Beam Time Report – ID15, October 2020

Proposal Summary

Colloidal metal oxide nanocrystals (NCs) based on group 4 metals (Ti, Zr, Hf) promise to play a central role in cancer therapy, solar cells, memristors etc. However, progress is hampered by poor control over nanostructure and lack of mechanistic insight into the formation of NCs. The highest quality colloidal zirconia NCs are synthesized by the non-hydrolytic reaction between $ZrCl_4$ and $Zr(OiPr)_4$ at 340 °C. We previously characterized the core structure of the NCs using *ex situ* total scattering. We now aim at elucidating the reaction mechanism (of nucleation and growth) using a two-pronged approach. (i) We will perform *in situ* total scattering experiments to probe the zirconium-oxo species from dissolved precursors, over nuclei, to the final nanocrystals. (ii) We will measure *ex situ* aliquots, sampled from a standard lab synthesis setup. We will learn about the structure of intermediates and nuclei and about the kinetics of nucleation and growth. Using these insights, we can design novel synthetic strategies to tune the nanocrystal size and to design more complex metal oxides based on group 4.

Proposal Decision

Initially, no beam time was allocated due to insufficient beam time available. But later beam time was allotted. Due to the corona pandemic, no site entrance permit was granted during the cycle. For that reason, experiments were restricted to *ex situ* samples on reaction aliquots only. Samples were handed over to the beamline scientist at the ESRF campus.

Measurement and Data Processing

Samples were prepared by the temporal sampling (both ramp and plateau) of reaction aliquot into a 2 mm glass capillary and 3 mm NRM tube which is then sealed under argon. A total of 110 samples were measured including background and silicon standard. Calibration, correction, and integration of the raw data were carried out by Dr. Stefano Checchia. The 2 mm glass capillaries were prone to breaking and the data quality was worse most likely due to the slight differences in the capillary size and shape. Data from 3 mm NMR tubes were used for the analysis. The program xPDFsuite with PDFgetX3 was used to perform the background subtraction, further corrections, and normalization to obtain the reduced total scattering structure function *F(Q)*, and Fourier transformation to obtain the pair distribution function (PDF), *G(r)*.[1, 2] Modeling was carried out using Diffpy-CMI.[3]

Analysis and Results

Figure 1A shows the observed PDF at 100, 200, 300, 340°C and after 90 minutes at 340°C. The corresponding interatomic distances are also indicated. There is no Zr-Zr atomic distance until the reaction reaches 340°C, indicating that the crystallization has not started yet. But the PDF after 90 minutes shows a strong Zr-Zr distance corresponding to the tetragonal zirconia structure. We performed a dual-phase refinement of tetragonal zirconia and the $ZrCl_4$ by-product **(2)**, see Figure 1B. For the complex, we used the $ZrCl_4$ complex with tripropylphosphine oxide (optimized by DFT) with distances: Zr-O (2.1 Å), Zr-Cl (2.5 Å), and Zr-P (3.5 Å). An excellent fit is obtained (R_w = 0.12), showing that the DFT structure is consistent

with the PDF data. We reported these results in our latest publication (Pokratath et al., JACS Au 2022).

We are currently preparing another detailed manuscript on the analysis of the aliquots at 340 °C, over time. We refined each data point, extracting a particle size (Figure 1C). We are comparing this with SAXS data to infer the mechanism of nucleation and growth (work in progress). Using the same strategy, the nanocrystal syntheses with other precursors (e.g., $ZrBr_4$) were also modeled (Figure 1B).

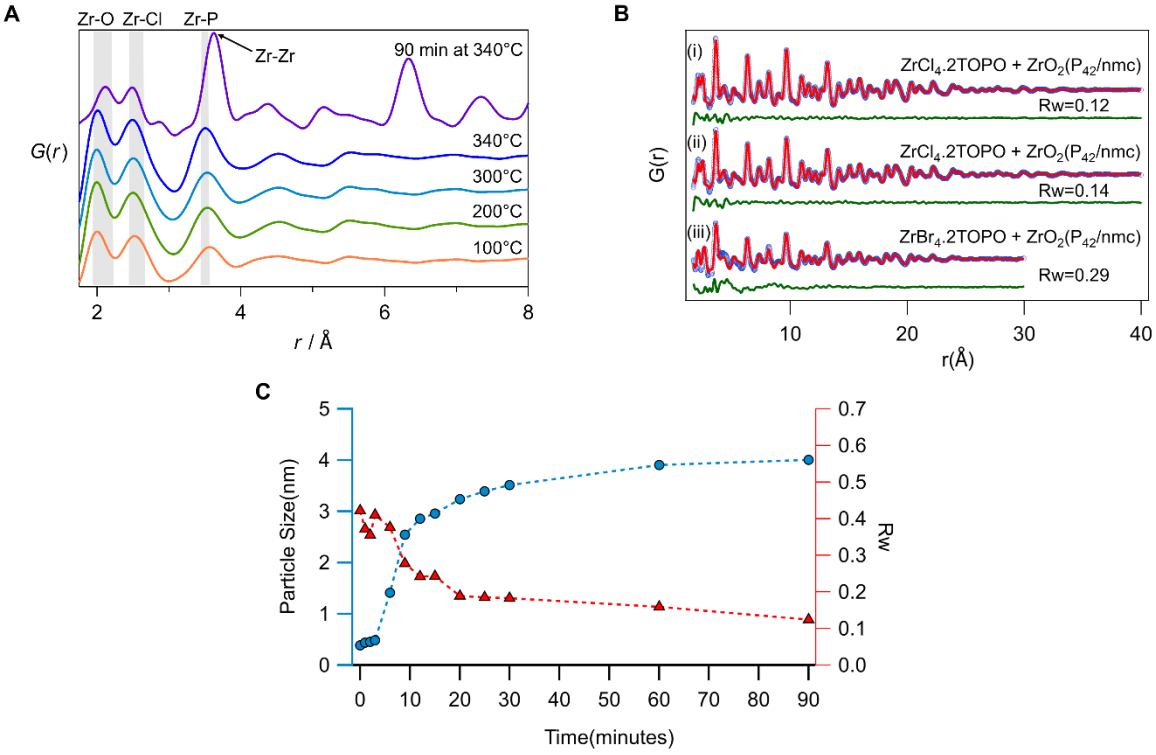

Figure 1: **(A)** X-Ray PDFs (acquired at 80 °C to melt TOPO) of reaction mixtures heated to different temperatures as indicated. The range of distances as determined from the DFT optimized structures of **(5)** and **(6)** are indicated by the grey zones. **(B)** *Ex- situ* experimental (blue circles), calculated (red line) XPDF and difference curve (green line) for the crude product from reaction mixture (i) 1:1 mixture of $ZrCl_4$:$Zr(O^iPr)_4$.^{i}PrOH (ii) 1:1 mixture of $ZrCl_4$.2THF : $Zr(O^iPr)_4$.^{i}PrOH (iii) 1:1 mixture of $ZrBr_4$: $Zr(O^iPr)_4$.^{i}PrOH.[4] **(C)** Evolution of nanocrystal size and with time, the Rw values corresponding to the refinement are indicated.

References

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3. P. Juhás, C. L. F., X. Yang, K. R. Knox and S. J. L. Billinge, Complex modeling: a strategy and software program for combining multiple information sources to solve ill posed structure and nanostructure inverse problems. *Acta Crystallographica* **2015,** *71*, 562-568.
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