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Preparation of La-Ti Composite Oxide Nanocrystal and Examination of Their Surface Topography with Atomic Force Microscope

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Abstract：With sol-gel method, nanometer La-Ti composite oxide was successfully prepared at a low temperature (750～800°C) using polyethylene glycol as dispersant. By means of atomic force microscope, the surface pattern, particle size distribution, and specific surface area were studied. The compound particle surface appears as a smooth sheet, the mean size of the compound is 25.38 nm. On the specific surface, the particle erects at a height of 4.69 nm. The surface area is 58.90 nm^2. The La-Ti composite oxide nanocrystal prefers to narrow and even particle size distribution and the homogeneity of surface topography.

Keywords: La-Ti composite oxide, nanocrystal, surface pattern, atomic force microscope.

Atomic force microscope (AFM) is a kind of scanning probe microscope (SPM) derived from scanning tunnel microscope (SCM)[1,2]. Enjoying such advantages as simple preparation of sample and nanometric differentiation scale [3], AFM is greatly welcome in chemistry, material and biology science research[4~7].

Composite oxides containing rare-earth element and transitional metal such as titanium as the third element enjoy many promising applications owning to their excellent physical and chemical properties. These compounds have been known to be applied to ceramic dielectric materials. With unique outer layer electronic construction ($La4f^05d^16s^2$, $Ti3d^24s^2$), which is full of empty orbits, La-Ti composite oxides are provided with high catalytic activity for organic compound dehydration. Since the activity of catalyst strongly depends on its surface area, to develop convenient and efficient preparation methods for the compounds with sufficiently high specific surface areas is of great importance. Traditionally, the monoclinic system of lanthanum-titanium composite oxide is usually prepared by flux growth method[8~10], and the La_2O_3-TiO_2 series are synthesized by solid phase reaction[11~13]. These methods need high calcination temperature (1300～1675°C) and often result in coarse aggregation. The grain size of the products obtained by these methods is large (in micron scale) and the specific surface area is rather small (less than 10 m^2/g). If they are used as catalyst for organic synthesis, they can not be dispersed well in reaction system, conglomerate easily,

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and can not alleviate embedded phenomenon of active center.

Sol-gelatin process has been widely used on synthesizing many kinds of oxide nanocrystal with narrow particle size distribution and phase homogeneity.

In this work, La-Ti composite oxide nanocrystal with high specific surface areas was successfully prepared through sol-gelatin process at a low temperature (750～800°C) using polyethylene glycol(PEG) as dispersant instead of citric acid or other micro-molecule dispersant agents. The surface topography of the compound particle was investigated by atomic force microscope. Nanometer-scale features of the particle size distribution and specific surface area range were described in detail.

Experimental

The precursors utilized for the preparation of La-Ti composite oxides nanocrystals were lanthanum oxide, nitric acid, deionized water, terta-*n*-butyl titanate, polyethylene glycol (PEG), all of analytical reagent grade. The synthesis procedures were as follows: a weighed amount of La_2O_3 was first dissolved by nitric acid, into this La_2O_3 solution an appropriate amount of PEG was added while stirring at ambient temperature, then a transparent solution sol (S1) formed. A stoichiometric amount of $(C_4H_9O)_4Ti$ dispersed in ethanol by swift stirring, a light yellow transparent solution sol (S2) formed. S2 was added dropwise in S1. After complete mixing , the sol was distillated of water entirely at 90°C by vigorous stirring throughout the whole evaporation process. After dehydration, the residue formed a complete homogeneous transparent sol. The sol was slowly cooled to ambient temperature to form a milk white gel. The gel was desiccated at 100°C for ten hours in air, the dry gel was obtained, then the dry gel underwent subsequent heat treatment in air at 750°C for three hours , bright white well-crystallized, and ultrafine La-Ti oxides particles were obtained. The crystalline structure has been reported in another paper[14].

The AFM used for these experiments was a microscope from SPM operating in contact mode and calibrated by imaging mica. A total of 32 images for different scanning scope were collected in the present study. The particle size distribution, the mean size, the mean height, and the specific surface areas were measured and calculated with the CSPM2000 Imager software.

Results and Discussion

Figure 1A shows an ideal representation of the composite oxides surface. The surface sheet consists of well-shaped even particles, which appear in the form of round shape with clear-cut brim and accumulate closely to form an even flake. The three dimensional surface topography patterns show the fluctuation of the compound surface (see **Figure 1B**), the surface is smooth and fluctuates a little and the largest height of the surface outline is 8.96 nm and the mean height of the outline is 4.69 nm, suggesting an accumulation of La-Ti composite oxide nanocrystal with a narrow and homogeneous particle size distribution.

Sixty-five particles are counted out in the scanning scope (see **Table 1**). The

particle size ranges from 5.18 nm to 98.48 nm, and the mean size is 25.38 nm. Eighty percent of the compound particles enjoy a size among 10 nm～32 nm. The compound particle is characterized with specific surface area ranging from 26.31 nm^2 to 1946.21 nm^2, and with a mean surface area of 58.90 nm^2, which is equal to the value examined by BET method[15].

