Journal of the Ceramic Society of Japan

2020
1. Introduction

Wettability of a solid surface is affected by its surface roughness and morphology. When roughness is created on a hydrophobic solid surface, the surface hydrophobicity is enhanced by the increase of the solid-water interface (Wenzel’s mode) and/or air intrusion at the solid–liquid interface (Cassie’s mode). A surface or a state in which the water contact angle is greater than 150° is commonly designated as superhydrophobic. The Cassie’s mode contribution is commonly greater than that of Wenzel’s mode for a superhydrophobic surface with excellent water shedding property because the practical contact area between solid and water is decreased. The dominant mechanism of hydrophobicity enhancement by imparting surface roughness generally switches from Wenzel’s mode to Cassie’s mode with increasing roughness. Although several revisions have been proposed on the equations for these two modes, they are commonly valid as an initial approximation of the wettability of hydrophobic solid surface with roughness.

When Wenzel’s mode is combined with Cassie’s mode, or when several hydrophilic points exist on the superhydrophobic surface, the water droplet on the surface is pinned at the position. These surfaces exhibit poor water shedding properties, and are often designated as a petal surface or gecko surface, which are phenomena named after the surfaces on which they were discovered. Such surfaces are important for natural creatures such as insects in dry areas to carry or obtain water droplets from the living environment.

A device for harvesting water from phenomena in living environments such as fog or dew condensation is commonly designated as a water harvester. Various systems have been proposed up to the present day by designing the morphology and wettability of the solid surface using biomimetic engineering. The water harvesting process involves (i) dew condensation, (ii) droplet growth, and (iii) droplet removal from the surface. Rapid dew condensation and growth, retention of large and numerous water droplets, and efficient droplet removal are the requirements for this system. Recent focus on this field is on fabricating hybrid surface with heterogenous wettability such as hydrophobic and hydrophilic. For the hydrophobic part, the surface with poor water shedding property can retain many large droplets on the surface. The water droplet surfaces possess good affinity with water vapor or fog particles. Therefore, the surface like a petal surface or gecko surface might be a candidate material for this use like insects in dry areas.

Very recently, we prepared zinc oxide (ZnO) nanorods (ZnO-NRs) with nanoscale roughness on the topmost surface of the rods through two-step hydrothermal
treatment. Hexagonal pillar-like ZnO-NRs with $c$-axis orientation were prepared from first-step hydrothermal treatment, hereinafter denoted as single-roughness ZnO-NRs. Nanoscale roughness was created by etching of the surface with alkaline chemicals in the precursor solution during the subsequent second-step hydrothermal treatment, hereinafter denoted as double-roughness ZnO-NRs. These samples exhibit a highly hydrophobic state after the coating of a hydrophilic silane. Single-roughness ZnO-NRs become hydrophobic by Cassie’s mode and thereby exhibit small sliding angles, whereas double-roughness ZnO-NRs became petal surfaces after the silane coating, which suggests Wenzel's mode by nanoscale roughness. This material might be applicable for use in a water-harvesting device, but its practical performance has not been evaluated. Given this background, we investigated the fog-harvesting performance of these ZnO-NRs in this study. Samples were prepared according to a description of an earlier study. Although we should set a hydrophilic part in this material as a water harvester, we evaluated the performance of this material by itself in this study as a primary research.

2. Experimental

2.1 Sample preparation and characterization
Monoethanolamine (MEA, NH$_2$CH$_2$CH$_2$OH; Fujifilm- Wako Pure Chemical Co., Tokyo, Japan) and zinc acetate dihydrate [Zn(CH$_3$COO)$_2$H$_2$O; Fujifilm-Wako] were dissolved respectively into 2-methoxyethanol (CH$_3$OCH$_2$-CH$_2$OH; Fujifilm-Wako) by 0.75 M. After reflux of the solution at 60 °C for 30 min, a solution of ZnO sol was prepared. The sol solution was coated onto a Si substrate [n-type Si (100); Aki Corp., Miyagi, Japan] by spin coating at 3000 rpm for 50 s. It was heated at 300 °C for 1 h. For this study, we applied this treatment only to the ZnO-NRs obtained from the conditions of $x = 12.5$ and 100 mM. After washing and drying, we were able to obtain ZnO nanorod samples with nanoscale roughness on their topmost surface. Then fluoroalkyl silane [CF$_3$(CF$_2$)$_2$(CH$_2$)$_2$Si(OCH$_3$)$_3$; FAS9; Tokyo Kasei Kogyo Co. Ltd., Tokyo, Japan] was coated onto the surface using chemical vapor deposition by heating the sample with 20 µL of FAS9 in a Petri dish at 155 °C for 1 h. For comparison, a smooth FAS9 coating was prepared by coating it onto a mirror polished Si substrate, hereinafter described simply as FAS9 coating. For this study, we designated the single-roughness ZnO-NRs obtained from $x = 25$ and 75 mM, and double-roughness ZnO-NRs obtained from $x = 12.5$ and 100 mM, respectively, as Rod-S, Rod-L, Rod-S-d, and Rod-L-d.

