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Synthesis of $La_2Mo_2O_9$ Nanocrystallites by Sol-Gel Process†

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$La_2Mo_2O_9$ nanocrystallites were synthesized successfully using sol-gel process with $(NH_4)_6Mo_7O_{24}·4H_2O$, $La(NO_3)_3·6H_2O$, citric acid and PEG400 as original materials. The result shows that spherical well-crystallized $La_2Mo_2O_9$ nanoparticles were formed at 500 ºC with sizes of *ca.* 80 and 20 nm, which indicates the secondary nucleation exists in the reaction process. The synthesized $La_2Mo_2O_9$ nanocrystallites were characterized by XRD, TEM, IR and UV-visible spectra.

Keywords: $La_2Mo_2O_9$, Sol-gel, Nanocrystallite.

INTRODUCTION

Nanocrystalline materials possess promising applications due to their grain size dependent phenomena in nano-scale. As one of functional materials, molybdates with Scheelite-type structure have attracted much attention for potential applications in photoluminescence, scintillators, photocatalyst hosts for lanthanide-activated lasers and humidity sensors[1-3]. Recently, oxide-ion conductors have a wide range of potential applications, including as the electrolyte in solid-oxide fuel cells, as oxygen sensors and acting as an oxygen-permeable membrane in catalytic systems. In particular, the lanthanum molybdate ($La_2Mo_2O_9$) has been proposed as an important oxide-ion conductor of intrinsic vacancy type. Its conductivity is about 0.06 S cm^{-1} at 1073 K, which is comparable to that of yttria-stabilized zirconia (YSZ) at 1273 K. So, it has potential applications in intermediate-temperature solid oxide fuel cells, oxygen sensors, oxygen permeable membrane, solid-state ionic devices, *etc*.

In recent years, several synthetic routes have been used to prepare this material, such as solid-state reaction[4] and wet chemical method[5-10]. These methods usually require high heat treatment temperatures, long processing times and expensive precursors. In order to overcome these problems, a new synthesis method known as ultrasonic assisted spray-pyrolysis process has been employed[11]. In fact, except for these techniques, the sol-gel method can also be considered as an alternative route because of its advantages such as high purity, high chemical homogeneity, lower calcination temperature and simple synthesis system. In this work, a simple sol-gel process has been used to synthesize $La_2Mo_2O_9$ nanocrystallites. The microcrystals were analyzed by X-ray diffraction (XRD), Fourier-transform infrared (FT-IR), transmission electron microscopy (TEM) and UV-visible spectrum.

EXPERIMENTAL

$La(NO_3)_3·6H_2O$, $(NH_4)_6Mo_7O_{24}·4H_2O$ and citric acid of analytic reagent grade were used to prepare the metal molybdate compound. The mixed solution of $La(NO_3)·6H_2O$, $(NH_4)_6Mo_7O_{24}·4H_2O$, citric acid and PEG400 (polyethylene glycol 400) was refluxed in a water bath at 80 ºC for 3 h under vigorous stirring to prepare the transparent sol. The sol was transformed into dried gel by drying at 100 ºC. Finally the dried gel powder was calcined in an oven in air at 500 ºC for 4 h to obtain nanocrystalline powders.

RESULTS AND DISCUSSION

Fig. 1 shows the IR spectrum of $La_2Mo_2O_9$ powders processed at 500 ºC for 4 h. The result displays several large absorption bands in range of 930-650 cm^{-1}, which are ascribed to the characteristic Mo=O and Mo-O-Mo stretching vibrations

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in $\{Mo_2O_9\}$ group. On the other hand, the origin of the weak absorption band at 550 cm^{-1} is due to the La-O bending vibration. In Fig. 1, it was detected other absorption bands caused by the presence of water and CO_2 arising from the room atmosphere in the $La_2Mo_2O_9$ powders.

