

Room-Temperature Liquid-Phase Synthesis of Aluminium Nanoparticles

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– Electronic Supporting Information –

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1. Analytical Equipment

Transmission electron microscopy (TEM). TEM and high-resolution transmission electron microscopy (HR)TEM were conducted with a FEI Tecnai Osiris microscope (FEI, USA) at 200 keV electron energy, equipped with a Super-X EDXS system comprising four silicon drift detectors. TEM samples of the Al(0) nanoparticles were prepared by evaporating THF suspensions on amorphous carbon (Lacey-) films mounted on 400 μm mesh Cu grids (Ted Pella Inc.). This deposition was performed under dry argon atmosphere in a glove box. Immediately after sample preparation, the samples were slowly heated to 130 °C under vacuum to remove surface adhered volatiles (e.g. solvent). Thereafter, the grids were transferred with a suitable vacuum/inert gas transfer module into the transmission electron microscope without any contact to air. Average particle diameters were calculated by statistical evaluation of at least 100 nanoparticles (ImageJ 1.48v). HRTEM images were evaluated by calculating their two-dimensional Fourier transform, which yields information on the crystal structure (lattice parameters and crystal symmetry) of single nanoparticles. Crystal structure analyses were performed by comparing experimental Fourier-transform patterns and calculated diffraction patterns, where the latter were obtained by using the Jems (Java version of the electron microscopy simulation) software.^{S1}

Centrifugation. All centrifugation of Al(0) nanoparticles was performed with a high-speed refrigerated centrifuge Sigma 3-30KS. To guarantee inert conditions (argon), the centrifuge was placed in a glove box. Tubes with a volume of 30 mL were used and allow a maximum speed of 30.000 rpm relating to about 65.000 \times g.

X-ray powder diffraction (XRD) was conducted on a Stadi-P diffractometer (Stoe, Germany) with Ge-monochromatized Cu-K_a radiation. Powder samples deposited in sealed glass capillaries with a diameter of 0.3 mm (Hilgenberg, Germany).

Thermogravimetry (TG) was performed with a STA409C device (Netzsch, Germany). All measurements were performed in air. Powder samples were heated to 1100 °C with a heating rate of 5 K min⁻¹ (20 mg, corundum crucibles).

Elemental analysis (EA, C/H/N/S analysis) was performed via thermal combustion with an Elementar Vario Microcube device (Elementar, Germany) at a temperature of about 1100 °C.

Fourier-transformed infrared (FT-IR) spectroscopy. FT-IR spectra were recorded on a Vertex 70 FT-IR spectrometer from Bruker Optics. Accordingly, the transmittance of pellets consisting of 300 mg of dried KBr and 1.0 mg of the respective sample was measured.

Ultraviolet-visible (UV-VIS) spectroscopy of Al(0) nanoparticles suspended in THF was performed on a Shimadzu UV-2700 spectrometer, equipped with an integrating sphere, in a wavelength interval of 250-800 nm. The suspensions were filled in gas-tight quartz cuvettes in a glovebox under argon.

2. Starting Materials and Recipe of Syntheses

Starting Materials. All experiments and purification procedures were performed under inert gas (argon), using standard Schlenk techniques or glove boxes. This also includes all centrifugation and washing procedures. Toluene (Tol, Merck, 99%) and THF (Sigma-Aldrich, 99%) were distilled over sodium with benzophenone as indicator. N,N,N',N'-tetramethylethylenediamin (TMEDA, Sigma-Aldrich, 99%) was dried over CaH₂ and freshly distilled. AlBr₃ (abcr, 99%), lithium (Sigma-Aldrich, 99%), and naphthalene (Sigma-Aldrich, 99%) were used as purchased.

Preparation of [LiNaph] solution. 42 mg (6 mmol) of lithium were added to a solution of 400 mg (3.1 mmol) of naphthalene in 80 mL of Tol. 1 mL (6.6 mmol) of TMEDA were added to the solution with intense stirring. Here, TMEDA is required to make [LiNaph] soluble in Tol. Moreover, it needs to be noticed that glass-covered stirring bars need to be used since teflon-covered stirring bars react with [LiNaph]). The formation of [LiNaph] was visibly indicated by the formation of a deep purple solution after addition of lithium. The solution was stirred for 2 days to guarantee complete dissolution of all lithium prior use.

