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Fabrication and photoluminescence of chemically stable $La_2O_3:Eu^{3+}$–$La_2Sn_2O_7$ core–shell-structured nanoparticles†

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Core–shell-structured $La_2O_3:Eu^{3+}$–$La_2Sn_2O_7$ nanoparticles were fabricated through SnO_2-coating of $LaOF:Eu^{3+}$ in an aqueous solution and subsequent heat treatments at a higher temperature. The nanoparticles exhibited high chemical stability under an ambient atmosphere and intense red photoluminescence upon irradiation with ultraviolet light.

Doped metal oxide phosphors such as $Y_2O_3:Eu^{3+}$ have been intensively studied for new applications in optoelectronic devices, as well as for improvements in fluorescent lighting equipment.[1,2] In designing new phosphor materials, various factors should be considered such as emission wavelengths, luminescence efficiencies, chemical and physical stabilities, morphology and microstructures *etc.* Electrical conductivity is also required for low-voltage cathodoluminescence applications such as field emission displays (FEDs).[3]

Inorganic compounds containing lanthanum are recognized as excellent host materials for rare-earth (RE) activators because RE doping levels can be controlled over a wide range without changing host crystal structures. RE ions can be homogeneously substituted for La^{3+} ions, which results in good luminescent properties. As such, $La_2O_3:Eu^{3+}$ and $LaOF:Eu^{3+}$ have been investigated as red phosphors.[4–7] Although $La_2O_3:Eu^{3+}$ has been demonstrated to exhibit high luminescence intensity and color purity, there is a serious drawback to its practical use due to its instability to moisture and carbon dioxide in the ambient atmosphere; La_2O_3 is easily converted into $La(OH)_3$. To overcome this problem, it is promising to passivate La_2O_3 particles with surface layers of chemically stable materials, as was successfully achieved in SiO_2–$Y_2O_3:Eu^{3+}$ composites.[8,9] Furthermore, core–shell-structured particles have been reported to be more suitable for viable applications such as phosphors.[10]

The sol–gel process is usually applied to coat particles. However, coating of La_2O_3 particles is not easy because of their high reactivity with water which is generally involved in sol–gel procedures. Our approach to coating technology utilizes multi-step processes: (1) preparation of $LaOF:Eu^{3+}$ nanoparticles that are stable in water, (2) coating of $LaOF:Eu^{3+}$ with SnO_2 layers through a chemical solution deposition (CSD) and (3) heat treatments of coated particles at higher temperatures. CSD is known as a technique for producing various kinds of thin films or layers on foreign surfaces through heterogeneous nucleation. In our work, $LaOF:Eu^{3+}$ nanoparticles were placed in an aqueous solution of sodium stannate (Na_2SnO_3)[11] at 60 °C, resulting in the coating of SnO_2 layers on the particles. The coated $LaOF:Eu^{3+}$ particles were then heat-treated at 1000 °C to be converted into $La_2O_3:Eu^{3+}$. During this process, surface reactions were found to occur between La_2O_3 and SnO_2, leading to a new core–shell structure of $La_2O_3:Eu^{3+}$–$La_2Sn_2O_7$ nanoparticles. This communication is focused on the characterization of the core–shell particles showing good chemical stability, as well as excellent luminescent properties.

$LaOF:Eu^{3+}$ (La : Eu = 10 : 1 mol) nanopowders were prepared following our previous report (see also Electronic Supplementary Information†).[12] $Na_2SnO_3{\cdot}3H_2O$ was dissolved in an aqueous NaOH solution (pH = 10.5). The $LaOF:Eu^{3+}$ powders were added to the Na_2SnO_3 solution and ultrasonicated for 10 min. The mixture was then heated at 60 °C for 1 h under reflux. After cooling to room temperature, the powders were centrifuged, washed with ethanol and dried. The powders obtained in this stage will be called "as-prepared" hereafter. Final heat treatments were typically performed at 1000 °C for 1 h in air to obtain the core–shell-structured nanoparticles.