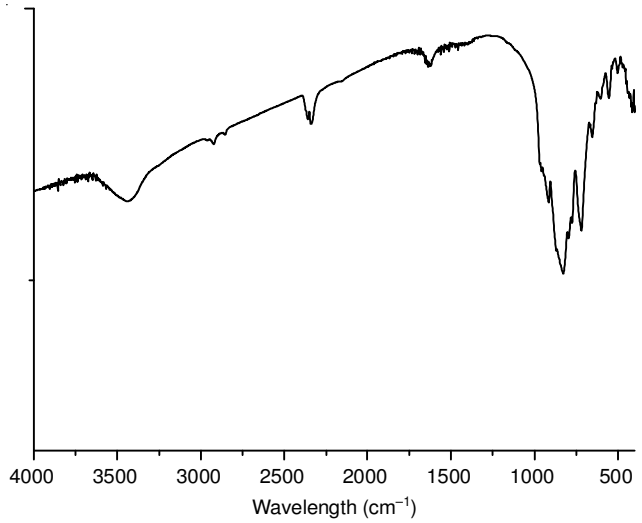

Fig. 1. IR spectrum of the sample

The XRD pattern of the sample calcined at 500 ºC for 4 h in air is shown in Fig. 2. It is observed that the precursor is fully decomposed to $La_2Mo_2O_9$ crystal particles. The diffraction peaks become more sharper, indicating the sample is in high degree of crystallinity. According to Scherrer formula, $D = K\lambda/\beta \cos\theta$ ($K = 0.89$, $\lambda = 0.1541$ nm), we can determine the corresponding crystal size of 45 nm and we can aslo calculate the crystal lattice parameter of a = 7.159 Å by using the following formula where (hkl) = 210 with corresponding d value from the obtained data (d = 3.202 Å). The result is in accordance with crystal parameter of the cubic structure of $La_2Mo_2O_9$[10].

$$d = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$$

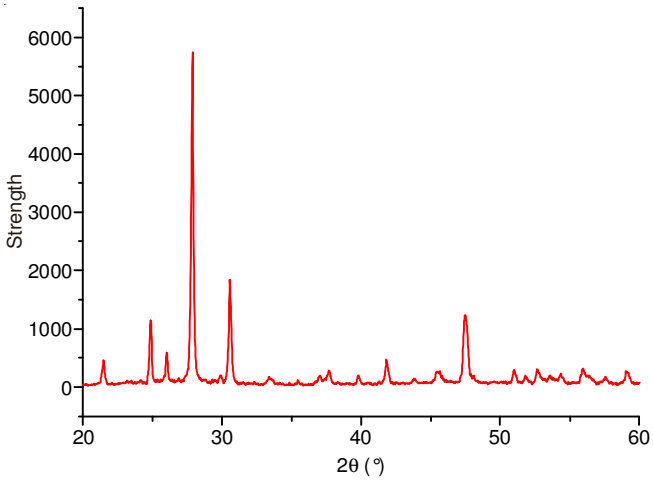

Fig. 2. XRD pattern of $La_2Mo_2O_9$

Transmission electron microscopic image of the $La_2Mo_2O_9$ particels is shown in Fig. 3, from which two sizes of spherical particles can be viewed. The large one is 80 nm with good dispersibility while the small one is 20 nm. The existence of the small particles indicates the secondary nucleation in the reaction process. The crystal nuclear is necessary for the crystal growth, in which the nucleation can be divided into primary and secondary nucleation. When there are no crystalline solid particles in the solution, the primary nucleation will happen. The secondary nucleation will occur in appropriate conditions with the existence of primary nucleation. In the present sample, the large particles should be from the primary nucleation and become the new crystalline centers, resulting in the secondary nucleation to form the small particles.

