Facile titania nanocoating using single droplet assembly of 2D nanosheets

Yue SHI1, Eisuke YAMAMOTO1, Makoto KOBAYASHI1 and Minoru OSADA1,2,†

1Institute of Materials and Systems for Sustainability (IMaSS) and Department of Materials Chemistry, Nagoya University, Nagoya 464–8601, Japan
2International Center for Materials Nanoarchitectonics (WPI-MANA), National Institute for Materials Science (NIMS), Tsukuba, Ibaraki 305–0044, Japan

Single droplet assembly is a new thin-film technology using drop casting of two-dimensional (2D) materials: controlled convection by a pipette and a hotplate causes a uniform deposition, suggesting new possibility of 2D nanosheet assembly. We extended this new assembly technique to titania nanocoating by including detailed investigations on fabrication procedure and characteristics as coating applications. The layer-by-layer approach using single droplet assembly is effective for the fabrication of atomically uniform and highly dense nanofilms. As a consequence of the effective tiling by controlled convection, the films appeared flat on the atomic scale and uniform over a large area. We also address characteristics of single droplet assembly in comparison with other deposition methods.

Key-words : 2D nanosheets, Titania, Drop casting, Nanocoating

[Received January 4, 2021; Accepted February 15, 2021]
2. Experimental

Figure 1 shows a typical procedure for single droplet assembly. Colloidal suspensions of Ti$_{0.87}$O$_2$ nanosheets (with lateral dimensions of 5–10 μm) were synthesized according to a well-established soft-chemical exfoliation procedure$^{20,21}$ starting from a layered titanate (K$_{0.8}$Ti$_{1.73}$Li$_{0.27}$O$_4$). The aqueous suspension can be directly used without any solvent exchange. For film deposition, the original nanosheet suspension (0.36 wt %) was first centrifuged at 2000 rpm for 15 min to remove the bulk sediments. Then, 40 μL of the suspension was diluted into 5 mL of ultrapure H$_2$O with 200 μL of ethanol as the precursor suspension.

Circular plates (such as 50 mm Si and 30 mm quartz glass) were used as substrates. The substrates were cleaned by immersing them in a mixed solution of CH$_3$OH/HCl [1:1 (v/v)] and concentrated H$_2$SO$_4$ for 30 min each. The substrates were heated on a heating plate at 100–120 °C for 3 min. The nanosheet suspension was loaded onto the cleaned substrate to cover the whole surface. Once the droplet settled, the liquid was immediately removed from the middle bottom of a droplet by the pipette. After all the liquid was removed, a well-packed film was assembled on the substrate. The resultant films were characterized by Atomic force microscopy (AFM) (SII Nanotech, E-Sweep).

Multilayer films of Ti$_{0.87}$O$_2$ nanosheets were fabricated by repeating the monolayer deposition described above. Before deposition of the next layer, the films were heated in air at 180–200 °C for 2–15 min. The procedure for monolayer deposition was repeated n times to fabricate multilayer films of (Ti$_{0.87}$O$_2$)$_n$. Build-up process was characterized by ultraviolet-visible (UV-visible) spectroscopy (Hitachi U-3900) and X-ray diffraction (XRD) (Rigaku SmartLab). The resultant films were characterized by high-resolution transmission electron microscopy (HRTEM) (Hitachi H-9000).

3. Results and discussion

3.1 Titania nanocoating using single droplet assembly

We prepared small-sized nanosheets by ultrasonication treatment and performed the single droplet assembly of Ti$_{0.87}$O$_2$ nanosheets with lateral sizes ranging from 10 μm to 100 nm. Figure 2 shows AFM images of Ti$_{0.87}$O$_2$ nanosheets with different lateral sizes. The AFM images clearly resolved individual nanosheets arranged edge to edge in a monolayer with negligible overlaps. The average coverage was >90 % with limited gaps. Clearly, a well-packed monolayer film was obtained with the samples even with a small dimension ~100 nm. In the case of 100-nm size, we observed some spherical bumps on the nanosheet surface. Since the thickness of Ti$_{0.87}$O$_2$ nanosheet is only 1 nm, the roughness of the substrate can be reflected in the morphology of the nanosheet films. Due to the experimental difficulty, we could not prepared nanosheets with a lateral dimension less than 100 nm. Although we still await further investigation of the critical lateral size for the single droplet assembly, the 2D aspect ratio would facilitate nanosheet tiling in the single droplet assembly.