Fig. 1(a) shows the X-ray diffraction (XRD) pattern of the as-prepared powder. Peaks due to LaOF with the rhombohedral fluorite-type structure are clearly observed, indicative of the high chemical stability of LaOF in the basic aqueous solution at 60 °C. At much higher temperatures, LaOF is known to decompose into La_2O_3 or $La(OH)_3$ due to pyrohydrolysis.[13] In Fig. 1(a), the as-prepared powder also shows diffraction peaks due to cassiterite (the rutile-type SnO_2); peaks at around $2\theta = 26.6$, 33.9 and 51.8° can be ascribed to the (100), (101) and (211) planes of the tetragonal SnO_2, respectively. It has been reported that gold nanoparticles could be coated with thin SnO_2 layers when maintained in the aqueous Na_2SnO_3 solution at 60 °C.[11] Nucleation of SnO_2 was promoted on the gold surface, resulting in Au–SnO_2 core–shell nanoparticles. Because we utilized a similar solution, the above XRD result may suggest that the LaOF nanoparticles were coated with SnO_2.

When the as-prepared powder was heated at 1000 °C, it was found to be converted into La_2O_3 and $La_2Sn_2O_7$, as indicated by the XRD pattern in Fig. 1(b). Formation of La_2O_3 results from the thermal decomposition of LaOF during the high-temperature heat treatment. Two possibilities should be considered about how $La_2Sn_2O_7$ is present in the heat-treated sample; one is that $La_2Sn_2O_7$ covers the core La_2O_3 particle, and the other is that La_2O_3 and $La_2Sn_2O_7$ exist separately as a mixture. The former case would be the result of successful SnO_2 coating on the LaOF particles in the as-prepared powder. We further analyzed the heat-treated powder maintained under an ambient atmosphere

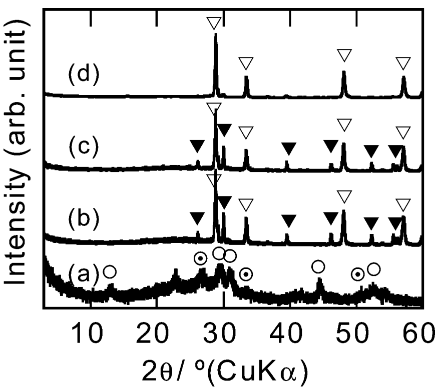

Fig. 1 XRD patterns of (a) the as-prepared powder, (b) the heat-treated powder, (c) the powder aged under an ambient atmosphere over 5 days and (d) the powder obtained through 24 h treatments for both SnO_2-coating and subsequent heating. LaOF, SnO_2, La_2O_3 and $La_2Sn_2O_7$ are labeled (○), (⊙), (▼) and (▽), respectively.

† Electronic Supplementary Information (ESI) available: experimental procedure and Fig. S1. See http://www.rsc.org/suppdata/cc/b4/b408495k/

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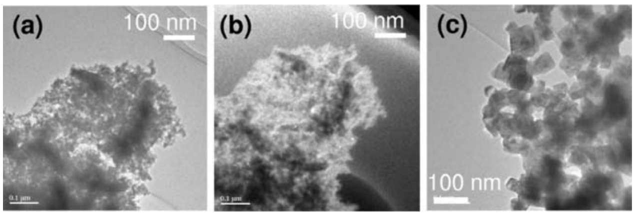

Fig. 2 (a) Bright and (b) dark field TEM images of the as-prepared powder. (c) TEM image of the heat-treated La_2O_3:Eu^{3+}–$La_2Sn_2O_7$ powder.

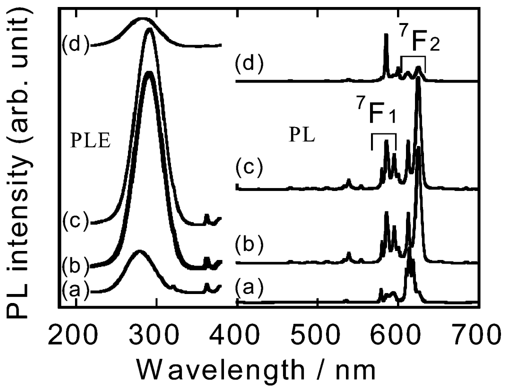

Fig. 3 PL and PLE spectra of (a) the as-prepared powder, (b) the heat-treated La_2O_3:Eu^{3+}–$La_2Sn_2O_7$ powder, (c) the La_2O_3:Eu^{3+}–$La_2Sn_2O_7$ powder aged under an ambient atmosphere over 5 days and (d) the $La_2Sn_2O_7$:Eu^{3+} powder.

containing H_2O and CO_2 at room temperature over 5 days. The XRD pattern of this sample (Fig. 1(c)) was found to be similar to that shown in Fig. 1(b). In our previous report, we have shown that La_2O_3 nanoparticles were converted completely into $La(OH)_3$ under the same conditions after typically 4 days.[12] The present results therefore suggest that the La_2O_3 particles were passivated by the surface $La_2Sn_2O_7$ layers, suppressing effectively the reaction with H_2O. Although the exact thickness of the $La_2Sn_2O_7$ layer could not be determined in the present work, it appeared that the thickness could be varied by changing the reaction time for the coating of SnO_2 onto LaOF in the Na_2SnO_3 solution, as well as the heating time for the formation of La_2O_3–$La_2Sn_2O_7$. Under extreme conditions, with 24 h treatments for both the solution reaction and the heat treatment, the powder was transformed into single-phase $La_2Sn_2O_7$, as indicated by Fig. 1(d), because of the thicker SnO_2 coating and the promoted solid-state reaction.

