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Multifractal Analysis of Morphology of TiO_2 Nano-films

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Abstract: The SEM and AFM images of three TiO_2 nano-films prepared at different conditions were obtained and transformed into digital format. The multifractal analyses for three films were made using height from a depth of thickness of film B and q from 55 to -55. The scale-invariance is very good for all $\ln\chi_q(\varepsilon)$~$\ln\varepsilon$ plots and $\tau(q)$~q plots at least close to three orders of magnitude. But the multifractal spectra f(a) of the films are quite distinct due to their different height distribution.

Keywords: TiO_2 nano-films, surface morphology, multifractal spectra.

TiO_2 nano-films have attracted considerable interests in recent years due to their potential applications in many fields like photocatalytic degradation of organic compounds in water or air, solarcells, gas sensors and photoelectric devices. It is realized that geometrical imperfections of surface play a key role in many interfacial processes. For example, it is necessary to increase roughness of the surface for the photocatalytic degradation of organic compounds. Fractal feature is used to characterize surface imperfections morphology. Since the complexity of the surface microstructure, the quantity characterization is still a major project. Xagas *et al*[1,2] have studied the fractal feature of titanium oxide film surface and discussed a relationship between photocatalysis, light absorption and fractal dimension. But they also found that the fractal dimension showed different value when the scan range was taken with different size R. In fact, simple fractal dimension only presents a total description of surface morphology, but can not show the detailed information of the surface. Regular fractal has ideal scale-invariance. However, the range of scale-invariance of random is related to calculation method. Sun *et al*[3] studied the multifractal features of ZnO films by using a surface height based on different zero levels. They found that the obtained results satisfied well the scaling law only when the heights were taken based on a depth from the surface or based on the bottom of the film. Such a method provide greater in sight into the morphology properties than the simple fractal dimension. This paper reports the results of multifractal analysi on three TiO_2 nano-films manufactured by dip-coating method from TiO_2 reverse micelle solution.

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Experimental

The TiO_2 nano-films were prepared by dip-coating method from a TiO_2 reverse micelle solution at different aging. The reverse micelle solution composition was H_2O: Triton X-100: titanium isobutoxide =4:2:1. Film A was dipped once immediately in the as-prepared reverse micelle solution, film B was dipped ten times in the as-prepared reverse solution, film C was dipped once in the reverse micelle solution which has been aging six hours. The films were heated to 450°C with a rate of 15°C/min, and then kept constant for 15 minutes. The SEM images were obtained using HITACHI S-520 scanning electronic microscope, and AFM images were obtained using THERMOMICROSCOPES AUTOPROBE CP. The images were transformed to digital by program Matlab 5. The multifractal analysis was done using Matlab 5 and Oringin 5. All calculations were carried out on Pentium III733 computer.

Results and Discussion

From the SEM and AFM images it was observed that the nano-particles with dimension about 60 nm were aggregated in different way formed second particle agglomerates, and thus lead a roughness increase in order from film A to film C.

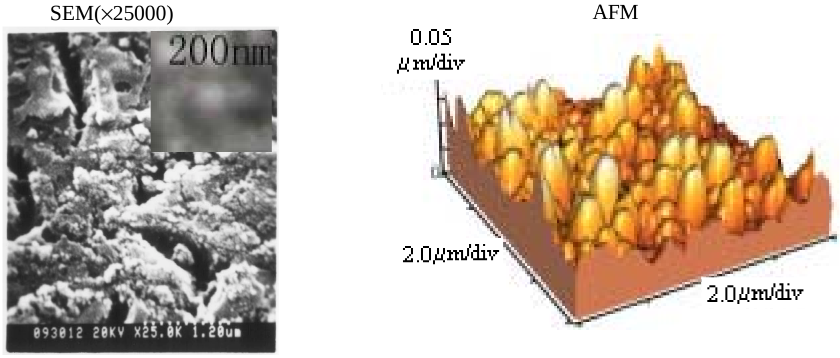
Figure 1 illustrates the SEM image and AFM image of film B. The multifractal analysis of a measure can be made using the following expression. Where ε is the box size of a measure, $P_{ij}(\varepsilon)$ is the probability of height distribution of film in the box(i,j) at the measure(ε), $\chi_q(\varepsilon)$ is the partition function for ε measure, q is a weight index of the partition function, a is Hölder singular index,and f(a) is the multifractal spectra, which describes a nature of inhomogeneous distribution in height of film(The f(a) presents the Hausdorff dimension for fractal subset x_a.)

