Utilization of La_2O_3 as a Support of Ga_2O_3 Photocatalyst to Enhance Activity on CO_2 Reduction with Water

Ryota Ito,^{a,†} Masato Akatsuka,^a Muneaki Yamamoto,^b Tetsuo Tanabe,^b Tomoko Yoshida^{b,‡}

^a Applied Chemistry and Bioengineering, Graduate School of Engineering, Osaka City University, 3-3-138 Sugimoto, Sumiyoshi-ku, Osaka, 558-8585, Japan

^b Advanced Research Institute for Natural Science and Technology, Osaka City University, 3-3-138 Sugimoto, Sumiyoshi-ku, Osaka, 558-8585, Japan

[†] Corresponding author: m18tc006@yf.osaka-cu.ac.jp

[‡] Corresponding author: tyoshida@ocarina.osaka-cu.ac.jp

Received: 3 December, 2019, Accepted 5 March, 2020, Published 21 March, 2020

We have prepared La_2O_3 supported Ga_2O_3 ($\text{Ga}_2\text{O}_3/\text{La}_2\text{O}_3$) photocatalyst to improve the photocatalytic activity of Ga_2O_3 for CO_2 reduction with water under ultraviolet light irradiation without a noble metal cocatalyst. Significant improvement on both CO_2 reduction and water splitting was attained compared with those for non-supported Ga_2O_3 and La_2O_3 . The improvement is attributed to the transformation of the La_2O_3 surface to $\text{NaLa}(\text{CO}_3)_2$ during the photocatalytic reduction tests in aqueous solution of NaHCO_3 . $\text{NaLa}(\text{CO}_3)_2$ was preferentially formed on the surface of La_2O_3 without changing Ga_2O_3 resulting in the structure of Ga_2O_3 supported by $\text{NaLa}(\text{CO}_3)_2$. Once $\text{NaLa}(\text{CO}_3)_2$ fully covered the surface of La_2O_3 , the high catalytic activity was kept long.

Keywords La_2O_3 supported Ga_2O_3 ; High activity and stability; Carbonate species; Structural change before and after reaction

I. INTRODUCTION

Nowadays, global warming and lack of energy fuel are serious concerns. Artificial photosynthesis is attracting much attention as one of the methods to mitigate these problems. Photocatalytic CO_2 reduction has been examined for conversion of CO_2 to useful chemicals such as CO , HCOOH , and CH_4 [1–5]. Semiconductor oxides have been extensively studied as the photocatalyst for water splitting and/or CO_2 reduction [4–18].

To improve the photocatalytic activity of the semiconductor oxides on CO_2 reduction to CO , Ag is often employed as a cocatalyst. Following Kudo *et al.*, who have reported that Ag cocatalyst loaded on $\text{ALa}_4\text{Ti}_4\text{O}_{15}$ ($A = \text{Ca}$, Sr , and Ba) promotes the photocatalytic CO_2 reduction [6], several groups have shown the promotion of the photocatalytic CO_2 reduction by the Ag cocatalysts loaded on composite oxides,

such as $\text{BaLa}_4\text{Ti}_4\text{O}_{15}$, $\text{KCaSrTa}_5\text{O}_{15}$ [7, 8], CaTiO_3 [9], $\text{La}_2\text{Ti}_2\text{O}_7$ [10], and SrO -modified Ta_2O_5 [11].

Although photocatalytic CO_2 reduction using Ga_2O_3 related oxides with the Ag cocatalyst has been studied by Yamamoto *et al.* for Ga_2O_3 [14–16] and Teramura *et al.* for Zn doped Ga_2O_3 and Yb modified Ga_2O_3 [17–19], the role of the Ag cocatalyst on the photocatalytic CO_2 reductions is not well understood yet. In addition, Ag loaded on Ga_2O_3 was sometimes unstable in reaction environments, oxidized or reduced resulting in the deterioration of the photocatalytic activity.