Surface morphology was observed using a scanning electron microscope (SEM) (JSM-7500F; JEOL Ltd., Tokyo, Japan). The contact angles were measured using a commercial contact-angle meter (Dropmaster DM-500; Kyowa Interface Science Co. Ltd., Japan) and 3.0 µL distilled water droplets using the sessile drop method. Sliding angles of a 1–30 µL distilled water droplet on the sample were measured using an automatic measurement system (SA-20; Kyowa Interface Science Co. Ltd.). This value was evaluated for five points, and then averaged.

2.2 Evaluation of fog-harvesting performance
For this study, we evaluated the water harvesting performance of the samples by exposing them in the fog stream under constant temperature and relative humidity, and with subsequent measurement of the entire harvested water amount. The yield of fog-harvesting in a unit time is expected to depend on the area ratio of water droplets adhered on the surface. Therefore, we have measured not only the entire harvested water amount from the samples in a certain time but also the area ratio of water droplets and corresponding adhered water amount on the sample surfaces, simultaneously. A schematic illustration of the experimental setup for the evaluation of fog-harvesting performance is presented in Fig. 1. The temperature and relative humidity inside of the thermostatic chamber were controlled using a commercial humidifier at a constant rate. After a certain period, photographs were taken vertically against sample surface. The obtained images were binarized into black (sample surface) and white (water droplets) respectively using Image-J software. Then the area ratio of water droplets that had adhered on the surface was calculated. The water droplets harvested in the water tray was also measured.
(IW222; Yamato Scientific Co., Ltd., Tokyo, Japan) were controlled to 25 °C and 90% RH. Fog was introduced into the chamber from a commercial humidifier (AHD-017; Apix International Co. Ltd., Osaka, Japan) at a constant rate (300 mL/h).

First, we measured the system background. The mass of a water tray \( W_{\text{tray-background, before}} \). The tray is a Petri dish; approx. 8.5 cm diameter) was measured and was set at a certain position (described below) in the chamber. Then fog was introduced into the chamber for 2–120 min in a controlled atmosphere (25 °C, 90% RH). After this period, the mass of the water tray with water droplets \( W_{\text{tray-background, after}} \) was measured again. The background value was obtained by subtracting \( W_{\text{tray-background, before}} \) from \( W_{\text{tray-background, after}} \) (\( W_{\text{tray-background, before}} \) was obtained again. The background value was obtained by subtracting \( W_{\text{tray-background, before}} \) from \( W_{\text{tray-background, after}} \).

As the next step, we set the sample and the water tray in the chamber after measuring their respective masses: \( W_{\text{sample, before}} \) and \( W_{\text{tray, before}} \). The sample was set vertically. The tray was set below the sample, with the distance between the sample bottom and the tray surface as approx. 7 cm. The distance between the nozzle tip of the humidifier and the sample surface was 10 cm. The sample area was set as a constant value: 12 cm².

Then a fog stream was introduced perpendicularly to the sample surface under atmospheric control (25 °C, 90% RH) for 2–120 min. After a certain period, photographs of the surface were taken. The mass of the sample with water droplets \( W_{\text{sample, after}} \) and that of the tray \( W_{\text{tray, after}} \) were measured. The image of the sample surface was binarized into black (sample surface) and white (water droplets) respectively using Image-J software. Then the area ratio of water droplets that had adhered on the surface was calculated. The corresponding adhered water amount on the sample surfaces was obtained by subtracting \( W_{\text{sample, before}} \) from \( W_{\text{sample, after}} \). The practical water amount harvested from the samples \( W \) was obtained from the following equation.

\[
W = (W_{\text{sample, after}} - W_{\text{sample, before}}) + (W_{\text{tray, after}} - W_{\text{tray, before}}) - W_{\text{tray-background}}
\]  

(1)

As shown later [Eq. (11)], the relation between \( W \) and exposure time \( t \) becomes linear. Therefore, we can discuss the yield of fog-harvesting in a unit time from the slope of this plot.

