Journal of Alloys and Compounds 506 (2010) 728–733

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

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

A facile one-pot hydrothermal method to prepare europium-doped titania hollow phosphors and their sensitized luminescence properties

Xuan Feng, Ling Yang, Nianchun Zhang, Yingliang Liu*

Department of Chemistry and Institute of Nanochemistry, Jinan University, 601 Western Huangpu Road, Guangzhou 510632, PR China

ARTICLE INFO

Article history:
Received 26 March 2010
Received in revised form 6 July 2010
Accepted 7 July 2010
Available online 15 July 2010

Keywords:
Titania hollow spheres
Europium-doped
Photoluminescence
Crystalline field
Energy transfer

ABSTRACT

Monodisperse europium-activated titania hollow phosphors had been synthesized by a facile one-pot hydrothermal method using carbon spheres as hard templates. Samples were characterized by X-ray powder diffraction, transmission electron microscopy, X-ray photoelectron spectroscopy, energy dispersive spectrometer and photoluminescence spectrum. The strongest emission intensity was observed with $TiO_2:Eu_{0.2}$ hollow spheres and $TiO_2:Eu_{0.2}$ hollow spheres calcining at 550 °C. Moreover, the strongest excitation of $TiO_2:Eu_{0.2}$ hollow spheres transferred from 400 to 500 °C and the effective nonradiative energy transfer from the TiO_2 hollow spheres host matrix to Eu^{3+} ions crystal field states was realized due to changes of crystalline field in the environment around Eu^{3+} ions occupying Ti^{4+} sites. The proposed energy transfer mechanism was that UV light is absorbed in the band of TiO_2 hollow spheres crystal and then the energy is relaxed to the defect states of TiO_2 host. The energy can transfer to the crystal states of Eu^{3+} ions (^7F_j, j = 0, 1, 2, 3 and 4), which results in efficient photoluminescence. The fluorescent intensity of $TiO_2:Eu_{0.2}$ hollow spheres was 2.2 times as strong as that of $TiO_2:Eu_{0.2}$ bulk material.

1. Introduction

Rare-earth-doped nanostructured materials as a new rising luminescent item have generated great interests due to a wide range of application in catalyst, sensors, and optical devices [1–4]. Compared with La^{3+} [5], Nd^{3+} [6], Er^{3+} [7], Tb^{3+} [8], and Sm^{3+} ions [9], Eu^{3+} ions have a unique advantage of tremendous applications in phosphors because of their high fluorescent efficiency [10,11].

Luminescence signals of the rare-earth ions are independent of the host matrix, but the nature of the matrix will affect the relative intensity of those signals. Luminescent performance of the rare-earth ions will be affected, when the rare-earth ions are located at different ligand environments. Up to date, a variety of materials have been investigated as the host matrix for rare-earth ions, including CeO_2 [12], ZnO [13], Y_2O_3 [14] and SnO_2 [15], because of their relatively wide band gaps, high chemical stability and physical refraction index.

In particular, titania as a valuable photocatalytic degradation material is used as a novel host material of rare-earth ions as a result of its unique optical and electrical capabilities [16,17]. Up to now, many different approaches including sonochemistry [18], nonionic surfactant-assisted soft-chemistry [19], microplasma oxidation [20], sol–gel [21] and hydrothermal method [22] had been developed to prepare europium-doped titania.

Moreover, hollow spheres are promising structures [23]. Holes and electrons can be effectively separated from time and space on the surface of hollow spheres. We had ever prepared preferable morphology, high thermal stability and good crystalline nature of anatase titania hollow spheres. So far, the photoluminescence properties of europium-doped titania hollow spheres have never been reported. So it is very essential to investigate these new materials.

In this paper, we report a facile one-pot method to prepare the monodisperse europium-doped titania hollow spheres using carbon spheres as hard templates. We study the photoluminescence properties of europium-doped titania hollow spheres. Red emission of Eu^{3+} ions and the concentration quenching were observed, because the trap depth of Eu^{3+} ions in crystalline field of titania hollow spheres had changed.

2. Experimental procedures

Europium nitrate was prepared by europium oxide and concentrated nitric acid. In a typical procedure, 4.5 g of glucose and 1 g of boric acid were dissolved in 30 mL of distilled water. The solution was transferred to a 50 mL Teflon-lined stainless-steel autoclave and maintained at 100 °C for 6 h and then heated to 147 °C for 48 h. After the autoclave was cooled down naturally, the products were centrifuged with absolute ethanol and distilled water. 30 mL of carbon spheres diluent as templates, different concentrations of europium nitrate (5.0, 10.0, 20.0 and 25.0 mol% compared to the concentration of titania), 1.44 g titanium sulfate and 5.4 g carbamide were mixed respectively. Then the solution was moved to the autoclave and heated to 120 °C for 1 h, and then heated to 180 °C for 10 h. Afterward, the reactor was cooled to room temperature naturally, all the resulting precipitates were harvested and

---

* Corresponding author. Tel.: +86 20 8522 1813; fax: +86 20 8522 1813.
E-mail address: tliuyl@jnu.edu.cn (Y. Liu).

