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Synthesis, Characterization, and Photoluminescence Property of $LaCO_3OH$ Microspheres

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Novel $LaCO_3OH$ microspheres with the hexagonal phase were synthesized by a hydrothermal method using $La(NO_3)_3 \cdot 6H_2O$ and urea $CO(NH_2)_2$ as the starting materials. Various experimental parameters were examined, such as the reaction temperature, the reaction time, and the molar ratios of the starting reagents. The as-synthesized products were characterized by powder X-ray diffraction, transmission electron microscopy, field-emission scanning electron microscopy, X-ray photoelectron spectroscopy, Fourier transform infrared spectroscopy, and photoluminescence (PL). The PL result showed one broad emission band centered at 438 nm ($\lambda_{ex} = 365$ nm) of the pure $LaCO_3OH$ microspheres. In addition, a possible formation mechanism of $LaCO_3OH$ microspheres and the PL property of pure $LaCO_3OH$ microspheres were discussed.

1. Introduction

Rare-earth materials have drawn much attention because of their wide range of applications in catalysis,[1,2] optics,[3−5] biological labeling,[6] magnetism,[7] etc. Most of their properties are dependent on the composition, crystal type, shape, and size. Among compounds of the rare-earth family, lanthanum compounds with various morphologies have been synthesized, such as nanorods,[8] macropores,[9] nanowires,[10] and nanoplates[11] of La_2O_3; nanospheres,[12] nanowires,[13] and nanorods[10] of $La(OH)_3$; needlelike and spherical[14] $La_2(CO_3)_3$; nanowires[15,16] of $LaPO_4$; triangular nanoplates[17,18] and flakes[19] of LaF_3, etc. Because of its low-temperature, cost-effective,

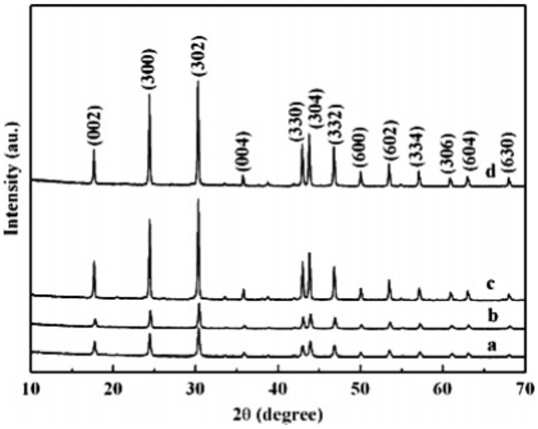

Figure 1. XRD patterns of the samples obtained at different reaction temperatures for 8 h: (a) 150 °C; (b) 190 °C; (c) 230 °C; (d) 270 °C.

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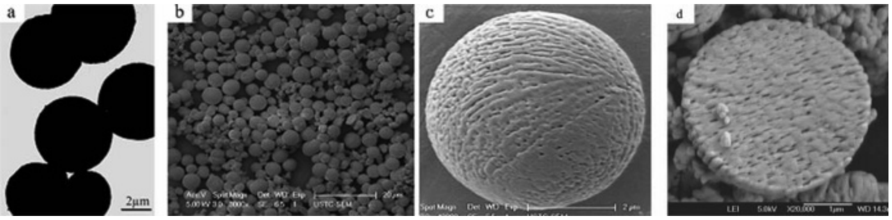

Figure 2. (a) Bright-field TEM image of the as-synthesized products. (b and c) FESEM image of the as-synthesized products. (d) Broken image of the microspheres.

