

## Time-resolved Microwave Conductivity Studies on the Chemical Treatment of the Nanocrystalline Porous TiO<sub>2</sub> Films

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**Abstract:** Effect of Ti(*iso*-C<sub>3</sub>H<sub>7</sub>O)<sub>4</sub> treatment on the photoinduced charge carrier kinetics of nanocrystalline porous TiO<sub>2</sub> films is studied by time-resolved microwave conductivity measurements. Analysis of the transient photoconductivity decays indicates that Ti(*iso*-C<sub>3</sub>H<sub>7</sub>O)<sub>4</sub> treatment leads to an increased concentration of photogenerated charge carriers and a fast interfacial transfer rate of holes *via* the surface modification of the freshly growing TiO<sub>2</sub> nanocrystallites.

**Keywords:** Nanocrystalline porous TiO<sub>2</sub> films, chemical treatment, transient photoconductivity, charge carrier kinetics, time-resolved microwave conductivity.

Our previous work revealed that the photoelectrical response of nanocrystalline TiO<sub>2</sub> films was increased efficiently by chemical treatment<sup>1</sup>. The effect of Ti(*iso*-C<sub>3</sub>H<sub>7</sub>O)<sub>4</sub> treatment on the surface topography and local conductivity of nanocrystalline TiO<sub>2</sub> films was examined previously by using AFM<sup>2</sup>. In this work, we present recent results concerning the influence of Ti(*iso*-C<sub>3</sub>H<sub>7</sub>O)<sub>4</sub> treatment on the charge carrier kinetics of nanocrystalline TiO<sub>2</sub> films studied by time-resolved microwave conductivity (TRMC) method.

In the TRMC measurements, a change of the transient photoconductivity induced by excess charge carriers under a laser pulse excitation is measured by the absorption of microwave power. The adsorbed microwave power related to the change of the transient photoconductivity is proportional to the photogenerated charge carrier concentration and their mobility. In the case of TiO<sub>2</sub>, the mobility of electron is much larger than that of hole, the change of the photoconductivity should be therefore attributed to the contribution of the electrons<sup>3</sup>. Microwave transient conductivity as a contactless measurement can provide detailed insights into charge carrier kinetics including photogeneration, recombination and interfacial transfer of charge carriers associated with the photoelectrochemical processes.

Nanocrystalline TiO<sub>2</sub> films prepared on the glass sheets (1×2 cm<sup>2</sup>) were used as

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samples. The average size of anatase particles was 12 nm and the film thickness was 8  $\mu\text{m}$ . Chemical treatment was performed by dipping the films in 0.2 mol/L solution of  $\text{Ti}(\text{iso-C}_3\text{H}_7\text{O})_4$  for 10 h and followed by sintering at 450 °C for 30 min. Adsorption of KSCN was prepared by adding a small amount of 0.1 mol/L KSCN solution to wet the sample. The prepared samples were fitted into the waveguide and were excited in a surface area of 0.2  $\text{cm}^2$  by 50 ns (FWHM) laser pulse at 326 nm through a cupric mesh which served as the short plate. Microwaves produced from the microwave source (10 GHz, 50 mw) injected into the sample through the isolator and circulator. The reflected microwaves were transformed into the voltage signals by a PIN diode detector and were recorded using a digital oscilloscope.

The transient photoconductivity decays after laser pulse excitation of nanocrystalline  $\text{TiO}_2$  films are shown in **Figure 1**. A rise of the photoconductivity signal indicates an increasing concentration of photogenerated carriers (electrons), whereas a decay occurs reflecting the electron decay kinetics which is different for the samples before and after adsorption of KSCN. The decay behavior of the sample before adsorption of KSCN (solid line) is attributed to the loss of electrons due to electron-hole recombination. A pronounced increase of the slower decaying part in the extended time range is probably resulted from the trapping of holes in the defects that leads to a diminished recombination probability. After adsorption of KSCN, photoconductivity decay (dashed line) is expected to involve the contribution of interfacial charge transfer kinetics which competes with charge carrier recombination yielding a complicated decay behavior.

