

# Self-Assembly and Photoluminescence Characterization of CaMoO<sub>4</sub>:Eu<sup>3+</sup>,Na<sup>+</sup> Superstructure via a Facile Surfactant-Free Hydrothermal Method

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The Eu<sup>3+</sup>, Na<sup>+</sup>-codoped CaMoO<sub>4</sub> microphosphors were successfully synthesized at low temperature via a facile hydrothermal method in a surfactant-free environment. Scanning electron microscopy, field-emission scanning electron microscope, and transmission electron microscopy images of the CaMoO<sub>4</sub> products prepared at 150°C for 6 h revealed three dimensional flake-ball and flake-disk superstructures, composed of densely packed nanoflakes. The formation mechanism of CaMoO<sub>4</sub> microstructures was discussed in detail based on the hydrothermal temperature. Meanwhile, other influencing factors on the morphology were also reported. Room-temperature photoluminescence properties of microsized CaMoO<sub>4</sub>:Eu<sup>3+</sup>, Na<sup>+</sup> phosphors were studied. Its excitation wavelengths ranging from 350 to 530 nm in the ultraviolet and visible regions significantly extend the excitation region of phosphor materials. In addition, the effect of reactional temperature, pH value, and Ca source on the photoluminescence properties was also studied systematically.

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In recent years, large-scale self-assembled micro- and nanoparticles in phosphors have attracted great attention due to their ease of processing into devices with high resolution, high screen coverage, intense emission, and long service life.<sup>1</sup> Herein, it is critical to have fine control over the structures and dimensions of micro- and nanoparticles which largely determine the properties and applications. At present, the conventional solid-state reaction technique, including cumbersome grinding and firing steps, normally results in irregular morphology and large grain size because of the high reaction temperature.<sup>2-4</sup> Therefore, various fabrication methods have been proposed to reduce the reaction temperature and obtain high-quality micro- and nanostructures for decades. Among them, the frequent one is the chemical solution route, which synthesizes the size- and shape-controlled micro- and nanostructures by using appropriate organic additives, such as surfactants, templates, and polymers as capping agents, stabilizing agents, modifying agents, directing agents, and soft templates.<sup>5-11</sup> However, these organic additives are usually difficult to effective removal and the most important is that the utilization of the organic additives increases the production cost, which restrict the popularization of the techniques in the further research and practical applications. So a facile surfactant-free method is highly preferred and desired to synthesize one dimensional (1D), two dimensional (2D), and three dimensional (3D) micro- and nanoparticles.

As an important class of lanthanide inorganic compounds, rareearth ions doped molybdates have gained much attention due to their attractive luminescence and structural properties, supporting various promising applications as phosphor materials in fields such as white light-emitting diodes (WLEDs), optical fibers, biolabel, lasers, and so on.<sup>12,13</sup> The molybdate family have promising trivalent cation conducting properties and most of the optical properties result from electron transitions of the 4f shell, which are greatly affected by the composition and structures of rare-earth compounds.<sup>14</sup> Recently, Eu<sup>3+</sup>-doped CaMoO<sub>4</sub> has been investigated extensively as a redemitting phosphor, originating from  ${}^5D_0 \rightarrow {}^7F_2$  transition of Eu<sup>3+</sup> upon near-ultraviolet (UV) excitation into the  ${}^5L_6$  state of Eu<sup>3+</sup> at 395 nm. Compared with the well-known red phosphors Y<sub>2</sub>O<sub>2</sub>S:Eu<sup>3+</sup> and CaS:Eu<sup>2+</sup>, molybdates also exhibit more stable physical and chemical properties.<sup>15</sup> Moreover, a few efforts have been devoted to improve luminescence efficiency of molybdate phosphors. For instance, Na<sup>+</sup> has been introduced into different phosphor host lattices to act as a coactivator and achieve charge compensation function.