$$\chi_q(\varepsilon) = \sum P_{ij}(\varepsilon)^q = \varepsilon^{\tau(q)} \quad (1)$$

$$\tau(q) = \lim[\ln \chi_q(\varepsilon) / \ln \varepsilon] \quad (2)$$

Figure 1 The images of SEM and AFM of film B

SEM(×25000) AFM

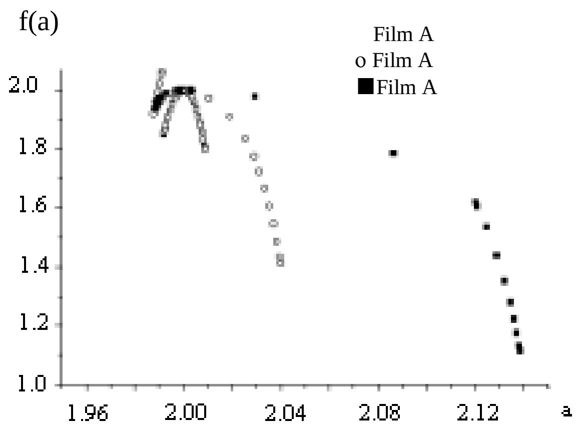


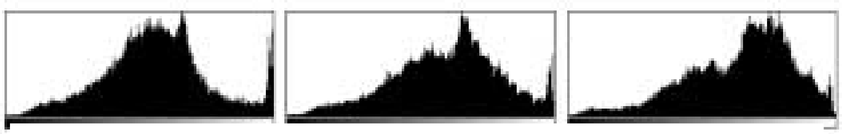
$$a = d[\tau(q)]/dq \qquad (3)$$

$$f(a) = aq - \tau(q) \qquad (4)$$

Here on the basis of the AFM images, the height from the depth that equals to the thickness of film B is used to calculate P_{ij} and q ranges from 55 to -55. The calculated results indicated that the scale-invariance is very good close to three orders of magnitude for all $\ln\chi_q(\varepsilon)$~$\ln\varepsilon$ plots and $\tau(q)$~q plots. The f(a) spectra are shown in **Figure** 2. It can be seen that the right-hand-side in the f(a) curves shows a distinct progression to larger values of a , showing the increase in the roughness from film A to film C. The f(a) curve of film A is bell-like and smooth, however, the left-hand-side of f(a) spectra of film B and film C appear some singular points, which is different from the results on ZnO_2 films calcined at different temperatures by Sun et.al[3] . According to the study by Sun[3] et.al, the f(a) curve shape should be bell-like and smooth if the scale-invariance is very good. But this is based on a hypothesis that the height distribution consists with Gauss model. In the present work, the height distribution of film A is close to Gauss model, but the height distribution of film B and film C seems to split gradually to two Gauss-close distributions. Moreover, two sub-distributions of the films are in an intercross (see **Figure** 2). Therefore, such a characteristic of f(a) plots in film B and C may relate to the two sub-distributions of the films, and show a coexisting nature of the original particles and secant particles (aggregates).

Figure 2 The f(a) spectra and height distribution from AFM images of three films





Film A Film B Film C

H distribution of AFM images

We also made the multifractal analysis for the SEM images of three films. A very good scale-invariance was obtained for all $\ln\chi_q(\varepsilon)$~$\ln\varepsilon$ plots and $\tau(q)$~q plots at least close to three orders of magnitude. The splitting of f(a)~a dot set was also observed. This is consistent with the multi-Gauss height distribution of surface of the films.

In summary, a good scale-invariance was obtained by using multifractal analysis for three TiO_2 films prepared at the different condition. The obtained multifractal spectra f(a) of the films showed significantly distinction between these films. These results indicate that the multifractal analysis may well characterize the morphology properties of TiO_2 nano-films, and may be an efficient tool for understanding the relationship of physical chemistry properties with morphology nature of films.

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