

Films prepared by both methods have film thicknesses of 5 to 15  $\mu\text{m}$  and film mass of about 1 to 2  $\text{mg cm}^{-2}$ . The optimum film thickness is 13 to 14  $\mu\text{m}$ . The films have porosity of 60 to 70% [76]. High porosity produces effective diffusion of the redox mediator into the film. The roughness factor (shown above) for a 10- $\mu\text{m}$  film reaches approximately 1000, allowing the adsorption of large amounts of photosensitizer and consequently increased light-harvesting efficiency, as described in Section 15.1.2.2.  $\text{TiO}_2$  film prepared from 10 to 20 nm particles of  $\text{TiO}_2$  is transparent.

The scattering property of the film is important for the improvement of the LHE of the dye-coated film, resulting in improved IPCE performance of the cell. This effect of the scattering in the  $\text{TiO}_2$  film has been investigated in detail [16, 76, 79–82]. The path length of the incident light and therefore the absorption due to the adsorbed dye can be increased by light scattering in the  $\text{TiO}_2$  film. This can be achieved by the addition of some larger  $\text{TiO}_2$  particles in small  $\text{TiO}_2$  particles during film preparation, since larger particles have small surface area and consequently cannot adsorb large amount of the dye. A simulation of light scattering in the  $\text{TiO}_2$  electrode of DSSC predicts that a suitable mixture of small  $\text{TiO}_2$  particles (e.g. 20 nm diameter) and of larger particles (250–300 nm diameter), which are effective light-scattering centers, have the potential to enhance solar light absorption significantly [80]. Actually, the photocurrent of DSSC increased by using a scattering film compared to that for a transparent film [81]. This improvement in the photoresponse of DSSC due to the scattering effect is observed especially in the low-energy region (e.g. 650–900 nm). As shown in Figures 15.4 and 15.7, the IPCE values obtained in the red region are higher than what is indicated by the absorption spectra of the dyes in solution (Figure 15.4,  $1 - T$ ). On the low-energy side, a significant part of the incident radiation penetrates the layer due to the low absorption coefficient of the dye, while photons of 500 to 650 nm can be mainly absorbed near the TCO/ $\text{TiO}_2$  interface because of the large absorption coefficient. Multiple reflections of the low-energy light in highly scattering films result in increased light absorption and hence increased photoresponse than what the solution absorption spectra indicate.

It has also been reported that  $\text{TiCl}_4$  treatment of the film significantly improves cell performance, especially the photocurrent [6]. After printing, the  $\text{TiO}_2$  films are immersed in 0.1 to 0.5 M  $\text{TiCl}_4$  aqueous solutions at room temperature and then sintered at 450°C for 30 min. It is possible that  $\text{TiCl}_4$  treatment improves the photocurrent by improving the connections between  $\text{TiO}_2$  particles.

### 15.2.3 Dye Fixation onto the $\text{TiO}_2$ Film

After preparation of the  $\text{TiO}_2$  films, the N3 dye photosensitizer is adsorbed onto the  $\text{TiO}_2$  surface. The films are immersed into the dye solution (0.2–0.3 mM in ethanol or *tert*-butanol–acetonitrile, 1:1 mixed solution) followed by storage at room temperature for 12 to 18 h. This treatment produces intense coloration of the film. Before use, the film is washed with alcohol or acetonitrile to remove excess nonadsorbed dyes inside the nanoporous  $\text{TiO}_2$  film.