The close ionic radius among  $Eu^{3+}$  (0.95 Å),  $Na^+$  (0.97 Å), and  $Ca^{3+}$  (0.99 Å) makes possible the easy substitution of  $Na^+$  and  $Eu^{3+}$  for  $Ca^{3+}$ . Meanwhile, adding  $Na^+$  into the CaMoO<sub>4</sub>:Eu<sup>3+</sup> scheelite structure also affects the structure and crystallization and, thereby, causes wide-ranging effects on the photoluminescence (PL) properties of the CaMoO<sub>4</sub>.<sup>16,17</sup>

In this paper, we successfully synthesized 3D europium and sodium codoped calcium molybdate superstructures via a facile hydrothermal method with no surfactant, catalysts, and templates at low temperature. The structure and luminescent properties of selfassembly CaMoO<sub>4</sub>:Eu<sup>3+</sup>,Na<sup>+</sup> microstructures with specific morphology and novel physical properties were systematically reported. It has been proved that the formation of CaMoO<sub>4</sub> flake-ball and flakedisk microstructures is affected by reaction temperature, pH value, and Ca source. In addition, the photoluminescence spectra of asprepared CaMoO<sub>4</sub>:Eu<sup>3+</sup>,Na<sup>+</sup> microstructures demonstrate bright red fluorescence, and its excitation wavelength ranging from 350 to 530 nm fits well with commercial near-UV GaN chip (380–410 nm) and blue light-emitting diode chips (450–480 nm) based on WLEDs. Moreover, comparison of the emission intensity, the optimal pH value, and Ca source are made.

# **Experimental Section**

*Chemicals.*— Sodium molybdate (Na<sub>2</sub>MoO<sub>4</sub>), ammonium molybdate ((NH<sub>4</sub>)<sub>6</sub>Mo<sub>7</sub>O<sub>24</sub>·4H<sub>2</sub>O), europium oxide (Eu<sub>2</sub>O<sub>3</sub>), nitrate acid (HNO<sub>3</sub>), sodium hydroxide (Na(OH)), calcium nitrate (Ca(NO<sub>3</sub>)<sub>2</sub>), and calcium chloride (CaCl<sub>2</sub>) were purchased from commercial sources (analytical-grade). 0.2 M Na<sub>2</sub>MoO<sub>4</sub> solution, 0.12 M Ca(NO<sub>3</sub>)<sub>2</sub> solution, and 0.12 M CaCl<sub>2</sub> solution were prepared by dissolving the corresponding Na<sub>2</sub>MoO<sub>4</sub>·4H<sub>2</sub>O, Ca(NO<sub>3</sub>)<sub>2</sub>, and CaCl<sub>2</sub> in distilled water at room temperature, respectively. 0.04 M Eu(NO<sub>3</sub>)<sub>3</sub> solution was prepared by dissolving the corresponding Eu<sub>2</sub>O<sub>3</sub> in nitrate acid and excess HNO<sub>3</sub> was removed by evaporation and dilution in distilled water. 1 M HNO<sub>3</sub> and 1 M Na(OH) solutions were prepared by dissolving the corresponding nitrate acid and Sodium hydroxide in distilled water.

Synthesis procedures.— The CaMoO<sub>4</sub> micro- and nanostructures were synthesized via a simple hydrothermal method. The required device is a 50 mL Teflon-lined stainless steel autoclave. The detailed description of reaction procedure is as follows: The Eu(NO<sub>3</sub>)<sub>3</sub> (0.04 M) solution was dropped into 0.12 M Ca(NO<sub>3</sub>)<sub>2</sub> solution to form the precursor Ca(NO<sub>3</sub>)<sub>2</sub>:Eu<sup>3+</sup> solution under vigorous stirring. Meanwhile, the given amounts of diluted nitric acid (1 M HNO<sub>3</sub>)

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Figure 1. The XRD pattern of as-synthesized sample at pH 1.5 and 150  $^\circ\mathrm{C}$  for 6 h.

