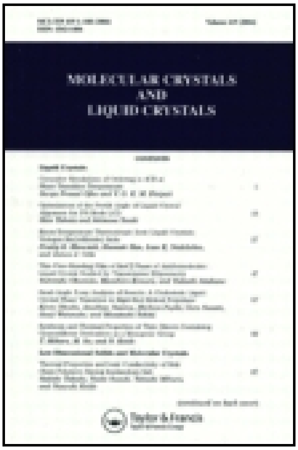

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Characterization of GrÄTzel Dye on Tio $_2$ Particles by Transmission Electron Microscopy

Yasutomo Yoshioka [a], Masahiko Tsujimoto [a], Masanori Koshino [a], Takashi Nemoto [a], Tetsuya Ogawa [a], Hiroki Kurata [a] & Seiji Isoda [a]
[a] Institute for Chemical Research, Kyoto University, Uji, Kyoto, Japan

Version of record first published: 18 Oct 2010

Mol. Cryst. Liq. Cryst., Vol. 424, pp. 95–102, 2004

ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400490505947

CHARACTERIZATION OF GRÄTZEL DYE ON TIO_2 PARTICLES BY TRANSMISSION ELECTRON MICROSCOPY

Yasutomo Yoshioka, Masahiko Tsujimoto, Masanori Koshino, Takashi Nemoto, Tetsuya Ogawa, Hiroki Kurata, and Seiji Isoda
Institute for Chemical Research, Kyoto University, Uji, Kyoto 611-0011, Japan

The structural characteristics of TiO_2 (anatase) nanocrystals covered with bis[(4,4′-carboxy-2,2′-bipyridine)(thiocyanato)] ruthenium (II) molecule known as Grätzel dye being developed for dye-sensitized solar cell were investigated by means of cryo-transmission electron microscopy (cryo-TEM) and elemental mapping with an energy-filtering TEM. The Grätzel dye is uniformly adsorbed on TiO_2 particles as non-crystalline phase with almost monolayer thickness.

Keywords: cryo-TEM; dye-sensitized solar cell; EELS; Grätzel dye; titanium oxide

INTRODUCTION

The structure of organic/inorganic interface plays an important role of physical and chemical properties of assembled materials. The system of TiO_2 nanocrystals coated with organic dyes like Ru polypridine complex is one of the functional organic/inorganic interfaces, which can be applied to photovoltaic cell. O'Regan and Grätzel [1] have reported a new type of solar cell consisting of nanometer-size TiO_2 colloidal particles sensitized by a newly developed charge-transfer organic dye, bis[(4,4′-carboxy-2,2′-bipyridine)(thiocyanato)]ruthenium (II) molecule known as Grätzel dye, which has shown the high efficiency for the conversion of incident photons to electrical current and the exceptional stability of solar cell. After this

Recevied 1 October 2003; accepted 1 December 2003.
This work was supported by a Grant-in-Aid from the Ministry of Education, Culture, Sports, Science and Technology, Japan (21st Century COE on Kyoto University Alliance for Chemistry) and a Grant-in Aid for Science Research (B) No. 15310089.
Address correspondence to Hiroki Kurata Division of State and Structure II, Institute for Chemical Research Kyoto University Uji Kyoto, 611-0011, Japan. Tel.: +81-774-38-3050, Fax: +81-774-38-3055, E-mail: kurata@eels.kuicr.kyoto-u.ac.jp

work the research on dye-sensitized solar cell has been carried out extensively, for example, the development of new dyes [2–5] and recently the use of TiO_2 nanotubes instead of nanocrystals [6,7]. However, there are few works related to the structural investigation for the adsorbed dyes. In the present work, we investigate the structural characteristics of the Grätzel dye adsorbed on TiO_2 (anatase) nanocrystals by means of analytical transmission electron microscopy.

EXPERIMENTAL

The Grätzel dye was obtained from Kojima Chemical Reagents INC. and used without further purification. The molecular structure of the Grätzel dye is shown in Figure 1. The crystal structure of this molecule has been reported [8] that the crystal is triclinic; $a = 1.14663\,\text{nm}$, $b = 1.25897\,\text{nm}$, $c = 1.89326\,\text{nm}$, $\alpha = 75.238°$, $\beta = 89.611°$, $\gamma = 66.446°$. The nanocrystalline powders of TiO_2 (anatase) with a diameter of 20 to 30 nm were supplied by

