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Preparation and Photoelectrochemical Properties of TiO_2 Films Consisting of Monodispersed Particles by Sol-Gel Method

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Monodispersed submicron TiO_2 particles have been prepared from $Ti(OC_2H_5)_4$solutions containing HPC, and deposited on mesa silica glass substrates to obtain particulate TiO_2 film electrodes. The particle size was controlled to be 0.7, 0.3 and 0.15 μm by changing the amount of water used for alkoxide hydrolysis. The particulate film electrode with the largest particles showed the highest anodic photocurrent under white light illumination and the highest anodic UV and visible light photoresponse. Based on the results obtained, the effects of the particle size on the photoelectrochemical properties have been discussed.

Keywords: monodispersed submicron TiO_2 particles; photoelectrochemistry; visible light response; TiO_2 films; sol-gel method

INTRODUCTION

Since in 1972 Fujishima and Honda found that water photolysis is possible using a single crystal TiO_2 as an anode in a liquid junction solar cell [1, 2], a large number of investigations have been conducted by focusing on photocleavage of water using TiO_2 electrodes. Yoko et al. have first applied the sol-gel dip-coating process to the preparation of TiO_2 thin film electrodes [3]. Grätzel and his co-workers also prepared dye-sensitized mesoporous TiO_2 films con-

sisting of nanometer particles reporting that such electrodes showed high quantum efficiency (12% under diffuse light illumination)[4]. The films they prepared had high specific surface area, and the dye (trinuclear ruthenium complex) which they used was very stable. Lindquist and his co-workers measured action spectra of nano-particulate and polycrystalline TiO_2 films on illumination either through the electrolyte or through the substrate[5]. They concluded that enough band bending does not form in the nano-particulate films, because the depletion layer thickness is about the same as the particle size. TiO_2 films consisting of submicron particles are expected to possess both high specific surface area and enough band bending.

So in this work, we investigated the photoelectrochemical properties of submicron particulate films and discussed the effect of the particle size on the photoelectrochemical properties.

EXPERIMENTAL

Submicron TiO_2 colloidal sols were synthesized from $Ti(OC_2H_5)_4$ solutions containing HPC (hydroxypropyl cellulose). Table 1 and 2 show the composition of the starting solutions. The colloidal sols were settled on a nesa silica glass substrate. The films were fired at 500°C for 10 min after every coating. Coating-firing process was repeated several times. Finally the films were post-heated at 800°C for 30 min. Hereafter the particulate films prepared from the solutions of R = 3, 10 and 60 are called R3, R10 and R60 films, respectively. For comparison, dip-coating films were also prepared.

Table 1 Compositions of starting solutions for particulate films (molar ratio)

	$Ti(OC_2H_5)_4$	H_2O	C_2H_5OH	HPC / $g \cdot l^{-1}$-soln.	Particle size/μm
R3	1	3	168	1.7	0.7
R10	1	10	166	1.7	0.3
R60	1	60	150	1.7	0.15

Table 2 Compositions of starting solutions for dip-films (molar ratio)

	$Ti(OC_3H_7^i)_4$	H_2O	C_2H_5OH	HNO_3
dip	1	1	10	0.2

RESULTS AND DISCUSSION

As clearly seen from the last column of Table 1, the particle size can be controlled by the water content added for hydrolyzing $Ti(OC_2H_5)_4$. That is, the increase of water content resulted in the decrease of particle size. In Fig. 1, XRD patterns of R3, R10 and R60 particulate films and dip-film post-heated at 800°C for 30 min. In dip-film rutile phase was precipitated while in particulate films anatase phase still remained.

Photoelectrochemical properties were measured for these film electrodes. Every film electrode showed a maximum photocurrent at a ceratain film thickness. This phenomena can be explained by the competition between the increase in the number of active sites and the increase of the film resistance.

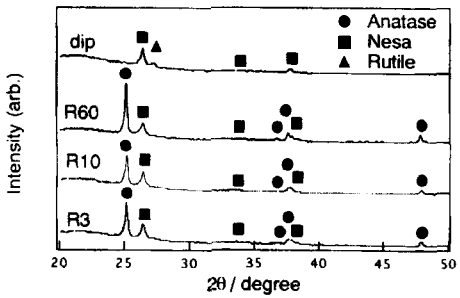

Fig. 1 XRD patterns of R3, R10 and R60 particulate films and dip-film heated at 800°C for 30 min.

In Fig. 2, action spectra of R3, R10 and R60 particulate films and dip-film are shown. It is obvious that the larger the particle size, the larger the photocurrent, and the peak position seems to shifts to longer wavelengths. Moreover, compared with the dense film derived by dip-coating method, the particulate films showed slightly higher photoresponse in the visible light region, which is attributable to photoexcitation of electrons from the surface states.

The surface states were estimated by the measurment of current-voltage curves under pulsed light illumination.

From TG-DTA analysis, a larger amount of Ti^{3+} species are expected to exist in the larger particle samples than the smaller ones. Higher donor densities and larger particle sizes make it possible to form the enough band bending in the particles to effectively separate the hole-electron pairs. Furthermore, the conductivity would be higher in the films consisting of larger particles because the cross-section of the necks formed via sintering would be larger in the samples of larger particles.

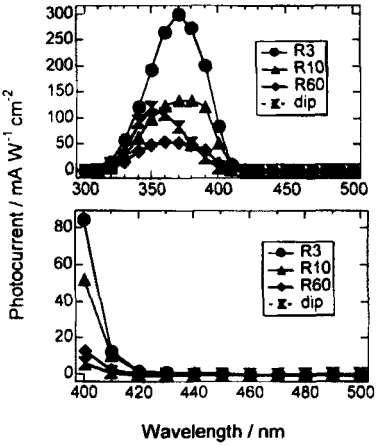

Fig. 2 Action spectra of R3, R10 and R60 particulate films and dip-film.

Acknowledgements

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