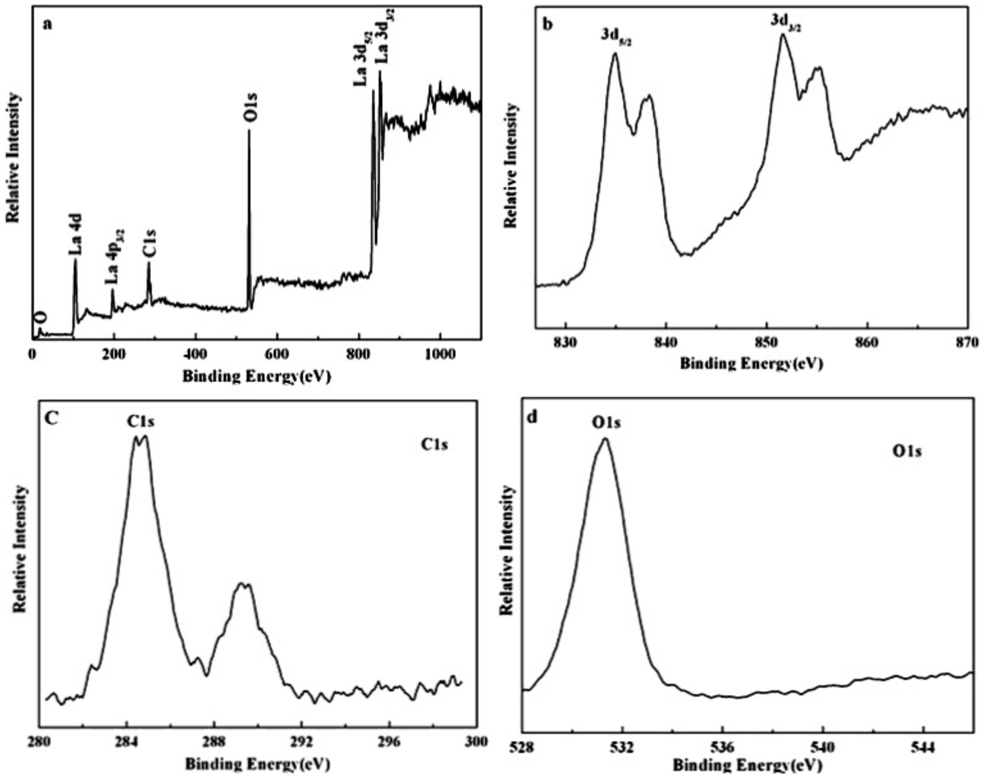

Figure 3. XPS spectra of the as-synthesized products: (a) survey spectrum; (b) La 3d region; (c) C 1s region; (d) O 1s region.

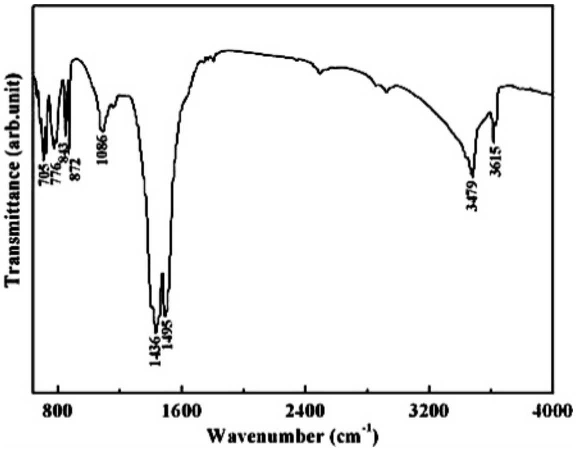

Figure 4. FTIR spectra of the as-synthesized product.

simple, and convenient advantages, the hydrothermal process has been widely used to synthesize lanthanum compounds.[20] However, there is still much attention focused on the lanthanum compound system, especially for the exploration of new research and application fields on the basis of the novel properties. For this reason, the synthesis of lanthanum hydroxycarbonate was investigated.

Most fluorescence of rare-earth compounds originate from electron transitions within the 4f shell. Lanthanum compounds doped with another activated phosphorus have been widely studied for application in luminescent materials,[21] but pure rare-earth hydroxycarbonates have rarely been investigated especially for lanthanum hydroxycarbonates. As far as we know, there is no report about the synthesis of $LaCO_3OH$ microspheres and their photoluminescence (PL) property. Herein, a systematic study of the reaction temperature, the reaction time, and the molar ratios of the starting reagents and a control experiment have been carried out to investigate the influence on the formation progress of the microspheres. In addition, the PL property of the pure $LaCO_3OH$ microspheres was investigated.