Transmission electron microscope (TEM) images shown in Fig. 2 compare the particle morphology of the as-prepared and the heat-treated powder. The as-prepared powder consists of large particles (approximately 50 nm in size) surrounded by small particles (approximately 14 nm in size) as shown in Fig. 2(a) with a bright field TEM image. The dark field image shown in Fig. 2(b) was taken by making a contrast with electrons diffracted only by SnO_2. Particles appearing white and black can then be characterized as SnO_2 and LaOF, respectively. These observations support the successful SnO_2 coating on LaOF. The particles were found to be well-defined with a spherical structure and uniform in size (approximately 60 nm) after heating at 1000 °C, as shown in Fig. 2(c). The particle growth was retarded probably due to the formation of the core–shell structure.

Fig. 3 shows the photoluminescence (PL) spectra of exactly the same powder samples as those that are shown in Fig. 1. The excitation wavelength used was 289 nm. The spectral feature of the as-prepared powder is typical of Eu^{3+} present in the rhombohedral LaOF lattice with C_{3v} or O_h site symmetries.[14] Emissions centered at approximately 611 and 622 nm are assigned to forced electric-dipole $^5D_0 \rightarrow {}^7F_2$ transitions. The PL spectrum of the heat-treated La_2O_3:Eu^{3+}–$La_2Sn_2O_7$ powder is very similar to that of La_2O_3:Eu^{3+} as reported in the literature.[4] Strong $^5D_0 \rightarrow {}^7F_2$ emissions appear at approximately 625 nm due to Eu^{3+} present in the hexagonal La_2O_3 lattice with C_{3v} symmetry. It can therefore be said that a major portion of the Eu^{3+} ions are preserved in La_2O_3 after the formation of the core–shell La_2O_3:Eu^{3+}–$La_2Sn_2O_7$ structure. Chemical stability of the core–shell-structured particles has also been supported by the PL measurement of the powder maintained under an ambient atmosphere containing H_2O and CO_2 over 5 days. That is, the PL spectrum of the aged powder is the same as that of the fresh powder. No change in the emission intensities was observed between the two powders, indicating that the La_2O_3:Eu^{3+} core was successfully passivated by the shell of $La_2Sn_2O_7$. We also observed the degradation of the PL properties in the bare (non-coated) La_2O_3:Eu^{3+} samples aged under the same conditions (see Fig. S1, ESI†).

As mentioned above, the powder could be transformed into single-phase $La_2Sn_2O_7$ under the specific conditions. PL of Eu^{3+} doped in $La_2Sn_2O_7$ was then examined. As shown in Fig. 3, emissions centered at approximately 585 nm were dominant due to magnetic-dipole $^5D_0 \rightarrow {}^7F_1$ transitions. This result is explained by the high symmetry of the La^{3+} site with eight-fold coordination in pyrochlore-type $La_2Sn_2O_7$. The electric-dipole transitions of Eu^{3+} are strictly forbidden in this type of crystal structure.

The PL excitation (PLE) spectra of the powders were monitored for the 625 nm emission and compared also in Fig. 3. For the as-prepared powder, a strong excitation band at around 278 nm was observed, resulting from an O^{2-}–Eu^{3+} charge transfer (CT) in LaOF:Eu^{3+}.[14] A similar O^{2-}–Eu^{3+} CT excitation was also promoted efficiently in the La_2O_3:Eu^{3+}–$La_2Sn_2O_7$ powders, indicating that these powders are suitable for applications such as UV-pumped phosphors. The CT band of $La_2Sn_2O_7$:Eu^{3+} exhibited a relatively weak intensity at least for the 625 nm emission.

In summary, our results suggest that we have achieved the fabrication of new chemically stable, core–shell-structured La_2O_3:Eu^{3+}–$La_2Sn_2O_7$ nanoparticles that exhibit red luminescence in response to UV light excitation.

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