UV/Thermally Driven Rewritable Wettability Patterns on TiO_2–PDMS Composite Films

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ABSTRACT Composite films of TiO_2 and polydimethylsiloxane (PDMS) are prepared by a sol–gel method, cured with UV irradiation, and then treated in hot water to crystallize the TiO_2 in the film. The presence of anatase TiO_2 contributes to the photoinduced superhydrophilicity of the film under UV irradiation. Contact angle studies reveal that the TiO_2–PDMS composite film recovers its original hydrophobic state. Hydrophobic–superhydrophilic patterns are successfully formed on the films. The wettability patterns can be erased by UV irradiation and thermal treatment. New wettability patterns can be reconstructed, demonstrating that the film exhibits rewritable wettability without the need for organic chemicals.

KEYWORDS: composite film • wettability • patterning • photocatalyst • TiO_2

Wettability patterns have been used in many fundamental and industrial applications such as fluidic devices (1, 2) and nanoparticle arrays (3) and for patterning cells (4, 5) and DNA (6). One of the designs used most commonly for the preparation of wettability patterns in industrial applications, such as offset printing plates and printed circuit boards (7–9), is a photosensitive polymer coated on a substrate. However, the fabrication of wettability patterns in this way has several problems: (i) the waste from the fabrication process is strongly basic, and (ii) the substrate is not recyclable.

TiO_2 is a useful material for the preparation of wettability patterns because it undergoes wettability conversion to a superhydrophilic state and it decomposes organic chemicals under UV irradiation (10–15). Suda et al. prepared superhydrophilic–hydrophobic patterns on a TiO_2-coated aluminum substrate that functioned as an offset printing plate (9). The TiO_2 surface was patterned with organic chemicals by photocatalytic decomposition of the organic molecules in selected areas by UV irradiation. The patterns can be removed and reconstructed by deposition of organic chemicals to form new superhydrophilic–hydrophobic patterns repeatedly, thus providing a reusable printing plate. However, the surface of the substrate requires repeated treatment with organic chemicals, which involves multiple steps and uses organic chemicals.

Construction of superhydrophilic–hydrophobic patterns without the use of organic chemicals is challenging. This is because it requires a hydrophobic surface that is able to undergo wettability conversion to a superhydrophilic state induced by external stimuli. Polydimethylsiloxane (PDMS), commonly used as a hydrophobic filler (16–18), is a candidate for the preparation of hydrophobic surfaces because it has low a surface energy. Thus, a blend of PDMS and TiO_2 should produce a surface that is hydrophobic with the ability to undergo wettability conversion to a superhydrophilic state under UV irradiation.

In this work, TiO_2–PDMS composite films were fabricated using a sol–gel method, cured under UV irradiation, and then treated with hot water. The changes in wettability of the films were characterized by measuring the contact angles before and after UV irradiation. Furthermore, a superhydrophilic–hydrophobic wettability pattern prepared by selective UV irradiation of the TiO_2–PDMS composite film was fabricated. The film demonstrates rewritability without requiring the use of organic chemicals.

Films prepared from titanium tetrabutoxide, benzoylacetone, and PDMS were cured by irradiation with UV light to form a TiO_2–PDMS composite. Structural changes occurring in the film upon curing under UV irradiation for 3 h were observed by UV–visible spectroscopy (see Figure S1 in the Supporting Information). An absorption band at around 360 nm is attributed to the π–π^* transition of a chelate ring of benzoylacetone coordinated to titanium. The intensity of this band decreases significantly, indicating that the chelate rings of benzoylacetone are dissociated by UV irradiation (19–22). After dissociation of the chelate rings, a Ti–O–Ti network was formed in the film, as confirmed by IR spectroscopy (see Figure S2 in the Supporting Information). The intensity of the peaks at 1600 and 1540 cm^{-1} attributed to $\nu(C{=}O)$ and $\nu(C{=}C)$ of the chelate ring of benzoylacetone, respectively, decreased after UV irradiation for 3 h due to dissociation of the chelate rings. Furthermore, a broad band appeared

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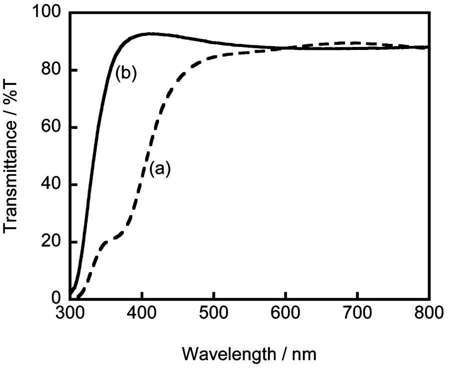

FIGURE 1. Optical transmittance spectra of TiO_2/PDMS composite films (a) before and (b) after hot water treatment.

below 1000 cm^{-1}, which is characteristic of the ν(Ti—O—Ti) vibration (21, 23). These results suggest that UV irradiation causes structural changes of the benzoylacetone chelate rings, allowing a TiO_2 network to form in the composite film.