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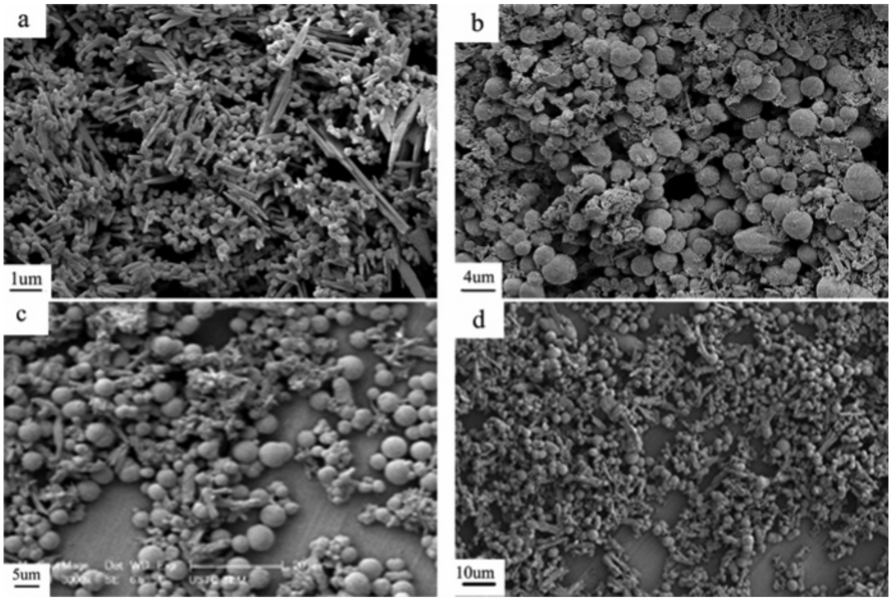

Figure 5. FESEM images of the samples obtained at different temperatures for 12 h with a molar ratio of urea to $La(NO_3)_3{\cdot}6H_2O$ of 3:1: (a) 210 °C; (b) 230 °C; (c) 250 °C; (d) 270 °C.

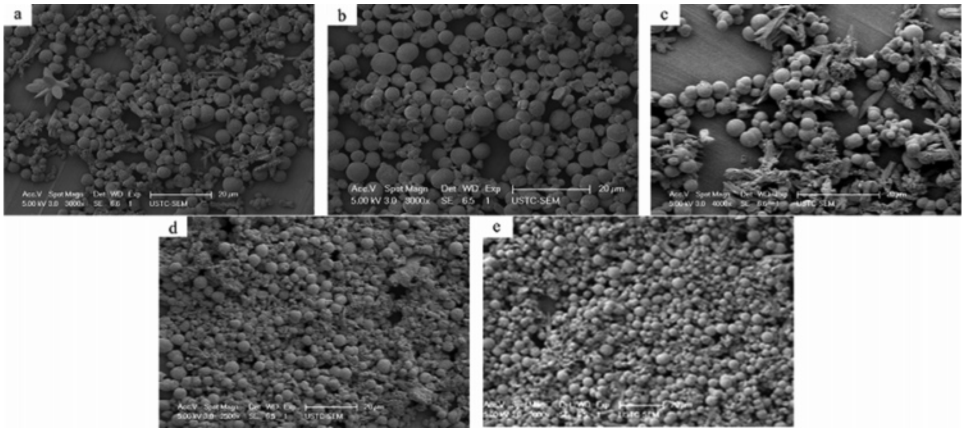

Figure 6. FESEM images of the samples obtained at 230 °C for 12 h under different molar ratios of urea to $La(NO_3)_3{\cdot}6H_2O$: (a) 1:1; (b) 2:1; (c) 3:1; (d) 4:1; (e) 5:1.

2. Experimental Section

All reagents used were of analytical purity, were obtained from Shanghai Chemical Reagent Ltd. Co. of China, and were used without further purification. The reactants were dissolved in 20 mL of deionized water with stirring. After several minutes, the mixture was transferred into a 60-mL Teflon liner and some distilled water was added up to 80% of the total volume. The autoclaves were heated at different temperatures for different times with different molar ratios of the starting reagents and then cooled to ambient temperature naturally. Then, the precipitates were washed with distilled water and absolute ethanol several times and dried at 80 °C for 6 h. The products were finally obtained. The procedure for the synthesis of $LaCO_3OH$ using NaOH and Na_2CO_3 as the precipitators was the same as the above process (the detailed procedure appears in the Supporting Information).