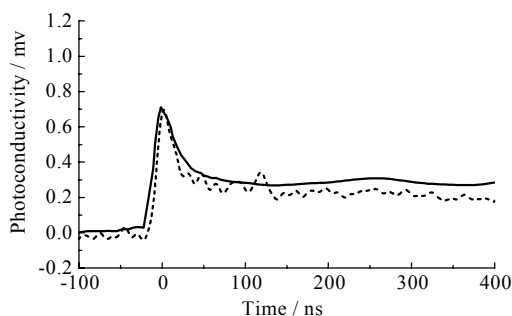
**Figure 2** illustrates the effect of  $\text{Ti}(\text{iso-C}_3\text{H}_7\text{O})_4$  treatment on the transient photoconductivity decays of nanocrystalline  $\text{TiO}_2$  films. As compared with **Figure 1**, there are significant differences in the decay behavior between untreated and  $\text{Ti}(\text{iso-C}_3\text{H}_7\text{O})_4$  treated samples. These differences include: 1. An increment of the maximum signal height is observed in the photoconductivity decay curve of treated sample (**Figure 2**) indicating that the concentration of separated electrons is increased. 2. A much faster decay in the treated sample before adsorption of KSCN manifests the increase of availability of holes for recombination due to eliminating hole-trapping defects by  $\text{Ti}(\text{iso-C}_3\text{H}_7\text{O})_4$  treatment. This would enhance the recombination probability leading to increase the electron decay rate drastically. 3. Photoconductivity decay in the treated sample after adsorption of KSCN is considerably slower than that of before adsorption of KSCN and also than that of untreated sample. This indicates the fast transfer of holes to KSCN taking place in the treated sample owing to eliminating hole-trapping defects effectively by this treatment. In this case, the decay behavior is dominated by the interfacial charge transfer kinetics. The fast interfacial transfer of holes results in a decrease of the recombination probability, that leads to a reducing of the electron decay rate significantly.

The effect of  $\text{Ti}(\text{iso-C}_3\text{H}_7\text{O})_4$  treatment on the transient photoconductivity decays can be explained by surface modification of the nanocrystalline films with freshly growing anatase nanocrystallites due to hydrolysis of  $\text{Ti}(\text{iso-C}_3\text{H}_7\text{O})_4$  during the treatment. The freshly growing anatase nanocrystallites yield an additional photo-generated charge carries and increase the interfacial transfer rate of holes *via* eliminating hole-trapping defects. As a consequence of increasing photogenerated charge carrier concentration and improving the interfacial transfer rate of holes, the photoelectrical

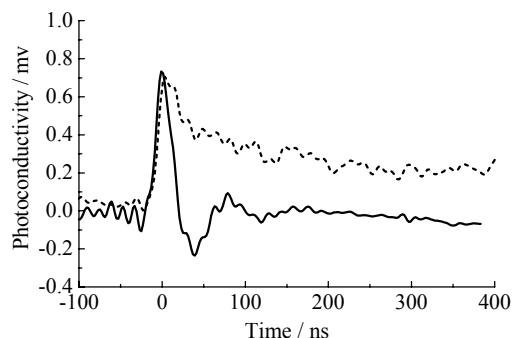
## 736 Time-resolved Microwave Conductivity Studies on the Chemical Treatment of the Nanocrystalline Porous TiO<sub>2</sub> Films

response of nanocrystalline TiO<sub>2</sub> films would increase efficiently.

**Figure 1** Transient photoconductivity decays of nanocrystalline TiO<sub>2</sub> films before (solid line) and after (dashed line) adsorption of KSCN



**Figure 2** Transient photoconductivity decays of Ti(*iso*-C<sub>3</sub>H<sub>7</sub>O)<sub>4</sub> treated nanocrystalline TiO<sub>2</sub> films before (solid line) and after (dashed line) adsorption of KSCN



In summary, TRMC measurements provide direct information on the photoinduced charge carrier kinetics of the nanocrystalline porous TiO<sub>2</sub> films. Ti(*iso*-C<sub>3</sub>H<sub>7</sub>O)<sub>4</sub> treatment influences the charge carrier kinetics in terms of increasing photogenerated charge carrier concentration and improving the interfacial transfer rate of holes *via* eliminating the hole-trapping defects.

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### References

1. D. S. Zhang, Y. Liu, W. B. Wang, X. R. Xiao, *Chin. Sci. Bull.*, **2000**, *45*, 1956.
2. Y. Lin, F. Z. Jiang, J. B. Zhang, Y. L. Song, L. Jiang, X. R. Xiao, *Chin. Chem. Letts.*, **2002**, *13*, 484.
3. K. M. Schindle, M. Kunst, *J. Phys. Chem.*, **1990**, *94*, 8222.

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