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Alumina nanoparticles generated from aqueous solutions of a "flat" aluminum-13 cluster.

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Supporting Information - Table of Contents

1. Experimental Details

1.1 General Information

Dynamic light scattering (DLS) was performed on a Wyatt Technologies Mobiuζ DLS-PALS using standard cumulant analysis methods. Samples were sonicated for 1 minute prior to filtration using 0.2-micron PTFE filter. The filtrate was immediately transferred to a quartz cuvette for analysis (t < 1 minute) using an incident wavelength of 532 nm at 20 °C. Dynamics Software 7.6.0.48 was used to average 20 measurements with an acquisition time of 5 seconds. This process was performed six times for each sample. Sizes and polydispersities presented in this manuscript are an average of all runs, and both the Cumulant and Regularization method within the Dynamics software package provided estimates of speciation percentages.

Elemental analysis by X-ray photoelectron spectroscopy (XPS) was performed on a Thermo Scientific ESCALAB 250 spectrometer using a monochromated Al Kα X-ray source (150 W, 20 eV pass energy, 500 µm spot size). Peak fitting was done with ThermoScientific Avantage 4.75 software using smart background subtraction. Isolated solid particulate was deposited onto conductive carbon tape, and measurements were averaged across three spots. Spectra were referenced to the C 1s hydrocarbon peak at 284.8 eV present from the conductive carbon tape. Infrared spectroscopy was performed on a Thermo Scientific Nicolet 6700 FTIR spectrometer averaging 64 scans per sample. Imaging by scanning electron microscopy was performed on a ThermoFisher Helios Hydra Plasma FIB.

1.2 Standard preparation of f-Al_{13} precursor solutions

Solutions of the flat-Al_{13} cluster $[Al_{13}(\mu\text{-}OH)_{24}(H_2O)_{24}](NO_3)_{15}$ were synthesized using previously reported literature methods.[1] In this facile mineral dissolution method, $Al(OH)_3$ (gibbsite, sourced from Sigma-Aldrich) was suspended in nanopure water (ρ=18.2 MΩ cm) under rapid stirring. Then, concentrated HNO_3 (sourced from Fisher Chemicals) was added to achieve a $(NO_3)^-$:Al^+ molar ratio of 15:13. The solution was then diluted with nanopure water to achieve a target concentration of 1 M [Al^+]. The reaction mixture was raised to 60 °C and allowed to stir for 24 hours. This results in an opaque white solution, which upon dilution and/or filtering takes on a blueish tinge.

1.3 Preparation of f-Al_{13} precursor solutions through "hot injection" method

For the "hot injection" method, adapted from the literature,[2] a dilute solution of nitric acid was heated to the target reaction temperature of 60 °C, followed by addition of a slurry of aluminum hydroxide, or the slow addition of the solid precursor to reduce pouring errors. The reaction was run for 24 hours measured from the initial addition of aluminum hydroxide.

1.4 Preparation of f-Al_{13} precursor solutions through "acid correction" method

The "acid correction" method involved the addition of extra nitric acid after the completion of the standard reaction. Following the overnight reaction period, the pH of the solution at 60 °C fell between the reported value for the f-Al13 (2.8-3.2). However, as the solution was allowed to cool to room temperature, the pH increased 3.9. To correct for this change, concentrated HNO_3 was added dropwise until the solution fell with the specified pH range. In general, this was achieved after the addition of 2-5 mL depending on the scale of the reaction. These additions represented a negligible change in the final concentration of the solutions, as the solutions were prepared in volumes greater than 100 mL.

1.5 Separation and calcination of solid particulate

Solids were isolated from the supernatant solution by centrifuge in an Argos Technologies C1000 FlexiFuge mini centrifuge at 6000 RPMs for 20 minutes. The supernatant was decanted or pipetted off, and samples were allowed to air dry. Samples set to be calcined were heated in a Thermo Scientific LBM Moldatherm 5.3L box oven using cleaned ceramic crucibles with a ramp rate of 12.5 °C/min. After the temperature ramp, samples were held at 600 °C (for gamma phase) or 1050 °C (for alpha phase) for 2.5 hours.

1.6 Key synthetic references

1 B. L. Fulton, C. K. Perkins, R. H. Mansergh, M. A. Jenkins, V. Gouliouk, M. N. Jr. Jackson, J. C. Ramos, N. M. Rogovoy, M. T. Gutierrez-Higgins, S. W. Boettcher, J. F. Jr. Conley, D. A. Keszler, J. E. Hutchison and D. W. Johnson, *Chem. Mater.*, 2017, **29**, 7760–7765.

2 E. Groeneveld and C. de Mello Donegá, in *Nanoparticles: Workhorses of Nanoscience*, ed. C. de Mello Donegá, Springer, Berlin, Heidelberg, 2014, pp. 145–189.