Synthesis of Al(0) nanoparticles. 500 mg (1.9 mmol) of AlBr₃ were dissolved in 20 mL of Tol to form a yellowish solution. 300 μ L (2.0 mmol) of TMEDA were injected with intense stirring, which resulted in the formation of a colourless suspension. Thereafter, the aforementioned [LiNaph] solution was injected and instantaneously lead to a black suspension. After centrifugation (20,000 \times g), the Al(0) nanoparticles were resuspended/centrifuged in/from THF or pyridine to remove remaining starting materials and salts. The as-prepared Al(0)

nanoparticles were redispersed in THF or dried in vacuum to obtain a dark grey powder samples.

3. Characterization of $\text{AlBr}_3(\text{TMEDA})$ Intermediate

In the synthesis of the $\text{Al}(0)$ nanoparticles (*see main paper: Figure 1*), $\text{AlBr}_3(\text{TMEDA})$ was formed as an insoluble intermediate in toluene upon addition of N,N,N',N' -tetramethylethylenediamin (TMEDA) to a solution of AlBr_3 in toluene. This $\text{AlBr}_3(\text{TMEDA})$ intermediate already consisted of nanoparticles and formed colloiddally highly stable suspensions (*see main paper: Figure 1*). Similar to the $\text{Al}(0)$ nanoparticles, the size of the intermediate nanoparticles was determined via electron microscopy (Figure S1a). According to bright-field scanning transmission electron microscopy (BF-STEM), spherical non-agglomerated nanoparticles were obtained with a mean diameter of 9.0 ± 3.1 nm (Figure S1b, according to statistical evaluation of >150 nanoparticles).

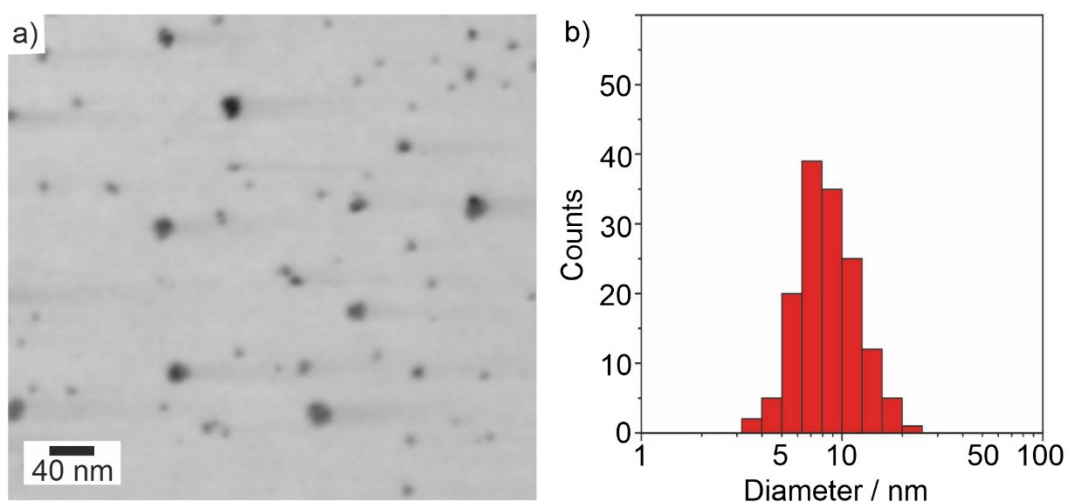


Figure S1. Electron microscopy of the $\text{AlBr}_3(\text{TMEDA})$ intermediate nanoparticles: (a) BF-STEM overview image, (b) size distribution based on a statistical evaluation of >150 nanoparticles on STEM images.