After curing under UV irradiation, the TiO_2—PDMS composite film was treated in boiling water to crystallize the amorphous TiO_2 in the film. Figure 1 shows the optical transmittance of the composite films before and after hot water treatment. Before the treatment, the transmittance of the composite films is 42—89% for light with wavelengths of 400—800 nm, which contains absorption from the chelate rings of the titanium complex below 500 nm. The transmittance of the composite film after hot water treatment is 87—90%, meaning that it is highly transparent to light of wavelengths longer than 380 nm. The increase in transmittance induced by hot water treatment is caused by decomposition of the titanium complex containing benzoylacetone chelate rings that remained in the film even after UV curing, and by the formation of TiO_2 crystals.

X-ray diffraction patterns (XRD) of the TiO_2—PDMS composite films were measured before and after hot water treatment (see Figure S3 in the Supporting Information). The XRD pattern of the film after hot water treatment has a peak at 25° that is consistent with the anatase phase of TiO_2 and can be indexed to the (101) plane. An equivalent peak is not observed in the XRD pattern of the film before hot water treatment, demonstrating that the TiO_2 in the film is crystallized by hot water treatment. Note that X-ray photoelectron spectroscopy (XPS) for the TiO_2—PDMS composite films reveals the presence of Ti $2p_{3/2}$ attributed to TiO_2 (458.8 eV) on the surface (see Figure S4 in the Supporting Information).

It is anticipated that the crystalline TiO_2 in the film has photocatalytic properties, such as photoinduced superhydrophilicity under UV irradiation (10). The contact angles for TiO_2—PDMS composite films prepared with different treatment times in hot water are shown in Figure 2. Contact angles gradually decreased for each film under UV irradiation. For the sample treated with hot water for 30 min, the contact angles decreased to 0° after 3.5 h of UV exposure. This photoinduced superhydrophilicity demonstrates the presence of crystallized TiO_2 in the film. The rate of the change in contact angle did not increase significantly if the hot water treatment was prolonged for more than 30 min.

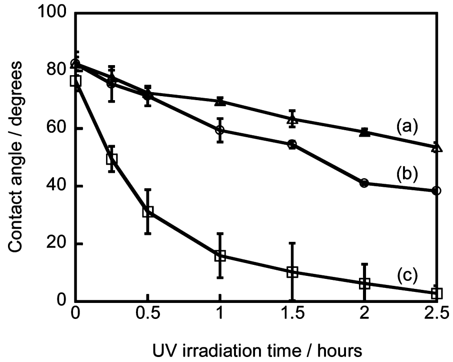

FIGURE 2. Water contact angles of TiO_2/PDMS composite films treated with hot water for (a) 5, (b) 10, and (c) 30 min.

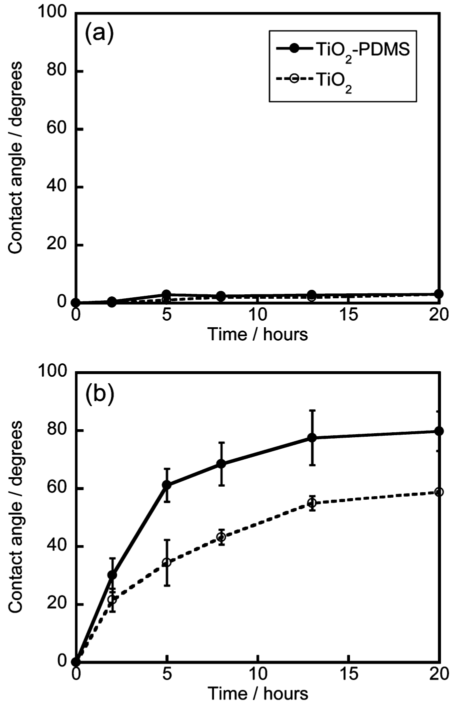

FIGURE 3. Recovery of the water contact angles of TiO_2 and TiO_2/PDMS composite films at (a) room temperature and (b) 100 °C.

