Wettability of ceramic surfaces –A wide range control of surface wettability from super hydrophilicity to super hydrophobicity, from static wettability to dynamic wettability

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Surface wettability is dependent on surface energy of the material. Therefore the surface wettability basically reflects its intrinsic surface property and it has been thought that it is hard to be controlled arbitrarily. For example, inorganic materials such like metal oxides usually exhibit relatively hydrophilic property as compared with organic materials. However recent series of studies by our group revealed that photo-induced surface reaction, nanometer scale roughness, nanometer scale physical and chemical heterogeneity affect wettability greatly. This fact clearly shows that the surface wettability of a metal oxide can be controlled from superhydrophilic state to superhydrophobic state. The target of control includes not only static wettability but also dynamic wettability. Oxide surface with high dynamic hydrophobicity can be obtained by optimizing these factors. Water repellency of developed hydrophobic ceramic surface turned out to be like a polymer surface. The novel technology to control wettability of ceramic surfaces is expected to contribute to various applications.

Key-words: Wettability, Surface, Hydrophilic, Hydrophobic, Dynamic hydrophobic, Photocatalyst

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1. Introduction

Surface wettability depends on the surface energy. In the simplest case, the wettability of a solid surface is evaluated by the contact angle given by Young’s equation. If one considers a drop of liquid on a solid substrate, there exist three different phases. Therefore, there are three surface tensions to consider: solid–liquid $\gamma_{SL}$, liquid–vapor $\gamma_{LV}$, and solid–vapor $\gamma_{SV}$. The relationship between the cosine of the contact angle $\theta$ that the drop makes with the surface and the three surface tensions is given by Young’s equation:

$$\gamma_{SV} = \gamma_{SL} + \gamma_{LV} \cos \theta$$  \hspace{1cm} (1)

This equation can be interpreted as a mechanical force balance for the line of the three-phase contact. The intrinsic surface energy of an inorganic ceramic surface such as metal oxide is considered to be higher as compared with organic material surface. In an ambient air atmosphere, OH groups and molecular water are adsorbed on the surface. Under the ordinary circumstances, surface organic contamination may change the wettability. In fact, a slight organic contamination is usually detected on the ceramic oxide surface which is kept in a laboratory room and it increases water contact angle gradually. Sometimes it changes several ten degree of contact angle. Despite this, at the industrial point of view, it does not make sense to measure the surface wettability in ultra vacuum or ultra clean atmosphere. It is necessary to control wettability in an ambient atmospheric condition to apply the wettability for practical uses. Alternatively, we can obtain more practical information by studying a profile of wettability change due to surface adsorption and contamination in usual atmosphere and evaluating the saturated values. In fact, ceramic surface usually exhibits more hydrophilic property than polymer surface even after longer exposure in usual atmosphere.

Saturated water contact angle of metal oxides such as SiO$_2$ or Al$_2$O$_3$ usually varies from 10° to 60°. Usual ceramic surface except carbon does not show contact angle above 90°. Our experimental study shows clearly that the profile of wettability change and saturated value of wettability stored in a usual clean laboratory depends strongly on surface structure, surface micro-structure and surface reaction etc. Even though, the surface with surface adsorption and slight contamination occur, intrinsic surface wettability affects the saturated wettability. Thus, in our experiments, we use such wettability data which are measured after longer enough storage in a clean glass chamber.

**Figure 1(a)** shows a photograph of water droplet on TiO$_2$ surface. The TiO$_2$ thin film was prepared by sputtering process and heat treated at 500°C for 10 min. The water contact angle is around 50°. This value is relatively high as metal oxide surface. However no sliding off of water droplet can be observed even on vertical surface. The enlarged image of the fringe of water is shown in Fig. 1(b). The fringe line is not uniform and shows irregular shape. There are some protruding points which are as

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Fig. 1. Water droplet on ceramic surface (ZrO$_2$ thin film).
like pined by projections. Water droplet on usual ceramic surface shows similar irregular shape. It seems difficult to change the wettability with complete control.

