THE PREPARATION OF LA-TI COMPOSITE OXIDE NANOCRYSTALLINES 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℃) using polyglcol(PEG) 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 even size of the compound ranges from 19.85nm to 25.38nm.the particle seems smooth, which erects at a high from 4.69nm to 5.88nm.The surface area ranges from $58.90nm^2$ to $1238.04nm^2$. The La-Ti composite oxide nanocrystallines enjoy a narrow and even particle size distribution and accumulate closely.

KEYWORDS: La-Ti composite oxide, nanocrystallines, surface pattern, atomic force microscope

INTRODUCTION

Atomic force microscope(AFM) is a kind of scanning probe microscope(SPM) derived from scanning tunnel microscope(SCM) (Radmacher M, Tillmann R W, Fritz M, et al.; Chunli BAI)[1,2].Based on the principle that oscillation frequency (ω) of atoms approximates to or is more than 10^{13}Hz,the atomic mass (m) is amount to 10^{-25}Kg,the atomic force elastic constant(k), $k=\omega^2 m$,then the scale of k is 10N/m,therefore with an elastic constant less than atomic elastic constant, the probe cantilever tip performs friction action with the sample surface, the cantilever fluctuates according to the appearance of sample surface, accordingly the reflecting light beam occurs excursion, thus by means of the variation of laser facula location detecting by photoelectric diode, the information of sample surface is obtained. Besides the surface pattern, coarseness, height, and particle granularity distribution can be characterized. Enjoying such advantages as simple preparation of sample and nanometric differentiation scale (de Gennes P G; Smith S B, Finzi L, Bustamante C)[3,4], AFM is greatly welcome in chemistry, material and biology (Shuping XING, Bingshi LI, Chen WANG, Yuxi HU, Jinxing LIN; Hongbin LI, Bingbing LIU, Xi ZHANG, Jiacong SHENG, Guangtian ZOU; Kowalewski T, Holtzman D M; Morris V J, Gunning A P, Kirby A R, et al)[5,6,7,8].

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Composite oxides containing rare-earth element and a 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 be applied to ceramic dielectric materials. With unique outer layer electronic construct （$La 4f^0 5d^1 6s^2$, $Ti\ 3d^2 4s^2$）,which is full of empty orbits, La-Ti composite oxides are provided with high catalytic activity for organic compound dehydration. Since the activity of a catalyst strongly depends on its surface area, the development of convenient and efficient preparation methods for the compounds with sufficiently high specific surface areas is of great importance. Traditionally, the monocrystal of Lanthanum-Titanium composite oxide is usually prepared by flux growth method (Mitsunori Yokoyama; Macchesney J B，Sauer H A; Sasaki H,Matsuo Y)[9，10，11],and the La_2O_3-TiO_2 series are synthesized by solid phase reaction (Michael Kestigian,Roland Ward; Yong XIANG, Jianmin HAO, Hao ZHANG, Daohua XIE, Wugang MEI; Tien T Y, Hummel F A) [12，13，14]. The methods needs a high calcinations temperature (1300～1675℃) for the reaction to occur and often results in simple crystalline composition and the formation of coarse aggregation which is difficult to disperse. The grain size of the products obtained by these methods is relatively large (in micron scale) and the specific surface area is rather small (less than $10m^2/g$). If they are used as catalyst for organic material synthesization, they can not be dispersed well in reaction system, conglomerate easily, and can not alleviate embedded phenomenon of active center.

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

In this work, La-Ti composite oxide nanocrystallines with high specific surface areas were successfully prepared through sol-gelatin process at a low temperature (750～800℃) using polyglcol(PEG) as dispersant in stead of citric acid or other micromolecule complexant. The surface topography of compound particles was investigated by Atomic Force Microscope employing laser beam deflection for force detection. Nanometer-scale features of the particle size distribution and specific surface area range were described in detail.

