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Influence of chemical treatments on the photoinduced charge carrier kinetics of nanocrystalline porous TiO_2 films

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Abstract

Effects of Ti(iso-$C_3H_7O)_4$ and $TiCl_4$ treatments on the photoinduced charge carrier kinetics of nanocrystalline porous TiO_2 films were studied by time-resolved microwave conductivity measurements. Both treatments greatly influence the transient microwave photoconductivity decay behaviors by increasing the photogenerated charge carrier concentration and diminishing the charge carrier recombination via suppressing the hole-trapping defects. This leads to improve the *I–V* behaviors of nanocrystalline porous TiO_2 films effectively. The results are discussed in terms of surface modification of anatase nanocrystallites which grow on the film surface by hydrolysis of Ti(iso-$C_3H_7O)_4$ and $TiCl_4$ during the treatments.

Keywords: Nanocrystalline porous TiO_2 films; Chemical treatments; Photoinduced charge carrier kinetics; Transient photoconductivity decays; Time-resolved microwave conductivity

1. Introduction

There are considerable interests to be attracted in developing semiconductor nanosized particulate thin films from colloidal suspensions or by chemical and electrochemical depositions [1–3]. These particulate films consist of interconnected nanoparticles constructing a porous network structure. A number of interesting physical and chemical properties exhibiting in the particulate films correlate to the particulate porous microstructure, which can be adjustable feasibly during the preparation and post-treatment by chemical modifications [4]. This indicates the potential use in developing a new kind of nanostructural semiconductor materials with expected properties for various applications including light energy conversion [5], electrochromatic [4,6] and non-linear optical devices [7] etc.

Nanocrystalline TiO_2 films are expected to be more importance for photovoltaic applications due to the good stability and inexpensiveness. To take the advantage of the large internal surface area and high porosity of nanocrystalline TiO_2 films, the efficiency of light to electrical conversion has been improved remarkably by dye-sensitization [8,9]. Our previous work revealed that photoelectrical response was increased by Ti(iso-$C_3H_7O)_4$ and $TiCl_4$ treatments in either case of nanocrystalline TiO_2 films with and without dye-sensitization [10]. In order to study the effects of chemical treatments on the photoelectrochemical performance of this films, the microstructure and surface properties after chemical treatments were examined previously by AFM measurements [11,12], which can provide direct information of surface topography and the correlated surface parameters. The results indicated that Ti(iso-$C_3H_7O)_4$ and $TiCl_4$ treatments led to modification of microstructure and improving the local conductivity significantly in the magnitude and uniformity, that would be advantageous to improve the electron transport through the porous network. In this work, we present recent results of the effects of chemical treatments on the photoinduced charge carrier kinetics of nanocrystalline TiO_2 films studied by using time-resolved microwave conductivity (TRMC) measurements.

2. Experimental details

2.1. Preparations and chemical treatments

Colloidal TiO_2 solution was synthesized by hydrolysis of titanium isopropoxide (Ti(iso-$C_3H_7O)_4$, Aldrich, 97%) in

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pH = 1 aqueous solution. Nanocrystalline TiO_2 films were prepared by spreading the synthesized colloidal TiO_2 solution on the SnO_2 conducting glass (F-doped, 30 Ω/sq.) and glass sheet for photoelectrochemical and TRMC measurements respectively and then sintering at 450 °C for 30 min. Prepared films consisted of anatase nanoparticles with average size of 12 nm measured by Raman spectra and STM. Film thickness was 8 μm determined by α-step profilometer and film porosity was 40%. Chemical treatments were performed by immersing the prepared films in 0.2 M aqueous solutions of Ti(iso-$C_3H_7O)_4$ and $TiCl_4$ respectively for 10 h and followed by sintering again at the temperature as mentioned above.

2.2. *Photoelectrochemical measurements*

Photocurrent–voltage (*I–V*) behaviors were measured using Potentiostat/Galvanostart Model 273 in a conventional three electrode system with pt counter electrode and saturated calomel reference electrode at 0.1 M KCNS solution. Two hundred and fifty watts halogen lamp was used as light source. The incident light intensity was 60 mW/cm^2.

