spectra and luminescence decay curves of SiO₂: 2mol%Eu, x mol% Ag (x=0, 0.2, 0.4, 0.6, and 0.8) 3DOM materials prepared by 750 °C were shown in the inset pattern of Figure 11 and Figure 13, respectively. The emission intensities and lifetimes of the SiO₂: 2 mol% Eu, x mol % Ag(x=0, 0.2, 0.4 and 0.6) 3DOM materials were observed to increase and decrease, respectively, with the increasing of Ag concentration from 0 to 0.6 mol%, suggested that enhanced luminescence of Eu³⁺ is indeed associated with the increasing of radiative decays rate in the SiO₂:Eu³⁺ 3DOM materials. The luminescence intensity of Eu³⁺ was decreased when the concentration of Ag is about 0.8 mol% in contrast to other 3DOM materials with lower concentration of Ag. The luminescence intensity decreasing of Eu³⁺ may be due to the concentration quenching when the concentration of Ag is about 0.8 mol%.

In the SiO₂-Ag-Eu 3DOM materials prepared by 550 °C and 750 °C, the emission of Eu³⁺ was significantly enhanced in contrast to that of the SiO₂-Eu 3DOM materials without Ag species. The enhancement factor (EF) of emission of SiO₂-Ag-Eu 3DOM materials was shown in Figure 14. Enhancement factor (EF) is defined as the ratio of the 614nm emission intensity observed from SiO₂-Ag-Eu 3DOM materials to that from SiO₂-Eu 3DOM materials without Ag. The maximum EF of emission caused by Ag nanoparticles is about 4 fold in the SiO₂-Ag-Eu 3DOM materials under the excitation of 245nm prepared by 750 °C without Ag⁺-Ag⁺, while about 12.8 and 8 folds enhancement was observed for the SiO₂-Ag-Eu 3DOM materials with Ag⁺-Ag⁺ and Ag⁺ under the excitation of 345 and 245nm prepared by 550 °C, respectively. The EF in the SiO₂-Ag-Eu 3DOM materials with Ag⁺-Ag⁺ and Ag⁺ prepared by 550 °C is larger than that of the SiO₂-Ag-Eu 3DOM materials

prepared by 750 °C without Ag⁺-Ag⁺ and Ag⁺, which indicates that coupling enhancement of Ag nanoparticles and Ag⁺-Ag⁺/Ag⁺ was also obtained in the Ag⁺-Ag⁺ and Ag⁺ including SiO₂-Ag-Eu 3DOM materials prepared by 550 °C. These results demonstrated the contribution of energy transfer from Ag⁺-Ag⁺ or Ag⁺ to Eu³⁺ in the SiO₂-Ag-Eu 3DOM materials prepared by 550 °C.

Conclusion

The influence of silver species on photoluminescence properties of Eu³⁺ was investigated systematically in the SiO₂ 3DOM materials. The results show that luminescence enhancement of Eu³⁺ ions was obtained by Ag species in the SiO₂ 3DOM materials. For the SiO₂ 3DOM materials prepared by 550 °C, the enhancement of Eu³⁺ luminescence is attributed to energy transfer from Ag⁺-Ag⁺ to Eu³⁺ under 345 and 280 nm excitation, while luminescence enhancement of Eu³⁺ is due to energy transfer from isolated Ag⁺ to Eu³⁺ under the excitation of 245 nm. For the SiO₂ 3DOM materials prepared by 750 °C, luminescence of Eu³⁺ were enhanced due to plasmon resonance effect of Ag nanoparticles.

Acknowledgements

This work was supported by Reserve Talents Project of Yunnan Province (2012HB068) and Applied Basic Research Program of Yunnan Province (2014FB127), and Talent Youth Science Foundation of College of materials science and technology (20140205), Kunming University of Science and Technology.

References

- (1) P. N. Bartlett, J. J. Baumberg, P. R. Birkin, M.A. Ghanem and M. C. Netti, *Chem. Mater.*, 2002, **14**, 2199.
- (2) W. Qian, Z. Z. Gu, A. Fujishima and O. Sato, *Langmuir*, 2002, **18**, 4526.
- (3) A. Stein and R. C. Schrodin, *Curr. Opin. Solid State Mater. Sci.*, 2001, **5**, 553.