0925-8388/$ – see front matter. Crown Copyright © 2010 Published by Elsevier B.V. All rights reserved.
doi:10.1016/j.jallcom.2010.07.052

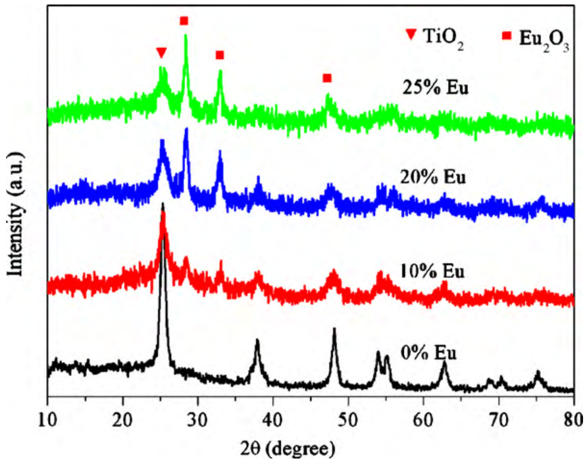

Fig. 1. XRD patterns of TiO_2 hollow spheres doped with different concentrations of europium.

washed several times with distilled water and absolute ethanol. After dying in a vacuum oven at 80 °C for more than 4 h, composites were obtained. Then composites were transferred to a crucible and calcined at 550 °C for 2 h in the air.

X-ray powder diffraction (XRD) data were collected by a MSAL-XD2 X-ray diffractometer with Cu Kα radiation (36 kV, 20 mA, $\lambda = 1.5406$ å). X-ray photoelectron spectroscopy (XPS) was used to evaluate the valence state of Eu atoms measured on an ESCALAB 250 spectrometer (Thermo Fisher Scientific). The XPS experiments were performed in an ultra high vacuum using AlKα (1486.6 eV) radiation. The recorded spectra were corrected due to the charge effect using the C1s line of the adventitious carbon at the sample surface at 284.8 eV as a reference. Transmission electron microscopy (TEM) was performed on Philips Tecnai-10. High-resolution transmission electron microscopy (HRTEM, JEM-2010 operated at 200 kV) with the energy dispersive spectrometer (EDS) analysis capability. The photoluminescence (PL) spectrum (Hitachi F-4500) with a Xe lamp was employed to record photoluminescence emission spectra for each sample at room temperature.

3. Results and discussion

Fig. 1 shows XRD analysis patterns of titania hollow spheres doped with different concentrations of europium. The samples show the peaks at 2θ angles of 25.3°, 37.9°, 48.1°, 54.0°, 55.2° and 62.8°, which are consistent with JCPDS card no. 89-4921 commendably. It is found that the diffraction peaks of titania become weak with increasing doping degree. But no shift of the anatase peaks is detected after doping Eu^{3+}. That is because Eu^{3+} ions enter the titania crystal lattice and occupy Ti^{4+} sites. Titania crystallinity decrease as a result of less Ti^{4+} amount. When the doping degree goes higher to about 10 mol%, some weak peaks from Eu_2O_3 located at 28.4°, 32.9° and 47.3° are detected. Those diffraction peaks are consistent with JCPDS card no. 86-2476, which indicates the well-dispersed Eu^{3+} ions in titania hollow spheres. They become stronger as the doping degree is further increased. This indicates that the loading content for Eu^{3+} ions in the samples may be saturated and some Eu^{3+} ions have to form Eu_2O_3 phase on the outer hollow spheres. Fig. 2 shows XRD patterns of TiO_2:$Eu_{0.2}$ hollow spheres before calcining and after calcining. Anatase titania had formed before calcining and the diffraction peaks of the precursor seemed to be very strong. After calcining to 400 °C, diffraction peaks of Eu_2O_3 begun to appear. When calcination temperature was raised, diffraction peaks of titania and Eu_2O_3 became stronger and no other new peaks turned up. However, after calcining to 900 °C, rutile did not emerge and $Eu_2Ti_2O_7$ appeared with the peaks at 30.4°, 50.7° and 60.1°, which are consistent with JCPDS card no. 87-1852 [24]. TiO_2 reacted with Eu_2O_3 under high temperature, because TiO_2 was an amphipathic compound. Three phases, including TiO_2, Eu_2O_3, and $Eu_2Ti_2O_7$, were existed simultaneously in the samples.

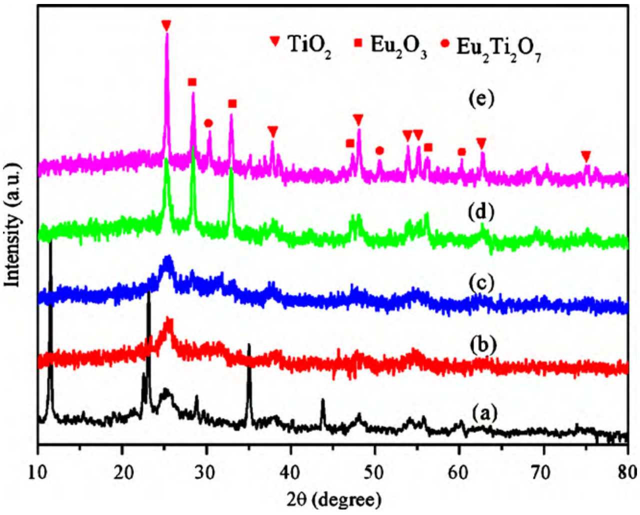

Fig. 2. XRD patterns of TiO_2:$Eu_{0.2}$ hollow spheres (a) before calcining and after calcining at (b) 400 °C, (c) 500 °C, (d) 800 °C, and (e) 900 °C, respectively.

