

# Morphology of a TiO<sub>2</sub> Photocatalyst (Degussa, P-25) Consisting of Anatase and Rutile Crystalline Phases

Teruhisa Ohno, Koji Sarukawa, Kojiro Tokieda, and Michio Matsumura<sup>1</sup>

Research Center for Solar Energy Chemistry, Osaka University, 1-3 Machikaneyama, Toyonaka, Osaka 560-8531, Japan

Received December 8, 2000; revised May 25, 2001; accepted June 23, 2001

The TiO<sub>2</sub> powder (Degussa, P-25), which is a standard material in the field of photocatalytic reactions, contains anatase and rutile phases in a ratio of about 3 : 1. Transmission electron microscopy showed that the anatase and rutile particles separately form their agglomerates. The average sizes of the anatase and rutile elementary particles are 85 and 25 nm, respectively. Diffuse reflectance spectra of the TiO<sub>2</sub> powder were successfully traced by physically mixing pure anatase and rutile particles in a ratio of 3 : 1. By the HF treatment of the TiO<sub>2</sub> powder, pure rutile particles were isolated. All these results indicate that the rutile phase does not exist as an overlayer on the surface of anatase particles, but it exists separately from anatase particles. We also found that photocatalytic oxidation of naphthalene is inefficient on pure anatase and rutile powders. However, the reaction is very efficient on the P-25 powder, as well as on a mixture of pure anatase and rutile particles. Under the conditions of the photocatalytic reactions, the anatase and rutile agglomerates are considered to be decomposed, and the anatase and rutile particles are in contact, leading to a synergy effect. © 2001 Academic Press

**Key Words:** photocatalyst; titanium dioxide; anatase; rutile; morphology; TEM.

## INTRODUCTION

Photocatalytic reactions on semiconductor powders have attracted much attention because of their applicability to the treatment of a variety of pollutants and wastes (1–11) and utilization of solar energy (12–18). To achieve high efficiency of the reactions, many kinds of TiO<sub>2</sub> powders have been examined. From the results, it has been concluded that anatase particles with a large surface area are efficient for the decomposition of pollutants in air and water (10, 11). In these reactions, the large surface area is especially important, because the concentrations of the pollutants are usually very low. On the other hand, for splitting water, which is an important reaction to convert light energy into chemical energy, rutile particles with a small surface area

are efficient (16–18). In this case, a band bending should be developed in each particle to oxidize water, and hence large particles are advantageous.

In the field of TiO<sub>2</sub>-photocatalyzed reactions, the powder called P-25 (Degussa) has been a standard material, which has a relatively large surface area (49 m<sup>2</sup> g<sup>-1</sup>). Interestingly, the P-25 powder consists of anatase and rutile phases. Because the P-25 powder shows high activity for many kinds of photocatalytic reactions, it has been used in many studies. In most studies, however, the effects of the mixed phases and the morphology have not been discussed in relation to the activity. The first extensive work to correlate the photocatalytic activity and the structure of P-25 was carried out by Bickley *et al.* (19). They obtained transmission electron microscopic (TEM) images and diffuse reflectance spectra of the P-25 powder, and they reported that the surface of anatase particles is transformed to the rutile structure. Afterward, based on precise TEM observation, Datye *et al.* (20) concluded that anatase and rutile single crystalline particles exist separately in the P-25 powder. However, they did not differentiate the morphology of the anatase and rutile particles. Under the circumstances, clarification of the morphology of the mixed phases is still of great importance to deepen the understanding of the activity of the TiO<sub>2</sub> photocatalysts.

We have reported that pure rutile particles are easily isolated from the P-25 powder by treatment with HF solution, because the anatase phase dissolves rapidly in this solution (21). By comparing the activities of the original P-25 powder and the isolated rutile particles, we also found that the presence of both anatase and rutile phases is important for some photocatalytic reactions where oxygen is used as the electron acceptor (21). To clarify the synergy between the anatase and rutile phases, we studied the morphology of the anatase and rutile phases in P-25 powder by measuring the TEM images and the diffuse reflectance spectra of the particles. From the results, we propose a model that is different from that reported by Bickley *et al.* (19). Our model is similar to that of Datye *et al.* (20) but different in the understanding of the synergy effect.

<sup>1</sup> To whom correspondence should be addressed. Fax: 81-6-6850-6699. E-mail: [matsu@chem.es.osaka-u.ac.jp](mailto:matsu@chem.es.osaka-u.ac.jp).