3. Results and discussion

Figure 2 displays SEM micrographs of the obtained samples. The pillar-like structure of ZnO-NRs was obtained from the first hydrothermal treatment. After the second hydrothermal treatment using DAP, nanoscale (approx. 10 nm) roughness was imparted onto the topmost surface (10001) of ZnO-NRs. The ZnO-NR film thickness was approx. 800 nm. This value was almost constant for all samples (Fig. S1-1 in Supporting Information). As demonstrated from an earlier study, the rod size depends on the precursor solution concentration. It seems like the diameter of ZnO nanorods grew after secondary hydrothermal treatment (see Rod-S and Rod-S-d). Although the reason is unclear, a plausible explanation is the precipitation of the dissolving species etched from the topmost surface onto the side wall of the ZnO-NRs.

After binarizing top-viewed SEM micrographs of the samples using Image-J software, we obtained the topmost surface area fraction from the black and white pixel ratios for the ZnO-NRs. The obtained ratios and the contact angles of the surface are depicted in Fig. 3. Presumably, this solid area corresponds to the practical solid–liquid contact area because the structures after the first hydrothermal treatment become hydrophobic by Cassie’s mode. The contact angle gradually decreases concomitantly with increasing solid–liquid contact area, except for Rod-L-d. The area ratio depicted in Fig. 3 does not incorporate the effect of nanoscale roughness imparted by the second hydrothermal treatment. The high contact angle of Rod-L-d should be given by the contribution of Wenzel’s mode from the nanoscale roughness on the topmost surface of the sample. Although the same discussion is applicable to Rod-S-d, the contribution of Wenzel’s mode from the nanoscale roughness was not remarkable between Rod-S and Rod-S-d. It is deduced that the effect of the growth of rod diameter and resultant increase of solid/water contact area ratio after the second-step hydrothermal treatment.
would be more significant than the effect of the contribution from the nanoscale roughness on the topmost surface of Rod-S-d.

The sliding angles for the droplet with different volume are presented in Fig. 4. The single-roughness ZnO-NRs (Rod-S and Rod-L) exhibit smaller sliding angles than the FAS9 coating. The Rod-S possesses a higher contact angle (Rod-S and Rod-L) exhibit smaller sliding angles than the Rod-L. These trends can be rationalized by the contribution of Cassie’s mode. The double-roughness ZnO-NRs exhibit higher sliding angles than the single-roughness ZnO-NRs, which suggests that the droplet adhesion capability was increased by the nanoscale roughness. This trend can also be rationalized by the contribution of Wenzel’s mode from the nanoscale roughness. Almost all these trends are the same as those reported in our earlier study.33)

The yield of fog-harvesting \( [E (g/s/m^2)] \) can be calculated as the following equation:

\[
E = \frac{W}{t \cdot S}
\]  

(2)

where \( t \) represents time, and \( S \) denotes the sample area (12 cm\(^2\)). The fog volume \( (V_{\text{fog}}) \) emitted from the humidifier is calculable by assuming the average fog size as 10 \( \mu \text{m} \), \( 5.2 \times 10^{-16} \text{m}^3 \). The relation between the number \( (N) \) and the volume \( (L) \) of fog reached on the sample surface in a unit time is \( L = N \times V_{\text{fog}} \). When the area fraction of droplet in the sample is “\( a \)”, that of the exposed solid area should be “1 − \( a \)”. Here we set the possibility of fog adhesion on the solid surface and that on the adhered droplet as \( P_{\text{sample}} \) and \( P_{\text{water}} \). We assume they have single value over time. Consequently, we can describe the adhered fog volume \( (\Delta W) \) in a short time scale \( (\Delta t) \) as presented below.

\[
\Delta W = NV_{\text{fog}} \Delta t \cdot [1 - a(t)]S \cdot P_{\text{sample}} + NV_{\text{fog}} \Delta t \cdot \cos \theta(t)S \cdot P_{\text{water}} \\
= LS[(1 - a(t))P_{\text{sample}} + a(t)kP_{\text{water}}] \Delta t
\]  