and sodium hydroxide solution (1 M Na(OH)) were added to regulate the pH value. Then, the Na<sub>2</sub>MoO<sub>4</sub> solution was slowly dropped into Ca(NO<sub>3</sub>)<sub>2</sub>:Eu<sup>3+</sup> solution under vigorous stirring. The vigorous stirring was continued for 45 min. Finally, the above solution was transferred into a 50 mL Teflon-lined stainless steel autoclave, which was subsequently sealed and maintained at 60–200°C for 6 h. Later, the autoclave was naturally cooled to room temperature. The products were collected by centrifugation and washing several times with distilled water and absolute ethanol. Then, these samples were obtained after being dried at 80°C for 6 h. The Eu<sup>3+</sup>-doped CaMoO<sub>4</sub> synthesized by replacing Na<sub>2</sub>MoO<sub>4</sub> with (NH<sub>4</sub>)<sub>6</sub>Mo<sub>7</sub>O<sub>24</sub>·4H<sub>2</sub>O and the synthesis procedure where CaCl<sub>2</sub> was used as Ca source was exactly the CaNO<sub>3</sub> at pH 1.5 and 150°C for 6 h.

Characterization.— The phase and purity of the samples were characterized by X-ray diffraction (XRD) [Rigaku DMAX 2000 powder diffractometer equipped with Cu target radiation resource ( $\lambda = 0.15405$  Å)]. The morphology and structure of the products were characterized by scanning electron microscopy (SEM, JEOL JEM-6460), field-emission scanning electron microscopy (FESEM, Hitachi S-4800) with an X-ray energy dispersive spectrometer (EDS), and transmission electron microscopy (TEM, JEOL JEM-2100, using an accelerating voltage of 200 kV). The luminescent properties were recorded on a Varian Cary-Eclipse 500 fluorescence spectrophotometer equipped with a 60 W xenon lamp as the excitation source.

### **Results and Discussion**

Structural characterization of calcium molybdate microcrystal.— The phase and purity of as-synthesized samples were determined by the XRD patterns. Figure 1 shows the XRD pattern of the product obtained by hydrothermal method at pH 1.5 and 150°C for 6 h. All diffraction peaks can be perfectly indexed to the standard JCPDS no. 29-0351 of CaMoO<sub>4</sub> tetragonal phase, belonging to space group I41/a, and with lattice parameters of a = 5.226 Å and c = 11.430 Å. The strong and sharp diffraction peaks prove good crystallinity in the as-synthesized product. No additional peaks can be found in this diffractogram, indicating that the hydrothermal products with high phase purity can be easily obtained under the current synthetic conditions.

The morphology and structure of the products were investigated by SEM and FESEM images. Figures 2a and 2b show the SEM images of CaMoO<sub>4</sub> samples prepared by hydrothermal method at pH 1.5 and 150°C for 6 h. We can clearly observe that there are two types of flake-ball and flake-disk superstructures in the CaMoO<sub>4</sub> product and the particles are monodisperse with an average diameter

**Figure 2.** (a) and (b) SEM images and (c) and d) FE-SEM images of asprepared typical CaMoO<sub>4</sub> microstructures at different magnifications.

of 5  $\mu$ m. As shown in Fig. 2c and 2d, from FESEM images of individual flake-ball and flake-disk, it can be concluded that such superstructures are composed of densely packed nanoflakes with an average 400 nm width and about 40 nm thickness (inset of Fig. 2c and 2d).

