Composite thin films prepared by electrophoresis using two types of TiO₂ nanoparticles

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Anatase titanium dioxide (TiO₂) films have attracted interest as a cathode material for dye-sensitized solar cells (DSSCs). In order to improve the power conversion efficiency (PCE) of DSSCs, it is necessary to create long electron conduction paths in the film and increase both the specific surface area and light harvesting efficiency (LHE) for incident light. To achieve these, the deposition of TiO₂ composite thin films by constant current electrophoresis was attempted using colloid mixtures of two types of TiO₂ nanoparticles with different sizes and surface properties: ca. 5 nm TiO₂ nanoparticles synthesized in this study (TNPs) and commercial TiO₂ nanoparticles of ca. 20 nm (P25) size. The size of TNPs is too small for visible light wavelengths and it is difficult to deposit thick films with TNPs, so the LHE of these films is low. Various TNP:P25 ratios were investigated to enhance the LHE and PCE for DSSCs. The P25 particles form a matrix structure in the thin film, and the TNPs are incorporated into this structure and fill the spaces between adjacent P25 nanoparticles. The upper limit of film thickness achieved without the film separating from the substrate increased with the mass content of P25. The LHE of the TiO₂ composite thin films was improved and could easily be controlled by adjusting the mass ratio of TNP:P25. The optimal PCE for DSSCs was obtained using TiO₂ composite thin films deposited using a TiO₂ colloid mixture with a TNP:P25 mass ratio of 2:7.

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1. Introduction

Anatase titanium dioxide (TiO₂) has attracted interest as a cathode material for dye-sensitized solar cells (DSSCs). The quality and structure of a thin film cathode are important factors that affect the DSSC characteristics. Electrophoresis has a high deposition rate and can be used to deposit thin films on any conductive substrate of any shape or area. Furthermore, the thickness of TiO₂ thin films can be easily controlled by adjusting the electrophoresis time and current density. The TiO₂ nano-particles synthesized for use in this study (hereafter, TNPs) are composed of 100% anatase and 20% rutile TiO₂. The P25 titanium dioxide nanoparticles (Degussa P25, average size ca. 20 nm) are commercially produced for semiconductor photocatalysis and environmental applications, and are composed of 80% anatase and 20% rutile TiO₂. On the other hand, TNPs are composed of 100% anatase. It is thus expected that highly transparent TiO₂ thin films with high specific surface areas could be electrophoretically deposited using TNPs. Moreover, TNPs can transport electrons through conduction paths formed by connections in the crystal lattice between adjacent TNPs in the thin film; these conduction paths result in relatively long electron diffusion lengths. TNPs are thus suitable for use as photocatalysts and as the cathode material for DSSCs.

Highly transparent TiO₂ nanoparticle thin films with only tiny cracks have been deposited by electrophoresis using a colloid of TNPs and ethanol as the dispersion medium, because the TNPs have a comparatively high zeta potential (ζ-potential) in ethanol. Moreover, the power-conversion efficiency (PCE) for the DSSCs was improved due to the increase in the specific surface area and diffusion length of electrons by the strong connections formed between TNPs when using the smallest size TNPs obtained by a centrifugal classification process. Higher quality thin cathode films for DSSCs are required to improve the light harvesting efficiency (LHE) in the thin film. The LHE is defined as 1 – (transmittance + reflectance), where transmittance and reflectance are the ratios of the intensities of transmitted light through the film and reflected light at the incident plane of the film to the intensity of the incident light, respectively. To achieve this, it is important to increase the light path length in the thin film by increasing the film thickness or to fabricate a thin film with an optical confinement structure. However, it is currently difficult to deposit thick films by electrophoresis, because many cracks are generated due to the low density of the TiO₂ film and contraction of the film during the drying process when the solvents are evaporated from the thin film. In other words, an upper limit exists for the thickness of the film with high quality for thin films deposited by electrophoresis. In particular, only long wavelength light is transmitted through a thin film without scattering, because the size of the TNPs is too small compared to the wavelength of light.