## EXPERIMENTAL

We used titanium dioxide (Degussa, P-25) powder obtained from Nippon Aerosil Co. Ltd. For comparison, various kinds of TiO<sub>2</sub> powders having anatase and rutile particles were used; these were obtained from Ishihara Co. Ltd. (ST-01, ST-21, PT-101) and Toho Titanium Co. Ltd. (NS-51). Contents of the anatase phase and relative surface areas of these powders are as follows—P-25: 75%, 49.2 m<sup>2</sup>/g; ST-01: 100%, 192.5 m<sup>2</sup>/g; ST-21: 100%, 56.1 m<sup>2</sup>/g; PT-101: 0%, 25 m<sup>2</sup>/g; NS-51: 0%, 6.5 m<sup>2</sup>/g. In some experiments, some of the pure anatase powders and the pure rutile powders were mixed in a ratio of 3 : 1, which is the same as that of the P-25 powder. For the mixing, the TiO<sub>2</sub> powders were dispersed in water, sonicated for 30 min, filtrated, and dried under reduced pressure successively at 50°C for 1 h and at 100°C for 2 h.

The morphologies of the TiO<sub>2</sub> powders were examined using a Hitachi H-800 TEM and a Hitachi S-5000 scanning electron microscope. The diffuse reflectance spectra of the powders were obtained using a Shimadzu UV-2500PC spectrophotometer equipped with an integrating sphere. The contents of anatase and rutile phases in the powders were determined using an X-ray diffraction meter (Philips X'Pert-MRD). The surface areas of the powders were

measured using a surface area analyzer (Micromeritics, FlowSorb II 2300).

Photocatalytic reactions were carried out at room temperature in Pyrex glass tubes ( $\phi = 15$  mm), which contain TiO<sub>2</sub> particles (0.015 g), naphthalene (0.1 g), and a mixture of acetonitrile and water (4.0 g). Details of the experimental conditions were reported in our previous papers (22, 23).

## RESULTS AND DISCUSSION

TEM images of the P-25 powder clearly indicate that the anatase and rutile particles exist separately by forming their agglomerates, as shown in Fig. 1. The crystal structures were assigned from the electron diffraction patterns. From these images, the average diameters of the anatase and rutile particles are estimated to be about 25 and 85 nm, respectively. By careful observation, we found amorphous particles in addition to the anatase and rutile particles, as shown in Fig. 2. The content of the amorphous particles is very low: about 1.0%. It should be emphasized that no images demonstrating that the crystal structure is partially transformed in a particle were obtained, as has been reported by Datye *et al.* (20).

The P-25 powder is manufactured by the Aerosil process, by which titanium tetrachloride is subjected to hydrolysis