-
- (4) R.C. Schroden, M.A. Daous, S. Sokolov, B.J. Melde, J.C. Lytle, A. Stein, M.C. Carbajo, J.T. Fernandez and E.E. Rodriguez, *J. Mater. Chem.*, 2002, **12**, 3261.
- (5) P. Jiang, K. S. Hwang, D. M. Mittleman, J. F. Bertone and V. L. Colvin, *J. Amer. Chem. Soc.*, 1999, **121**, 11630.
- (6) Y. Y. Song, D. Zhang, W. Gao and X. H. Xia, *Chem. Eur. J.* 2005, **11**, 2177.
- (7) Y. Bai, K. Yang, Y. wang, X. Zhang and Y. Song, *Opt. Commun.*, 2008, **28**, 2930.
- (8) D. Jia, X.J. Wang, W. Jia and W.M. Yen, *J. Appl. Phys.*, 2003, **93**, 148.
- (9) F. Liu, G. Aldea and J.M. Nunzi, *J. Lumin.*, 2010, **130**, 56.
- (10) T. Hayakawa, S.T. Selvan and M. Nogami, *J. Non-Cryst. Solids*, 1999, **259**, 16.
- (11) D. Zhang, X. Hu, R. Ji, S. Zhan, J. Gao, Z. Yan, E. Liu, J. Fan and X. Hou, *J. Non-Cryst. Solids*, 2012, **358**, 2788.
- (12) S. Lai, Z. Yang, J. Liao, J. Li, B. Shao, J. Qiu, Z. Song, *RSC Adv.* 2014, **4**, 33607.
- (13) D. Manikandan, S. Mohan and K.G.M. Nair, *Mater. Res. Bull.*, 2003, **38**, 1545.
- (14) J. A. Jiménez, S. Lysenko, H. Liu, E. Fachini, O. Resto and C.R. Cabrera, *J. Lumin.*, 2009, **129**, 1546.
- (15) I. Rabin, W. Schulze and G. Ertl, *Chem. Phys. Lett.*, 1999, **312**, 394.
- (16) L. Li, Y. Yang, D. Zhou, X. Xu and J. Qiu, *J. Non-Cryst. Solids*, 2014, **385**, 95.
- (17) I. Belharouak, F. Weill, C. Parent, G. Le Flem and B. Moine, *J. Non-Cryst. Solids*, 2001, **293**, 649.
- (18) L. P. Naranjo, C. B. de Araújo, O. L. Malta, P. A. Santa Cruz and L. R. Kassab, *Appl. Phys. Lett.*, 2005, **87**, 241914.
- (19) H. Guo, X. Wang, J. Chen and F. Li, *Opt. Express*, 2010, **18**, 18900.
- (20) M. Guzzi, M. Martini, A. Paleari, F. Pio, A. Vedda, C. B. Azzoni, *J. Phys.: Condens. Matter*, 1993, **5**, 8105.
- (21) P. Gangopadhyay, R. Kesavamoorthy, Santanu Bera, P. Magudapathy, K. G. M.

-
- Nair, B. K. Panigrahi, and S.V. Narasimhan, *Phys. Rev. Lett.* 2005, **94**, 047403
- (22) H. Nishikawa, R. Tohmon, Y. Ohki, K. Nagasawa and Y. Hama, *J. Appl. Phys.*, 1989, **65**, 4672.
- (23) F. Meinardi and A. Paleari, *Phys. Rev. B*, 1998, **58**, 3511.
- (24) J. A. Jiménez, S. Lysenko and H. Liu, *J. Appl. Phys.*, 2008, **104**, 054313.
- (25) M. El Masloumi, Université Sciences et Technologies-Bordeaux I; Université Cadi Ayyad (Marrakech, Maroc). Faculté des sciences Semlalia, 2008.
- (26) M. Dubiel, R. Schmitz, K. Scheerschmidt, H. Hofmeister, *J. Non-Cryst. Solids*, 1995, **192**, 632.
- (27) M. Jansen, *Angew. Chem.* 1987, **99**, 1136.
- (28) N. Nishikawa, Y. Miyake, E. Watanabe, D. Ito, K.S. Seol, Y. Ohki, K. Ishii, Y. Sakurai and K. Nagasawa, *J. Non-Cryst. Solids*, 1997, **222**, 221.
- (29) L. S. Liao, X. M. Bao, N. S. Li, X. Q. Zheng, N.B. Min, *J. Lumin.*, 1996, **68**, 199.
- (30) J. A. Jiménez, S. Lysenko, G. Zhang and H. Liu, *J. Mater. Sci.*, 2007, **42**, 1856.
- (31) R. Pang, C. Li, L. Shi and Q. Su, *J. Phys. Chem. Solids*, 2009, **70**, 303.
- (32) D. Andsager, J. Hilliard, J. M. Hetrick, L. H. AbuHassan, M. Plisch, M. H. Nayfeh, *J. Appl. Phys.*, 1993, **74**, 4783.
- (33) S. Murakami, M. Herren, D. Rau and M. Morita, *Inorg. Chim. Acta*, 2000, **300**, 1014.
- (34) J.R. Lakowicz, *Anal. Biochem.*, 2001, **298**, 1.

