Improvement of Wettability of Photocatalytic TiO$_2$–Coated Wafers by Microwave/UV Pre-treatment

Minh Quang Tran$^{1, 2}$, Kazuya Nakata$^{2, 3}$*, and Satoshi Horikoshi$^{1, 2}$

1 Department of Materials and Life Sciences, Faculty of Science and Technology, Sophia University, 7-1 Kioicho, Chiyodaku, Tokyo, 102-8554, JAPAN
2 Photocatalytic International Research Center, Research Institute of Science and Technology, Tokyo University of Science, 2641 Yamazaki, Noda, Chiba, 278-0022, JAPAN
3 Department of Applied Biological Science, Faculty of Science and Technology, Tokyo University of Science, 2641 Yamazaki, Noda, Chiba, 278-0022, JAPAN

Abstract: The wettability efficiency of TiO$_2$-coated Ti substrate wafers was improved using a microwave/UV pre-treatment method. With the assistance of microwave heating, TiO$_2$ substrates coating with P25 completely achieved super hydrophilic state within 5 min, which is twice as fast compared with only UV irradiation condition. Moreover, when the microwave power was increased, improvement in the wettability activity was observed. Apart from P25, coating with brookite also resulted in a good performance. The contact angle was 0° with only 10 min of irradiation.

Key words: TiO$_2$, microwave, super hydrophilic, wettability, electromagnetic wave effect

1 INTRODUCTION

Wettability is one of the most important basic physical properties of material surfaces in nature. The control of this property has received significant attention in recent years in regard to fundamental and industrial applications. Moreover, by separating the specific super-hydrophobic and super hydrophilic area, or patterning, controllable-wettability material could be used to control fluidic devices or applied to offset printing. Recently, wettability applications have not been limited only to water. Other solutions such as oil, tea, blood, methanol, and ethanol have been investigated.

The photocatalyst TiO$_2$ which has been studied as an environmental catalyst was reported to exhibit super hydrophilicity when irradiated with ultraviolet rays by Hashimoto and others in 1997. The contact angle of water on a clean TiO$_2$ surface can be repeatedly cycled between approximately zero (after UV irradiation) and 50-60° (after irradiation with visible light or storage in the dark). This phenomenon is exploited in commercially available materials with properties which include antifouling and anti-fogging of glass. To improve the performance of the self-cleaning effect, Kazuo Yamaguchi was successful in increasing the contact angle of the surface using a self-assembled monolayer method (SAM). Based on his research, we deposited TiO$_2$ substrate with SAM to create a super-hydrophobic surface with a contact angle of approximately 160°. This material was irradiated with UV light to convert the surface to super hydrophilic with a contact angle lower than 5°. The improvement of the wettability of TiO$_2$ with respect to ultraviolet radiation is needed for numerous applications.

The microwave-/photo-assisted photocatalytic methodology has many advantages in regard to the treatment of polluted water. However, the photocatalytic performance could be significantly improved by using both microwave heating and UV light irradiation. The advantage of this method is that the amount of ·OH radicals, which are oxidation active species generated from the photocatalyst under UV irradiation, is simultaneously increased by microwave irradiation. This is because the recombination of electrons inside TiO$_2$ is suppressed at this wavelength. In addition, it is reported that microwave has an effect on the interaction with oxygen defect inside TiO$_2$ in terms of an electromagnetic wave, but this is not a thermal effect. Based on this phenomenon, it can be predicted that micro-

*Correspondence to: Kazuya Nakata, Department of Materials and Life Sciences, Faculty of Science and Technology, Sophia University, 7-1 Kioicho, Chiyodaku, Tokyo, 102-8554, JAPAN
E-mail: horikosi@sophia.ac.jp
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waves may improve the wettability of the surface of TiO₂. In part, this explains the strong interest in solid surfaces whose wettability can be reversibly controlled using an external stimulus such as microwaves.

2 EXPERIMENTAL PROCEDURES

2.1 Materials

The preparation of photocatalytic TiO₂-coated Ti wafers was adopted from our earlier report. Titanium plate (size: 0.1×10×10 cm) was purchased from Nilaco corporation for use with the substrate materials. Sulfuric acid 70% purchased from Yoneyama Yakuhin Kyogo Co., Ltd was used to etch the Titanium plate. Commercial higher activity TiO₂ powder was purchased from Evonik Industries AG. Rutile TiO₂ powder was purchased from Soekawa chemical Co., Ltd, anatase TiO₂ powder was purchased from Ishahara Sangyou Kaisha, Ltd and brookit TiO₂ powder was purchased from Kohundo Chemical Laboratory Co., Ltd. These materials were used for coating purposes. Self-assembled monolayer (SAM) chemical octadecyltrimethoxysilane (ODS) bought from Tokyo chemistry Industry Company was prepared to create the super-hydrophobic surface.

2.2 Apparatus

P25 TiO₂ powder (0.10 g, 0.25 g, and 0.50 g) was dispersed in 100 mL ultrapure water, mixed with a magnetic stir for 2 h, and then the TiO₂ suspended aqueous solution was dispersed in an ultrasound bath for 30 min at 35°C. Similarity, other dispersion of anatase TiO₂ powder, rutile TiO₂ powder and brookite TiO₂ powder were also prepared.

