

Multicolor Photochromism of TiO<sub>2</sub> Films Loaded with Ag Nanoparticles:  
Mechanisms of Photo-bleaching by Visible Light

Tetsu Tatsuma, Yoshihisa Ohko, Kenji Naoi,  
and Keisuke Kawahara

*Institute of Industrial Science, University of Tokyo,  
Komaba, Meguro-ku, Tokyo 153-8505, Japan*

Recently, we have reported multicolor photochromism<sup>1,2</sup> of a nanoporous TiO<sub>2</sub> film loaded with Ag nanoparticles. Ag nanoparticles were photocatalytically deposited in nanopores of the TiO<sub>2</sub> film under UV light. The color of the film, initially brownish-gray, changes under a monochromatic visible light (a Xe lamp with a bandpass filter or a laser) to almost the same color as that of the incident light. The colored TiO<sub>2</sub> film turns brownish-gray again by irradiation with UV light. This is the first multicolor photochromic material with apparently uniform structure, to the best of our knowledge. There are a number of potential applications including a rewritable color copy paper, a multicolor smart glass, and a high-density multi-wavelength optical memory. A color-changeable paint is an additional application, since the film is easy to prepare, low cost, and applicable to a large area. On the other hand, it is of great scientific interest that such a simple material exhibits the multicolor photochromism. Elucidation of the mechanism might facilitate development of other functional materials.

In the present work, we prepared a nanoporous TiO<sub>2</sub> film loaded electrochemically with Ag, and compared its photochromic characteristics with those of nanoporous ITO and silica films loaded with Ag.<sup>3</sup> The TiO<sub>2</sub> film loaded electrochemically with Ag exhibited multicolor photochromic behavior. In contrast, both of the nanoporous ITO and silica films loaded with Ag have exhibited no such behavior so far. The Ag-silica film was not even bleached under white light. In the case of the Ag-ITO film, the bleaching was observed under white light, although it was much slower than that of the Ag-TiO<sub>2</sub> film, by more than three orders of magnitude.

Roles of TiO<sub>2</sub> in the Ag-TiO<sub>2</sub> system may therefore be not only (1) a photocatalyst catalyzing the reduction of Ag<sup>+</sup> to Ag nanoparticles by electrons taken from water,<sup>1</sup> (2) templates for the Ag nanoparticles,<sup>2</sup> and (3) a matrix with high refractive index that redshifts the resonance wavelength of the Ag nanoparticles.<sup>2</sup> TiO<sub>2</sub> seems to facilitate photo-bleaching of Ag nanoparticles under visible light, in the presence of oxygen. One of the possible mechanisms for this acceleration is that the contact with TiO<sub>2</sub> raises the Fermi level of Ag nanoparticles, resulting in acceleration of electron transfer to oxygen. Another possibility is that TiO<sub>2</sub> takes photoexcited electrons from Ag to facilitate the charge separation, and gives the electrons to oxygen (Figure 1). Actually, we observed that Ag-TiO<sub>2</sub> and Au-TiO<sub>2</sub> electrodes exhibit negative potential shifts in response to visible light, in oxygen-free solutions; the photoexcited electrons may be transferred from the metal nanoparticles to TiO<sub>2</sub>.<sup>4</sup>

In the meantime, we found that modification with a fluoroalkylthiol of Ag nanoparticles deposited by

UV light in the nanoporous TiO<sub>2</sub> film retarded the photo-bleaching of the Ag-TiO<sub>2</sub> system (Figure 2).<sup>5</sup> The self-assembled monolayer of the thiol formed on the Ag nanoparticles may interfere with dissolution of Ag<sup>+</sup> from the Ag nanoparticles and/or transfer of the photoexcited electrons from Ag to oxygen. Further elucidation of this process will give important information about the mechanisms of the photo-bleaching.

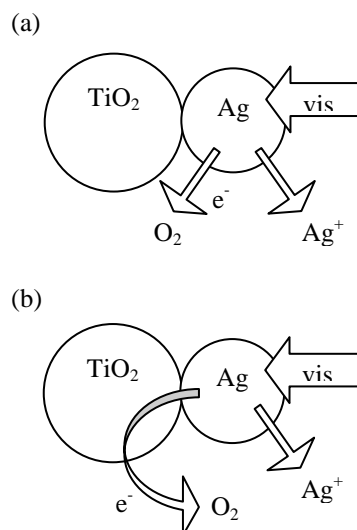


Figure 1. Possible mechanisms of visible light-induced bleaching of the Ag-TiO<sub>2</sub> system; (a) direct electron transfer from Ag to oxygen and (b) electron transfer via TiO<sub>2</sub>.

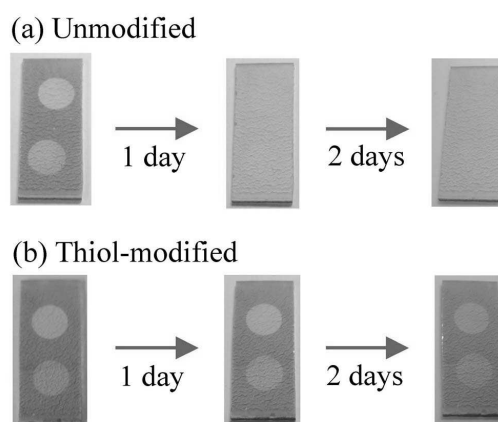


Figure 2. Deceleration of photo-bleaching of the Ag-TiO<sub>2</sub> system by a fluoroalkylthiol.

References

1. Y. Ohko, T. Tatsuma, T. Fujii, K. Naoi, C. Niwa, Y. Kubota, and A. Fujishima, *Nature Mater.*, **2**, 29 (2003).
2. K. Naoi, Y. Ohko, and T. Tatsuma, *J. Am. Chem. Soc.*, **126**, 3664 (2004).
3. K. Kawahara, Y. Ohko, and T. Tatsuma, in preparation.
4. Y. Tian and T. Tatsuma, *2004 Joint Intl. Meeting*, Honolulu (2004).
5. K. Naoi, Y. Ohko, and T. Tatsuma, in preparation.