Figure Captions:

Figure 1 The low (a) and high (b) magnification SEM images of SiO₂: 2%Eu, 0.6%Ag 3DOM material; (c) the EDS spectrum of SiO₂: 2%Eu, 0.6%Ag 3DOM material.

Figure 2 (a) The TEM image of SiO₂-Eu-Ag 3DOM material. (b) The absorption spectra of pure SiO₂, SiO₂-Eu, SiO₂-Ag and SiO₂-Eu-Ag 3DOM materials sintered at 550 °C; (c) The XPS spectrum of SiO₂-Ag-Eu 3DOM material.

Figure 3 The excitation spectra of pure SiO₂ and SiO₂-Ag 3DOM materials sintered at 550 °C by monitoring the 360, 396 or 540 nm emissions; Inset pattern is the excitation spectrum of SiO₂-Eu 3DOM materials by monitoring the 614 nm emission.

Figure 4 The emission spectra of pure SiO₂, SiO₂-Ag, SiO₂-Eu and SiO₂-Ag-Eu 3DOM materials under the excitation of 280 nm.

Figure 5 (a) The decay curves of 360 nm emission in the pure SiO₂, SiO₂-Eu, SiO₂-Ag and SiO₂-Ag-Eu 3DOM samples under the 280 nm excitation; (b) The decay curves of 540 nm emissions in the pure SiO₂, SiO₂-Ag and SiO₂-Ag-Eu 3DOM samples under the 280 nm excitation.

Figure 6 (a) The emission spectra of pure SiO₂, SiO₂-Eu, SiO₂-Ag and SiO₂-Ag-Eu 3DOM samples under excitation at the 345 nm; (b) The decay curves of 540 nm emission in the SiO₂-Ag and SiO₂-Ag-Eu 3DOM samples under the 345 nm excitation.

Figure 7 (a) The emission spectra of pure SiO₂, SiO₂-Ag, SiO₂-Eu and SiO₂-Ag-Eu 3DOM samples under the excitation of 245 nm; (b) The decay curves of 396 nm emission in the SiO₂-Ag and SiO₂-Ag-Eu 3DOM samples under the 245 nm excitation.

Figure 8 Energy level diagram and energy transfer process.

Figure 9 The chromaticity coordinates (CIE) of the SiO₂-Ag and SiO₂-Ag-Eu 3DOM materials under the excitation of 245, 280, 345 nm.

Figure 10 The TEM (a) and high-resolution TEM (b) images of the SiO₂: 2mol% Eu, 0.6mol% Ag 3DOM material prepared by 750 °C; (c) The absorption spectra of SiO₂: 2mol%Eu 3DOM materials with and without 0.6 mol% Ag prepared by 750 °C. Inset pattern is the absorption spectra of SiO₂-Eu 3DOM materials with different Ag concentration prepared by 750 °C; (d) The excitation spectra of SiO₂: 2mol% Eu, 0.6mol% Ag 3DOM material prepared by 550 and 750 °C by monitoring the 614 nm emission.

Figure 11 The emission spectra of SiO₂:2 mol% Eu 3DOM materials with and without 0.6 mol% Ag prepared by 750°C. Inset pattern is the emission spectra of SiO₂-Eu 3DOM materials with different Ag concentration prepared by 750°C.

