Switchable rewritability of Ag–TiO_2 nanocomposite films with multicolor photochromism

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Received (in Cambridge, UK) 21st October 2004, Accepted 1st December 2004
First published as an Advance Article on the web 25th January 2005
DOI: 10.1039/b416139d

The photochromism and rewritability of Ag–TiO_2 films were deactivated by modification with thiols to make it possible to retain color images displayed on the films (for more than 3 days under white fluorescent lamps), while the deactivated properties were fully reactivated by UV-irradiation.

Recently, we have found a new phenomenon, multicolor photochromism, of Ag–TiO_2 films prepared by loading nanoporous TiO_2 films with Ag nanoparticles by photocatalytic means.[1,2] The color of the Ag–TiO_2 film, initially brownish-gray, changes under a monochromatic visible light to almost the same color as that of the incident light. Potential applications of the material include rewritable color papers, rewritable paints, and a new class of optical memories. However, it is inevitable that color images displayed on the film are bleached gradually in air by ambient white light due to photochromism. In the present study, we developed a technique to suppress the bleaching by modification of the Ag–TiO_2 film with an alkanethiol or a fluoroalkanethiol to deactivate the photochromism temporarily. The photochromism can be reactivated by sufficiently irradiating the film with UV light. These techniques not only improve applicability of the material dramatically but also provide important information about the mechanism of the multicolor photochromism.

A commercial anatase TiO_2 sol (STS-01, ~7 nm diameter, Ishihara Sangyo Kaisha) was diluted seven-fold with ethanol. A nanoporous TiO_2 thin film was prepared on a Pyrex glass substrate (25 × 50 × 1 mm) from the sol by a spin-coating technique (at 1500 rpm for 10 s) and sintering at 500 °C for 1 h. The film was soaked in 1 M aqueous $AgNO_3$ for 3 min. The thoroughly rinsed and dried film was irradiated with 310 nm UV light and 420 nm light[2] (0.1 and 5 mW cm^{-2}, respectively) for 30 min to deposit Ag nanoparticles in the nanoporous TiO_2 film. Hg–Xe and Xe lamps (Luminar Ace LA-300UV and LA-250Xe, respectively, Hayashi Watch Works) were used as UV and visible light sources, respectively, with bandpass filters (fwhm, 10 nm). We also prepared much thicker TiO_2 films for visual observation of images. Anatase TiO_2 powders (ST-01, ~7 nm diameter, Ishihara Sangyo Kaisha) were suspended (11 wt%) in 9 mM $AgNO_3$ ethanol solution containing a silicone binder (NDC-100A, NISSO), and irradiated with UV light for 2 h. The film was prepared on a Pyrex glass plate from the resulting suspension by a spin-coating technique (at 700 rpm for 10 s), and annealed at 120 °C for 1 h, followed by further irradiation with UV light for 30 min.

A nanoporous TiO_2 film is treated with $AgNO_3$ to adsorb Ag^+, and is irradiated with UV light to reduce the Ag^+ ions to Ag nanoparticles with various sizes and shapes in the nanopores; the TiO_2 photocatalyst[3] reduces Ag^+ and oxidizes water simultaneously (Fig. 1(A), process a). Each Ag nanoparticle absorbs light of a specific wavelength (its plasmon resonance wavelength).[4,5] The electrons are photoexcited due to plasmon resonance transfer to oxygen in air either directly or *via* TiO_2,[6] at a relatively low