2.3. *TRMC measurements*

Nanocrystalline TiO_2 film prepared on a glass sheet (1 × 2 cm^2) was used as sample. Adsorbing KCNS was achieved by adding a small amount of 0.1 M KCNS solution onto the sample surface and drying in the air. The sample was fitted into the waveguide and fixed the position at the distance of 15 nm from the short plate using a plastic block, which was adhered to the inside wall of the waveguide. A cupric mesh was served as the short plate for entering the excitation light and reflecting back the microwave into the waveguide. The sample was excited in a surface area of 0.2 cm^2 by a 50 ns (FWHM) laser pulse at 355 nm generated from a 190 series Nd-YAG laser with 35 mJ per pulse.

Microwaves produced from the microwave source (10 GHz, 50 mW) inject into the sample through the isolator and circulator. The reflected microwaves pass through the circulator to a PIN diode detector, which transforms the microwave power into voltage signals. The voltage signals enlarging 25-fold by a fast preamplifier (Standford Research) and taking an average over 1000 times were recorded in a digital oscilloscope (Lecory 9350). The scheme of the set-up for TRMC measurements is illustrated in Fig. 1.

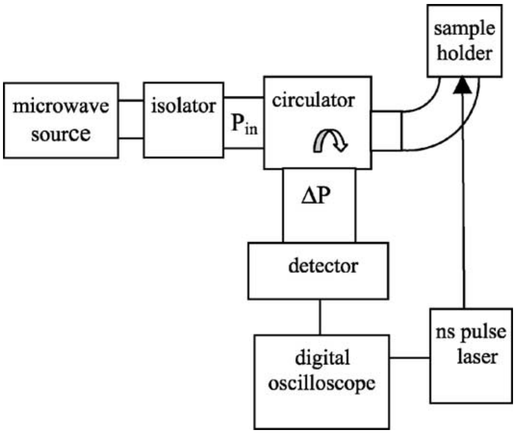

Fig. 1. Scheme of the set-up for TRMC measurements.

3. Results and discussion

Photoelectrochemical (PEC) performance of nanocrystalline TiO_2 films before and after Ti(iso-$C_3H_7O)_4$ and $TiCl_4$ treatments was compared by measuring the photocurrent–voltage (*I–V*) behaviors in 0.1 M KCNS solution. The results are shown in Fig. 2. The increases in the photocurrents over the scanning range of applied voltages are observed obviously for the samples after Ti(iso-$C_3H_7)_4$ and $TiCl_4$ treatments. However, the increased photocurrents are larger in the $TiCl_4$ treated sample as compared to that of the sample treated by Ti(iso-$C_3H_7O)_4$. In order to know the effects of both chemical treatments on the *I–V* behaviors, photoinduced charge carrier kinetics, which is of importance for determining the PEC performance of semiconductor electrodes were studied by TRMC measurements. TRMC method has been developed to study the excess charge carrier kinetics in either semiconductor systems of electrode [13–15] and particulate suspension recently [16–20]. As a contactless technique, this method has the advantage of studying the kinetic processes in a large time range with high resolution and therefore can provide detailed insights into photoinduced charge carrier kinetics including photogeneration, recombination and interfacial transfer processes.

The principles of TRMC method has been discussed previously by a number of authors [13,14,16,18,19]. In this method, a change of the transient photoconductivity $\Delta\sigma(t)$ induced by excess charge carriers of semiconductor after

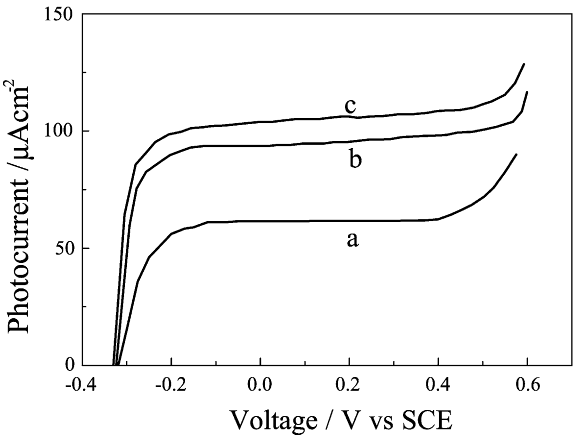

Fig. 2. Photocurrents vs. applied voltages of nanocrystalline porous TiO_2 films (a), after Ti(iso-$C_3H_7O)_4$ treatment (b) and $TiCl_4$ treatment (c), measured in 0.1 M KCNS solution.

