Processing of transparent superhydrophobic films using cerium oxide particles with different aspect ratios

Takuya HIROSAWA¹, Toshihiro ISOBE¹, Sachiko MATSUSHITA¹ and Akira NAKAJIMA¹,‡

¹Department of Materials Science and Engineering, School of Materials and Chemical Technology, Tokyo Institute of Technology, 2-12-1 O-okayama, Meguro-ku, Tokyo 152-8552, Japan

Rod-like cerium dioxide (CeO₂) powder was prepared using hydrothermal processing. Then ceria thin films were prepared by coating of ethanol suspensions with a sublimation agent and a mixture of the rod-like ceria with commercial irregular nanoparticles onto glass substrates, followed by firing. Transparent superhydrophobic ceria films were obtained from samples with more than 50% rod-like ceria after coating hydrophobic fluoroalkyl silane on the surface. Both sliding angles and contact angles increased concomitantly with increase of the ratio of rod-like ceria. The trend of the contact angle increase was rationalized by the increase of the pore structure in the film. The sliding angle increase was accountable by consideration of the depth of droplet penetrating into the surface obtained by assuming normal pillar-array structure models calculated from the packing of particles with a high aspect ratio.

Key-words : Aspect ratio, Ceria, Particle, Rod, Superhydrophobic

1. Introduction

Surface roughness is well known to have a strong influence on the wettability of a hydrophobic solid surface. A surface with roughness possesses a greater surface area than a smooth one. The ratio of the actual area of a rough surface to the geometrically projected area is defined as roughness factor r. Wenzel modified Young’s equation to the following Eq. (1) by considering roughness factor effects on the surface energy ratio in Young’s equation.¹

\[
\cos \theta' = r \cos \theta
\]  

(1)

In that equation, \( \theta' \) represents the contact angle at a surface with roughness. In this equation, \( r \) is always greater than unity. Therefore, surface roughness enhances the hydrophobicity of solid when the contact angle of the smooth surface is higher than 90°. With increasing surface roughness, air intrudes into the hydrophobic solid–liquid interface. When a unit area of the surface has a wetted solid surface area fraction \( f \) with a water contact angle \( \theta \), the interface is assumed to comprise a mixture of solid and air. Cassie and Baxter expressed the contact angle of this state as the following Eq. (2) by assuming a 180° water contact angle for air.²⁻³

\[
\cos \theta' = f \cdot \cos \theta + (1 - f) \cdot \cos 180° \\
= f \cos \theta + (f - 1)
\]  

(2)

Wetting states for which water contact angles are higher than 150° are commonly designated as superhydrophobic. This state is not attainable merely by decreasing the surface energy.⁵ All superhydrophobic surfaces have been prepared by combining surface roughness with lowering of the surface energy.⁵⁻⁷ In a practical hydrophobic surface with roughness, both modes exist. Excellent water shedding property for a superhydrophobic surface is therefore attainable with an increasing contribution of Cassie’s mode because of the decrease of the practical contact area between a solid and liquid.⁸

Although surface roughness is necessary to obtain the superhydrophobic state, the provision of surface roughness implies the introduction of sources for light scattering. To maintain transparency in the visible wavelength range, surface roughness should be controlled precisely to be smaller than the visible wavelength range (preferably less than 100 nm). One effective approach to prepare a transparent superhydrophobic coating is the accumulation of nanoparticles. Various innovative processes have been developed to prepare transparent superhydrophobic coatings using this approach, such as control of coagulation and rheological behavior;⁹⁻¹⁰ addition of sublimation material,¹¹ and the mixture of different roughness dimensions.¹² Miwa et al. prepared various transparent highly hydrophobic coatings with roughness by adding a sublimation material [aluminum acetylacetonate (AACA)] to the suspension of spherical boehmite particles and ethanol. They investigated the relation among contact angles, sliding angles, and surface structure.⁸ Based on images

† Corresponding author: A. Nakajima; E-mail: anakajima@ceram.titech.ac.jp

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obtained using scanning electron microscopy (SEM) and atomic force microscopy, they modeled the coating surface with the sequence of the same conical roughness array. In their model, roughness factor \( r \) is assumed as a constant value. Then the solid–liquid contact area fraction \( f \) can be increased concomitantly with increasing droplet penetration depth into the surface with roughness. They described contact angles of the coatings by combining Wenzel’s equation as shown below.

\[
\cos \theta' = fr \cos \theta + f - 1
\]  

(3)

Many related studies have been conducted to date using spherical or irregular nanoparticles. Although particles with a high aspect ratio, such as rod-like particles, are apparently beneficial for the processing of superhydrophobic coatings because of the difficulty of dense packing, the experimental and theoretical studies of the effects of particles with a high aspect ratio are few. Moreover, an earlier study demonstrated that the mixture of roughness with different shapes and dimensions increases fractional dimensions and the resultant hydrophobicity. Mixture of a powder with different morphology and size might be an effective approach to attain a highly hydrophobic state. However, the effects of accumulated structures of rod-like particles on contact angles and sliding angles have not been investigated for a bimodal powder mixture.

