I. INTRODUCTION

Lanthanide compounds, such as oxides, sulfides, hydroxides and fluorides have attractive applications in medicine, biology, chemistry, magnetism and optics [1−5] due to the unique electronic structure of 4f shell and the numerous transition modes [6]. Among all the studies, much attention has been paid to the synthesis of lanthanide compounds with different morphologies because the morphologies of the materials have important effect on their physical and chemical properties, thus leading to the different applications [7−10].

As one of the most important lanthanide compounds, molybdates display some excellent performances in the field of catalysis, lasers and ionic conductors [11−13]. Many researches focused on luminescence properties of NaY(MoO₄)₂ doped with rare earth ions. Huang et al. generated self-assembled NaY(MoO₄)₂:Eu³⁺ microarchitecture with Y₂O₃, Eu₂O₃, and Na₂MoO₄·2H₂O as the starting materials by a glycine-assisted hydrothermal method [14]. Xu et al. successfully synthesized novel 3D urchin-like NaY(MoO₄)₂ microarchitectures by a complexing-agent-assisted hydrothermal process followed by a subsequent heat treatment process [15]. Liu et al. established a capping agent free hydrothermal process using Y(OH)₃ nanorods as a precursor for the synthesis of nearly monodisperse NaY(MoO₄)₂ architectures with various shapes. The results showed that the volume ratio of water/ethanol in the mixed solvents and temperature had crucial influences on the formation of the multi-morphologies NaY(MoO₄)₂ particles and the NaY(MoO₄)₂:0.05Eu³⁺ bipyramid microstructure showed the strong red emission [16]. The hydrothermal process assisted solid state reaction at room temperature was reported by Yan and co-workers [17], who successfully synthesized NaY(MoO₄)₂:Eu³⁺ and NaY₀.₉Bi₀.₁(MoO₄)₂:Eu³⁺ submicrometer phosphors with the average size of about 200 nm. The luminescent lifetimes and quantum efficiencies of the two products indicated that the introduction of Bi³⁺ was favorable for the luminescence of Eu³⁺. Neeraj et al. synthesized the NaLn(WO₄)₂−x(MoO₄)ₓ and NaY₁−yBiₓ(WO₄)₂ (Ln=Y, Gd) doped with Eu³⁺ ion by the solid-state reaction. The materials could be used as red phosphors for white lighting devices under GaN-based excitation in the near UV [18].

As a heating method, microwave irradiation has been developed in chemistry and ceramic processing [19−21]. The microwave assisted reaction in the synthesis is the kinetics of the reaction, the initial heating is rapid which can lead to the energy saving and the selective formation of the phase [22−25]. So the microwave synthesis has the advantages of short reaction time, small and narrow particle size distribution and high purity.

In this work, flower-like NaY(MoO₄)₂ particles were successfully synthesized by a microwave-assisted hydrothermal process followed by a subsequent calcination process. The products were characterized by X-ray diffraction, X-ray photoelectron spectroscopy, field-emission scanning electron microscopy, and photoluminescence. As far as we know, the flower-like NaY(MoO₄)₂ particles by a microwave-assisted hydrothermal process followed by a subsequent calcina-
tion process had not been reported. Furthermore, the optical property of the flower-like NaY(MoO$_4$)$_2$:Eu$^{3+}$ was studied.

II. EXPERIMENTS

A. Synthesis of flower-like NaY(MoO$_4$)$_2$

All chemical reagents in this work are analytical grade and used as purchased without further purification. In a typical procedure, 1 mmol Y(NO$_3$)$_3$·6H$_2$O and 2 mmol Na$_2$MoO$_4$ were dissolved in 5 mL distilled water to form two colorless solution, respectively. Then the aqueous solution of Na$_2$MoO$_4$ was added into the aqueous solution of Y(NO$_3$)$_3$·6H$_2$O and the white colloidal solution was formed. The white colloidal solution was treated for 40 s by microwave irradiation of 400 W. After then, the as-obtained white colloidal solution was transferred into a 50 mL Teflon liner and some distilled water was added up to 80% of the total volume. The system was sealed and treated at 160 $^\circ$C for 24 h. The precipitate was washed several times with distilled water and dried at 80 $^\circ$C for 6 h. After calcinating at 800 $^\circ$C for 4 h, the product was obtained.

B. Characterization

The microwave treatment was carried out in the microwave oven (WBFY-201, 800 W and 2450±50 MHz). X-ray diffraction (XRD) was examined by a Japan Rigaku D/max rA X-ray diffractometer equipped with graphite-monochromatized high-intensity Cu-Ka radiation ($\lambda$=0.15478 nm). The scanning rate was 0.05 $^\circ$/s in the 2$\theta$ range from 10$^\circ$ to 80$^\circ$. X-ray photoelectron spectroscopy (XPS) analysis was performed on an ESCALAB MK II X-ray photoelectron spectrometer, using Mg Kr radiation as the excitation source. Field-emission scanning electron microscopy (FESEM) images were obtained on a JEOL-6300F field-emission scanning electron microscope with an accelerating voltage of 15 kV. Photoluminescence (PL) was carried out using a Jobin Yvon Fluorolog-3-TAU steady-state/lifetime spectrophotometer.

