Time- and Frequency-resolved Photoelectrochemical Investigations on Nano-honeycomb TiO₂ Electrodes

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Time- and frequency-resolved photoelectrochemical studies have been performed on nano-honeycomb porous TiO₂ electrode prepared by photoelectrochemical etching of single crystal TiO₂, both for its bare surface and when sensitized by cis-di(thiocyanato)-N,N-bis(2,2'-bipyridyl-4,4'-dicarboxylate)ruthenium(II). Since the remaining wall in the porous layer become as thin as the double thickness of the space charge layer by photoetching, electron diffusion comes to play the main role in the charge transport rather than field-driven migration. Intensity modulated photocurrent spectroscopy revealed much faster electron diffusion in the honeycomb electrode than that in colloid based porous electrode, because of the smaller electron trap density in the nano-honeycomb structure owing to the non-existence of grain boundaries.

Key Words : Titanium Dioxide, Nano-porous, Charge Transport, Dye-sensitization

1 Introduction

Titanium dioxide (TiO₂) is one of the most important semiconductor materials being essential in photocatalysis¹⁻⁴⁾ and dye-sensitized solar cells.⁵⁾ As all the photoelectrochemical events take place at the surface of semiconductors, enlargement of active surface area should maximize their functions. The crystallographic structure is important as well, especially when used as photoelectrodes, in order to achieve fast charge transport in the semiconductor materials.

We have recently developed a method to create an ordered porous surface on highly crystallized TiO₂ electrodes by photoelectrochemical etching (photoetching) in aqueous sulfuric acid.⁶⁻⁸⁾ A unique porous structure named "nano-honeycomb" was formed as it consists of square deep cells separated by interconnected thin walls of TiO₂. Because photoetching can enlarge the surface area of TiO₂ in a controlled manner, while maintaining the crystallinity of the original material, photoelectrochemical properties of the nano-honeycomb TiO₂ electrode are of significant interest in the above mentioned view points.

The present study has been dedicated to the photoelectrochemical characterization of the nano-honeycomb TiO₂ electrodes both under UV illumination and when sensitized to visible light by surface modification with cis-di(thiocyanato)-N,N-bis(2,2'-bipyridyl-4,4'-dicarboxylate)ruthenium(II) complex, known as N3 dye.⁹⁾ Colloid based nano particulate porous film electrodes of TiO₂, typically used in dye-sensitized solar cells, have also been studied for comparison. Time- and frequency-resolved photoelectrochemical methods such as photocurrent transient measurements during a light flash in the

ms regime¹⁰⁾ and intensity modulated photocurrent spectroscopy (IMPS)^{11,12)} have been utilized to elucidate the charge transport mechanism within the honeycomb layer and to determine kinetic parameters relevant to the charge transport.

2 Experimental

TiO₂ single crystals polished for the (001) face were purchased from High Purity Chemicals Laboratory, Co., Ltd. They were reduced at 1000°C for 1 h in a 10% H₂ + N₂ gas to obtain an n-type semiconductivity. A Cu wire was soldered on the back side by In and insulated with epoxy except for the front surface. Nano crystalline porous TiO₂ films of 8 μm thickness were prepared from JRC-TIO-4 reference catalyst (The Catalysis Society of Japan) according to a method described in literature¹³⁾ on a F-doped SnO₂ coated glass substrate (Central Glass, Co., Ltd.).

The photoetching was carried out by illuminating the electrodes with a 500 W high pressure Hg arc lamp (intensity = 350 mW cm⁻²) in a 1 M H₂SO₄ aqueous solution at +1.0 V vs. SCE and for the total charge of 100 C cm⁻².⁸⁾ This etching quantity corresponds to the honeycomb layer thickness of 5 μm as estimated from the faradaic efficiency of the photoetching reaction.⁷⁾

Photoelectrochemical studies were carried out both for the bare TiO₂ electrodes and those modified by N3 dyes. All the measurements were performed under a potentiostatic condition at +0.17 V vs. SCE in an acetonitrile/ethylene carbonate (v/v = 1/4) mixed solution containing 0.5 M KI. Light was illuminated from the front side of the electrodes.

Photocurrent transients were measured during illumi-

nation for 120 ms regulated by a mechanical shutter and monitoring the current by an oscilloscope. A 500 W high pressure Hg arc lamp was used for the bare TiO₂ electrodes, while a 500 W Xe arc lamp with a $\lambda > 420$ nm long pass and an IR-cutoff filters was used for the sensitized electrodes. The light intensity was set to 100 mW cm⁻².

