MS23- Advances in electron crystallography methods

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Continuous rotation electron diffraction: an approach for better understanding of beam sensitive materials

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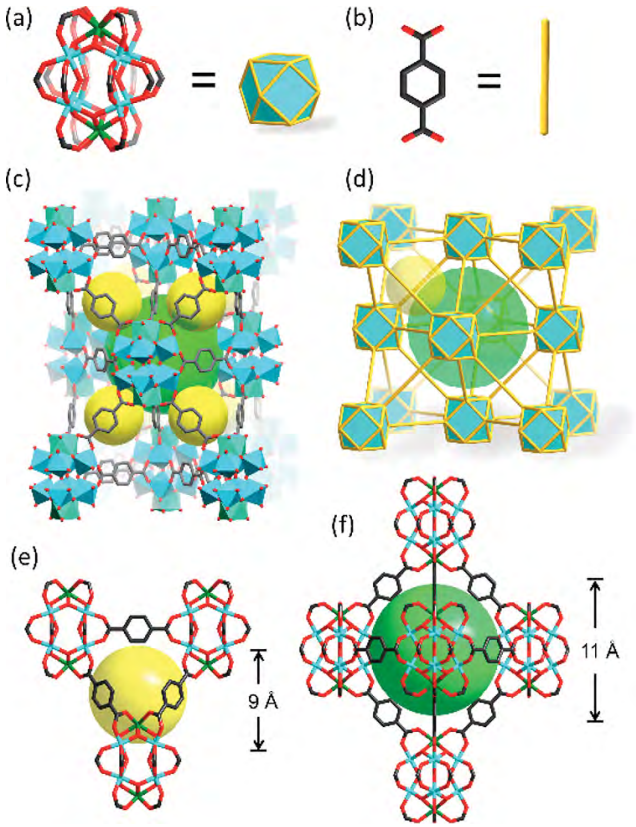
Nanoporous materials, such as metal-organic frameworks (MOFs) and zeolites are attracting increasing interest because of their particular high performance in catalysis, gas storage, separation, ion exchange, fuel cells, supercapacitor, etc. A crucial problem in the study of porous materials is to determine the structure, more specifically, the atomic positions. The novel properties of nanoporous materials can be revealed by knowing the atomic positions, and then specific applications could be designed. However, MOFs and zeolites are often resulted in nano-size, and high beam sensitivities, which leads to difficulties in structural determination. A newly developed method, continuous rotation electron diffraction (*c*RED) method, is extended from electron crystallography[1,2]. Due to the high signal to background ratio and high frame rate of the direct electron detector, we are capable of collecting the dataset in less than one minute. Thus, the major problem in electron diffraction, the beam damage, could be minimized. As a consequence, more details of the beam sensitive materials can be revealed.

*c*RED method was applied to reveal the structural details of a MOF, PCN-415[3]. The crystal size of PCN-415 is less than 1 mm, which is too small to be solved by single X-ray diffraction. Ultrafast data collection (17 s – 3 min per dataset) was carried out to minimize beam damage on the MOF. From 3D reciprocal lattice of PCN-415, unit cell and possible space groups were easily determined. The structures were solved and refined by using Shelx software against the *c*RED data. They were further refined against synchrotron PXRD data by Rietveld method. The structure models refined against *c*RED and PXRD show excellent agreement with each other, and the atomic positions differ on average only by 0.032 Å for Zr/Ti and by 0.071 Å for O/C.

Inspecting the structural details, PCN-415 is consisted by a new type of cluster, $[Ti_8Zr_2O_{12}(COO)_{16}]$. Each of them is connected to 16 terephthalic acid (BDC) linkers to form a 3D framework. There is a tetragonal cage with a diameter of 9 Å and an octahedral cage with a diameter of 11 Å. Two types of symmetrically independent BDC linkers are observed. Topologically, a pair of parallel BDC linkers within the equatorial plane is regarded as one edge. Therefore, eight equatorial BDC linkers are simplified into four edges. On the other hand, eight BDC linkers above and below the equatorial plane are simplified into eight edges. As a result, the $[Ti_8Zr_2O_{12}(COO)_{16}]$ cluster acts as a 12-connected node, affording a network with **fcu** topology. Because of the new cluster, PCN-415 has outstanding photoactive property. The optical band gap was calculated to be 3.3 eV based on the UV-Vis spectrum, and can be further turned by amine-functionalization of BDC linkers. In combination with the high porosity (BET surface area of 1050 $m^2 \cdot g^{-1}$), and excellent chemical stability (in pH range of 0–13), PCN-415 provides ideal platforms for the design of MOF photocatalysts. Among all the tested materials, amine-functionalized PCN-415-NH_2 shows the highest activity with an H_2 evolution rate of 594 μmol g^{-1} h^{-1}. These results highlight the effect of new clusters in PCN-415 as photoactive species for photochemical hydrogen production as well as *c*RED method as a powerful tool for the structural study of beam sensitive materials.



References:

[1] Wan, W.; Sun, J.; Su, J.; Hovmöller, S.; Zou, X. J. Appl. Crystallogr., 2013, 46, 1863–1873.
[2] Zhang, D.; Oleynikov, P.; Hovmöller, S.; Zou, X. Z. Kristallogr., 2010, 225, 94–102.
[3] Yuan, S.; Qin, J.; Xu, H.; Su, J.; Rossi, D.; Chen, Y.; Zhang, L.; Lollar, C.; Wang, Q.; Jiang, H.; Son. D.; Xu, H.; Huang, Z., Zou X.; and Zhou, H. ACS Cent Sci., 2018, 4, 105–111.

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