

Article

# Large-Area Patterning of Oil-Based Inks on Superhydrophobic TiO<sub>2</sub> Nanotubular Layers by Photocatalytic Wettability Conversion

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**Abstract:** Patterning an oil-based ink on a solid surface based on a wettability difference is of significant importance for the application of offset printing. Herein, we describe a large-area patterning of oil-based ink on a self-organized TiO<sub>2</sub> nanotubular layer based on a photocatalytic wettability conversion. The TiO<sub>2</sub> nanotubular layer was fabricated by electrochemical anodization, which demonstrated a superhydrophobic wettability after modification with a self-assembled molecular layer. Subsequently, area-selective ultraviolet (UV) irradiation through a pre-designed pattern of water-based UV-resistant ink formed by an ink-jet technique was used to form a wettability difference. After removing the water-based ink, an oil-based ink was capable of depositing selectively on the superhydrophobic area to form the same pattern as the pre-designed pattern of water-based ink. This large-area patterning of an oil-based ink based on the photocatalytic wettability conversion is potentially applicable in offset printing.

**Keywords:** patterning; wettability difference; TiO<sub>2</sub>; offset printing; photocatalysis

## 1. Introduction

The creation of a wettability difference on a solid surface has attracted significant attention for practical applications [1–23]. One of the applications is to use the wettability difference to pattern an oil-based ink on a solid surface for offset printing [21–23]. Titanium oxide (TiO<sub>2</sub>) is one of the most important materials for fabricating a wettability difference [15–23]. A rough TiO<sub>2</sub> surface, which typically exhibits superhydrophilicity [24–26], can be converted to be superhydrophobic through the modification of self-assembled molecular layers (SAMs) with a low surface free energy [27,28]. The photocatalysis of TiO<sub>2</sub> under ultraviolet (UV) irradiation is capable of decomposing the SAMs, which achieves a photocatalytic wettability conversion of the TiO<sub>2</sub> surface from superhydrophobicity to superhydrophilicity [15–22,27,28]. Therefore, area-selective UV irradiation through a photomask on a SAMs-modified superhydrophobic TiO<sub>2</sub> surface can be used to fabricate a wettability difference.

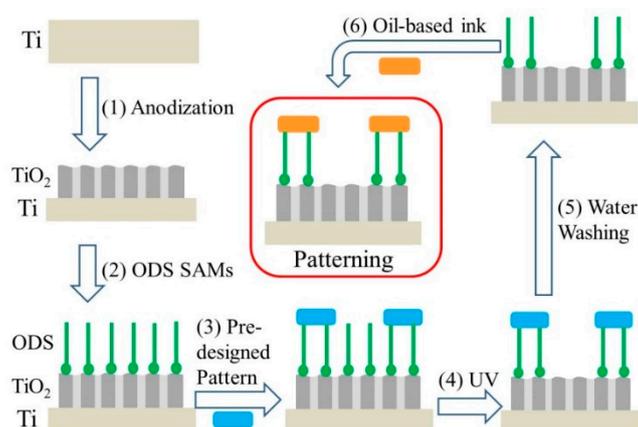
The patterning of oil-based inks on a TiO<sub>2</sub> surface with a wettability difference exhibited a promising potentiality for offset printing [21–23]. Compared with the conventional wettability difference between hydrophobicity and hydrophilicity on an aluminum plate based on a photosensitive polymer coating for offset printing [22,29], the wettability difference on the TiO<sub>2</sub> surface demonstrated several advantages, such as the reusability, environmental friendship and a large wettability contrast. Nishimoto et al. described the patterning of oil-based inks on a TiO<sub>2</sub>-coated aluminum plate with a wettability difference between superhydrophobicity and superhydrophilicity for offset printing [21]. Nakata et al. prepared the patterns of oil-based inks on a rough TiO<sub>2</sub> substrate by annealing etched Ti metal in a concentrated sulfuric acid for use as a printing plate in offset printing [22]. However, for

the future application of offset printing, the fabrication of a large-area pattern of oil-based inks on a superhydrophobic  $\text{TiO}_2$  film, specifically attached to the substrate with a robust surface wettability and a low environmental cost, is very necessary.