To solve these problems, we attempted to deposit TiO₂ composite thin films by electrophoresis using a mixture of two types of TiO₂ nanoparticles with different sizes and different surface properties: TNPs and P25. It is expected that P25 will form a matrix structure in the thin film and the TNPs will be incorporated into the matrix structure. As such, the electron conduction paths in the film should be long and both the specific surface area and LHE for incident light should be improved. Thus, the aim of this study was to investigate the effectiveness of cathode thin films deposited from a colloid mixture of TNPs and P25 to...
enhance the LHE and PCE of DSSCs.

2. Experimental procedure

TNPs were synthesized according to the method described in Ref. 2. The TNPs were centrifugally classified using a centrifugal separator using isopropyl alcohol as the dispersion medium by a process to eliminate agglomeration. First, large size TNPs were precipitated and removed at 10,000 rpm by centrifugal classification. Small size TNPs were precipitated from the supernatant of the colloidal solution at 13,500 rpm. Agglomeration of P25 were also classified using the same process with water as the dispersion medium. The gel state of the classified TNPs includes residual isopropyl alcohol of approximately 85 wt % and that of classified P25 includes water of approximately 48 wt %. These particles were used in the wet state including the solvent because it is difficult to disperse dried particles in a dispersion medium. A mixture of wet-powder with a total mass of 0.8 g and with various mass ratios of TNP:P25 was added to 50 cm³ of ethanol as the dispersion medium in a glass beaker. Dispersion of the colloidal solution was performed using an ultrasonic processor (ECLIPSE-ME600, Nikon) at an accelerating voltage of 5 kV. The thickness of the thin films was measured using a profilometer (DEKTAK150, Veeco). The TNPs and P25 particles were observed using a transmission electron microscope (TEM; JEM-2100F, JEOL) at an accelerating voltage of 200 kV. After the thin films were heated at 350°C for 30 min in air, the thin films were sensitized by immersion in an ethanol solution containing 3 × 10⁻⁴ M of cis-di(thiocyanate)bis(2,2′-bipyridyl-4,4′-di-carboxy-late)-ruthenium(II)bis-tetra-butyl-ammonium (N719 dye, Tokyo Chemical Industry Co.) for one day. The LHE of the thin films with absorbed dye was measured using a visible-light spectrometer with an integrating sphere (U-3900, Hitachi). The amount of adsorbed dye was determined by desorbing the dye from the TiO₂ surface into a 0.1 M sodium hydroxide aqueous solution and measuring its absorbance by a visible-light spectrometer. The electrolyte solution was prepared by the addition of LiI, I₂, 1,2-dimethyl-3-propyl-imidazolium iodide, and 4-tet-butylpyridine into 3-methoxy propionitrile. The active area of the cell exposed to light was 0.25 cm² (0.5 × 0.5 cm²). A solar simulator (XES-40S1, San-Ei Electric Co.) was used as the light source with the radiation power density set to 100 mW/cm² (AM1.5). The characteristics of the DSSCs were measured using a digital multimeter (34401A, Agilent Technologies).

3. Results and discussion

Figure 1 shows a schematic diagram of the setup used for the constant-current electrophoresis. An indium–tin oxide (ITO) glass substrate and an aluminum plate (99.99% purity) were used as the negative and positive electrodes, respectively. The electrodes were positioned at a distance of 15 mm from each other, perpendicular to the liquid surface in the glass beaker. TiO₂ composite thin films were deposited onto the ITO glass substrate by constant-current electrophoresis for various electrophoresis times. The deposition continued until the film fell away from the substrate during electrophoresis. The thickness at this time was defined as the upper limit of the film thickness. The current density for electrophoresis was set to 0.1 mA/cm². The colloid temperature was approximately 25°C. After deposition, the thin films were dried in air for one day.