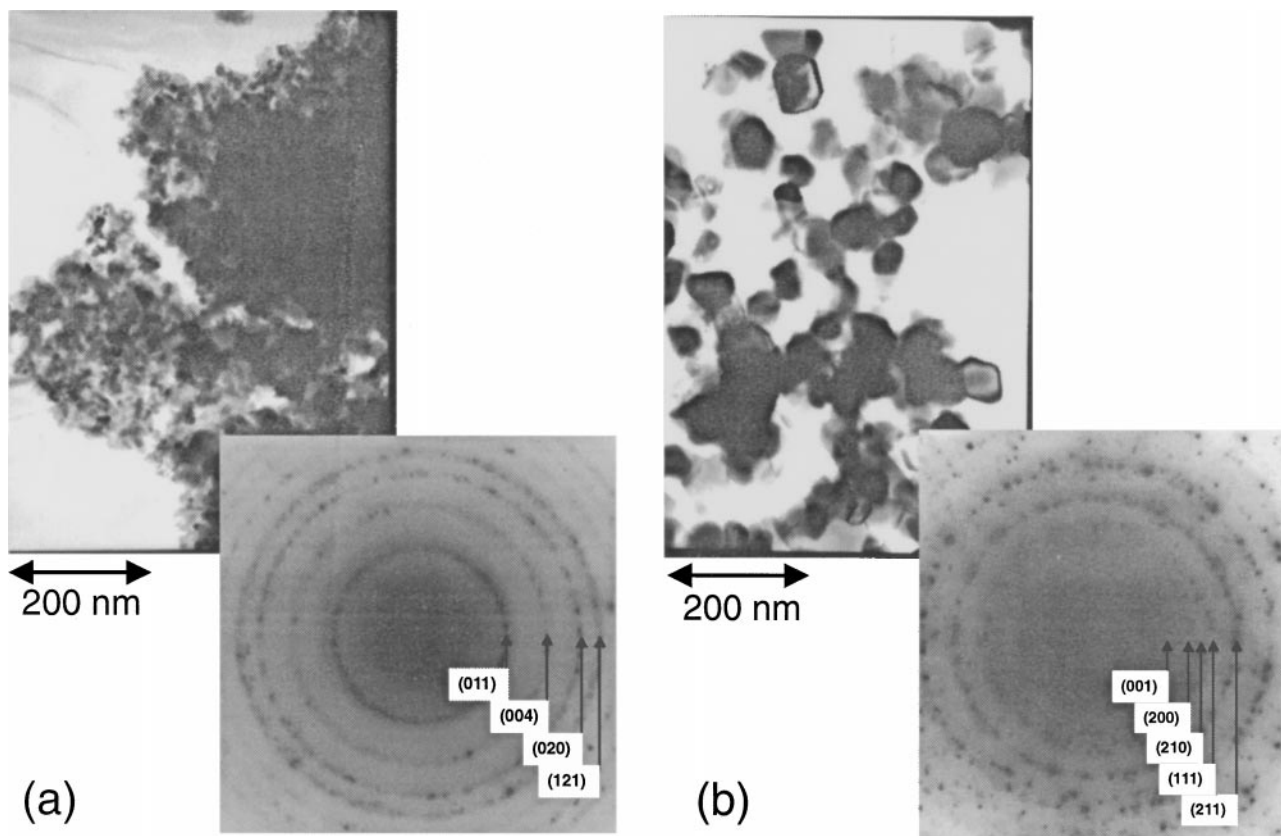


FIG. 1. TEM photographs and electron diffraction patterns of the P-25 powder in the regions of (a) the anatase phase and (b) the rutile phase.

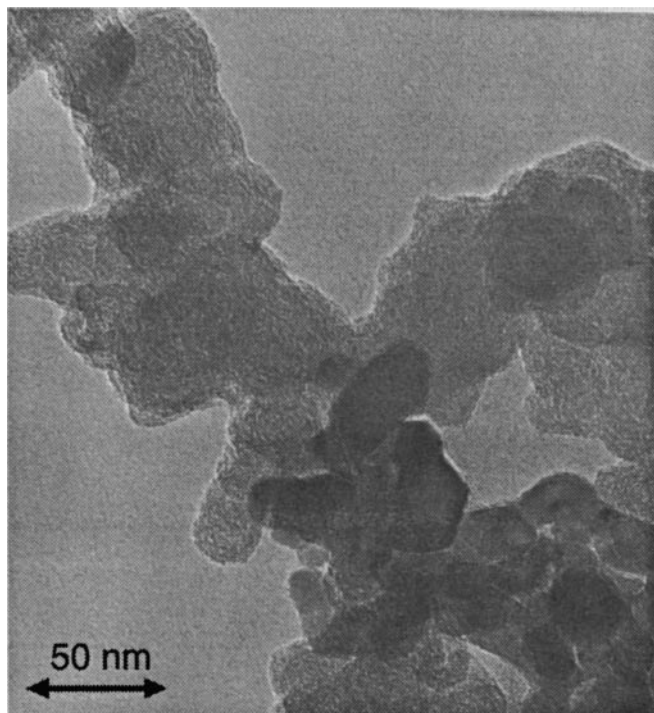


FIG. 2. TEM photograph of the amorphous phase included in the P-25 powder.

in the vapor phase at an elevated temperature (19, 20). During this process, the growth of particles is quenched when the particles (or the agglomerates) reach a certain size, since the grown particles (or the agglomerates) are removed from the reaction zone because of their increased weight. The TEM pictures of the P-25 powder shown in Fig. 1 suggest that the anatase and rutile particles grow on different nuclei during the process. In contrast to our observation, Bickley *et al.* (19) reported that anatase and rutile phases in the P-25 powder often appeared in close proximity. On the basis of their results, they suggested that the rutile phase forms an overlayer on the surface of anatase particles during the manufacturing process. However, our TEM images are strongly against the model. The difference in TEM images obtained by Bickley *et al.* and us is probably caused by the different sample preparation conditions. We sprinkled directly the particles on carbon films, which were supported Cu meshes. On the other hand, Bickley *et al.* placed the particles on the substrates from the suspension of butanol. Their method is not adequate to observe the morphology of the powder, because the anatase and rutile particles mix, once they are suspended in solution, as discussed later.

