Formation of Crystalline-Oriented Titania Thin Films on ITO Glass Electrodes by EPD in a Strong Magnetic Field

Mamiko Kawakita¹,²,ᵃ, Tetsuo Uchikoshi²,ᵇ, Laxmidhar Besra²,ᶜ, Tohru S. Suzuki²,ᵈ, Jin Kawakita²,ᵉ and Yoshio Sakka¹,²,ᶠ

¹Graduate School of Pure and Applied Sciences, University of Tsukuba, 1-2-1 Sengen, Tsukuba, Ibaraki 305-0047, Japan
²National Institute for Materials Science (NIMS), 1-2-1 Sengen, Tsukuba, Ibaraki 305-0047, Japan
ᵃkawakita.mamiko@nims.go.jp,ᵇuchikoshi.tetsuo@nims.go.jp,ᶜbesra.laxmidhar@nims.go.jp,ᵈsuzuki.tohru@nims.go.jp,ᵉkawakita.jin@nims.go.jp,ᶠsakka.yoshio@nims.go.jp

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Abstract. Crystal-oriented and crack-free thin TiO₂ films with a good interfacial adhesion on indium-tin oxide (ITO) glass substrates for photoelectrodes were fabricated by the electrophoretic deposition (EPD) method in a 12 T strong magnetic field. A binder-free suspension for the EPD was prepared by dispersing TiO₂ in the mixture of 2-propanol and 2,4-pentanediol. The electrophoretic mobility and the sedimentation rate were measured at various ratios of the mixed solution. The optimized state of the suspension exhibiting the highest surface charge potential and producing deposits with the highest green density was obtained at the 50:50 mixing ratio. The TiO₂ films were characterized by XRD and SEM analyses. The photo-current measurement was also conducted to investigate the relation between the photo-anode characteristics of a dye-sensitized solar cell and the plane orientation of the TiO₂ films.

Introduction

The dye-sensitized solar cell (DSSC)[¹] is promising since it can convert light at longer wavelengths into electricity and can be manufactured using less energy as compared to the semiconductor-type cells with a p-n junction. Despite these advantages, DSSC commercialization is still limited because of its low reliability of the liquid electrolyte and of its low conversion efficiency due to the nonuniformity of the electrode components. In order to significantly enhance the cell performance, it is important to optimize the photo-anode structure of the DSSC on the basis of its fundamental properties. Most of the photo-electrodes of the DSSC are composed of TiO₂ (anatase) nano-particles covered with a dye stacked on a conductive glass substrate. The desirable thickness of the TiO₂ layer is under 50 microns to ensure the transparency of sunlight through it. Recently, it was reported that some functional properties of anatase TiO₂ show a crystalline-orientation dependence[²,³]. For example, water reduction and photo-oxidation take place at more negative potentials on the anatase (001) surface than on the anatase (101) surface[³]. It is also expected that the photo-electricity conversion behavior depends on the crystalline orientation of the anatase TiO₂, and its battery performance can be improved by the surface-texture...
control. To obtain oriented planes of anatase TiO$_2$, various kinds of techniques have been used;[4-11] however, it is difficult to obtain a crystal-oriented anatase layer of around 10 µm thick with a high crystallinity on a transparent and conductive substrate which is appropriate for a photo-anode electrode. In this study, textured titania thin films and preferred crystalline orientation on ITO glass substrates were fabricated by EPD in a strong magnetic field[12-14]. First, the optimization of the colloidal suspension of TiO$_2$ nanopowder, which is indispensable for the EPD process under a strong magnetic field, was performed. The fabrication and characterization of the crystal-oriented, crack-free TiO$_2$ thin films on the ITO glass were then carried out using the optimized suspension. At the end, the relation between the photo-anode characteristics of the DSSC and the plane orientation of the TiO$_2$ particles was investigated.