EXPERIMENTAL

The precursor utilized for the preparation of La-Ti composite oxides nanocrystals were lanthanum sesquioxide,nitric acid, deionized water,titanium butoxide, polyglycol (PEG), all of analytical reagent grade.The systhesis 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 appeared a transparent solution sol (S1);a stoichiometric amount of Ti(oBu)4 dispersed in ethanol by swift stirring,a light yellow transparent solution sol (S2) was formed;into S1,S2 was added in the form of little drop,after complete mixing ,the sol was evaporated to eliminate the water entirely at 90℃ 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℃ for ten hour in air, the dry gel was obtained, then dry gel underwent subsequent heat treatment in air at 750℃ for three hour in air, quite fluffy bright white well-crystallized ultrafine La-Ti composite oxides particles were obtained. The crystalline structure has been reported in another paper (Yuanliang WAN, Li GU, Jianhua WANG, Jun PAN)[15].

The AFM used for these experiments was a microscope (nanoscope II head with nanoscope III data acquisition system) from SPM operating in contact mode and calibrated by imaging mica. La-Ti composite oxides were put into the mould of compactor, and an appropriate force was employed on the sample, a few minutes later a round thin flake was obtained. The AFM tip was carefully placed in the middle of a flake. The images reported contain 512 x 512 data points and nearly all images were acquired at a scan rate of 10～20 lines/s. The Si_3N_4 cantilevers (with integral tips) used for imaging were 120 μ m in length and possessed a spring constant of 0.6N/m.The force applied was about 1nN;this information was obtained using the force calibration technique contained in the AFM software package. A total of 32 images for different scanning scope were obtained 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.

RESULT AND DISCUSSION

When an AFM is operated in a contact mode, the tip of the cantilever is in contrast contact with the surface where it fluctuates according to the surface topography in a manner controlled by repulsive forces. This mode of operation provides high resolution but it can also provide artifacts resulting from morphologic deformation induced by the shape of the probe and by the rigidity of the cantilever in use. The imaging force, the large contact area between the tip and the surface, the tip profile, and the viscoelastic properties of the samples are the main source of image artifacts while studying hard surfaces.Contact mode image artifacts resulting from tip-surface interactions can be minimized by operating the AFM in a tapping mode but at the expense of resolution.

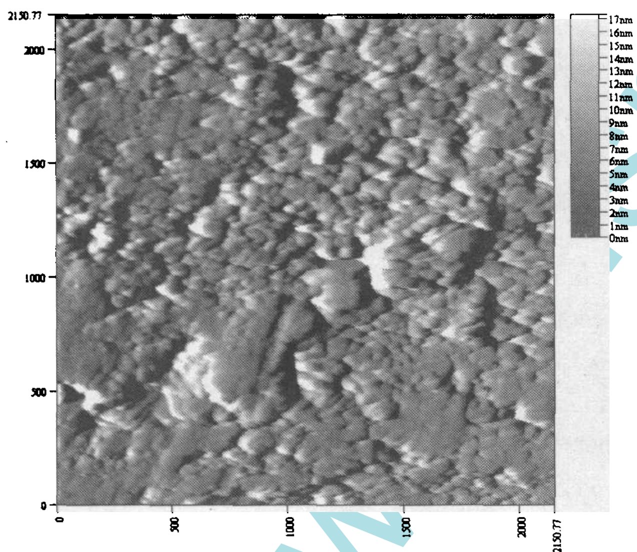


Fig.1a Two dimensional AFM picture patterns of La-Ti composite oxide with a scanning scope of 2150.77nm＊2150.77nm

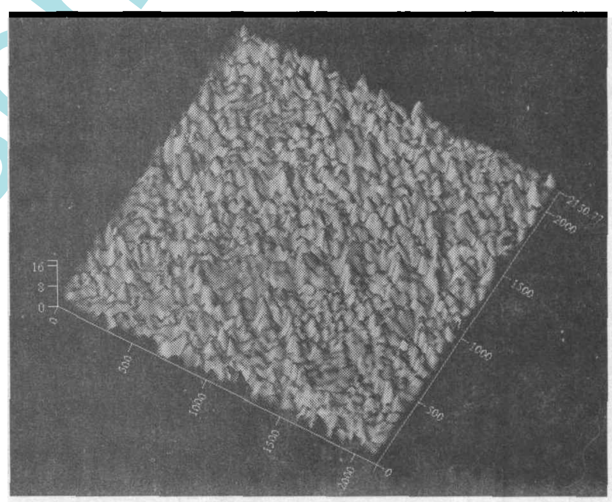


Fig.1b Three dimensional AFM picture patterns of La-Ti composite oxide with a scanning scope of 2150.77nm ＊2150.77nm