Surface wettability attracts attention not only because of genuine scientific curiosity but because it is important at industrial standpoint. Adhesiveness of stains, adsorbability of contaminations and surface cleaning ability are strongly dependent to surface wettability. To optimize surface wettability is critical issue to apply material for wider applications in mechanical engineering, chemical engineering and architectural applications.7)–9) For these purposes, the understanding of mechanism of surface wettability of ceramic surface is inevitable. Photo-induced hydrophilic conversion on photocatalyst thin film which has been discovered by our group is one of the breakthrough to control hydrophilic conversion on photocatalyst thin film which has been discovered by our group is one of the breakthrough to control hydrophilicity of ceramic surface. 7), 8) Utilizing this reaction, it became possible to obtain self-cleaning ceramic surface. On the contrary, superhydrophobic surface can be obtained by utilizing ceramic manufacturing process to give rough surface. 9)

Recently, not only static hydrophobicity, but also dynamic hydrophobicity is attracting much attention. Figure 2 shows schematic illustration of water contact angle and sliding angle. The wettability which is evaluated by sliding angle or sliding speed represents dynamic wettability. The relationship between static and dynamic wettability is complicated than it is usually expected. In this review, the fundamental technology to control wettability of ceramic surface from hydrophilicity to hydrophobicity and also from static to dynamic property is described on the basis of experimental works by our groups.

2. Hydrophilicity

2.1 Wenzel equation

As shown in the previous chapter, surface wettability depends on the surface energy and is subject to Young’s equation. However, this equation is not applicable to rough surfaces. It is known well that water on porous surface cannot form a droplet because it is absorbed into pores by a capillary effect. However the roughness even on the dense surface also affects contact angle. According to Wenzel’s modification of Young’s equation, the roughness factor r enhances both hydrophilicity and hydrophobicity.

$$\cos \theta' = r \frac{\gamma_{SV}}{\gamma_{SL}/\gamma_{LV}} = r \cos \theta$$

According to this equation, when the intrinsic water contact angle is larger than 90° on a flat surface, the hydrophobicity of the surface is enhanced by this effect. In contrast, when the intrinsic water contact angle is smaller than 90° on a flat surface, the hydrophilicity of the surface is enhanced by this effect. Because usual intrinsic water contact angle of ceramic surface is below 90° as mentioned earlier, more hydrophilic surface can be obtained by preparing rougher ceramic surfaces. On the contrary, more hydrophobic surface can be obtained by preparing flatter surfaces.

Figure 3 shows the relationship between surface roughness of various metals (Au, Ag, Cu, Al, Cu, Ti, Cr, Ni, Sn, Pt, Ge) and oxides (TiO2, SnO2 and SiO2) and water contact angles. The roughness was measured by AFM and also a mechanical surface roughness measuring machine. Because it includes various compounds, the dependence of roughness on water contact angle cannot be attributable to Wenzel effect alone. Even so, it is clear that the effect of roughness is dominantly large. It is noted that although the dependence of roughness in μm scale is not so clear, it in nanometer scale is significant.

The Wenzel equation is fundamentally based on a thermodynamic model and the assumption that the average surface energy is identical to that enhanced by surface area. A surface with a roughness on a micrometer scale can be treated as a macroscopically uniform surface when it interacts with water droplets. However, surfaces that have a roughness in the nanometer scale may interact with water molecules in a different way. These surfaces have a typical roughness that is comparable to the size of water molecule and may be smaller than the size of water cluster. In this case, the thermodynamically uniform interaction may not be expected. Therefore the effect of roughness in nanometer scale shown in Fig. 3 is not considered to be caused by conventional Wenzel effect, but by a different mechanism caused by interaction between an inorganic surface and water molecule.

Even on the same TiO2, the wettability is so much different between samples when the surface roughness is altered. For example, water contact angle of single crystal TiO2 is usually much higher than polycrystalline TiO2 surface because the surface roughness of single crystal is much smaller than polycrystalline TiO2. In this paper, several measurements of wettability on the same TiO2 with different roughness show different values. It is noted that these deviation are mainly due to surface roughness.

