Picometer-level core-shell structure in Pd nanocrystals revealed by total scattering

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Most nanocrystals are expected to show deviations from a perfect crystal lattice inside the grains, which is referred to as *modulation waves* [1], because of their significant surface effects, leading to exceptional physical and chemical properties. Conventional X-ray diffraction fails to reveal *modulation waves* owing to the assumption of the periodic structure, whereas electron diffraction from a single grain is one of the most powerful probes to distinguish the core structure from the surface structure on the atomic level. It is, however, still challenging to investigate *modulation waves* from the core to the surface, which is the atomic-level core-shell structure. In this study, we have demonstrated that synchrotron X-ray total scattering makes it possible to visualize the core-shell structure on the picometer level in Pd nanocrystals.

X-ray total scattering provides a potential for visualization of *modulation waves* [2]; nevertheless, its applications have been very limited because the approach is extremely demanding of experimental data. We have developed the high-resolution and high-accuracy total scattering measurement system, OHGI (Overlapped High-Grade Intelligencer), at SPring-8[3,4] to overcome the limitations. Recent studies have demonstrated that our total scattering data are of the highest quality in terms of both Bragg and diffuse scattering [5-7]. With this system, Pd nanocrystals were measured under hydrogen pressure. The total scattering data were converted into atomic pair distribution functions (PDF) based on the principle of maximum entropy [8]. The resulting PDFs were virtually free from spurious ripples at no expense of real-space resolution. We have attempted to model *modulation waves* from the PDFs on the basis of an fcc Pd lattice. The model suggests that the interatomic distances between Pd atoms in the shell region are longer than those in the core by a few picometers. In addition, we found that the core-shell structure undergoes significant changes by hydrogenation. The picometer-level core-shell structure can explain that implied by neutron diffraction, where both tetrahedral and octahedral sites are occupied by hydrogen atoms in the surface [9]. In this presentation, I will discuss the relationship between the modified core-shell structure and hydrogen-storage kinetics in Pd nanocrystals.

[1] Hudry, D., Howard, I. A., Popescu, R., Gerthsen, D. & Richards, B. S. (2019). *Adv. Mater.* **31**, 1900623.

[2] Palosz, B., Grzanka, E., Gierlotka, S. & Stelmakh, S. (2010). *Z. Kristallogr.* **225**, 588.

[3] Kato, K., Tanaka, Y., Yamauchi, M., Ohara, K. & Hatsui, T. (2019). *J. Synchrotron Rad.* **26**, 762.

[4] Kato, K. & Shigeta, K. (2020). *J. Synchrotron Rad.* **27**, 1172.

[5] Svane, B., Tolborg, K., Kato, K. & Iversen, B. B. (2021). *Acta Cryst.* **A77**, 85.

[6] Pinkerton, A. (2021). *Acta Cryst.* **A77**, 83.

[7] Beyer, J., Kato, K. & Iversen, B. B. (2021). *IUCrJ* **8**, 387.

[8] Kato, K. *et al.*, to be submitted.

[9] Akiba, H., Kofu, M., Kobayashi, H., Kitagawa, H., Ikeda, K., Otomo, T. & Yamamuro, O. (2016). *J. Am. Chem. Soc.* **138**, 10238.

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