Insight of Local Atomic Structure of Metal Organic Frameworks via 4D STEM Imaging

Metal organic frameworks (MOFs) have been named as one of "the top ten emerging technologies in chemistry" by the International Union of Pure and Applied Chemistry (IUPAC)[1]. A wide range of MOFs have distinctive features including adjustable chemical compositions, tunable topologies, and large specific surface areas, which make MOFs highly promising for numerous applications in clean energy. These applications include gas storage and separation, bioimaging, catalysis, batteries, supercapacitors, and drug delivery. The properties of MOFs are directly influenced by various microstructures, including surfaces, interfaces, defects, and the interactions between the framework and guest species[2]. Guest species, such as ions, particles, clusters, and molecules, can be accommodated within the well-defined frameworks of MOF crystals, resulting in unique porosity and long-range orderly structures. However, our understanding of the molecular-level interactions between the framework and guest molecules, which play a crucial role in these applications, remains limited.

Conventional transmission electron microscopy (TEM), including scanning TEM (STEM), stands as the most powerful imaging technique at the atomic level. However, achieving atomic-resolution imaging of the host framework and guest molecules poses significant challenges due to the delicate bonding between the guest molecule and framework. Even under low electron doses, this bonding is highly susceptible to damage. As a result, current studies rely on ensemble measurements utilizing X-ray/neutron diffraction, nuclear magnetic resonance, or theoretical simulations. Nonetheless, these methods provide structural information averaged over bulk particles.

The rapid advancement of low-dose 4D STEM has presented an unprecedented opportunity to explore the atomic-scale structure of porous materials, such as zeolites, across multiple dimensions and scales (Fig. 1)[3]. Electron ptychography, an emerging computational microscopy technique based on 4D STEM, enables the capture of high-resolution images that surpass the limitations imposed by lenses. Its potential applications in super-resolution imaging[4], high-contrast light-element detection detection[5], 3D imaging[6], spectroscopic data acquisition[7], and low-dose imaging[8] using direct electron detectors have garnered significant interest. Furthermore, cryo-EM has contributed to investigating the structural details of beam-sensitive materials by preserving their stability over prolonged irradiation periods. The combination of ptychography and cryo-EM has recently demonstrated 2D and 3D high-contrast phase imaging of organic matter, such as unstained virus particles, even at low doses as shown in Fig. 2 [9, 10], by the PI.

Building on our previous work in cryogenic electron ptychography[5-10], our objective is to investigate the atomic-level structures of porous crystalline materials, including MOFs and COFs, allowing us to observe previously unattainable details such as atomic defects, host-guest interactions, and surface structures. To address the challenge of sample thickness for high-resolution, low-dose imaging, we will employ cryofocused ion beam (cryo-FIB) to prepare the crystals with sizes beyond the nanoscale, making them suitable for TEM observation. By leveraging cryogenic electron microscopy (cryo-EM), we will stabilize beamsensitive MOFs and generate near-atomic-resolution images, providing molecular-level insights into hostguest interactions. These observations will enhance our understanding of particle growth and gas adsorption kinetics. Additionally, we will explore the preferred adsorption sites for guest molecules in the porous materials and reveal the atomic surface structure through crvo-ptychography, shedding light on the growth mechanisms. Through the use of various examples involving guest molecules or atomic insertion into the porous materials, we will demonstrate the potential of cryo-electron ptychography in this extensive research field. This study will unlock opportunities for further exploration of host-guest interactions and the development of a comprehensive understanding of adsorption kinetics at the atomic level. The discoveries made will provide valuable insights into the fundamental operation of these materials, shaping future designs of these tunable substances and opening up possibilities to study numerous host-guest interactions across a wide range of materials.

This PhD studentship is available for an immediate start. To discuss this project further contact: peng.wang.3@warwick.ac.uk

More Details of the project: <u>https://warwick.ac.uk/fac/sci/physics/staff/academic/pwang/openpositions/</u>



Fig. 1 | Strategy for 4D-STEM imaging of small molecules by host-guest interactions. a, Schematics of 4D-STEM imaging of the pyridines adsorbed in ZSM-5 channels. b,c, images of empty ZSM-5 straight channels (b) and the channels after the saturated pyridine adsorption (c), compared with the structural models (d). [2]



Fig. 2 | **Strategy for crogenic electron ptychography imaging of macro biomolecues. a**, Schematics of ptychographic imaging experimental setup. **b**, 3D Reconstruction of Rotavirus DLPs at a low dose of 25 e/A². [8,9]

References:

- 1. Gomollon-Bel, Chemistry International, 2019. **41**: 12.
- 2. Zhu, et al., Nat Mater, 2017. 16: 532-536.
- 3. Shen, et al., Nature, 2022. **607**: 703-707.
- 4. Jiang, et al., Nature, 2018. **559**: 343-349.
- 5. Wang, et al., Scientific Reports, 2017. **7**: 1-8.
- 6. Gao, et al., Nature Communications, 2017. 8.
- 7. Song, et al., Physical review letters, 2018. **121**: 146101.
- 8. Song, et al., Scientific reports, 2019. 9: 1-8.
- 9. Zhou, et al., Nature Communications, 2020. 11: 1-9.
- 10. Pei#, et al., Nature Communications, 2023. 14: 3027.