TiO_2 surfaces exhibit the recovery of water contact angles from the superhydrophilic state induced by UV irradiation (24, 25). The water contact angles of the TiO_2—PDMS composite and TiO_2 films were therefore investigated at various temperatures after the transition to superhydrophilicity (see Figure 3). At room temperature, the water contact angles recovered quite slowly for both of the films. However, the rate of recovery of the water contact angles significantly increases at 100 °C. The recovery of water contact angles relates to conformational changes in the molecular bonding around Ti atoms on the TiO_2 surface and replacement of the adsorbed hydroxyl groups by oxygen (24—26). At high temperature, the rate of recovery is enhanced because the changes on the surface of TiO_2 are thermally stimulated (27, 28). Furthermore, the rate of recovery of water contact angle is faster for the TiO_2—PDMS film than for the TiO_2 film at 100 °C because PDMS behaves as a hydrophobic filler.

The combination of photoinduced superhydrophilicity and thermally stimulated recovery of water contact angles on the TiO_2—PDMS surface offers the potential to form

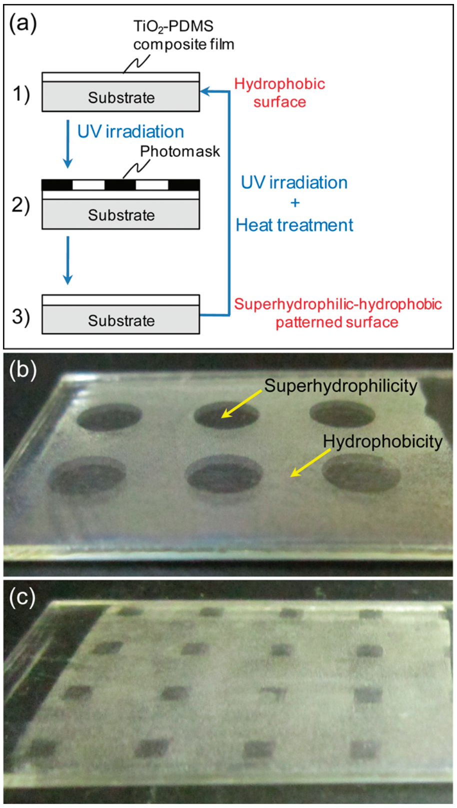

FIGURE 4. (a) Schematic representation of the preparation procedure of the wettability patterns on the TiO_2/PDMS composite film, and photographs of hydrophobic—superhydrophilic patterns formed by UV irradiation through photomasks after (b) first and (c) secondary processing.

rewritable surfaces controlled by external stimuli. A TiO_2—PDMS composite film with rewritable wettability was produced. The film contained patterns that were formed by UV irradiation, and then erased by subsequent thermal treatment. To fabricate the wettability patterns, we irradiated TiO_2—PDMS films that had undergone curing and hot water treatment with UV light through a photomask patterned with a square array of dots with diameters of 5 mm (Figure 4a). The film was then cooled below the dew point on a cooling stage to visualize the contrast in wettability. Water molecules from the air condensed on the surface of the film, resulting in a pattern of water adhesion on the film surface as shown in Figure 4b. The transparent regions correspond to superhydrophilic areas that were formed by UV irradiation, where water molecules spread over the film surface. The opaque areas are hydrophobic. To demonstrate the rewritability of the wettability patterns, we irradiated the film with UV light to make the surface superhydrophilic, and then dried in an oven at 100 °C to convert the surface back to a hydrophobic state. Different wettability patterns were then fabricated by UV irradiation through a photomask patterned with a square array of squares with diameters of 2 mm. The film was cooled below the dew point to check for the formation of wettability patterns prepared by this secondary process. A wettability pattern corresponding to the photomask used was successfully obtained as shown in Figure 4c. It should be noted that that the patterns that were prepared in the first fabrication process were not observed. These results demonstrate that the prepared substrate exhibits rewritable wettability.

In conclusion, TiO_2—PDMS composite films were prepared by a sol—gel method followed by curing with UV light and hot water treatment. The film was transparent to visible light after hot water treatment, and exhibited photoinduced superhydrophilicity under UV irradiation. Contact angle studies showed that the films recover their initial wettability, and that the rate of this recovery increases at high temperature. Wettability patterns prepared on a film using a photomask during UV irradiation can be erased by UV irradiation followed by thermal treatment. The TiO_2—PDMS composite films exhibit rewritable wettability that is stimulated by UV irradiation and thermal treatment. The rewritable wettability does not require the use of organic chemicals, which means TiO_2—PDMS composite films offer a new, efficient, and environmentally friendly substrate for high contrast wettability patterns, and could be used for offset printing plate.

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Supporting Information Available: Detailed experimental for the preparation of TiO_2/PDMS composite films and TiO_2 films; the determination of wettability patterns and recyclability; UV—visible absorption spectra, IR spectra, and XRD data for the TiO_2—PDMS composite films before and after hot water treatment (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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