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Atomic Force Microscopy Studies on the Chemical Treatment of Nanocrystalline Porous TiO_2 Films

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Abstract: AFM has been utilized to study the surface topography and the local conductivity of nanocrystalline TiO_2 films. Improving the local conductivity by Ti(*iso*-$C_3H_7O)_4$ treatment is characterized by quantitative analysis of the simultaneous current image. The mechanism of Ti(*iso* $C_3H_7O)_4$ treatment is discussed.

Keywords: Nanocrystalline TiO_2 films, chemical treatments, AFM topography, local conductivity.

Dye-sensitized solar cell based on the nanocrystalline TiO_2 films exhibits a high light-to-electrical conversion efficiency. Our recent work revealed that the chemical treatments to modify the microstructure and the surface properties of nanocrystalline TiO_2 films could successfully improve the photovoltaic behaviors of this cell[1]. In this work, we examine the modification of nanocrystalline TiO_2 films by chemical treatment of Ti(*iso*-$C_3H_7O)_4$ using atomic force microscopy (AFM).

Nanocrystalline TiO_2 films consisted of anatase nanoparticles with average size of 12 nm were prepared. The detailed procedures of preparation were indicated elsewhere[1]. Chemical treatment were performed by dipping the TiO_2 films in 0.2 mol/L Ti(*iso*-$C_3H_7O)_4$ solution for 10 h and followed by sintering at 450°C for 30 min..

AFM was measured on Seiko SPL-3800N scanning probe microscope. Topographies and current images were simultaneously recorded by using conductive Si cantilever coated with Au under bias in air *via* AFM feedback control.

AFM capable of simultaneous imaging the topography and the local current allow for a direct comparison between the surface topographic structure and local conductivity of nanocrystalline TiO_2 films. AFM topographies and the simultaneous current images are illustrated in **Figure 1**. The aggregated TiO_2 nanoparticles with different sizes constructing a porous structure are observed in the topographies of **Figure 1(a)** and **Figure 1(b).** The surface shows jagged features with different heights indicated in the respective gray scales. A great difference appeared in the simultaneous current images of **Figure 1(c)** and **Figure 1(d)**. The

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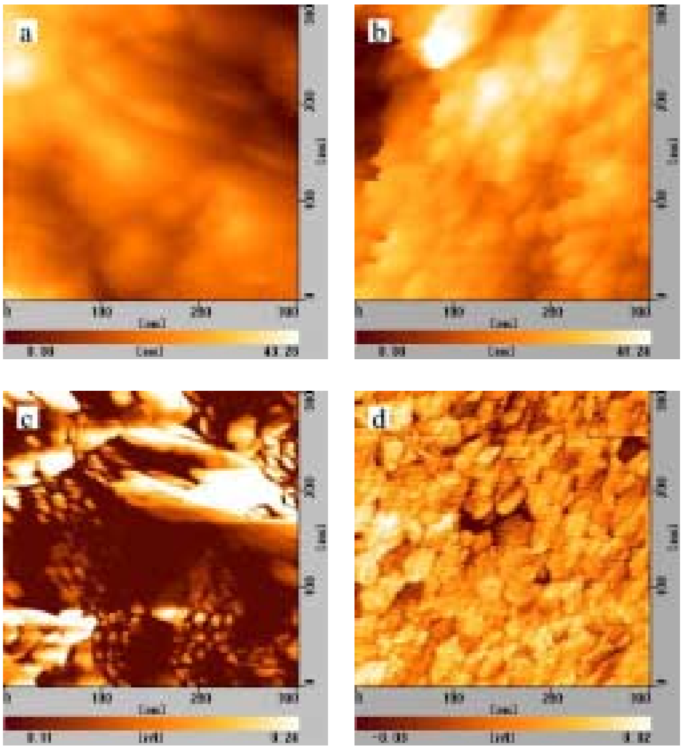
Figure 1 AFM topographies (a,b) and the simultaneous current images (c,d) of TiO_2 films before (a,c) and after (b,d) Ti(*iso*-$C_3H_7O)_4$ treatment, bias is 6V(c) and 2V (d).



