

# Self-assembly and multicolor emission of core/shell structured $\text{CaWO}_4:\text{Na}^+/\text{Ln}^{3+}$ spheres†

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**A novel core/shell  $\text{CaWO}_4$  microsphere co-doped with  $\text{Na}^+$  and  $\text{Ln}^{3+}$  ( $\text{Ln} = \text{Dy}, \text{Tb}, \text{Sm}, \text{Eu}$ ) was successfully prepared by the self-assembly of 8.5 nm particles, and shows a unique multicolor emission in the visible region when excited by single-wavelength light.**

The self-assembly of nanocrystals of specific morphology has drawn great attention because of their interesting properties and many applications.<sup>1</sup> To fabricate the nanodevices of the future, nanocrystals have to be taken as the building blocks for the nanoarchitectures. There have been plenty of reports on the synthesis of nanocrystals<sup>2</sup> in which self-assembly appears to be more effective for assembling the nanocrystals into two or three dimensional superstructures, and therefore becomes an essential part of the nanotechnology.<sup>3</sup> It is well documented<sup>4–6</sup> that further understanding of self-assembly phenomena is fundamentally important, which may help to translate the chemical language of molecular self-assembly into the organization of various nanocrystals for certain functions.

Luminescent materials activated by  $\text{Ln}^{3+}$  are important parts of many applications such as fluorescent tubes, field emission displays, laser materials, efficient light-conversion molecular devices, luminescent labels, and even fiber amplifiers.<sup>7</sup> Such applications are highly dependent on the fundamental factors that govern the luminescence. For instance, morphology and size are primarily responsible for the luminescent properties and moreover the device performance of  $\text{Ln}^{3+}$  doped phosphors.<sup>8</sup> Phosphors with spherical morphology of a fine size (1–4  $\mu\text{m}$ ) are advantageous in achieving high packing densities and low light scattering, and therefore can significantly improve screen brightness.<sup>9</sup> Besides the merits of the spherical morphology, phosphors should be able to be excited to show different emission colors for multiplexing applications using a single wavelength light.<sup>10</sup> Such a goal appears very difficult, but is highly possible by the effective energy transfer process *via* exchange and dipole–dipole interactions for both energy migration and energy transfer from the host matrix to the central  $\text{Ln}^{3+}$  ions.<sup>11</sup> Therefore, self-assembly of multicolor spherical phosphors excited by a single wavelength light is very important, and may help to unlock a realm of new

possibilities in practical applications through a simple one-pot technique.

We initiated the self-assembly of novel core/shell structured  $\text{CaWO}_4$  spheres *via* a simple hydrothermal route in the presence of citric acid and polyvinylpyrrolidone (PVP). It was found that citric acid modulated the nucleation and growth of  $\text{CaWO}_4$  nanocrystals, which enables the co-incorporation of  $\text{Na}^+$  and  $\text{Ln}^{3+}$  into the  $\text{CaWO}_4$  matrix. PVP controlled the aggregation of  $\text{CaWO}_4$  nanocrystals, which assembles the nanoparticles into a core/shell spherical structure. Such a core/shell sphere shows a surprising multicolor emission ranging from dark cyan, green and pink to red emissions under a single excitation of 265 nm.

All chemicals were of analytical grade and were used without further purification. A typical synthetic procedure toward the core/shell structured  $\text{CaWO}_4:\text{Na}^+/\text{Ln}^{3+}$  ( $\text{Ln} = \text{Dy}, \text{Tb}, \text{Sm}, \text{Eu}$ ) spheres can be described briefly as follows. Given amounts of rare earth oxides of  $\text{Ln}_2\text{O}_3$  were first dissolved into diluted nitric acid to form a  $\text{Ln}(\text{NO}_3)_3$  solution. 0.0045 mol  $\text{CaCl}_2$ , 0.0005 mol  $\text{Ln}(\text{NO}_3)_3$ , and 0.005 mol citric acid were added to 15 ml distilled water, into which 15 ml of 0.005 mol  $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$  was carefully added. Then, 10 ml of 0.6 g PVP was dropped into the above solution. A well controlled NaOH solution was used to adjust the pH value to 8 to obtain a clear solution which was then carefully adjusted to a volume of 50 ml. This solution was transferred to Teflon-lined autoclaves, which were heated at 180 °C for 12 h and then cooled to room temperature.