The thin film samples were evaluated using optical microscopy (ECLIPSE-ME600, Nikon) and scanning electron microscopy (SEM; JSM7500FA, JEOL) at an accelerating voltage of 5 kV. The thickness of the thin films was measured using a profilometer (DEKTAK150, Veeco). The TNPs and P25 particles were observed using a transmission electron microscope (TEM; JEM-2100F, JEOL) at an accelerating voltage of 200 kV. After the thin films were heated at 350°C for 30 min in air, the thin films were sensitized by immersion in an ethanol solution containing 3 × 10⁻⁴ M of cis-di(thiocyanate)bis(2,2′-bipyridyl-4,4′-di-carboxy-late)-ruthenium(II)bis-tetra-butyl-ammonium (N719 dye, Tokyo Chemical Industry Co.) for one day. The LHE of the thin films with absorbed dye was measured using a visible-light spectrometer with an integrating sphere (U-3900, Hitachi). The amount of adsorbed dye was determined by desorbing the dye from the TiO₂ surface into a 0.1 M sodium hydroxide aqueous solution and measuring its absorbance by a visible-light spectrometer. The electrolyte solution was prepared by the addition of LiI, I₂, 1,2-dimethyl-3-propyl-imidazolium iodide, and 4-tet-butylpyridine into 3-methoxy propionitrile. The active area of the cell exposed to light was 0.25 cm² (0.5 × 0.5 cm²). A solar simulator (XES-40S1, San-Ei Electric Co.) was used as the light source with the radiation power density set to 100 mW/cm² (AM1.5). The characteristics of the DSSCs were measured using a digital multimeter (34401A, Agilent Technologies).

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Figure 2 shows TEM images of the classified TNPs and P25 particles. The TNPs were connected to each other by an interparticle crystal lattice as shown in Fig. 2(b) and as a result, formed a net-like structure as shown in Fig. 2(a). No agglomeration was observed. The smallest particle diameter was approximately 5 nm. The P25 particles had uniform particle size and that of classified P25 includes water of approximately 48 wt %. These particles were used in the wet state including the solvent because it is difficult to disperse dried particles in a dispersion medium. A mixture of wet-powder with a total mass of 0.8 g and with various mass ratios of TNP:P25 was added to 50 cm³ of ethanol as the dispersion medium in a glass beaker. Dispersion of the colloidal solution was performed using an ultrasonic processor (ECLIPSE-ME600, Nikon) at an accelerating voltage of 5 kV. The thickness of the thin films was measured using a profilometer (DEKTAK150, Veeco). The TNPs and P25 particles were observed using a transmission electron microscope (TEM; JEM-2100F, JEOL) at an accelerating voltage of 200 kV. After the thin films were heated at 350°C for 30 min in air, the thin films were sensitized by immersion in an ethanol solution containing 3 × 10⁻⁴ M of cis-di(thiocyanate)bis(2,2′-bipyridyl-4,4′-di-carboxy-late)-ruthenium(II)bis-tetra-butyl-ammonium (N719 dye, Tokyo Chemical Industry Co.) for one day. The LHE of the thin films with absorbed dye was measured using a visible-light spectrometer with an integrating sphere (U-3900, Hitachi). The amount of adsorbed dye was determined by desorbing the dye from the TiO₂ surface into a 0.1 M sodium hydroxide aqueous solution and measuring its absorbance by a visible-light spectrometer. The electrolyte solution was prepared by the addition of LiI, I₂, 1,2-dimethyl-3-propyl-imidazolium iodide, and 4-tet-butylpyridine into 3-methoxy propionitrile. The active area of the cell exposed to light was 0.25 cm² (0.5 × 0.5 cm²). A solar simulator (XES-40S1, San-Ei Electric Co.) was used as the light source with the radiation power density set to 100 mW/cm² (AM1.5). The characteristics of the DSSCs were measured using a digital multimeter (34401A, Agilent Technologies).

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Figure 3 shows the film thickness as a function of the electrophoresis time for various TNP:P25 mass ratios. The film thickness increased with electrophoresis time for each mass ratio. When the mass ratio of P25 was low, the upper limit of the film thickness was low; the upper limit of the film thickness for the TiO₂ composite thin films with TNP:P25 of 2:7 and 1:32 was higher than that for thin films with only P25. SEM images of the composite thin film surfaces and a cross-section are shown in Fig. 4. No apparent crack with large size was observed.

Fig. 1. Schematic diagram of the constant-current electrophoresis setup.

