Hydrothermal Synthesis of Highly Ordered Micropompon of Lanthanum Molybdate Nanoflakes

Yun-Peng Xu, Dan-Yu Jiang, Wen-Bo Bu, and Jian-Lin Shi*
State Key Laboratory of High Performance Ceramics and Superfine Microstructures, Shanghai Institute of Ceramics, Chinese Academy of Sciences, Shanghai 200050, P. R. China

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A novel micrometer-scale spherical structure composed of nanoflakes, named micropompon, has been achieved in the $La_2(MoO_4)_3$ system through a simple surfactant-free hydrothermal approach. Possible formation mechanisms for the nanoflakes and micropompons have been preliminarily discussed.

In the recent years, nanostructured materials have attracted great attention owing to their novel properties and potential usages in many fields, such as electronics, optoelectronics, and nanosensors.[1] The synthesis of nanostructured materials and guiding these nanometer-scaled building blocks to ordered complex functional architectures would offer great opportunities to explore their novel properties and lead to the construction of ordered and complex one-dimensional (1D) nanostructures,[2] such as multiarmed,[3] selfsustained,[4] and penniform[5] nanostructures. However, the complex architectures, which can be self-assembled with two-dimensional (2D) nanoflakes, and their large-scale manufacturing at low cost in particular, remain crucial challenges to unfold the very promising future of nanotechnology. In addition, various types of surfactants have been widely used in the synthesis of complex-structured materials thanks to their efficient self-assembly properties.[6] But the use of surfactants introduces heterogeneous impurities and increases the production cost, which may restrict the wide development of researches and applications.[7] Therefore, the development of methods for the synthesis of the novel microarchitectures composed of two-dimensional (2D) nanoflakes through a low cost and easy approach is a major challenge in the field of nanoscale science.

Metal molybdates and tungstates are two families of inorganic materials that have a high application potential in various fields, such as in photoluminescence, optical fibers, and scintillator materials.[8] Previous work has been focused on the synthesis of the nanorods and nanoparticles.[9] But to the best of our knowledge, micrometer-scale architectures composed of nanoflakes have not been achieved. Here we demonstrate a surfactant-free hydrothermal crystallization procedure to the large-scale synthesis of lanthanum molybdate micropompons.

In a typical procedure, 1.30 g of $La(NO_3)_3 \cdot 6H_2O$ and 0.79 g of $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ were dissolved in 25 mL of deionized water, respectively. The solution of $La(NO_3)_3 \cdot 6H_2O$ was slowly added to the $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ solution under strong magnetic stirring. The amorphous white precipitate was achieved. The pH value was adjusted to 8 using concentrated NaOH solution. The resulting precursor suspension was transferred into a Teflon-lined stainless steel autoclave, which was subsequently sealed and maintained at 180 °C for 12 h, then cooled to room temperature. The product was filtered, washed for several times with deionized water and absolute ethanol, and then dried in vacuum at 60 °C for 6 h.

The crystal structure and phase purity of the samples achieved by hydrothermal treatment at 180 °C can be identified from the powder XRD (Model D/MAX-C, Rigku, Tokyo, Japan) pattern, as showed in Figure 1. All the peaks can be perfectly indexed as the monoclinic $La_2(MoO_4)_3$ [space group: $C2/c$] which are consistent with the literature values (JCPDS No. 70-1382), indicating that the samples achieved by our current synthetic methods are pure monoclinic $La_2(MoO_4)_3$ phase. The calculated cell parameters based on XRD data are $a = 16.6249$ Å, $b = 11.8119$ Å, $c = 15.3681$ Å, $\beta = 105.1017°$, which are slightly smaller than bulk material (JCPDS No. 70-1382). It may be caused by the size effect of the nanomaterials.

The morphology and the microstructure of the products were further investigated with a field emission scanning electron microscope (FE-SEM, JSM-6700F, JEOL, Japan), transmission electron microscope (TEM, JEOL JEM-2010, operated at an accelerating voltage of 200 kV), and selected area electron diffraction (SAED). Representative SEM image (Figure 2a) shows that the products obtained at pH = 8, 180 °C for 12 h are composed of micropompons of 3–4 μm in diameter, which was consistent with Figure 2b. TEM images (Figure 2c) from the same sample after prolonged ultrasonic dispersion show that the micropompon is composed of striplike nanoflakes, and these nanoflakes are 20–200 nm in width and 30–40 nm in thickness, as can be judged from Figures 2a and 2c. Figure 2d shows the nanoflake and its corresponding SAED pattern at the top right corner which reveals that the nanoflake diffraction spots characteristic of a monoclinic $La_2(MoO_4)_3$, in accordance with the XRD result. Moreover, the SAED patterns taken from the different nanoflakes were found to be identical within experimental accuracy, indicating that all $La_2(MoO_4)_3$ nanoflakes are single crystalline.