a laser pulse excitation is measured by the absorption of microwave power $\Delta P(t)$. The absorbed microwave power correlated to the change of the transient photoconductivity is proportional to the concentration and mobility of photogenerated charge carriers. In the case of TiO_2, the mobility of electron is much larger than that of hole, the changes of transient photoconductivity should be attributed to the contribution of electron and the surface trapping electron, which has the mobility comparable to that of free electron [19]. The relations are expressed as follows:

$$\frac{\Delta P(t)}{P} = A\sigma(t) = Ae(\Delta n(t)\mu_n + \Delta n_T(t)\mu_{n_T}) \qquad (1)$$

where P is the incident microwave power, A the proportionality constant, e the quantity of elementary charge, $\Delta n(t)$, $\Delta n_T(t)$ and μ_n, μ_{n_T} the concentration changes and the mobilities of free electron and surface trapping electron, respectively.

Transient microwave photoconductivity decays after laser pulse excitation were measured for chemical treated and untreated samples of nanocrystalline TiO_2 films. A rise of the photoconductivity signal indicates an increasing concentration of photogenerated electrons, whereas a decay takes place reflecting the decrease of electron concentration due to the loss of electrons by the charge carrier recombination and interfacial charge transfer processes. The kinetic mechanisms of the electron loss processes are different for the samples before and after adsorption of KCNS. Before adsorption of KCNS, the transient photoconductivity decays of chemical treated and untreated samples corresponding to the electron decay processes are dominated by the charge carrier recombination due to the absence of interfacial charge transfer. In the case of the samples after adsorption of KCNS, the transient photoconductivity decays resulting from the loss of electrons are attributed to the competition between interfacial charge transfer and charge carrier recombination. Analysis of the transient photoconductivity decay behaviors of Ti(iso-$C_3H_7O)_4$ and $TiCl_4$ treated and untreated samples in the cases of before and after adsorption of KCNS, the effects of chemical treatments on the photoinduced charge carrier kinetics can be studied.

3.1. Before adsorption of KCNS

Transient microwave photoconductivity decays of untreated and Ti(iso-$C_3H_7O)_4$, $TiCl_4$ treated samples of nanocrystalline TiO_2 films are shown in Figs. 3–5. The solid and dashed lines in these figures represent the transient photoconductivity decays of the samples before and after adsorption of KCNS respectively. In order to analyze the transient photoconductivity decay behaviors, the following bi-exponential equation was used to fit the decay curves,

$$\sigma(t) = A_1 \exp\left(\frac{-t}{\tau_1}\right) + A_2 \exp\left(\frac{-t}{\tau_2}\right) \qquad (2)$$

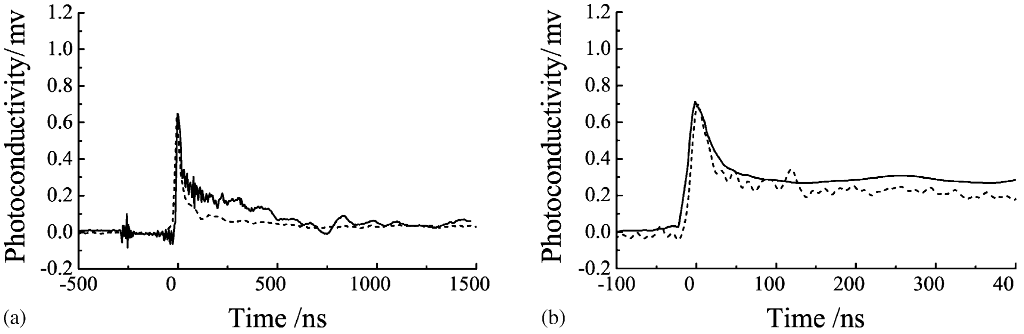

Fig. 3. Transient microwave photoconductivity decays of nanocrystalline porous TiO_2 films at the time-base of 250 ns/div. (a), 50 ns/div. (b), solid line: before adsorption of KCNS, dashed line: after adsorption of KCNS.