(3)

In this equation, the first term \( NV_{\text{fog}} \Delta t \cdot [1 - a(t)] S \cdot P_{\text{sample}} \) represents the volume of fog adhered on the sample surface. The second term \( NV_{\text{fog}} \Delta t \cdot \cos \theta(t) S \cdot P_{\text{water}} \) denotes the volume of fog absorbed into the droplets on the sample surface. Because the droplet surface is curved three-dimensionally, the surface area value differs from \( aS \). Therefore, we introduced a correction factor \( (k) \) in Eq. (3). This factor is obtainable from the contact angle of water droplet on the sample surface as shown below (Fig. 5).

\[
k = 2/(1 + \cos \theta) \quad (\theta > 90^\circ)
\]

(4)

The integration of Eq. (3) provides the following Eq. (5).

\[
W = LS[P_{\text{sample}} + (a(t)kP_{\text{water}} - P_{\text{sample}})] \Delta t
\]  

(5)

Ascertaining the practical value of \( W \) requires clarification of \( A(t) \). This \( A(t) \) is the integration of droplet area fraction \( [a(t)] \) over time \( t \). At the initial state, \( a(0) = 0 \). When fog is introduced continuously to the chamber at a certain rate, \( a(t) \) is expected to be saturated to a certain value under the repetition of dew condensation and droplet sliding. This value can be set as \( a(\infty) \). It is deduced that \( a(t) \) increases rapidly in the early stage of fog-harvesting. When a certain amount of fog is harvested on the surface, it would gradually increase. Therefore, we assumed the following function as \( a(t) \) in this study.

\[
2(1 - \cos \theta) \cdot S_{\text{droplet}}
\]

\[
2/(1 + \cos \theta) \cdot S_{\text{droplet}}
\]
\[ a(t) = -\frac{r}{t+p} + a(\infty) \quad (6) \]

\[ a(0) = 0 \text{ gives } p = -\frac{r}{a(\infty)}, \text{ and} \]

\[ a'(0) = \frac{r}{(0-p)^2} = \frac{[a(\infty)]^2}{a'(0)} \text{ gives } r = \frac{[a(\infty)]^2}{a'(0)} \]

Therefore, we can describe \( a(t) \) as the following Eq. (7),

\[ a(t) = -\frac{[a(\infty)]^2}{a'(0)t + a(\infty)} + a(\infty) \quad (7) \]

\( a'(0) \) is the initial slope of \( a(t) \) against time \( t \). This value is calculable from \( \Delta W \) at \( t = 0 \). The \( \Delta W \) is described as Eq. (8) by substituting \( a(0) = 0 \) to Eq. (3). Consequently, \( a'(0) \) is described as Eq. (9). In this equation, \( S_{\text{fog}} \) means the occupied area for one fog droplet on the sample surface by adhesion.

\[ \Delta W = NV_{\text{fog}}SP_{\text{sample}}\Delta t \quad (8) \]

\[ \Delta W = \frac{V_{\text{fog}}\Delta t}{S} \times S_{\text{fog}} \]

\[ a'(0) = \frac{[a(\infty)]^2}{a'(0)t + a(\infty)} = NS_{\text{fog}}P_{\text{sample}} \quad (9) \]

The practical value of \( S_{\text{fog}} \) is calculable from the assumed fog droplet size and the contact angle of the solid. Integrating Eq. (7) provides the following Eq. (10) as \( A(t) \).

\[ A(t) = -\frac{[a(\infty)]^2}{a'(0)} \left[ \frac{a'(0)}{a(\infty)} t + 1 \right] + a(\infty)t \quad (10) \]

Then, substituting Eq. (10) to Eq. (5) gives \( W \) as shown below.

\[ W = LS \left\{ P(\infty)_{\text{ave}} - \frac{[a(\infty)]^2}{a'(0)} (kP_{\text{water}} - P_{\text{sample}}) \right\} \times \log \left[ \frac{a'(0)}{a(\infty)} t + 1 \right] \]

\[ P(\infty)_{\text{ave}} = [a(\infty)kP_{\text{water}} + [1 - a(\infty)]P_{\text{sample}}] \quad (11) \]