IMPS was carried out using a UV LED ($\lambda_{\text{max}} = 380$ nm) and a blue LED ($\lambda_{\text{max}} = 475$ nm) for the bare and sensitized TiO₂ electrodes, respectively. The dc components of the illumination were 570 $\mu\text{W cm}^{-2}$ for UV and 940 $\mu\text{W cm}^{-2}$ for blue. Sinusoidal ac modulation of about 10% was superimposed on the dc component over a frequency range between 0.2 Hz and 10 kHz. The phase shift between the excitation light and photocurrent response, as well as the amplitude of the ac component of the photocurrent, were analyzed by a frequency response analyzer.

3 Results and Discussion

The SEM photograph of nano-honeycomb surface created on a single crystal TiO₂ after photoetching is shown in Fig. 1. The photoetching proceeds along the c-axis of rutile and the inner surfaces of the honeycomb are of (100) planes as previously found.⁸⁾ We have found that the size of the square holes as well as the thickness of the remaining TiO₂ walls change as a function of the carrier density.¹⁴⁾ For the heavily reduced TiO₂ used here, a carrier density of $1.53 \times 10^{20} \text{ cm}^{-3}$ was estimated from Mott-Schottky analysis of the impedance measurement. As the photoetching was carried out at +1.0 V (vs. SCE) corresponding to an anodic bias of 1.2 V with respect to the flatband potential of TiO₂ in 1 M H₂SO₄ ($= -0.2$ V vs. SCE), a space charge layer of 12.3 nm thickness should be built up for the both sides of the TiO₂ thin wall during photoetching, as calculated from the carrier density and taking usual significance of relative permittivity of rutile TiO₂ along the a-axis. The average thickness of 18 nm for the thin walls seen in Fig. 1, which is slightly smaller than the double thickness of the space charge layer. It is supposed that the photoetching reaction ceases when the wall thickness becomes as thin as that needed for the ef-

Fig. 1 SEM photograph of a nano-honeycomb single crystal TiO₂ electrode prepared by photoetching.

fective band bending for charge separation.

Photocurrent transients were measured during a flash of UV light to the TiO₂ electrodes (Fig. 2). The TiO₂ before photoetching shows a rectangular response, with the sharp rise and fall of photocurrent which are as fast as the shutter speed. The photocurrent of the honeycomb electrode rises obviously slower than the shutter speed and a slight delay of photocurrent declination is also noticed. Because the applied bias cannot build an effective field in the thin walls of the honeycomb, field-driven transport of photogenerated charge carriers may not contribute to the current generation. It can be considered that diffusion of electron is the predominant mechanism of charge transport in the honeycomb layer, just like the case of nano-particulate semiconductor films.¹⁵⁾ A similar slowdown of photocurrent transient was indeed observed at crystalline porous n-GaP electrodes prepared by anodic etching, as reported by Vammaekelbergh *et al.*, and they also suggested the absence of field-driven charge transport in the porous layer as a reason for this behavior.¹⁶⁾

TiO₂ surfaces have been modified by N3 dye both for the honeycomb TiO₂ and the colloid based porous TiO₂ electrode which is typically used in dye-sensitized solar cells. The amount of dye adsorbed on the honeycomb electrode was $4.6 \times 10^{-8} \text{ mol cm}^{-2}$, whereas that adsorbed on the plane TiO₂ was smaller than the detection limit by UV-Vis spectroscopy, indicating a significant increase of surface area by photoetching, although still higher amount was adsorbed on the 8 μm thick colloid based film ($1.1 \times 10^{-7} \text{ mol cm}^{-2}$). Using the area occupied by one dye molecule,¹⁷⁾ a roughness factor of 256 is estimated for the honeycomb electrode, which is in close agreement with the calculated value (230) based on the geometry seen in Fig. 1 and the layer thickness of 5 μm , suggesting a complete monolayer coverage of dye on the honeycomb surface.

Photocurrent transients at the sensitized honeycomb electrode exhibits a response similar to that observed

Fig. 2 Photocurrent transients measured at a plane TiO₂ single crystal electrode before photoetching and a nano-honeycomb TiO₂ electrode after photoetching during a flash of UV light. The inset is given to show the difference for the photocurrent declination with enlarged scales.