Since Ga_2O_3 shows polymorphs, correlation of the crystalline structure of synthesized Ga_2O_3 and its photocatalytic activity has been examined [14–23]. For example, Ga_2O_3 consisting of different two phases shows high photocatalytic activity on the CO_2 reduction with water without the Ag

cocatalyst [20–22]. We have succeeded to improve the photocatalytic activity of Ga_2O_3 for water splitting and CO_2 reduction without the Ag cocatalyst but employing Al_2O_3 as a support of Ga_2O_3 [24, 25]. Ga_2O_3 supported by Al_2O_3 was consisted of two phases (α and γ) and their particle size was changed depending on the amount of Ga_2O_3 loaded on the Al_2O_3 support. Thus, the control of the crystal phase and the particle size of Ga_2O_3 is likely a key factor for the improvement of its photocatalytic activity. In a separate work [26], we have examined various metal oxides as the support of the Ga_2O_3 photocatalyst. Among all examined oxides, La_2O_3 supported Ga_2O_3 ($\text{Ga}_2\text{O}_3/\text{La}_2\text{O}_3$) showed the highest photocatalytic activity.

This motivates us to investigate the structure of $\text{Ga}_2\text{O}_3/\text{La}_2\text{O}_3$ and the reason for its high photocatalytic activity for CO_2 reduction in detail. After confirming the high activity of $\text{Ga}_2\text{O}_3/\text{La}_2\text{O}_3$ synthesized here on the photocatalytic reduction of CO_2 with water, $\text{Ga}_2\text{O}_3/\text{La}_2\text{O}_3$ was characterized by X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), Ga K-edge X-ray absorption near edge structure (XANES), La L_1 -edge XANES, and field emission scanning electron microscope (FE-SEM), and the role of La_2O_3 on the photocatalytic activity was discussed.

II. EXPERIMENTAL

A. Preparation of $\text{Ga}_2\text{O}_3/\text{La}_2\text{O}_3$ photocatalyst

$\text{Ga}_2\text{O}_3/\text{La}_2\text{O}_3$ photocatalyst samples were prepared by an impregnation method. La_2O_3 (Kishida Chemical) was calcined at 1273 K to remove carbonate before mixing with $\text{Ga}(\text{NO}_3)_3 \cdot 8\text{H}_2\text{O}$ (Kishida Chemical, purity; 99.0%) [27]. The amounts of them were selected to be 6 : 4 for the mass ratio of Ga_2O_3 and La_2O_3 (referred as 40 wt% Ga_2O_3 hereafter). It was the optimum loading amount for $\text{Ga}_2\text{O}_3/\text{Al}_2\text{O}_3$ in our previous work [24]. Then, they were dispersed into 200 mL of distilled water. The dispersion was stirred with a magnetic stirrer in air and dried up, followed by calcination at 823 K for 4 h, resulting the $\text{Ga}_2\text{O}_3/\text{La}_2\text{O}_3$ samples [21]. Unsupported Ga_2O_3 and La_2O_3 were also prepared in a similar way to compare their photocatalytic activities with that of $\text{Ga}_2\text{O}_3/\text{La}_2\text{O}_3$.

B. Characterization

Crystalline structures of all $\text{Ga}_2\text{O}_3/\text{La}_2\text{O}_3$ samples were examined by XRD analysis. XRD patterns of the samples were recorded on a MiniFlex600 (Rigaku) using $\text{Cu K}\alpha$ as a radiation source with an operating voltage of 40 kV and current of 15 mA. The XRD patterns were collected at 2θ angles of 20° – 70° . The 2θ step size was 0.02° with the scanning rate of $2^\circ/\text{min}$. To examine the surface composition of the samples, XPS measurements were carried out using ESCA 3400 (Shimadzu). Mg $\text{K}\alpha$ was used as an X-ray source with an electron acceleration voltage of 10 kV and a current of 20 mA. Ga K-edge XANES and La L_1 -edge

XANES were measured with the transmission mode using the beam line of BL5S1 at Aichi Synchrotron Radiation Center. Morphology of the samples were observed by a FE-SEM (JSM-6500F, JEOL) with a backscattered electron mode under acceleration voltage of 15 kV.

C. Photocatalytic CO_2 reduction and water splitting tests

Photocatalytic CO_2 reduction with H_2O under UV light irradiation was tested for 0.1 g of a sample in aqueous solution of NaHCO_3 with using a fixed-bed flow reactor cell under CO_2 gas flow. The reactor cell is shown in Figure S1 in [Supplementary Material](#). The ultraviolet (UV) light intensity was 40 mW cm^{-2} in the range of $254 \pm 10 \text{ nm}$. Before the test, the sample was irradiated with a 300 W Xe lamp for 1 h under CO_2 gas flow with a flow rate of 20.0 mL min^{-1} . Then, the reduction test was started by introducing 10.0 mL of the NaHCO_3 aqueous solution (1.0 M) and the CO_2 gas with the flow rate of 3.0 mL min^{-1} under the UV light irradiation. The reaction products (CO , H_2 , and O_2) were analyzed by a gas chromatograph equipped with a thermal conductivity detector (GC-TCD). To confirm that the CO production was caused by the photocatalytic process, the CO_2 reduction tests without UV light or NaHCO_3 were also conducted.