In addition to the TEM images, Bickley *et al.* argued that the rutile phase is generated as a result of transformation at the surface of anatase particles on the basis of the diffuse reflectance spectrum of the P-25 powder. They observed

that the diffuse reflectance spectrum of the P-25 powder was different from that of a powder prepared by physically mixing anatase and rutile particles. Based on this result, they proposed that morphology of the P-25 powder is different from that of the physically mixed powder, and the spectrum of the P-25 powder was attributed to the partly transformed crystalline structure. However, they might have erroneously selected the anatase and rutile powders for preparing the mixed powder. In particulate systems, the scattering of light is strongly dependent on the particle size. Hence, we selected the pure anatase (ST-21, average diameter about 30 nm) and rutile (PT-101, average diameter about 75 nm) particles, the diameters of which are similar to those of anatase and rutile particles included in the P-25 powder. We mixed them in the ratio of 3:1, which is identical to the ratio of the components in the P-25 powder. The detailed procedure for preparation of the mixed  $\text{TiO}_2$  powder is described in the Experimental section. The diffuse reflectance spectra of P-25 and the mixed powder show the onset of the reflection in the region between the onsets of pure anatase and rutile powders, as shown in Fig. 3. Importantly, the spectrum of the mixed powder was in good agreement with that of the P-25 powder. Therefore, in contrast to the report by Bickley *et al.*, the diffuse reflectance spectra did not give evidence supporting that partly transformed phases exist on a particle of the P-25 powder.

We have found that pure rutile particles are easily isolated from the P-25 powder by treatment with 10% HF solution for 24 h (21). The diffuse reflectance spectrum of the isolated powder is shown by a bold line in Fig. 3. The onset wavelength of the absorption (i.e., the band gap) is in good agreement with that of the pure rutile powder (PT-101). It should be noted that the reflectance of the HF-treated P-25

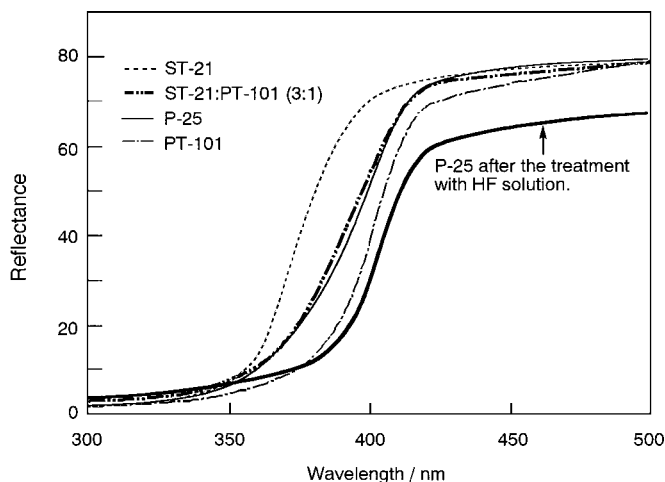


FIG. 3. Diffuse reflectance spectra of pure anatase powder (ST-21), pure rutile powder (PT-101), the mixture of the pure anatase and rutile powders (3:1), and the P-25 powder. The spectrum of the P-25 powder after the treatment with HF solution is shown by the bold line.

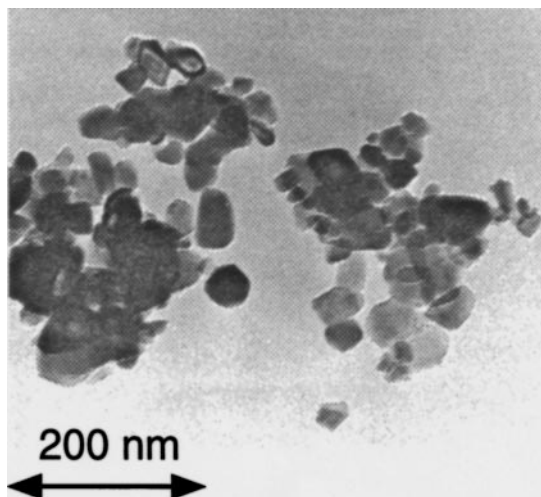


FIG. 4. TEM photograph of the rutile particles isolated from the P-25 powder.

powder at a wavelength longer than 400 nm is lower than those of the powders, as shown in Fig. 3. Consistent with the spectrum, the isolated rutile powder is grayish. Before the HF treatment, however, the reflectance of the P-25 powder is high. This is probably because of the strong light scattering by the small anatase particles, whose content is 75%. It is known that TiO<sub>2</sub> powders show absorption in the wavelength region longer than 400 nm, if they are reduced at elevated temperature and the absorption of these powders is attributed to the Ti<sup>3+</sup> ions (24). Hence, the rutile particles in the P-25 powder are considered to contain the Ti<sup>3+</sup> ions, which form the electron donors. Accordingly, it is considered that a fairly large band bending is generated in the rutile particles despite their rather small particle size (85 nm). This is probably an important reason for the high reactivity of the P-25 powder for many kinds of reactions.

