

TiO₂ Films Loaded with Silver Nanoparticles: Control of Multicolor Photochromic Behavior

Kenji Naoi, Yoshihisa Ohko,[†] and Tetsu Tatsuma*

Contribution from the Institute of Industrial Science, University of Tokyo,
4-6-1, Komaba, Meguro-ku, Tokyo 153-8505, Japan

Received November 7, 2003; E-mail: tatsuma@iis.u-tokyo.ac.jp.

Abstract: Ag–TiO₂ films exhibiting multicolor photochromism were prepared by photoelectrochemical reduction of Ag⁺ to Ag nanoparticles in nanoporous TiO₂ films under UV light. Color of the Ag–TiO₂ film, initially brownish-gray, changes under a colored visible light to the color of the light and reverts to brownish-gray under UV light. Their chromogenic properties were improved by simultaneous irradiation for Ag deposition with UV and blue lights to suppress the formation of anisotropic Ag particles. Nonvolatilization of a color image was also achieved by removing Ag⁺ that was generated during the irradiation with a colored light. Once nonvolatilized, the image can be reproduced by UV light, even after the image is discolored under white light. This new effect evidenced that nanopores in the TiO₂ film determine the resonance wavelengths of the Ag particles, as their molds. In addition, solvatochromic behavior of the Ag–TiO₂ film proved that nanospaces left around the Ag nanoparticles affect the resonance wavelengths of the Ag particles.

Introduction

Recently, we have reported multicolor photochromism¹ of a TiO₂ film that is loaded with Ag nanoparticles by photocatalytic reaction² under UV light. The color of the film, initially brownish-gray, changes under a colored visible light (a Xe lamp with a band-pass filter or a laser is used) to almost the same color as that of the incident light. The colored TiO₂ 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 multiwavelength 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.

Under UV light, electrons in the valence band of TiO₂ are excited to the conduction band, resulting in generation of holes in the valence band. It is known that Ag⁺ ions are reduced by the excited electrons of TiO₂ to Ag nanoparticles.³ It is also known that Ag nanoparticles absorb visible light of various wavelengths due to surface plasmon resonance and that the wavelength depends on particle size, particle shape, and local

refractive index.^{4,5} Thus, the brownish-gray color of the Ag–TiO₂ film should be ascribed to Ag nanoparticles with various sizes and shapes deposited in the nanopores of the TiO₂ film. The deposition has been observed by transmission electron microscopy (TEM).¹ Those particles absorb the light of different wavelengths, and the characteristic broad absorption band appears in the visible range.

When the brownish-gray film is irradiated with a colored light, the absorption at around the excitation wavelength decreases. Thus, an “absorption hole” is formed. This is probably because electrons of Ag nanoparticles are excited only when they are irradiated with the light of their resonance wavelength. The excited electrons transfer to oxygen in air, and thus the Ag nanoparticles are oxidized to colorless Ag⁺ ion. As a result, only the light of the excitation wavelength is reflected or transmitted, while the remaining particles absorb the lights of the other wavelengths. Thus, the color corresponding to the excitation wavelength appears.¹

Incidentally, this phenomenon, which is based on photo-oxidation of Ag particles to Ag⁺, is different from conventional silver halide photography, which is based on photoreduction of silver halide to Ag particles.⁶ No similar phenomenon has been reported to date, to the best of our knowledge.

In the present study, we improved chromogenic properties of the Ag–TiO₂ thin film and elucidated the origin of the diversity in the resonance wavelengths of the Ag particles in the film. The obtained findings were exploited to develop new

* Corresponding author: Tel +81-3-5452-6336; fax +81-3-5452-6338.

[†] Concurrent address: PRESTO, Japan Science and Technology Agency (JST), 4-1-8 Honcho, Kawaguchi-shi, Saitama 332-0012, Japan.

(1) Ohko, Y.; Tatsuma, T.; Fujii, T.; Naoi, K.; Niwa, C.; Kubota, Y.; Fujishima, A. *Nat. Mater.* **2003**, *2*, 29–31.

(2) Fujishima, A.; Honda, K. *Nature* **1972**, *238*, 37–38.

