

## Electronic Supplementary Information

### Large-scale solution synthesis of $\alpha$ - $\text{AlF}_3 \cdot 3\text{H}_2\text{O}$ nanorods under low supersaturation conditions and their conversion to porous $\beta$ - $\text{AlF}_3$ nanorods

Marc Estruga, Fei Meng, Linsen Li, Lianyi Chen, Xiaochun Li and Song Jin\*

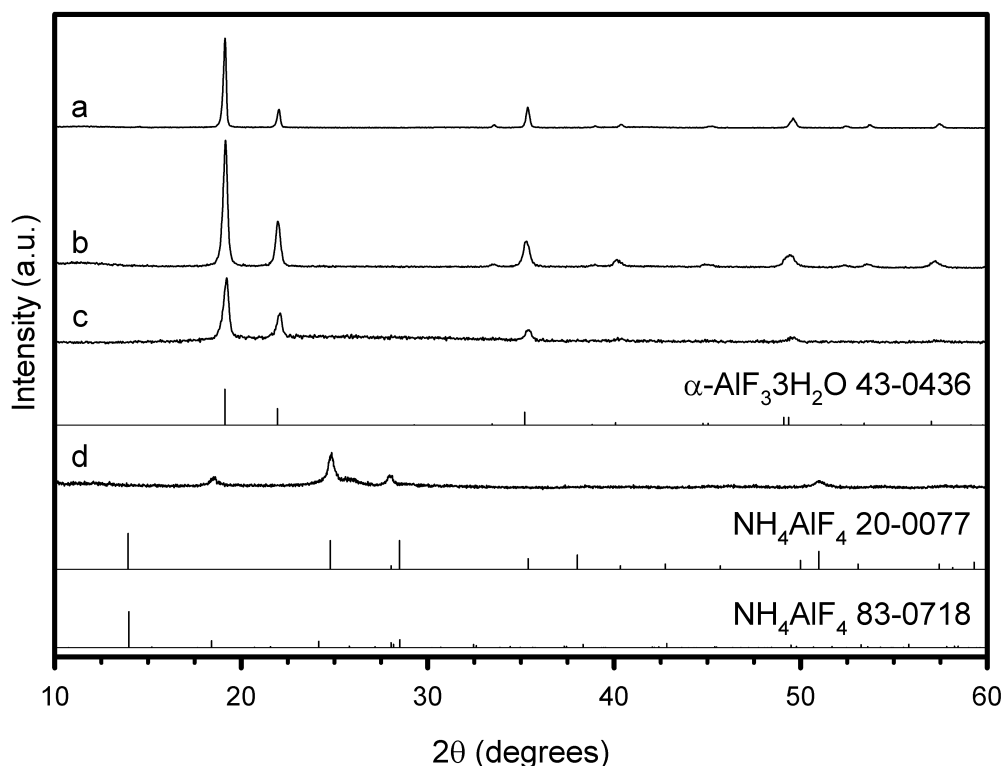


Fig S1. PXRD of additional samples in Figure 2: Sample 2 (a), Sample 5 (b), Sample 6 (c) and Sample 7 (d). Standard patterns of  $\alpha$ - $\text{AlF}_3 \cdot 3\text{H}_2\text{O}$  (JCPDS #43-0436), and  $\text{NH}_4\text{AlF}_4$  (JCPDS #20-0077 and 83-0718) are included for comparison.

At higher  $[\text{HF}]/[\text{Al}^{3+}]$  ratio (550:1, Sample 7) and also after 60 °C heating, the product is no longer  $\alpha$ - $\text{AlF}_3 \cdot 3\text{H}_2\text{O}$  (Fig. S1 plot d). By comparing the experimental pattern to the known phases in the Al-F systems, it appears that a mixture of two  $\text{NH}_4\text{AlF}_4$  phases was obtained. We suspect that the hydronium analogue, that is,  $(\text{H}_3\text{O})\text{AlF}_4$ , is the product that precipitates out after heating the solution to 60 °C for 24 h. The ammonium compounds have a layered structure with cations occupying the interstices between  $\text{AlF}_6$  octahedra chain layers,<sup>1</sup> so it is reasonable that the hydronium ions can substitute the  $\text{NH}_4^+$  ions at the interlayer positions, which leads to isostructural phases. This would explain the similarity of the PXRD patterns.