The morphology and the size of resulting products depend on templates [25]. So controlling the parameters of templates was very important. Carbon spheres were utilized as the sacrificial templates, which can be seen from TEM characterized to be monodisperse and spherical (Fig. 3a). It should be noted that the centrifugal speed of templates has been optimized. Moreover, the overall morphology was uniform. This qualification is essential for the template approach, where templates are soaked in the titanium sulfate solution, allowing adsorption of heterogeneous ions such as Ti^{4+} ions and OH^- ions through electrostatic interaction. Fig. 3b displays TEM image of core-shell structures. We found that core-shell structures could be seen clearly and titania loaded on carbon spheres well. As seen from the TEM image in Fig. 3c, the diameter of monodisperse TiO_2:$Eu_{0.2}$ hollow spheres was about 350 nm presented through calcination of templates. Fig. 3d displays HRTEM image of the shells of TiO_2:$Eu_{0.2}$ hollow spheres. The shell of hollow spheres was ca. 25 nm and the surface of hollow structures was very rough due to the doping of Eu^{3+} ions. Fig. 3e presents a typical HRTEM lattice image of the shells of TiO_2:$Eu_{0.2}$ hollow spheres. By measuring the lattice fringes, the resolved interplanar distance is about 0.35 nm, corresponding to the low energy (1 0 1) plane of the anatase TiO_2. The typical selected area electron diffraction (SAED) patterns (inset in Fig. 3e) indicate that the shells consist of a weak polycrystalline nature of anatase phases for TiO_2 hollow spheres. The shell of hollow spheres was round and coarse. As shown in Fig. 3f, the peaks for titanium (4.5, 4.9 and 0.3 keV), oxygen (0.5 keV) and europium (0.9, 5.9 and 6.5 keV) are observed. EDS analysis of the titania shells shows that the contents of the constituent atoms are 70.19% (C), 5.25% (O), 5.92% (Ti), 0.64% (Eu), 0.17% (Cr) and 17.83% (Cu). The peak of Cu comes from the TEM mesh. Some carbon contents are from the TEM mesh and others are from the sample. We insist carbon element can be removed even after calcining at 550 °C.

It is well known that XPS probes the surface of the particles. But carbon signal is always present in XPS as a result of hydrocarbon deposits in the vacuum. The XPS spectra of TiO_2:$Eu_{0.2}$ hollow spheres calcined at 550 °C recorded in the energy region of the Eu($3d_{5/2}$, 4d) transition, are presented in Fig. 4. The former spectrum shows the coexistence of two oxidation states for the Eu and Eu^{3+} ions. Each of them splits because of the spin–orbit coupling. On the basis of the published Eu($3d_{5/2}$) spectrum of Eu_2O_3, we can assign the prominent peak around 1135.5 eV to an $Eu^{3+}{}_{5/2}(3d4f^6)$ configuration, and the other small peak around 1125.6 eV is attributed to an Eu configuration. The latter spectrum shows Eu(4d) level occurring at 135.2 eV (main peak) and at 141.7 eV (satellite peak), which are attributed to Eu^{3+} ions con-