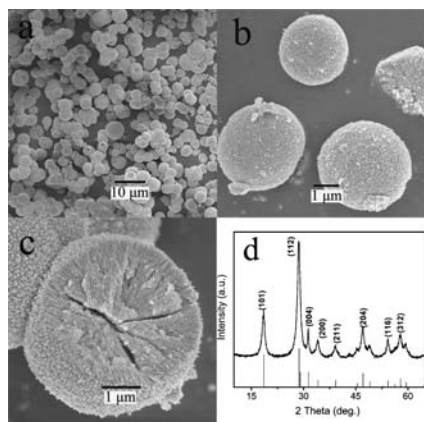
The morphologies examined by scanning electron microscopy (SEM) indicated that all samples  $\text{CaWO}_4:\text{Na}^+/\text{Ln}^{3+}$  ( $\text{Ln} = \text{Eu}$ ) were spherical with an average diameter of about 2–4  $\mu\text{m}$  (Fig. 1a, b). An SEM image of the cross section of a single sphere of  $\text{CaWO}_4:\text{Na}^+/\text{Eu}^{3+}$  clearly demonstrated that these spheres had a core/shell structure (Fig. 1c). The shell, with a thickness of about 0.1  $\mu\text{m}$ , is composed of tiny  $\text{CaWO}_4$  nanocrystals with an acicular shape, while the core is an aggregation of small particles with cracks. To confirm the chemical stoichiometry of the as-synthesized core/shell spheres, we performed chemical analysis using inductively coupled plasma-atomic emission spectrometry (ICP-AES). Besides the rare earth elements, sodium was also detected for all samples.† Therefore,  $\text{Ln}^{3+}$  should be doped in the  $\text{Ca}^{2+}$  sites due to the similar ionic radius.  $\text{Na}^+$  substitution in the  $\text{CaWO}_4$  lattice is also most likely to occur due to the charge compensation effect *via*  $2\text{Ca}^{2+} = \text{Ln}^{3+} + \text{Na}^+$ .

The impact of the ionic substitution on the structure of the core/shell spheres was examined by X-ray diffraction (XRD). As indicated in Fig. 1d, all XRD data of  $\text{CaWO}_4:\text{Na}^+/\text{Ln}^{3+}$

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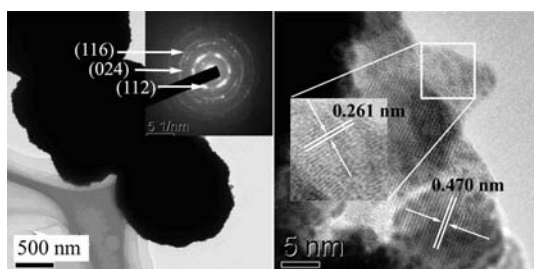
† Electronic supplementary information (ESI) available: Details of chemical analysis, XRD, TEM, SEM images and luminescence properties of the spheres doped with other rare earth ions. See DOI: 10.1039/b810648g



**Fig. 1** (a) Low magnification and (b) high magnification SEM images of the as-prepared sample  $\text{CaWO}_4:\text{Na}^+/\text{Eu}^{3+}$ ; (c) SEM image of the cross section of a single  $\text{CaWO}_4:\text{Na}^+/\text{Eu}^{3+}$  sphere; and (d) XRD pattern of the as-prepared  $\text{CaWO}_4:\text{Na}^+/\text{Eu}^{3+}$  sample. Vertical bars represent the standard diffraction data of  $\text{CaWO}_4$  (JCPDS, No. 41-1413).

spheres ( $\text{Ln} = \text{Eu}$ ) can be readily indexed to a pure scheelite phase of  $\text{CaWO}_4$ , while no traces of impurity peaks of other phases were observed. For  $\text{Ln} = \text{Dy}$ ,  $\text{Tb}$ , and  $\text{Sm}$ , similar XRD patterns were also obtained.<sup>†</sup> It is noted that all diffraction peaks in Fig. 1d are broadened, which indicates the fine nature of the constituent nanoparticles. Using the Scherrer formula for the (101) diffraction peak of  $\text{CaWO}_4:\text{Na}^+/\text{Ln}^{3+}$  ( $\text{Ln} = \text{Eu}$ ), the mean crystallite size was calculated to be 8.5 nm, which is two orders of magnitude smaller than the sphere diameter observed by SEM (Fig. 1a–c). It is thus demonstrated that  $\text{CaWO}_4:\text{Na}^+/\text{Ln}^{3+}$  spheres are assembled from tiny nanocrystals.