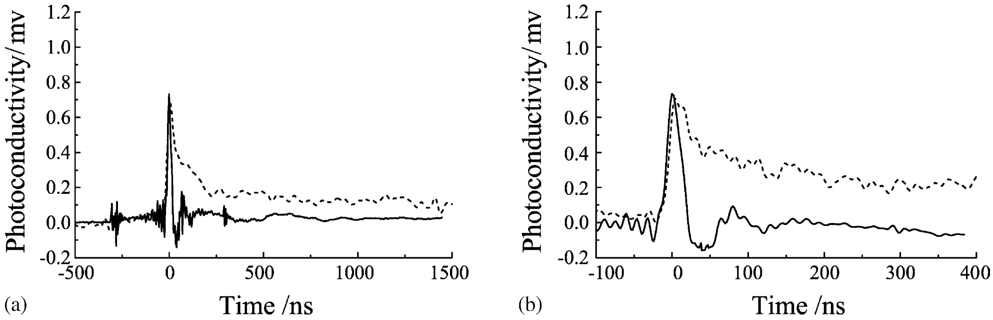

Fig. 4. Transient microwave photoconductivity decays of Ti(iso-$C_3H_7O)_4$ treated nanocrystalline porous TiO_2 films at the time-base of 250 ns/div. (a), 50 ns/div. (b), solid line: before adsorption of KCNS, dashed line: after adsorption of KCNS.

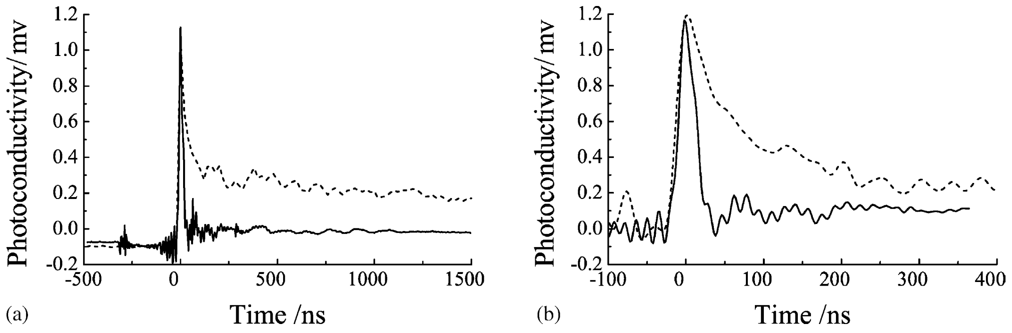

Fig. 5. Transient microwave photoconductivity decays of $TiCl_4$ treated nanocrystalline porous TiO_2 films at the time-base of 250 ns/div. (a), 50 ns/div. (b), solid line: before adsorption of KCNS, dashed lines: after adsorption of KCNS.