Large scope scanning images of surface topography: Figure1A shows an ideal representation of the composite oxides surface. The surface sheet consists of well-shaped even particles, which arrange in order closely. Three hundred particles are counted out in the scanning scope. The mean size of particles is 28.84nm, the mean surface area is 2612.70nm^2.The three dimensions surface topography pattern is shown in figure1B. The largest height of the surface outline is 17.04nm, and the even height of the outline is 2.95nm.The surface of the compound appears smooth and fluctuates a little, which suggests the narrow size distribution of compound particles and the homogeneity of surface topography.

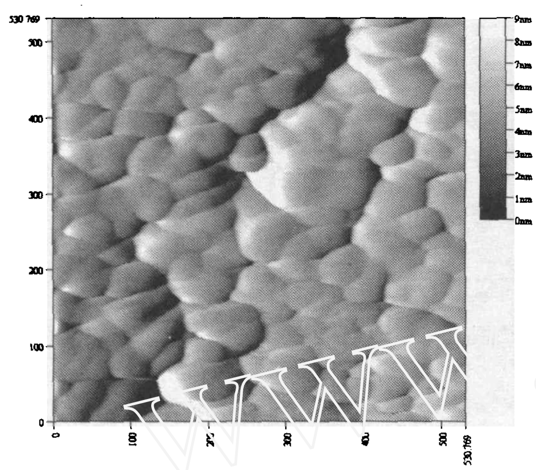


Fig.2a Two dimensional AFM picture patterns of La-Ti composite oxide with a scanning scope of 530.77nm＊ 530.77nm

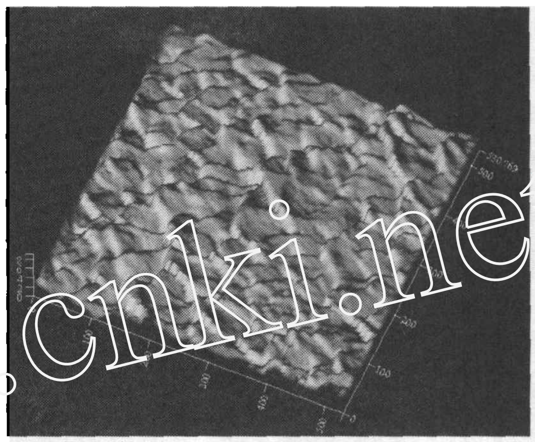


Fig.2b Three dimensional AFM picture patterns of La-Ti composite oxide with a scanning scope of 530.77nm＊ 530.77nm

Small scope scanning images of surface topography: Zooming out the image by reducing scanning scope, figure2A shows a quite clear image of the compound surface sheet. The particles appear in the form of round shape with clear-cut brim and accumulate closely to form an even sheet. Sixty-five particles are counted out in the scanning scope (seeing table 1).

