

Electronic Supporting Information

Probing the hydrolytic degradation of UF₄ in humid air

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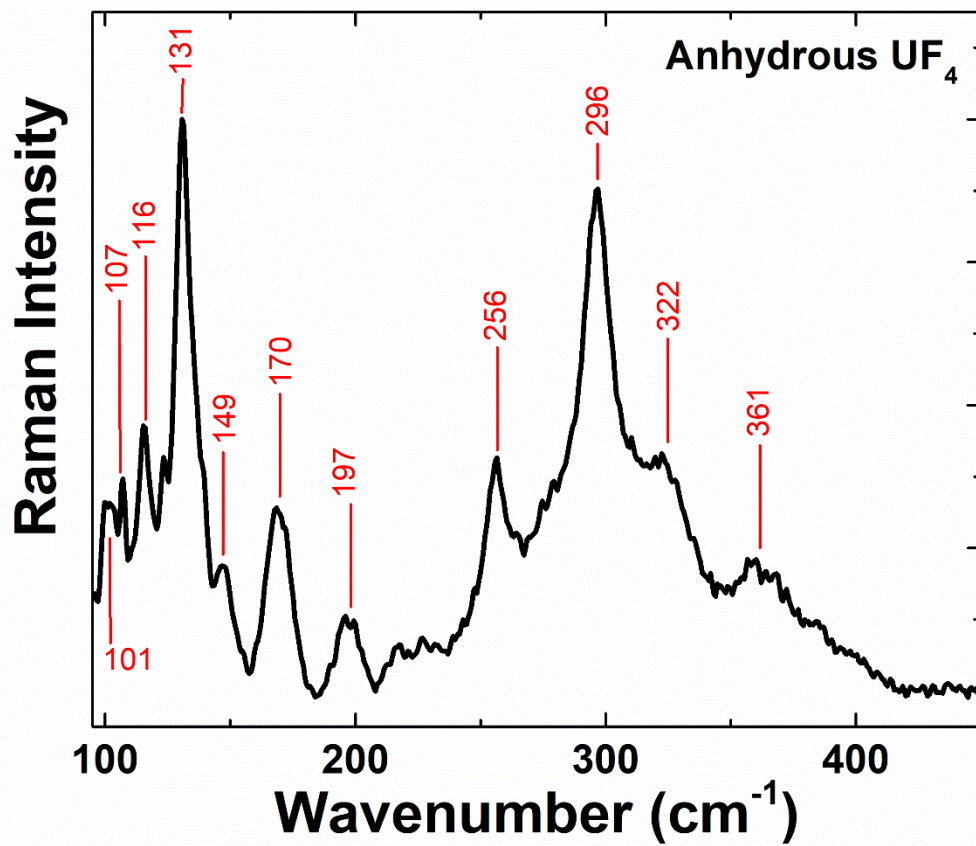


Figure S1. Raman spectrum of commercially-purchased UF₄ taken upon receipt.