III. RESULTS AND DISCUSSION

A. Phase formation and structure of NaY(MoO$_4$)$_2$ crystals

The XRD pattern of the as-synthesized product and the standard XRD data for NaY(MoO$_4$)$_2$ are shown in Fig.1. The diffraction peaks of the product can be indexed to the tetragonal phase NaY(MoO$_4$)$_2$ (JCPDS card No.01-082-2369, $a=b=0.5199$ nm, $c=1.1330$ nm).

The product was also characterized by XPS for the evaluation of its composition on the particle surface (Fig.2). The binding energies obtained in the XPS analysis are corrected for specimen charging by referencing the C1s to 284.60 eV. The survey XPS spectrum of the product indicates that there are metal elements Y and Mo in the product (Fig.2(a)). The Y3d$_{5/2}$ and Y3d$_{3/2}$ peaks centered at 157.8 and 159.7 eV, respectively (Fig.2(b)) [10]. The binding energies of 232.4 and 235.6 eV are Mo3d$_{5/2}$ and Mo3d$_{3/2}$, respectively (Fig.2(c)). No characteristic peaks of other metals are detected.

B. The morphologies of the as-synthesized products

The morphologies of the products were investigated by FESEM (Fig.3). The as-synthesized flower-like precursor obtained at 160 $^\circ$C for 24 h and for 40 s by
Flower-like NaY(MoO$_4$)$_2$

FIG. 3 FESEM images of the products obtained at 160°C for 24 h and for 40 s by 300 W of microwave irradiation. (a) The precursor, (b) NaY(MoO$_4$)$_2$.

FIG. 4 FESEM images of the samples obtained at (a)–(d) different reaction temperatures. (a) 120 °C, (b) 160 °C, (c) 200 °C, (d) 240 °C; and (e)–(h) 160 °C for different reaction times: (e) 0 h, (f) 12 h, (g) 24 h, (h) 48 h.

400 W of microwave irradiation is shown in Fig.3(a). Figure 3(b) shows the FESEM image of the product NaY(MoO$_4$)$_2$ particles obtained by calcinating the precursor at 800 °C for 4 h. The samples were composed of uniform flower-like structures with the average diameter of about 1 μm.

To study the influence of the hydrothermal reaction temperature on the formation of the flower-like NaY(MoO$_4$)$_2$ precursor, several experiments at different hydrothermal temperatures under the same other conditions were carried out. Figure 4 (a)–(d) showed the FESEM images of the samples obtained at different reaction temperatures. When the reaction temperature was 120 °C, the small plate particles were found in the product. The flower-like product could be found as increasing the reaction temperature to 160 °C (Fig.4(b)). When the reaction temperature was further increased to 200 or 240 °C, the flower-like structures in the product could not be found (Fig.4 (c) or (d)).

The hydrothermal reaction time-dependent experiments were carried out at 160 °C and the resultant products were analyzed by FESEM. Figure 4 (e)–(h) show the FESEM images of the samples obtained at 160 °C for different reaction times. As increasing the time, the self-assembling process was observed clearly from Fig.4 (e)–(g). In Fig.4 (e) and (f), NaY(MoO$_4$)$_2$ micro-flakes were found. When the reaction time was prolonged to 24 h, flower-like particles could be clearly detected (Fig.4(g)) in the product. The flower-like structures were not found any more as prolonging the reaction time to 48 h (Fig.4(h)).

The influence of the microwave irradiation time on the morphology of the product was further investigated. Figure 5 shows the FESEM images of the as-synthesized products obtained at 160 °C for 24 h with different microwave irradiation times. When the microwave irradiation time was 20 s, micro-flakes were found (Fig.5(a)). The self-assembling flower-like particles could be detected in Fig.5(b) when the microwave irradiation time was 40 s. As prolonging the microwave irradiation time...
FIG. 5 FESEM images of the samples obtained at 160 °C for 24 h and with different microwave irradiation times: (a) 20 s, (b) 40 s, (c) 60 s.

FIG. 6 FESEM images of the products obtained at 160 °C for 24 h and by different microwave powers for 40 s. (a) 240 W, (b) 400 W, (c) 640 W, and (d) 800 W.

to 60 s, the flower-like structures could not be found (Fig.5(c)).

Figure 6 shows the FESEM images of the as-synthesized products obtained at 160 °C for 24 h and by different microwave powers for 40 s. When the microwave power was 240 W, the samples appeared as aggregates of many micro-flakes particles (Fig.6(a)). As the microwave power increasing to 400 W, flower-like particles could be detected (Fig.6(b)). But when the microwave power was increased to 640 or 800 W, flower-like particles could not be found clearly (Fig.6 (c) and (d)).