The microstructure of as-prepared CaMoO<sub>4</sub>:Eu<sup>3+</sup>, Na<sup>+</sup> samples was further investigated with TEM and selected-area electron diffraction (SAED). As shown in Fig. 3a-3d, TEM micrograph of a single flake-disk with a diameter of about 5 µm. Observing the edge of the flake-disk, the nanoflakes are very thin and, therefore, relatively transparent to the electron beam (inset of Fig. 3a). The highresolution TEM (HRTEM) image and SAED pattern, taken from the edge of a randomly chosen nanoflake (Fig. 4) of CaMoO<sub>4</sub> microstructure after prolonged ultrasonic treatment, are shown in Fig. 3b and 3c, respectively. HRTEM image shows well-defined lattice fringes with an interplanar spacing of 0.2532 nm for the (200) face of tetragonal CaMoO<sub>4</sub> crystals, indicating the single-crystal nature of nanoflake. The corresponding SAED pattern (Fig. 3c) with regular dotted lines can be indexed to the tetragonal CaMoO<sub>4</sub> structure and confirms the nanocrystals grow preferentially along the (100) face. Here, this can be explained from the viewpoint of the intrinsic structure feature of the CaMoO<sub>4</sub>. If we view the (100) face



Figure 3. (a) TEM image of a single flake-disk microstructure. (b) and (c) HRTEM image and SAED pattern of single nanoflake. (d) EDS spectrum of the CaMoO<sub>4</sub>:Eu<sup>3+</sup>,Na<sup>+</sup> superstructure.



Figure 4. TEM image of a single nanoflake of CaMoO4 superstructure after prolonged ultrasonic treatment.

of CaMoO<sub>4</sub> structural along the *a*-axis, it is known that all the negative  $[MoO_4^{2-7}]$  chains lied on the (100) face are exposed outwardly, while all the positive Ca<sup>2+</sup> chains are shielded. In particular, the (100) face is perpendicular to the *a*-axis with the highest chemical potential among all the facets, such as (001) and (010). This structural feature makes the (100) face very active to the surrounding growth conditions, so the nanocrystals grow preferentially along the (100) plane.<sup>20</sup>

The chemical compositions of flake-ball and flake-disk microstructures were determined by EDS. The EDS analysis (Fig. 3d) shows strong peaks from Ca, Mo, and O elements and weak peaks from Na and Eu elements. No impurities were observed from the spectra, revealing the high purity of these microstructures. Quantitative analysis shows that the atom ratio of Ca:Mo:O:Na:Eu is about 0.8:1:4:0.1:0.1 which agrees with the formula  $Ca_{0.8}MoO_4:0.1Eu^{3+},0.1Na^+$  in which the concentration of Na<sup>+</sup> is equal to that of Eu<sup>3+</sup> to achieve charge compensation.

Growth mechanism of the superstructure.— The formation mechanism of the superstructures was discussed on the basis of temperature-dependent experiments. As shown in Fig. 5, these samples prepared at different temperatures ( $60-200^{\circ}C$ ) for 6 h (the pH value maintained 1.5) display the interesting morphologies of nanoflakes, self-assembly flake-ball and flake-disk, and slippery microparticles, respectively. When the reaction was carried out at  $60^{\circ}C$ , the product is composed of 2D nanoflakes with an average 9  $\mu$ m width and about 20 nm thickness (Fig. 5a). At 80°C, it consists of some short flakelike aggregation and parallel and intercrossed morphologies coexist in the sample (Fig. 5b). When the hydrothermal temperature was 100°C, the nanoflakes began directed



Figure 5. SEM images and XRD patterns of  $CaMoO_4$ : Eu<sup>3+</sup>, Na<sup>+</sup> phosphors synthesized at (a) 60°C, (b) 60°C, (c) 100°C, (d) 150°C, and (e) 200°C for 6 h.

aggregation and self-assemble layer by layer into compacted flakeball and flake-disk morphologies (Fig. 5c). While the reaction temperature was held at 150°C, the plumpy and round microstructures indicate a large development of the flake-ball and flake-disk morphologies, with an average diameter of 5  $\mu$ m (Fig. 5d). When the hydrothermal temperature was increased to 200°C, the nanoflakes of the CaMoO<sub>4</sub> superstructures seem to melt into one phase and the products become 3D slippery microparticles (Fig. 5e).