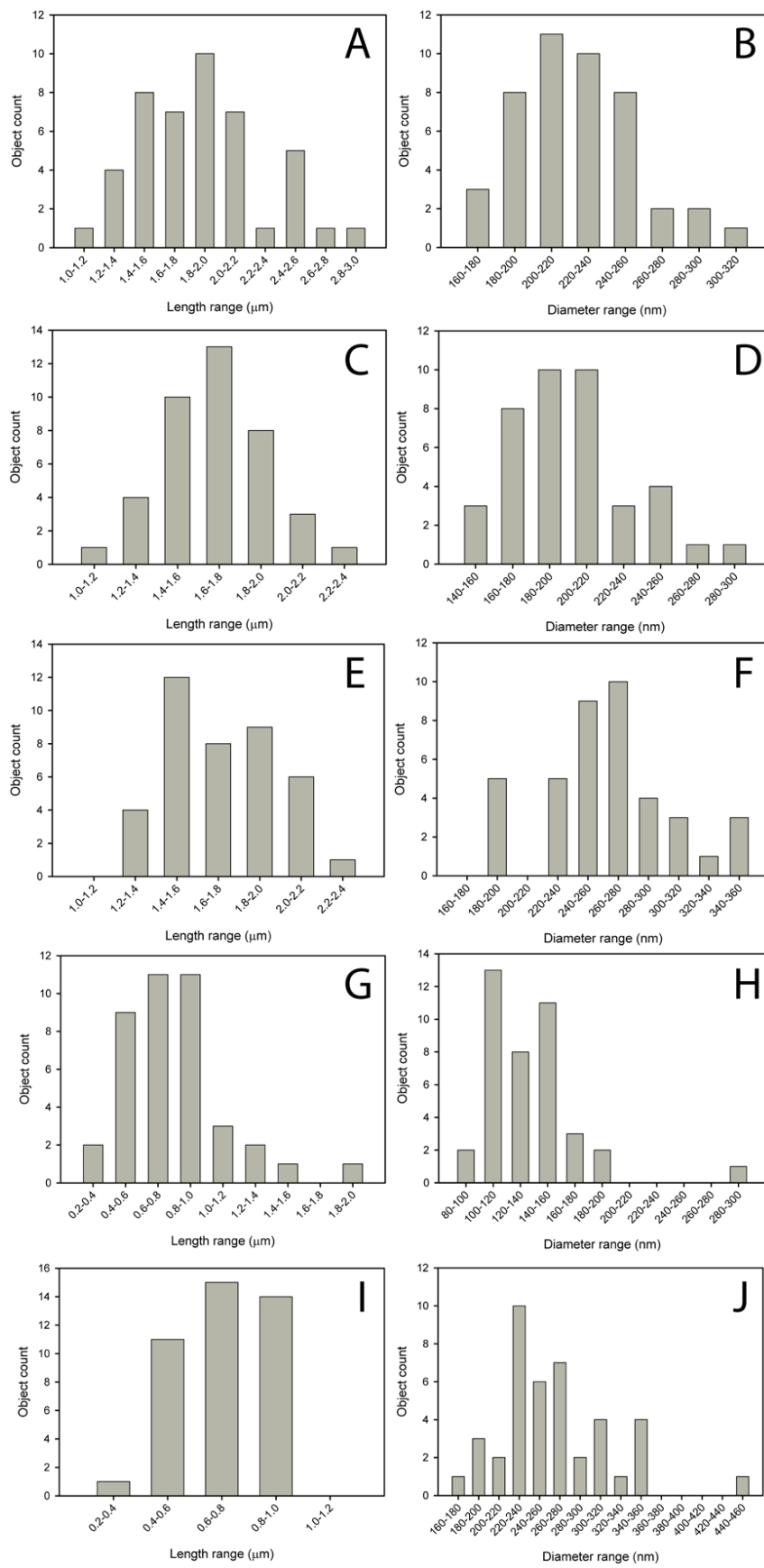


Fig S2. Size distribution survey of the as-prepared  $\alpha\text{-AlF}_3 \cdot 3\text{H}_2\text{O}$  nanomaterials: Sample 1 (A, B), Sample 2 (C, D), Sample 3 (E, F), Sample 4 (G, H), Sample 5 (I, J).

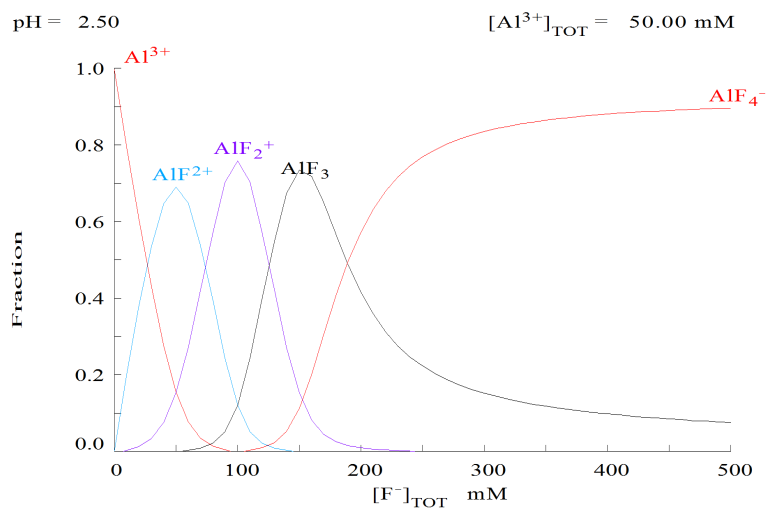


