

sheet resistance and high transparency. In addition, sheet resistance should be nearly independent of the temperature up to 500°C because sintering of the TiO<sub>2</sub> electrode is carried out at 450 to 500°C. Indium–tin oxide (ITO) is one of the most famous TCO materials. In spite of having low resistance at room temperature, ITO resistance increases significantly at high temperature in air. Usually, fluorine-doped SnO<sub>2</sub> is used as the TCO substrate for DSSCs (e.g. Nippon Sheet Glass Co.,  $R = 8\text{--}10 \Omega/\text{square}$ ).

### 15.1.2.2 TiO<sub>2</sub> photoelectrode

Photoelectrodes made of such materials as Si, GaAs, InP, and CdS decompose under irradiation in solution owing to photocorrosion. In contrast, oxide semiconductor materials, especially TiO<sub>2</sub>, have good chemical stability under visible irradiation in solution; additionally, they are nontoxic and inexpensive. The TiO<sub>2</sub> thin-film photoelectrode is prepared by a very simple process. TiO<sub>2</sub> colloidal solution (or paste) is coated on a TCO substrate and then sintered at 450 to 500°C, producing a TiO<sub>2</sub> film about 10 μm in thickness. Because this film is composed of TiO<sub>2</sub> nanoparticles (10–30 nm), giving it a nanoporous structure, the actual surface area of TiO<sub>2</sub> compared to its apparent surface area, roughness factor (rf), is >1000; that is, a 1-cm<sup>2</sup> TiO<sub>2</sub> film (10 μm thickness) has an actual surface area of 1000 cm<sup>2</sup>. The dye is considered to be adsorbed on the TiO<sub>2</sub> surface in a monolayer. Thus, if the nanoporous TiO<sub>2</sub> film has a high rf, the amount of dye adsorbed is drastically increased (on the order of 10<sup>-7</sup> mol cm<sup>-2</sup>), resulting in an increase of LHE that is near 100% at the peak absorption wavelength of the dye. In comparison, the amount of adsorbed dyes on the surface of single-crystal and polycrystal materials is quite small, with only 1% LHE even at the peak wavelength.

Normally, the TiO<sub>2</sub> film contains large TiO<sub>2</sub> particles (250–300 nm), which can scatter incident photons effectively, to improve the LHE as shown later. The porosity of the film is also important because the electrolyte, which contains the redox ions, must be able to penetrate the film effectively to suppress the rate-determining step via diffusion of redox ions into the film. Appropriate porosity, 50 to 70%, is controlled in the sintering process by the addition of a polymer such as polyethylene glycol (PEG) and ethyl cellulose (EC) into the TiO<sub>2</sub> colloidal solution or paste. Figure 15.2 shows a scanning electron microscope (SEM) photograph of a typical nanocrystalline TiO<sub>2</sub> film. A detailed description of the procedure for preparing the TiO<sub>2</sub> film is given in Section 15.2.2.

### 15.1.2.3 Ru complex photosensitizer

The Ru complex photosensitizer, which contributes the primary steps of photon absorption and the consequent electron injection, is adsorbed onto the TiO<sub>2</sub> surface. The chemical structure of typical Ru complex photosensitizers developed by Grätzel's group are shown in Figure 15.3 (TBA is tetrabutylammonium cation, (C<sub>4</sub>H<sub>9</sub>)<sub>4</sub>N<sup>+</sup>), and Figure 15.4 shows absorption properties of the complexes in solution. The y-axis is represented by absorbance ( $A$ ) and  $1 - T (= 1 - 10^{-A})$ , where  $T$  is the transmittance. The *cis*-bis(4,4'-dicarboxy-2,2'-bipyridine)dithiocyanato ruthenium(II) (RuL<sub>2</sub>(NCS)<sub>2</sub> complex), which is referred to as N3 dye (or red dye), can absorb over a wide range of the visible regions from 400 to 800 nm. The trithiocyanato 4,4'4''-tricarboxy-2,2':6',2''-terpyridine ruthenium(II) (black dye) (RuL'(NCS)<sub>3</sub> complex), absorbs in the near-IR region up to