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# Surface topography of La-Ti composite oxide nanocrystallines examined with atomic force microscope①

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**Abstract:** By means of atomic force microscope, the surface pattern, particle size distribution, and specific surface area of La-Ti composite oxide were studied. The compound particle surface appears as a smooth sheet, the even size of the compound ranges from 19.85 nm to 25.38 nm. The particle seems smooth, which erects at a height from 4.69 nm to 5.88 nm. The surface area ranges from 58.90 $nm^2$ to 1 238.04 $nm^2$. The La-Ti composite oxide nanocrystallines enjoy a narrow and even particle size distribution and accumulate closely.

**Key words:** La-Ti composite oxide; nanocrystallines; surface pattern; atomic force microscope

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## 1 INTRODUCTION

Atomic force microscope (AFM) is a kind of scanning probe microscope (SPM) derived from scanning tunnel microscope (STM)[1, 2]. Based on the principle that oscillation frequency ($\omega$) 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 $k = \omega^2 m$, whose scale is 10 N/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[3, 4], AFM is greatly welcome in chemistry, material and biology[5, 6].

Composite oxides containing rare-earth element and a transitional metal such as titanium as the third element enjoy many promising applications owing to their excellent physical and chemical properties. These compounds have been known to 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 was usually prepared by flux growth method[7, 8], and the $La_2O_3$-$TiO_2$ series were synthesized by solid phase reaction[9, 10]. The methods need a high calcinations temperature (1 300~ 1 675 ℃) for the reaction to occur and often resulted in simple crystalline composition and the formation of coarse aggregation which was difficult to disperse. The grain size of the products obtained by these methods was relatively large (in micron scale) and the specific surface area was rather small (less than 10 $m^2/g$). If they were used as catalyst for organic material synthesis, they could not be dispersed well in reaction system, conglomerate easily, and could not alleviate embedded phenomenon of active center.

Sol-gel process has been widely used in synthesizing many kinds of oxide nanocrystallines with narrow particle size distribution and phase homogeneity.

In this work, La-Ti composite oxide nanocrystallines with high specific surface areas were success-

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fully prepared through sol-gel process. 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.

## 2 EXPERIMENTAL

Fluffy bright white well-crystallized ultrafine La-Ti composite oxides particles were obtained by sol-gel method and the crystalline structure was reported in Ref. [11] .

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 × 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 μm in length and possessed a spring constant of 0.6 N/m. The force applied was about 10 N; 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 Image software.

## 3 RESULTS 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 sources 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.

**Large scope scanning images of surface topography:** Fig. 1 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 28.84 nm, the mean surface area is 2 612.70 $nm^2$. The three dimensions surface topography pattern is shown in Fig. 2. The largest height of the surface outline is 17.04 nm, and the even height of the outline is 2.95 nm. 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.

**Small scope scanning images of surface topography:** Zooming out the image by reducing scanning scope, Fig. 3 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.