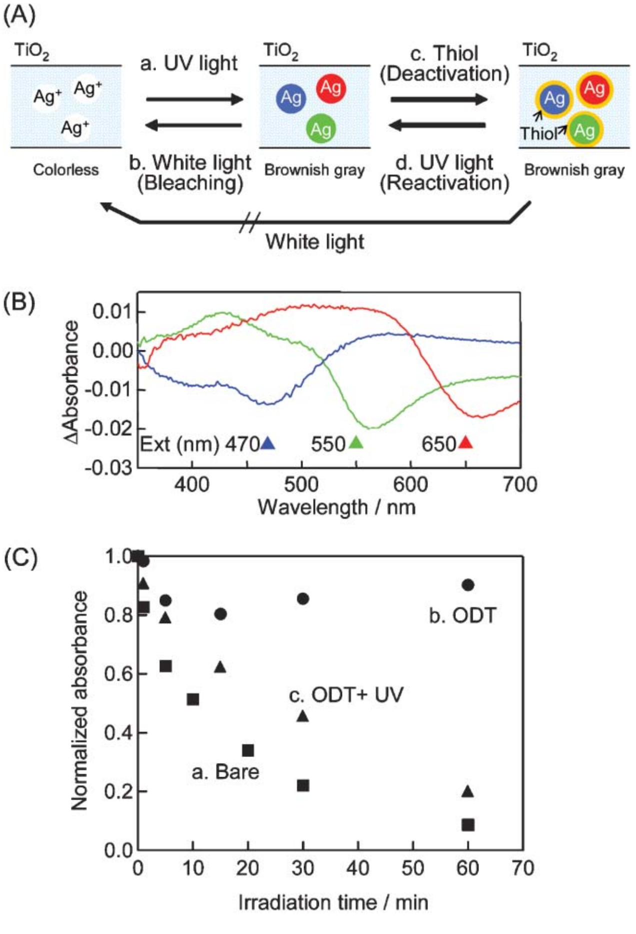

Fig. 1 (A) Schematic illustrations for photochromism of the Ag–TiO_2 film (a, b) and deactivation (c) and reactivation (d) of the photochromism. (B) Typical spectrum changes upon excitation by monochromatic lights (5 mW cm^{-2}, 5 min). (C) Absorbance change (450 nm, normalized by the initial value) of the Ag–TiO_2 films (thickness, 200 nm) during white light irradiation (>400 nm, 10 mW cm^{-2}). Bare (a), octadecanethiol (ODT)-modified (b), and ODT-modified and UV irradiated (1 mW cm^{-2}) (c) films were used.

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quantum yield. Thus, the Ag nanoparticle is reoxidized to Ag^+, and the Ag–TiO_2 film loses absorption at the excitation wavelength (Fig. 1(B)).[1,2] If the Ag–TiO_2 film is irradiated with strong green light for instance, the sufficiently irradiated film no longer absorbs green light and reflects it, while it absorbs the lights of the other colors. Therefore, it looks green. This mechanism holds for both coloring by a monochromatic light and bleaching by white light (Fig. 1(A), process b).

Plot (a) of Fig. 1(C) shows the bleaching of the Ag–TiO_2 film (thickness, *ca.* 200 nm) during white light irradiation (a Xe lamp, with a UV-cut filter, 10 mW cm^{-2}). In contrast, the bleaching was almost totally suppressed for the Ag–TiO_2 film treated with octadecanethiol (ODT) (1 mM ethanol solution for 5 min followed by evaporation of ethanol) (Fig. 1(C), plot b). An ODT self-assembly monolayer (SAM) formed on a Ag particle (Fig. 1(A), process c) may simply prevent the oxidative dissolution of Ag. The ODT layer may also block the electron transfer from Ag to oxygen. In addition, since the ODT layer is hydrophobic, the amount of adsorbed water, which may be necessary for dissolution of Ag^+, should be decreased in the vicinity of the Ag nanoparticles. These effects would inhibit the photooxidation of the Ag nanoparticles, resulting in the suppressed absorbance change.

In the meantime, plasmon resonance wavelength of a Ag nanoparticle is generally sensitive to the refractive index of its matrix.[7] This means that coating a Ag nanoparticle with a certain material may change its color. Actually, coating the Ag–TiO_2 film with a silica or nitrocellulose film changed its spectrum. However, the modification of the Ag–TiO_2 film with ODT did not change its spectrum significantly. In the case of silica and nitrocellulose, a Ag particle should have been deeply immersed in those materials, so that the resonance wavelength was shifted according to the refractive indexes of the materials. On the other hand, in the case of ODT, each Ag particle was coated with a SAM of ODT, which should have been sufficiently thinner than visible light wavelengths, so that the resonance wavelength of Ag was almost insensitive to the refractive index of the ODT layer.