Figure 3 depicts a series of photographs during the single droplet assembly. After dropping the diluted suspension onto the substrate [Fig. 3(a)], a pipette was used to withdraw the liquid from the bottom center of the droplet. During the liquid removal, the height and contact angle of the sessile droplet decreased while maintaining the contact area between the droplet and substrate [Figs. 3(b) and 3(c)]. Then the height of the droplet was reduced to a critical value, shrinkage of the contact area was observed along with a reduced height of the residual droplet [Figs. 3(d) and 3(e)]. After the removal of all the liquid, a neatly packed monolayer film was deposited [Fig. 3(f)].
Based on these observations, we assume that the nanosheet tiling is driven by the thermal convection force in the sessile droplet, which is caused or enhanced by the temperature difference between the cold droplet and hot substrate. In the case of typical drop casting, the formation of patterns after the evaporation of colloidal droplets has often been discussed in terms of capillary and Marangoni flows. In the single droplet assembly, we consider that the co-occurrence of capillary and Marangoni flows plays a key role for 2D nanosheet tiling. Usually, water-based suspensions are not suitable for drop casting due to its high surface tension ($\sim 72$ mN m$^{-1}$), low viscosity ($\sim 1$ mPa s) and very weak Marangoni flow. We thus added ethanol as a modifier to reduce the surface tension and enhance the Marangoni flow.

Figure 4 illustrates a plausible model for 2D nanosheet tiling. Once the evaporation began, the dried nanosheets were pinned at the edge of the droplet, providing a force maintaining the frame of the film against the action of surface tension. The Marangoni flow remained at the edge part could introduce the cycling inward movement of nanosheets and orientate the nanosheets uniformly. During the meantime, the velocity of surface movement near the edge ($v_e$) was enhanced by the drag force toward the center to exceed the velocity of the nanosheet movement ($v_M$). According to previous studies in drop casting, the typical velocity of the generated Marangoni flow could be calculated by $v_M \sim (\beta \theta_c \Delta T)/32 \mu$, where $\beta$ is the surface tension gradience regards to temperature, $\theta_c$ the contact angle and $\mu$ the dynamic viscosity in Ns m$^{-2}$, respectively.

Fig. 3. A series of photographs during the single droplet assembly of Ti$_{0.87}$O$_2$ nanosheets, along with the variation of contact angle ($\theta_c$). (a) 0 s (just after loading a droplet before the liquid removal), (b) 3 s, (c) 5 s, (d) 7 s, (e) 10 s, (f) 15 s (after the removal of all the liquid).

Fig. 4. Plausible model for 2D nanosheet tiling. (Right panel) Surface capture process during the middle stage of the single droplet assembly.
The $\theta_c$ decreased from 30° to 7°, $\beta = 1.544 \times 10^{-4}$ N m$^{-1}$ °C$^{-1}$, $\mu = 1.25 \times 10^{-3}$ Ns m$^{-2}$. Suppose there was no change in $\Delta T = 75$ °C, $v_{M}$ at $\theta_c = 7^\circ$ was estimated to be 4.3 mm s$^{-1}$. At $\theta_c = 12^\circ$ Marangoni flow might be completely suppressed; the real velocity would be $\ll 4.3$ mm s$^{-1}$. Meanwhile, the surface velocity of the droplet near the edge can be directly calculated by $v_e = R/t_f$ where $R$ is the radius of the substrate 25 mm and $t_f$ is the time for completing the shrinkage of the contact area. From Fig. 3, $t_f$ was 5 s and $v_e$ was estimated to be 5 mm s$^{-1} > v_{M}$ (4.3 mm s$^{-1}$). Then, the surface capture would happen near the edge (the right panel of Fig. 4). During the process, the surface of the droplet acts like the fishing net, while the nanosheets refer to fish. When the speed of fishing net is faster than fish, fish would be caught by the fishing net. Similarly, the nanosheets moved along the droplet surface could be captured at the air/liquid interface, when the velocity of the edge surface is faster than that of nanosheets movement. The affinity of such surface capture can be even enhanced for more hydrophobic particles. In this context, the nanosheets have a very high 2D aspect ratio (> 10$^9$) with a negatively charged nature; the nanosheet surface is most likely covered with TBA$^+$ ions (exfoliation agent), which act as surfactants. With the continuous loss of the suspension via liquid removal and evaporation, the fluid layer becomes thinner and nearly flat at the final stage of the single droplet assembly. In such a thin fluid layer, the 2D nanosheets are forced to align in parallel to the substrate.