Figure 5f is the corresponding XRD patterns of  $CaMoO_4$ :Eu<sup>3+</sup>,Na<sup>+</sup> crystals obtained at different reaction temperatures for 6 h; all diffraction peaks of the products can be indexed to pure CaMoO<sub>4</sub> phase, according to JCPDS no. 29-0351. With the increase in hydrothermal temperatures, the intensity of the diffraction peaks is gradually enhanced, showing the improvement in crystallinity of as-prepared phosphors.

In general, the crystal growth is controlled by the intrinsic and extrinsic factors, such as the degree of supersaturation, solution parameters, diffusion of the reaction, surface energy, crystal structure, etc.<sup>8</sup> We believe crystal nucleation is very fast and subsequent crystal growth might be better described by Ostwald-ripening process



Scheme 1. Formation mechanism of CaMoO<sub>4</sub> superstructures.



**Figure 6.** SEM images and XRD patterns of the samples synthesized at different pH values (hydrothermally treated at 150°C for 6 h, no surfactant): (a) pH 1.5, (b) pH 4.5, (c) pH 6.0, (d) pH 7.5, and (e) pH 9.0.

and aggregation mechanism. Ostwald-ripening process expounds the crystal growth route by growth of larger particles at the cost of smaller particles according to the well-known Gibbs–Thomson equation.<sup>20</sup> The aggregation mechanism by oriented attachment or random aggregation involves self-assembly crystal growth process, which is an efficient and often preferred manner to build micro- and nanoparticles into ordered multidimensional macroscopic structure.

In the formation of the as-prepared CaMoO<sub>4</sub>:Eu<sup>3+</sup>,Na<sup>+</sup> superstructures, we believe the self-assembly process plays a key role in this process. On the basis of the above analysis, a possible arranging mechanism of the influence of the reaction temperature on the morphology in the hydrothermal process is schematically shown in Scheme 1. In the heating process, CaMoO<sub>4</sub>:Eu<sup>3+</sup>,Na<sup>+</sup> nuclei were generated via the reaction between Ca<sup>2+</sup>/Eu<sup>3+</sup>/Na<sup>+</sup> and MoO<sub>4</sub><sup>2-</sup> when the CaMoO<sub>4</sub>:Eu<sup>3+</sup>,Na<sup>+</sup> solution achieves the given degree of super-

saturation at different temperatures. The freshly formed nuclei have a strong tendency to grow into larger particles to reduce the surface energy. Then, the CaMoO<sub>4</sub> nuclei gradually grow into flakelike nanoparticles (Scheme 1b) through selective adsorption and desorption on various faces at different rates. This phenomenon may be explained by the Ostwald ripening process, due to the difference of surface energy of various particles and crystal faces. Here, reduction in surface energy is the important driving force for crystal growth and morphology evolution.<sup>19</sup> Subsequently, the nanoflakes tend to aggregate face to face to reduce the surface energy of the CaMoO<sub>4</sub> system. It is worth pointing out that the round morphology is beneficial to reduce the surface energy in the context of thermodynamics.<sup>21,22</sup> So, layer-by-layer self-assembly process, by the directed aggregation along the specific crystal face, follows a round growth style that lead to the development of flake-ball and flake-disk microstructures, which is confirmed by the evolvement of flake-ball and flake-disk CaMoO4 microcrystals (Scheme 1 C  $\rightarrow$  D  $\rightarrow$  E).

