



TiO₂-based superhydrophobic–superhydrophilic pattern with an extremely high wettability contrast



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ABSTRACT

Rough nanostructured anatase TiO₂ surfaces containing many pores were prepared by the hydrothermal-based method. Surface modification with self-assembled monolayers (SAMs) of octadecylphosphonic acid (ODP) resulted in the superhydrophobic surface with an extremely high static water contact angle (CA) of $173.6^\circ \pm 1.7^\circ$. This superhydrophobic surface could be converted into a superhydrophilic surface with a water CA of nearly 0° by irradiating it with ultraviolet (UV) light, which induced photocatalytic decomposition of the ODP SAM. A superhydrophobic–superhydrophilic pattern with an extremely high wettability contrast (a water CA difference of over 170°) could be fabricated on the ODP-modified TiO₂ surface by area-selective UV irradiation through a photomask. This is the report of the TiO₂-based superhydrophobic–superhydrophilic pattern with a water CA difference of over 170° , and it may be possible to use such patterns for various applications.

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1. Introduction

Fabrication of surface patterns displaying contrasting wettability has received increasing interest due to their potential widespread applications including offset printing, cell growth and cell screening, spotting of biomolecules, fluidic microchips, and site-selective immobilization of functional materials [1–6]. To further develop such functional interfaces, it is important to enhance contrast in the wettability on the patterned surfaces. In particular, the high wettability contrast on such surfaces is required for the accurate manipulation of water-soluble or water-dispersed materials [7–9].

It is well known that the ultraviolet (UV)-irradiated TiO₂ film surface becomes superhydrophilic with water contact angles (CAs) of less than 5° due to a photocatalytic reaction [1–5,10–14]. On the other hand, TiO₂ films with fairly rough surfaces can be readily converted to superhydrophobic with water CAs of over 150° via the deposition of self-assembled monolayers (SAMs) of hydrophobic compounds, such as octadecylphosphonic acid (ODP) or octadecyltrimethoxysilane [10–12,14–16]. Accordingly, some examples of superhydrophobic–superhydrophilic dual functional surfaces with a water CA difference of 150° – 170° have been reported, based on the above concept, by patterning TiO₂ surfaces with hydrophobic SAMs, which are then carefully decomposed by area-selective UV irradiation through a photomask to expose the bare TiO₂ [1–6,17,18]. Because high contrast in the

wettability on the patterned surface can be easily achieved on this surface, TiO₂ film surface is considered highly suitable as a platform for such applications. Moreover, the TiO₂ film surface is chemically stable and bio-compatible, which provides the material with special advantages in micro-chemical systems and bio-related applications [19].

Some TiO₂ materials with unique architectures including TiO₂ nanotubes and nanowires have been prepared by the hydrothermal treatment of TiO₂ powder or Ti plates by aqueous alkaline solutions [20,21]. These nanostructured surfaces have the potential to be used as filtration membranes, high-surface-area electrodes, and photocatalysts for environmental purification and hydrogen evolution [22–29]. Recently, extreme superhydrophobic TiO₂ surface (a water CA of over 170°) has been reportedly achieved by hydrophobic SAM modified-rough TiO₂ surface prepared by the hydrothermal-based method [30]. However, the report on the wettability on the TiO₂ surface has just been the measurements of water and oil CAs. There have been no reports on the photocatalytic wettability patterning on such extreme superhydrophobic TiO₂ surface. Moreover, there are few reports on the superhydrophobic–superhydrophilic pattern with a water CA difference of over 170° . Accordingly, we report the photocatalytic wettability patterning on the extreme superhydrophobic TiO₂ surface prepared by the hydrothermal-based method and ODP surface modification. Herein, we first present a TiO₂-based superhydrophobic–superhydrophilic pattern with an extremely high wettability contrast (a water CA difference of over 170°). We also characterize a water–ethanol mixture, *n*-hexadecane (oil), and an under-water *n*-hexadecane CAs on the obtained superhydrophobic and

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superhydrophilic areas to investigate the possibility of the pattern on various applications such as offset printing and site-selective immobilization of functional materials.