### 3.2 Multilayer assembly using single droplet assembly

The construction of multilayer nanosheet films is also of significant importance for their practical applications in functional thin films and coatings. Common requirements for such applications are atomically uniform, highly dense and void-free characteristics. Currently, physical methods such as vapor deposition techniques are favorably employed to achieve such high-quality films with a nanometer precision. We utilized the single droplet assembly for applications of titania coatings. One precaution to take was fixing the nanosheets tightly enough to the substrate so that they were not peeled off in the following coating steps. We found that heating the film to 100–200°C was effective for improving the adhesion between the nanosheets and substrate.

**Figure 5** depicts the multilayer assembly of Ti$_{0.87}$O$_2$ nanosheets. The droplet driven deposition procedure was repeated 10 times. After each deposition cycle, heat treatment at 200°C for 15 min was conducted to improve the adhesion between the nanosheets and substrate. Multilayer deposited (Ti$_{0.87}$O$_2$)$_n$ films were characterized by UV–visible spectroscopy and XRD. The bandgap absorption at 265 nm arising from Ti$_{0.87}$O$_2$ was linearly enhanced with the deposition cycle ($n$), clearly indicating multilayer buildup [Fig. 5(a)]. XRD data exhibited a basal diffraction peaks with $d$ spacing of ~1.4 nm, which can be ascribed to the lamellar structure of Ti$_{0.87}$O$_2$ nanosheets with TBA$^+$ ions. As a function of the deposition cycles, the peaks became more intense and sharper, strongly supporting the layer-by-layer growth of the film [Fig. 5(b)]. The as-fabricated films were irradiated by UV/white light from a Xe lamp for 48 h to decompose the TBA$^+$ ions used in the exfoliation process. Cross-sectional HRTEM observations [Fig. 5(c)] revealed the homogeneous film over the substrate surface. The thickness of the film was approximately 10.4 nm, in good agreement with that for a 10-layer film of Ti$_{0.87}$O$_2$ nanosheets. In the HRTEM image, the lamellar fringes from the layer-by-layer assembled nanosheets were also clearly resolved, revealing the uniform and highly ordered architecture of the film.

Finally, we address a few remarks on the single droplet assembly as a coating technique. **Table 1** summarizes...
some characteristics of the single droplet assembly in comparison with other deposition methods. Currently, the deposition of well-packed nanosheet films were mainly fabricated by three techniques involving electrostatic sequential adsorption,9),10) LB deposition11),12) and spin coating.13) Electrostatic sequential adsorption is one of the most simple and powerful methods for layer-by-layer thin-film growth using 2D nanosheets. However, attempts at uniform depositions of 2D nanosheets have been frustrated by uncontrolled overlapped patches and gaps. For improved film quality, complicated operations with ultrasonication treatment are needed.10),25) On the other hand, the LB and spin coating films tend to have a gap rather than an overlap while vice versa for the film via the single droplet assembly. The film quality was comparable to the best films fabricated through electrostatic sequential adsorption with ultrasonication.

The obvious benefit of the single droplet assembly include its short processing time and simple operation. Electrostatic sequential adsorption and LB deposition usually take 1 h; serious drawbacks associated with long processing times and complicated deposition operations have impeded practical applications. Spin coating has been applied for overcoming these issues; highly organized monolayer films can be fabricated within 1 min.13) Despite this potential impact, spin coating also faces some disadvantages, such as pretreatments for solvent exchange, small processing windows and sample consumption. In the single droplet assembly, on the contrary, a monolayer deposition can be completed in ~30 s, even shorter than the time for spin coating (1 min). We also note that the single droplet assembly requires a tiny amount of diluted suspension (~100 µL, ~0.007 wt%), which constitutes a highly efficient deposition with sample saving. In contrast, spin coating and LB deposition typically waste over 95% suspension for the monolayer coating. These results clearly indicate the versatility of single droplet assembly for various functional nanocoatings.

Table 1. Summary of the characteristics of different deposition methods

| Operation          | Single droplet assembly | Electrostatic sequential adsorption | LB deposition | Spin coating |
|--------------------|-------------------------|--------------------------------------|---------------|--------------|
| Solvent            | Water                   | Water                                | Water         | Organic      |
| Time for 1L deposition | 30 s                   | ×                                    | ×             | 1 min        |
| Cost               | Highly efficient deposition| Waste > 90%                        | Waste > 95%   | Waste > 95%  |

4. Conclusion

We have demonstrated successful fabrication of highly organized monolayer and multilayer films composed of titania nanosheets by single droplet assembly. The single droplet assembly is extremely simple. The highly organized monolayer films can be fabricated in ~30 s using only a tiny amount of diluted suspension. Due to the highly anisotropic nature, titania nanosheets can be easily managed at the surface of the droplet, driven by capillary and Marangoni flows. AFM observations confirmed that TiO2 nanosheets were well-packed with negligible overlapped patches and gaps. Repetition of this monolayer deposition led to the highly ordered multilayer structure of the stacked nanosheets. With these unique features, our approach of titania coating opens new opportunities for ceramic nanocoatings with advanced functionalities.