Figure 4 shows the TEM image of the rutile particles isolated from the P-25 powder by the treatment with 10% HF solution for 24 h. The structure is almost the same as that observed in the rutile particles observed in the P-25 powder, which is shown in Fig. 1b. In contrast, the anatase particles, as shown in Fig. 1a, completely disappeared after the treatment with 10% HF solution. The disappearance of the anatase particles also contradicts the argument that the rutile phase exists as an overlayer on the surface of anatase particles.

We found a clear synergy effect between the anatase and rutile phases for the photocatalytic oxidation of naphthalene, as shown in Table 1. The main product is 2-formylcinnamaldehyde (25), which was erroneously assigned to 1,8-dihydroxynaphthalene in our previous papers (22, 23). As seen in Table 1, the mixture of ST-01 (anatase) and NS-51 (rutile) showed the activity as high as that of P-25, whereas the activity of pure ST-01 and NS-51 powders is low.

TABLE 1

Photocatalytic Oxidation of Naphthalene on TiO<sub>2</sub> Powders

TiO <sub>2</sub> powder	Amount of 2-formylcinnamaldehyde <sup>a</sup> /μmol
P-25	13.4
ST-01 (anatase)	1.4
NS-51 (rutile)	4.3
ST-01 : NS-51 (3 : 1)	11.5

<sup>a</sup> Product was quantitatively analyzed by HPLC after photoirradiation for 1 h.

The synergy effect can be expected, if rutile and anatase particles are in contact. Figure 5 shows the scanning electron microscopic image of the mixture of pure anatase (ST-01) and pure rutile (NS-51) powders, which were mixed by sonication in water. Before the mixing, the powders form agglomerates, as the anatase and rutile phases in the P-25 powder. Since the sizes of the anatase and rutile particles in these two kinds of powders are largely different, one can easily see that the anatase particles are loaded on the rutile particles as shown in Fig. 5. In the case of the P-25 powder also, the anatase and rutile particles are mixed in a similar fashion after the same treatment. However, such a clear mixed image as shown in Fig. 5 was not obtained for P-25, because the difference in the sizes of anatase and rutile particle is not large enough. In the photocatalytic reactions, the solution is sonicated to suspend the TiO<sub>2</sub> particles before photoirradiation, and the anatase particles are

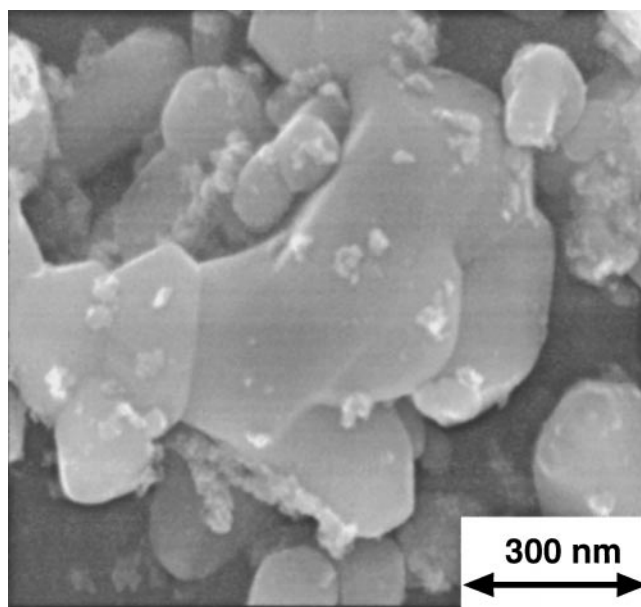


FIG. 5. Scanning electron microscopic photograph of a mixture of ST-01 (pure anatase) and NS-51 (pure rutile) powders. The elementary particle sizes of the powders are 7.0 and 220 nm, respectively. From the difference in the particle sizes, the small dots deposited on the large rutile particles are assigned to the agglomerates of fine anatase particles.

probably loaded on the rutile particles. This is why synergy effect appears for the mixture of anatase and rutile particles, which make separated agglomerate before sonication.