III. RESULTS

A. Photocatalytic reduction tests

Figure 1 shows the time course of the production rates of H_2 , O_2 , and CO for $\text{Ga}_2\text{O}_3/\text{La}_2\text{O}_3$. All production rates continuously increased within 4 h and then saturated to keep nearly constant for 5 h of the reaction. After 24 h of the reaction, the CO production rate was reduced to around 2/3 of the highest rate observed at 5 h.

Figure 1: Time course of production rates of CO , H_2 , and O_2 for photocatalytic CO_2 reduction with aqueous solution of NaHCO_3 under UV light irradiation on $\text{Ga}_2\text{O}_3/\text{La}_2\text{O}_3$ from 1 h to 5 h and 24 h. Circles of white, gray, and black correspond to the production rates of H_2 , O_2 , and CO , respectively. The production rate of O_2 after 24 h could not measure.

Figure 2: Production rates of CO (black), H₂ (white), and O₂ (gray), and the selectivity toward CO evolution in the photocatalytic CO₂ reduction on Ga₂O₃/La₂O₃, Ga₂O₃, and La₂O₃ after 5 h of the reaction tests.

Figure 2 compares H₂, O₂, and CO production rates for Ga₂O₃/La₂O₃, La₂O₃, and Ga₂O₃ after 5 h of the photocatalytic reduction test. Ga₂O₃/La₂O₃ showed significantly higher activities in the production rates of CO and H₂ compared with those of Ga₂O₃ by 4.3 and 2 times, respectively. Furthermore, Ga₂O₃/La₂O₃ also showed a higher CO selectivity. Both kept stoichiometry among the products. La₂O₃ did not show the catalytic activity. Thus, the photocatalytic activity of Ga₂O₃ was significantly improved by the La₂O₃ support.

Additional tests changing the reaction conditions were done as shown in Table 1. It should be noted that without the UV light or NaHCO₃ dissolution, Ga₂O₃/La₂O₃ showed no CO production.

B. XRD measurements

Figure 3 showed XRD pattern of Ga₂O₃/La₂O₃ before and after use as the photocatalyst. After use, the part of La₂O₃ in Ga₂O₃/La₂O₃ changed its structure to be carbonate which was assigned as NaLa(CO₃)₂ later. Although the XRD pattern before use was broad, no other components than α-Ga₂O₃, γ-Ga₂O₃, and La₂O₃ were found. However, after use, the carbonate assigned as NaLa(CO₃)₂ appeared and dominated [shown in Figure 3(b)] [28–30]. On the other hand, Ga₂O₃ was left unchanged in XANES measurements as shown later.

The formation of NaLa(CO₃)₂ was observed in all samples after use except entry e which was tested without NaHCO₃ as shown in Figure 4. Without NaHCO₃, as depicted in Figure 4(e), the hydrated La carbonate with a chemical form of La(CO₃)₃·8H₂O was produced. Therefore, NaLa(CO₃)₂ was formed in the reaction of NaHCO₃ with La₂O₃ of Ga₂O₃/La₂O₃. NaLa(CO₃)₂ was disappeared with annealing at 773 K in vacuum [compare (b) and (c) in Figure 3].

Figure 3: XRD patterns of Ga₂O₃/La₂O₃ (a) before and (b) after use, and (c) annealed in vacuum at 773 K after use.

Figure 4: XRD patterns of Ga₂O₃/La₂O₃ and La₂O₃ after use under conditions given in Table 1; (a) Ga₂O₃/La₂O₃, (b) Ga₂O₃/La₂O₃ after use under He flow, (c) La₂O₃, (d) Ga₂O₃/La₂O₃ after use without UV light, and (e) Ga₂O₃/La₂O₃ after use without NaHCO₃.

C. XANES spectra

Figure 5 shows La L₁-edge and Ga K-edge XANES spectra. The former are clearly different before and after use, indicating the change of a bonding nature of La from the oxide (La₂O₃) to the carbonate [NaLa(CO₃)₂] [31]. On the other hand, the Ga K-edge XANES spectra did not show an appreciable change, indicating that most of Ga remained as the oxide.