Cerium dioxide (CeO\(_2\)) has been the subject of many studies investigating its use as a three-way catalyst for automobile exhaust gas treatment, as a chemical mechanical polishing agent, as a solid oxide fuel cell, and for ultraviolet (UV) filtration. Several recent reports have described that ceria exhibits antibacterial properties. Highly hydrophobic surfaces can suppress bacterial contact and bleeding. Therefore, high antibacterial activity is anticipated for superhydrophobic ceria coatings. Moreover, morphology control from spherical shape to rod-like structure is feasible for ceria through hydrothermal treatment. Given this background, we first prepared rod-like ceria particles for this study using hydrothermal processing. Subsequently, using the obtained particles or mixing them with commercial ceria nanoparticles, we tried to prepare transparent superhydrophobic ceria coatings following the processing method described in work by Miwa et al. Using these samples, we investigated the effects of the accumulated structure of rod-shaped ceria particles on contact angles and sliding angles in relation to the bimodal powder mixture.

2. Experimental

Rod-like ceria was prepared as described in a report of a study by Jiang et al. Cerium(III) nitrate hexahydrate [1.737 g, Ce(NO\(_3\))\(_2\)·6H\(_2\)O; Fujifilm Wako Pure Chemical Corp., Tokyo, Japan] was dissolved into 4M HNO\(_3\) (5 mL). Sodium hydroxide (10.24 g NaOH; Fujifilm Wako Pure Chemical Corp.) was also dissolved into distilled water (35 mL). This NaOH solution was added to the Ce(NO\(_3\))\(_2\) solution with stirring. Thereby, a suspension with white precipitate was obtained. The suspension was placed into a 50-mL Teflon reactor of a stainless steel autoclave, which was heated to 100 °C for 72 h; then it was allowed to cool. After washing several times with distilled water and ethanol, rod-like ceria was obtained. This sample was dispersed into ethanol (5.0 g). Then a rod-like ceria suspension was obtained by sonication (7 mL, 30 min., US CLEANER US-4R, 180 W; AS One Corp., Osaka, Japan) and by the subsequent addition of citric acid [0.005 g, C(OH)\((CH_2)COOH\)·2COOH; Fujiﬁlm Wako Pure Chemical Corp.]. The obtained rod-like ceria suspension or the mixture of the suspension with a commercial ceria sol with ceria nanoparticles (Needral B-10E; Taki Chemical Co. Ltd., Hyogo, Japan) was mixed with ethanol and AACA [Al(C\(_3\)H\(_7\)O\(_2\))\(_3\); Tokyo Kasei Kogyo Co. Ltd., Tokyo, Japan] by sonication (7 mL, 30 min.). The AACA was dissolved completely in ethanol. The ratio of solid CeO\(_2\):ethanol:AACA in the mixture was fixed as 0.025:5:0.025. The ratio between rod-like ceria and ceria sol was changed as 100:0:0; 50:50, 10:90, and 0:100. Hereinafter, sample names are stated as the percentage of rod-like particles, as Rod-X%. Although AACA was added to Rod-10%, Rod-50%, and Rod-100%, it was not added to Rod-0% because the sample was prepared for the evaluation of roughness effects of the ceria nanoparticles alone. The sonicated suspensions were coated onto Pyrex glass plates [50 mm (length) × 50 mm (width) × 1.0 mm (thickness)] by spin coating at 1000 rpm for 10 s. The coated glass plates were dried at room temperature for 30 s. During drying, the glass plates became opaque because of precipitation of AACA. Heating of the glass plates was conducted on a hot plate heated at 470 °C for 20 s. White smoke was emitted from the coated films because of the sublimation of AACA. After this coating and heating procedure was repeated five times, transparent ceria films were obtained on the glass plates. Finally, all samples were fired at 500 °C for 1 h in ambient air.