2. Experimental details

Ti plates (10×50 mm; thickness: 0.25 mm; purity: 99.5%) were sonicated in acetone for 5 min, dried in air, and heated at 400°C for 1 h to form TiO_2 layers on their surfaces. The Ti plates were immersed in a 10 M NaOH solution (45 mL) in TeflonTM-lined stainless-steel (DuPont Co., Wilmington, DE) autoclaves. The autoclaves were placed in an oven and heated at 110°C for 6 h. After hydrothermal treatment, the samples on the Ti substrates were washed with deionized water and 0.1 M HCl solution and then heated at 500°C for 1 h. The thus-prepared TiO_2 surfaces were modified with an ODP monolayer by a previously reported method involving immersion in a 0.5 mM (10^{-3} mol/dm³) 2-propanol solution of ODP for 20 h [1,3,14]. The substrates were then removed from the solution and rinsed thoroughly with 2-propanol before being heat treated at 110°C for 2 h.

The crystalline phases of the samples were characterized by X-ray diffraction (XRD) using a conventional $\theta/2\theta$ diffractometer (RINT 2100/PC, Rigaku Co., Tokyo, Japan) with monochromated Cu K α radiation operated at 40 kV–30 mA. Surfaces and fractured sections of the samples were observed by scanning electron microscopy (SEM; JSM-6380A and JSM-7500FA, JEOL Co., Tokyo, Japan) operated at an acceleration voltage ranging from 2 to 20 kV. The compositions of the samples were analyzed by energy-dispersive X-ray spectroscopy (EDS; EX-23000BU, Jeol Co., Tokyo, Japan) operated at an acceleration voltage of 15 kV. In the EDS spectra, we observed the presence of Ti, Na, and O. The surface roughness of the samples was measured using an optical microscope (VH-Z100, Keyence Co., Osaka, Japan).

Wettability conversions of the TiO_2 surfaces by UV illumination were examined. A water–ethanol mixture and *n*-hexadecane were employed as model liquids for these measurements. The ethanol concentration was varied from 0 to 30 mass%; the liquid's corresponding surface energy was varied from 72 to 33 mJ/m² [31,32]. A 300 W Xe lamp was used as the UV light source. The UV intensity was set to be about 15 mW/cm². The static and dynamic (advancing/receding) CAs of the samples were measured using contact angle meters (DM-300 and CA-V, Kyowa Co., Tokyo, Japan) at room temperature and analyzed using commercial software. In addition, an underwater oil CA was measured using *n*-hexadecane as oil and deionized water as the water environment, and the oil droplet was supported by a needle when it did not adhere to the surface, i.e., an underwater oil CA $> 165^\circ$. At least five different positions were measured for the same sample. The wettability patterns were obtained by area-selective UV irradiation (intensity: about 15 mW/cm²) for 5 min onto the ODP-modified TiO_2 surfaces by using a photomask. The photomask was placed directly on the ODP-modified TiO_2 surfaces. The resulting samples were characterized by optical microscopy (KH-2700, Hirox Co., Tokyo, Japan).

3. Results and discussion

SEM observations (Fig. 1) indicated the formation of an approximately 2- μm -thick porous film on the sample surface. The sample surface contained many pores with diameters ranging from about 100 nm to 1 μm and the average surface roughness (R_a) of the sample was $0.84 \pm 0.03 \mu\text{m}$. In addition, the porous film contains nanowires with diameters of about 30 nm; these imparted double roughness. EDS analysis (Fig. 2) revealed that washing with deionized water and 0.1 M HCl solution after hydrothermal treatment completely removed Na from the sample. Furthermore, XRD peaks of the anatase phase were observed (at approximately $2\theta = 25.3^\circ, 36.9^\circ, 37.8^\circ, 38.5^\circ, 48.0^\circ, 53.9^\circ$, and 55.0°) as well as peaks due to the rutile phase and the Ti metal plate (Fig. 3). Thus, the nanostructured film mainly consists of the crystalline anatase TiO_2 phase.