(3) Ohtani, B.; Okugawa, Y.; Nishimoto, S.; Kagiya, T. *J. Phys. Chem.* **1987**, *91*, 3550–3555.

(4) Jin, R.; Cao, Y.; Mirkin, C. A.; Kelly, K. L.; Schatz, G. C.; Zheng, J. G. *Science* **2001**, *294*, 1901–1903.

(5) Mock, J. J.; Barbic, M.; Smith, D. R.; Schultz, D. A.; Schultz, S. *J. Chem. Phys.* **2002**, *116*, 6755–6759.

(6) *Photography for the Scientist*; Engel, C. E., Ed.; Academic Press: London, 1968.

functionalities. As for the chromogenic properties, we have had a problem that absorption holes are formed not only at the excitation wavelength but also at around 420 nm simultaneously, probably due to anisotropic Ag particles.¹ This problem was solved by simultaneous irradiation for Ag deposition with UV and blue (420 nm) lights.

We also found evidence indicating that nanopores in the TiO₂ film function as molds for Ag nanoparticles and that they determine the resonance wavelengths of the particles. On the basis of this finding, we achieved nonvolatilization of a color image by removing Ag⁺ ion from specific pores. We also investigated solvatochromic behavior of the Ag–TiO₂ film. The findings presented here would be of importance for improvement of the characteristics and applicabilities of the Ag–TiO₂ material, as well as development of a new class of photochromic materials.

Experimental Section

Preparation of the TiO₂ Films. A commercial anatase TiO₂ sol (STS-01, ~7 nm diameter, Ishihara Sangyo Kaisha) was diluted 7-fold with ethanol. We prepared a TiO₂ film on a Pyrex glass substrate (25 × 50 × 1 mm) from the sol by a spin-coating technique (at 1500 rpm for 10 s). The TiO₂ film was then sintered at 500 °C for 1 h. The obtained nanoporous TiO₂ film was colorless and transparent.

Loading of the TiO₂ Film with Ag Nanoparticles. An aqueous solution containing 1 M silver nitrate (AgNO₃) (1 mL) was mixed with ethanol (1 mL), and a 0.6 mL aliquot of the solution was uniformly cast on the TiO₂ thin film. The film was irradiated with UV light for 1 min, to deposit Ag nanoparticles in the porous film by photocatalytic reduction of Ag⁺. During the UV irradiation, the sample turned brownish-gray due to surface plasmon absorption of the deposited Ag nanoparticles.^{7,8} The UV light source was a Hg–Xe lamp (Luminar Ace LA-300UV, Hayashi Watch Works Co., Ltd.) with a band-pass filter [310 nm; full width at half-maximum (fwhm), 10 nm]. The light intensity measured by a radiant power energy meter (Model 70260, Oriel Instruments) was 0.1 mW cm⁻². The resulting Ag–TiO₂ film was thoroughly rinsed with ultrapure water and dried by blowing air with an electric duster.

In experiments for improvement of the film chromogenicity, the film was further irradiated with the 310 nm UV light with or without 420 nm light for 30 min. The light source used for the irradiation with 420 nm light was a Xe lamp (Luminar Ace LA-250Xe, Hayashi Watch Works) with a band-pass filter (fwhm, 10 nm). The light intensity was 5 mW cm⁻².

We also prepared much thicker TiO₂ films for visual demonstration of color changes. We suspended anatase TiO₂ powder (ST-01, Ishihara Sangyo Kaisya, 7 nm particle diameter) at 11 wt % in 9 mM AgNO₃ ethanol solution containing silicone binder (NDC-100A, NISSO), and irradiated it with UV light for 2 h. The film was prepared on a Pyrex glass plate from the resulting suspension by spin-coating technique (700 rpm, 10 s) and annealed at 120 °C for 1 h, followed by further irradiation with UV light for 30 min.