where A_1, A_2 refer to the maximum signal heights and τ_1, τ_2 the time constants of the fast and slow components. The accuracy of fitting parameters was <4%. Fitting the solid lines of Fig. 3 shows that the transient photoconductivity decay of untreated sample consists of a fast and a slow processes. As mentioned above, the photoconductivity decay including the fast and slow processes of untreated sample is dominated by the charge carrier recombination kinetics. The fast process of photoconductivity decay is referable to the recombination between electrons (or surface trapping electrons) and holes, which may occur in the timescale of ns. However, the slow process of photoconductivity decay extending to μs probably results from the recombination of electrons (or surface trapping electrons) with the holes trapping on the defects. The recombination of electrons (or surface trapping electrons) with trapped holes may be a slow process. Comparing the fitting results of solid lines in Figs. 4 and 5 with that of Fig. 3, it is found that the transient photoconductivity decays of Ti(iso-$C_3H_7O)_4$ and $TiCl_4$ treated samples are significant different from the decay behavior of untreated sample. The differences include (1) the maximum signal heights in the transient photoconductivity decays of both chemical treated samples are larger than that of the untreated sample indicating that the concentration of separated electrons is increased by both treatments. $TiCl_4$ treatment is seemed to be more efficient for increasing the concentration of electrons leading to a much larger maximum signal height than that of Ti(iso-$C_3H_7O)_4$ treatment; (2) transient photoconductivity decays of Ti(iso-$C_3H_7O)_4$ and $TiCl_4$ treated samples involve only the fast processes and without the slow processes. This result reveals the hole-trapping defects presented in the untreated sample are suppressed effectively by both chemical treatments. As the result, the slow processes caused by the recombination between electrons (or surface trapping electrons) and trapped holes may not occur in the transient photoconductivity decays of both chemical treated samples.

3.2. After adsorption of KCNS

Transient microwave photoconductivity decays after adsorption of KCNS are expected to involve interfacial charge transfer processes which compete with charge carrier recombination processes yielding complicated decay behaviors. The decay behaviors of these samples after adsorption of KCNS illustrated as dashed line in Figs. 3–5 were fitted well to the bi-exponential decay processes. Usually, the rate of hole transfer is in the timescale of ns, which is faster than the rate of electron transfer with the timescale extending from ns to ms [19]. Therefore, the electron decay process determined by the competition between charge carrier recombination and hole fast transfer induces the fast process of the photoconductivity decays, the slow process extending to μs should be assigned to the electron transfer process. The identical time constants of the slow processes in the photoconductivity decays of chemical treated and untreated samples obtained from the fitting results indicate that the electron transfer kinetic processes are not influenced by Ti(iso-$C_3H_7O)_4$ and $TiCl_4$ treatments.

The effects of Ti(iso-$C_3H_7O)_4$ and $TiCl_4$ treatments on the transient microwave photoconductivity decays can be explained by surface modification of nanocrystalline TiO_2 with freshly grown anatase nanocrystallites due to the hydrolysis of Ti(iso-$C_3H_7O)_4$ and $TiCl_4$ during the treatments. Surface modification of freshly grown anatase nanocrystallites yields an additional numbers of charge carriers after laser pulse excitation and diminishes the charge carriers recombination via suppressing the hole-trapping defects. As a consequence of increasing the photogenerated charge carrier concentration and diminishing the charge carrier recombination, the photoelectrical response of nanocrystalline TiO_2 films is improved reasonably.

4. Conclusions

TRMC measurements provide direct information about the influence of Ti(iso-$C_3H_7O)_4$ and $TiCl_4$ treatments on the photoinduced charge carrier kinetics of nanocrystalline porous TiO_2 films. Comparing the different transient microwave photoconductivity decay behaviors between the chemical treated and untreated samples reveals that Ti(iso-$C_3H_7O)_4$ and $TiCl_4$ treatments result in the increases of the photogenerated charge carrier concentration. Diminution of charge carrier recombination via suppressing the hole-trapping defects by these treatments is manifested in the decay behaviors measured before adsorption of KCNS. The transient photoconductivity decays of after adsorption of KCNS is analyzed in terms of the kinetic processes of competition between the charge carrier recombination and interfacial charge transfer indicating that the Ti(iso-$C_3H_7O)_4$ and $TiCl_4$ treatments have no influence on the electron transfer processes. The results are explained by surface modification of the nanocrystalline TiO_2 films with freshly grown anatase nanocrystallites due to the hydrolysis of Ti(iso-$C_3H_7O)_4$ and $TiCl_4$ during the treatments. $TiCl_4$ treatment is more efficient for increasing the photogenerated charge carrier concentration leading the larger increase of the photocurrent response in the *I*–*V* behaviors of nanocrystalline porous TiO_2 films.

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