Figure 12 Three Energy level diagram for the calculation of population of excited level of Eu³⁺.

Figure 13 The decay curves of 614 nm emission of SiO₂: 2mol%Eu, x mol% Ag (x=0, 0.2, 0.4, 0.6, and 0.8) 3DOM materials.

Figure 14 (a) Enhancement factor of 614 nm emission from Eu³⁺ in 3DOM materials prepared by 550 °C under various excitation wavelength; (b) Enhancement factor of 614 nm emission from Eu³⁺ in the 3DOM materials with different Ag concentration prepared by 750 °C

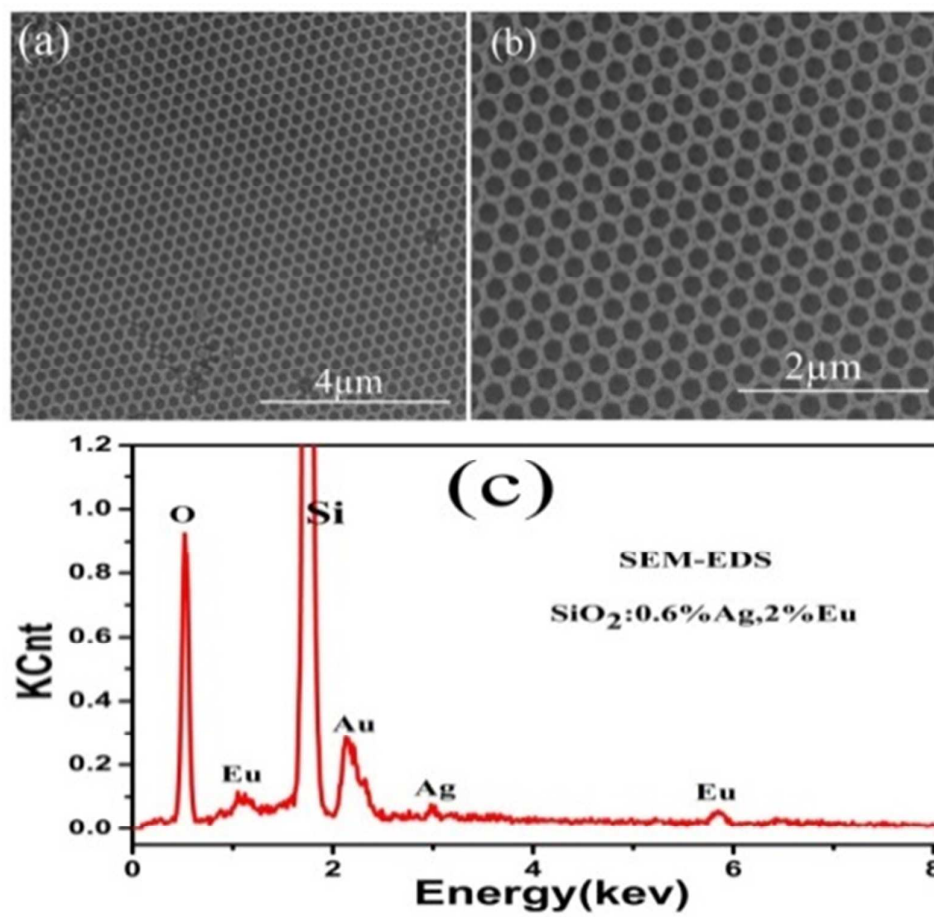


Figure 1

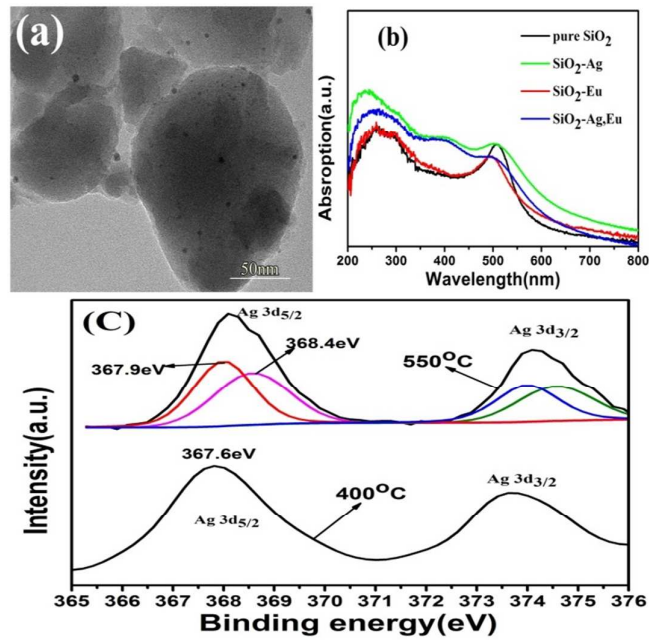


Figure 2

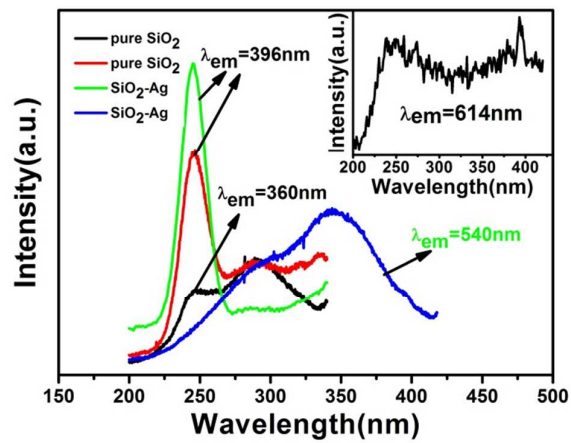


Figure 3

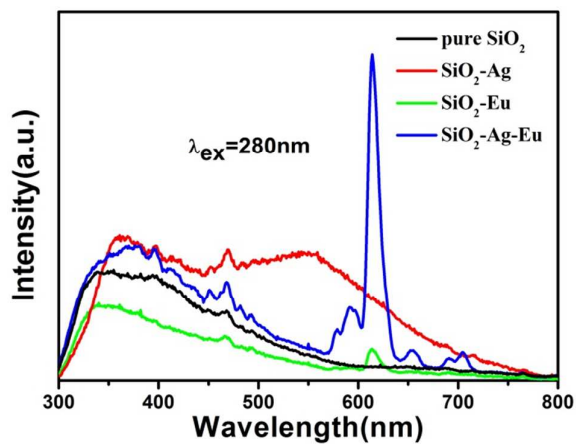


Figure 4

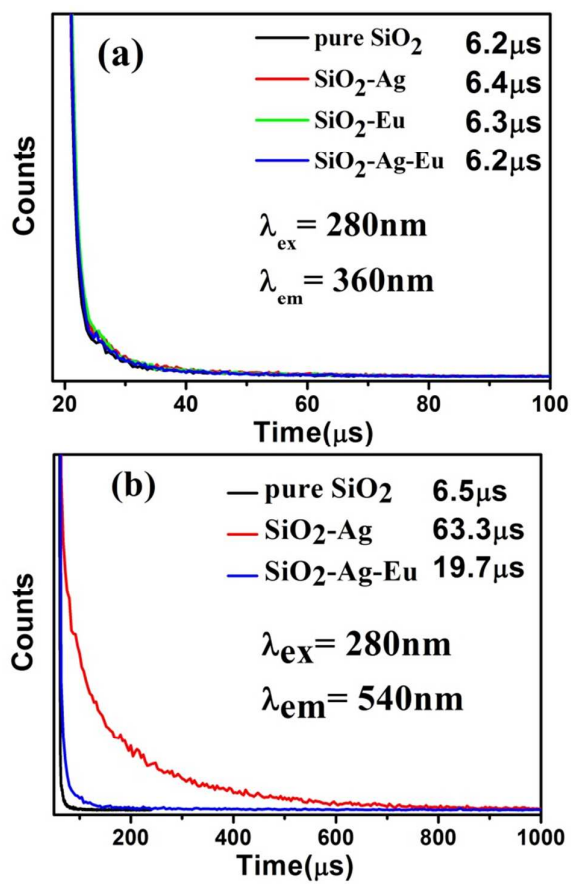


Figure 5

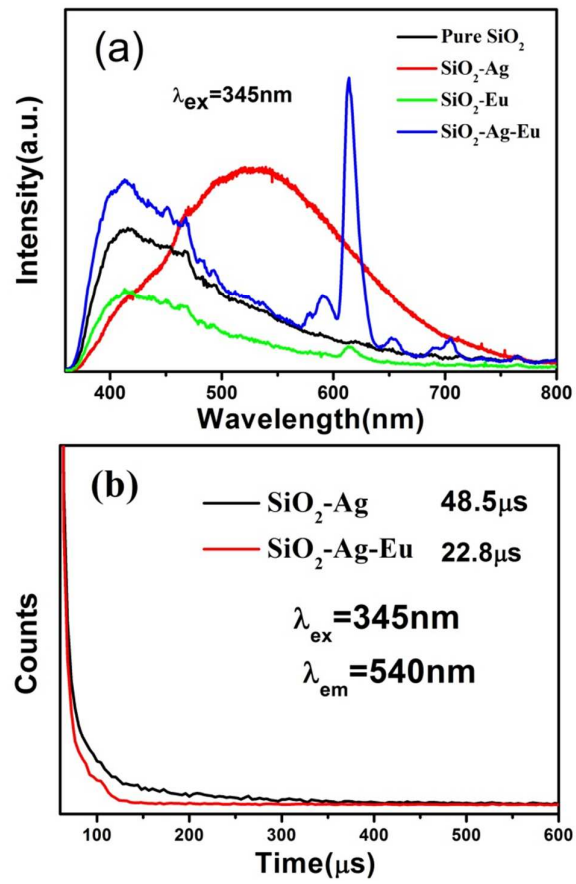


Figure 6

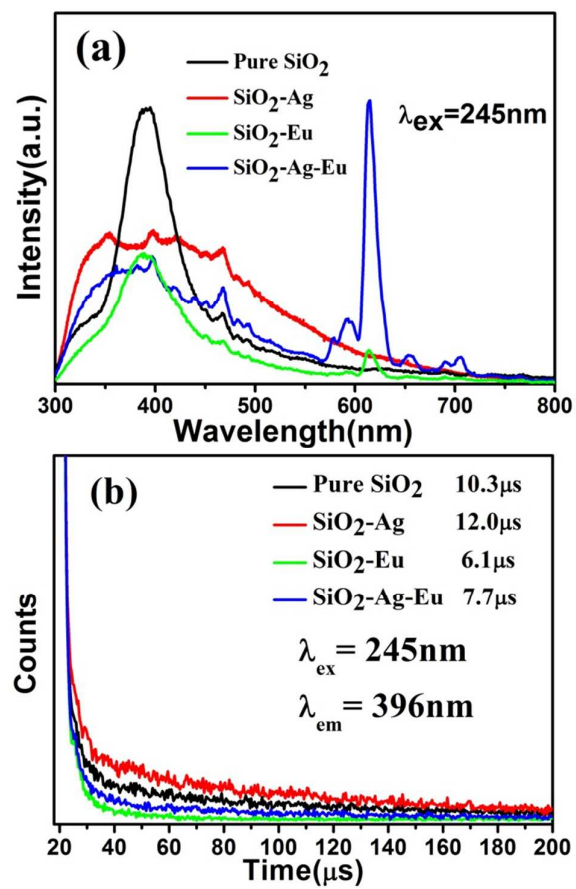


Figure 7

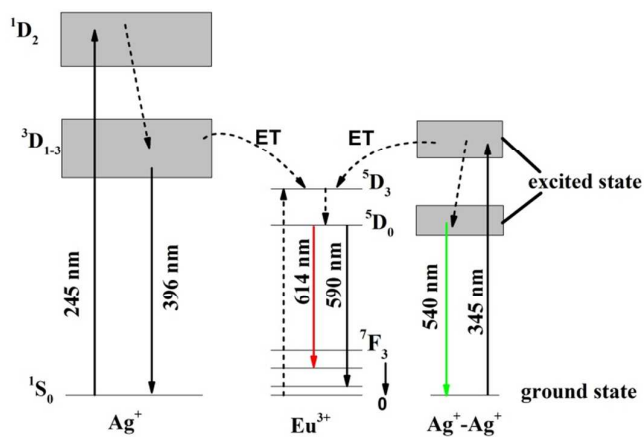


Figure 8

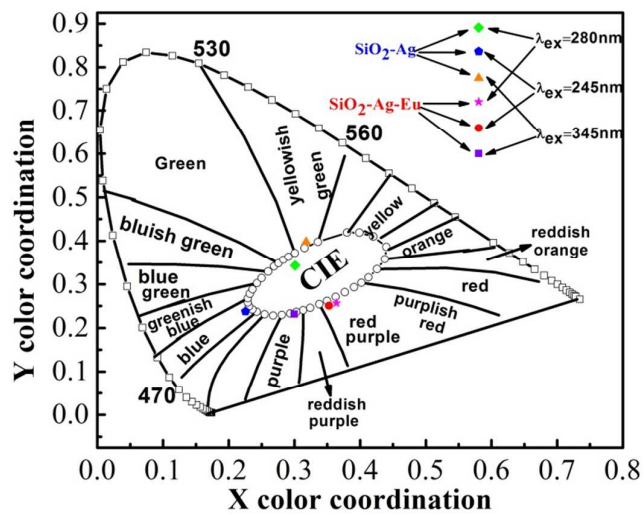


Figure 9

