Modulated Solvothermal Synthesis of Large (3 mm) Single Crystals of $Cu_3(BTC)_2$ Metal-Organic Framework

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Metal-organic frameworks (MOFs) are a new class of crystalline, porous materials that consist of metal units linked by organic ligands. These materials have gained huge attraction due to their ultra-high surfaces areas, large porosity, tunable framework construction, and availability for post-synthetic modification. With these advantages, MOF materials are promising candidates for applications including hydrogen storage, capture of CO_2, separations, and catalysis. However, MOF powders (μm-scale crystals) obtained via conventional methods may not be the desired configuration for some applications, and large MOF single crystals are in demand for the bulk properties yet to explore. Here, we report a new synthesis method to dramatically increase the size of $Cu_3(BTC)_2$ MOF (or HKUST-1) crystals. Taking advantage of the competition effect between acetic acid (monocarboxylic acid) and 1,3,5-benezenetricaboxylic acid (ternary linker), we were able to control the rate of homogeneous nucleation at low temperature (55°C), making heterogeneous nucleation and growth favored. Large $Cu_3(BTC)_2$ crystals (up to 1mm) were successfully obtained within 3 days of synthesis using this approach. In addition, liquid-phase epitaxial growth was achieved on MOF crystal seeds allowing for $Cu_3(BTC)_2$ crystals greater than 3mm in size to be obtained after multiple reaction sequences. Optical, SEM, and TEM images and analysis of single-crystal XRD data will be presented and discussed for these large $Cu_3(BTC)_2$ MOF crystals.