The self-organized  $\text{TiO}_2$  nanotubular layer on Ti metal can be fabricated by a facile electrochemical anodization technique in a fluoride-contained electrolyte [30–33]. The anodization strategy is time-saving without the use of a concentrated acid, which is a versatile technique to form a  $\text{TiO}_2$  nanotubular layer on any Ti metal independent of its geometry and size [34,35]. After being modified with SAMs with a low surface free energy, the  $\text{TiO}_2$  nanotubular layer demonstrated a superhydrophobic wettability [15,36–39]. Moreover, a  $\text{TiO}_2$  nanotubular layer generally demonstrates a higher photocatalytic activity when compared with a  $\text{TiO}_2$  nanoparticulate film [40], which is favorable for the photocatalytic wettability conversion. Herein, we reported the fabrication of a wettability difference on a large area  $\text{TiO}_2$  nanotubular layer by selectively decomposing the self-assembled molecular layers under ultraviolet irradiation, using a pre-designed pattern of water-based UV-resistant ink as a photomask. After removing the water-based ink, the oil-based ink was able to deposit selectively on the superhydrophobic area to form the same pattern as the pre-designed pattern of water-based ink.

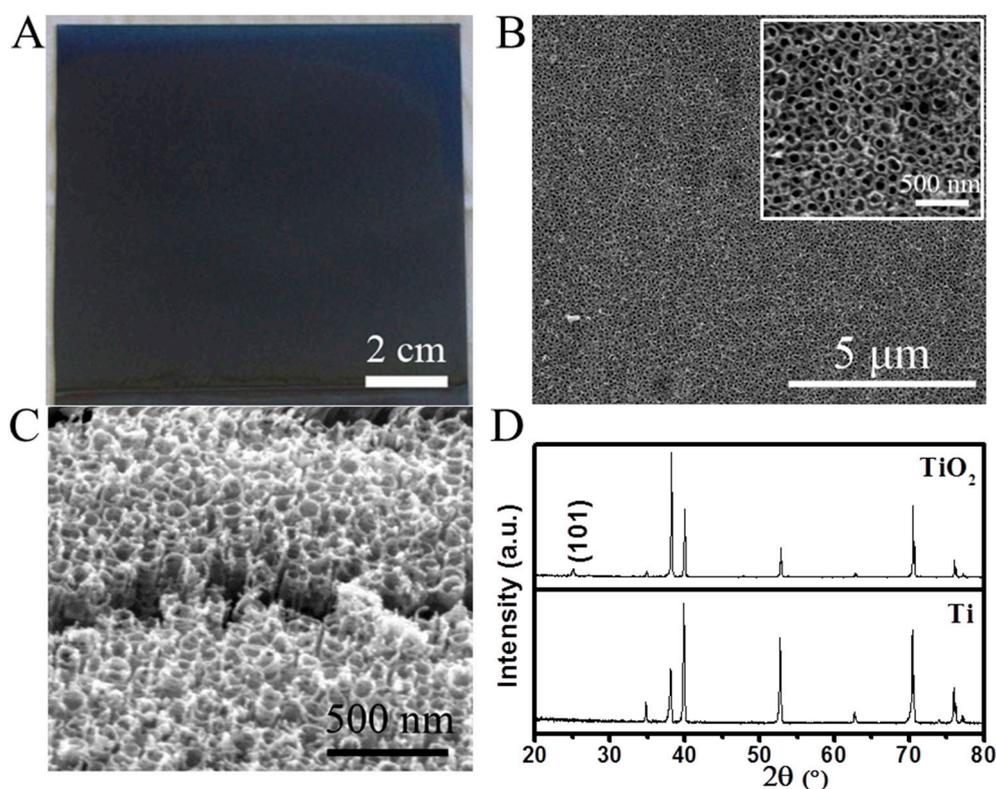
## 2. Results and Discussion

The process for the large-area patterning of oil-based ink on a  $\text{TiO}_2$  nanotubular layer is summarized in Scheme 1. A large-area  $\text{TiO}_2$  nanotubular layer with a crystallization of anatase phase was first formed on Ti metal by electrochemical anodization (Step 1). After modification with octadecyltrimethoxysilane (ODS) self-assembled molecular layers (SAMs), a superhydrophobic surface was obtained (Step 2). Then, a pre-designed pattern of water-based ink was formed on the superhydrophobic surface by an ink-jet technique, which functioned as a UV-resistant photomask (Step 3). Under UV irradiation, the ODS SAMs that were not covered by the water-based ink were photocatalytically decomposed, which converted the surface to be superhydrophilic (Step 4). The surface that was covered by the water-based ink remained to be superhydrophobic. After the water-based ink pattern was removed by water washing (Step 5), an oil-based ink was deposited selectively on the superhydrophobic area (Step 6), which developed a corresponding pattern the same as the pre-designed pattern of water-based ink.