XRD indicates the $\text{AlBr}_3(\text{TMEDA})$ intermediate to be crystalline (Figure S2). High-intensity Bragg peaks below 20 degree of two-theta and the great number of Bragg peaks indicate a unit cell with great lattice axis (>150 pm) and low lattice symmetry (triclinic or monoclinic). Data related to powder diffraction data or single-crystal structure analysis that could be used as a reference are not available in the literature.

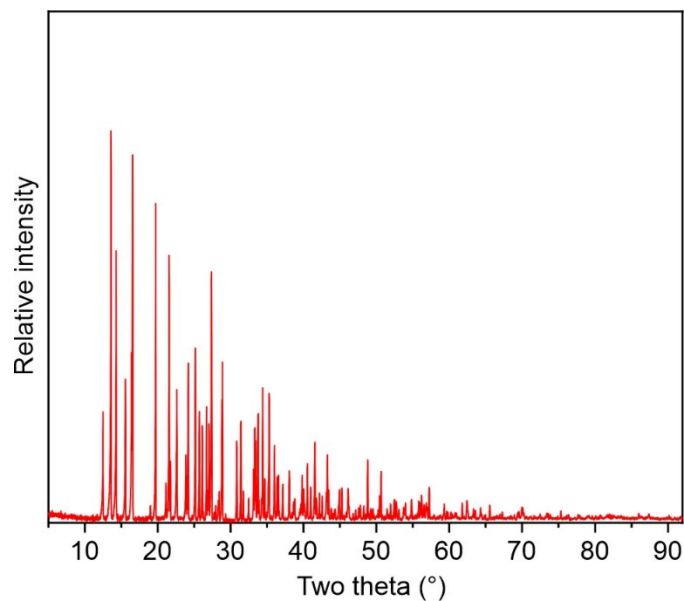


Figure S2. XRD of the $\text{AlBr}_3(\text{TMEDA})$ intermediate.

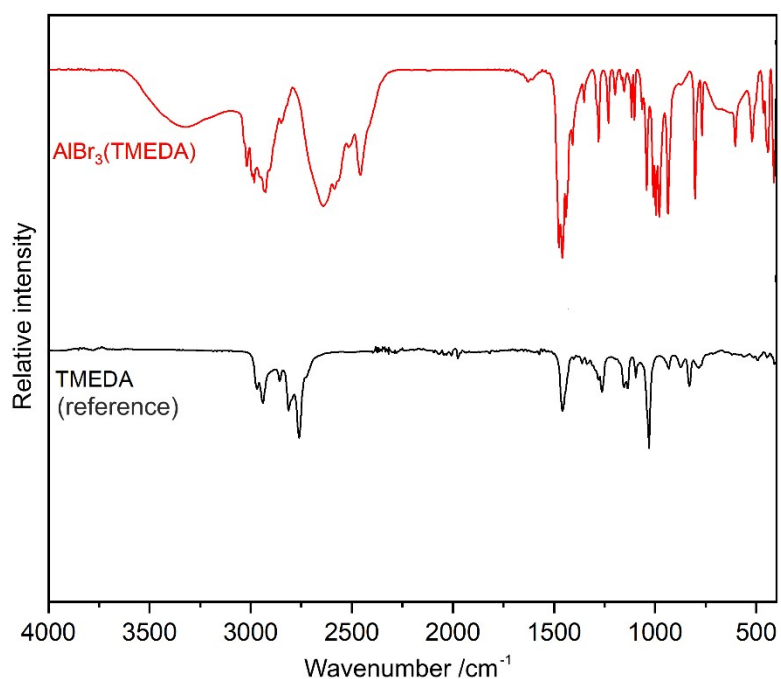
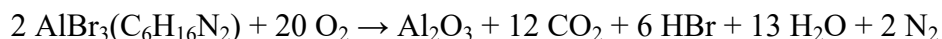


Figure S3. FT-IR spectrum of the $\text{AlBr}_3(\text{TMEDA})$ intermediate (with TMEDA as a reference).

FT-IR spectra prove the presence of TMEDA in the $\text{AlBr}_3(\text{TMEDA})$ intermediate (Figure S3). Thus, the observed vibrations are very comparable to pure TMEDA as a reference. Certain shifts of vibrations to lower wavelength in the case of the $\text{AlBr}_3(\text{TMEDA})$ intermediate indicate the coordination of the ligand to the metal center.