Fig. S3. Simulated speciation distribution of sample 6.

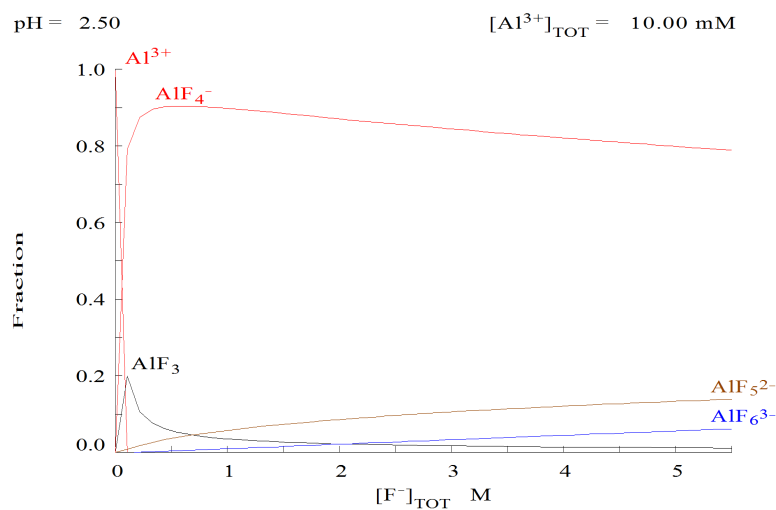


Fig. S4. Simulated speciation distribution of sample 7.

## References

1. N. Herron, D. L. Thorn, R. L. Harlow, G. A. Jones, J. B. Parise, J. A. Fernandez-Baca and T. Vogt, *Chem. Mater.*, 1995, **7**, 75-83.