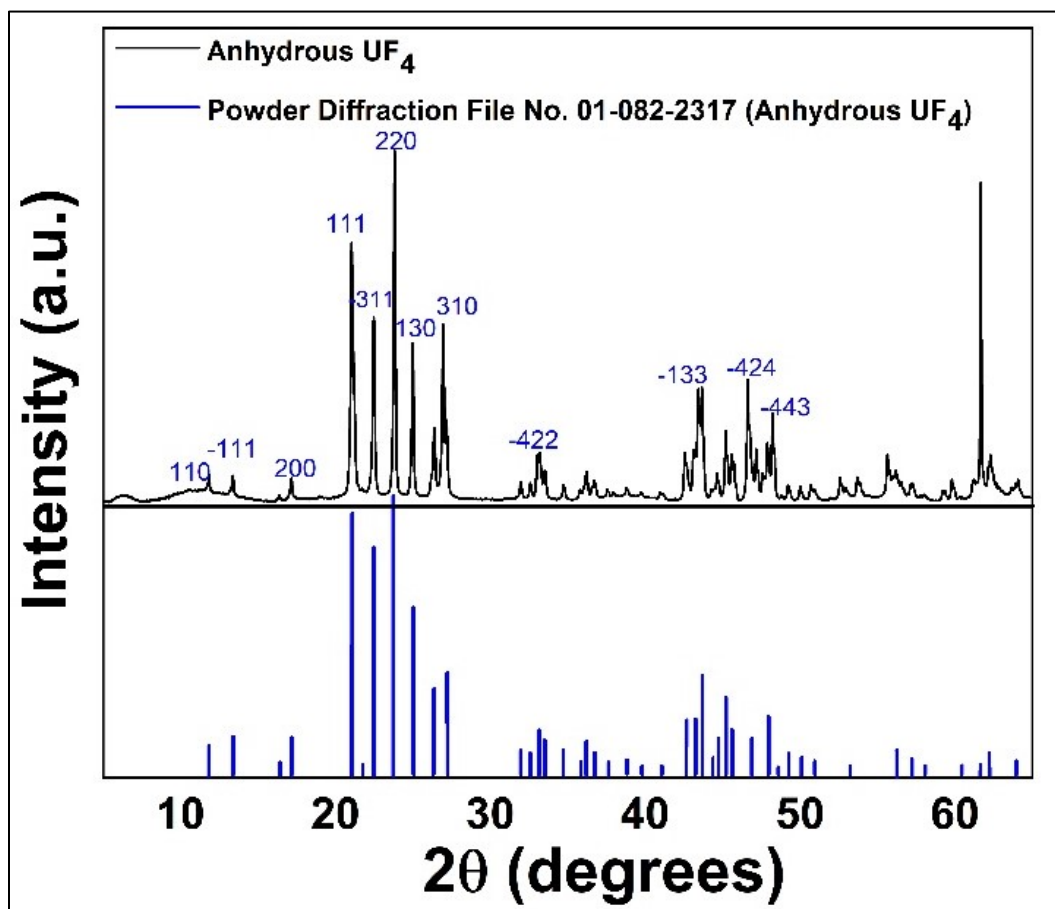


Figure S2. TOP: pXRD pattern of commercially purchased UF₄ obtained upon receipt (Note: The intense reflection at ~62° is an errant reflection from the sample holder). Miller Indices labels are shown above several of the more intense diffraction lines. Bottom: Database powder diffraction file for anhydrous UF₄.¹