The bleaching of the Ag–TiO_2 film was suppressed by deactivating the photochromism using ODT, as described above (Fig. 1(A), process c). However, simultaneously, the rewritability of the film was deactivated as well. Then, to reactivate the photochromism and rewritability, we irradiated the ODT-modified sample with UV light using black fluorescent lamps (1 mW cm^{-2}) for 1 h so as to decompose ODT by TiO_2 photocatalysis (Fig. 1(A), process d). Subsequently, the UV-irradiated film could be bleached by irradiation with white light (Fig. 1(C), plot c); the rewritability was reactivated. This bleaching behavior was similar to that of the bare sample before modification with ODT (Fig. 1(C), plot a). This is because the ODT molecules on the Ag nanoparticles were decomposed under UV light by active oxygen species, such as •OH radicals, which were photocatalytically generated on the TiO_2 surface and diffused either on the TiO_2 surface[8,9] or in the gas phase.[10,11] There may also be a possibility that the photoexcited electrons of TiO_2 transfer to the Ag nanoparticles, giving rise to reductive desorption of the ODT molecules, which are in turn decomposed by photocatalytic oxidation.[12] The slightly slower bleaching of the reactivated film is probably explained in terms of incomplete removal of the ODT molecules; remaining reaction products and/or intermediates might interfere slightly with the photooxidation of Ag or the accompanying mass transport.

Next, we demonstrated this effect visually by using a much thicker film. A brownish-gray Ag–TiO_2 film (thickness, 100 μm) was irradiated with a blue (450 nm) and red (650 nm) monochromatic spotlight (5 mW cm^{-2}; fwhm, 10 nm), for 30 min each (Fig. 2(A), left). Under relatively strong white fluorescent lamps (~80 μW cm^{-2}), the image with the color spots was gradually deteriorated, and was completely bleached within 24 h (Fig. 2(A)). When the film was treated with the ODT solution for 24 h in the dark immediately after the irradiation with the color spotlights, no obvious retardation of the bleaching was observed visually. The ODT might have been decomposed by trace UV light[12] contained in the white fluorescent light.

Then, we used fluorodecanethiol (FDT), instead of ODT, because fluoroalkyl groups are more resistant to photocatalytic oxidation than alkyl groups.[13] No color change was caused by the modification with FDT. As shown in Fig. 2(B), the FDT-modified sample retained the color image for more than 72 h (gradual deterioration of the image was observed after 96 h); the bleaching was clearly suppressed.

As described above, the possible reasons why the photooxidation of the Ag nanoparticles was inhibited by thiols include blocking of electron transfer to oxygen and water repulsion, so we examined which effect is predominant. Bleaching of the bare and ODT-treated Ag–TiO_2 thin films under a Xe lamp (with UV-cut filter; 10 mW cm^{-2}; 5 min) was examined in O_2–N_2 mixed gases at various mixing ratios and humidity. The bleaching rate for the bare Ag–TiO_2 film was almost independent of the humidity at the normal O_2 concentration of 20% while it strongly depended on the O_2 concentration. In addition, the bleaching rate for the ODT-modified film was gradually increased as the O_2 concentration increases under dry conditions. These results led us to conclude that the blocking effect of ODT on the electron transfer to oxygen might be more effective for the suppression of bleaching, rather than the water-repellent effect. A similar effect of thiol SAMs deposited on Au electrodes was reported; the thiol SAMs blocked electron transfer from the electrode to oxygen.[14,15]

In this work, suppression of the bleaching of the Ag nanoparticles loaded in the nanoporous TiO_2 films was achieved by modification with thiol molecules. Color images displayed on the film remained almost the same for more than 3 days under white fluorescent lamps. The photochromism and rewritability were

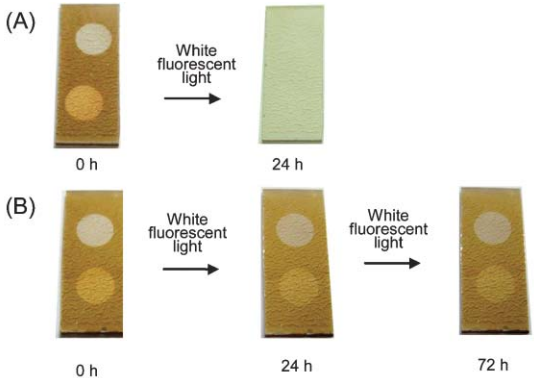

Fig. 2 Changes of the color images displayed (see text for details) on TiO_2 films (thickness, 100 μm) under white fluorescent lamps (~80 μW cm^{-2}); (A) a bare sample and (B) a sample modified with fluorodecanethiol after the image was displayed.

reactivated by UV-irradiation. These techniques would expand the applicabilities of the Ag–TiO_2 films.

This work was supported by a Grant-in-Aid for Scientific Research on Priority Areas (Area No. 417, Research No. 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.).

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