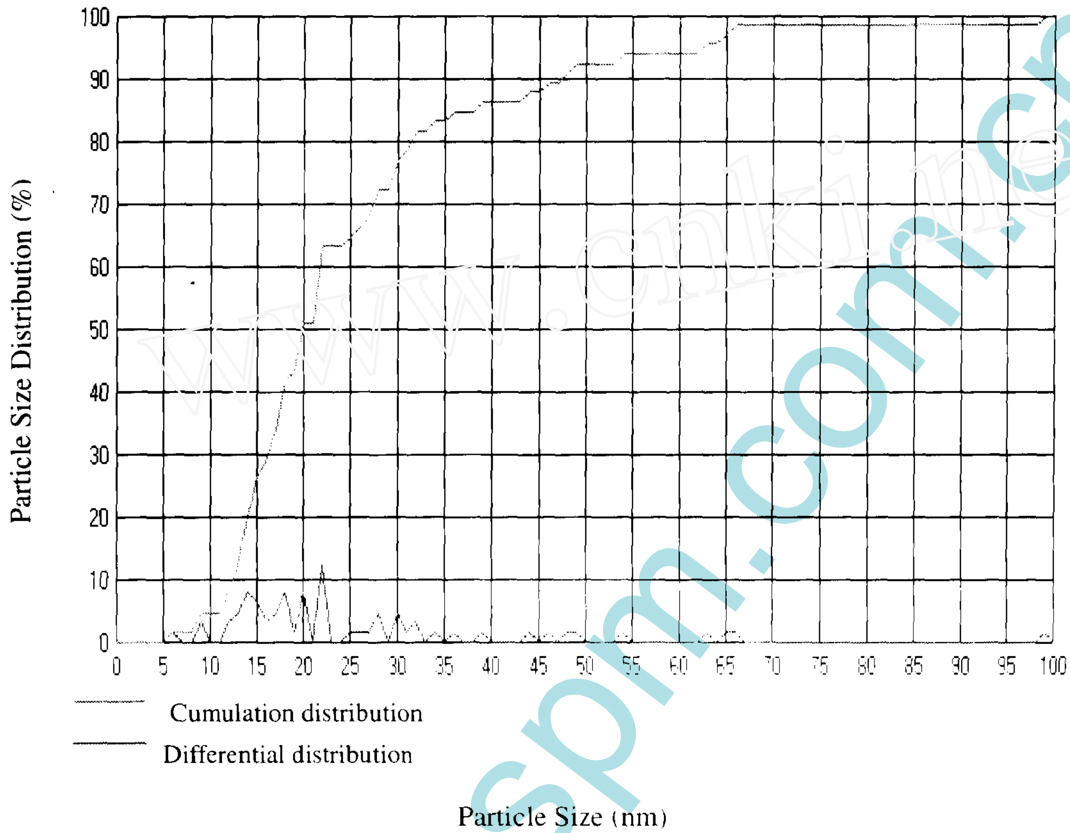
Table2. The diameter data of La-Ti composite oxide nanocrystallines

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

The particle size ranges from 98.483nm to 5.183nm, and the mean size is 25.38nm. Eight percent of the compound particles enjoy a size among 10nm～32nm (seeing figure 3). The compound particle is characterized with specific surface area ranging from 1946.21nm^2 to

26.31nm^2, and with a mean surface area of 58.90nm^2, which is equal to the value examined by BET method (Li GU, Yuanliang WANG, Jianhua WANG, et al.)[16]. The three dimensional surface topography patterns show the fluctuation of the compound surface (seeing figure2B), The largest height of the surface outline is 8.96nm and the mean height of the outline is 4.69nm, which suggesting an accumulation of La-Ti composite oxide nanocrystallines with an narrow and even particle size distribution.

Fig.3 Particle diameter curve of La-Ti composite oxide



Scanned by AFM and calculated by calculated with the CSPM2000 Imager software, the compound particle size is equal to the value calculated by Sherri formulae according to X-ray powder diffraction spectrum (Li GU, Yuanliang WANG, Jianhua WANG, et al.)[16]. So the result examined by AFM is confirming.

CONCLUSION

The La-Ti composite organic complexant precursor was prepared by sol-gel method, and the precursor decomposed at a low calcinations temperature (750～800℃), the La-Ti composite oxide nanocrystallines were 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 ranges from 19.85nm to 25.38nm.the particle seems smooth, which erects at a high from 4.69nm to 5.88nm.The surface area ranges from 58.90nm^2 to 1238.04nm^2. The La-Ti composite oxide nanocrystallines enjoy a narrow and even particle size distribution and accumulate closely.

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