D. XPS spectra

Figure 6 shows C1s XPS spectra of Ga₂O₃/La₂O₃ before and after use. After use, the small peak appeared around 290

Figure 5: (A) La L1-edge XANES spectra (a) before and (b) after use. (B) Ga K-edge XANES spectra (a) before and (b) after use.

eV became appreciable. The main peak was caused by surface contamination of C. From the peak energy, the small peak was attributed to the carbonate [32], agreeing with the XRD analysis. The carbonate peak observed in the sample before use was probably caused by the reaction of La_2O_3 with CO_2 in atmosphere. With a curve fitting method, peak areas of the carbonate and the main peak were determined. It was indicated that the area ratio of the carbonate peak and

Figure 6: XPS spectra of $\text{Ga}_2\text{O}_3/\text{La}_2\text{O}_3$ (a) before and (b) after use. Small peaks around 290 eV represent carbonate.

the main peak increased from 4.3 % before use to 13.4 % after use.

E. FE-SEM observation

Figure 7 shows FE-SEM images of the sample before and after use taken with a back scattered electron mode, of which contrast well corresponds to the mass of consisting atoms of the sample. Before use, needle-like fine particles of Ga_2O_3 were on larger La_2O_3 particles, which confirms that Ga_2O_3 was supported by La_2O_3 . After use, the sizes of the supporting La_2O_3 particles became large probably owing to the formation and growth of the carbonate on the surface of La_2O_3 , while the Ga_2O_3 fine particles kept their original structure. Thus, $\text{Ga}_2\text{O}_3/\text{La}_2\text{O}_3$ turned to be Ga_2O_3 supported by $\text{LaNa}(\text{CO}_3)_2$.

IV. DISCUSSION

The photocatalytic activity of $\text{Ga}_2\text{O}_3/\text{La}_2\text{O}_3$ was increased almost linearly with the reaction time until 4 h, and afterward they became nearly constant or saturated. Even after

Figure 7: FE-SEM image of $\text{Ga}_2\text{O}_3/\text{La}_2\text{O}_3$ (a) before and (b) after use.

Table 1: CO production rates for photocatalytic CO₂ reduction with water under various conditions. Symbols, ○ and ×, mean the presence or absence, respectively, of CO₂, the UV light, and NaHCO₃ during the reaction.

Entry	Catalyst	CO ₂	UV light	NaHCO ₃	CO production rate (μm h ⁻¹)
a	Ga ₂ O ₃ /La ₂ O ₃	○	○	○	7.1
b	Ga ₂ O ₃ /La ₂ O ₃	He ^a	○	○	0.15
c	La ₂ O ₃	○	○	○	0.04
d	Ga ₂ O ₃ /La ₂ O ₃	○	×	○	N.D. ^b
e	Ga ₂ O ₃ /La ₂ O ₃	○	○	×	N.D.
f	Ga ₂ O ₃	○	○	○	1.64

^a Under He flow.

^b Not detected.

24 h, the reaction rates almost kept the highest values, which were achieved at 5 h, as seen in Figure 1. At the same time, the crystalline structure of La₂O₃ changed to NaLa(CO₃)₂ as seen XRD (Figure 3). The full conversion from La₂O₃ to NaLa(CO₃)₂ occurred after 3–4 h as shown in Figure S2 in Supplementary Material. Accordingly, its morphology changed as seen in Figure 7. On the other hand, Ga₂O₃ remained mostly as prepared without some possible modification at the boundary between Ga₂O₃ and La₂O₃ as shown in Figure 5(A). Correspondingly, the catalytic activity was improved until the surface of La₂O₃ was fully converted with NaLa(CO₃)₂.

There remains the possibility of CO production by dissociation of NaHCO₃ and/or during the formation of NaLa(CO₃)₂. Therefore, we have conducted four additional photocatalytic reduction tests as shown in Table 1. As given in entry **b** of Table 1, without the CO₂ flow, CO production was quite small even with NaHCO₃. This indicates that the CO production was not caused by the decomposition of NaHCO₃ but by CO₂ introduced into the reaction cell. Entry **c** shows that bare La₂O₃ in NaHCO₃ without Ga₂O₃ hardly showed the photocatalytic activity but La₂O₃ was converted to NaLa(CO₃)₂. This confirms that, without Ga₂O₃, NaLa(CO₃)₂ did not show the photocatalytic activity. Without UV irradiation, no reaction occurred indicating that the CO₂ reduction was caused photocatalytically but not by pyrolysis of NaLa(CO₃)₂. Entry **e** shows that without the formation NaLa(CO₃)₂, Ga₂O₃/La₂O₃ did not show catalytic activity. NaHCO₃ is essential for the CO₂ reduction reaction, because it raised pH of its aqueous solution accompanying the increase of CO₂ solubility [33].