In this equation, \( S \) is a constant. \( k \) and \( S_{\text{fog}} \) are calculable from the contact angle and the fog droplet size. Also, \( a(\infty) \) and \( W \) are obtainable from the experiment. For this study, \( P_{\text{water}} \) is assumed as unity. We measured \( \Delta W \) using a wetted highly hydrophilic glass plate to obtain the \( L \) value. It is assumable that \( P_{\text{sample}} = 0, P_{\text{water}} = 1, k = 1, \) and \( a = 1 \) for the wetted highly hydrophilic glass plate. Consequently, \( \Delta W \) for this sample is equal to \( L \times \Delta t \times S \) from Eq. (3). Then we could be able to obtain the \( L \) value as \( 1.1 \times 10^{-3} \text{mL/min/cm}^2 \). Therefore, the only unknown term is \( P_{\text{sample}} \). The value of \( W \) given by Eq. (11) is a function of \( a(\infty) \). It can be regarded as the sum of droplet on the sample surface and the water in the tray.

Differentiation of Eq. (11) and subsequent divergence of time to infinity \((t \to \infty)\) give \( \text{LSP}_{\text{ave}} \). This is equivalent to the slope of the first term in Eq. (11). It represents the saturated fog adhesion rate. Consequently, the first term in Eq. (11) [\( P(\infty)_{\text{ave}} \)] affects the water harvesting amount after the saturation of fog adhesion. Also, differentiation of Eq. (11) and subsequent time approaching to zero \((t \to 0)\) give \( \text{LSP}_{\text{sample}} \). It represents the initial fog adhesion rate on the sample surface. Therefore, the second term \(- \left( [a(\infty)]^2/a'(0) \right) (kP_{\text{water}} - P_{\text{sample}}) \log \left[ \frac{a'(0)}{a(\infty)} t + 1 \right] \) relates the water harvesting amount in the early stage of fog adhesion.

Figure 6 displays practical images of the sample surface during evaluation of the fog-harvesting performance. The images are binarized into black (solid surface) and white (droplet part) regions. The Rod-S, a single-roughness ZnO-NR, is a superhydrophobic surface. Only very fine droplets remained on the surface during the experiment. Because of the small sliding angles, this surface can retain only small droplets. The droplet sliding initiates in 2–5 min. The Rod-L, another single-roughness ZnO-NR, retained larger droplets on the surface than Rod-S. The sliding angles of Rod-L are greater than those of Rod-S because of the higher solid–liquid contact area ratio. However, even for Rod-L, droplet sliding was observed in 5 min.

The double-roughness ZnO-NRs retained large droplets on their surface by their nanoscale roughness and the resultant contribution of Wenzel’s mode. Droplet sliding was observed for all samples in 5–10 min. The surface state was apparently saturated at around 20 min. The area ratios of water droplets at each time for these samples are presented in Fig. 7. The area ratio increased rapidly in the initial stage, and saturated in approximately 20 min. The saturated value of the area ratio of water droplets for FAS9 coating was 0.424. The single-roughness ZnO-NRs exhibited smaller values than FAS9 coating (0.196 for Rod-S, and 0.305 for Rod-L). The values for the double-roughness ZnO-NRs were greater than those for the single-roughness ZnO-NRs (0.398 for Rod-S-d, and 0.487 for Rod-L-d) because of the adhesion of large droplets on the surface by Wenzel’s mode. Another plausible explanation is the heterogeneous coating of FAS9 on the topmost surface with nanoscale roughness. The roughness scale
The FAS9 molecule size is 0.5–1 nm. If FAS9 was coated onto the surface heterogeneously, then the hydrophilic point remains, consequently becoming an adhesion spot for water droplets. Confirmation of the homogeneity of FAS9 on this surface is difficult. That point is therefore left as a subject to be addressed in future works.