To further characterize the structural and self-assembly properties, transmission electron microscopy (TEM) and high resolution TEM (HRTEM) were performed. Fig. 2, left, shows a typical TEM image of  $\text{CaWO}_4:\text{Na}^+/\text{Ln}^{3+}$  spheres ( $\text{Ln} = \text{Eu}$ ) and its selected-area electron diffraction (SAED) pattern. The SAED pattern shows distinct rings: the rings from the innermost to the outside correspond to the (112), (024), and (116) planes of  $\text{CaWO}_4$ . This observation reveals the polycrystalline nature of the as-prepared  $\text{CaWO}_4:\text{Na}^+/\text{Eu}^{3+}$  spheres. The HRTEM image gave further evidence for the polycrystalline behavior of  $\text{CaWO}_4:\text{Na}^+/\text{Eu}^{3+}$  spheres. As can be seen in Fig. 2, right, the spacing between adjacent lattice fringes of  $\text{CaWO}_4:\text{Na}^+/\text{Eu}^{3+}$  nanocrystals was 0.261 and 0.470 nm, which are very close to those

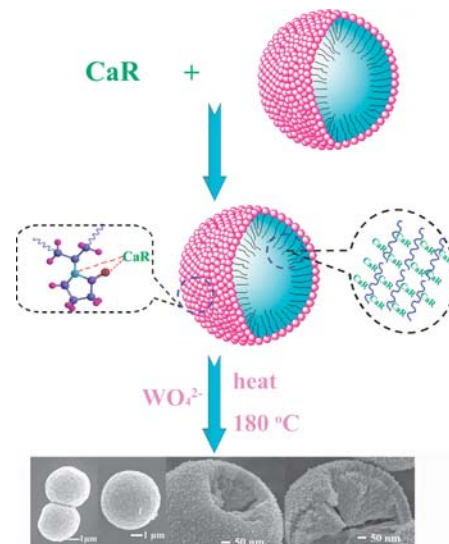


**Fig. 2** TEM and HRTEM images of the as-prepared  $\text{CaWO}_4:\text{Na}^+/\text{Eu}^{3+}$  spheres. Inset indicates the SAED pattern.

of 0.258 nm for the (020) plane and 0.468 nm for the (011) plane of  $\text{CaWO}_4$ . The crystallite size of  $\text{CaWO}_4:\text{Na}^+/\text{Eu}^{3+}$  nanocrystals was estimated to be 9 nm, which is compatible with that calculated using the Scherrer formula.

It is well documented that citric acid and PVP can play critical roles in reducing the activity of nanocrystals (building blocks) to promote or tune the ordered self-assembly of core/shell structured spheres.<sup>12</sup> To shed light on the growth process of these novel core/shell  $\text{CaWO}_4$  spheres, we explored the preparation conditions by modulating the concentration of citric acid and PVP.

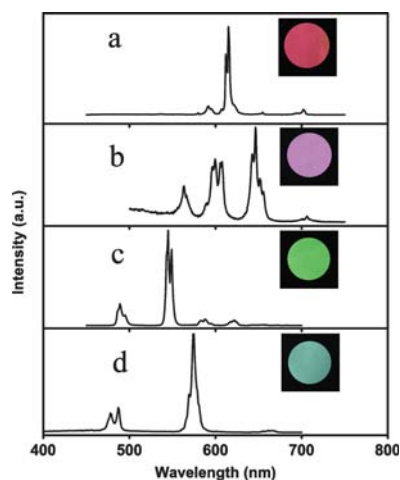
When the reaction was performed in the citric acid free system, large size  $\text{CaWO}_4$  was obtained<sup>12b</sup> as demonstrated by a weak red emission characteristic of  $\text{Eu}^{3+}$  (see ESI<sup>†</sup>) in comparison to the  $\text{CaWO}_4$  nanocrystals prepared in the presence of citric acid. It is evident that citric acid can regulate the kinetic growth of  $\text{CaWO}_4$  nanocrystals and enable the incorporation of rare earth ions into the  $\text{CaWO}_4$  matrix. Nevertheless, citric acid itself cannot achieve the controlled growth of  $\text{CaWO}_4$  nanocrystals toward regular morphology.<sup>†</sup> PVP, as a directing reagent, was then introduced in cooperation with citric acid to motivate the self-assembly of core/shell structured  $\text{CaWO}_4$  spheres. The possible formation process of the core/shell structured  $\text{CaWO}_4$  spheres is proposed in Scheme 1. Firstly, citric acid adds into the reaction system and may form two types of complexes with calcium ions (named as CaR) to reduce the relative activity of reactive species ( $\text{Ca}^{2+}$ ) via van der Waals forces.<sup>12b</sup> Once PVP is introduced in aqueous solution, spherical micelles would be formed with carbonyl groups on the outside.<sup>13</sup> Meanwhile, more complicated polymer-metal complexes form between PVP molecules and CaR, which are similar to that of PVP with  $\text{Ni}^{2+}$  and  $\text{Ag}^+$  ions.<sup>13a,14</sup> The coordinated atoms are oxygen on the carbonyl group and the heteroatom (N atom) adjoining on the pyrrolidone ring<sup>13</sup> as is seen in Scheme 1. It should be noted that the CaR complexes are in a largely stoichiometric excess in comparison with PVP, which results in incorporation of a large amount of CaR complexes into the spherical micelles attached near the carbon chains. As the temperature increases,  $\text{CaWO}_4$  tiny crystals could be formed by