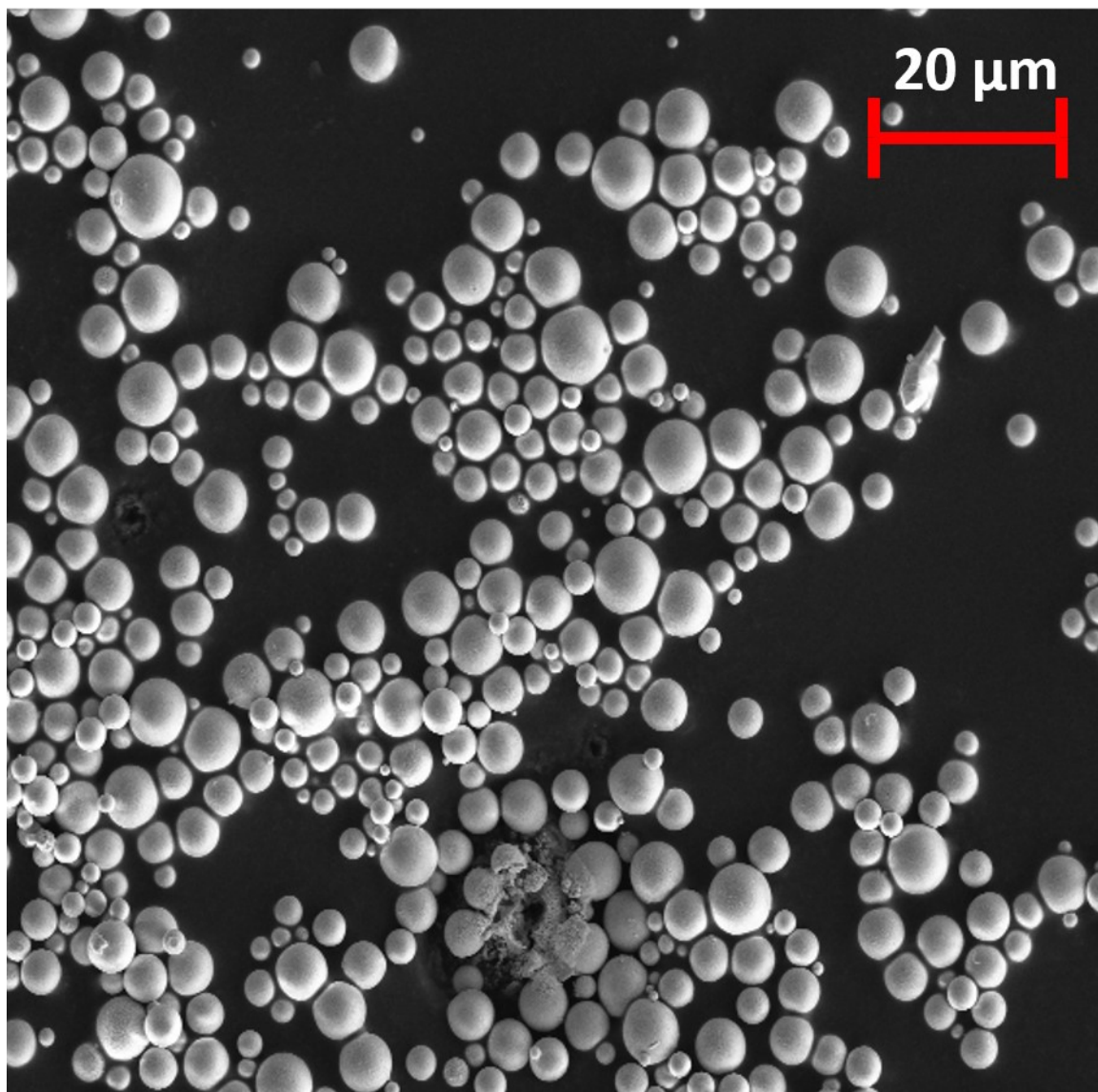


Figure S3. SEM image of commercially purchased UF_4 obtained upon receipt.