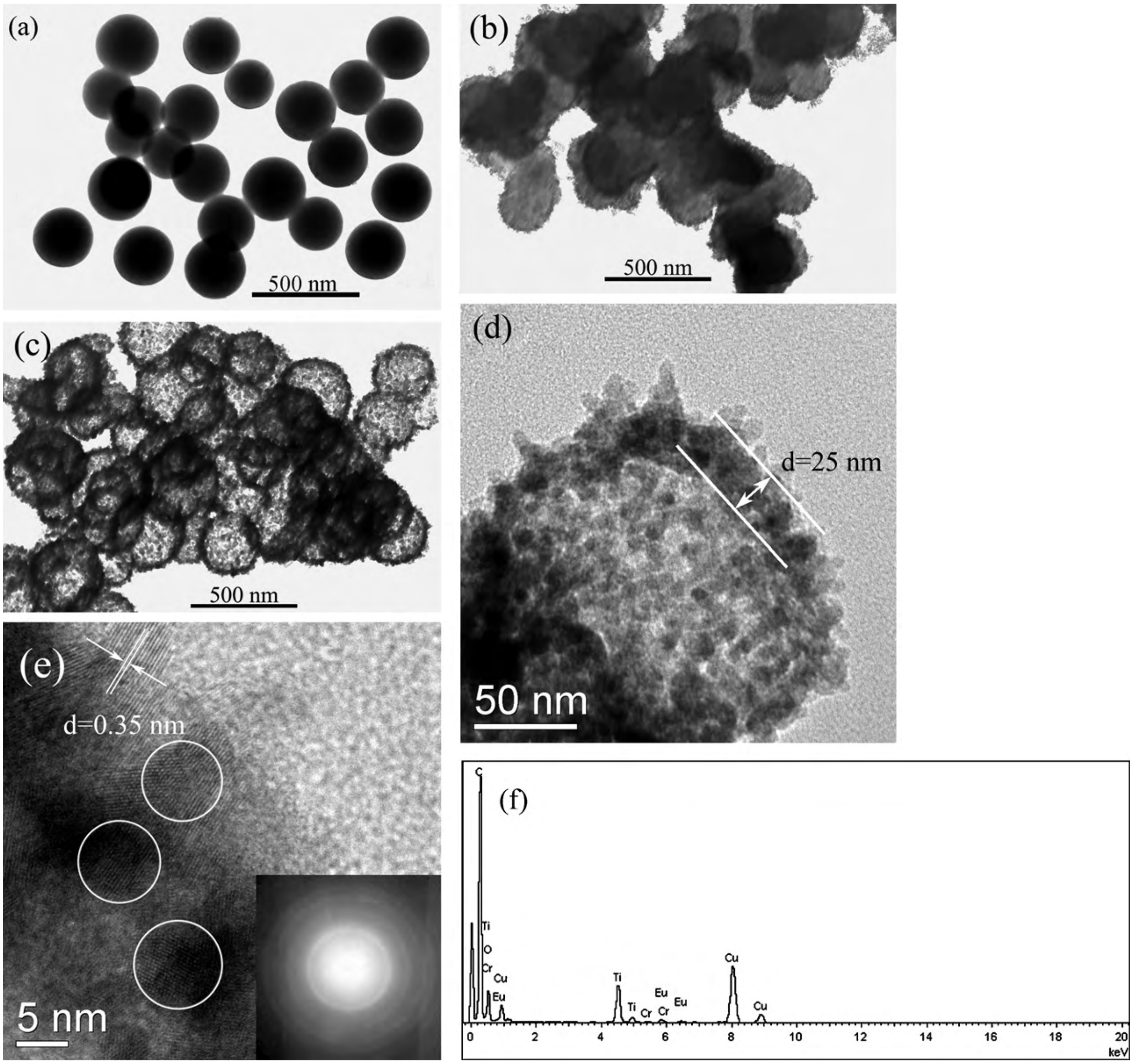

Fig. 3. TEM images of (a) carbon spheres, (b) core-shell structures, (c) TiO_2:$Eu_{0.2}$ hollow spheres calcined at 550 °C, and (d, e) HRTEM images and (f) EDS analysis of TiO_2:$Eu_{0.2}$ hollow spheres.

figuration. Trace amounts of Eu to which the small peak around 128.1 eV is attributed can also been seen. Pol et al. have explained its appearance due to the divalent component whose ground state is different from the bulk because of different geometric environments [18]. Here, we insist that Eu exists in the TiO_2:$Eu_{0.2}$ hollow spheres.

PL spectrum is an important detection means of luminescence properties of the materials. Fig. 5 compares emission spectra of titania hollow spheres with different concentrations of europium. Europium-doped titania hollow spheres exhibited characteristic emission located at 583, 591, 613, 650 and 698 nm which were assigned to $^5D_0 \rightarrow {}^7F_0$, $^5D_0 \rightarrow {}^7F_1$, $^5D_0 \rightarrow {}^7F_2$, $^5D_0 \rightarrow {}^7F_3$ and $^5D_0 \rightarrow {}^7F_4$ transition, respectively. TiO_2 was a host matrix to sensitize the luminescence of Eu^{3+} ions and Eu^{3+} ions were a luminescence center. Eu^{3+} ions occupy the sites of non-homogeneous central position in the hollow spheres and forbidden transition was rescinded because of its electric-dipole character. It is found that the photoluminescence intensity initially increases with doping degree. This is easily understood that the luminescent intensity increases due to more Eu^{3+} ions amount occupying Ti^{4+} sites. When the Eu:Ti ratio exceeds a critical level about 20 mol%, the concentration quenching occurs due to pair formation [26]. Hollow spheres have a large surface area, but it is still limited after all. According to the structure characterizations above, some Eu^{3+} ions cannot well incorporate into titania hollow spheres and they form the independent Eu_2O_3 phase, when the doping degree is too high. Therefore, these Eu_2O_3 clusters might have increased ion–ion interaction and decreased the photoluminescence intensity. However, it should be pointed out that the quenching concentration in these europium-doped titania hollow spheres is higher compared with results in other literatures. We insist that hollow spheres accommodate high concentration Eu^{3+} ions and the interface effect of hollow spheres might induce good dispersion state of the Eu^{3+} ions.