**Scheme 1** Schematic illustration of the possible growth mechanism for the core/shell structured  $\text{CaWO}_4$  spheres.

two processes: the reaction between the complicated polymer-metal with  $\text{WO}_4^{2-}$  ions at the surfaces of the micelles, and the reaction of CaR and  $\text{WO}_4^{2-}$ . The  $\text{CaWO}_4$  tiny crystals at the surfaces of the micelles are covered by the citric acid and polar carbonyl groups<sup>12,15</sup> which would inhibit the growth of certain facets, resulting in an oriented growth of  $\text{CaWO}_4$  nanocrystals with acicular shape as confirmed by SEM and TEM images. However, the growth of tiny crystals inside the micelles would be dominated by the effect of citric acid because of their very weak absorbing effect and polarity of carbon chains. Finally, the core/shell structured  $\text{CaWO}_4$  is obtained due to the different growth process at the surface and inside the micelles. In order to test the growth mechanism, we modulated the PVP content while fixing other experimental parameters. It was seen that all of the obtained products exhibited core/shell spherical morphology except for the dimension and dispersity.<sup>†</sup>

The luminescent properties of the self-assembly core/shell structured  $\text{CaWO}_4:\text{Na}^+/\text{Ln}^{3+}$  spheres were explored by monitoring their multicolor emission in the visible region on single-wavelength light excitation. When the samples were excited at 265 nm, high luminescence was observed (see ESI<sup>†</sup>) due to efficient energy transfer from the tungstate groups to the activators.<sup>16</sup> Fig. 3 shows the emission spectra of the as-prepared  $\text{CaWO}_4:\text{Na}^+/\text{Ln}^{3+}$  spheres. The emission spectrum of  $\text{CaWO}_4:\text{Na}^+/\text{Eu}^{3+}$  consists of lines ranging from 580 to 720 nm that come from the transitions of  $^5\text{D}_0$  to  $^7\text{F}_J$  ( $J = 1, 2, 3, 4$ ) levels of the  $\text{Eu}^{3+}$  activators. The most intense emission is the  $^5\text{D}_0$ - $^7\text{F}_2$  transition, which is located in the range 600–620 nm and gives a red color. The intensity of the red emission for the core/shell structured  $\text{CaWO}_4:\text{Na}^+/\text{Eu}^{3+}$  spheres is largely enhanced in comparison with the sample prepared in the PVP system.<sup>†</sup> Emissions characteristic of the other luminescent lanthanide ions can also be observed after excitation in the charge-transfer band of the tungstate groups. For  $\text{Ln} = \text{Sm}$  spheres (Fig. 3b), a pink light was observed, which consists of the typical emissions at 565, 602, 646 nm that originate from the transitions from the  $^4\text{G}_{5/2}$  level to the  $^6\text{H}_{5/2}$ ,  $^6\text{H}_{7/2}$ , and  $^6\text{H}_{11/2}$  levels, respectively. For  $\text{Ln} = \text{Tb}$ , as indicated in Fig. 3c, the emissions at 489, 542, 587, and



**Fig. 3** Emission spectra of  $\text{CaWO}_4:\text{Na}^+/\text{Ln}^{3+}$  under  $\lambda_{\text{ex}} = 265$  nm for  $\text{Ln} =$  (a) Eu; (b) Sm; (c) Tb; and (d) Dy. Insets are the direct view photos of the corresponding samples when excited at 254 nm.

620 nm are associated with the typical transitions from the  $^5\text{D}_4$  level to the  $^7\text{F}_6$ ,  $^7\text{F}_5$ ,  $^7\text{F}_4$ , and  $^7\text{F}_3$  levels. Fig. 3d exhibits the emission spectrum of  $\text{CaWO}_4:\text{Na}^+/\text{Ln}^{3+}$  spheres ( $\text{Ln} = \text{Dy}$ ) which originates from the transitions  $^4\text{F}_{9/2}$ - $^6\text{H}_{15/2}$  and  $^4\text{F}_{9/2}$ - $^6\text{H}_{13/2}$  at 478, 487 and 574 nm. These observations strongly demonstrate that the novel core/shell  $\text{CaWO}_4$  spheres co-doped with  $\text{Na}^+$  and  $\text{Ln}^{3+}$  ( $\text{Ln} = \text{Dy}, \text{Tb}, \text{Sm}, \text{Eu}$ ) could show merits of multicolor emissions in the visible region when excited by a single-wavelength light.

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