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Top-down delamination of the two-dimensional metal–organic frameworks

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Porous materials are used in a wide range of applications. In the last few decades, metal-organic frameworks (MOFs), porous crystalline coordination compounds allowing compositional and structural diversity beyond conventional solid-state materials, were reported to be powerful catalysts, energy storage materials, membranes or separators. Although crystallinity and modularity provides remarkable advantages, and the specific surface areas of MOFs range up to 7600 m^2 g^{-1}, the limiting pore window diameters and corresponding diffusion limitations are still an issue for application involving larger (bio)molecules. The possibility of having individual layers (cutouts) of materials would help to overcome such limitations and to achieve unsurpassed accessibility of the surface. Moreover, single-layered MOF based materials (MOFenes) would combine the peculiarity of two-dimensional matter and the versatile properties of MOFs.

In the following, amine assisted top-down approach for the synthesis of 2D MOF nanosheets is described on the model compounds $M_2(L)_2$ (M – metal, L = linker) which are based on 2D layers connected by hydrogen bonds within the bulk crystal. This method benefits from a gentle delamination process, since no mechanical stress affects the initial bulk material and directly exploits the affinity of open metal sites of the paddle wheels to the amine containing reagents, in order to break the weak interlayer interactions in the structure and to separate the stabilized single layers. The best results could be achieved using combination of surfactant-assisted synthesis of MOF (polyvinylpyrrolidone) with post-synthetic delamination with ethylamine yielding ultrathin square-shaped nanoplates with a thickness of 4–14 nm (Fig. 1).

References

[1] Kutzscher, A. Gelbert, S. Ehrling, C. Schenk, I. Senkovska and S. Kaskel, *Dalton Trans.*,46 (**2017**), 16480-16484.

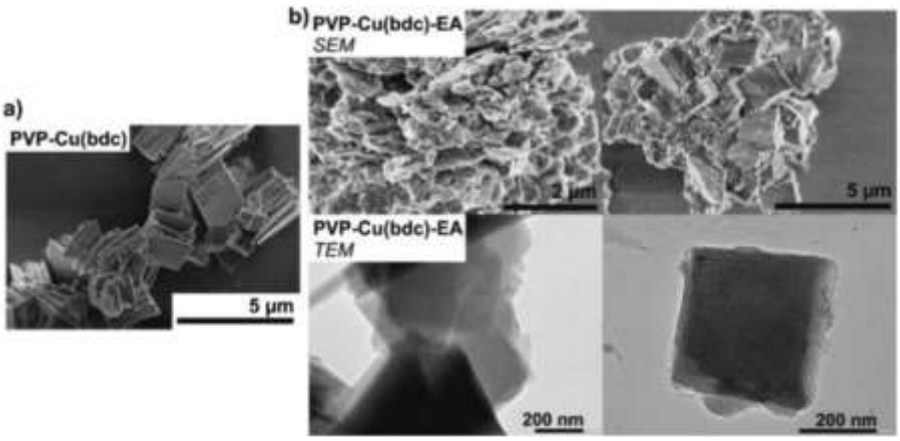

Figure 1: (a) SEM image of polyvinylpyrrolidone (PVP) derived $Cu_2(bdc)_2$ (bdc – 1,4-benzenedicarboxylate), and (b) SEM and the TEM images of delaminated PVP-$Cu_2(bdc)_2$ with ethylamine (EA).