Fig. 6 shows emission spectra of TiO_2:$Eu_{0.2}$ hollow spheres at different calcination temperatures. The emission of Eu^{3+} ions cannot been almost seen before calcining. Because the nonradiative relaxation decreases with increasing the temperature of heating. When samples were calcinated at different temperatures and excitated at 466 nm, TiO_2:$Eu_{0.2}$ hollow spheres exhibited characteristic emission from the $^5D_0$ level to ^7F_j level and the emission of Eu^{3+}

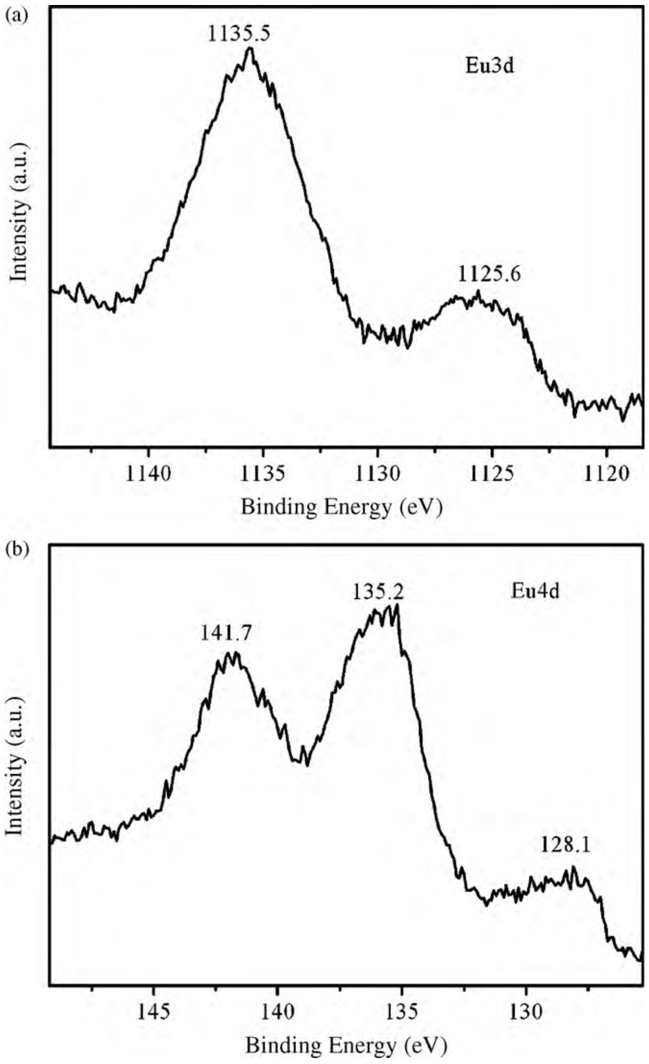

Fig. 4. XPS spectra of (a) the Eu($3d_{5/2}$) level and (b) the Eu(4d) level in the TiO_2:$Eu_{0.2}$ hollow spheres.

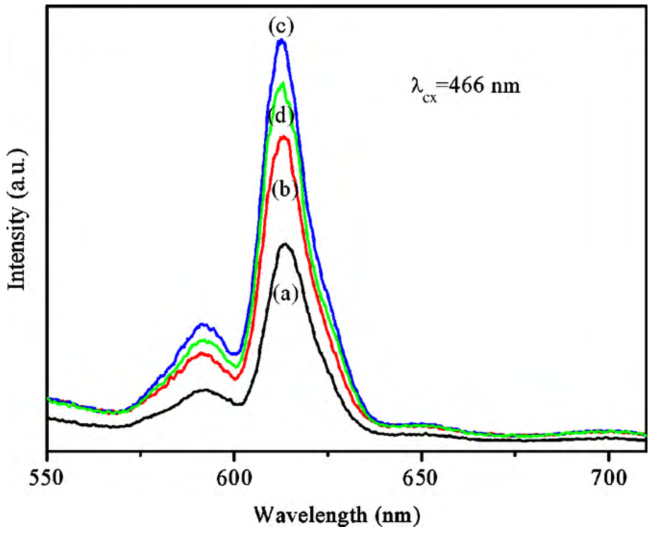

Fig. 5. Photoluminescence emission spectra of TiO_2 hollow spheres doped with (a) 5 mol%, (b) 10 mol%, (c) 20 mol%, and (d) 25 mol% of europium, respectively.

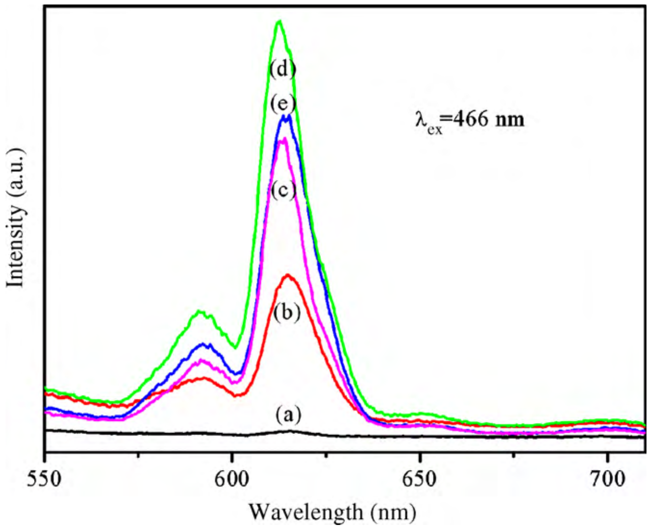

Fig. 6. Photoluminescence emission spectra of TiO_2:$Eu_{0.2}$ hollow spheres (a) before calcining and calcined at (b) 400 °C, (c) 500 °C, (d) 550 °C, and (e) 600 °C, respectively.