Thus, we can conclude that Ga₂O₃/La₂O₃ shows high photocatalytic activity of CO₂ reduction in NaHCO₃ aqueous solution owing to the conversion of La₂O₃ into NaLa(CO₃)₂. To confirm this conclusion, it is necessary to prepare Ga₂O₃ supported by NaLa(CO₃)₂ as a photocatalyst and to conduct the reduction test with using it. However, it is hardly possible to carry out such a confirmation study. This is because the preparation of the Ga₂O₃ catalyst supported by NaLa(CO₃)₂ is difficult if the catalyst would be prepared by the impregnation method, in which annealing at temperatures higher than 773 K, a decomposition temperature of NaLa(CO₃)₂, is necessary. Thus, confirmation of our claim remains for future works.

V. SUMMARY AND CONCLUSION

We have succeeded to improve photocatalytic activity of Ga₂O₃ employing La₂O₃ as a supporting material for CO₂ reduction with the aqueous solution of NaHCO₃ under UV light irradiation. The improvement of the activity is not directly caused by the La₂O₃ support but caused by the conversion of La₂O₃ to NaLa(CO₃)₂ during the photocatalytic reduction in aqueous solution of NaHCO₃ under the UV light. It is also confirmed that CO₂ production was not caused the decomposition of NaHCO₃. The conversion continued rather long time accompanying the improvement of the photocatalytic activity.

It should be noted that Ag was not used as a cocatalyst in the present work. Hence, as noted in our previous papers [24, 25], some lattice distortion in Ga₂O₃ should be introduced during the conversion of the La₂O₃ support to NaLa(CO₃)₂ which would provide high activity for CO₂ reduction without using the Ag cocatalyst.

Appendix

The reaction cell for CO₂ reduction tests and the change of the XRD patterns of Ga₂O₃/La₂O₃ with the reaction time are available in Supplementary Material at <https://doi.org/10.1380/ejssnt.2020.110>.

Note

This paper was presented at the 12th International Symposium on Atomic Level Characterizations for New Materials and Devices '19 (ALC '19), in conjunction with the 22nd International Conference on Secondary Ion Mass Spectrometry (SIMS-22), Miyako Messe, Kyoto, Japan, 20–25 October, 2019.

References

- [1] A. D. Handoko, K. Li, and J. Tang, *Curr. Opin. Chem. Eng.* **2**, 200 (2013).
- [2] M. Anpo, *J. CO₂ Util.* **1**, 8 (2013).
- [3] L. Yu, G. Li, X. Zhang, X. Ba, G. Shi, Y. Li, P. K. Wong, J. C. Yu, and Y. Yu, *ACS Catal.* **6**, 6444 (2016).
- [4] A. Kubacka, M. Fernández-García, and G. Colón, *Chem. Rev.* **112**, 1555 (2012).