Characterization. Powder X-ray diffraction (XRD) were carried out with a Japan Rigaku D/max rA X-ray diffractometer equipped with graphite-monochromatized high-intensity Cu KR radiation ($\lambda = 0.154\,78$ nm). The scanning rate was 0.05° s^{-1} in the 2θ range from 10° to 70°. The transmission electron microscopy (TEM) images were carried out on a Hitachi model H-800 transmission electron microscope working at 200 kV. The 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. The X-ray photoelectron spectroscopy (XPS) analysis was performed on an ESCALAB MK II X-ray photoelectron spectrometer, using Mg Kα radiation as the excitation source. The Fourier transform infrared (FTIR) spectroscopic study was performed on a MAGNA-IR 750 FTIR spectrometer. The PL was carried out using a Jobin Yvon Fluorolog-3-TAU steady-state/lifetime spectrofluorometer, and the analysis range was 240−1700 nm.

3. Results and Discussion

Figure 1 shows typical XRD patterns of samples obtained at different reaction temperatures for 8 h. In each XRD pattern, all of the reflections can be indexed to the pure hexagonal phase (JCPDS card 26-0815) with lattice constants $a = 1.261$ nm and $c = 1.002$ nm. No other peaks exist in the figure, showing the high purity and crystallinity of the

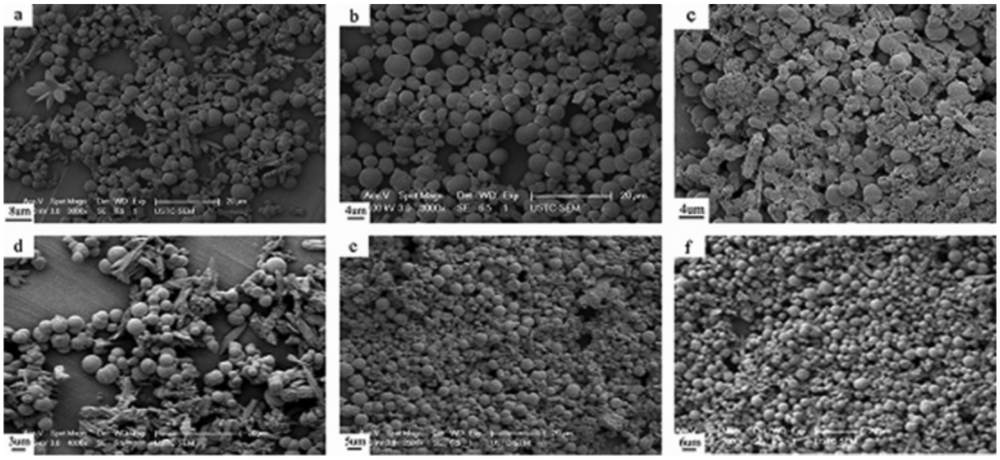

Figure 7. FESEM images of the samples obtained at 230 °C: (a) 4 h; (b) 8 h; (c) 12 h; (d) 16 h; (e) 20 h; (f) 24 h.

samples. When using NaOH and Na_2CO_3 as the precipitators to synthesize $LaCO_3OH$ at 230 °C for 8 h, the reflections can also be indexed to the pure hexagonal phase $LaCO_3OH$ (JCPDS card 26-0815) (XRD patterns of the samples appear in the Supporting Information).

The TEM images of these microspheres show the solid nature on basis of a strong contrast between the dark edge and pale center (Figure 2a). Figure 2b shows an overview of the FESEM image of the samples obtained at 230 °C for 8 h; from this, it can be seen that the yield of microspheres in the products exceeds 90%, with the diameter in the range of 2−6 μm. There are some small gaps on the surface and in the inner portion of the microspheres (Figure 2c,d).