ions was increased slightly. Because the amounts of hydroxy or other organic groups decreased after calcining. When samples were further calcinated at 600 °C, the emission of Eu^{3+} ions suddenly declined because of the photoluminescence quenching. Temperatures influenced crystalline of samples highly, while they impacted on the action between TiO_2 and Eu^{3+} ions. This may be the fact that most of Eu^{3+} ions have been transformed into Eu_2O_3 or even $Eu_2Ti_2O_7$ phase rather sitting close to the semiconductor crystallite surface resulting in little Eu^{3+} ions occupying Ti^{4+} sites due to change of crystalline field. This undesired Eu–Eu interaction acting as luminescence quenching decreases the PL intensity.

Fig. 7 shows excitation spectra of TiO_2:$Eu_{0.2}$ hollow spheres before calcining and calcined at 400 and 500 °C for an emission at 613 nm. The characteristic excitation of Eu^{3+} ions located at 364, 384, 396, 414, 466, 534 and 556 nm was very weak before calcining, but excitation of 396 nm from the $^7F_0$ level to the $^5L_6$ level was stronger than excitation of 466 nm from the $^7F_0$ level to the $^5D_2$ level. The wide bands from 200 to 300 nm were due to the excitation of TiO_2 host matrix. When samples were calcinated at 400 °C, TiO_2:$Eu_{0.2}$ hollow spheres exhibited stronger characteristic

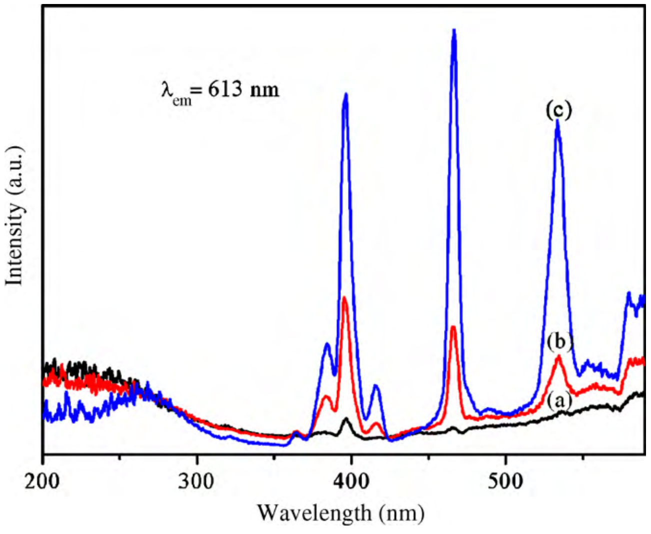

Fig. 7. Photoluminescence excitation spectra of TiO_2:$Eu_{0.2}$ hollow spheres (a) before calcining and calcined at (b) 400 °C, and (c) 500 °C, respectively.

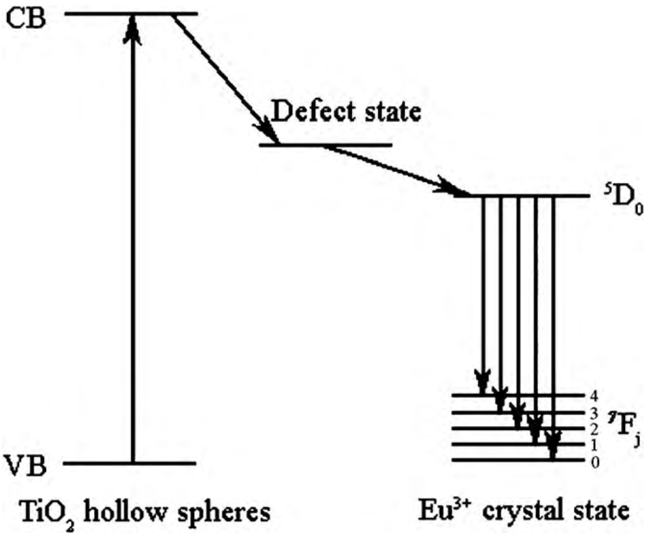

Fig. 8. Schematic representation of proposed energy transfer mechanism.

excitation. When samples were further calcinated at 500 °C, excitation of 466 nm became stronger than excitation of 396 nm. So the excitation of 466 nm was the most sensitive excitation wavelength instead of 396 nm. This can be explained due to changes of crystalline field in the environment around Eu^{3+} ions occupying Ti^{4+} sites [27]. Compared with bulk materials, we found the excitation bands had red shift and the excitation spectrum consists of a broad band in 200–280 nm. This is interesting because it clearly provides evidence that there is a host band-gap excitation. The peak at 265 nm is attributed to the charge transfer between Eu^{3+} and O^{2-}, i.e. for an electron transferring from the O^{2-} ($2p^6$) orbital to the empty orbital of Eu^{3+} ($4f^6$). Similar broad peaks have been reported in other works [28,29], while the peak positions ranged from 200 to 280 nm. For the excitation spectrum of samples, one excitation band centered at 322 nm is observed, which corresponds to the anatase TiO_2 host absorption. It is well known that Eu^{3+} ions have no crystal field absorption transition around 320 nm [30]. Therefore, the excitation peak at 322 nm is attributed to the effective nonradiative energy transfer from the TiO_2 hollow spheres host matrix to Eu^{3+} ions crystal field states.

