Microscale structure designing of nanoparticle-based photocatalyst films for enhanced functionalities and efficient energy utilization

Yuki Kameya* and Hiroki Yabe
Department of Mechanical Engineering, Chiba Institute of Technology, 2-17-1 Tsudanuma, Narashino, Chiba 275-0016, Japan
*E-mail: yuki.kameya@it-chiba.ac.jp

Abstract. Photocatalysts have increasingly become important materials to utilize renewable solar energy for decomposing pollutants, producing clean water, achieving self-cleaning surface, and so on. Therefore, it is desirable to expand the applications of photocatalysts by enhancing the functionalities and allowing ample design flexibility. Here the potential of nanoparticle-based photocatalyst films with microscale surface structures was investigated in order to enhance their useful functionalities. Photocatalyst films with microscale surface structures were prepared using the suspension of titanium dioxide (TiO$_2$) nanoparticles. The micro-scale structural features of prepared films were evaluated using a scanning electron microscope. Also, an atomic force microscope (AFM) was used. The AFM analysis of a film consisting of nanoparticle spherical aggregates revealed a surface profile of subwavelength surface structure. Then the optical and wetting characteristics were investigated. It was found that the visible-light transmittance increased due to subwavelength surface structures and that the microstructured TiO$_2$ films exhibited the contact angles below 10 degrees, i.e., superhydrophilic behavior, without ultraviolet-light illumination. On the basis of the presented results, it was suggested that the microscale surface structures of photocatalyst film can be designed to achieve enhanced functionalities. It is expected to effectively utilize the energy of sunlight in many applications using functional photocatalyst films with optimized design.

Keywords: Energy, Photocatalyst, Surface microstructure, Optical property, Hydrophilicity

1. Introduction
Sustainable energy system requires effective use of functional materials. Photocatalysts have increasingly become important materials to utilize renewable solar energy for decomposing pollutants, producing clean water, achieving self-cleaning surface, and so on. Most typical photocatalyst material is titanium dioxide, or TiO$_2$: it can decompose organic pollutants and also increase water wettability at its surface [1]. Photocatalyst films of TiO$_2$ generally appear white, because TiO$_2$ has a high refractive index and there is no absorption band in visible wavelength range. This property limits the color designing of TiO$_2$ coating surface. In addition, titanium dioxide has super-hydrophilic characteristics under the condition of ultra-violet (UV) light illumination. However, to utilize this interesting property, it is necessary to supply UV light. Hence, functional titanium dioxide films are promising if it is possible to achieve superhydrophilicity without UV light irradiation.
It is possible to improve the transmission of visible light at optical interfaces by fabricating micro-scale surface structure called anti-reflection structures. As a typical example of such surface, a subwavelength micro-texture can be used to make a graded refractive index at the optical interface, which results in reduced reflection. In addition, micro-scale surface texture affects the wetting characteristics; intrinsic hydrophilic material increases its hydrophilicity because of the surface texture. If the micro-scale structure of titanium dioxide film is modified, it may possible to observe the enhancement of hydrophilic property because titanium dioxide is a hydrophilic material itself.

It is also necessary to consider the photocatalytic activity of TiO$_2$ films. At the initial stage of photocatalyst reaction, an incident light is absorbed in a TiO$_2$ film. The pairs of electron and hole recombines after these carriers diffuse in titanium dioxide crystal (Figure 1a), which causes energy loss [2]. However, if nanoparticles of titanium dioxide are used as a photocatalyst, the distance of carrier diffusion can be limited by the solid surface. At the solid surface, the carriers can produce the radical species in gas phase (Figure 1b) [3]. Therefore, it is promising to use titanium dioxide nanoparticles in order to reduce the possibility of carrier recombination.

To fabricate the microscale surface structure of TiO$_2$ film, spherical nanoparticle aggregate (NSA) can be used [4]. The top layer of packed NSA film has an intrinsic subwavelength surface structure by when using NSA with the diameter of 100–200 nm. Also, it is possible to make microscale patterns, such as an array of micropillars, by using a softlithography process [5].

In the present study, the influence of microscale surface structures of a titanium dioxide nanoparticle-based film on its light transmission and wetting properties was investigated. Applying an NSA-based and a micropillar structures, the visible-light transmittance and hydrophilic property were examined. On the basis of experimental results, the effect of surface microstructure on the surface functionalities is discussed.

![Figure 1. Schematic of photocatalytic reaction phenomena in (a) nonporous film and (b) nanoparticle.](image)

2. Experimental

2.1. Fabrication of titanium dioxide films
An aqueous dispersion of TiO$_2$ nanoparticle Evonik P25 was prepared. This material consisted of nanoparticles (the mean diameter was 21 nm). This material has been widely applied in many areas as a standard photocatalyst particles. NSA (Ujiden Chemical) was also used in this study. To fabricate the array of micropillars, the softlithography process was applied [5]. All the samples were fabricated at a standard laboratory condition. The detailed fabrication process can be found in the reference [3].

2.2. Surface structure characterization
Micro-scale structural characteristics can be generally examined using a scanning electron microscope (SEM). So the film samples prepared here were analysed using a Hitachi S-4700 SEM. Also, atomic
force microscopy (AFM) observation was performed to quantitatively evaluate the surface microstructures. We used nGauge AFM (ICSPI) to scan the sample surface and acquire AFM data. The AFM data were then analysed using the software Gwyddion [6].

2.3. Normal light transmission experiment
The light transmission experiment was conducted via an optical-fiber-based spectrometer. Visible lights were supplied with a halogen light source. The light was normally irradiated to a sample. The obtained data was analysed with a software provided by the manufacturer of spectrometer, and then the transmittance was determined over the visible light wavelengths.

