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PHOTOTHERMAL CHARACTERIZATION OF HIGHLY POROUS, POLYCRYSTALLINE TiO_2 ELECTRODES FABRICATED BY CHEMICAL SYNTHESIS

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Abstract

We report the optical absorption characteristics of highly porous, polycrystalline TiO_2 electrodes and the influence of hydrolysis period for the preparation processes by photoacoustic (PA) spectroscopy together with photoelectrochemical (PEC) current ones. The PA spectra show peaks which are attributed to the lowest transition energy due to the quantum confinement effect. The peak intensity decreases with the increase of hydrolysis periods, indicating the possibilities of the changes in the thermal properties and the densities due to hydrolysis processes. The PEC spectra indicate that the photocurrent intensity also show peak and that of the longer hydrolysis periods is somewhat smaller than others, indicating the increase of interface states due to the formation of grain boundaries with the increase of hydrolysis processes.

Keywords: anatase-type TiO_2 films, chemically synthesized TiO_2 films, photoacoustic spectroscopy, photoelectrochemical current spectroscopy, photothermal effect, porous electrode

Introduction

Titanium dioxide, TiO_2, is a promising candidate for photoanode material because of its high chemical and photoelectrochemical durability [1]. However, TiO_2 has a low solar energy conversion efficiency of less than 4% because of its wide band-gap (~3.0 eV). Dye sensitization is one of the methods used to extend the photoresponse of TiO_2 electrodes to the visible region, where the photoexcited electrons of the dye molecules are transferred to the conduction band of TiO_2. Another method to increase solar energy conversion efficiency of TiO_2 was developed by Graetzel's group. They prepared highly porous, polycrystalline anatase TiO_2 electrodes to increase the surface area by chemical synthesis. The electrodes exhibited high yields for the collection of photoexcited electrons from the absorbed dyes owing to their large surface

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area [2–5]. To realize a more efficient solar energy conversion method than that by organic dye sensitization, Vogel *et al*. used quantum-sized semiconductors (termed nanocrystals of quantum dots) [6] as sensitizers which were adsorbed on highly porous, polycrystalline anatase TiO_2 electrodes [7, 8]. Due to the spatial confinement of the photogenerated charge carriers, they showed that the size quantization effect is useful for band-gap adjustment. In addition to this effect, semiconductor nanocrystals are more stable against photodegradation than laser-grade dyes.

It is necessary to obtain information on the optical absorption properties to investigate the electronic states of the highly porous, polycrystalline TiO_2 matrix. However, few investigations have been carried out on the optical absorption of this material because of the difficulty in using conventional transmission methods caused by the strong scattering in the highly porous structure of TiO_2 electrodes and the presence of a substrate. However, scattering effects can be minimized by employing a photothermal (PT) method. It relies on the existence of a thermal de-excitation branch (Fig. 1), which occurs for most materials. In the PT method, one detects a signal directly proportional to the thermal energy (heat production by non-radiative processes) induced by the absorbed photons. Heat production has been detected by several methods [9]. The PT signal is less sensitive to light scattering effects than conventional spectroscopy signals, and the ability of the PT methods to produce absorption spectra from strongly scattering media has been demonstrated [9–12]. Thus, the PT method is useful for obtaining the absorption spectra of the highly porous, polycrystalline TiO_2 electrodes. The PA method is a PT technique which detects acoustic energy produced by non-radiative processes in materials [13]. PA spectroscopy is useful for obtaining the absorption characteristics of TiO_2 films without removing the substrate [14]. The application of PA spectroscopy for the characterization of semiconductors (including ceramics and nanocrystals) is important because it yields direct information on non-radiative de-excitation energy channels [15–21].