To date, there are mainly two proposed formation mechanisms involved in the hydrothermal/solvothermal crystallization process: the self-aggregation or the oriented attachment mechanism[10] for the polymers/surfactants/chelating ligands-existing

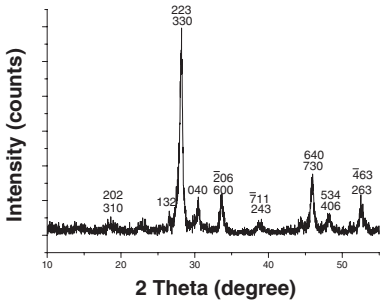

Figure 1. X-ray diffraction pattern for $La_2(MoO_4)_3$ samples obtained at pH = 8, 180 °C for 12 h.

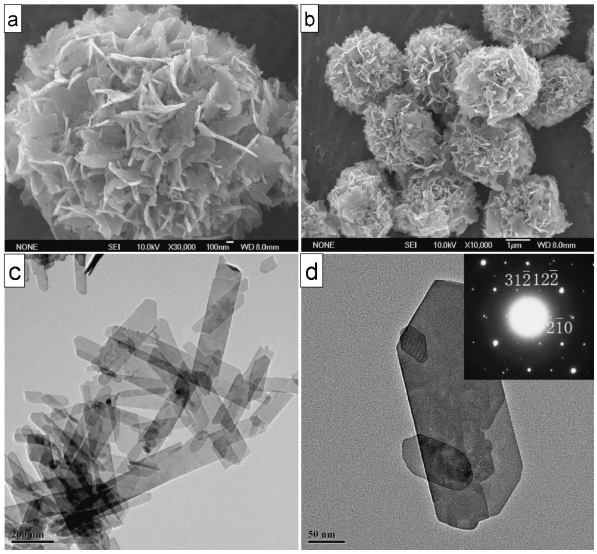

Figure 2. (a) and (b) SEM images of $La_2(MoO_4)_3$ micropompon; (c) TEM images of $La_2(MoO_4)_3$ nanoflakes; (d) A single $La_2(MoO_4)_3$ nanoflake. Right inset: selected area electron-diffraction (SAED) pattern obtained from the nanoflake. Scale bar: (a) 100 nm; (b) 1 μm; (c) 20 nm; (d) 50 nm.

system and the Ostwald ripening process[11] in which the spherical diffusion model was proposed to expound the anisotropic lateral crystal growth.[12] Because of the absence of the surfactant in the present study, the formation mechanism for the $La_2(MoO_4)_3$ nanoflakes can be simply depicted as an Ostwald ripening process: tiny crystalline nuclei of $La_2(MoO_4)_3$ in a supersaturated medium formed in advance which was followed by the crystal growth at the cost of the amorphous precipitates and/or the small crystals. Because the growth rate of different facets are different, $La_2(MoO_4)_3$ nanoflakes are formed.

Compared with the formation mechanism for the nanoflakes, the formation mechanism for the micropompons seems difficult to depict. Liu et al.[13] have synthesized CuO "dandelions" using surfactant-free hydrothermal method and believed that the geometrical shape of building blocks played a key role. However, the synthesized nanoflakes are not uniform in size, and the nanoflakes on the micropompon are irregularly oriented, so the shape of the nanoflakes does not play an important role in the micropompon formation. In the hydrothermal crystallization procedure, the pH value is a very important factor that influences the phase structure, the crystallinity and the growth rate of different crystal faces of the product.[9b,14] We suppose that with the proper OH^- concentration, the following reaction exists:

$$La^{3+} + nOH^- = La(OH)_n^{3-n}. \quad (1)$$

Some of the La^{3+} exists in the form of the $La(OH)_n^{3-n}$ complex ion, so the concentration of La^{3+} reduces, which leads to the reduction of the $La_2(MoO_4)_3$ nuclei number at the beginning period. Then the nanoflakes tends to aggregate and grow together. And because of the homogeneity of the solution, spherical micropompons are yielded. The study of the detailed mechanism is still in progress.

In summary, for the first time we synthesized $La_2(MoO_4)_3$ micropompon which composes of nanoflakes through simple and mild surfactant-free hydrothermal approach and the formation mechanisms of the nanoflakes and the micropompon have been preliminarily discussed.

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