Fig. 3 Sensitized photocurrent transients measured at a dye-modified nano-honeycomb TiO_2 electrode and a colloid based porous TiO_2 film electrode during a flash of visible light.

during UV illumination, indicating charge transport by electron diffusion (Fig. 3). However, it is noticed that the colloid based porous electrode shows a much slower response than the honeycomb electrode, although the steady photocurrent is much larger. The smaller sensitized photocurrent for the honeycomb electrode can be attributed to the limited photon harvesting efficiency, which is not only due to the low amount of dye, but also due to the facts that the majority of dyes are attached as monolayer on the TiO_2 surfaces aligned parallel to the incident light and that the reduced TiO_2 is black because of the formation of Ti(III) , thus hindering penetration of visible light. The low sensitized photocurrent does not necessarily mean poor efficiency of the honeycomb electrode. The observed photocurrent transients in fact suggest a faster electron diffusion in the honeycomb layer than that in the colloid based film.

Charge transport kinetics of each electrode was studied by IMPS.¹⁸⁾ The results are shown in Fig. 4 as complex plane plots for the measurements on bare TiO_2 single crystal, honeycomb TiO_2 and colloid based porous TiO_2 electrodes using a UV LED as a light source. For the flat single crystal TiO_2 electrode in which charge transport is extremely fast, the minimum frequency ($f_{\min} = 447 \text{ Hz}$) is determined by the system delay which reflects the RC constant of the electrochemical cell.¹⁹⁾ For any system which indicates the $f_{\min}$ value lower than this, the $f_{\min}$ is related to the delay caused by the slow charge transport in the electrode. The $f_{\min}$ value determined for the honeycomb electrode is 56.2 Hz, whereas that for the colloid based porous TiO_2 is as low as 0.79 Hz. When the electron transport is achieved by diffusion, the diffusion time, τ_D , is the reciprocal of the minimum modulation frequency,

$$\tau_D = \frac{1}{2\pi f_{\min}}$$

The diffusion coefficient, D_n , is related to τ_D by,

$$\tau_D = \frac{d^2}{D_n}$$

Fig. 4 Complex plane plots of IMPS for a plane single crystal TiO_2 before photoetching (a), a nano-honeycomb TiO_2 after photoetching (b), and a colloid based porous TiO_2 film (c) measured under illumination by a UV LED.

Table 1 The $f_{\min}$ values the electron diffusion times, τ_D , diffusion layer thicknesses, d , and electron diffusion constants, D_n , determined from IMPS on honeycomb TiO_2 and colloid based porous TiO_2 film both as bare and dye-modified electrodes.

	$f_{\min}$ (Hz)	τ_D (10^{-3} s)	d (μm)	D_n ($10^{-5} \text{ cm}^2 \text{ s}^{-1}$)
Honeycomb TiO_2	56.2	2.83	5	8.82
Colloid based TiO_2	0.79	160	8	0.32
Honeycomb $\text{TiO}_2/\text{N3}$	31.6	5.04	5	4.96
Colloid based $\text{TiO}_2/\text{N3}$	7.08	22.5	8	2.85

where d is the thickness of the layer across which electron diffuses, being 5 and 8 μm for the honeycomb and colloid based electrodes, respectively. The values of D_n have been calculated from the $f_{\min}$ values of IMPS plots for the results shown in Fig. 4, as well as for corresponding IMPS measurements at dye-sensitized electrodes (Table 1). The electrons in the honeycomb electrode are much more mobile than those in the colloid based TiO_2 film, as indicated by the D_n value nearly 30 times greater under UV illumination. Dye sensitization significantly improves D_n in case of the colloid based TiO_2 owing to the increased density of mobile electron, as the electron traps can be filled up. The dependence of D_n on the electron density in the conduction band as controlled by light intensity has been well documented for colloid based TiO_2 film electrodes which have a high density of electron traps due to the presence of many grain boundaries.^{20, 21)} By contrast, the D_n values of the honeycomb electrode do not vary so much in the two measurements. As the honeycomb structure originates from a single piece of TiO_2 crystal, there are absolutely no grain

boundaries in the porous layer. Accordingly, the electron trap density is expected to be very low.

It has been found in the present study that the photoetching creates a regular porous structure in which the wall thickness becomes as thin as the double thickness of space charge layer. Consequently, effective electrical field can no longer be formed within the porous layer, so that electron diffusion comes to play the main role in the photoelectrochemical events at the honeycomb electrode. Very fast electron diffusion was observed owing to the perfect crystalline nature of the honeycomb electrode.

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