**Experimental procedure**

The mixed system of 2,4-pentanedione and 2-propanol was selected as a dispersion medium in this study. 2,4-Pentanedione is known to dissociate an H$^+$ ion by keto-enol tautomerism according to the catalytic action of a coexisting aid[15]. In the mixed solvent of 2,4-pentanedione and 2-propanol, the liberated protons adsorb on the surface hydroxyl groups of the TiO$_2$ by acid-base interactions and make the powder surface positively charged. This positive surface charge enables the particles to deposit on the cathode. Commercial TiO$_2$ particles with a spherical shape (Nanotek, 80% in anatase content, 30 nm in average size, 99.95% in purity) were dispersed in the solvent and ultrasonicated for 15 min to break up any agglomerates. The TiO$_2$ solid content of the suspensions was 0.10 g/ml. The ratio of 2-propanol in the mixture with 2,4-pentanedione was varied from 0~100 in vol% to investigate the influence of the solvent composition on the stability of the suspension and the following deposition. Generally, binders, such as PVA and PVB, are added to the suspension for the EPD process to prevent cracking and peeling off the film during drying. However, we didn’t use any binders because a binder-free suspension is preferable for the electron mobility in the electrodes of the DSSCs. The electrophoretic mobility of the TiO$_2$ suspensions was measured by an electrophoretic light-scattering spectrophotometer. The densities of the deposits before and after sintering at 673 K for 30 min were measured by Archimedes’ method in kerosene using thick deposits prepared by the EPD at the constant voltage of 20 V for 70 minutes. Preparation of the bulk deposits for the density measurements were conducted external to the magnetic field. The stability of the suspensions was also evaluated by a sedimentation

![Fig. 1 Schematic diagram of the electrophoretic deposition in a strong magnetic field.](image-url)
test. Fabrication of the textured titania films was conducted by the EPD in a 12 T strong magnetic field. A schematic diagram of the electrophoretic deposition in a strong magnetic field is shown in Fig. 1. The suspension was placed in the magnetic center of a superconducting magnet and then a strong magnetic field was applied to the suspension. The EPD was carried out at the constant voltage of 40V. The direction of the electric field $E$ relative to the magnetic field $B$ was altered ($\phi B - E = 0^\circ, 67.5$ and $90^\circ$) in order to control the dominant crystal faces of the deposits[12]. It was intended that $\phi B - E = 0^\circ$ is to align the c-plane of the TiO$_2$ parallel to the ITO substrate, $\phi B - E = 67.5^\circ$ is for the preferred orientation of (101) plane, and $\phi B - E = 90^\circ$ is to align the c-plane of the TiO$_2$ perpendicular to the ITO substrate. Randomly-oriented TiO$_2$ films were also prepared by EPD external to the magnetic field for comparison with the oriented electrodes’ performance. An ITO glass substrate was used as the cathode and a palladium sheet was used as the anode. The distance between the electrodes was fixed at 2 cm. The deposition time was 30~35 s for most of the samples. After the deposition, the samples were kept in the strong magnetic field for more than 20 min during drying. The TiO$_2$ films were then thermally treated at 673 K for 30 min. The X-ray diffraction (XRD) was carried out to investigate the crystalline orientation of the specimens. A digital microscope and scanning electron microscope (SEM) were used for the observation of the surface appearance and fractured microstructure of the electrophoretically deposited TiO$_2$ films on the ITO. The photo-current measurement was also conducted to investigate the relation between the photo-anode characteristics of a dye-sensitized solar cell and the plane orientation of the TiO$_2$ films. The detailed experimental procedure is shown elsewhere[16].

Results and discussion

The electrophoretic mobility of the suspensions as a function of the composition of the solvent is shown in Fig. 2. The electrophoretic mobility increased with an increase in the amount of 2-propanol and reached the highest value for 2,4-pentanedi:2-propanol = 50:50 and then decreased with a further increase in the 2-propanol proportion. As the electrophoretic mobility is proportional to the zeta-potential of a colloidal particle, this result indicates that the highest surface charge potential is achieved in the 50:50 solvent mixtures. The relative densities of the TiO$_2$ bulk compacts as a function of the mixed ratio of 2,4-pentanedi:2-propanol are shown in Fig. 3. The density was measured for the deposits of green and sintered at 673 K for 30 min. For the electrode of the DSSCs, the heat treatment around 673~773 K is generally conducted after coating to improve the adhesion of the deposited layer to the substrate which enhances the conversion efficiency. In the relation between the relative densities and the mixture ratio of the suspension, both the green and sintered relative densities showed the
Dispersed medium composition (2-propanol Vol. %)

Fig. 3 The relative density of the deposits as a function of the dispersed medium composition.

Fig. 4 The sedimentation testing results of the suspensions dispersed after 2 weeks.