Acknowledgements This work was in part supported by World Premier International Research Center Initiative (WPI Initiative on Materials Nanoarchitronics), MEXT, the Grant-in-Aid for Scientific research KAKENHI, JSPS, A-STEP, JST, Creation of Life Innovation Materials for Interdisciplinary and International Researcher Development Satellite, MEXT, and the joint usage/research program of the Institute of Materials and Systems for Sustainability (IMaSS), Nagoya University.

References
1) D. G. Schlom, L.-Q. Chen, X. Pan, A. Schmehl and M. A. Zurbuchen, J. Am. Ceram. Soc., 91, 2429–2454 (2008).
2) H. Y. Hwang, Y. Iwasa, M. Kawasaki, B. Keimer, N. Nagaosa and Y. Tokura, Nat. Mater., 11, 103–113 (2012).
3) D. G. Schlom, *APL Mater.*, 3, 062403 (2015).
4) R. Ramesh and D. G. Schlom, *Nat. Rev. Mater.*, 4, 257–268 (2019).
5) R. Ma and T. Sasaki, *Adv. Mater.*, 22, 5082–5104 (2010).
6) M. Osada and T. Sasaki, *Adv. Mater.*, 24, 210–228 (2012).
7) M. Osada and T. Sasaki, *Polym. J.*, 47, 89–98 (2015).
8) P. Xiong, B. Sun, N. Sakai, R. Ma, T. Sasaki, S. Wang, J. Zhang and G. Wang, *Adv. Mater.*, 31, 1902654 (2019).
9) T. Sasaki, Y. Ebina, T. Tanaka, M. Harada, M. Watanabe and G. Decher, *Chem. Mater.*, 13, 4661–4667 (2001).
10) T. Tanaka, K. Fukuda, Y. Ebina, K. Takada and T. Sasaki, *Adv. Mater.*, 16, 872–875 (2004).
11) K. Akatsuka, M. Haga, Y. Ebina, M. Osada, K. Fukuda and T. Sasaki, *ACS Nano*, 3, 1097–1106 (2009).
12) B. W. Li, M. Osada, Y.-H. Kim, Y. Ebina, K. Akatsuka and T. Sasaki, *J. Am. Chem. Soc.*, 139, 10868–10874 (2017).
13) K. Matsuba, C. Wang, K. Saruwatari, Y. Uesusuki, K. Akatsuka, M. Osada, Y. Ebina, R. Ma and T. Sasaki, *Sci. Adv.*, 3, e1700414 (2017).
14) B. W. Li, M. Osada, T. C. Ozawa, Y. Ebina, K. Akatsuka, R. Ma, H. Funakubo and T. Sasaki, *ACS Nano*, 4, 6673–6680 (2010).
15) B.-W. Li, M. Osada, Y. Ebina, S. Ueda and T. Sasaki, *J. Am. Chem. Soc.*, 138, 7621–7625 (2016).
16) M. Osada and T. Sasaki, *APL Mater.*, 7, 120902 (2019).
17) R. D. Deegan, O. Bakajin, T. F. Dupont, G. Huber, S. R. Nagel and T. A. Witten, *Nature*, 389, 827–829 (1997).
18) D. Mampallil and H. B. Eral, *Adv. Colloid Interfac.*, 252, 38–54 (2018).
19) Y. Shi, M. Osada, Y. Ebina and T. Sasaki, *ACS Nano*, 14, 15216–15226 (2020).
20) T. Sasaki and M. Watanabe, *J. Am. Chem. Soc.*, 120, 4682–4689 (1998).
21) T. Tanaka, Y. Ebina, K. Takada, K. Kurashima and T. Sasaki, *Chem. Mater.*, 15, 3564–3568 (2003).
22) M. R. Barmi and C. D. Meinhart, *J. Phys. Chem. B*, 118, 2414–2421 (2014).
23) M. Parsa, S. Harmand and K. Sefiane, *Adv. Colloid Interfac.*, 254, 22–47 (2018).
24) C. Diddens, H. Tan, P. Lv, M. Versluis, J. Kuerten, X. Zhang and D. Lohse, *J. Fluid Mech.*, 823, 470–497 (2017).
25) M. Osada, Y. Ebina, H. Funakubo, S. Yokoyama, T. Kiguchi, K. Takada and T. Sasaki, *Adv. Mater.*, 18, 1023–1027 (2006).