We have reported the photoacoustic (PA) and photoelectrochemical current (PEC) spectra of highly porous, polycrystalline TiO_2 electrodes fabricated by chemical synthesis on which CdS nanocrystals were adsorbed [22]. The PA spectrum shifts

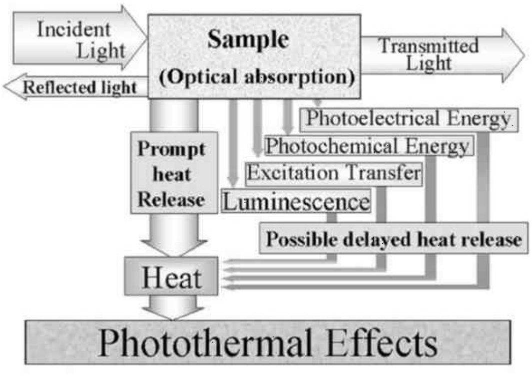

Fig. 1 Schematics of optical absorption and de-excitation channels

to the lower energy region and the PA intensities below the band-gap of TiO_2 increase rapidly with the increase of in the number of CdS coating layers and becomes almost constant. The increase in PEC intensity and a clear shift to lower energy region are also observed with increasing number of CdS coating layers, indicating the possibility of the transfer of photoexcited electrons of CdS nanocrystals to the conduction band of TiO_2 [22]. Also, we have already reported the PA and PEC spectra of highly porous, polycrystalline TiO_2 electrodes to show the effect of the applied voltage treatments [23, 24].

In the present paper, we report for the first time the influence of the hydrolysis period for the preparation processes of TiO_2 electrodes [7] on PA and PEC spectra to clarify the changes of the electronic and thermal conditions of the TiO_2 electrodes. Vogel *et al.* carried out the hydrolysis only at a period of 30 min for the preparation processes of highly porous, polycrystalline TiO_2 electrodes fabricated by chemical synthesis [7].

Experimental

The preparation of TiO_2 films is carried out according to the reference [7]. Ti foil (thickness: 0.2 mm) was washed with chloroform, boiled in 18% HCl for 30 min and then washed with water. Ti sheets were transferred to a hydrolysis box after drying at 60°C. Methanol mixture with $TiCl_4$ was prepared: 10 mL $TiCl_4$+90 mL CH_3OH. First, two drops of solution were dropped onto the horizontally adjusted Ti foil and care was taken to spread the solution uniformly. After a certain hydrolysis time (15, 30 and 60 min), the sheet was heated to 125°C, maintained at this temperature for 5 min, then heated to 450°C for 25 min in air. This procedure was carried out five times for each hydrolysis periods.

The PA cell was composed of an aluminum cylinder with a small channel at its periphery in which a microphone was inserted. The inside volume of the cell was approximately 0.5 cm^3. The cell was suspended by four rubber bands to prevent outside vibration. The light source was a 300 W xenon arc lamp. Light was focused on the sample at an impinging area of 0.20 cm^2. The cell window was highly transparent throughout the observed wavelength range, and the sample holder could be easily re-

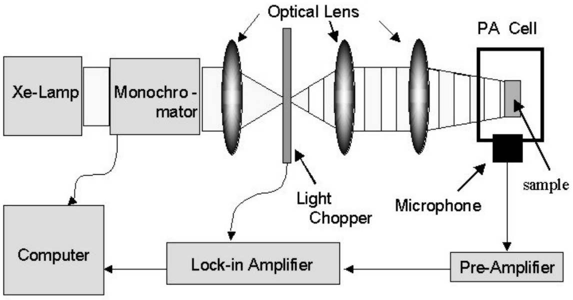

Fig. 2 Block diagram of photoacoustic spectroscopy system

moved from the cell to maintain the optical configuration. Figure 2 shows the block diagram of the PA apparatus. The modulation frequency for the spectroscopic measurements was 333 Hz obtained using a mechanical chopper to get the optical absorption information for TiO_2 films. Measurements of the PA spectra were carried out at room temperature in the wavelength range of 250–1200 nm. The PA signal intensities were monitored by first passing the microphone signal through a preamplifier and then into a two-phase lock-in amplifier. The data were averaged to improve the signal-to-noise ratio (S/N). The spectra were normalized using PA signals from a carbon black sheet. The conditions for each of the PA measurements were fixed as far as possible to compare the PA signal directly.