Influencing factors on the morphology and structure.— Transformation of CaMoO<sub>4</sub>:Eu<sup>3+</sup>, Na<sup>+</sup> morphology by pH-controlled surfactant-free route.- The effect of pH values on the structure and morphology of CaMoO4:Eu3+,Na+ were prepared without any surfactant being studied. The CaNO<sub>3</sub>:Eu<sup>3+</sup> solution was adjusted to the desired pH values by adding HNO3 and NaOH solution, and then was hydrothermally treated at 150°C for 6 h. Figures 6a-6e show the morphological evolution of CaMoO<sub>4</sub>:Eu<sup>3+</sup>,Na<sup>+</sup> samples synthesized at different pH values of the precursor solution. When the pH value is 1.5, 3D flake-ball and flake-disk superstructures of CaMoO<sub>4</sub>:Eu<sup>3+</sup>,Na<sup>+</sup> sample are formed and the nanoflakes serve as the building units of the  $CaMoO_4:Eu^{3+}, Na^+$  superstructures, as shown in Fig. 6a. When the pH value is adjusted to 4.5, the flakeball and flake-disk microstructures start the aggregated process (Fig. 6b). Subsequently, when the pH value of the precursor solution reaches 6.0, the large masses are obtained (Fig. 6c). Moreover, with increasing pH values, the flakelike building units disappear and the nanoflake self-assembly superstructures gradually disintegrate, which is clearly shown in Fig. 6d and 6e.

It is obvious in our case that the pH value of the precursor solution greatly affects the structure and dispersivity of the final product CaMoO<sub>4</sub>:Eu<sup>3+</sup>,Na<sup>+</sup>. When the reaction occurs at low pH values (1–4.5) the concentration of H<sup>+</sup> ions is much higher than that of OH<sup>-</sup> ions, which restrains the hydrolysis of the Ca<sup>2+</sup>. Thus, the nucleation rate of CaMoO<sub>4</sub>:Eu<sup>3+</sup>,Na<sup>+</sup> is much faster than the rate of crystal growth due to the existence of a large quantity of Ca<sup>2+</sup>. Large quantities of CaMoO<sub>4</sub>:Eu<sup>3+</sup>,Na<sup>+</sup> nuclei tend to aggregate together to form larger and more thermodynamically stable particles. Subsequently, Ostwald-ripening growth and self-assembly take place, which leads to the formation of CaMoO<sub>4</sub>:Eu<sup>3+</sup>,Na<sup>+</sup> superstructures constructed from nanoflake substructures (Fig. 6a and 6b). With the



Figure 7. SEM image (left) and XRD pattern (right) of the prepared sample using CaCl<sub>2</sub> as Ca source.



**Figure 8.** The PLE (monitoring under 615 nm) and PL (under 465 nm excitation) spectra of  $Eu^{3+}$ -doped and  $Eu^{3+}$ , Na<sup>+</sup>-codoped CaMoO<sub>4</sub> samples, prepared at pH 1.5 and 150°C for 6 h.

increasing pH values, the concentration of  $Ca^{2+}$  ions is greatly reduced due to the hydrolysis of the  $Ca^{2+}$ . The rate of  $CaMoO_4:Eu^{3+},Na^+$  nucleation is then depressed, which also slows down the intrinsic anisotropic growth and the aggregation of  $CaMoO_4:Eu^{3+},Na^+$  nuclei during the hydrothermal process. Therefore, the nanoflake self-assembly superstructures disintegrate and gradually disappear, and the flakelike building units are replaced by nanoparticles (Fig. 6d and 6e).<sup>23</sup> XRD diffraction peaks shown in Fig. 6f suggest that at different pH values the prepared samples are all consistent with the tetragonal  $CaMoO_4$  phase. Simultaneously, the crystallinity of  $CaMoO_4$  phosphors gradually becomes weaker as the pH values increase.

Using  $CaCl_2$  instead of  $CaNO_3$ .— Keeping the other reaction conditions used before, replacing only  $CaNO_3$  with  $CaCl_2$  (0.2 M aqueous solution) as the Ca source, it was observed the formation of ellipselike microstructure, as shown in Fig. 7 (left). The ellipselike structure has lengths of about 3  $\mu$ m and diameters of 1  $\mu$ m. All



Figure 9. The PL and PLE spectra of undoped CaMoO4 samples prepared at pH 1.5 and 150  $^\circ C,$  respectively, for 6 h.