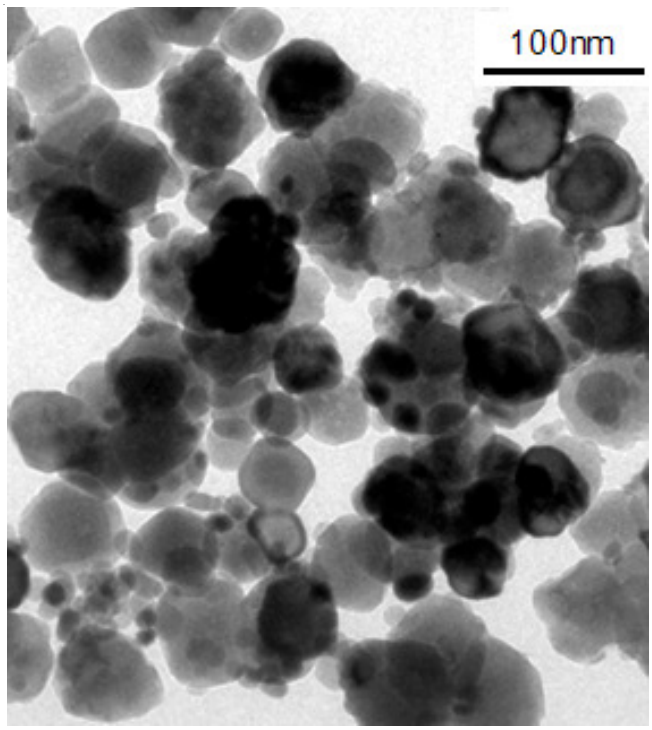

Fig. 3. TEM image of the sample

The UV-visible spectrum of the sample in solid state was studied at room temperature. The result shows the sample exhibits an absorption at 320 nm, which is due to charge-transfer transitions (O→Mo) in the $\{Mo_2O_9\}$ group.

Conclusion

The nanocrystallites of $La_2Mo_2O_9$ were prepared by sol-gel process with $(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$, $La(NO_3)_3{\cdot}6H_2O$, citric acid and PEG400 as original materials. The result shows that the precursor can be entirely decomposed to $La_2Mo_2O_9$ at 500 ºC. The TEM image shows that the well-defined spherical nanoparticles with sizes of 80 and 20 nm can be obtained. The product displays the UV-visible absorption at 320 nm.

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REFERENCES

1. Z.C. Shan, Y.M. Wang, H.M. Ding and F.Q. Huang, *J. Mol. Catal. A*, **302**, 54 (2009).
2. S. Rajagopal, V.L. Bekenev, D. Nataraj, D. Mangalaraj and O.Y. Khyzhun, *J. Alloys Comp*., **496**, 61 (2010).
3. T. Thongtem, S. Kungwankunakorn, B. Kuntalue, A. Phuruangrat and S. Thongtem, *J. Alloys Comp*., **506**, 475 (2010).
4. S. Georges, F. Goutenoire, P. Lacorre and M.C. Steil, *J. Eur. Ceram. Soc*., **25**, 3619 (2005).
5. C. Tealdi, G. Chiodelli, L. Malavasi and G. Flor, *J. Mater. Chem*., **14**, 3553 (2004).
6. A. Tarancon, G. Dezanneau, J. Arbiol, F. Peiró and J.R. Morante, *J. Power Sources*, **118**, 256 (2003).
7. S. Basu, P.S. Devi and H.S. Maiti, *Appl. Phys. Lett*., **85**, 3486 (2004).
8. Z.G. Yi, Q.F. Fang and X.P. Wang, *Solid State Ion*., **160**, 117 (2003).
9. D. Marrero-López, J. Pena-Martínez, D. Pérez-Coll and P. Núnez, *J. Alloys Comp*., **422**, 249 (2006).
10. A. Subramania, T. Saradha and S. Muzhumathi, *Mater. Res. Bull*., **43**, 1153 (2008).
11. S. Georges, R.A. Rocha and E. Djurado, *J. Phys. Chem. C*, **112**, 3194 (2008).