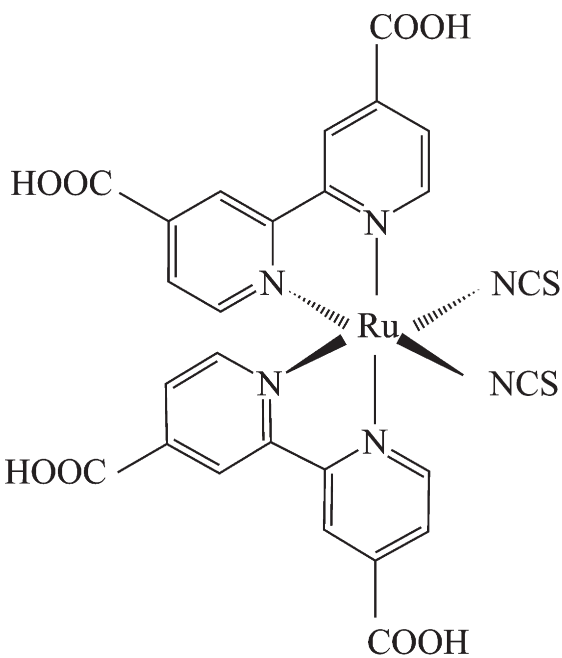

FIGURE 1 Molecular structure of bis[(4,4′-carboxy-2,2′-bipyridine)(thiocyanato)] ruthenium (II).

Wako Pure Chemical Industries. The specimens were prepared by dispersing TiO_2 powders into an ethanol solution of Grätzel dye for 12 hours. After washing with ethanol, the nanocrystalline powders were dispersed on a carbon or germanium thin film supported by microgrid mounted on a cupper mesh for electron microscope observations. Transmission electron microscopy (TEM) investigations were performed on a JEM-4000SFX, operated at 400 kV, which made it possible to examine the specimen at temperatures around 4.2 K [9], diminishing considerably the electron irradiation damage of specimens. The elemental distribution images on TiO_2 surface were observed with an ARM-1000 (JEOL) equipped with a Gatan imaging filter for an 1 MV operation [10]. The elemental distribution was also observed with a scanning transmission electron microscope (STEM) mode combined with an electron energy-loss spectroscopy (EELS) using a JEM-2010F [11].

RESULTS AND DISCUSSION

A high-resolution TEM image and an electron diffraction pattern of TiO_2 particles coated with Grätzel dye observed at room temperature are shown in Figures 2(a) and (b), respectively. The adsorbed layer is uniformly covered on the particle surface with a thickness of 1 to 2 nm with weaker contrast. This thickness was almost the same even if the concentration of dye in ethanol solution or the dipping time was changed in sample preparation.

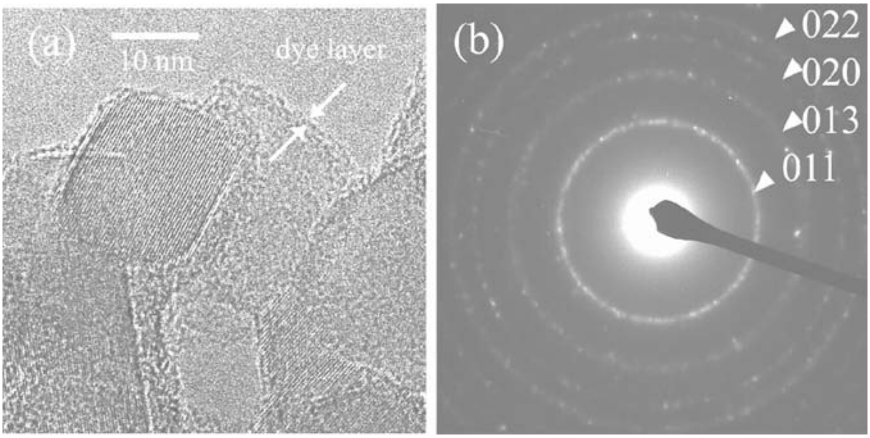

FIGURE 2 High-resolution TEM image of TiO_2 nanocrystals coated with Grätzel dye (a) and the selected area electron diffraction pattern (b). The diffraction pattern can be indexed as shown in (b) with the anatase TiO_2.

The lattice fringes are clearly observed in TiO_2 particles but the adsorbed layers seem to be amorphous phase. Indeed, the electron diffraction pattern shows only diffraction rings assigned to reflections from the anatase TiO_2 crystal. Such an amorphous-like appearance could be originated from electron irradiation damage because organic molecules are generally sensitive to the high-energy electron beam.