**Scheme 1.** The schematic process for the patterning of oil-based ink on a  $\text{TiO}_2$  nanotubular layer. Firstly, a  $\text{TiO}_2$  nanotubular layer was formed on Ti metal by anodization (Step 1). A superhydrophobic surface was obtained by modified octadecyltrimethoxysilane (ODS) self-assembled molecular layers (Step 2). Then, a pre-designed pattern of water-based ink was formed on the superhydrophobic surface by an ink-jet technique (Step 3). After UV irradiation (Step 4) and a subsequent water washing (Step 5), a wettability difference was formed on the surface. Finally, an oil-based ink was deposited selectively on the superhydrophobic area (Step 6), which developed a corresponding pattern the same as the pre-designed pattern of water-based ink. The diagram was not drawn to scale.

The electrochemical anodization is a versatile technique to form a TiO<sub>2</sub> nanotubular layer on any Ti metal independent of its geometry and size. Compared with the conventional dip-coating and thermal calcination technique, electrochemical anodization can be used facilely to prepare a large-area and uniform TiO<sub>2</sub> layer specifically attached to Ti metal because electrochemical anodization occurs at a solid-liquid interface using Ti metal as the precursor of TiO<sub>2</sub>. Figure 1A shows a representative photograph of a large-area TiO<sub>2</sub> nanotubular layer (around 10 × 10 cm) prepared by anodizing a Ti sheet in a 0.5% HF solution, followed by calcination under ambient air. An oxide surface with a uniform visible color was obtained. The SEM images (Figure 1B,C) indicate that the oxide surface showed a clear nanotubular configuration with a tube internal diameter of ~87 nm, a wall thickness of ~18 nm and a tube length of ~228 nm. The nanotubular morphology significantly increased the occupied fraction of air pockets on the entire surface, which was considered to be of prime importance to achieve a superhydrophobic surface. The XRD investigation identified the anatase phase existed in the TiO<sub>2</sub> nanotubular layer, as evidenced by the diffraction peak of anatase (101) crystal face at 2θ = 25.0° (Figure 1D).