2.2 Photo-induced hydrophilicity

The intrinsic wettability of a solid surface can be sustained by conventional photocatalytic oxidation processes by decomposing surface contamination. In addition to this reaction, some photocatalysts themselves exhibit surface wettability conversion by photo irradiation. Figure 4 shows the change in the water contact angle on TiO2, 7), 8) ZnO, 11) SnO2, 12) and TiO2/WO313) composite

![Fig. 2. Concept of dynamic and static wettability. (a) Young’s relation is described. Here the relationship between solid–liquid γSV, liquid–vapor γLV, and solid–vapor γSV and the contact angle θ is described. (b) The figure shows sliding angle, advancing contact angle and receding contact angle. Here: α: sliding angle, θa: advancing contact angle, θr: receding contact angle.](image)

![Fig. 3. Relationship between average roughness and water contact angle of various inorganic oxides and metals.](image)
when they are brought about by photoillumination in which the photon energy was sufficient to produce electrons and holes in these semiconductors.

The samples were irradiated by UV light at first and kept in dark storage in a clean atmosphere for a sufficiently long duration until the wettability stabilized. After this process, UV irradiation was conducted again and the water contact angle was measured.

As shown in Fig. 4, these oxides show an apparent decrease in the water contact angle under UV illumination. Although all the samples in this figure exhibited similar photo-oxidation power, the hydrophilizing effect is different between them, e.g., some were more hydrophilicized than others and some showed less change in wettability.\textsuperscript{14} In fact, some photocatalysts show no photo-induced wettability change even though they show high photocatalytic oxidation power. Figure 5 shows water contact angle of hydroxyapatite doped with Ti ions (TiHAP)\textsuperscript{15} and SrTiO\textsubscript{3}.\textsuperscript{16} No wettability change was observed on these samples.

We have examined the photo-oxidation capability of these materials by conducting the photodecomposition of IPA with the same UV light sources. These experiments show that all these samples exhibit photocatalytic activity upon the oxidation of IPA. It is clear that even though the photocatalyst has higher photo-oxidation power, it does not always show photo-induced hydrophilic conversion.

As for photo-induced hydrophilic conversion of TiO\textsubscript{2}, detailed analytical experiments have been conducted to investigate mechanism of the conversion. These studies indicate that hydrophilic conversion occurs not only because of the removal of organic substances from the TiO\textsubscript{2} surface but also because of the change in the surface structure of the TiO\textsubscript{2}. The photo induced hydrophilic conversion on the surface of TiO\textsubscript{2} was discovered in 1995 and this phenomenon is currently called as "superhydrophilicity".\textsuperscript{17,18}

To induce hydrophilic conversion, the pairs of photogenerated electrons and holes are essential as like usual photo-oxidation process. However, they react in a different way. The holes transfer to water as in the case of conventional photocatalytic oxidation, but the electrons react with the lattice oxygen instead of the adsorbed oxygen. This reduces the number of oxygen ions, creating oxygen vacancies. Water molecules then heal these oxygen vacancies in order to produce a highly hydrophilic surface. Figure 6 shows a schematic illustration of the mechanism of photo-induced hydrophilic conversion.\textsuperscript{19-23}

In addition to the contact angle, there are several important parameters that describe the phenomena related to photoinduced hydrophilic conversion. Photo induced hydrophilic conversion sometimes occurs along with oleophobicizing. Therefore, not only the measurement of the water contact angle but also the measurement of the oil contact angle is important. It is known that some inorganic surfaces exhibit hydrophilic and oleophobic properties at the same time. However, some surfaces exhibit higher hydrophilic and higher oleophilic at the same time. This property is called amphiphilic and has been reported for both single crystal TiO\textsubscript{2}\textsuperscript{7} and polycrystalline TiO\textsubscript{2}.\textsuperscript{24}

The rate of the hydrophilic conversion is a fundamental parameter that correlates with conventional photocatalytic activity in many cases. The rate is also affected by surface microstructure especially surface roughness as shown previously. A rough surface usually has a faster hydrophilicizing rate.