- [5] B. AlOtaibi, S. Fan, D. Wang, J. Ye, and Z. Mi, *ACS Catal.* **5**, 5342 (2015).
- [6] K. Iizuka, T. Wato, Y. Miseki, K. Saito, and A. Kudo, *J. Am. Chem. Soc.* **133**, 20863 (2011).
- [7] T. Takayama, K. Tanabe, K. Saito, A. Iwase, and A. Kudo, *Phys. Chem. Chem. Phys.* **16**, 24417 (2014).
- [8] T. Takayama, A. Iwase, and A. Kudo, *Bull. Chem. Soc. Jpn.* **88**, 538 (2015).
- [9] H. Yoshida, L. Zhang, M. Sato, T. Morikawa, T. Kajino, T. Sekito, S. Matsumoto, and H. Hirata, *Catal. Today* **251**, 132 (2015).
- [10] Z. Wang, K. Teramura, S. Hosokawa, and T. Tanaka, *Appl. Catal. B* **163**, 241 (2015).
- [11] K. Teramura, H. Tatsumi, Z. Wang, S. Hosokawa, and T. Tanaka, *Bull. Chem. Soc. Jpn.* **88**, 431 (2015).
- [12] A. Kudo and Y. Miseki, *Chem. Soc. Rev.* **38**, 253 (2009).
- [13] Y.-X. Pan, Z.-Q. Sun, H.-P. Cong, Y.-L. Men, S. Xin, J. Song, and S.-H. Yu, *Nano Res.* **9**, 1689 (2016).
- [14] M. Yamamoto, T. Yoshida, N. Yamamoto, T. Nomoto, Y. Yamamoto, S. Yagi, and H. Yoshida, *J. Mater. Chem. A* **3**, 16810 (2015).
- [15] N. Yamamoto, T. Yoshida, S. Yagi, Z. Like, T. Mizutani, S. Ogawa, H. Nameki, and H. Yoshida, *e-J. Surf. Sci. Nanotechnol.* **12**, 263 (2014).
- [16] M. Yamamoto, T. Yoshida, N. Yamamoto, H. Yoshida, and S. Yagi, *e-J. Surf. Sci. Nanotechnol.* **12**, 299 (2014).
- [17] Z. Wang, K. Teramura, S. Hosokawa, and T. Tanaka, *J. Mater. Chem. A* **3**, 11313 (2015).
- [18] Z. Wang, K. Teramura, Z. Huang, S. Hosokawa, Y. Sakata, and T. Tanaka, *Catal. Sci. Technol.* **6**, 1025 (2016).
- [19] H. Tatsumi, K. Teramura, Z. Huang, Z. Wang, H. Asakura, S. Hosokawa, and T. Tanaka, *Langmuir* **33**, 13929 (2017).
- [20] Y. Kawaguchi, M. Yamamoto, A. Ozawa, Y. Kato, and T. Yoshida, *Surf. Interface Anal.* **51**, 79 (2019).
- [21] X. Wang, Q. Xu, M. Li, S. Shen, X. Wang, Y. Wang, Z. Feng, J. Shi, H. Han, and C. Li, *Angew. Chem. Int. Ed.* **51**, 13089 (2012).
- [22] S. Jin, X. Wang, X. Wang, M. Ju, S. Shen, W. Liang, Y. Zhao, Z. Feng, H. Y. Playford, R. I. Walton, and C. Li, *J. Phys. Chem. C* **119**, 18221 (2015).
- [23] Y. Kato, M. Yamamoto, M. Akatsuka, R. Ito, A. Ozawa, Y. Kawaguchi, T. Tanabe, and T. Yoshida, *Surf. Interface Anal.* **51**, 40 (2019).
- [24] R. Ito, M. Akatsuka, A. Ozawa, Y. Kato, Y. Kawaguchi, M. Yamamoto, T. Tanabe, and T. Yoshida, *ACS Omega* **4**, 5451 (2019).
- [25] M. Akatsuka, T. Yoshida, N. Yamamoto, M. Yamamoto, S. Ogawa, and S. Yagi, *J. Phys.: Conf. Ser.* **712**, 012056 (2016).
- [26] R. Ito, M. Akatsuka, A. Ozawa, M. Yamamoto, T. Tanabe, and T. Yoshida, submitted to *Bull. Chem. Soc. Jpn.*
- [27] A. Tsoukalou, Q. Imtiaz, S. M. Kim, P. M. Abdala, S. Yoon, and C. R. Müller, *J. Catal.* **343**, 208 (2016).
- [28] O. K. Nikol'skaya and L. N. Dem'yanets, *Inorg. Mater.* **41**, 1206 (2005).
- [29] V. Philippini, T. Vercouter, A. Chaussé, and P. Vitorge, *J. Solid State Chem.* **181**, 2143 (2008).
- [30] H. Hao, Y. Wang, and B. Shi, *Water Res.* **155**, 1 (2019).
- [31] H. Asakura, T. Shishido, K. Teramura, and T. Tanaka, *J. Chem. Phys.* **142**, 164507 (2015).
- [32] M. Ni and B. D. Ratner, *Surf. Interface Anal.* **40**, 1356 (2008).
- [33] K. Teramura, K. Hori, Y. Terao, Z. Huang, S. Iguchi, Z. Wang, H. Asakura, S. Hosokawa, and T. Tanaka, *J. Phys. Chem. C* **121**, 8711 (2017).

All articles published on e-J. Surf. Sci. Nanotechnol. are licensed under the Creative Commons Attribution 4.0 International (CC BY 4.0). You are free to copy and redistribute articles in any medium or format and also free to remix, transform, and build upon articles for any purpose (including a commercial use) as long as you give appropriate credit to the original source and provide a link to the Creative Commons (CC) license. If you modify the material, you must indicate changes in a proper way.

Published by The Japan Society of Vacuum and Surface Science