Figures 8 and 9 respectively present adhered water amounts on the sample surfaces and the entire harvested water amounts from the samples (the sum of droplet on the
surface and the water in the tray, namely $W$). The required time for the saturation of adhered water amount on the sample surfaces is almost equivalent (20–30 min) to that of the area ratios of water droplets on FAS9 and the single-roughness ZnO-NRs. Compared to FAS9, the adhered water amount (Fig. 8) decreases concomitantly with increasing contact angles in the case of the single-roughness ZnO-NRs. This decreasing adhesion is expected to be attributable to the small solid–liquid contact area ratio and the resultant decrease of sliding angles. The black lines for FAS9 and the single-roughness ZnO-NRs in Fig. 9 show fitting using Eq. (11), respectively assuming $P_{\text{sample}} = 0.9$, 0.95 and 0.85 for FAS9, Rod-S, and Rod-L. The practical $W$ values in the fog-harvesting experiment for these three samples can be fitted by Eq. (11) using almost equivalent $P_{\text{sample}}$ values. This result implies that the entire water amount harvested from these ZnO-NRs was almost equivalent to that from FAS9 under these experimental conditions. It is noteworthy that the contact angle contributes to the overall performance as well as sliding angle in the fog-harvesting process. A high contact angle is beneficial for fog-harvesting because the entire droplet surface area is large. FAS9 and Rod-L exhibited high droplet area fractions (Fig. 7), but their contact angles are low (Fig. 3). Rod-S exhibited a small droplet area fraction but its contact angle is high. Similar fog-harvesting performance among FAS9, Rod-S, and Rod-L might be attributable from their contact angle difference. Differences might be more conspicuous when the sample is tilted.

Compared to these samples, the required time for the saturation of adhered water amount on the sample surfaces was longer (approx. 60 min) for the double-roughness ZnO-NRs. That finding suggests that a certain time is required for the equilibrium droplet size distribution during repetition of dew condensation and droplet sliding on the surface of the double-roughness ZnO-NRs. For double-roughness ZnO-NRs, the increase of water adhesion capability leads to a remarkable increase of the adhered water amount. Because of the high contact angle, the droplet layer thicknesses on these ZnO-NRs are also greater than that on FAS9. In the case of these ZnO-NRs, the practical $W$ values in the fog-harvesting experiment were large and could not be fitted by Eq. (11), even when $P_{\text{sample}}$ was assumed as 1 (see black line in Fig. 9). A plausible explanation of this result is the contribution of droplet overlapping as pictured in Fig. 10. Because of high water adhesion capability and the contact angle, the water droplet overlap increases, which might lead to a difference in $a(t)$ and resultant greater $W$ values than the amount expected from theoretical calculation. Although the sliding angle on Rod-L-d was greater than that on Rod-S-d, the entire water amount harvested from Rod-L-d was smaller than that from Rod-S-d. Similarly to findings obtained for FAS9, Rod-S, and Rod-L, a high adhered water amount on Rod S-d might be attributable to its high contact angle.

When the same fog-harvesting experiment was conducted using a pristine hydrophilic Si substrate, the area ratios of water droplets saturated to 1 and both adhered water amount on the sample surface and the entire harvested water amount from the sample were much smaller than those of other samples, which suggests advantages of hydrophobicity in the use of water-harvesting (Fig. SI-2 in Supporting Information). This relative advantage is probably attributable to the difference in the practical water-air interface area amount.

For the collection efficiency of a surface, both the drop collection and the drop transportation are crucial. Sometimes, lower sliding angle becomes more beneficial for fog-harvesting. It depends on the entire system and surrounding environmental condition. This work is a primary research on the ZnO-NRs combined with nanoscale roughness for the design of a water harvester, and practical system assembly using this material should also be addressed in future works.

4. Summary

For this study, we prepared single-roughness ZnO-NRs and double-roughness ZnO-NRs using one-step or two-step hydrothermal treatment. All these samples were highly hydrophobic after the coating of FAS9. The sliding angles for the double-roughness ZnO-NRs were greater than those for the single-roughness ZnO-NRs. The entire
harvested water amount for FAS9 and the single-roughness ZnO-NRs can be fitted by theoretical calculation. The entire harvested water amount for the double-roughness ZnO-NRs was greater than that for FAS9 and the single-roughness ZnO-NRs. It could not be fitted by the theoretical calculation, suggesting the contribution of droplet overlapping.

Acknowledgments The authors are grateful to the staff of the Center of Advanced Materials Analysis (CAMA) at the Tokyo Institute of Technology for various characterizations and for helpful discussion related to this study. The authors also thank Prof. Munetoshi Sakai at Ibaraki University for helpful discussion related to this study. The authors acknowledge the Center of Advanced Materials Analysis (CAMA) at the Tokyo Institute of Technology for various characterizations of the Center of Advanced Materials Analysis (CAMA) at the Ministry of Education, Culture, Sports, Science, and Technology of Japan (18K19125).

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