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Composite thin films of titanium dioxide nanoparticles with particle size distribution prepared by electrophoresis

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HIGHLIGHTS

- Investigation of the effect of a cathode film comprising two types of TiO_2 particles for dye-sensitized solar cells (DSSCs).
- Proposition of method to form film with gradient of particle size (GPS).
- Proposition of method to theoretically estimate particle behavior.
- Light harvesting and power conversion efficiencies of DSSCs fabricated using GPS thin film as a cathode material were improved.

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ABSTRACT

In order to improve the energy conversion efficiency of dye-sensitized solar cells (DSSCs), deposition of anatase titanium dioxide (TiO_2) composite thin films as the negative electrode was attempted using constant-current electrophoresis with a colloidal mixture of two types of TiO_2 nanoparticles with different sizes and surface properties. The first type was synthesized in the present study and had a size of about 5 nm; these are referred to as TNPs. The second type was commercially obtained TiO_2 nanoparticles (P25) with a size of about 20 nm. The P25-to-TNP mass ratio was changed during electrophoresis. Because the TNPs were small and the film had a high specific surface area, the film was deposited to minimize the P25-to-TNP mass ratio in the region close to the entrance window of the DSSC. The upper limit of the film thickness was markedly increased compared to deposition in a colloid consisting of one or two kinds of TiO_2 nanoparticles, but without a particle size gradient. A method for calculating the P25-to-TNP mass ratio, the gradient of the number average particle size, and the specific surface area of thin films with a particle size gradient was proposed. The harvesting efficiency for incident light was improved over a wide wavelength range, and as a result, the energy conversion efficiency of DSSCs fabricated using these thin films was increased.

1. Introduction

Anatase titanium dioxide (TiO_2) has attracted great interest as a cathode material for dye-sensitized solar cells (DSSCs) [1]. Currently, TiO_2 films are mainly prepared by the squeegee, spin-coating, and spray methods [1–4]. The quality and structure of a thin film cathode are important factors that affect the DSSC characteristics. The electrophoresis method for forming thin films has a high deposition rate and can be used to deposit thin films on any conductive substrate with any shape or area [5–16]. Furthermore, the thickness of the TiO_2 films can be easily controlled by adjusting the electrophoresis time and current density.

TiO_2 nanoparticles approximately 5–15 nm in size (hereafter, TNPs) were synthesized and used for the fabrication of DSSCs [12,13,15–17]. The size of these TNPs is smaller than that for commercially available TiO_2 nanoparticles such as P25. 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 TiO_2 [1]. On the other hand, the TNPs are composed of 100% anatase TiO_2. It is thus expected that TiO_2 films with high specific surface areas could be electrophoretically deposited using TNPs. The TNP network can also allow electron transport through conduction paths formed via the oriented attachment mechanism, by which the crystal lattices in

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adjacent particles are connected and electron diffusion lengths become relatively long [12,13,15–17]. It has been reported that the maximum practical energy conversion efficiency of a DSSC using TNPs is approximately 9%, comparable to that using P25 particles. The TNPs used in the present study also are suitable for use as photocatalysts and as a negative electrode material for DSSCs.

Highly transparent TiO_2 nanoparticle thin films with only tiny cracks have been deposited by electrophoresis using a colloid of TNPs or P25 particles and ethanol as the dispersion medium, because both types of particles have a comparatively high positive zeta potential (ζ-potential) in commercially available ethanol or dehydrated ethanol [12,13,15]. Moreover, when the smallest TNPs obtained by a centrifugal classification process were used, it was found that the energy conversion efficiency for the DSSCs was improved due to an increase in the specific surface area and electron diffusion length resulting from the strong connections between the TNPs [15,16]. Higher quality thin cathode films for DSSCs are required to improve the light harvesting efficiency (LHE) of thin films with sensitizing dye. The LHE is defined as $[1-(\text{transmittance} + \text{reflectance})]$, where the transmittance and reflectance are the ratios of the intensities of the transmitted light through the film and the reflected light at the incident plane of the film to the intensity of the incident light, respectively [16]. To improve the LHE, it is important to reduce the reflectance at the entrance window and to increase the optical path length in the film by increasing the film thickness or by fabricating a film with an optical confinement structure.

Currently, it is difficult to deposit thick films by electrophoresis because a large number of cracks are generated due to the low density of the TiO_2 film and contraction of the film during the drying process after the solvents evaporate. In other words, there is an upper limit to the film thickness that can be achieved while maintaining high quality. Also, because the TNPs are small relative to the wavelength of visible light, only long wavelengths are transmitted through the film without scattering.