The photoelectrochemical setup consisted of a quartz illumination cell equipped with a working-electrode (TiO_2) and a Pt counterelectrode in 1 M KCl+0.1 M Na_2S electrolyte [7]. PEC measurements were carried out under short current conditions using the same apparatus and conditions as those used for the PA measurements. Measurements of the PEC current spectra were carried out at room temperature in the wavelength range of 250–800 nm with a modulation frequency of 33 Hz. The spectra were normalized using PA signals from a carbon black sheet. The conditions for each of the PEC measurements were fixed as far as possible to compare the PEC signal directly.

Results and discussion

Figures 3 and 4 show the scanning electron microscopy (SEM) observations of the TiO_2 electrodes prepared with hydrolysis periods of 15 and 30 min, respectively. They showed high surface roughness and crevices in the films. A rugged structure was recognized similar to the observations reported previously [7]. The average surface area was obtained by averaging the grain sizes in Figs 3 and 4 (both Figures have the same scale in photographs). The average surface area of the single grain in Fig. 4 (hydrolysis time of 30 min) is smaller than that in Fig. 3 (hydrolysis time of 15 min), indicating that the average area decreases with the increase of hydrolysis period. Also, the surface area of the single grain with the hydrolysis time of 60 min is somewhat smaller than that of 30 min with much smaller boundaries in crevices.

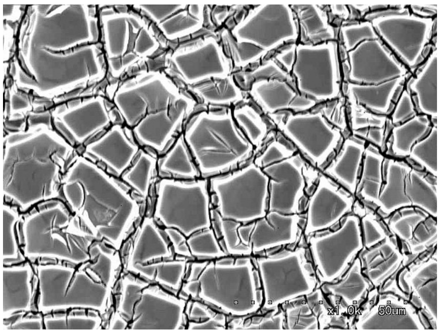

Fig. 3 Scanning electron microscopy observation of the TiO_2 electrode with hydrolysis period of 15 min

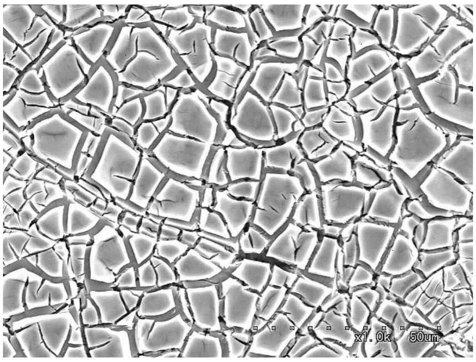

Fig. 4 Scanning electron microscopy observation of the TiO$_2$ electrode with hydrolysis period of 30 min

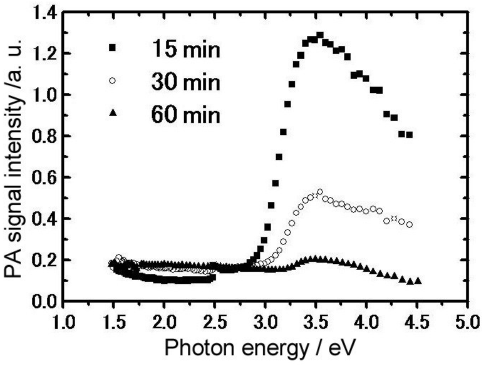

Fig. 5 Photoacoustic spectra of the TiO$_2$ electrode with different hydrolysis periods