Evaluation of Photochromic Characteristics. The light source of visible light for coloring the film was the Xe lamp with an appropriate band-pass filter (fwhm, 10 nm). The intensity was 5 mW cm⁻² each, unless otherwise noted. The UV absorption spectra of the films were collected by use of a UV spectrophotometer (UV-2400PC, Shimadzu). If necessary, the irradiation of the films with visible light was conducted in water or a 18 mM Na₂S₂O₃ aqueous solution, to remove the photogenerated Ag⁺ from the nanopores in the TiO₂ film.

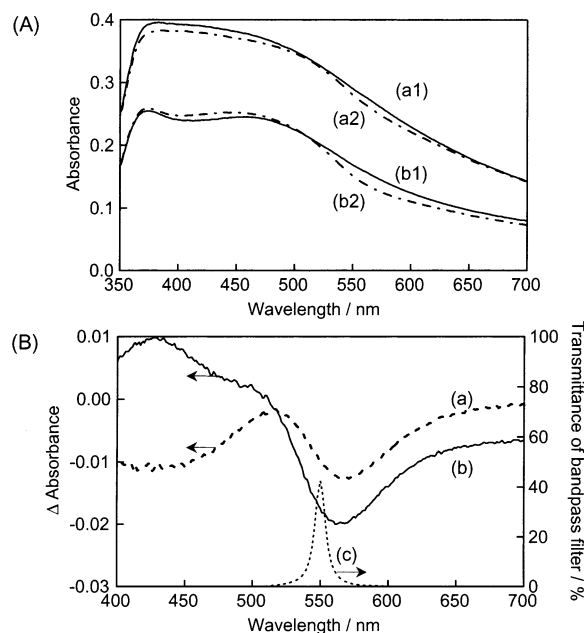


Figure 1. (A) Absorption spectra of the Ag–TiO₂ films before (a1, b1) and after (a2, b2) irradiation with 550 nm light (5 mW cm⁻², 5 min). Prior to the irradiation, Ag nanoparticles have been deposited by UV light (310 nm, 0.1 mW cm⁻², 30 min) without (a) or with (b) simultaneous irradiation with 420 nm light (5 mW cm⁻²). (B) Differential absorption spectra for the data in panel A. Transmission spectrum of the band-pass filter used is also shown (c).

Results and Discussion

Improvement in the Chromogenic Properties. To obtain Ag–TiO₂ film, the AgNO₃ solution was applied onto the TiO₂ film, and the film was irradiated with UV light (310 nm, 0.1 mW cm⁻²) for 30 min. The obtained brownish-gray Ag–TiO₂ film (curve a1, Figure 1A) was irradiated with green light (550 nm, 5 mW cm⁻²; spectrum of the band-pass filter used is curve c, Figure 1B) for 5 min (curve a2, Figure 1A). The absorbance change is shown in Figure 1B (curve a) as a differential absorption spectrum. Absorption at around the excitation wavelength (550 nm) decreased, accompanied by an absorption decrease at 420 nm. Similar behavior was also observed when the film is excited at a different excitation wavelengths (e. g., 500, 600, or 650 nm). This might be due to anisotropic Ag nanoparticles, which have two different resonance wavelengths, in the porous TiO₂ film. Actually, it has been shown theoretically and experimentally that some ellipsoidal Ag nanoparticles have two absorption peaks (or bands) at around 400 nm and 400–700 nm.⁹ Excitation of such an anisotropic particle at 500, 550, 600, or 650 nm should result in formation of two absorption holes at the excitation wavelength and at around 400 nm.

Here we envisaged suppressing the undesired absorption decrease at 420 nm. In the present system, selective oxidation of specific Ag nanoparticles is possible by irradiation with the light of their resonance wavelength. Therefore, if the Ag nanoparticles are deposited by simultaneous irradiation with UV light (310 nm) and 420 nm light, the formation of the anisotropic Ag nanoparticles that are excitable at 420 nm would be inhibited, while other isotropic nanoparticles would be deposited normally. If this is correct, subsequent irradiation with colored visible light

(7) Stathatos, E.; Lianos, P.; Falaras, P.; Siokou, A. *Langmuir* **2000**, *16*, 2398–2400.

(8) He, J.; Ichinose, I.; Fujikawa, S.; Kunitake, T.; Nakao, A. *Chem. Commun.* **2002**, 1910–1911.