The product was also characterized by XPS for the evaluation of its composition and purity. The binding energies obtained in the XPS analysis were corrected for specimen charging by referencing the C 1s orbital to 284.60 eV. The survey XPS spectrum of the products (Figure 3a) suggests that there are no other elements on the surface of the samples. Figure 3b shows that the binding energies of La $3d_{5/2}$ and La $3d_{3/2}$ are 834.88 and 851.64 eV, respectively. The binding energy of C 1s is 289.60 eV, which can be assigned to the C−O peak (Figure 3c). The O 1s spectrum for the surface of the sample demonstrates a O^{2-} peak at 531.30 eV (Figure 3d).

Our FTIR investigation also affirms the formation of $LaCO_3OH$. Figure 4 presents the sample obtained at 230 °C for 8 h with a ratio of 3:1 urea/$La(NO_3)_3 \cdot 6H_2O$. The peaks at 3615 and 3479 cm^{-1} are assigned to structural OH and adsorbed H_2O in the materials, respectively.[22] The other strong peaks at 1495−1436 cm^{-1} are attributed to the ν_3 mode of carbonate, and the rest of the minor bands at 1086−872, 843, and 776−705 cm^{-1} are assigned to ν_1, ν_2, and ν_4 modes of carbonate, respectively.[23,24]

The morphologies of the products obtained at different reaction temperatures, molar ratios of the starting reagents, and reaction times were examined by a field-emission scanning electron microscope. Temperature has been found to play an important role in the crystallization and shape control of $LaCO_3OH$. If the temperature was below 210 °C, no microspheres could be obtained; $LaCO_3OH$ was mainly composed of asymmetric microrods with diameters of around 80−200 nm and lengths of about 1−3 μm (Figure 5a). When the temperature reached 230 °C, the microspheres were formed in about 70% morphological yield (Figure 5b), which is higher than those at 250 and 270 °C (Figure 5c,d).

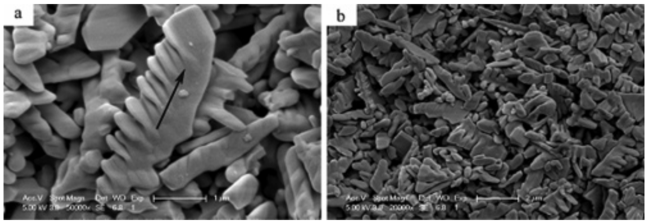

Figure 8. FESEM images of the samples obtained at 230 °C for 8 h, using NaOH and Na_2CO_3 as the precipitators.

For a lack of urea (the molar ratio of urea to $La(NO_3)_3 \cdot 6H_2O$ was 1:1), the sample was composed of all anomalous particles (Figure 6a). However, when the molar ratio was increased to 2:1, the microspheres were formed with a low yield (Figure 6b), and the yield sharply ascended after the molar ratio was changed to 3:1 or 4:1 (Figure 6c,d). It can be found that when the molar ratio was 5:1, the superfluous urea produced a lot of CO_2 and NH_3 bubbles that resulted in most of the microspheres being broken (Figure 6e).

Time-dependent experiments indicated that the reaction time has a weak influence on the morphological yield. Exiguous microspheres were formed when the reaction time was 4 h (Figure 7a), and the yield of the microspheres exceeded 90% after 8 h (Figure 7b). When the time exceeded 8 h, a small decrease occurred in the yield (Figure 7c−f).

On the basis of the above experimental results, it can be seen that the most important factors that affect the morphology of $LaCO_3OH$ crystals in the present work are the reaction temperature and the molar ratio of urea to $La(NO_3)_3 \cdot 6H_2O$ in the reaction system. The preferable experimental parameters are a reaction temperature of 230 °C, a reaction time of 8 h, and a molar ratio of urea to $La(NO_3)_3 \cdot 6H_2O$ of 3:1.