Fig. 2. TEM images of classified TNPs and P25s. (a) TNP, (b) P25. (b) The domain D in (a) is expanded.
However, many pores with small size were observed in all film. TNPs filled up the space between adjacent P25 particles that form the matrix structure, as shown in Fig. 4(f). These structural factors contribute to make the film-density high and provide high resistance to contraction of the film during the drying process. As a result, the upper limit of the film thickness was increased. It is hard to estimate the pore volume from SEM images. If the specific surface can be estimated, it is possible to estimate roughly the pore volume. However, it is hard to measure the specific surface using measuring instrument, such as BET method, for a thin film.

Figure 5 shows the dependence of the deposition rate of the composite films and the electrical field intensity $E$ between electrodes on the mass ratio of P25 to the total mass of TNP and P25 particles in colloid mixtures.

$$R_{\text{ep}} = n_{\text{TNP}} v_{\text{TNP}} V_{\text{TNP}} + n_{\text{P25}} v_{\text{P25}} V_{\text{P25}} + V_{\text{pore}},$$ (1)

where $n_{\text{TNP}}$ and $n_{\text{P25}}$ are the number of particles, $v_{\text{TNP}}$ and $v_{\text{P25}}$ are the particle speeds for TNP and P25 in the colloid. $V_{\text{TNP}}$ and $V_{\text{P25}}$ are the volumes of the TNP and P25 particles, respectively. $V_{\text{TNP}}$ and $V_{\text{P25}}$ were assumed to be $4/3\pi r_{\text{TNP}}^3$ and $4/3\pi r_{\text{P25}}^3$, respectively, where $r_{\text{TNP}}$ and $r_{\text{P25}}$ are the radii of TNP and P25 particles, respectively. $V_{\text{pore}}$ is the pore volume per unit area of the thin film. The ratio of $V_{\text{pore}}$ to the total volume of the thin film (pore volume ratio) is approximately 26% for the closest packing of particles. From SEM images shown in Fig. 4, the pore volume ratio will be larger than approximately 26%. $v_{\text{TNP}}$ and $v_{\text{P25}}$ are dependent on $E$ and are given by

$$v_{\text{TNP}} = \mu_{\text{TNP}} E,$$ (2)

$$v_{\text{P25}} = \mu_{\text{P25}} E,$$ (3)

where $\mu_{\text{TNP}}$ and $\mu_{\text{P25}}$ are the mobilities of TNP and P25 particles, respectively. From Eqs. (1)-(3), $R_{\text{ep}}$ can be expressed as

$$R_{\text{ep}} = (n_{\text{TNP}} \mu_{\text{TNP}} V_{\text{TNP}} + n_{\text{P25}} \mu_{\text{P25}} V_{\text{P25}}) E + V_{\text{pore}}.$$ (4)

$E$ can be measured, as shown in Fig. 5. Table 1 shows the mobility, particle speed, and $\zeta$-potential for pure colloids of TNP and P25 particles for the closest packing of particles at 25°C. The particle speeds were calculated from the relationship between the deposition rate of a TiO$_2$ composite thin film and the number of...
particles incident from a colloid into the substrate. $\mu_{\text{TNP}}$ and $\mu_{\text{P25}}$ were calculated from $v_{\text{TNP}}$ for a pure TNP colloid and $v_{\text{P25}}$ for a pure P25 colloid using Eqs. (2) and (3). The actual particle speeds becomes small, so that $v_{\text{pore}}$ becomes large. $\zeta$-potentials were calculated using the Henry equation:9)–11)

$$\zeta_{\text{TNP}} = \frac{\mu_{\text{TNP}} \eta}{\varepsilon_0 \varepsilon_r f}, \quad \zeta_{\text{P25}} = \frac{\mu_{\text{P25}} \eta}{\varepsilon_0 \varepsilon_r f}$$

(5)

where $\zeta_{\text{TNP}}$ and $\zeta_{\text{P25}}$ are the $\zeta$-potentials for TNP and P25, respectively, $\eta$ is the viscosity of the dispersion medium, $\varepsilon_0$ is the permittivity in vacuum, $\varepsilon_r$ is the relative permittivity of the dispersion medium, and $f$ is the Henry coefficient, which is related to the electrophoretic delay.9)–11) The specific surface, $S_{\text{sp}}$, of particles in a TiO$_2$ composite thin film is given by

$$S_{\text{sp}} = \frac{s_{\text{TNP}} v_{\text{TNP}} S_{\text{TNP}} + s_{\text{P25}} v_{\text{P25}} S_{\text{P25}}}{R_{\text{p}}},$$