(9) Hilger, A.; Tenfelde, M.; Kreibitz, U. *Appl. Phys. B* **2001**, *73*, 361–372.

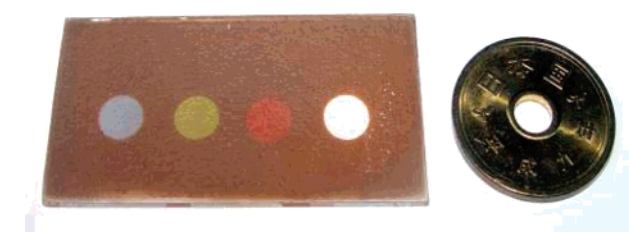


Figure 2. Multicolored Ag–TiO₂ film. Each spot (6 mm diameter) was irradiated successively with a blue, green, red, or white light. A xenon lamp and an UV-cut filter (blocking light below 400 nm) were used with an appropriate band-pass filter (blue, 460 nm, 10 mW cm⁻², 1 h; green, 520 nm, 11 mW cm⁻², 30 min; red, 630 nm, 10 mW cm⁻², 30 min) or without any band-pass filter (white, 480 mW cm⁻², 10 min).

would give a single absorption hole at the excitation wavelength and no surplus absorption decrease at around 420 nm.

Although the Ag–TiO₂ film obtained by the dual light irradiation was also brownish-gray, its absorption at around 420 nm was smaller than the conventional one (curve b1, Figure 1A). Further irradiation with 550 nm light gave rise to a single absorbance hole at around 550 nm (curve b2, Figure 1A; curve b, Figure 1B). No absorption hole was observed at 420 nm, and rather, in most cases, an absorption increase was observed, probably due to a decrease in the size of the oxidized nanoparticles. It is known that the resonance wavelength is blue-shifted as the dimension of a silver nanoparticle decreases.^{4,5} Similar results were also obtained when the film was irradiated with 470 or 650 nm light.

Thus, we conclude that the undesired absorption decrease at 420 nm can be suppressed by the dual-light irradiation. This might reflect that the formation of the anisotropic Ag nanoparticles can be inhibited to a considerable degree. In the present stage, observation of the nanoparticles by transmission or scanning electron microscopy (TEM or SEM) is difficult, because they are formed within the TiO₂ film.¹ X-ray diffraction (XRD) measurements were also unsuccessful, due probably to very low density of Ag particles in the film (<1 wt %). However, our technique to remove the undesirable absorption hole is essential for further investigation of the mechanism and further development of the functionalities of the Ag–TiO₂ film.

Possible Molding Effect of Nanoporous TiO₂ Films. The present Ag–TiO₂ material can display various colors, as shown in Figure 2, by irradiating the thick film (25 × 50 mm) with various excitation lights. As mentioned in the introduction, Ag nanoparticles of various sizes and shapes should be prerequisite to displaying various colors. It is reasonable to consider that nanopores of various sizes and shapes are present in the TiO₂ films prepared and that the nanopores act as molds for Ag nanoparticles with various sizes and shapes. We call this a “molding effect”. If this effect holds, the nanopores may determine sizes, shapes, and thereby resonance wavelengths of Ag nanoparticles. A specific nanopore may produce Ag nanoparticles with the same specific resonance wavelength repeatedly, in repeated writing–erasing cycles. This proposed mechanism is illustrated in Figure 3.

Various nanoparticles are generated under UV light (Figure 3b). Assume that this sample is irradiated with green light. Only the Ag nanoparticles that absorb the green light are excited. The excited electrons are transferred to oxygen, and the nanoparticles are oxidized to Ag⁺ ion (Figure 3c; the green particle symbol represents a nanoparticle absorbing only green light).