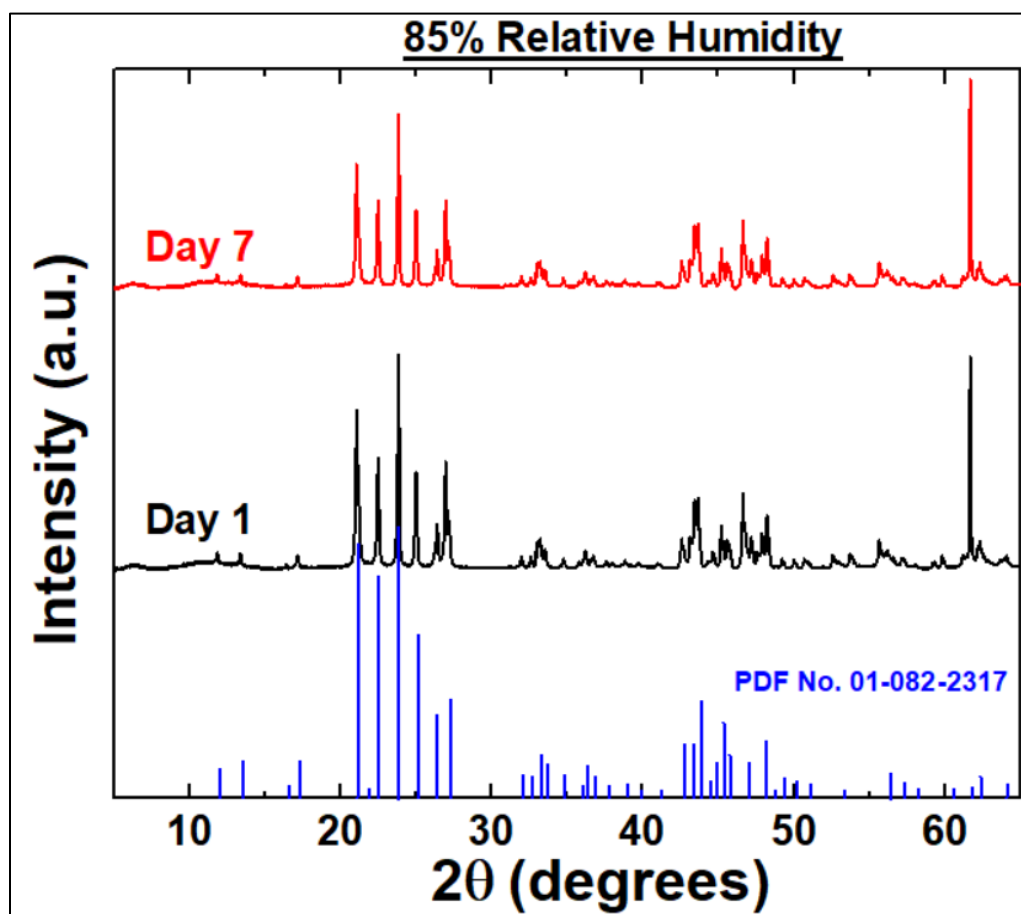


Figure S4. Bottom: Database powder diffraction file for anhydrous UF₄.¹ Middle: pXRD pattern of commercially purchased UF₄ after 1 day of exposure to 85% RH (Note: The intense reflections at 62° is an errant reflection from the sample holder). Top: pXRD pattern of commercially purchased UF₄ after 7 days of exposure to 85% RH (Note: The intense reflections at 62° is an errant reflection from the sample holder).

