Structure-Texture-DFT Correlation in Defect-Rich UiO-66-NH_2

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Controlled defect engineering in zirconium-based metal–organic frameworks offers an effective strategy to tune crystallinity, pore architecture, and the local electrostatic environments that ultimately govern material–ion interactions. In this work, we synthesized UiO-66-NH_2 using acetic-acid-modulated solvothermal routes at 45, 70, and 120 ℃, enabling systematic control over missing-linker defect density and textural properties.

Powder X-ray diffraction confirms that the cubic UiO-66 topology is preserved across the series, while coherent domain sizes decrease from ~35 to ~24 nm with increasing synthesis temperature, consistent with faster nucleation under elevated thermal conditions. SEM observations reveal sub-100 nm particles composed of aggregated crystalline domains, with progressively smaller and more uniform particles obtained at higher temperatures.

Nitrogen physisorption show a clear structure–texture relationship. The sample synthesized at 70 ℃ exhibits the highest BET surface area (1004 $m^2\ g^{-1}$) and well-preserved microporosity ($V_{mi} \approx$ 0.4 $cm^3\ g^{-1}$), suggesting an optimal balance between defect generation and framework integrity. In contrast, synthesis at 120 ℃ leads to pronounced mesoporosity ($V_{tot} \approx$ 1.50 $cm_3\ g^{-1}$; $D_{av} \approx$ 8 nm) and a reduced micropore fraction, indicating partial over-disruption of the framework. FT-IR spectroscopy confirms proper linker coordination and reveals temperature-dependent signatures associated with defect formation and activation.

To gain deeper insight into adsorption behavior, periodic DFT calculations were performed to map electrostatic potential distributions within the octahedral and tetrahedral cavities. The results identify electrophilic regions along linker edges and near μ_3-OH groups. These intrinsic electrostatic features, together with defect-exposed Zr–OH sites, provide a mechanistic explanation for the inner-sphere binding motifs observed experimentally by post-adsorption FT-IR analysis.

As a functional validation under realistic conditions, the defect-optimized UiO-66-NH_2(70) demonstrates rapid arsenic removal from naturally contaminated groundwater at near-neutral pH.

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