(6)

where $s_{\text{TNP}}$ and $s_{\text{P25}}$ are the surface area of the TNP and P25 particles, respectively. $S_{\text{TNP}}$ and $S_{\text{P25}}$ were assumed to be $4\pi r_{\text{TNP}}^2$ and $4\pi r_{\text{P25}}^2$, respectively. Figure 6 shows the relationships between the amount of dye per unit volume in the film and $S_{\text{sp}}$ for closest packing calculated using Eq. (6) on the mass ratio of P25 to the total mass of TNP and P25. It was confirmed that the amount of dye was proportional to the specific surface $S_{\text{sp}}$ roughly. This result suggests that the pore volume ratio for arbitrary TNP:P25 mass ratios is almost constant and the ratio of actual $\mu_{\text{TNP}}$ and $\mu_{\text{P25}}$ is roughly the same as that for closest packing shown in Table 1. However, the absolute value of the pore volume ratio is still unknown. Therefore, $\zeta_{\text{TNP}} = \zeta_{\text{P25}}$. When the particles are in the nano size region, the total charge $q$ on the surface of the particle is given by $q \approx 4\pi \varepsilon_0 \varepsilon_r f r$, where $r$ is the particle radius.11) Therefore, the total charge $q_{\text{TNP}}$ on the TNP particles is approximately 4 times as large as $q_{\text{P25}}$ on the P25 particles, because the size of the P25 particles is approximately 4 times as large as that of the TNP particles. Figure 7 shows the deposition rate calculated using Eq. (4) for each mass ratio of P25, which agrees well with the measured values. This result indicates that P25 and TNP particles are transported without significant interaction and the deposition rate of a composite thin film with arbitrary TNP:P25 can be estimated.

Figure 8 shows LHE at a wavelength of 533 nm (specific absorption peak of N719 dye) and 650 nm (long wavelength side from peak) for composite thin films with sensitized-dye and various TNP:P25 mass ratios as a function of film thickness. The LHE at 533 nm was larger than that at 650 nm. This indicates that light is mainly absorbed by the dye. The LHE increased with increasing film thickness, because the absorption of light correlates with the amount of dye, which increases with film thickness. The LHE increased as the mass ratio of P25 to TNP decreased, because the reflectance decreased as the mass ratio of P25 to TNP decreased. The upper limit of the film thickness for the composite thin film became a maximum at a TNP:P25 mass ratio of 1:32.

### Table 1. Mobility, particle speed, $\zeta$-potential, and Henry coefficient of TNP and P25 nanoparticles in pure colloid form at 25°C

<table>
<thead>
<tr>
<th></th>
<th>Particle speed $\mu$m/s</th>
<th>Mobility $\mu$m$^2$/V·s</th>
<th>$\zeta$-potential V</th>
<th>Henry coefficient</th>
</tr>
</thead>
<tbody>
<tr>
<td>TNP</td>
<td>4.1</td>
<td>$1.4 \times 10^4$</td>
<td>0.10</td>
<td>0.7</td>
</tr>
<tr>
<td>P25</td>
<td>95</td>
<td>$1.5 \times 10^4$</td>
<td>0.11</td>
<td>0.7</td>
</tr>
</tbody>
</table>

Fig. 6. Relationships between the amount of dye per unit volume in the film and $S_{\text{sp}}$ for closest packing on the mass ratio of P25 to the total mass of TNP and P25.
mass ratio of P25 to the total mass of TNP and P25 particles in colloid mixtures. The adsorption coefficients between the amount of dye in the composite thin films and averaged adsorption coefficient of the composite films on the mass ratio of P25 to the total mass of TNP and P25. The adsorption coefficient showed a similar mass ratio dependence to the adsorption coefficient on the mass ratio of P25 to TNP.