### CONCLUSIONS

We have found that the anatase and rutile particles exist separately in the P-25 (Degussa) powder. By the TEM observation, the agglomerates made of either anatase or rutile particles are clearly observed. However, under the practical operational conditions of the photocatalytic reactions, the agglomerates are expected to be decomposed, and the anatase particles and rutile particles are in contact. This mixed structure must be the key to the high activity of the P-25 powder.

### REFERENCES

- Schwitzgebel, J., Ekerdt, J. G., Gerischer, H., and Heller, A., *J. Phys. Chem.* **99**, 5633 (1995).
- Zang, L., Lange, C., Abraham, I., Storck, S., Maier, W. F., and Kisch, H., *J. Phys. Chem. B* **102**, 10765 (1998).
- Ohnishi, H., Matsumura, M., Tsubomura, H., and Iwasaki, M., *Ind. Eng. Chem. Res.* **28**, 719 (1989).
- Matsumura, M., Furukawa, S., Saho, Y., and Tsubomura, H., *J. Phys. Chem.* **81**, 1327 (1985).
- Jackson, N. B., Wang, C. M., Luo, Z., Schwitzgebel, J., Ekerdt, J. G., Brock, J. R., and Heller, A., *J. Electrochem. Soc.* **138**, 3660 (1991).
- Hoffmann, M. R., Martin, S. T., Choi, W., and Bahnemann, D. W., *Chem. Rev.* **95**, 69 (1995).
- Fujishima, A., Cai, R. X., Otsuki, J., Hashimoto, K., Itoh, K., Yamashita, T., and Kubota, Y., *Electrochim. Acta* **18**, 153 (1993).
- D'Oliveira, J. C., Minero, C., Pelizzetti, E., and Pichat, P., *J. Photochem. Photobiol. A* **72**, 261 (1993).
- Yamashita, H., Miwa, H., Harada, M., Ichihashi, Y., Anpo, M., *J. Phys. Chem. B* **102**, 10707 (1998).
- Rao, M. V., Rajeshwar, K., Vernerker, V. R., and Kubow, J., *J. Phys. Chem.* **84**, 1987 (1980).
- Nishimoto, S., Ohtani, B., Kajiwarra, H., and Kagiya, T., *J. Chem. Soc., Faraday Trans. 1* **81**, 61 (1985).
- Sato, S., and White, J. M., *J. Catal.* **69**, 128 (1981).
- Sayama, K., and Arakawa, H., *J. Phys. Chem.* **97**, 531 (1993).
- Bard, A. J., and Fox, M. A., *Acc. Chem. Res.* **28**, 141 (1995).
- Takata, T., Furumi, Y., Shinohara, K., Tanaka, A., Hara, M., Kondo, J. N., and Domen, K., *Chem. Mater.* **9**, 1063 (1997).
- Ohno, T., Haga, D., Fujihara, K., Kaizaki, K., and Matsumura, M., *J. Phys. Chem. B* **101**, 6415 (1997); Errata, **101**, 10605 (1997).
- Fujihara, K., Ohno, T., and Matsumura, M., *J. Chem. Soc., Faraday Trans.* **94**, 3705 (1998).
- Ohno, T., Fujihara, K., Sarukawa, K., Tanigawa, F., and Matsumura, M., *Z. Phys. Chem.* **213**, 165 (1999).
- Bickley, R. I., Gonzalez-Carreno, T., Lees, J. S., Palmisano, L., and Tilley, R. D., *J. Solid State Chem.* **92**, 178 (1991).
- Datye, A. K., Riegel, G., Bolton, J. R., Huang, M., and Prairie, M. R., *J. Solid State Chem.* **115**, 236 (1995).
- Ohno, T., Sarukawa, K., and Matsumura, M., *J. Phys. Chem. B* **105**, 2417 (2001).
- Jia, J., Ohno, T., Masaki, Y., and Matsumura, M., *Chem. Lett.* **963** (1999).
- Jia, J., Ohno, T., and Matsumura, M., *Chem. Lett.* **908** (2000).
- Rothenberger, G., Moser, J., Grätzel, M., Serpone, N., and Sharma, D. K., *J. Am. Chem. Soc.* **107**, 8054 (1985).
- Soana, F., Sturini, M., Cermenati, L., and Albin, A., *J. Chem. Soc., Perkin Trans. 2* **4**, 699 (2000).