Figure 10. Emission spectra of as-prepared samples and relative intensity of the  ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$  transition in the inset at different temperature.

diffraction peaks of the XRD pattern shown in Fig. 7 (right) are in well accordance with the standard pattern (JCPDS no. 29-0351) of CaMoO<sub>4</sub>.

Photoluminescence properties.— Photoluminescence properties of calcium molybdate superstructures.-- Room-temperature photoluminescence properties of the as-obtained samples are studied. Figure 8 shows the photoluminescent excitation (PLE) and PL spectra of Eu3+-doped and Eu3+, Na+-codoped CaMoO4 superstructures prepared at pH 1.5 and 150°C for 6 h via hydrothermal method. Comparison with Eu3+-doped sample, Eu3+, Na+-codoped CaMoO4 samples play more stronger photoluminescence intensity, where Na<sup>+</sup> acts as a charge compensator. This can be explained by charge compensation in the phosphor system CaMoO<sub>4</sub>:Eu<sup>3+</sup>.<sup>16</sup> From Supporting Information Fig. 9, we can observe the undoped CaMoO<sub>4</sub> superstructure sample emits blue light around 480 nm and is excitated only under UV region. Moreover, from Refs. 16, 17, and 24, it can be seen that the excitation wavelengths of the bulk crystals of rareearth doped CaMoO<sub>4</sub> products are generally up to 490 nm. For the codoped samples in our case, the excitation spectra monitoring 615 nm emission line are composed of an intense broad band and some sharp lines in the range of 350-530 nm which is assigned to the combination of the f-f transition of  $O^{2-}-Mo^{6+}$  and  $O^{2-}-Eu^{3+}$ .<sup>15</sup> The effective excitation peaks at about 395 and 465 nm, ascribed to the  ${}^7F_0 \rightarrow {}^5L_6$  and  ${}^7F_0 \rightarrow {}^5D_2$  transitions of Eu<sup>3+</sup>, respectively,



**Figure 11.** Relative intensity of  ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$  transition of as-prepared samples at different pH values: 1.5, 4.5, 6, 7.5, 9.



Figure 12. Emission spectra of as-prepared samples using different Ca precursors.

agree well with the commercial near-UV and blue light-emitting diodes.<sup>7,16</sup> Under 465 nm excitation, all the PL spectra consist of two main emission peaks at about 595 and 615 nm in the region of 550–650 nm, corresponding to the characteristic  ${}^{5}D_{0} \rightarrow {}^{7}F_{1}$  and  ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$  transitions of Eu<sup>3+</sup>, respectively. As it is well known, CaMoO<sub>4</sub> has scheelite structure in which the Mo metal ion is surrounded by four oxygen atoms in tetrahedral symmetry (Td), and the large cations (Ca<sup>2+</sup>/Eu<sup>3+</sup>/Na<sup>+</sup>) are bounded to eight oxygen atoms from different tetrahedra. Among these peaks, the predominated red emission at about 615 nm is corresponding to the characteristic  ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$  electric dipole transition of Eu<sup>3+</sup> and results from the noncentrosymmetrical sites for the occupying Eu<sup>3+</sup>. The orange emitting one at about 595 nm is assigned to the  ${}^5D_0 \rightarrow {}^7F_1$  magnetic dipole transition of Eu<sup>3+</sup>, which is insensitive to the site symmetry.<sup>17</sup> The lack of centrosymmetry of Eu<sup>3+</sup> sites in CaMoO<sub>4</sub>:Eu<sup>3+</sup>,Na<sup>+</sup> implies that the  ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$  transition has much stronger emission intensity than the  ${}^{5}D_{0} \rightarrow {}^{7}F_{1}$  transition, as it is shown in Fig. 8. The Commission Internationale del'Eclairage (CIE) chromaticity coordinates under 465 nm excitation are (0.65, 0.35) with high color purity and are closer to the NTSC standard values (0.67, 0.33) and  $Y_2O_2S:Eu^{3+}$  (x = 0.63, y = 0.35).<sup>2</sup>