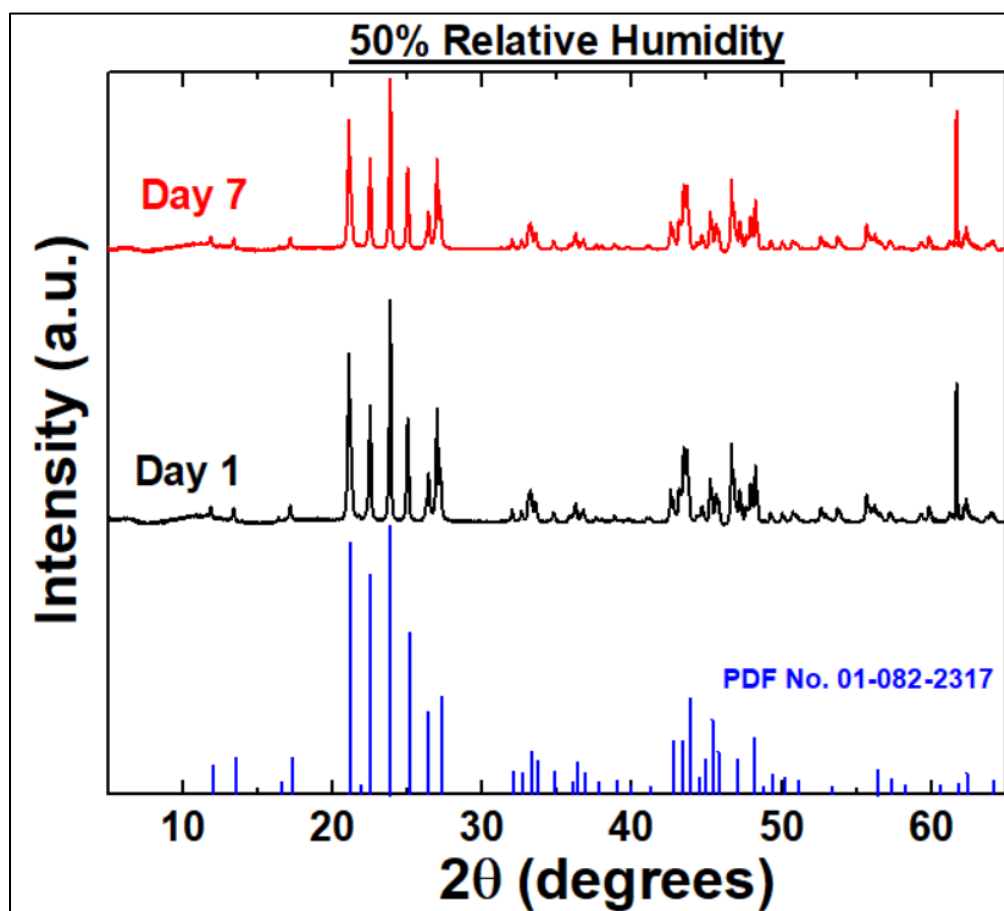


Figure S5. Bottom: Database powder diffraction file for anhydrous UF_4 .¹ Middle: pXRD pattern of commercially purchased UF_4 after 1 day of exposure to 50% RH (Note: The intense reflections at 62° is an errant reflection from the sample holder). Top: pXRD pattern of commercially purchased UF_4 after 7 days of exposure to 50% RH (Note: The intense reflections at 62° is an errant reflection from the sample holder).

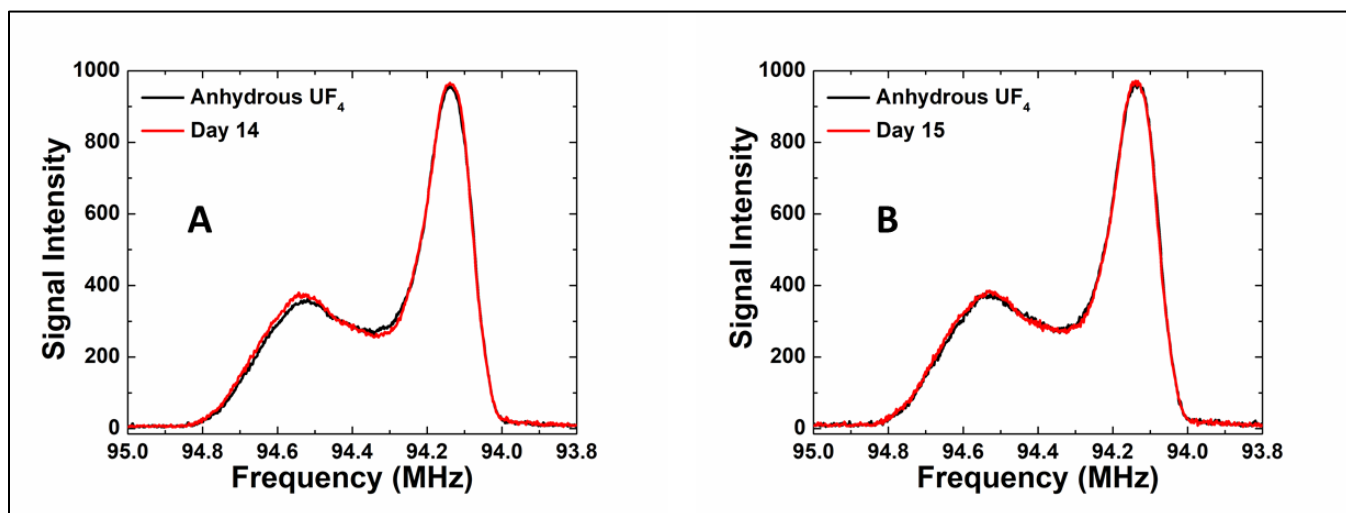


Figure S6. ^{19}F NMR spectra of UF_4 before (black trace) and after (red trace) exposure to air at 85% RH. These spectra resulted from the sum of 11 sub-spectra using an automated acquisition method a) with a wait time of 4 ms between scans; b) with a wait time of 4 s between scans. The total number of scans for each sub-spectrum was a) 2048 and b) 1024.