Vacuum ultraviolet (VUV) light was illuminated on the films using a Xe excimer lamp (172 nm wavelength; Ushio Inc., Tokyo, Japan) for 15 min at room temperature in air to remove organic compounds from the coating surface. The illumination intensity of the VUV light was 7 mW/cm\(^2\). Then fluoroalkyl silane [FAS9, CF\(_3\)(CF\(_2\))\(_3\)(CH\(_2\))\(_2\)-Si(OCH\(_3\))\(_3\); Tokyo Kasei Kogyo Co. Ltd., Tokyo, Japan] was coated onto the surface by heating the sample with 20 μL of fluoroalkyl silane in a Petri dish at 150 °C for 1.5 h. For comparison, a smooth fluoroalkyl silane coating was prepared by coating onto a Pyrex glass plate, hereinafter described simply as FAS9 coating. After the coatings were rinsed with toluene and water, they were dried.

The crystalline phase of the sample was evaluated using X-ray diffraction (XRD, XRD-6100; Shimadzu Corp., Tokyo, Japan) with Cu Kα radiation. The microstructure of the obtained samples was observed using SEM (JSM-7500F; JEOL Ltd., Tokyo, Japan) and a transmission electron microscope (TEM, JEM-2100F; JEOL Ltd., Tokyo, Japan). The transmittance of the samples in the visible wavelength range was measured using a UV–Vis spectro-
photometer (V-630; Jasco Corp., Tokyo, Japan) with a Pyrex glass plate used as a reference. The water contact angle and sliding angle of the obtained samples were measured using a commercial measurement system (Dropmaster 500; Kyowa Interface Science Co. Ltd., Saitama, Japan). Five contact angles were measured for a 3 μL water droplet using sessile drop method. Sliding angles were measured at five points for a 10 μL droplet. Then they were averaged.

3. Results and discussion

3.1 Structure and hydrophobicity

Figure 1 displays SEM and TEM micrographs of the starting ceria particles. The morphology of ceria particles prepared through hydrothermal treatment was rod-like. That of commercial ceria sol was irregular. The primary particle size of the ceria sol was approx. 5 nm. The particles form aggregates with size of approx. 20 nm. Figure 2 presents XRD patterns of these samples. All peaks in the XRD patterns of the obtained samples were identified as CeO$_2$ (JCPDS 34-0394). All these results correspond to work by Jiang et al.\textsuperscript{22)}

Figure 3 portrays SEM micrographs of the obtained thin film samples. The microstructure changed according to the mixing ratio of starting ceria sources. However, no extremely heterogeneous (segregated) portion was observed in the structure. In Rod-50%, irregular ceria nanoparticles were accumulated on the surface of rod-like ceria. Miwa et al. reported that films prepared from a suspension with AACA have many 100–200 nm pores because of the sublimation of AACA, although such voids were not observed on the film surface for the suspension without AACA.\textsuperscript{9,12)} Similar pores were observed in Rod-10%, but were not so remarkable in Rod-0%, which is formed from the suspension without AACA. With increase of the rod-like ceria ratio (Rod-50% and Rod-100%), pores originated from the loose packing of rod-like ceria seem to become more remarkable than those created by the sublimation of AACA. The average length and diameter for the rod-like ceria calculated from the 290 particles were, respectively, 235.6 (average) ± 11.9 (standard deviation) nm and 21.6 ± 0.8 nm. Data used for this calculation were collected from four SEM images (magnification: ×50,000). The value of the average aspect ratio of the particles was calculated as approx. 11. The film thickness for Rod-100%, as measured from 50 points, was 916 ± 33 nm (Fig. 4). The average thicknesses for Rod-50%, Rod-10%, and Rod-0% were, respectively, 946 ± 23, 632 ± 24, and 289 ± 4 nm.

The visible light transmittance of samples is depicted in Fig. 5. Rod-10%, Rod-50%, and Rod-100% possess more than 80% transmittance in the visible wavelength range. The film sample transmittance decreased concomitantly with increase of the concentration ratio of the rod-like ceria, which is attributable to the increase of light scattering by the large pores from the packing of the particles with a large aspect ratio.