probability distribution of the local conductivity calculated from the simultaneous current images can give an insight into the difference between the simultaneous current images before and after chemical treatment. As shown in **Figure 2(a),** the probability distribution of the local conductivity of nanocrystalline TiO_2 films is in the low conductive range of 0.018 nS-0.040 nS. Further evaluation from the integrated probability distribution indicates the probability of 45% is < 0.022 nS and only 10% is > 0.038 nS. After Ti(*iso*-$C_3H_7O)_4$ treatment, the probability distribution of local conductivity shown in **Figure 2(b)** is mainly in the larger conductive ranges of 0.060 nS-0.085 nS. The standard deviations calculated from **Figure 2(a)** and **Figure 2(b)** are 0.007 and 0.004 respectively. This results give a strong evidence that the local conductivity of the nanocrystalline TiO_2 films is improved significantly in the magnitude and the uniformity after the Ti(*iso*-$C_3H_7O)_4$ treatment.

Figure 3 shows the FFT results of the simultaneous current images of nanocrystalline TiO_2 films. The symmetrical diffraction lines have appeared in the FFT results of simultaneous current image after treatment of Ti(*iso*-$C_3H_7O)_4$ indicating a regular feature in the simultaneous current image. This may be attributed to the effects of Ti(*iso*-$C_3H_7O)_4$ treatment which modified the microstructure and the surface properties by fresh growth of anatase nanocrystallites on the porous network due to the hydrolysis of Ti(*iso*-$C_3H_7O)_4$ during the treatment. The freshly grown nano- crystallites increase the electrical contact between the TiO_2 nanoparticles and consequently improving the local conductivity and the photovoltaic behaviors.

Figure 2 Probability distribution and the integrated probability distribution of the local conductivity of TiO_2 films before (a) and after treatment (b).

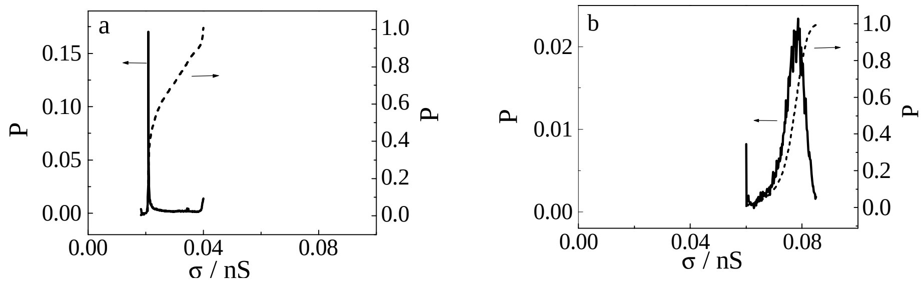
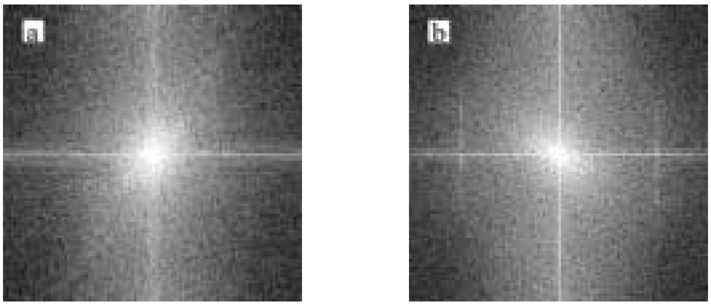


Figure 3 FFT results of current images of TiO_2 films before(a), and after treatment (b)



Conclusions

A direct comparison between the surface topographic structure and the local conductivity of nanocrystalline TiO_2 films are performed by using AFM. Quantitative analysis of the simultaneous current images indicates an improvement of the local conductivity of nanocrystalline TiO_2 films by Ti(*iso*-$C_3H_7O)_4$ treatment.

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Reference

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