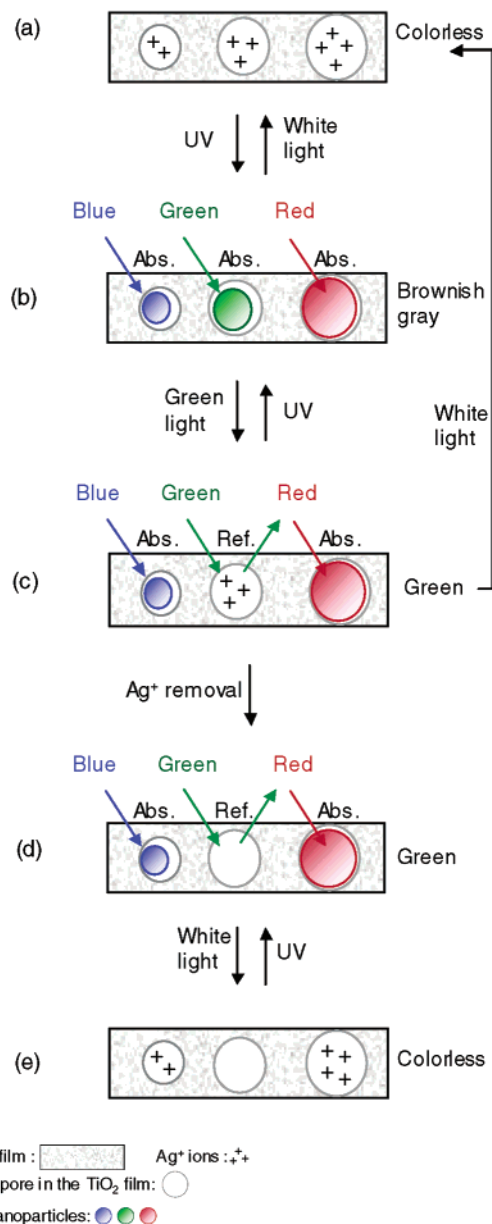


Figure 3. Proposed model for the molding effect of a porous TiO₂ thin film (a–c) and the mechanism of nonvolatilization of a color image (d, e). (a) Ag⁺-adsorbed porous TiO₂ film (film looks colorless). (b) Ag nanoparticles deposited by UV light (film looks brownish-gray). (c) Ag particles absorbing green light are photoelectrochemically oxidized to Ag⁺ by green light (film looks green) (the blue, green, or red particle symbol represents a nanoparticle absorbing only blue, green, or red light, respectively). (d) Ag⁺ generated in panel c is removed (film looks green). (e) Ag particles left in panel d are also photoelectrochemically oxidized to Ag⁺ (film looks colorless).

light for simplicity). As a result, the Ag–TiO₂ film turns green, since the green light is not absorbed but reflected (or transmitted). In this case, if the Ag⁺ ions generated during the green light irradiation are removed (Figure 3d), the film should stay green even if it is irradiated with UV light.

If this sample is irradiated with white light, all the Ag nanoparticles left are also photooxidized to Ag⁺ ions, and the film becomes colorless (Figure 3e). In this stage, the nanopores that produce Ag nanoparticles absorbing green light contain no Ag⁺ ions. Therefore, even when the film is irradiated with UV light again, Ag particles that absorb green light may not be formed, while the other particles, which absorb blue and red

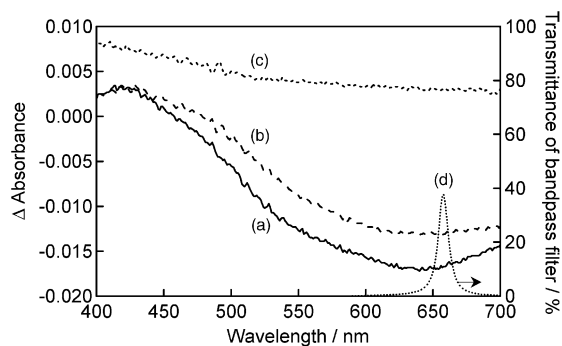


Figure 4. Differential absorption spectra of the Ag–TiO₂ film after irradiation with 660 nm light in water (5 mW cm⁻², 10 min) (a) (corresponding to Figure 3d) and following irradiation with UV light (310 nm, 0.1 mW cm⁻², 30 min) (b). Spectrum c is obtained after successive irradiation with 660 nm light (5 mW cm⁻², 10 min) (corresponding to Figure 3c) and UV light (30 min) in air (corresponding to Figure 3b). Transmission spectrum of the band-pass filter used is also shown (d).

lights, are generated. Thus, the film turns green again (Figure 3d). The color information is kept as a “latent image” in Figure 3e, although the film is colorless. However, if the molding effect does not hold, regenerated particles are not specific, and the film should turn brownish-gray under UV light.