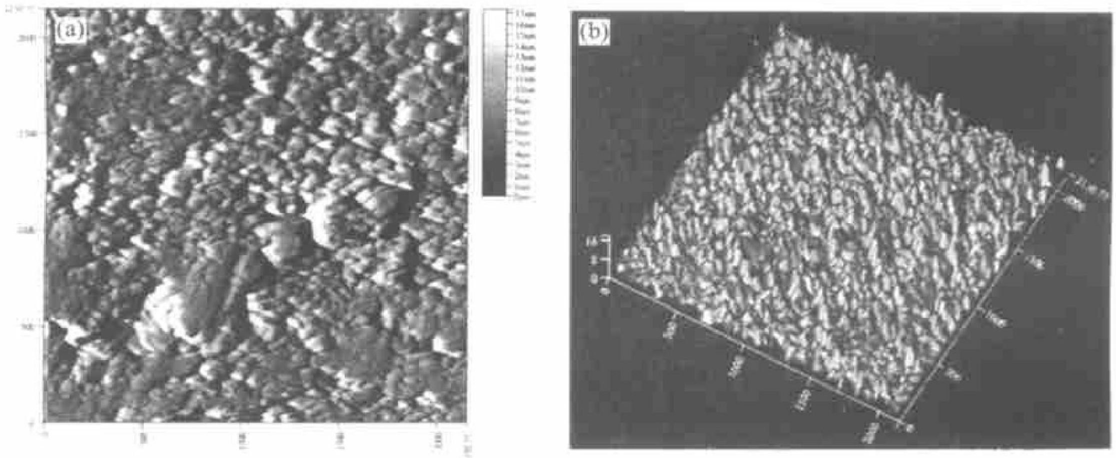


**Fig. 1** AFM picture patterns of La-Ti composite oxide with scanning scope of 2 150.77 nm × 2 150.77 nm

(a) —Two dimensional; (b) —Three dimensional

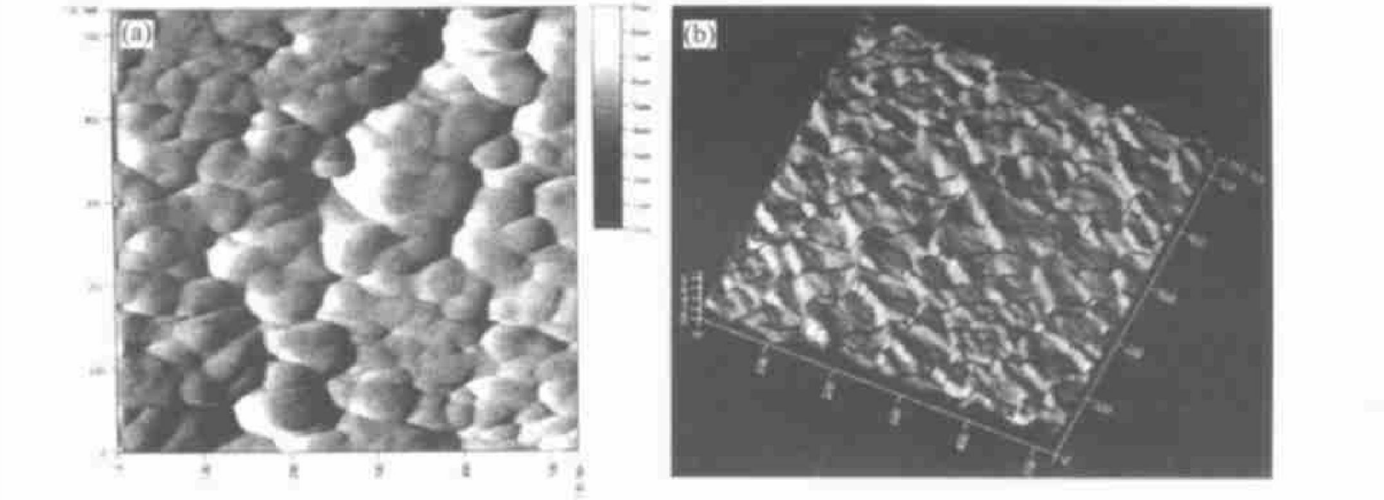

**Fig. 2** AFM picture patterns of La-Ti composite oxide with scanning scope of 530.77 nm × 530.77 nm
(a) —Two dimensional; (b) —Three dimensional

There are sixty-five particles in the scanning scope (see Table 1). The particle size ranges from 98.483 nm to 5.183 nm, and the mean size is 25.38 nm. Eighty percent of the compound particles enjoy a size among 10 nm~ 32 nm (see Fig. 3). The compound particle is characterized with specific surface area ranging from 1 946.21 $nm^2$ to 26.31 $nm^2$, and with a mean surface area of 58.90 $nm^2$, which is equal to the value examined by BET technology [11]. The three dimensional surface topography patterns show the fluctuation of the compound surface, the largest height of the surface outline is 8.96 nm and the mean height of the outline is 4.69 nm, which suggesting an accumulation of La-Ti composite oxide nanocrystallines with an narrow and even particle size distribution.

Scanned by AFM and calculated with the CSPM2000 Image software, the compound particle size is in close agreement with the value calculated by Sherri formula according to X-ray powder diffraction spectrum [11]. So the result examined by AFM is confirming.

**Table1** 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 |

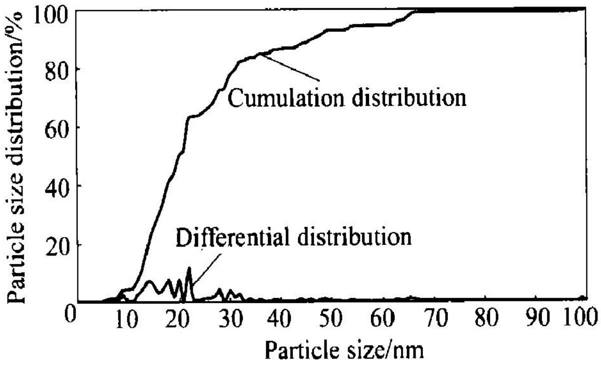


**Fig. 3** Particle diameter curve of La-Ti composite oxide

## 4 CONCLUSIONS

The La-Ti composite organic complexant precursor was prepared by sol-gel method. 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. 85 nm to 25. 38 nm. the particle seems smooth , which erects at a height from 4. 69 nm to 5. 88 nm. The surface area ranges from 58. 90 $nm^2$ to 1 238. 04 $nm^2$. The La-Ti composite oxide nanocrystallines enjoy a narrow and even particle size distribution and accumulate closely.

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