In addition, it has been reported that the different crystal faces of a single crystal of rutile exhibit different rates of hydrophilic conversion.\textsuperscript{25} Figure 7 shows hydrophilic conversion rates on two different crystal faces of a TiO\textsubscript{2} single crystal caused by repeated UV illumination. The (110) surface shows higher hydrophilic conversion rate from the beginning of the first time UV illumination. The repeated illumination affects the rate slightly. On the other hands, repeated illumination affects wettability change behavior of the (001) surface greatly. The hydrophilic conversion on (001) surface is hardly induced at the beginning of UV illumination when it is illuminated at first time. However repeated illumination leads to faster hydrophilic conversion and lower contact angle even after dark storage.\textsuperscript{26}

It is thought that the face with rich oxygen vacancy sites is
likely to be more sensitive to photo induced surface crystal change. The initial difference of hydrophilic conversion rate between (110) and (001) faces is attributable to the difference of the bridging oxygen sites i.e. they on (110) faces are larger than those on (001) sites. However repeated illumination changes the hydrophilic conversion behavior. It was reported that change of roughness of TiO$_2$ surface is observed during photo-illumination.$^{27}$ Although it is known that photocorrosion occurs upon ZnO, the structure of TiO$_2$ is believed to remain no change even under UV illumination. However our studies clearly show that surface crystal layer of TiO$_2$ is changed during UV illumination and to some extent, the structural change remains after UV illumination to induce internal stress. In fact, the internal stress is also a parameter that might affect the hydrophilic conversion process.$^{28}$

Even if once hydrophilicized, a surface will gradually convert to its original wettability when it is kept in dark. The sustainability of a hydrophilic state is also an important parameter for practical applications. It is found that the addition of SiO$_2$ improves hydrophilic sustainability greatly. Recently several paper reports that just SiO$_2$ does exhibit hydrophilicity without UV illumination.$^{29}$ However SiO$_2$ does not have mechanism to maintain hydrophilicity$^{30}$ and it cannot be expected that such surfaces without photocatalyst show stable hydrophilicity for long term.

3. Static hydrophobicity

Figure 3 clearly shows the surface with nanometer scale flatness exhibits higher contact angle. In fact, careful preparation of oxide thin film to suppress surface roughness is effective to increase water contact angle. One of the fabrication processes to increase surface flatness is plasma crystallization process of TiO$_2$.31–33

We recently studied that the effect of post-plasma treatment on the surface roughness and wettability of a TiO$_2$ film deposited by magnetron sputtering. The crystallization of anatase by the plasma treatment was optimized by the selection of an amorphous thin film that was deposited at 20% oxygen partial pressure. The anatase film crystallized by the plasma treatment had a flatter surface with a lower average roughness than a heat-treated sample. The flat surface of the thin film exhibited improved hydrophobicity. The highest value of the water contact angle was around 70°.

On the contrary, the surface with much larger roughness may exhibit higher water contact angle. In the case of such roughened surface, the surface can be assumed to be the composite of solid and air on a specific condition. The wettability of a composite was studied by Cassie.$^{34}$ He proposed an equation describing the contact angle $\theta'$ at a surface composed of two phases:

$$\cos \theta' = f \cos \theta_1 + (1-f)\cos \theta_2$$

The equation describes the effect of surface heterogeneity on the contact angle. In this equation, $\theta'$ is the Cassie angle, which is the weighted average of the contact angles of the two phases of the surface. In the above equation, $f$ represents the fraction of the surface covered by one phase, and $\theta_1$ and $\theta_2$ represent the contact angle of each phase.