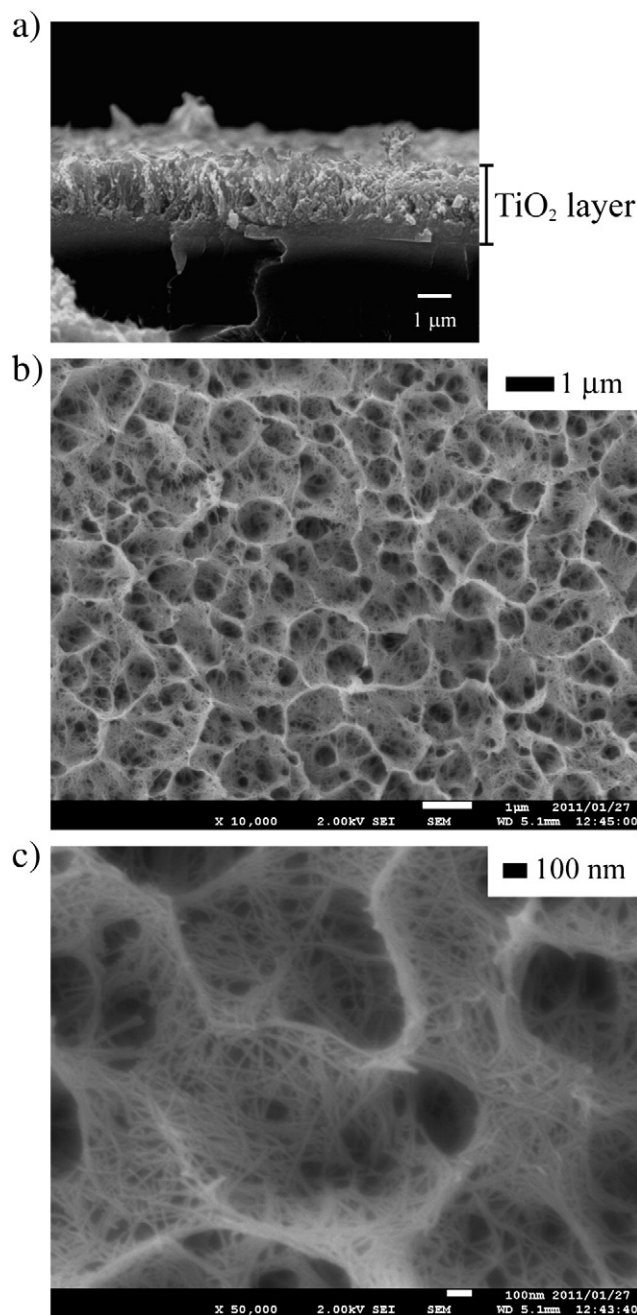


Fig. 1. Scanning electron microscopy images of porous TiO_2 layers prepared by hydrothermal treatment: (a) cross-sectional view, (b) top view, and (c) enlarged top view.

Table 1 shows the static water, *n*-hexadecane, and underwater *n*-hexadecane CAs before and after UV irradiation for 10 min. Before UV irradiation, the ODP-modified surface exhibited superhydrophobicity, superoleophilicity and underwater superoleophilicity. It was noted that the static water CA was measured to be $173.6^\circ \pm 1.7^\circ$ (volume of water droplets: 8.3 μL), although the static water CA of the surface before the ODP modification was 5° – 10° . Furthermore, the sliding angle of a stationary 10 μL water drop on the surface was found to be about 3° and the advancing and receding water CAs were measured to be $171.1^\circ \pm 0.6^\circ$ and $167.7^\circ \pm 1.2^\circ$ (volume of water droplets: 6.3 μL), respectively. These results indicate the ODP-modified nanostructured TiO_2 surfaces exhibit extremely high water repellency, as described in the previously reported TiO_2 surfaces [30]. In addition, we conducted the nonsticking test proposed by Gao and McCarthy to further characterize the superhydrophobic surface [33]. Fig. 4(a) shows a sequence

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