Schematic representation of proposed energy transfer mechanism is shown in Fig. 8. Frindell et al. had ever reported energy transfer mechanism from TiO_2 host matrix to rare-earth ions [31]. In this process, UV light is absorbed in the valence band (VB) of TiO_2 hollow spheres crystal and some of the excited electrons in conduction band (CB) transit nonradiatively to the defect states of TiO_2 host. Other excited electrons are captured by trap to form self-trapped excitons. The energy of the defect states is higher than that of the emitting state of Eu^{3+} ions ($^5D_0$ level). To excite the Eu^{3+} 4f–4f intrashell transitions by self-trapped excitons, the energy is relaxed to the crystal states of Eu^{3+} ions ($^5D_0$ level) resulting in efficient photoluminescence, when the electron transmits to the ^7F_j ($j = 0$, 1, 2, 3 and 4) ground state shown in Figs. 6 and 7. By this way we can say that the energy transfer occurs between self-trapped excitons and Eu^{3+} 4f shell after doping Eu^{3+} in TiO_2 hollow spheres.

Fig. 9 shows emission spectra of $TiO_2{:}Eu_{0.2}$ bulk material and $TiO_2{:}Eu_{0.2}$ hollow spheres calcined at 550 °C. It is found that the emission of Eu^{3+} ions in crystalline field of TiO_2 bulk material or TiO_2 hollow spheres is similar. But characteristic emission of Eu^{3+} ions in crystalline field of titania hollow spheres is stronger than that of TiO_2 bulk material. It can be imaged that depth of trap of Eu^{3+} ions in crystalline field of titania hollow spheres is deep than that of TiO_2 bulk material.

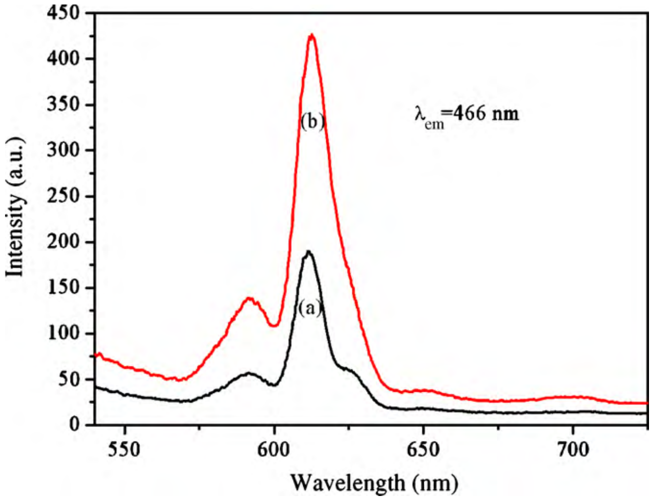

Fig. 9. Photoluminescence emission spectra of (a) $TiO_2{:}Eu_{0.2}$ bulk material and (b) $TiO_2{:}Eu_{0.2}$ hollow spheres calcined at 550 °C.

4. Conclusions

In summary, monodisperse europium-doped titania hollow phosphors had been synthesized by a facile one-pot hydrothermal method using carbon spheres as the hard templates and titanium sulfate as the titanium source. By calcination of core-shell structures at 550 °C for 2 h, the morphology of hollow spheres was presented. When europium-doped titania hollow spheres were excitated at 466 nm, their emission spectra exhibited five groups of characteristic emission associated with Eu^{3+} 4f–4f transitions from $^5D_0$ level to the ^7F_j level. The dominated radiation was 613 nm in the red emission area. The strongest emission intensity was observed with $TiO_2{:}Eu_{0.2}$ hollow spheres and the luminescence quenching phenomenon of europium-doped titania hollow spheres had also happened. The emission intensity of $TiO_2{:}Eu_{0.2}$ hollow spheres calcining at 550 °C was the strongest. Moreover, the fluorescent intensity of $TiO_2{:}Eu_{0.2}$ hollow spheres was 2.2 times as strong as that of $TiO_2{:}Eu_{0.2}$ bulk material. We also found the strongest excitation of $TiO_2{:}Eu_{0.2}$ hollow spheres transferred from 400 to 500 °C and the effective nonradiative energy transfer from the TiO_2 hollow spheres host matrix to Eu^{3+} ions crystal field states was realized. This could be explained by the present evidence of XRD data due to changes of crystalline field in the environment around Eu^{3+} ions occupying Ti^{4+} sites.

Acknowledgements

This work has been supported financially by the National Natural Science Foundations of China (SFC-20671042 and NSFC-50872045), the National Natural Science Foundations of Guangdong (GDSF-05200555 and GDSF-7005918), the National Natural Union Foundation of China and Guangdong Province (U-0734005) and the Fundamental Research Funds for the Central Universities (21610102).