The ITO glass was excellent as shown in Fig. 5. These results indicate that dense deposits are obtained from a well-dispersed suspension. To prepare the film with a better crystalline orientation, the suspension should also be well-dispersed so that the particles can freely rotate in the magnetic field[12]. Therefore, the mixture ratio at 2,4-pentandione:2-propanol = 50:50 was adopted for the following experiments. Fig. 4 shows the sedimentation state of the suspensions which passed two weeks after they were dispersed. The suspension prepared with the 100% 2-propanol immediately sedimented when the stirring was stopped probably due to the absence of the keto-enol tautomerism that produces protons and the lower surface charge potential of the particles. In the suspension of only 2,4-pentanedione, the sedimentation gradually occurs since their repulsive potential is not sufficient to disperse the powder. In the mixed system of 2,4-pentanedione and 2-propanol, the stability of the suspensions remained well dispersed even after two weeks; it was especially prominent in the 20~50 vol % 2-propanol solvent. However, gradual sedimentation occurred in the 60 vol % and 80 vol % 2-propanol suspensions. The increase in the ionic concentration probably causes compression of the electrical double layer. As a result, the electrostatic repulsive force between the particles became weak.

Fig. 5 shows surface appearance of a thin film on an ITO glass substrate prepared by the EPD in a 12 T magnetic field. This film was thin but uniform and crack-free. This thin film had no flaking or cracking even after the heat treatment at 673 K for 30 minutes, and adhesion of the film on the ITO glass was excellent as shown in Fig. 5.
Fig. 7 XRD patterns of the prepared TiO$_2$ films; 
(a) c-plane of TiO$_2$ parallel to ITO face ($\varphi_{B-E}=0^\circ$); (b) preferential-orientation of (101) plane ($\varphi_{B-E}=67.5^\circ$); (c) c-plane of TiO$_2$ perpendicular to ITO face ($\varphi_{B-E}=90^\circ$); (d) randomly-oriented film.

Fig. 8 Photo current dependence of oriented TiO$_2$ photoelectrodes; (a) c-plane of TiO$_2$ parallel to ITO face ($\varphi_{B-E}=0^\circ$); (b) preferential-orientation of (101) plane ($\varphi_{B-E}=67.5^\circ$); (c) c-plane of TiO$_2$ perpendicular to ITO face ($\varphi_{B-E}=90^\circ$); (d) randomly-oriented film.

Fig. 6 shows the tilted view and the fractured microstructure of the thin film on an ITO glass substrate prepared by the EPD in a 12 T magnetic field. The thickness of the thin film estimated from the SEM micrograph in was about 10 $\mu$m. Our results show that the combination of 2,4-pentanedione and 2-propanol is appropriate to prepare the suspension which produces crack-free TiO$_2$ films without any binders.

The XRD patterns of the thin TiO$_2$ films on the ITO substrates obtained by the EPD in and out of a strong magnetic field are shown in Fig. 7. The relative intensity of the diffraction peaks corresponding to the (004), (101) and (200) planes of the anatase phase shown in Fig. 7a~c, respectively, is higher than that of the randomly-oriented specimen in Fig. 7d. These results indicated that the preferential orientation of each plane, and especially in case of Figs. 7a and 7c, was found to be parallel and perpendicular to the ITO substrate, respectively. These XRD results of the thin film were consistent with the report regarding the bulk TiO$_2$[12]. It was possible to control the specific face orientation in the thin films composed of the TiO$_2$ particles on the ITO substrate by the EPD in a strong magnetic field.

Fig. 8 compares the photo-current among the specimens with the three types of plane orientations and random orientation. The highest photo-current was observed for case (a). The c-plane corresponds to the (004) plane of the anatase phase. Therefore, this result was consistent with the report that the DSSC based on the (001) oriented TiO$_2$ nanocrystalline showed a remarkable improvement in battery performance when compared with that based on the polycrystalline TiO$_2$[17]. The second highest photo-current was observed in case of (c) and the lowest photo-current was observed for (b). The specimen with a random orientation had a value between the highest and the lowest values derived from the different plane orientations. It was considered that this value corresponds to the average photo-current. The photo-current showed a clear difference in plane orientation of the TiO$_2$.

Conclusions

Crystalline-orientated, crack-free TiO$_2$ thin films with a good interfacial adhesion to the ITO glass substrates were obtained by the EPD method in a strong magnetic field using the non-aqueous
mixed solvent of 2,4-pentanedione / 2-propanol. The binder-free mixed solvent of 2,4-pentanedione and 2-propanol provided positive surface charging of the TiO$_2$ particles. The optimized state of the stable suspension appropriate for the EPD process was the 50:50 mixture of 2,4-pentanedione and 2-propanol. The adhesiveness did not deteriorate even after heat treatment at 673 K for 30 min. The thickness was controlled at around 10 microns. The photo-current of the (004) plane of the anatase phase showed the highest value. The second highest was the preferred orientation of the (100) plane, and the lowest photo-current was observed in case of the preferred orientation of the (101) plane. The photo-current of the randomly-oriented specimen was between those of the oriented planes.

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**References**