In order to minimize the effects of electron irradiation damage on the adsorbed layer during the experiment, high-resolution cryo-TEM observation was performed as shown in Figure 3. Figure 3(a) is a cryo-TEM image of TiO_2 particles coated with the Grätzel dye as observed at about 4.2 K, which shows the amorphous-like feature at the dye layers observed at room temperature. Figure 3(b) is a high-resolution cryo-TEM image observed from a small crystal of Grätzel dye itself that was found occasionally in areas isolated from TiO_2 particles. The fringes with a lattice-plane spacing of 0.560 nm and 0.539 nm are observed in this image, which corresponds to $(1\bar{1}1)$ and $(21\bar{1})$ lattice plane spacings of the dye crystal, respectively. This fact means that the cryo-TEM experiment could protect

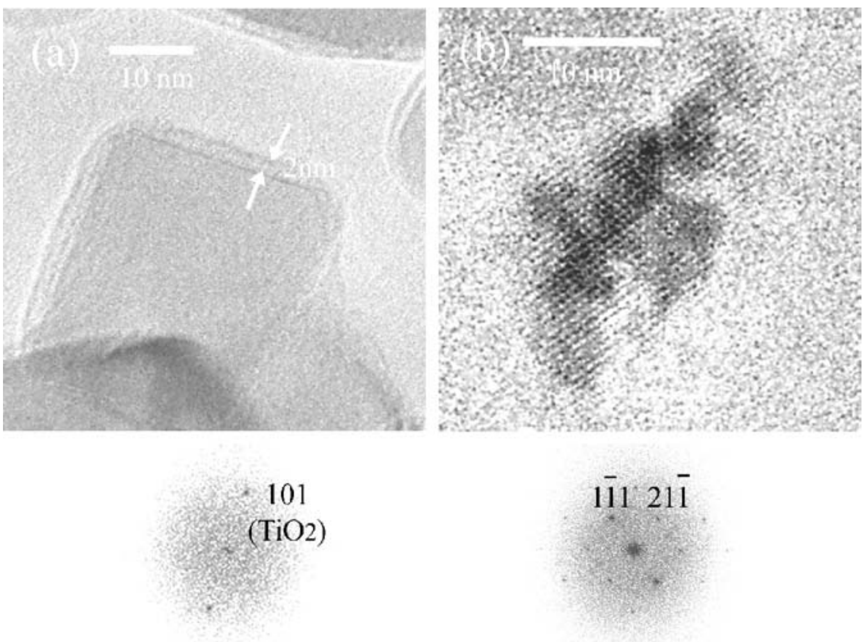

FIGURE 3 High-resolution cryo-TEM images of TiO_2 nanocrystals coated with Grätzel dye (a) and the nanocrystal of Grätzel dye (b). Attached figures show the Fourie transform patterns.

the radiation damage in taking lattice images on the dye crystal. If the dye adsorbed on TiO_2 particles has a crystalline phase, the lattice fringe of dye crystal should be observed together with the fringes of TiO_2 crystal. However, only the lattice fringes of TiO_2 crystal are observed in Figure 3(a). The attached figure is the Fourier transform of the image showing only the spots due to TiO_2 lattices of 0.35 nm. It has been reported [12] that the TEM observation for TiO_2 nanocrystals coated with another sensitized dye similar to the Grätzel dye has shown the extra contrast like a Moiré fringes coming from the lattice superposition of an adsorbed layer and a TiO_2 particle. Such an extra contrast has never even observed in the present case. These results suggest obviously that the adsorbed layer is not crystalline phase.

In order to make sure that the amorphous layers are the organic dye, the elemental distribution image has been examined by means of the energy filtering TEM method based on the EELS. Figures 4(a) and 4(b) show a TEM image and an EELS spectrum obtained from a TiO_2 particle covered with dye. The inner-shell excitation spectra of carbon, titanium and oxygen were observed in the EELS spectrum. Carbon is one of the constituent elements of the dye, so carbon distribution is important to reveal an existence of the dye. Other elements included in the dye molecule except oxygen have not been detected with a large S/N ratio because of the small number of atoms and the smaller cross-sections. Figures. 4(c) and 4(d) show the elemental distribution images of titanium and carbon constructed by use of inelastically scattered electrons due to the titanium 2p-shell and carbon 1s-shell excitations observed at about 460 and 300 eV energy-loss, respectively. Although the elemental signals were superimposed on background intensity coming from the pre-edge region as shown in Figure 4(b), these background intensities were subtracted to construct pure elemental maps by using the three windows technique [13]. In the elemental map the bright contrast indicates the existence of the element of interest. The carbon distribution is high in the peripheral regions of TiO_2 particle, which means that the thickness of adsorbed layers along the electron beam direction is large compared to that on the center of particles. The carbon distribution with a thickness of 1 to 2 nm observed on TiO_2 surface is attributed to the adsorbed Grätzel dye and corresponds to the non-crystalline layer as discussed in the TEM images.