Ag⁺ Removal from the Colored Film and Retention of the Color under UV. To examine the molding effect, the thin TiO₂ film was soaked in a 1 M AgNO₃ aqueous solution for 3 min, rinsed with ultrapure water, and dried. The film was irradiated simultaneously with UV light (0.1 mW cm⁻²) and 420 nm light (5 mW cm⁻²) for 30 min. The obtained brownish-gray film was irradiated further with 660 nm light (curve d, Figure 4; 5 mW cm⁻²) in water for 10 min. As shown in Figure 4 (curve a), an absorption hole was observed. In this case, the Ag⁺ ions generated by photooxidation of the Ag nanoparticles were expected to be removed from the nanopores to water. This film was irradiated again with UV light (0.1 mW cm⁻²) and 420 nm light (5 mW cm⁻²) simultaneously for 30 min. Although the absorbance increased slightly, the absorption hole was retained (curve b).

On the other hand, when the irradiation with 660 nm light was conducted in air (the generated Ag⁺ ions remained in the film), the absorption reverted to the original level upon the following simultaneous irradiation with UV and 420 nm lights (curve c).

In conclusion, if the brownish-gray Ag–TiO₂ film is irradiated with colored (e.g., red) light in air, the photooxidatively generated Ag⁺ is retained in the nanopores (Figure 3c), so that the colored (e.g., red) film turns original brownish-gray under UV light. This should be because the Ag nanoparticles absorbing the colored (e.g., red) light form again in the nanopores (Figure 3b). In contrast, if the Ag–TiO₂ film is irradiated with colored (e.g., red) light in water, the generated Ag⁺ is removed from the pores (Figure 3d), so that the film retains its color (e.g., red) even under UV light.

Reproduction of a Color Image by UV. In another experiment, the brownish-gray Ag–TiO₂ film was irradiated with 450 nm light (2 mW cm⁻²) in pure water for 5 min. As a result, the differential absorption spectrum of curve a in Figure 5A was obtained. The sample was left under weak white light (fluorescent lamps, <50 nW cm⁻²) for 1 h, and the sample became almost colorless (curve b in Figure 5A). Since the original absorption in the long-wavelength range was relatively small