To solve these problems, in a previous study, we attempted to deposit TiO_2 composite films by electrophoresis using a mixture of two types of TiO_2 nanoparticles, TNPs and P25, with different sizes and surface properties [16]. The P25 particles were found to form a matrix structure in the film, with the TNPs becoming incorporated into this matrix. The upper limit of the film thickness increased with increasing P25-to-TNP mass ratio, the electron conduction paths in the film became long, and both the specific surface area and the LHE were improved [16]. However, the P25-to-TNP mass ratio was constant throughout the film and P25 particles existed at the boundary of the transparent electrode and the film. As a result, it was expected that the surface reflectance of the film at the entrance window would increase with the P25-to-TNP mass ratio. In the present study, we therefore attempted to deposit TiO_2 composite films that were both thick and had a gradient of number average particle size (*GPS*). This was performed by constant-current electrophoresis using two types of TiO_2 nanoparticles with different sizes and surface properties, in order to reduce the reflectance by depositing TNPs near the entrance window. Hereafter, the thin film with a non-zero *GPS* is called a GPS thin film.

Fig. 1 shows a schematic drawing of the ideal structure of a GPS thin film. This film has a low P25-to-TNP mass ratio near the entrance window. The number average particle size increases with increasing film thickness and P25-to-TNP mass ratio. This structure is expected to decrease the reflectance of the film because the incident light would not be scattered at the boundary between the substrate and the film. Moreover, as the P25-to-TNP mass ratio increases with increasing film thickness, the light becomes more and more scattered within the film, and this confinement effect

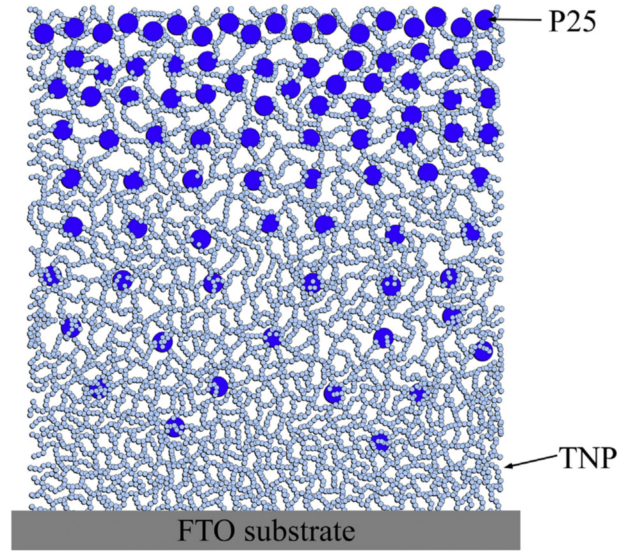

Fig. 1. Schematic drawing of the structure of a GPS thin film.

increases the optical path. Therefore, the aim of this study was to investigate the effectiveness of thin film cathodes deposited from a colloid in which the P25-to-TNP mass ratio was gradually changed as a function of electrophoresis time, at enhancing the LHE and, as a result, increasing the energy conversion efficiency of DSSCs.

2. Experimental procedure

2.1. Sample preparation

The TNPs were synthesized according to the method described in Ref. [17]. The TNPs were classified by size in a centrifugal separator with isopropyl alcohol as the dispersion medium using a surfactant removal process [15]. First, the TNPs were precipitated at 10,000 rpm by centrifugal classification and this process was repeated several times. Agglomerations of P25 were also classified with water as the dispersion medium. First, large P25 particles were precipitated and removed at 10,000 rpm by centrifugal classification. Small P25 particles were then precipitated from the supernatant of the colloidal solution at 13,500 rpm. The gel states of the classified TNPs and P25 included residual isopropyl alcohol at approximately 85 wt% and water at approximately 48 wt%, respectively. These particles were used in a wet state that included the solvent because it was difficult to disperse dry particles in a dispersion medium.

Two types of TiO_2 colloid were prepared in separate containers. 15.6 mg of TNPs with a small amount of isopropyl alcohol was added to 20 cm^3 of ethanol as the dispersion medium in a glass beaker. P25 particles in a small amount of water was added to ethanol as the dispersion medium in a burette container. The colloid was dispersed by stirring it, and then ultrasonication was performed.

Fig. 2 shows a schematic diagram of the fabrication method for GPS thin films by constant-current electrophoresis. The film-forming and stirring chambers were divided using a separator with a tiny hole to allow the solution to diffuse into the film-forming chamber from the stirring chamber. A fluorine-doped tin oxide (FTO) 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 10 mm from each other, perpendicular to the liquid surface in the glass beaker. GPS thin