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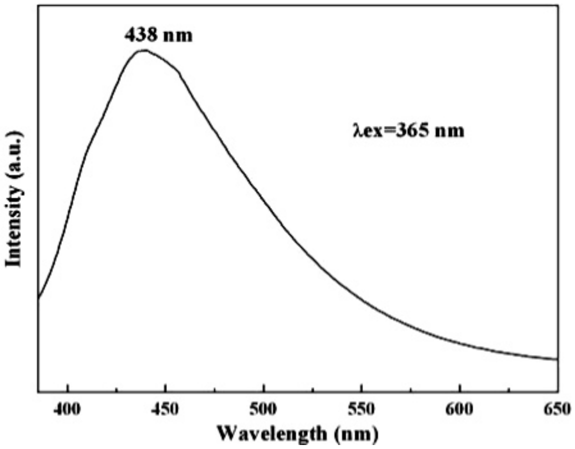

Figure 9. PL spectra of the $LaCO_3OH$ microspheres at room temperature.

The reaction process for the formation of $LaCO_3OH$ could be described as follows:

$$CO(NH_2)_2 + 3H_2O \rightarrow CO_2(g) + 2NH_3 \cdot H_2O \quad (1)$$

$$NH_3(g) + H_2O \rightleftharpoons NH_4^+ + OH^- \quad (2)$$

$$La^{3+} + OH^- + CO_3^{2-} \rightarrow LaCO_3OH \quad (3)$$

The urea plays a significant role in the formation of $LaCO_3OH$ microspheres. The hydrolyzation process of the urea provides a small quantity of CO_3^{2-} and OH^- ions in the alkalescent system; this can slow the growth rate of $LaCO_3OH$, which is different from the alkali system composed of NaOH and Na_2CO_3, just like the proposed mechanism for the formation of CdSe nanocrystals.[25] According to that mechanism, when the overall growth rate is fast, the growth of an anisotropic material is generally faster along an axis, and a rodlike nanoparticle is obtained. If the overall growth rate is slow, a nearly spherical morphology is favored. In the present work, the growth rate of anisotropic $LaCO_3OH$ is properly slow, which is favored to form a spherical morphology. When using NaOH and Na_2CO_3 as the precipitators, the growth of the $LaCO_3OH$ crystal is faster along an axis, and asymmetric trunks are formed (Figure 8). It is believed that the alkaline condition in the reaction system has a vital influence on the morphology of $LaCO_3OH$. In addition, the CO_2 and NH_3 gas bubbles in the growth progress could make some small gaps on the surface and on the inner portion of the microspheres.

The optical properties of pure rare-earth hydroxycarbonates have rarely been investigated up to now. The room-temperature PL spectrum of the pure $LaCO_3OH$ microspheres obtained at 230 °C for 8 h is shown in Figure 9. The emission spectrum has only one broad band centered on 438 nm with the 365 nm excitation, and no filter was used. It is known that the fluorescence of rare-earth ions mainly comes from the interior electron transitions of the 4f shell,[26] but the 4f shell of La^{3+} is empty and no f−f transitions exist in our products. Herein, the emission spectrum of the $LaCO_3OH$ microspheres consists of a broad band located between 350 and 600 nm and can be attributed to the self-trapped exciton (STE) luminescence.[27,28] Many of the free holes and free electrons were created after the lattice was irradiated, and the STEs can be formed directly from electron−hole pairs. During the diffusion of the STEs, they can be an irradiative recombination, leading to luminescence,[29,30] the possible origin of the visible PL, but further work is definitely necessary to understand the details of the PL mechanism in the $LaCO_3OH$ microspheres.

4. Conclusion

In summary, novel $LaCO_3OH$ microspheres with the hexagonal phase were synthesized by a hydrothermal method. Various experiment parameters were examined and a possible formation mechanism of $LaCO_3OH$ microspheres was discussed. This method brings forward a broad idea to synthesize other rare-earth compounds with various morphologies and novel properties. The XRD, TEM, FESEM, XPS, and FTIR were used to characterize the products, and the PL properties of pure $LaCO_3OH$ microspheres were discussed. This brings a new opportunity to research and apply luminescence fields.

Supporting Information Available: Procedure for the synthesis of $LaCO_3OH$ and XRD patterns. This material is available free of charge via the Internet at http://pubs.acs.org.

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