References

[1] V. Štengl, S. Bakardjieva, N. Murafa, Mater. Chem. Phys. 114 (2009) 217–226.
[2] W. Li, A.I. Frenkel, J.C. Woicik, C. Ni, S.I. Shah, Phys. Rev. B 72 (2005) 155315.
[3] M. Saif, M.S.A. Abdel-Mottaleb, Inorg. Chim. Acta 360 (2007) 2863–2874.
[4] T.H. Fang, Y.S. Chang, L.W. Ji, S.D. Prior, W. Water, K.J. Chen, C.F. Fang, C.N. Fang, S.T. Shen, J. Phys. Chem. Solids 70 (2009) 1015–1018.
[5] S. Dikmen, J. Alloys Compd. 491 (2010) 106–112.
[6] W.Q. Luo, R.F. Li, X.Y. Chen, J. Phys. Chem. C 113 (2009) 8772–8777.
[7] S.A. Klimin, E.P. Chukalina, M.N. Popov, E. Antic-Fidancev, P. Aschehoug, N.V. Gaponenko, I.S. Molchan, D.A. Tsyrkunov, Phys. Lett. A 323 (2004) 159–163.

[8] M. Zalewska, A.M. Kłonkowski, Opt. Mater. 30 (2008) 725–729.
[9] G.P. Dong, X.D. Xiao, Y.Z. Chi, B. Qian, X.F. Liu, Z.J. Ma, S. Ye, E. Wu, H.P. Zeng, D.P. Chen, J.R. Qiu, J. Phys. Chem. C 113 (2009) 9595–9600.
[10] C. Molina, K. Dahmouche, C.V. Santilli, A.F. Craievich, S.J.L. Ribeiro, Chem. Mater. 13 (2001) 2818–2823.
[11] C.M. Leroy, T. Cardinal, V. Jubera, M. Treguer-Delapierre, J. Majimel, J.P. Manaud, R. Backov, C. Boissière, D. Grosso, C. Sanchez, B. Viana, F. Pellé, ChemPhysChem 9 (2008) 2077–2084.
[12] A. Kumar, S. Babu, A.S. Karakoti, A. Schulte, S. Seal, Langmuir 25 (2009) 10998–11007.
[13] P.A. Tanner, L.X. Yu, J. Nanosci. Nanotechnol. 8 (2008) 1307–1311.
[14] M.H. Zahir, T. Suzuki, Y. Fujishiro, M. Awano, J. Alloys Compd. 476 (2009) 335–340.
[15] G.F. Wang, Y.P. Yang, Q.Y. Mu, Y.D. Wang, J. Alloys Compd. 498 (2010) 81–87.
[16] K.L. Frindell, M.H. Bartl, A. Popitsch, G.D. Stucky, Angew. Chem. Int. Ed. 41 (2002) 959–962.
[17] J.J. Wu, X.J. Lü, L.L. Zhang, Y.J. Xia, F.Q. Huang, F.F. Xu, J. Alloys Compd. 496 (2010) 234–240.
[18] V.G. Pol, R. Reisfeld, A. Gedanken, Chem. Mater. 14 (2002) 3920–3924.
[19] J.B. Yin, L.Q. Xiang, X.P. Zhao, Appl. Phys. Lett. 90 (2007) 113112.
[20] X.H. Wu, W. Qin, X.B. Ding, Y. Wen, H.L. Liu, Z.H. Jiang, J. Phys. Chem. Solids 68 (2007) 2387–2393.
[21] P. Ghosh, A. Patra, J. Phys. Chem. C 111 (2007) 7004–7010.
[22] S. Sreekantan, L.C. Wei, J. Alloys Compd. 490 (2010) 436–442.
[23] G. Li, F. Liu, Z. Zhang, J. Alloys Compd. 493 (2010) L1–L7.
[24] J.G. Li, X.H. Wang, K. Watanabe, T. Ishigaki, J. Phys. Chem. B 110 (2006) 1121–1127.
[25] X.M. Sun, J.F. Liu, Y.D. Li, Chem. Eur. J. 12 (2006) 2039–2047.
[26] S. Yi, J.S. Bae, B.K. Moon, J.H. Jeong, J.H. Kim, Opt. Mater. 28 (2006) 610–614.
[27] L.A. Rocha, E.F. Molina, K.J. Ciuffi, P.S. Calefi, E.J. Nassar, Mater. Chem. Phys. 101 (2007) 238–241.
[28] H.W. Song, B.J. Chen, H.S. Peng, J.S. Zhang, Appl. Phys. Lett. 81 (2002) 1776–1778.
[29] A.V. Murugan, A.K. Viswanath, V. Ravi, B.A. Kakade, V. Saaminathan, Appl. Phys. Lett. 89 (2006) 123120.
[30] K.L. Frindell, M.H. Bartl, A. Popitsch, G.D. Stucky, Angew. Chem. 114 (2002) 1001–1004.
[31] K.L. Frindell, M.H. Bartl, M.R. Robinson, G.C. Bazan, A. Popitsch, G.D. Stucky, J. Solid State Chem. 172 (2003) 81–88.