2. X-Ray photoelectron spectroscopy (XPS) data

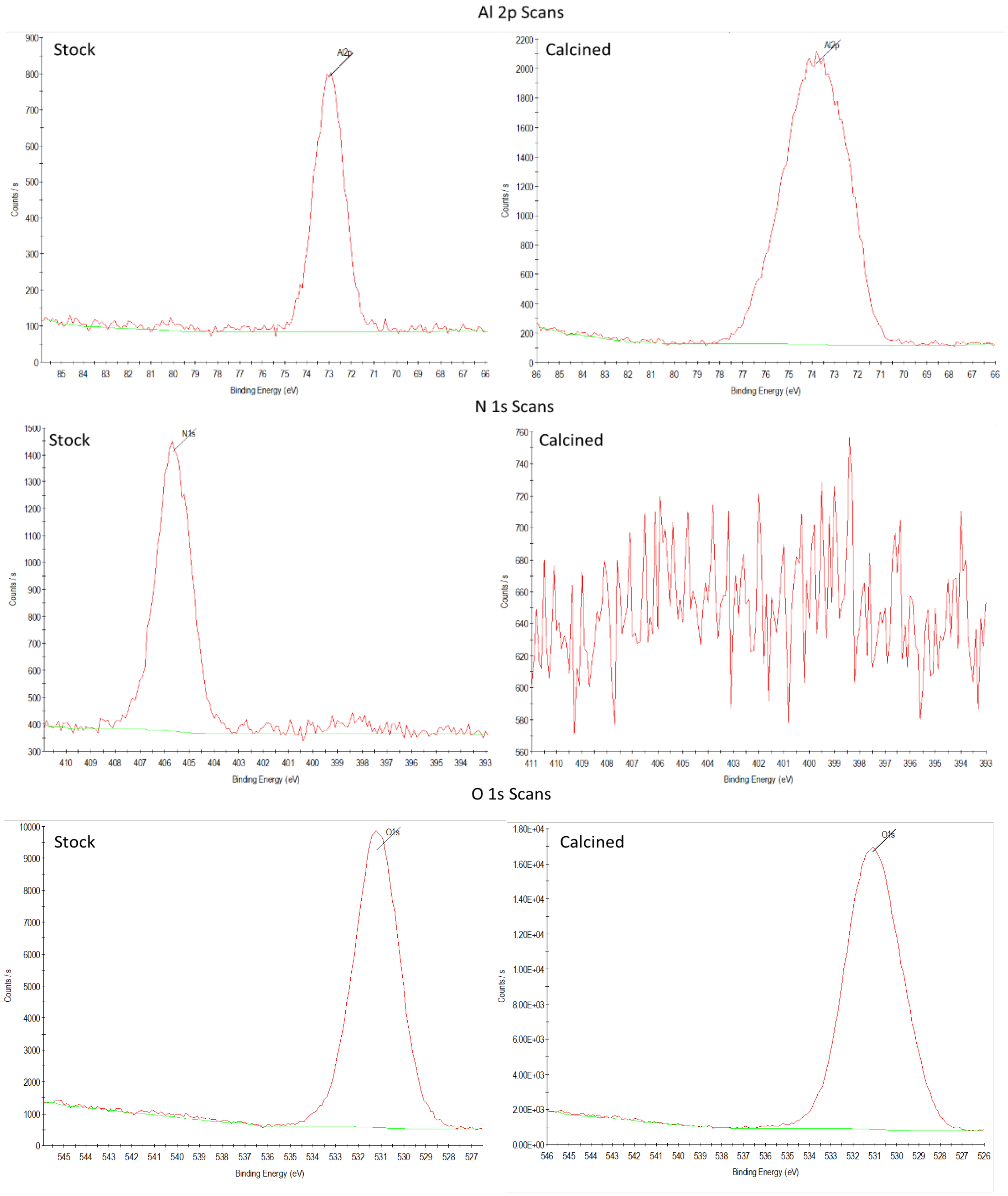

Figure S1: XPS single element high-resolution plots of isolated solid particulate. Elemental plots of the stock NPs, and NPs calcined at 1050 °C for 2.5 hours, are shown for comparison. Importantly, the N 1s plots show a large peak in the stock particulate from the nitrate counterions, which is completely gone in the calcined sample. The elemental Al:N ratio in the stock sample aligns with the f-Al_{13} cluster (13:15), and the Al:O ratio in the calcined sample matches Al_2O_3 (2:3).

3. Dynamic light scattering (DLS) data

Table S1: The raw data for each measured DLS method reported in this paper is included below. The averages of each method are reported in the main text in table 1. Each preparation method listed below is referenced to its relevant preparation section above.

Method	**Run number**	**Radius (nm)**	**Polydispersity index**
Standard Prep (SI 1.2)	1	52.1	0.206
	2	55.9	0.214
	3	56.95	0.208
	4	57.25	0.210
	5	57.0	0.208
	6	57.25	0.204
Hot injection (SI 1.3)	1	96.15	0.183
	2	105.05	0.184
	3	108.85	0.180
	4	110	0.192
	5	111.2	0.190
	6	111.2	0.180
Acid Correction (SI 1.4)	1	58.95	0.221
	2	63.35	0.224
	3	64.85	0.227
	4	65.3	0.229
	5	65.45	0.229
	6	65.7	0.228