Resolving exotic structure and polar ordering using advanced STEM

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Novel functional materials are usually characterized by emerging ordering beyond the conventional unit-cell level. Examples include artificial superlattices, self-assembled nanostructures, ferroic domain structures, and charge-density waves. Such complex ordering, even though occurring collectively, commonly suffers nanoscale fluctuations that destroy the long-range periodicity that is required for conventional diffraction-based structure analysis, posing a formidable challenge for accurate structure determination. On the other hand, the maturation of aberration-corrected TEM/STEM presents an alternative real-space approach to probe the local complex ordering, through directly imaging the atomic structure with picometer precision. In this talk, I will give several examples demonstrating the power of advanced STEM on resolving the complex atomic and polar ordering in perovskite oxides and 2D materials: i) By developing an imaging condition optimized for oxygen contrast, we can image sensitively the octahedral structure in perovskite oxides with picometer precision. It further enabled us to reveal an extraordinary 2D ordered octahedral tilting in the solid electrolyte $Li_{0.5-3x}Nd_{0.5+x}TiO_3$ (Fig. 1a and 1b), and to demonstrate its dependence on the competition between Li content and lattice strain.[1] ii) Through atomic displacement mapping based on high-resolution imaging, and electric polarization mapping based on 4D-STEM, we made the first experimental discovery of 2D antiferroelectricity in vdW In_2Se_3 (Fig. 1c), and resolved the true nature of its superstructure that had been under debate for over four decades.[2] We also demonstrated the 2D ferroelasticity coupled with this antiferroelectricity through the spontaneous lattice strain.[3] iii) Lastly, iDPC technique in STEM allowed us to unravel the exotic polar textures associated to the modulated octahedral tilting in complex perovskites. The characterization strategy and capability in our work demonstrate a powerful tool to probe the structure-property interplay in emerging functional materials at the atomic scale.

[1] Zhu, Y.*, Withers, R. L., Bourgeois, L., Dwyer, C. & Etheridge, J.* (2015). *Nat. Mater.* **14**, 1142.
[2] Xu, C., Chen, Y., Cai, X., Meingast, A., Guo, X., Wang, F., Lin, Z., Lo, T. W., Maunders, C., Lazar, S., Wang, N., Lei, D., Chai, Y., Zhai, T., Luo, X. & Zhu, Y.* (2020). *Phys. Rev. Lett.* **125**, 047601.
[3] Xu, C., Mao, J., Guo, X., Yan, S., Chen, Y., Lo, T. W., Chen, C., Lei, D., Luo, X., Hao, J., Zheng, C. & Zhu, Y.* (2021). *Nat. Commun.* **12**, 3665.

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