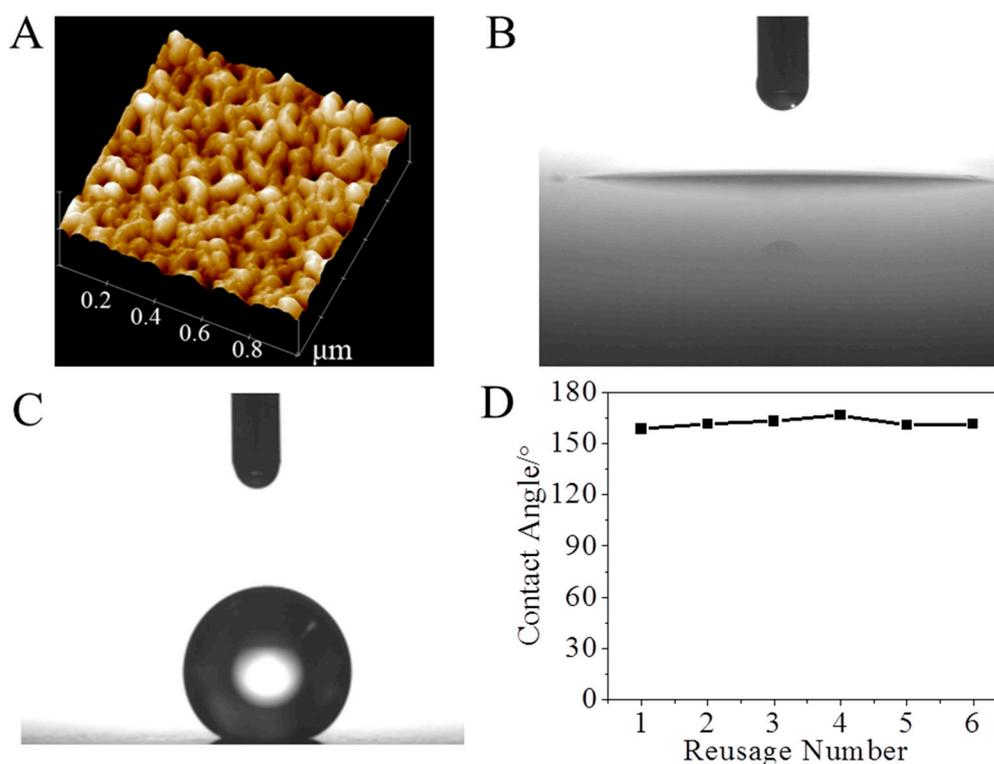
**Figure 1.** (A) A photograph of a large-area TiO<sub>2</sub> nanotubular layer, which demonstrated a uniform surface visible color. (B,C) Top-viewed (B) and cross-sectional (C) SEM images of the TiO<sub>2</sub> nanotubular layer. (D) The XRD investigation identified the anatase phase of the TiO<sub>2</sub> nanotubular layer.

The TiO<sub>2</sub> nanotubular layer was further analyzed by atomic force microscope (AFM) measurement. As shown in Figure 2A, the AFM image also revealed the porous surface of a TiO<sub>2</sub> nanotubular layer. The Root Mean Square (RMS) roughness was determined to be ~10.3 nm based on a scanning range of 1.0 × 1.0 μm. Figure 2B shows the static water contact angle (CA) of the as-prepared TiO<sub>2</sub> nanotubular layer, which demonstrated superhydrophilicity because of the high roughness resulting from the porous surface [41]. After being modified with ODS SAMs, the TiO<sub>2</sub> nanotubular layer showed a superhydrophobic state with a static water CA of ~156° (Figure 2C). The relation between the apparent

water CA ( $\theta'$ ) of a composite surface with two phases of solid and gas, and the water CA ( $\theta$ ) of a smooth surface with one phase of solid, can be described by the Cassier equation as follows [42–44]:

$$\cos \theta' = f_1 \cos \theta - f_2 \quad (1)$$

Herein,  $f_1$  is the fraction of the solid/water interface and  $f_2$  is the fraction of the gas/water interface, respectively, with a prerequisite of  $f_1 + f_2 = 1$ . Based on this equation, the large fraction ( $f_2$ ) of the gas/water interface in the TiO<sub>2</sub> nanotubular layer contributed to this large water CA.

