Multicolor Photochromism of TiO₂ Films Loaded with Ag Nanoparticles

<u>Yoshihisa Ohko</u>¹, Tetsu Tatsuma², Tsuyoshi Fujii¹, Kenji Naoi¹, Chisa Niwa³, Yoshinobu Kubota⁴ and Akira Fujishima^{*1}

- ¹Department of Applied Chemistry, Graduate School of Engineering, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan
- ²Institute of Industrial Science, University of Tokyo, 4-6-1 Komaba, Meguro-ku, Tokyo 153-8505, Japan
- ³Kanagawa Academy of Science and Technology, KSP

Bldg. East 412, 3-2-1 Sakado, Takatsu-ku, Kawasaki-shi, Kanagawa 213-0012, Japan

⁴Department of Urology, School of Medicine, University of Yokohama City, 3-9 Fukuura, Kanazawa-ku, Yokohama-shi, Kanagawa 236-0004, Japan

Very recently, we found a new phenomenon, multicolor photochromism of TiO2 films loaded with Ag nanoparticles¹. The color of the Ag-TiO₂ film (initially brownish gray due probably to plasmon resonance) was changed to various colors, by irradiating it with corresponding visible light in air under ambient conditions. The film was bleached to colorless by white light, and was colored again in brownish gray by UV light. Multicolor photochromism was thus achieved with this apparently uniform, easily prepared film, while the multicolor display with conventional monochromic photochromism has been difficult unless several different materials were combined. The photochromic devices using our material would be much more informative and find a greater number of applications, including a rewritable color copy paper or electronic paper² and a high density multi-wavelength optical memory.

A Ag-TiO₂ film for spectroscopic measurements was prepared as follows: a TiO₂ film was coated on a glass substrate from anatase sol (Ishihara Sangyo Kaisha, Ltd., STS-21, 20 nm particle diameter, 50 m² g⁻¹ surface area) by a spin coating technique (sintered at 723 K for 1 h). The resulting film was soaked in 1 M AgNO₃ aqueous solution for 3 min and rinsed with pure water. After dried, the film was irradiated with UV light (300-400 nm, 1 mW cm⁻²) for 15 min in air at room temperature by using commercial black-fluorescent lamps to reduce the adsorbed Ag⁺ to Ag nanoparticles.

One of the typical differential absorbance spectra is shown in Figure 1. In the case of irradiation with a laser beam with a He-Ne laser (632.8 nm, ~200 mW cm⁻²) for 10 sec, an absorbance hole was observed. The holes were relatively persistent; decay of the holes by 20% took 30 min under a conventional fluorescent lamp (~60 μ W cm⁻²) and one day in dark. After the monochromatic visible light irradiation, the Ag-TiO₂ film showed corresponding colors (blue, green, yellow, orange, red, and colorless). This multicoloring is because the film became reflective at around the corresponding wavelength.

In general, metal nanoparticles exhibit unique colors due to plasmon resonance absorption of surface electrons³⁻⁷. We deduce the following model for this process: Under UV light, TiO_2 should generate Ag nanoparticles with different absorption wavelengths. Upon irradiation with a monochromatic visible light, the corresponding nanoparticle absorbs the light, and the thus

excited electrons are accepted by O_2 , resulting in oxidation of the Ag nanoparticle to Ag^+ and an absorption decrease at the corresponding wavelength. Since the other remaining particles absorb the all other wavelengths, the color of the excitation wavelength appears.



Figure 1. Differential absorbance spectrum of the Ag-TiO₂ film after irradiation with a laser beam of a He-Ne laser (632.8 nm, ~200 mW cm⁻²) for 10 sec (spot diameter, 2 mm).

References

- 1. Y. Ohko, T. Tatsuma, T. Fujii, K. Naoi, C. Niwa, Y.
- Kubota, and A. Fujishima, submitted.
- 2. Ditlea, S. Sci. Am. 285, 5, 38 (2001).
- 3. W. Kleemann, Z. Phys. 215, 113 (1968).
- 4. B. K. Russell, J. G. Mantovani, V. E. Anderson, R. J.
- Warmack, T. L. Ferrell, Phys. Rev. B 35, 2151 (1987).
- 5. R. H. Doremus, J. Chem. Phys. 42, 414 (1965).
- 6. R. C. Jin, Y. W. Cao, C. A. Mirkin, K. L. Kelly, G. C.
- Schatz, J. G. Zheng, Science 294, 1901 (2001).
- 7. J. J. Mock, M. Barbic, D. R. Smith, D. A. Schultz, S.
- Schultz, J. Chem. Phys. 116, 6755 (2002).