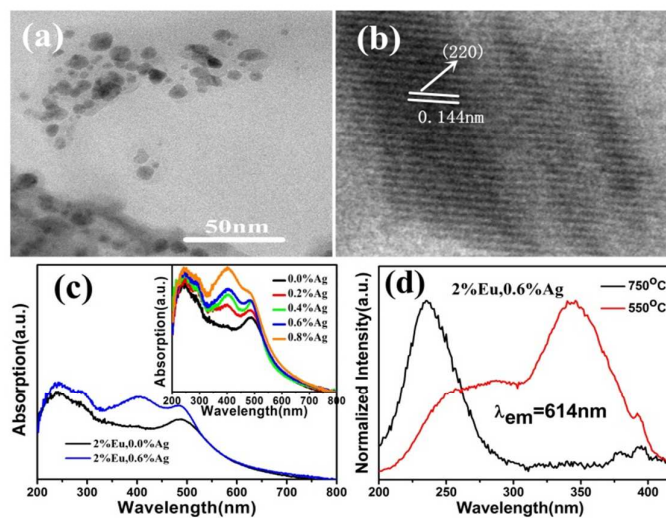


Figure 10

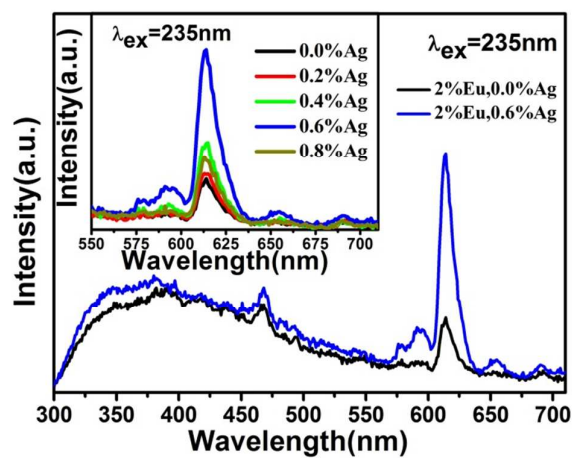


Figure 11

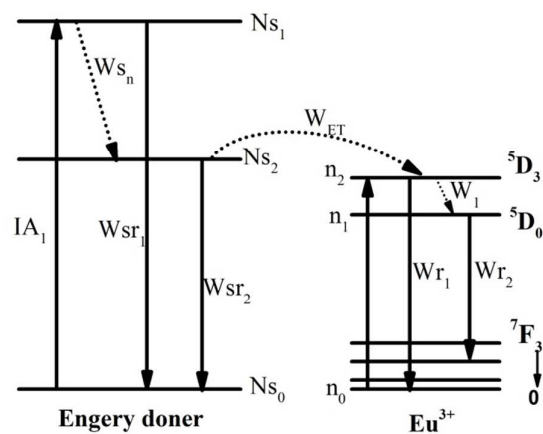


Fig.12

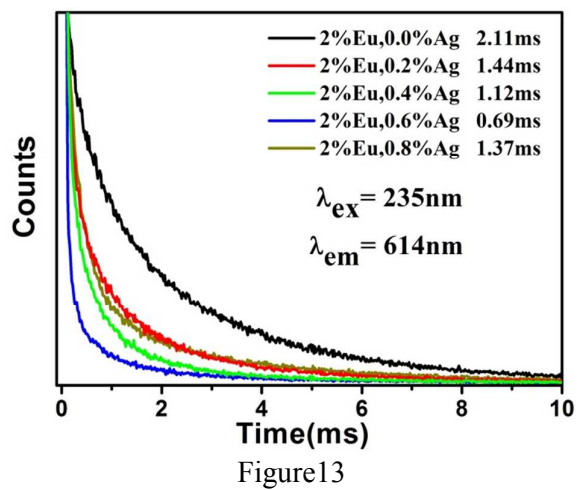


Figure13

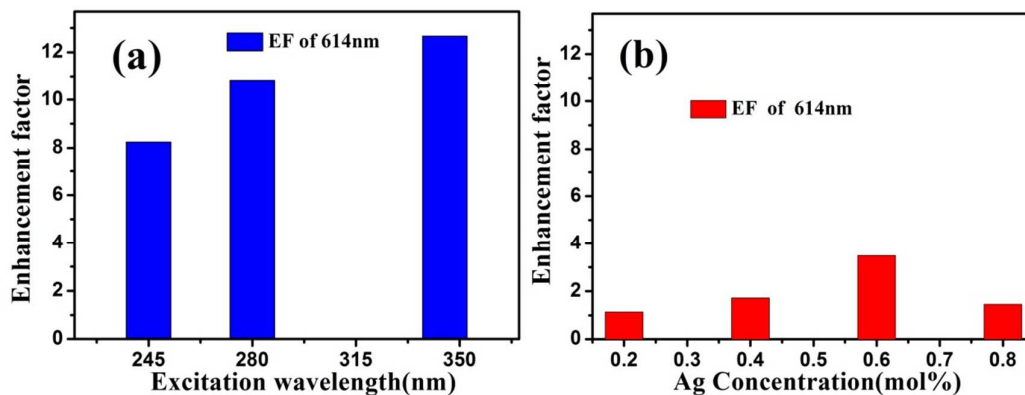


Figure 14

Table I The fitting parameters as A_1 , τ_1 , A_2 , τ_2 and luminescence lifetime (τ) of 360 and 540 nm emissions in the pure SiO_2 , SiO_2 -Eu, SiO_2 -Ag and SiO_2 -Ag-Eu 3DOM samples under the 280 nm excitation.

Samples	A_1	τ_1	A_2	τ_2	τ