The wettability of a rough surface with considerably less surface energy can be suitably predicted by the Cassie equation under particular circumstances. This prediction is based on the assumption that a rough surface is composed of a solid and air. If the second phase is considered to be air, the contact angle is considered to be 180° because the interaction between air and water is negligibly small. Then,

$$\cos \theta' = f \cos \theta + f - 1$$

There have been many reports of superhydrophobic surfaces utilizing this Cassie effect. Figure 8 shows various micro-structures with roughness to exhibit superhydrophobicity. In these cases, hydrophobic polymers such like CF$_3$ compound were coated on the surface to lower the surface energy. Therefore mechanical durability of these coatings is insufficient for practical uses. Moreover, these roughened surfaces themselves usually show less mechanical durability than a flat surface. For example, a needle-like structure or a pillar like structure (as shown in Fig. 8(a)) that is ideal for a superhydrophobic surface exhibits mechanically insufficient properties when abrasion tests are applied. We have also created a surface with a crater-like structure (as shown in Fig. 8(b)). This surface exhibits higher durability than needle like structure. However, also in this case, the mechanical properties are still not sufficient for practical uses.$^{35–37}$

Even though numerous previous papers on highly hydrophobic materials have been reported, a superhydrophobic surface with sufficient mechanical durability is rarely seen even now.

Another approach for wettability control is wettability switching by photo illumination. Figure 9 shows an example showing such effects. The sample material is TiO$_2$ prepared by CVD process implanted by Cr ion. This surface show hydrophilicizing effect when it is illuminated by UV and hydrophobicizing effect by visible light illumination. It is considered that the hydrophobicizing
is not induced by photon but by heat from light irradiation.38

4. Dynamic hydrophobicity

4.1 Design of dynamic hydrophobicity

In addition to the static contact angle, there are dynamic parameters that define hydrophobicity. Even though the static contact angle is sufficiently high (more than 150°), the water droplet does not always slide off easily. It is well known that a water droplet on the surface treated with a CF3 group cannot be removed easily even on a vertical surface. As this fact shows, static hydrophobicity and the sliding angle seem to have no direct correlation. In fact, fluorine compounds have been believed to have a high sliding angle even though their static contact angle is high.

Hydrophobicity should not be evaluated by only the static contact angle but also by dynamic parameters such as sliding angle and sliding speed. Although static hydrophobicity can be controlled by surface energy and roughness, it is difficult to intuitively understand the practical dynamic hydrophobicities just by studying these parameters. While the sliding angle has been extensively reported, there are only a few reports on sliding behavior.39–43

Recently, the dynamic hydrophobicity on self-assembled monolayer surfaces was studied by our group. In this study, ultrasmooth hydrophobic surfaces composed by FAS17 (1H,1H,2H,2H-perfluorodecyltrimethoxysilane) or ODS (octadecyltrimethoxysilane) were prepared by optimizing conditions such as solvent, concentration, and reaction time. The water contact angle and surface roughness increases with respect to reaction time, and sliding properties show maximal values at optimized condition. It has been found that the optimized conditions provide excellent static and dynamic hydrophobicity to a Si wafer surface. It also shows clearly that the dynamic hydrophobicity is strongly affected by the differences in surface roughness of only a few nanometers. In other words, dynamic hydrophobicity is decreased when roughness is becoming larger than nanometer scale. On the basis of this result, the fact that a water droplet on the surface treated with a CF3 group cannot be removed easily even on a vertical surface is attributable to insufficient surface flatness.44

Similarly, it is expected that even ceramic surface with higher surface energy can be modified to show higher dynamic hydrophobicity by controlling its surface roughness.

4.2 Dewetting process

One of the important equations to show dynamic hydrophobicity is Furmidge equation,45 which shows sliding angle as

\[
\sin \alpha = w \gamma L (\cos \theta_r - \cos \theta_a) / mg
\]

Where, \( \alpha \): sliding angle, \( m \): weight of water, \( g \): gravity, \( w \): width of water, \( \theta_r \); advancing contact angle, \( \theta_a \); receding contact angle.