Figure 6 displays contact angles and sliding angles of the obtained ceria films. Error bars show the standard deviation. The contact angle of Rod-0% was increased approx. 10 degrees from FAS9 coating, probably because of fine
roughness given by irregular ceria nanoparticles. Both contact angles and sliding angles were increased concomitantly with the increase of the concentration ratio of rod-like ceria in the film. Packing of the particles with a high aspect ratio is looser than that of irregular ceria nanoparticles, which is beneficial for air intrusion in the structure and which engenders the increase of contact angles. This trend corresponds to the result of transmittance in the visible wavelength range. This finding implies that the film surface fractal dimension was increased appropriately by the particle mixture in Rod-50% and that the resultant contact angle was increased to the same level of Rod-100%. As presented in this study, Rod-50% and Rod-100% became transparent superhydrophobic films. However, the sliding angle increase that occurred concomitantly with the increase of the contact angle showed a reverse trend to that reported by Miwa et al., which might be responsible for the use of particles with a high aspect ratio. This result suggests that different modeling is necessary for samples with high concentrations of rod-like ceria such as Rod-50% and Rod-100%. Therefore, we tried modeling of the film structure with consideration of the packing of particles with a high aspect ratio.

3.2 Modeling of hydrophobicity of the film structure with rod-like ceria

For this study, we assume that both Wenzel’s mode and Cassie’s mode contribute simultaneously to surface hydrophobicity. As described in the Introduction, this assumption is valid for various superhydrophobic surfaces. Moreover, we assume that the entire film surface is coated
homogeneously with fluoroalkyl silane used in this study. Therefore, we can describe contact angles on the surface as Eq. (3). Furthermore, the roughness size is assumed to be much smaller than the droplet size. Under this assumption, we can infer that the bottom part of the droplet penetrating into the film surface is flat and parallel to the substrate. The droplets are of millimeter scale. Therefore, this assumption is also valid for the system examined in this study.

Random packing structures of particles with a high aspect ratio were reported by Wouterse et al. They used mechanical contraction and molecular dynamics method for their simulation. Simply stated, they set a certain number of the particles in the space and elongated their shape while retaining its diameter. When the elongated particles were impinged, the particle was moved to a different coordinate by force using a Newtonian equation. This elongation, movement, and rotation were repeated until the minimum energy state in the system was reached. According to their simulation result, the volume fraction of solids ($\phi$) in the closest packing of particles for which the aspect ratio was 11 under the random packing condition was approximately 0.43. The packing state in the film is expected to depend on the capillary force of the solvent in the coating suspension during drying. Although AACA precipitates during drying after coating the suspension, the packing inhibition effect for particles by AACA does not seem remarkable in Rod-50% and Rod-100% from SEM observation. Therefore, we assumed that the Rod-100% structure is equivalent to the closest packing of particles with aspect ratio of 11 under the random packing condition. By this structure, one can assume that the solid area ratio at the solid–water interface is constant even if the penetration depth of the droplet into the film differs, except near the topmost portion of the film (see Fig. 7). This property is equivalent to that for the normal pillar-array structure, although the morphology differs. Therefore, we tried to convert the film structure of Rod-100% into an equivalent virtual surface with the normal pillar-array structure.

Particle number ($N$), which Wouterse et al. used in their simulation was 2048. Using this number and the practical average length ($L = 235.56$ nm) and diameter ($D = 21.60$ nm) of the rod-like ceria, one can calculate the packing volume ($V$), the number density of the particles in the system ($\rho$), and the entire surface area of the particle ($S_{\text{surface}}$) from the following equations.

$$V = \frac{\pi LD^2}{4\phi} \cdot N$$  \hspace{1cm} (4)

$$\rho = \frac{N}{V}$$  \hspace{1cm} (5)

$$S_{\text{surface}} = N \cdot \left( \frac{\pi D^2}{4} + \pi DL \right)$$  \hspace{1cm} (6)

A system of 1000 nm (length) × 1000 nm (width) × 900 nm (height) is considered. The system volume is $V' = 9.0 \times 10^3$ nm$^3$. The solid–liquid contact area fraction is an important parameter of the wetting of the solid surface.
with roughness. Therefore, we set the total surface area of the normal pillar-array structure equal to the entire surface area of the particles in Rod-100%. Moreover, the solid part occupies 0.43 of the system volume. Under these conditions, we calculated the number \( n \) and the size \( a \) of the rods in the normal pillar-array structure from the following Eqs. (7) and (8). In this calculation, we fixed the pillar shape as a rectangle for which the cross-cut section parallel to substrate is square, and for which the pillar height is 900 nm.

\[
\begin{align*}
    n \cdot a^2h &= V', \Phi \\
    n \cdot (4ah + a^2) &= S_{\text{surface}}
\end{align*}
\]  

