Tracking and modelling the in situ formation of NiCo layered double hydroxides using pair distribution function analysis

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Layered double hydroxides (LDHs) are promising materials for green energy technologies, particularly as electrocatalysts for the oxygen evolution reaction (OER) [1-2]. To optimize their performance, it is crucial to understand how they form from precursor solution to solid product, and how chemical composition influences this process.

In this work, in situ total scattering data from DanMAX combined with pair distribution function (PDF) analysis were used to investigate the formation of NiCo LDHs synthesized via solvothermal methods. While this work offers insight into the formation of NiCo LDHs, particular emphasis is placed on modelling turbostratically disordered layered materials.

Existing modelling approaches for turbostratic disorder rely on large supercell simulations that are computationally prohibitive for sequential refinement of in situ datasets [3-5]. Here, we introduce a computationally efficient hybrid modelling approach, where in-plane correlations are described using a single-sheet structural model, while out-of-plane correlations arising from stacking disorder are represented using damped sine functions. This approach enables efficient sequential refinement of time-resolved PDF data, allowing extraction of in-plane structural parameters such as bond lengths, atomic displacement factors (ADPs), and reaction kinetics, while also tracking the evolution of interlayer spacing. We further show that the integrated square of the damped sine wave between 7.1 and 80 Å, tracks the same structural evolution as the integrated intensity of the 003 reflection.

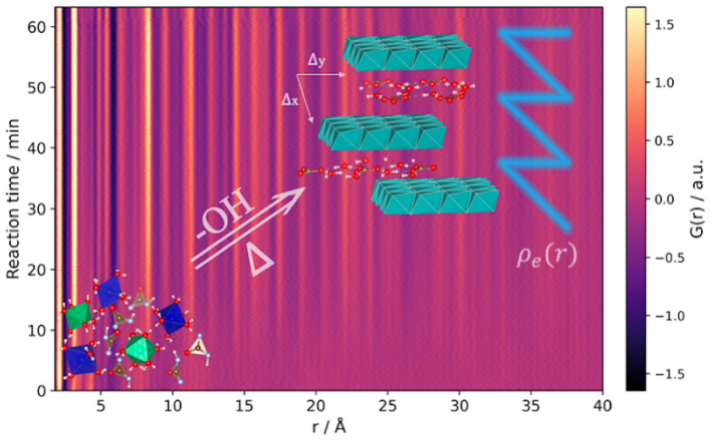


Figure 1. *Contour plot of the time-resolved pair distribution function (PDF) during the formation of NiCo layered double hydroxides. The overlaid schematic illustrates the proposed reaction pathway, where hydrated Ni and Co ions nucleate into LDH layers under alkaline conditions. The resulting turbostratically disordered structure preserves in-plane correlations, while out-of-plane correlations appear as a characteristic sawtooth oscillation in the PDF.*

The results suggest that Ni and Co hydrates in solution nucleate and grow into the LDH structure through an olation mechanism once urea hydrolysis generates sufficiently alkaline conditions. The resulting material forms turbostratically disordered LDH structures with interlayer spacings of ~7.1 Å. Comparison across different Ni:Co ratios reveals clear composition-dependent trends in the formation process, where increasingly asymmetric Ni:Co ratios tend to slow the LDH evolution. Furthermore, increasing Co content leads to lattice expansion, and a higher degree of structural disorder.

Overall, this work demonstrates an efficient PDF-based strategy for modelling turbostratically disordered layered materials and provides new insight into the formation of NiCo LDHs during solvothermal synthesis.

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