Structure analysis of the large dimension of pseudo-polyrotaxane nanosheet in a solvent via neutron scattering

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Our groups have been studied the morphology, self-assembly/disassembly mechanism, and application of the supramolecular self-assembled nanosheet, pseudo-polyrotaxane nanosheet (PPRNS).[1,2] This nanosheet material has potential to be tailored its chemical and geometrical structure by adopting the fabrication method. However, the structure analysis methods of the PPRNS in the solvent (water) is limited. The optical microscopy can observe the PPRNS structure with rough scale (1~10 μm) in a real image and the scattering method (using X-ray and/or light) can analyze the nanometer-scale structure of PPRNS from the scattering pattern. The structure with the size around 100 nm in a solvent is sometimes difficult, although we can see them by the microscopy (AFM, SEM and TEM) in a dried state. In this experiment, we analyze the structure of fragmented PPRNS in a very small size by sonication which is difficult to be characterized by the versatile equipment with the lab-scale size.

Fig. 1 shows the images of optical microscope observation for the normal PPRNS and PPRNS fragmented by sonication in water. For the normal PPRNS, the rhombus shaped structures could be seen with the size of around 1–2 μm. The thickness is around 11 nm [1]. By sonicating the PPRNS in water, the particles were fragmented in very small pieces, which is estimated to be less than 100 nm.

To estimate the edge length of PPRNS, we perform the neutron scattering experiment (Fig. 1). For the normal PPRNS, the intensity at the low q range (around 0.002) are increased with the decrease of the q value. This indicate the size of the larger dimension (edge length) of the PPRNS is over 1200 Å. Although this means the size of normal PPRNS is too large to be determined by this method, the roughly estimated value is consistent with the size evaluated by the optical microscopy (around 1–2 μm). On the other hands, the edge length of fragmented PPRNS could be determined from the neutron scattering profiles, which is 461 Å. This is characterized in the scattering intensity around 0.002. The suppression of the increase of the intensity with the decrease of the q value clearly indicate the size of the large dimension of the fragmented PPRNS is smaller than that of the normal PPRNS. The value (461Å) is reasonable which was roughly assessed by the optical microscopy.

From this experiment, we succeeded in the evaluation of the edge length of normal and fragmented PPRNS in the solvent for the first time. Although the analysis of this size rage of the particle in a solvent is not easy, this is important for the dynamic behavior of the particle *in vivo*. We believe this method is effective to distinguish the size of this range, and would be helpful for the investigation of the behavior of the size-characterized PPRNS in/for bio-materials in our future experiment.

[1] S. Uenuma, R. Maeda, H. Yokoyama, K. Ito, *Chem Commun*, 2019, **55**, 4158.
[2] S. Uenuma, K. Endo, N. Yamada, H. Yokoyama, K. Ito, *ACS Appl. Mater. Interfaces.*, 2021, **13**,60446.

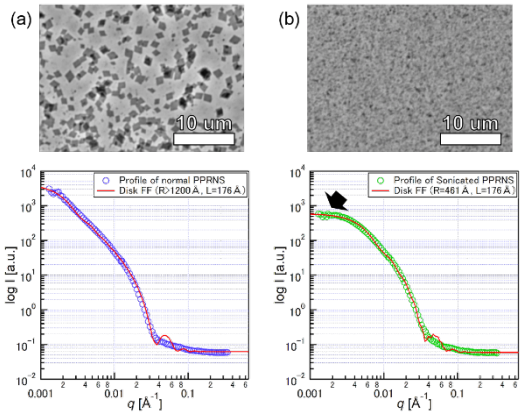

Fig. 1. Optical microscope images and neutron scattering patterns of (a) the normal PPRNS and (b) the fragmented PPRNS.