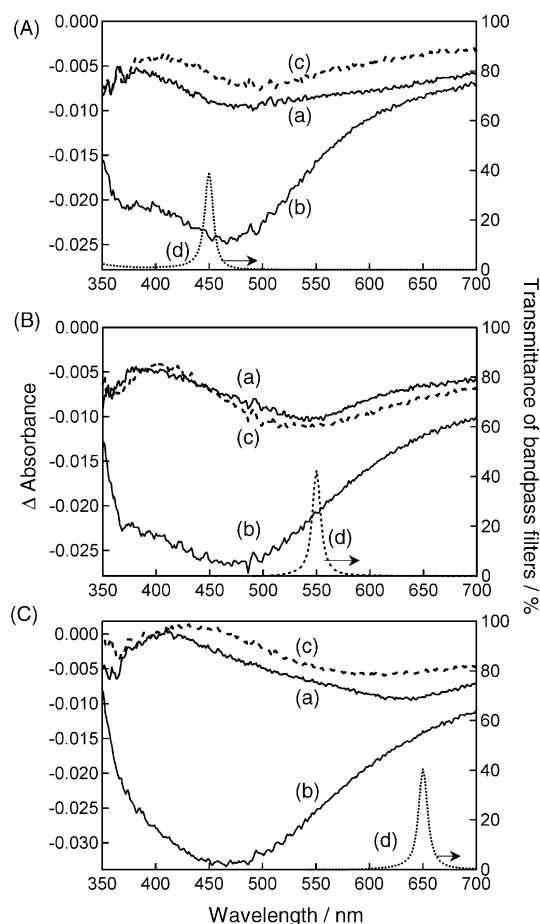


Figure 5. Reproduction of absorption holes. Differential absorption spectra of the Ag–TiO₂ film after irradiation with a colored light in water (spectra a) (panel A, 450 nm, 2 mW cm⁻², 10 min; panel B, 550 nm, 2 mW cm⁻², 5 min; panel C, 650 nm, 2 mW cm⁻², 10 min) and following irradiation with weak white light (<50 nW cm⁻², 1–5 h) (spectra b). Spectra c is obtained after further irradiation with UV light (0.1 mW cm⁻², 2 min). Transmission spectra of the band-pass filters used are also shown (spectra d).

for the initial brownish-gray sample (Figure 1A), the absorbance decrease in this range was also relatively small. The colorless sample was irradiated with the UV light, and the absorption hole was almost reproduced (curve c in Figure 5A). Similar results were obtained when 550 and 650 nm lights were employed (Figure 5, panels B and C, respectively).

Namely, absorption holes could be reproduced, as we have anticipated on the basis of the possible molding effect. We could also demonstrate this “nonvolatilization” of a color image visually by using a thicker film (Figure 6). This film was basically identical with that used for Figure 2, but the amount of the binder used was 1/4. Also, sodium thiosulfate aqueous solution (Na₂S₂O₃ (aq), 18 mM) was used instead of pure water to remove Ag⁺ ions more effectively. The initial brownish-gray film (Figure 6a) was irradiated with a blue spotlight (450 nm, 2 mW cm⁻², 6 mm diameter) for 60 min (Figure 6b). The film was then left under white light (50 mW cm⁻²) for 6 h; the film became almost colorless (Figure 6c). Finally, the film was irradiated with UV light (0.1 mW cm⁻²) for 15 min, and the bluish spot of the same size was reproduced (Figure 6d). Thus, nonvolatilization of a color image has been achieved. The film with a nonvolatilized image can be initialized by recharging the film (rather, the vacant nanopores) with Ag⁺ ions to reactivate the rewritability.

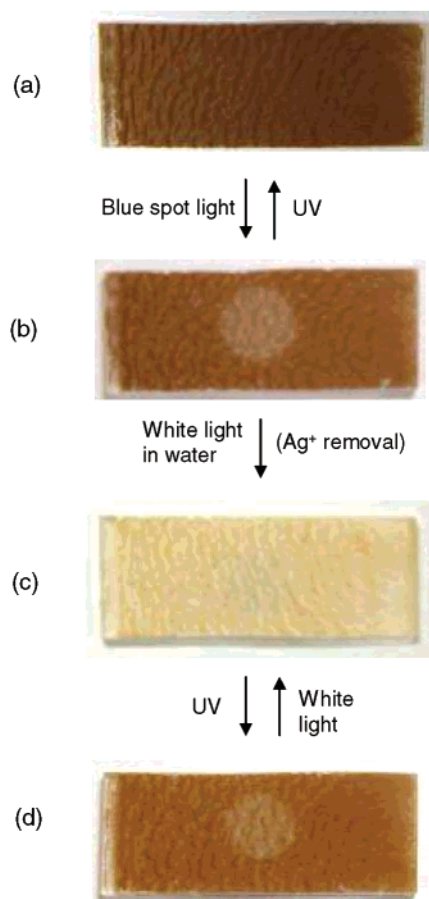


Figure 6. Reproduction of a color image (bluish spot). (a) TiO₂ film loaded with Ag nanoparticles (brownish gray). (b) The film irradiated with a blue spot light (450 nm; fwhm, 10 nm; 2 mW cm⁻²; 60 min; diameter, 6 mm), (c) followed by irradiation with white light (50 mW cm⁻², 6 h). (d) The film was further irradiated with UV light (310 nm, 0.1 mW cm⁻², 15 min).

The results presented in the previous and the present sections support the molding effect of the nanopores of the TiO₂ film, which we have proposed. In the future, on the basis of this effect, it is expected that the chromogenic properties would be improved and controlled furthermore by controlling the size, shape, and distribution of the nanopores.