Therefore critical parameters dominating sliding angle is represented by \( (\cos \theta_r - \cos \theta_a) \). In this framework, dynamic hydrophobicity is defined by the deference between advancing contact angle and receding contact angle (contact angle hysteresis). When the hysteresis is smaller, sliding angle becomes smaller. Advancing angle is usually correlates with static contact angle. Therefore, the key parameter to affect the hysteresis is receding angle. It depends on how easy the water can remove from the surface.

Actually receding of water droplet is not homogeneous process and it is disturbed so often by many causes. Figure 10 shows the photograph of receding face of water droplet on several samples with various contact angles. We can observe many points of resistance which disturbs receding of water droplet by optical microscope. A rupture of a thin liquid film from the solid surface is called as dewetting. Therefore the image suggests that easy dewetting process is the key process to enhance dynamic hydrophobicity.

Dewetting process associated with considerable energy barriers results hysteresis of contact angles. Although systematic study has not been conducted to clarify the cause of the energy barrier, it is considered to be possibly because of surface roughness, surface chemical inhomogeneous state and surface physical chemical inhomogeneous state.46 Therefore we expect to be able to obtain higher dynamic hydrophobic ceramic surface by reducing these factors as much as possible.
4.3 Surface treatment to accelerate dewetting

In order to obtain dynamic hydrophobic surface, surface roughness, surface chemical inhomogeneous state and surface physical chemical inhomogeneous state should be reduced as much as possible. It is considered that various manufacturing processes might be effective to reduce these values. We have studied effective methods to reduce them and recently found several processes are effective to enhance dynamic hydrophobicity. One of the processes is the post plasma treatment of oxide thin film which is described previously in this paper.

The crystallization of anatase TiO$_2$ by the plasma treatment can be optimized by the selection of an amorphous thin film. It is shown that the anatase film crystallized by the plasma treatment has a flatter surface with a lower average roughness than a heat-treated sample. Because of such flatness, the surface of the thin film exhibited improved hydrophobicity. The highest value of the water contact angle was around 70° and this value itself is not so high. While the film which was fabricated by optimized condition showed excellent water removability. The sliding angle of the water droplet was only 20°. Even the thin film with the same flatness does not always show such high level of dynamic hydrophobicity. It was found that the film with higher water removability has an amorphous top layer formed on the crystallized layers. To summarize the results, a TiO$_2$ photocatalyst surface which has amorphous top layer with nanometer scale flatness exhibits superior dynamic hydrophobicity. Generally speaking, the chemical and physical property of amorphous surface is more homogeneous than these of crystallized surface. Optimized plasma treatment leads to nanometer scale flat and amorphous surface which enhances dynamic hydrophobicity.

Besides plasma treatment, we have found that water vapor treatment in special condition during thin film preparation process is effective to enhance dynamic hydrophobicity of sol–gel derived thin film recently. Figure 11 summarizes the effect by these treatments. In many cases, not only decrease in sliding angle but also improvement in water contact angle is observed. However some samples show clear decrease of sliding angles while maintaining similar contact angle. As a result, we can obtain high dynamic hydrophobic oxide surfaces with relatively low contact angle. The water repellency on tilted surface of the developed hydrophobic oxide films is really like them on a polymer surfaces. Although shape of water droplet is not so round but semicircular, it can removed easily by tilting the substrate. This property is novel and not known for inorganic oxide surfaces.
5. Conclusion

Based on Young’s equation which is fundamental thermodynamic theory, wettability of ceramic surface should be constrained to be usual hydrophilic state. However, utilizing photo-induced reaction, Wenzel effect, nanometer scale roughness effect, Cassie effect and treatment to enhance dewetting process, we can obtain ceramic surfaces with various wettabilities. The variation of wettability includes not only static one but also dynamic wettability. Even though its surface energy is relatively high, we can fabricate high dynamic hydrophobic ceramic thin film as like polymer surface.

Figure 12 shows schematic illustration of wettability controlled surface of ceramics. It shows that the shape of water droplet can be controlled arbitrarily by several methods mentioned above. Such technologies to change surface wettability are interesting not only at scientific viewpoint but also at industrial viewpoint. It is expected that further study in this field will lead to the novel applications in various fields in near future.

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