Figure 5 shows the PA spectra of highly porous, polycrystalline TiO$_2$ films with different hydrolysis period from 15 to 60 min. The PA spectra in Fig. 5 show a clear increase of the signal intensity above the band-gap (~3.0 eV) region which is independent of the hydrolysis period. Figure 5 shows a broad band at approximately around a photon energy of 3.5 eV, indicating a possibility of quantum confinement effects. The peaks at 3.5 eV might be attributed to the lowest transition energy due to the quantum confinement effects. The peak intensity decreases with the increase of hydrolysis periods, indicating the possibilities of changes in the optical absorption, the thermal properties and the density due to the hydrolysis processes. According to the RG theory [13], our situation in the PA spectrum below a photon energy of 3.5 eV might be the case of optically transparent and thermally thick samples. In that case, the PA signal intensity is proportional to the optical absorption coefficient β and the inverse of the ($\rho_s C_s$), where ρ_s and C_s are density and specific heat of the materials, respectively. The optical absorption coefficient β is not much influenced by the hydrolysis processes because of the results of PEC current data shown later. Hence, the decrease of PA signal intensity with the increase of hydrolysis periods might be attributed to the changes of the densities and the specific heats of the TiO$_2$ films.

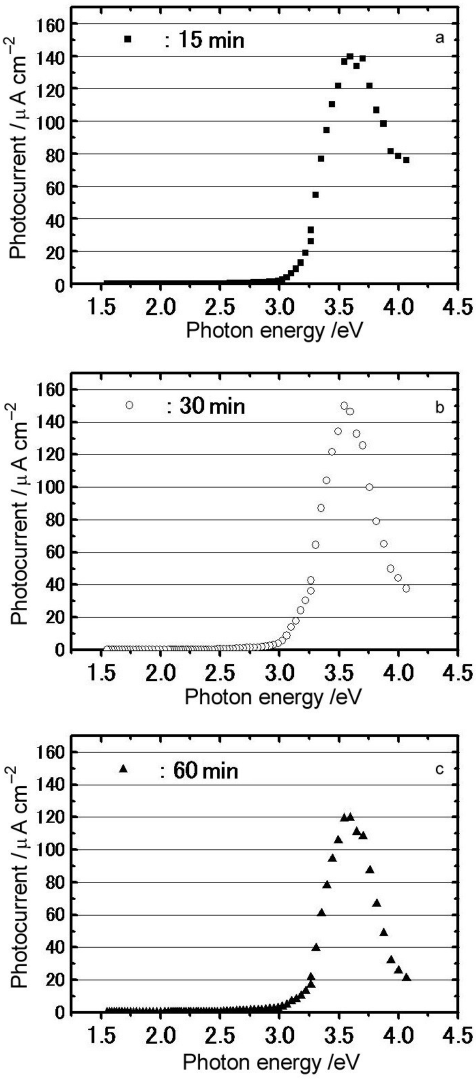

Fig. 6 Photoelectrochemical current spectra of the TiO_2 electrode with different hydrolysis periods of a – 15 min, b – 30 min and c – 60 min

Figure 6 shows the PEC spectra of highly porous, polycrystalline TiO_2 films with different hydrolysis periods ((a) 15 min, (b) 30 min, (c) 60 min). The PEC spectra in Fig. 6 show a clear increase of the signal intensity above the band-gap (~3.0 eV) region which is independent of the hydrolysis period. Figure 6 shows a broad band at approximately around 3.5 eV similar to that of the PA spectra, also indicating a possibility of a quantum confinement effects. Figure 6 shows that the PEC current peak intensities of the sample with hydrolysis periods of 15 and 30 min agree with each other within the experimental accuracy and that of the sample with the hydrolysis period of 60 min is somewhat smaller than others, indicating the small increase of interface states due to the formation of smaller grain boundaries with the longer hydrolysis period. The peak intensity is not much modified by the hydrolysis periods, indicating that the optical absorption coefficient β still remains unchanged.

Conclusions

The PA spectra of highly porous, polycrystalline TiO_2 films with the different hydrolysis periods show broad peaks at approximately around a photon energy of 3.5 eV, indicating a possibility of quantum confinement effects. The peak intensity decreases with the increase of hydrolysis periods, indicating the possibilities of changes in thermal properties and the densities due to the hydrolysis processes. The PEC spectra also show broad peaks at approximately around a photon energy of 3.5 eV and the peak intensity is independent of the hydrolysis processes, indicating that the optical absorption coefficient remains unchanged during the hydrolysis processes.

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