“Latent images” have been extensively studied, especially in the field of silver halide photography. In those cases, a latent image is based on silver clusters generated by photoreduction of silver halide.⁶ On the other hand, in the present system, a latent image is based on the nanopores containing no Ag⁺. These are completely different phenomena.

Effect of the Local Refractive Index. We can assume that the Ag nanoparticles are formed at the gas–solid interface between TiO₂ and air (rigorously, some adsorbed water should also coexist). Thus, the Ag nanoparticles are probably in contact with not only TiO₂ but also air. It is known that surface plasmon resonance wavelength of Ag nanoparticles depends on the particle size and shape as well as the refractive index of surrounding materials.¹⁰ The absorption wavelength is red-shifted as the refractive index increases. Therefore, the absorption wavelength of the Ag nanoparticles would depend on the local composition of the matrix, namely, the TiO₂/air ratio. This might be one of the origins of the diversity in the absorption wavelengths of the Ag particles.

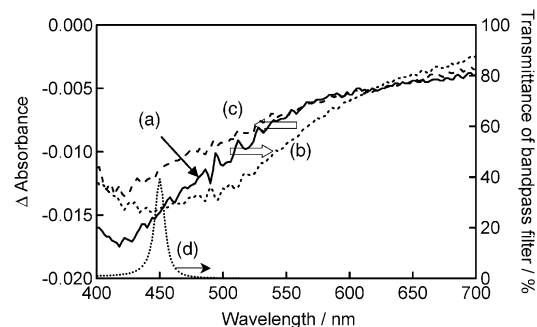


Figure 7. Differential absorption spectra of the Ag–TiO₂ film after irradiation with 450 nm light (2 mW cm⁻², 10 min) (a) and subsequent immersion in ethanol (b). The absorption peak was shifted back by evaporation of ethanol (c). Transmission spectrum of the band-pass filter used is also shown (d).

If so, the absorption wavelength should be red-shifted, when the air filling the vacant nanopores is replaced with a solvent whose refractive index is higher than that of air. An absorption hole generated by a colored light should also be red-shifted. However, if no shift is observed, we should conclude that the Ag nanoparticles are surrounded only by TiO₂.

To examine this, the thin Ag–TiO₂ film in brownish-gray was irradiated with a blue light (curve a, Figure 7), and the film was impregnated with ethanol (refractive index = 1.36). This red-shifted the absorption hole by about 30 nm (curve b). As the ethanol was evaporated, the absorption hole reverted to the original wavelength again (curve c). A larger peak shift (by about 50 nm) was observed when quinoline (refractive index = 1.63) was used instead of ethanol.

Such solvatochromic characteristics indicate that the absorption wavelength of the Ag nanoparticles before the impregnation depends not only on the refractive index of TiO₂ but also on that of air. The particles must be in contact with TiO₂ and air at various ratios. The diversity in the ratio should contribute to the diversity in the resonance wavelength of the Ag particles to some extent. These results suggest that chromogenic properties of this material can be controlled by tuning the refractive index of the matrix. Also, the present solvatochromic property might be exploited for new functions, such as optical sensing of chemical species.

Conclusions

We have achieved the improvement of the chromogenic properties of the Ag–TiO₂ film and the introduction of new functions, namely, nonvolatilization and solvatochromism. In addition, we have obtained evidence for the molding effect of the nanopores in the TiO₂ film. We have also revealed that we can control the multicolor photochromic behavior and the chromogenic properties by regulating irradiation conditions as well as geometry and matrix materials of nanopores.

Acknowledgment. We are grateful to Emeritus Professor A. Fujishima for many valuable discussions and T. Fujii for some preliminary experiments. This work was supported in part by a Grant-in-Aid for Scientific Research on Priority Areas (Area 417, Research 14050028 for T.T.) from the Ministry of Education, Science, Sports and Culture of Japan, Japan Science and Technology Agency (for Y.O. and T.T.), and Nippon Paint Co., Ltd. (for T.T.).

(10) Doremus, R. H. *J. Chem. Phys.* **1965**, *42*, 414–417.