The calculated values of \( a \) and \( n \) were, respectively, 27.34 nm and 564 (Fig. 7). This \( a \) value was close to the cross-cut diameter of the average rod-like ceria. Using these values and Eq. (3), one can calculate the penetration depth of the droplet into the normal pillar-array structure. Because of the roughness morphology, \( f \) is expected to be equal to \( \Phi \) (0.43) in this structure. Also, \( r \) increases concomitantly with increasing penetration depth of the droplet into the structure. The relation for the constant and parameter between \( r \) and \( f \) was inverse of that referred by Miwa et al.\(^{27}\) The value of the calculated penetration depth for Rod-100% obtained by substituting the average contact angle of FAS9 coating (105°) to \( \theta \), the practically measured contact angle (154°) to \( \theta' \) in Eq. (3), was 13.4 nm.

The packing structure and the solid volume fraction in the case of closest packing for the mixture of the particles with different aspect ratios such as the case of Rod-50% have been calculated as reported by Kyrylyuk et al.\(^{27}\) using an approach similar to that reported by Wouterse et al. In the case of a 1:1 powder mixture between spherical particles and elongated ones with aspect ratio of 11, the solid volume fraction in the case of closest packing is reported as 0.60. Using the same system (1000 nm \( \times \) 1000 nm \( \times \) 900 nm) as Rod-100%, we modeled a thicker normal pillar-array structure from the following Eqs. (7) and (8). In this calculation, we fixed the pillar shape as a rectangle for which the cross-cut section parallel to substrate is square, and for which the pillar height is 900 nm.

Water droplets are known to slide down a hydrophobic solid surface by a caterpillar-like rolling motion with or without slippage at the solid–liquid boundary.\(^{29-31}\) A high contribution of slipping mode is reported on superhydrophobic surfaces.\(^{29}\) The large penetration depth implies a large moving resistance against slipping motion. The surfaces of Rod-50% and Rod-100% are assumed, respectively, to be the same as those of Rod-0% and FAS9. The sliding angle on Rod-0% is less than that on FAS9 (Fig. 9). Despite a large apparent solid–liquid contact area ratio, these results might contribute to the smaller sliding angle for Rod-50% than that for Rod-100%. It is noteworthy that calculations presented by Kyrylyuk et al. were conducted by assuming the same size (diameter) between spherical particles and rod-like ones. In this study, the rod diameter is almost equivalent to the size of aggregates of irregular ceria nanoparticles.

However, calculation of the penetration depth for Rod-10% was infeasible. In fact, the study by Kyrylyuk et al. was not conducted with this ratio. The effect of packing inhibition for particles by AACA is inferred from SEM observations of Rod-10%, which means that the closest packing structure is difficult to assume. Moreover, because of the small concentration ratio of rod-like ceria, the Rod-10% microstructure is similar to that of films prepared by Miwa et al. Therefore, the relation for constants and parameters between \( r \) and \( f \) might be the same as that in a study described by Miwa et al. If so, then the definitions for \( r \) and \( f \) in the structure are also different from the models for Rod-50% and Rod-100%. Consequently, the normal pillar-array structure might not be applicable to this sample. This model is expected to be applicable to a film.
with a high concentration ratio of rod-like particles. Detailed investigations of the applicable range of this model are expected to be addressed in future works. All these discussions are based on the homogeneous coating of fluorooalkyl silane onto both rod-like ceria and irregular ceria nanoparticles. Unfortunately, it is infeasible to confirm the practical coating state on these particles.

These results demonstrate the value of using particles with a high aspect ratio. They produce a superhydrophobic state with high contact angles and sliding angles by increasing pore space in the coating and the penetration depth of the droplets into the coating surface. Such surfaces are important for natural organisms such as insects in dry areas to carry or obtain water droplets from their living environment.32),33) This approach might be effective for the processing of highly hydrophobic surfaces using cerium oxide particles with different aspect ratios.

4. Summary

For this study, we prepared rod-like ceria through hydrothermal processing. Then transparent ceria films were prepared by mixing the rod-like ceria with irregular ceria nanoparticles and subsequent spin coating of the powder suspensions with AACA. Both contact angles and sliding angles increased concomitantly with the increase of the concentration ratio of rod-like ceria in the films after FAS9 coating. The contact angle increase trend was elucidated by the increase of the pore structure in the film. The sliding angle increase was explained by modeling of the equivalent normal pillar-like structure from the packing of the particles with a certain aspect ratio and the resultant penetration depth difference of the droplet into the film structure. Using particles with a high aspect ratio is expected to be beneficial for the processing of highly hydrophobic surfaces for water harvesting.

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