To determine the composition of the $\text{AlBr}_3(\text{TMEDA})$ intermediate, TG analysis was performed in air to perform a total organics combustion (Figure S4). Here, one-step

decomposition up to 750 °C was observed with a weight loss of 86%, which can be ascribed to the following reaction:



The observed weight loss is well in agreement with the expectation (87%). Al_2O_3 (observed: 14%, calculated: 13%) remains as solid residue.

EA further confirms the composition of the $\text{AlBr}_3(\text{TMEDA})$ intermediate with values of 19.5% C, 6.7% N, and 4.4% H, which are in good agreement with the calculated values (18.8% C, 7.3% N and 4.2% H).

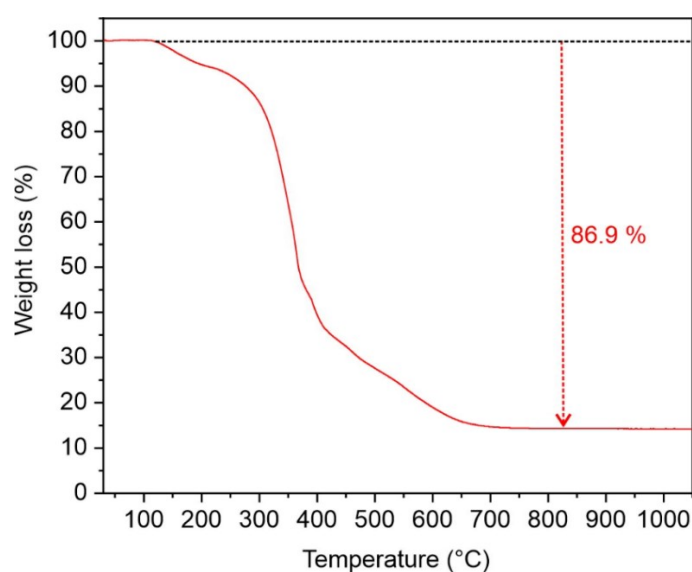


Figure S4. Thermogravimetry of the $\text{AlBr}_3(\text{TMEDA})$ precursor (atmosphere: air; heating rate: 5 K/min).

4. Characterization of Al(0) Nanoparticles

After TG analysis of THF-treated Al(0) nanoparticles with air as atmosphere, a solid remain of Al_2O_3 . The latter was identified by XRD (Figure S5).

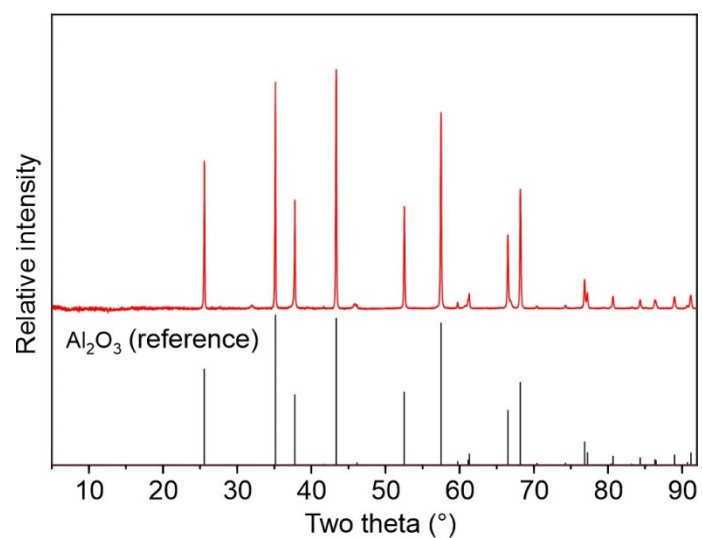


Figure S5. Thermal remnant of the TG of THF-washed Al(0) nanoparticles (bulk α - Al_2O_3 as a reference, ICDD-No. 00-046-1212).

References

(S1) <http://www.jems-saas.ch/>