In the carbon map of Figure 4(d) it is not clear whether the dye molecules coat the whole surface of TiO_2 particles because of the low sensitivity of the elemental mapping. Alternative way to examine the elemental distribution with higher sensitivity is to measure the EELS spectrum from each point of the specimen area by scanning the electron probe focused into sub-nanometer in diameter, so-called STEM-EELS method. Figure 5 shows the carbon and titanium distributions measured by a line scanning of

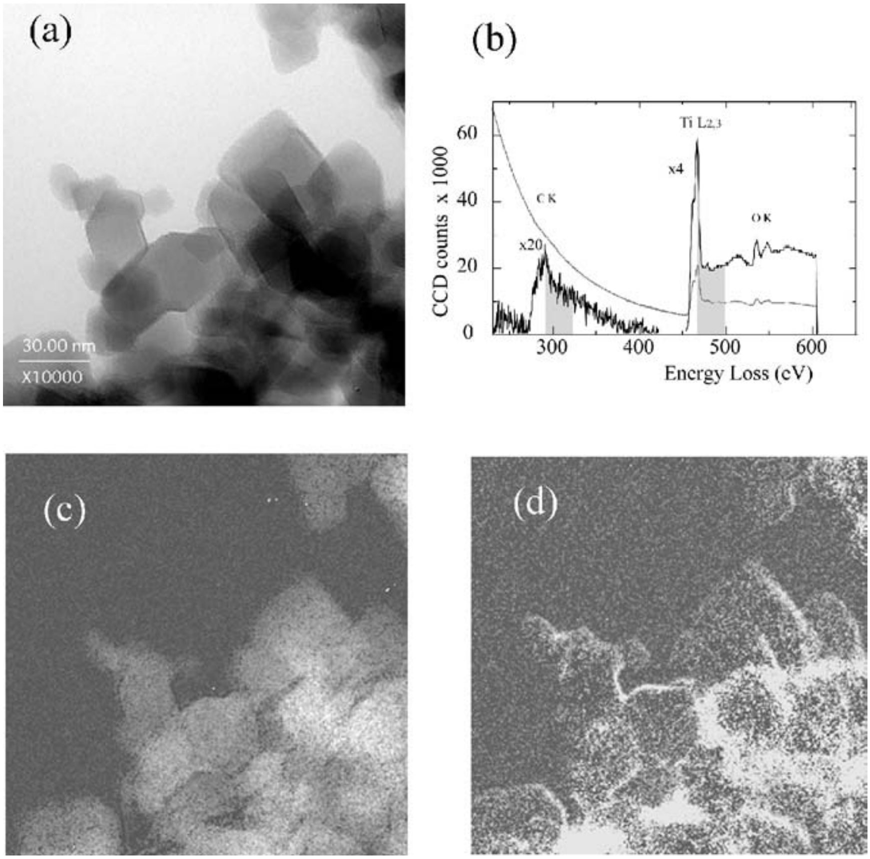

FIGURE 4 TEM images of TiO_2 nanocrystals coated with Grätzel dye (a) and an EELS spectrum (b). Elemental distribution images of titanium and carbon are shown in (c) and (d), respectively.

electron probe across the edge region of TiO_2 nanocrystal covered with the dye using the STEM-EELS method. The 50 spectra were measured along the line of about 25 nm lengths with an interval of 0.5 nm. The intensity distribution of titanium corresponds to the TiO_2 particle region in this plot. The high intensity of carbon is mainly observed in the edge region as well as in the particle region, which means that the dye coats the whole surface of TiO_2 particles. Consequently, the Grätzel dye sensitizing the TiO_2 nanocrystals is adsorbed on the particle surface uniformly with the thickness of 1 to 2 nm, which is consistent with the results of X-ray diffraction, XPS and XAFS spectroscopy studies reported recently [14].