Influencing factors on photoluminescence properties.— Recently, Cavalcante et al.<sup>25</sup> reported the great dependence of the PL properties on the morphology and crystallinity of the  $BaMoO_4$  powders.<sup>25</sup> In addition, M. Longo et al.<sup>26</sup> observed and reported different origins of the PL emission of  $CaMoO_4$  microcrystals and showed that the PL emission of disorder CaMoO<sub>4</sub> is relevant with structural defects and the PL emission of ordered CaMoO<sub>4</sub> is attributed to an intrinsic slightly distorted tetrahedral symmetry in the short range. It is believed that luminescence property of calcium molybdate in the paper is associated with several factors, such as distortion on the [MoO<sub>4</sub>] tetrahedron groups caused by Ca/Na/Eu, particle size, morphology, and crystallinity degree.<sup>2</sup>

Figure 10 shows the hydrothermal temperature-dependent emission brightness. The PL intensity is evidently improved as the hydrothermal temperatures are increased from 60 to 200°C. In the inset, we can clearly observe the intensity of the  ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$  transition showing an upward tendency. As the reactional temperatures increase, the crystallinity of the as-prepared phosphors gradually enhanced (Fig. 5f), thereby improving the emission brightness.

In this case, pH value and Ca source also have a great effect on the luminescent properties of CaMoO<sub>4</sub>:Eu<sup>3+</sup>,Na<sup>+</sup> phosphors. Figure 11 discusses the influence of pH values on the intensities of the Eu<sup>3+</sup>  ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$  transition under the 465 nm excitation. Apparently, different morphologies and structures have different PL intensity and the flake-ball and flake-disk samples present the strongest emission

intensity. As the pH values increase, the PL intensity is gradually weaker, which is in accordance with the crystallinity of the asprepared phosphors (Fig. 6f). Hence, luminescence property is highly sensitive to the morphology changes of CaMoO<sub>4</sub> phosphors. Figure 12 shows the PL spectra under 465 nm excitation using different Ca source (the precursor solution fixed pH = 1.5,  $150^{\circ}C$  for 6 h). Obviously, the luminescent intensity of utilization of CaNO<sub>3</sub> is stronger than that of CaCl<sub>2</sub>. In this case, we can find the nanoflakes self-assembly flake-ball and flake-disk superstructures prepared by CaNO<sub>3</sub> are different from the ellipselike microstructures prepared by CaCl<sub>2</sub> at morphology, superstructure and particle sizes (shown in Fig. 2 and 7). Therefore, these factors together promote the formation of different emission properties.

#### Conclusions

In summary, we have provided a convenient, environment friendly, non-surfactant assisted and low-cost approach for preparing self-assembly 3D superstructure. The self-assembly CaMoO<sub>4</sub>:Eu<sup>3+</sup>,Na<sup>+</sup> superstructures with an average diameter of 5 µm, composed of multilayered nanoflakes, are successfully synthesized, presenting specific morphology and physical properties. The formation mechanism of CaMoO<sub>4</sub> superstructures mainly focuses on the aggregation behavior of CaMoO<sub>4</sub> nanoflakes as a function of the heating temperature. Meanwhile, the pH value and Ca source also have effect on the structure and dispersivity of the  $CaMoO_4$  products. In the PLE spectra, the excitation wavelengths, ranging from 350 to 530 nm in the UV and visible region, significantly extend the excitation region of photoluminescent materials. The PL spectra indicate the products emit bright red fluorescence and have high color purity. In addition, we also conclude the pH value of 1.5 and CaNO3 as Ca source are the optimal choice for the best optical properties of these materials.

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