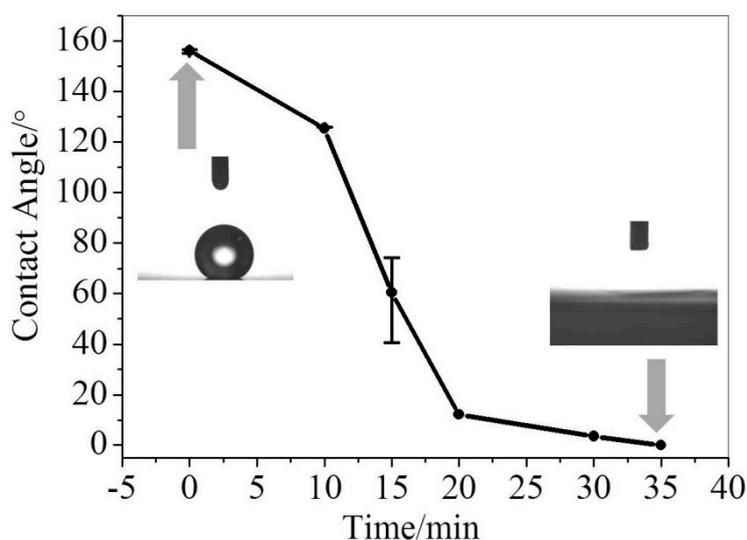


**Figure 2.** (A) The atomic force microscope (AFM) morphology of a TiO<sub>2</sub> nanotubular layer. (B) The static water contact angle (CA) of an as-prepared TiO<sub>2</sub> nanotubular layer, which demonstrated a superhydrophilicity. (C) After being modified with ODS self-assembled molecular layers (SAMs), the TiO<sub>2</sub> nanotubular layer showed a superhydrophobic state. (D) The static water CAs of six samples containing ODS-modified large-area TiO<sub>2</sub> nanotubular layers were prepared in one HF electrolyte successively.

The reusability of the HF electrolyte during the electrochemical anodization is important from the standpoint of reducing the environmental cost in a practical process. We fabricated six samples with a size of around 10 × 10 cm containing a TiO<sub>2</sub> nanotubular layer in one HF electrolyte successively. As shown in Figure 2D, after modification with ODS SAMs, all of the samples demonstrated an almost constant static water CA of ~160°, which indicated that electrochemical anodization could be used for the large-area fabrication of a TiO<sub>2</sub> nanotubular layer for a superhydrophobic surface in a practical process.

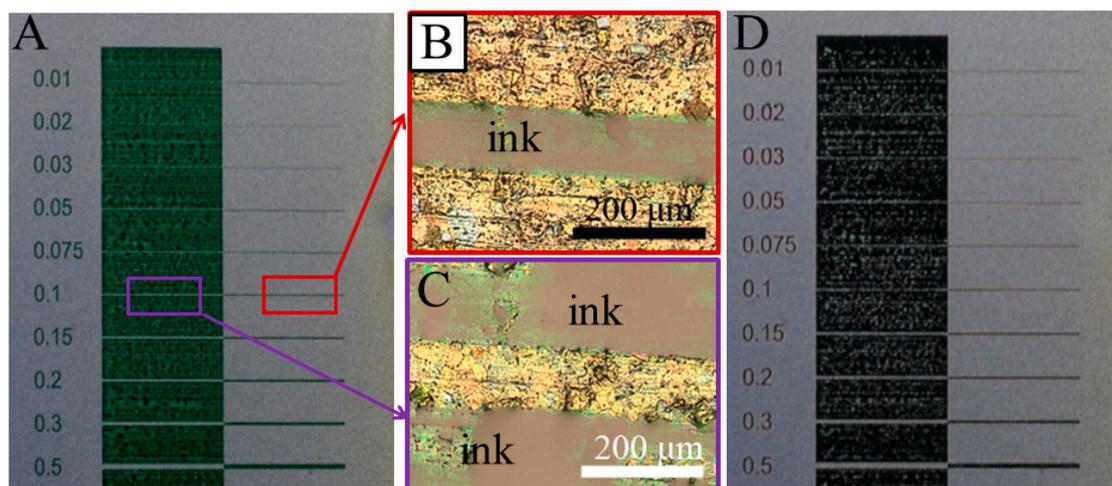
It has been well-known that the photocatalysis of TiO<sub>2</sub> under UV irradiation can decompose the ODS SAMs, which converts the superhydrophobic ODS-modified TiO<sub>2</sub> nanotubular layer to be superhydrophilic. Figure 3 depicts the evolution of the static water CAs of the ODS SAMs-modified TiO<sub>2</sub> nanotubular layer under UV irradiation. A series of water CAs were obtained between ~156° and ~0°, which was dependent on the time of UV irradiation. After UV irradiation for enough time, the superhydrophobic TiO<sub>2</sub> nanotubular layer with a CA of ~156° could be converted to be superhydrophilic with a CA of ~0°, indicating that almost all the long-chain alkyls of ODS were decomposed by TiO<sub>2</sub>