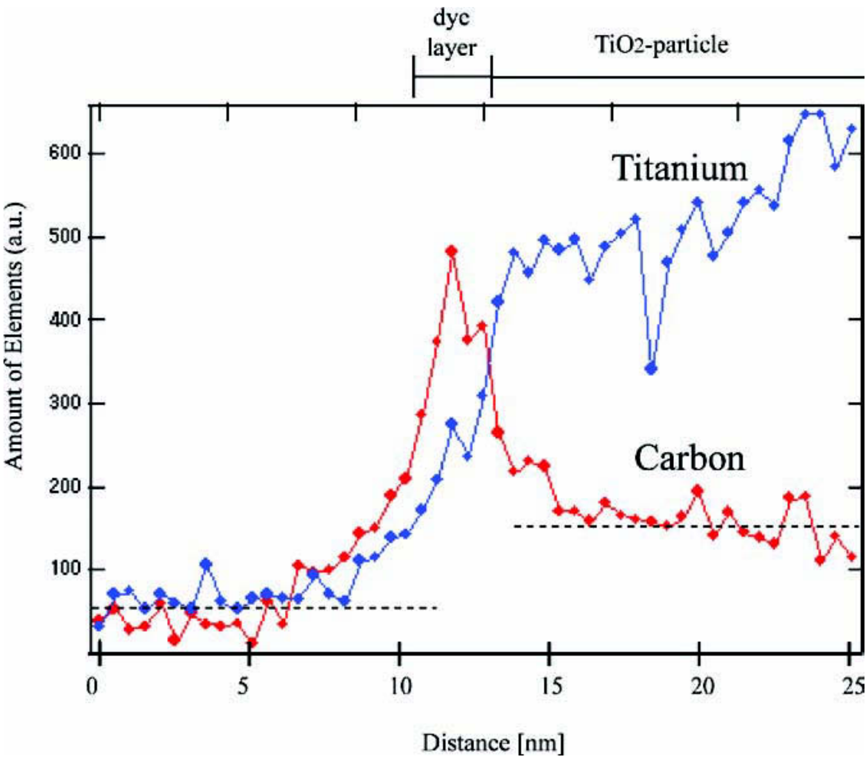

FIGURE 5 Elemental distribution profiles of titanium and carbon measured along a line across the edge region of TiO_2 nanocrystals coated with Grätzel dye.

CONCLUSIONS

High-resolution transmission electron microscopy for TiO_2 nanocrystals coated with the Grätzel dye molecules was performed at low temperature of about 4.2 K. The elemental distributions were also observed by using the energy-filtering TEM and STEM-EELS methods. The adsorbed dye forms a non-crystalline layer at the surface of TiO_2 nanocrystals with a thickness of 1 to 2 nm.

REFERENCES

[1] O'Regan, B. & Grätzel, M. (1991). *Nature*, *353*, 737.
[2] Nazeeruddin, M. K., Humphry-Baker, R., Grätzel, M., & Murrer, B. A. (1998). *Chem. Commun.*, 719.

[3] Ferrerre, S., Zaban, A., & Gregg, B. A. (1997). *J. Phys. Chem. B.*, *101*, 4490.
[4] Sayama, K., Sugino, M., Sugihara, H., Abe, Y., & Arakawa, H. (1998). *Chem. Lett.*, 753.
[5] Cherepy, N. J., Smestad, G. P., Grätzel, M., & Zhang, J. Z. (1997). *J. Phys. Chem. B.*, *101*, 9342.
[6] Adachi, M., Okada, I., Ngamsinlapasarhian, S., Murata, Y., & Yoshikawa, S. (2002). *Electrochemistry*, *70*, 449.
[7] Uchida, S., Chiba, R., Tomita, M., Masaki, N., & Shirai, M. (2002). *Electrochemistry*, *70*, 418.
[8] Shklover, V., Ovchinnikov, Y. E., Braginsky, L. S., Zakeeruddin, S. M., & Grätzel, M. (1998). *Chem. Mater.*, *10*, 2533.
[9] Ogawa, T., Isoda, S., & Kobayashi, T. (1997). *Acta Cryst.*, *B53*, 831.
[10] Kurata, H., Moriguchi, S., Isoda, S., & Kobayashi, T. (1996). *J. Electron Microsc., 45*, 79.
[11] Kurata, H., Kumagai, H., & Ozasa, K. (2001). *J. Electron Microsc., 50*, 141.
[12] Shklover, V., Haibach, T., Bolliger, B., Hochstrasser, M., Erbudak, M., Nissen, H. U., Zakeeruddin, S. M., Nazeeruddin, Md. K., & Grätzel, M. (1997). *J. Solid State Chem.*, *132*, 60.
[13] Reimer, L. (1995). *Energy-filtering transmission electron microscopy.* Springer-Verlag: Berlin, Germany.
[14] Zubavichus, Y. V., Slovokhotov, Yu. L., Nazeeruddin, M. K., Zakeeruddin, S. M., Grätzel, M., & Shklover, V. (2002). *Chem. Mater., 14*, 3556.