Based on the above experiment results, the preferable experiment conditions to synthesize the uniform flower-like NaY(MoO$_4$)$_2$ precursor could be obtained: 160 °C, 24 h, microwave time of 40 s and microwave power of 400 W.

A self-assembly growth mechanism for the formation of the flower-like NaY(MoO$_4$)$_2$ precursor can be proposed. The micro-flakes were formed by the fresh nuclei due to the anisotropic growth at first, and then the micro-flakes piled up to assemble into multilayer sheets, which further assembled to the flower-like structure (Fig.7). When the colloidal solution was treated by microwave irradiation, the micro-flakes piled up to assemble multilayer micro-sheets. In the process, microwave heating increased the collision rate, which resulted in the faster flower-like structure growth [22, 23]. And further high temperature and pressure were provided in the process of hydrothermal synthesis. The assembling process is shown in Fig.7, no flower-like NaY(MoO$_4$)$_2$ precursor could be found without microwave.

C. Photoluminescence property

The photoluminescence spectra of NaY(MoO$_4$)$_2$ with microwave irradiation and without microwave irradiation were also studied in this work (Fig.8). In fact, when the morphologies of NaY(MoO$_4$)$_2$ are changed from the flake to the flower-like under microwave irradiation, the red/orange ratio became from 0.066 to 0.074. The reason may be that the density of the flower-like particles was lower than that of the flake particles and the strength of the red light and the orange light decreased, moreover, the strength of the orange light decreased more than that of the red light, which resulted in the larger red/orange ratio.
FIG. 8 Photoluminescence spectra of NaY(MoO$_4$)$_2$ (a) with microwave irradiation $\lambda_{ex}=393$ nm and (b) without microwave irradiation.

FIG. 9 (a) Photoluminescence spectra and (b) excitation spectrum of the flower-like NaY(MoO$_4$)$_2$:Eu$^{3+}$.

The room temperature photoluminescence properties of the flower-like NaY(MoO$_4$)$_2$:Eu$^{3+}$ materials were investigated under the excitation at 393 nm. The excitation spectrum and the photoluminescence spectra (different amount of Eu$^{3+}$) of the flower-like NaY(MoO$_4$)$_2$:Eu$^{3+}$ samples could be seen in Fig. 9. The excitation spectrum of the sample consists of a strong absorption band with a maximum at 393 nm and many weak bands monitored with 618 nm emission of Eu$^{3+}$. So we choose the 393 nm as the excitation source. The doping molar ratios of the Eu$^{3+}$:Y$^{3+}$ in our experiments were from 0 to 10%. The efficient and sharp peaks were attributed to $^5D_0\rightarrow^7F_J$ ($J=1$, 2, 4) emission transitions [14], indicating the presence of Eu$^{3+}$ cations in the NaY(MoO$_4$)$_2$ lattices. The efficient red PL emission peak centered at around 612 nm corresponded to the forced electric dipole transition ($^5D_0\rightarrow^7F_2$), and the $^5D_0\rightarrow^7F_1$ at around 590 nm was magnetic dipole allowed. The other peak at around 699 nm corresponded to the transition of $^5D_0\rightarrow^7F_4$. As the molar ratio of doped Eu$^{3+}$ increasing from 0 to 5%, the intensity of the emission peaks increased obviously. But the intensity of the emission peaks did not increase any more as the molar ratio of doped Eu$^{3+}$ increased from 5% to 10%. So the preferable molar ratio of doped Eu$^{3+}$ might be 5%. The flower-like NaY(MoO$_4$)$_2$:Eu$^{3+}$ materials with the emission peak at 612 nm could be used potentially as a red phosphor for white light-emitting diodes [26].

IV. CONCLUSION

In summary, flower-like NaY(MoO$_4$)$_2$ particles were successfully synthesized by a microwave-assisted hydrothermal process followed by a subsequent calcination process. The influence of experiment parameters on the morphologies of products had been investigated, and the preferable experiment parameters for preparing the regular flower-like NaY(MoO$_4$)$_2$ precursor were 160 °C, 24 h, microwave time of 40 s and microwave power of 400 W. A possible formation mechanism of the regular flower-like NaY(MoO$_4$)$_2$ precursor was suggested. Furthermore, the optical property of flower-like NaY(MoO$_4$)$_2$:Eu$^{3+}$ was studied, and the preferable molar ratio of doped Eu$^{3+}$ was 5%. The two efficient and sharp PL emission peaks at around 590 and 612 nm showed a potential application as a red phosphor for light-emitting diodes. This approach could be extended for the synthesis of the other lanthanide molybdates with flower-like morphology.

V. ACKNOWLEDGMENT

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