2.4. Wetting evaluation
Surface wetting property can be examined by simply depositing a water droplet. The shape of water droplet reflects the surface wetting property, so it is necessary to analyse the contact angle of water. Static contact angle was determined using the setup shown in Figure 2(a). A monochromatic high-speed camera HAS-U2M (DITECT) was also used to observe rapid water motion due to the strong capillary force of microstructured TiO$_2$ film surface (Figure 2b).

![Figure 2](image)

Figure 2. Schematic of experimental setup for evaluating surface wettability: (a) static contact angle measurement, and (b) dynamic measurement using a high-speed camera.

3. Results and discussion

3.1. Prepared samples
Prepared TiO$_2$ film samples were observed via an SEM. The acquired images are shown in Figure 3. No unique geometrical features were observed for P25 film (Figure 3a). The agglomeration of nanoparticles during the fabrication process might cause the surface roughness. Concerning NSA film, the structural characteristics of NSA (i.e., subwavelength spheres) were still observable (Figure 3b). These two samples have predictable surface texture considering the particles constituting the final form of films. Figure 3c shows the perspective view of micropillar structure. A remarkable difference was confirmed regarding the qualitative characteristics of surface structure between these samples.

In addition, it was examined whether the subwavelength structure was fabricated on the NSA film. Figure 4 summarizes the AFM results. The surface structure is characterized by the size and shape of NSA as shown in two-dimensional (Figure 4a) and three-dimensional (Figure 4b) views, which is consistent with the SEM image shown above. Figure 4c shows the surface profile at $y = 0.93$ μm (the coordinate is defined in Figure 4a), and the subwavelength surface structure of NSA film was confirmed.
3.2. Optical property
Figure 5 shows the spectral transmittance of TiO$_2$ nanoparticle photocatalyst films in the visible wavelength range. The NSA film exhibited higher transmittance than the P25 film. The enhanced transmittance appears to be achieved by the subwavelength structure fabricated at the film surface. Even though the P25 film also has the surface roughness, the enhanced transmittance was not observed; this might be due to insufficient refractive index gradient at surface. Furthermore, the micropillar structure film was pale white, which would be caused by the scattering of visible lights by the micropillars.

3.3. Wettability
Wettability is an important property for achieving a water-spreading (self-cleaning) functionality. As described in Section 2.4, the static contact angle was first determined for each sample. As a result, every sample showed the contact angle less than 10°. The water contact angles below 10° is a typical threshold of superhydrophilic character. Because of superhydrophilicity, a supplied water drop rapidly spread immediately after contacting the surface as shown in Figure 6a. It was suggested to use a special technique when quantitatively evaluating superhydrophilic surfaces [7], so additional experiment was performed using the setup shown in Figure 2b. Water was contained in a PTFE tube...
with an outer diameter of 1.1 mm. The PTFE tube was suspended above the TiO$_2$ film surface. Water flow was initiated when the bottom of cylindrical water made contact with the film surface. The snapshots taken by a high-speed camera are shown in Figure 6b, and it was confirmed that a detectable amount of water spread within 15 ms.

As described above, superhydrophilic behavior for nanoparticle-based samples was observed without UV light illumination. The surface roughness appeared to play an important role especially for the P25 film. P25 film consisted of fine nanoparticles and its nano-scale surface texture appears to be large enough for water molecules. By using microstructures, such as an array of micropillars, it would be possible to enhance the water transport function on the TiO$_2$ photocatalyst film surface.

3.4. Effect of surface structure dimension

Figure 7 summarizes the effect of surface structure dimension on the functionalities of nanoparticle-based photocatalyst films. A nonporous film needs UV light irradiation to obtain superhydrophilic surface, while microstructured films have enhanced water wetting due to its surface structures. Concerning the optical characteristics, subwavelength structure is effective to achieve the increased transmission because larger structures such as micropillars would cause light scattering.

4. Conclusion

The effect of surface microstructures of TiO$_2$ nanoparticle-based films on its optical and wetting characteristics was investigate. Several kinds of surface microstructures can be fabricated: a sub-wavelength surface structure using submicron-scale NSA, and a micropillar structure using a soft-lithography process. Enhanced light transmission was demonstrated for sub-wavelength structured
surface. Also, for all nanoparticle-based films without ultraviolet-light illumination, superhydrophilic behavior was observed due to the surface roughness. The experimental data shown in this study clearly indicated the novel usefulness of surface microstructures to obtain the functionalities of photocatalyst films. Further enhancement of surface functionalities can be expected by designing the surface microstructures. On the basis of the presented results, it was suggested that microscale surface structures of photocatalyst film can be designed to achieve enhanced functionalities. It is expected to effectively utilize the energy of sunlight in many applications using photocatalyst films with optimized design.

Figure 7. Enhanced functionalities of nanoparticle-based photocatalyst films depending on the dimension of surface structure.

Acknowledgments
The authors thank Tomohiro Okazoe of Ujiden Chemical Industry for supplying the TiO$_2$ materials. A part of the experiments was performed by Kasumi Masuda and Takahiro Yamada as an undergraduate research program of Chiba Institute of Technology.

References
[1] Teoh WY, Scott JA and Amal R 2012 J. Phys. Chem. Lett. 3 629
[2] Luttrell T, Halpegamage S, Tao J, Kramer A, Sutter E and Batzill M 2014 Sci. Rep. 4 4043
[3] Kameya Y, Torii K, Hirai S and Kaviany M 2017 Chem. Eng. J. 327 831
[4] Kameya Y and Yabe H 2019 Coatings 9 547
[5] Kameya Y, Yamaki H, Ono R and Motosuke M 2016 Mater. Lett. 175 262
[6] Nečas D and Klapetek P 2011 Open Physics 10 181
[7] Allred TP, Weibel JA and Garimella SV 2017 Langmuir 33 7847