Next, absorption of the light by the dye is discussed in detail. Figure 9 shows the dependence of the adsorption coefficients of the composite films with a TNP:P25 mass ratio of 2:7 was the highest. As a result, the LHE of the composite thin films was almost the same as that for the thin film of P25. Figure 11 shows the short-circuit current density (SCCD) and PCE for DSSCs fabricated using composite thin films with various TNP:P25 mass ratios.

Table 2. Electrophoresis time $t_p$ for a single lamination, number of laminations $N_l$, and film thickness for laminated composite thin films with various TNP:P25 mass ratios.

<table>
<thead>
<tr>
<th>TNP:P25</th>
<th>$t_p$</th>
<th>$N_l$</th>
<th>$t_f$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1:0</td>
<td>60 s</td>
<td>8</td>
<td>3.46 x 10^4</td>
</tr>
<tr>
<td>8:3</td>
<td>180 s</td>
<td>5</td>
<td>5.37 x 10^3</td>
</tr>
<tr>
<td>2:7</td>
<td>240 s</td>
<td>10</td>
<td>8.33 x 10^3</td>
</tr>
</tbody>
</table>

various mass ratios of TNP and P25 as a function of film thickness. The photocurrents of the DSSCs correspond to the LHE for the composite thin films. Therefore, the dependence of SCCD and PCE on the thickness had the same tendency as that for the LHE. The highest PCE was obtained for the composite thin films with a TNP:P25 mass ratio of 2:7.

The absorption properties and DSSC characteristics with a high mass ratio of TNP have not yet been clarified, because thick films could not be obtained. Therefore, thick laminated composite films were fabricated by repeated deposition under the conditions shown in Table 2 and annealing processes at 350°C for 30 min in air. In particular, the upper limit of the film thickness for the composite thin film with TNP:P25 of 2:7 was extended to approximately 23 μm. Figure 12 shows the dependence of LHE, transmittance, and reflectance on the wavelength for the laminated composite thin films without a dye with TNP:P25 of 1:0, 8:3, and 2:7. The thickness of all films was fixed at approximately 6 μm. The transmittance of the film increased and the reflectance decreased as the mass ratio of P25 to TNP decreased. As a result, the LHE of the film with TNP:P25 of 2:7 was the highest at 533 nm (specific absorption peak of the N719 dye) and
the value was approximately 20%. **Figure 13** shows the LHE for all the laminated composite thin films fabricated under the conditions shown in Table 2 with the dye for various TNP:P25 mass ratios as a function of film thickness, while that for SCCD and PCE of the DSSCs is shown in **Fig. 14**. In **Fig. 13**, the LHE for the composite thin films shown in **Fig. 8** are shown together. The maximum film thickness shown in Figs. 13 and 14 corresponds to the upper limit. The LHE at the wavelength with an absorption peak exceeded 90% above a certain film thickness and sufficiently large LHEs were obtained for all films. Notably, the LHE for the laminated thin film of the TNP was higher than those for the other films. The path length of the incident light in the film deposited using a colloid with only TNPs was the longest due to high transparency, as shown in **Fig. 12(b)**. The path length became shorter by light scattering with increasing mass ratio of P25. It is thus speculated that for the TNP films, more photons are absorbed by dye molecules as shown in **Fig. 10** when incident light from the surface arrives at the other surface of the
film and then returns; therefore, the SCCD and PCE of these DSSCs was the highest. This result indicates that the light absorption properties of the film can be easily controlled by adjusting the mass ratio of the two different sized TiO₂ particles. Thus, it is concluded that deposition of composite thin films by electrophoresis is an effective technique that can be utilized to design improved efficiency for DSSCs. Moreover, it is expected that LHE can be improved by reducing the reflection losses in the film according to the mass ratios of the various sized TiO₂ particles deposited.

4. Summary

TNPs fill the spaces between adjacent P25 particles that form the matrix structure in electrophoretically deposited cathode films. The upper limit of the film thickness was increased with increasing mass ratio of P25 to TNP. The light absorption properties of the composite thin films can be easily controlled by adjusting the mass ratio of two different sized TiO₂ particles. The LHE and PCE of the DSSCs were significantly improved for a composite thin film deposited using a TiO₂ colloid mixture.

References