photocatalysis and removed from the surface of TiO<sub>2</sub> nanotubes. Two possible pathways are proposed for the photocatalytic oxidation of ODS molecules on the surface of TiO<sub>2</sub> nanotubes [45–47]. Firstly, the photo-generated holes in TiO<sub>2</sub> nanotubes can oxidize the long-chain alkyls in ODS molecules directly. Secondly, the trap of photogenerated electrons and holes by the oxygen and H<sub>2</sub>O in the surroundings under UV irradiation generates some active oxygen species, such as hydroxyl radicals (OH•), superoxide anions (O<sub>2</sub><sup>•-</sup>) and hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>), which also contributes to the oxidation of the long-chain alkyls in ODS molecules. Based on this special characteristic of UV-induced wettability conversion, area-selective UV irradiation through a pre-designed photomask on the superhydrophobic TiO<sub>2</sub> nanotubular layer can be used to fabricate the wettability difference between superhydrophobicity and superhydrophilicity.



**Figure 3.** The evolution of the static water CAs of the ODS SAMs-modified TiO<sub>2</sub> nanotubular layer under UV irradiation. Inset: the corresponding images for the measurement of water CA. After UV irradiation, the superhydrophobic TiO<sub>2</sub> nanotubular layer converted to be superhydrophilic.

The pre-designed pattern of water-based ink on the superhydrophobic TiO<sub>2</sub> surface formed by an ink-jet technique was a highly effective photomask to fabricate the wettability difference between superhydrophobicity and superhydrophilicity [21,22]. This water-based ink has a low surface free energy, which therefore can spread over the superhydrophobic TiO<sub>2</sub> surface. Moreover, the water-based ink is able to absorb UV light, which can function as a UV-resistant film [22]. As shown in Figure 4A, a pre-designed pattern of water-based ink with a resolution of 133 lpi (lines per inch) was formed on the surface of a superhydrophobic TiO<sub>2</sub> nanotubular layer by an ink-jet technique, which functioned as a photomask. The pre-designed pattern included some numbers, lines and areas. The morphologies of the lines with and without ink were imaged with an optical microscope (Figure 4B). A clear boundary between the TiO<sub>2</sub> nanotubular substrate and ink was observed, indicating that the TiO<sub>2</sub> nanotubular layer could be used as a substrate for the large-area patterning of water-based ink. Subsequently, the surface with a pre-designed pattern was illuminated by UV light. The ODS SAMs that were not covered by the water-based ink were photocatalytically decomposed, which converted the surface to be superhydrophilic, as shown in Figure 3. On the contrary, the surface that was covered by the water-based ink remained to be superhydrophobic because of the highly effective absorption of UV light. As a result, a wettability difference between superhydrophobicity and superhydrophilicity was formed on the TiO<sub>2</sub> nanotubular layer after UV irradiation.



**Figure 4.** (A) A pre-designed pattern of water-based ink was formed on the surface of a superhydrophobic TiO<sub>2</sub> nanotubular layer by an ink-jet technique, which functioned as a UV-resistant photomask. (B,C) The morphologies of the line with (B) and without (C) ink imaged with an optical microscope. A clear boundary between the TiO<sub>2</sub> nanotubular substrate and ink was observed. (D) The patterning of the oil-based ink after the TiO<sub>2</sub> nanotubular layer with a pre-designed pattern of water-based ink was illuminated by UV light and subsequently washed by water.