The titanium plate was modified to an appropriate size of 0.1×5.0×5.0 cm and immersed in sulfuric acid 70% for 48 h at room temperature (Fig. 1). After the surface was sufficiently etched, it was calcined at 500°C for 3 hrs. The obtained material was cut again (0.1×2.5×2.5 cm) and immersed in the prepared P25, rutile, anatase, and brookite dispersed aqueous solutions, respectively. Samples were recovered, and after drying, they were calcined again at 500°C for 3 h. The recovered sample was in super hydrophilic condition. Lastly, the materials were deposited with a self-assembled monolayer of octadecyltrimethoxysilane (ODS) at a temperature of 120°C for 3 h to allow the surface to become super-hydrophobic.

3 RESULTS

The wettability efficiency of the microwave/UV irradiation on the coating amount of P25 TiO₂ powder (0.25 g, 0.50 g, and 0.10 g) was investigated. During this process, the microwave was continuously irradiated at 30 W (Fig. 2). Note that during the experiment, the temperature of the P25 TiO₂-coated wafers was less than 30°C. The TiO₂ coating with 0.5 g P25 had the highest wettability efficiency After 10 min, the surface of the TiO₂ coating with 0.5 g P25 became super hydrophilic with a contact angle of 0°. Furthermore, the difference of the contact angle of the surface was negligible. On the contrary, the TiO₂ substrate coating with 0.1 g P25 had a poorly uniform surface. Some regions on the surface even had high contact angles such as 110° and 95°. In the case of the TiO₂ sample coating with 0.25 g P25, although the surface becomes super hydrophilic after 10 min of irradiation with UV, the fluctuation of contact angles was still higher than for the sample coating with 0.5 g P25. Based on this result, it can be concluded that coating with 0.5 g P25 resulted in the highest uniformity...
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and the most efficient surface. The temporal changes of the contact angle with microwave/UV pre-treatment P25 TiO$_2$-courted Ti wafers and pristine P25 TiO$_2$-coated wafers (no microwave) are shown in Fig. 2. According to the result, with the assistance of microwave/UV pre-treatment, the efficiency of wettability greatly increased compared with pristine P25 TiO$_2$-courted Ti wafers. Because they exhibited the highest surface uniformity, the TiO$_2$ substrate coating with 0.50 g P25 reached the super-hydrophilic state within 5 minutes, which is two times faster compared with irradiation without microwave heating. TiO$_2$ substrate coated with 0.10 g P25 with support heating from microwaves also exhibited a higher efficiency. However, due to the lack of uniformity, the contact angle result showed high fluctuation. Similarity, although the TiO$_2$ sample coating with 0.25 g P25 had the same efficiency as the TiO$_2$ sample coating with 0.5 g P25, the difference in the result for the two surfaces was still significant.

To determine whether the increase of photoactivity was caused by the heating effect or via the electromagnetic wave effect of the microwave, the sample was heated at 30°C using a commercial electric heater (Yonezawa mini oven MD-100) under UV light irradiation, and the temporal change in the contact angle was observed. Note that the conditions used for the UV light experiment are the same as those used for the microwave investigation. The contact angle of the P25 TiO$_2$-courted Ti wafers using electric furnace heating was almost the same as the naked P25 TiO$_2$-courted Ti wafers.

The hollow triangle (dotted line) shown in Fig. 2a is confirmation of the wettability of the microwave pre-treatment without UV irradiation. If only microwaves are used for irradiation of the TiO$_2$, this does not lead to an improvement in wettability. Simultaneous irradiation with microwaves and ultraviolet irradiation is necessary. In summary, it could be concluded that microwave irradiation under UV irradiation plays an important role in increasing the wettability efficiency by the microwave electromagnetic wave effect(s).

Changes in wettability to microwave power were studied...
at 80 W and 100 W from 30 W. 0.50 g P25 TiO$_2$-coated Ti wafers were used as the sample (Fig. 3). In the case of a microwave power setting of 100 W, the contact angle of the sample was swiftly reduced to 0° after 2 min irradiation with microwave heating support. When a microwave power of 80 W was used, the wettability change was slower. However, high efficiency near 3 min was still obtained compared with 5 min for 30 W. Initially, we researched the number of ·OH radical produced from the photocatalytic reaction with P25 TiO$_2$ particles under microwave irradiation at 3 W and 16 W. The amount of ·OH radicals increased with microwave irradiation, moreover, the results show that the increase of the ·OH radicals at a power of 16 W was more than at 3 W. This could be explained by considering that a higher microwave power will increase the number of ·OH radical produced from P25$^{15}$. As a result, it is anticipated that the wettability would improve.

TiO$_2$ substrate coating with 0.5 g P25, anatase, rutile and brookite was irradiated under UV light with microwave heating. The efficiency of each sample is shown in Fig. 4. It can be seen that TiO$_2$ substrate coating with P25 had the highest wettability efficiency, with only 5 min to convert the contact angle from super-hydrophobic condition (higher than 160°) to 0°. The time to change the super-hydrophobic surface to super hydrophilic of TiO$_2$ substrate coating with anatase and rutile were similar, though the efficiency of anatase was higher. After 20 min, the contact angle of anatase was 0°, while the contact angle of rutile was 4.3°. In addition, the result of the brookite case also indicates a significant result, in that the contact angle was only approximately 50° after 5 min irradiation and reached 0° after 10 min.

5 CONCLUSION

In this research, we confirmed that the combination of microwave and UV irradiation as pre-treatment of the TiO$_2$ substrate improves overall wettability. It was concluded that this result is due to the synergistic effect of ultraviolet light and microwave because the outcome cannot be replicated by irradiation with only microwaves. Furthermore, even when both electric furnace heating and ultraviolet irradiation are used, wettability is not promoted in the same way, which suggest that the phenomenon is an electromagnetic wave effect.

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