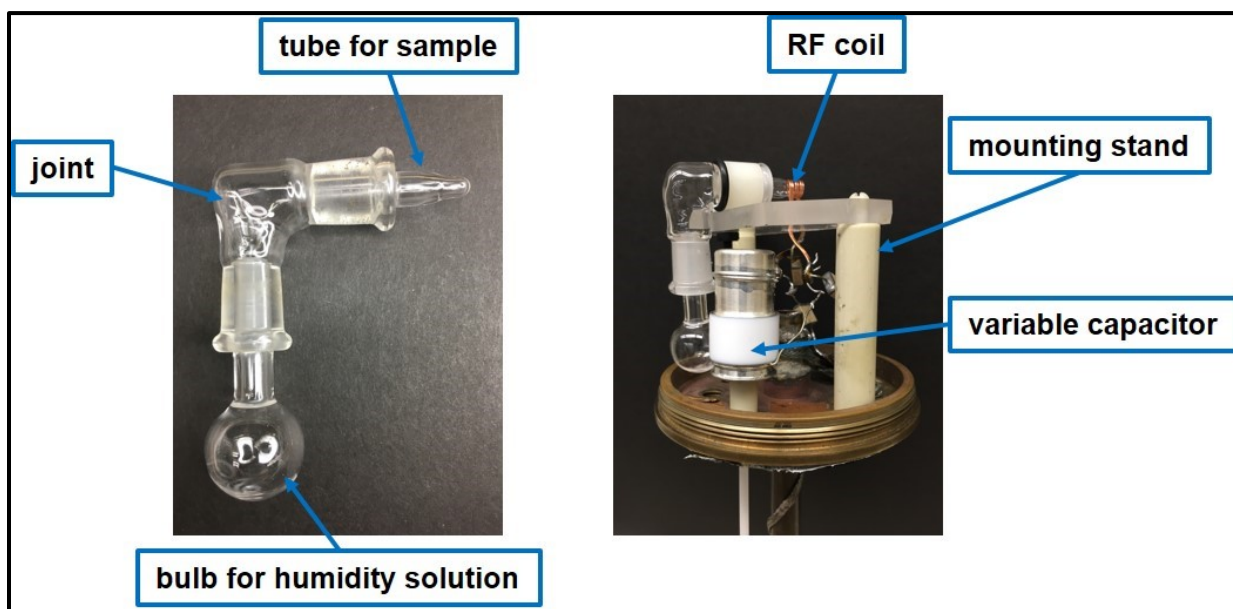


Figure S7. Left: Custom three-piece glassware for constant humidity experiments. Right: incorporation of custom glassware into custom NMR probe head.