Figure 1a Two dimensional AFM picture patterns of La-Ti composite oxide with a scanning scope of 530.77nm ×530.77nm

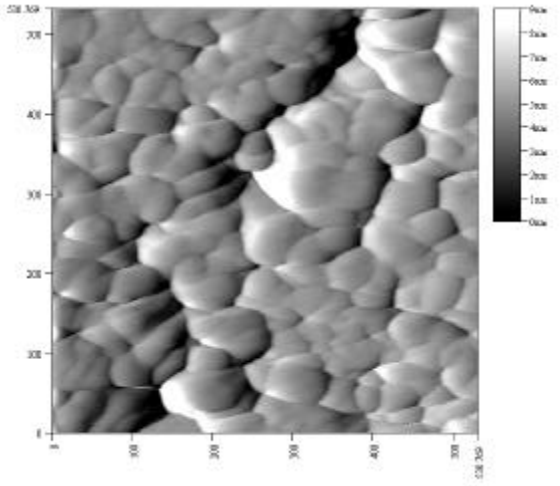
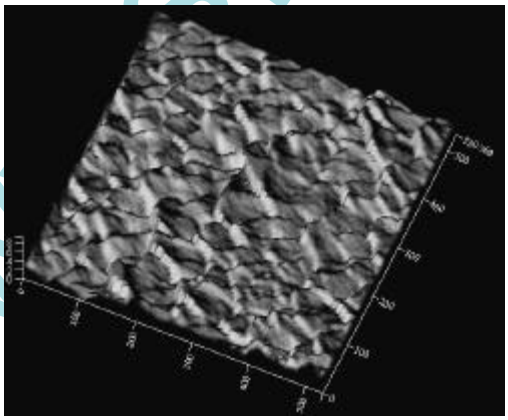


Figure 1b Three dimensional AFM picture patterns of La-Ti composite oxide with a scanning scope of 530.77 nm ×530.77nm



Conclusion

The La-Ti composite organic complexant precursor was prepared by sol-gel method, and the precursor decomposed at a low calcination temperature (750～800°C), the La-Ti composite oxide nanocrystal was successfully obtained. By means of atomic force microscope, the surface pattern, particle size distribution, and specific surface area were studied. The compound particle surface appears as a smooth sheet, the even size of the

compound is 25.38 nm. The surface particle erects at a height of 4.69 nm. The even specific surface area is 58.90 nm^2. The La-Ti composite oxide nanocrystal enjoys a narrow particle size distribution and homogeneity of surface topography.

Table 1 The diameter data of La-Ti composite oxide nanocrystal

Serial number	Particle size(nm)	Serial number	Particle size(nm)	Serial number	Particle size(nm)	Serial number	Particle size(nm)	Serial number	Particle size(nm)
0	13.477	1	19.697	2	17.623	3	19.697	4	27.990
5	30.063	6	17.623	7	62.199	8	8.293	9	14.513
10	15.550	11	11.403	12	13.477	13	21.770	14	21.770
15	11.403	16	65.309	17	38.356	18	31.100	19	12.440
20	17.623	21	12.440	22	5.183	23	21.770	24	31.100
25	16.587	26	98.483	27	27.990	28	29.026	29	13.477
30	18.660	31	14.513	32	12.440	33	53.906	34	21.770
35	16.587	36	19.697	37	13.477	38	14.513	39	26.953
40	25.916	41	19.697	42	21.770	43	29.026	44	64.273
45	13.477	46	29.026	47	27.990	48	8.293	49	35.246
50	45.613	51	21.770	52	15.550	53	33.173	54	19.697
55	48.723	56	14.513	57	21.770	58	47.686	59	43.540
60	17.623	61	17.623	62	24.880	63	16.587	64	21.770

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References

1. M. Radmacher, R. W. Tillmann, M. Fritz, *et al., Science*, **1992**, *257*, 1900.
2. C. l. BAI, *Application of Scanning Tunnel Microscope Technology* (in Chinese), **1992,** 91.
3. S. B. Smith, L. Finzi, C. Bustamante, *Science*,**1992**, *258*,1122.
4. S. P. XING, B.S. LI, C. WANG, Y.X. HU, J. X. LIN, *Chin. Sci. Bull.*, **2000**, *45* (3), 306. (Chinese).
5. H. B. LI, B.B. LIU, X. ZHANG, J.C. SHENG, G.T. ZOU, *ACTA Polymerica Sinica* (in Chinese), **1998**, (4),444.
6. T. Kowalewski, D. M. Holtzman, *Proc. Natl. Acad. Sci.* , **1999**, *96*, 3688.
7. V. J. Morris, A. P. Gunning , A. R. Kirby, *et al., Biological Macromolecules*, **1997**, *21*, 61.
8. M. Yokoyama, *Journal of Crystal Growth*, **1986**, *96*, 90.
9. J. B. Macchesney, H. A. Sauer, *J. Am. Ceram. Soc.* , **1962**,*45* (9), 16.
10. H. Sasaki, Y. Matsuo, *J. Am .Ceram .Soc.*, **1965**,*48* (8),434.
11. M. Kestigian, R. Ward, *J .Am. Soc.*, **1995**, *77* (12), 199.
12. Y. Xiang, J. M. Hao, H. Zhang, D. H. Xie, W. G. Mei, *Silicate Bull.*(in Chinese), **2001**, *2*, 51.
13. T. Y.Tien, F. A. Hummel, *Brit. Ceram. Soc.*, **1967**, *66*, 233.
14. Y. L. Wang, L. Gu, J. H. Wang, J. Pan, China *Patent*, **2002**, No.02113313.1
15. L. Gu, Y. L. Wang, J. H. Wang, *et al., Chinese Powder Technology* (in Chinese), **2002**, *8* (2), 50.

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