In order to check the preliminary application of the wettability difference on the TiO<sub>2</sub> nanotubular layer as a printing plate for the offset printing, the water-based ink patterns were removed by water washing. Subsequently, an oil-based ink was deposited on the same surface by a hand roller. As shown in Figure 4C, the oil-based ink was able to selectively deposit on the superhydrophobic area, which developed a corresponding pattern the same as the pre-designed pattern of water-based ink. This result indicated clearly that the large-area TiO<sub>2</sub> nanotubular layer derived from electrochemical anodization could be applied as a substrate for the patterning of oil-based ink.

### 3. Materials and Methods

#### 3.1. Fabrication of a Large-Area Superhydrophobic TiO<sub>2</sub> Nanotubular Layer

A large-area TiO<sub>2</sub> nanotubular layer on Ti metal was prepared following our previous method with a slight change [33,40]. Briefly, a large-area Ti foil, with a size of around 10 × 10 cm (Nilaco), was anodized in 3 L of a 0.5 wt% HF solution (Wako Chemicals) under stirring. The counter electrode was a Pt-sputtered stainless steel electrode with a size of around 10 × 10 cm. The voltage was provided by a custom-built direct-current (DC) power supply. The as-prepared TiO<sub>2</sub> nanotubular layer was annealed at 500 °C under ambient air for 3 h to induce anatase crystallization.

Octadecyltrimethoxysilane (ODS, TCI, C<sub>21</sub>H<sub>46</sub>O<sub>3</sub>Si) molecules were deposited on the surface of a TiO<sub>2</sub> nanotubular layer by a vapor reaction in a N<sub>2</sub> atmosphere at 120 °C for 3 h [48]. The static water contact angles (CAs) were measured with a contact angle meter (Kyowa CA-X, Saitama, Japan). The evolution of water CAs under UV irradiation was performed with a 2 mW/cm<sup>2</sup> mercury-xenon lamp.

#### 3.2. Fabrication of a Pre-Designed Pattern and the Patterning of Oil-Based Ink

The pre-designed pattern on the TiO<sub>2</sub> nanotubular layer for use as a UV-resistant photomask was fabricated by an ink-jet technique using a water-based ink [21,22]. The water-based ink was prepared by mixing a commercial dye (Tokyo Chemical Industry Co., Ltd., Tokyo, Japan, Direct Blue 86, 3 wt%) and pigment (BASF Japan Ltd., Tokyo, Japan, UVINUL3050, 2 wt%) into a mixed solvent of triethanolamine, diethylene glycol and deionized water (1:3:25, w/w/w). The water-based ink was effective in absorbing UV light, which functioned as a UV-resistant photomask. The TiO<sub>2</sub> nanotubular layer with a pre-designed pattern was irradiated with a 7 mW/cm<sup>2</sup> UV light (Philips-TUV75W) for

30 min. Then, the water-based ink patterns were removed by water washing. Finally, the oil-based ink (TOYO Ink) was then deposited on the surface of the TiO<sub>2</sub> nanotubular layer by a hand roller.

### 3.3. Characterizations

The morphologies of the TiO<sub>2</sub> nanotubular layer were studied using an FEI Quanta FEG 250 environmental scanning electron microscope (Hillsboro, OR, USA) (SEM) and a Bruker Dimension Icon atomic force microscope (Santa Barbara, CA, USA) (AFM). X-ray diffraction (XRD) patterns were measured on a Shimadzu XRD-6000 X-ray diffraction meter (Kyoto, Japan).

## 4. Conclusions

In summary, a large-area patterning of oil-based ink was achieved on a superhydrophobic TiO<sub>2</sub> nanotubular layer based on a UV-induced photocatalytic wettability conversion. The pre-designed pattern of water-based UV-resistant ink on a superhydrophobic TiO<sub>2</sub> nanotubular layer formed by an ink-jet technique was used as a photomask to selectively decompose the self-assembled molecular layers under UV irradiation. After removing the water-based ink patterns, the oil-based ink was selectively deposited on the superhydrophobic areas, which developed the corresponding pattern the same as the pre-designed pattern of water-based ink. This large-area patterning of an oil-based ink on a TiO<sub>2</sub> nanotubular layer could be potentially applied for offset printing.

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**Conflicts of Interest:** The authors declare no conflict of interest.

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