Supplementary Document

Experimental Procedures:

The experiments were performed at the Hamburger Synchrotronstrahlungslabor (HASYLAB) at the Deutsches Elektronen-Synchrotron (DESY). The bending magnet based X1 beam line was used for the experiments. This beam line is optimized for X-Ray Absorption Fine-Structure Spectroscopy (XAFS). It spans an energy range of 6 - 80 keV, offering a photon flux of the order of 10^9 photons s^{-1}.

The ultrasonic spray system has been described elsewhere in detail(Allsop *et al.*, 2006). Figure 1 shows a schematic of the essential parts. Briefly, a commercial household nebulizer was used to nebulize the $InCl_3$ solution. Three solution concentrations of 50, 100 and 200 mmol/L were used for the experiments. The aerosol formed in the nebulizer chamber was extracted through a continuous N_2 flow across the upper part of the nebulizer chamber. This resulted in a continuous aerosol flow at the nebulizer exit (see movie posted in the supplementary documents section, which shows the setup in action). The N_2 flow rate was measured with a flow meter. Investigated flow rates were 1 and 1.9 L/min. The exit of the nebulizer chamber was connected to a plastic tube (1.7 cm diameter). A 1.7 cm long section of the plastic tube was partially removed to create an unobstructed path for the x-ray beam. The cutout section of the tube was protected from air turbulence by a plastic box with appropriate openings for the x-ray beam. The opposite end of the tube was connected to a scroll pump. Before entering the pump the aerosol was scrubbed from the gas flow using four wash bottles connected in series filled with water. The exit of the pump was fed into a suction hose connected to the laboratory exhaust system. The hose connecting the plastic tube end to the wash bottles was outfitted with a flow restrictor that was used to adjust the aerosol flow towards the pump in such a way that the aerosol "fog" appeared to flow straight through the cutout section with a minimum of aerosol escaping into the surrounding space. This aimed to keep the mass density of the aerosol constant within the cutout section.

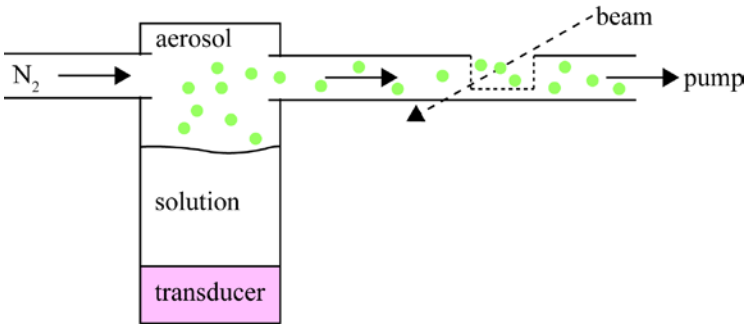

Fig.1: Schematic of the experimental set-up.

The nebulizer transducer amplitude could be adjusted on a scale from 1 to 10 (arbitrary units). The settings used for the experiments were 1, 4 and 8. These settings had a strong influence on the aerosol formation rate. In a separate supporting experiment the nebulization rates depending on gas flow and nebulizer setting were determined. Table 1 summarizes the determined values.

Once a stable flow into the exit hose was established by adjusting the flow restrictor, the x-ray absorption spectroscopy measurement was started. Due to the limited run time of the nebulizer per

solution filling and about 2 hrs time intervals between refills of the storage ring, the measurement was split up into several runs, whose data were subsequently integrated to achieve a sufficiently good signal-to-noise ratio. The low concentration of In-atoms in the spray plume made it necessary to measure the XAFS spectra in fluorescence yield mode. The used energy dispersive Ge detector (Canberra GL0110*7, Olen, Belgium) had seven individual Ge detector crystals with an active surface of 80 mm² each. The detector was read out using Canberra 2026x spectroscopy amplifiers and Canberra 8715 ADCs. The shaping time was set to 0.2 µs, allowing count rates of up to 50 kHz per pixel without significant losses due to detector dead time. The detector was mounted at 5.6 cm distance to the interaction volume in the tube cutout. It was oriented perpendicularly to the x-ray beam axis. The selected distance was chosen as a compromise between maximizing the solute In K-edge absorption related fluorescence signal, and preventing the detector from going into overflow due to the background radiation from the solvent/air matrix.

The Si 311 double crystal monochromator of the X1 beam line was used for the production of the monochromatic X-ray beam for In K-edge XAFS measurements. The 2nd crystal was detuned to 70 % of the maximum intensity at the start of each scan to suppress higher harmonics. The size of the monochromatic beam on the sample was 1*10 mm² (v*h). The incoming beam intensity was measured using a 10 cm long ionization chamber filled with Kr at 140 mbar.

Scans were made between 27.8 keV and 28.1 keV with varying step size (pre-edge: 5 eV, edge: 0.5 eV, post-edge: 1.0 eV). The accumulation time per point was 1 s. The resulting data were evaluated using the Athena program within the iXAFS package(Newville, 2011). The spectra measured on a particular sample were added up, then normalized and background removed following standard procedures.

References:

Allsop, N. A., Schonmann, A., Belaidi, A., Muffler, H. J., Mertesacker, B., Bohne, W., Strub, E., Rohrich, J., Lux-Steiner, M. C. & Fischer, C. H. (2006). Thin Solid Films **513**, 52-56.

Newville, M. (2011). *IFEFFIT: Interactive XAFS Analysis,* http://cars9.uchicago.edu/ifeffit/Ifeffit.