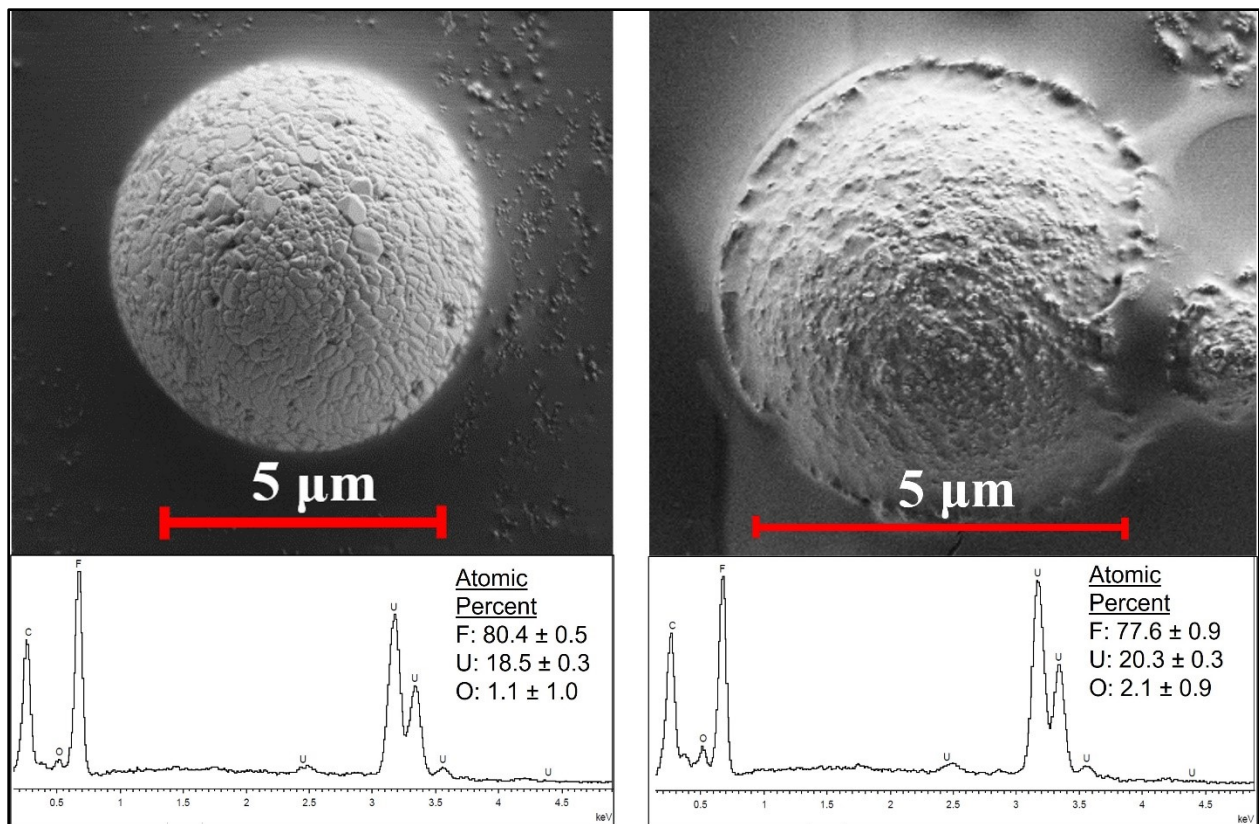


Figure S8. Left: Representative UF_4 sample after exposure to air at 85% RH for 13 days and corresponding EDS spectrum. Right: Representative UF_4 sample after exposure to air at 50% RH for 11 days.

Table S1. Previously published Raman resonance bands for UF₄ and several uranium-bearing compounds.

Formula	Laser (nm)	Raman shift bands (cm ⁻¹)	SI Reference
Anhydrous UF ₄	785	59.4, 66.8, 78.9, 91.0, 101.3, 107.2, 115.9, 131.4, 148.5, 170.4, 197.3, 255.8, 296.1, 322.4, 360.8, 603.6	2
UF ₄ (H ₂ O) _{2.5}	785	82, 95, 106, 118, 156, 185, 235, 257, 282, 320, 333, 340, 364, 427, 3283, 3390, 3481, 3535	3
Hydrated UO ₂ F ₂	514	867, 174	4
Anhydrous UO ₂ F ₂	514	915, 442, 180	4
UO ₂	514	445	5
UO ₂	514	448, 630, 1104, 1152	6
UO ₂	514	445	7
UO ₂	514	232, 445, 1151	8
UO ₂	488	450, 585, 1595	9
UO ₂	488	448, 585, 920, 1150	9
UO ₂	785	445, 583, 640, 1160, 1360	9
U ₄ O ₉	---	210, 465	10
U ₃ O ₇	---	210, 465	10
U ₃ O ₇	---	410, 445, 500	7
U ₃ O ₈	514	343, 351, 412, 483, 738, 811	5
U ₃ O ₈	514	236, 342, 408, 480, 752, 798	7
U ₃ O ₈	488	235, 340, 405, 480, 640, 745, 800, 885	9
U ₃ O ₈	514	236, 342, 408, 480, 638, 752, 798, 888	11
γ-UO ₃	514	768, 846	5
UO ₂ (OH) ₂	---	838, 855	12
Schoepite	1064	843, 845	13

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