Pure SiO_2 ($\lambda_{\text{em}}=360$ nm)	15292.89	1.17	1590.001	11.28	6.2 μs
SiO_2 -Ag ($\lambda_{\text{em}}=360$ nm)	14404.58	1.275	884.405	13.99	6.4 μs
SiO_2 -Eu ($\lambda_{\text{em}}=360$ nm)	14629.4	1.304	1211.704	12.53	6.3 μs
SiO_2 -Ag-Eu ($\lambda_{\text{em}}=360$ nm)	15047.72	1.252	1493.922	11.62	6.2 μs
Pure SiO_2 ($\lambda_{\text{em}}=540$ nm)	15840.43	0.956	910.231	13.42	6.5 μs
SiO_2 -Ag ($\lambda_{\text{em}}=540$ nm)	2485.399	155.18	40021.64	20.846	63.3 μs
SiO_2 -Ag-Eu ($\lambda_{\text{em}}=540$ nm)	1683.62	37.717	14337.6	5.7197	19.7 μs

Table II The luminescence lifetime (τ) of 396 nm emission in the pure SiO_2 , SiO_2 -Eu, SiO_2 -Ag and SiO_2 -Ag-Eu 3DOM samples under the 245 nm excitation.

Samples	Pure SiO_2	SiO_2 -Ag	SiO_2 -Eu	SiO_2 -Ag, Eu
τ ($\lambda_{\text{ex}}=245$ nm, $\lambda_{\text{em}}=396$ nm)	10.3 μs	12.0 μs	6.1 μs	7.7 μs

Graphical abstracts

Luminescence enhancement was observed in the SiO₂: Ag, Eu 3DOM materials

