Structure Selection Dynamics of Cobalt Nanoparticles from Solution Synthesis

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Resolving the three-dimensional structure of transition metal oxide nanoparticles (TMO-NPs), upon self-restructuring from solution, is crucial for tuning their structure–functionality. Yet, this remains challenging as this process entails complex structure fluctuations, which are difficult to track experimentally and, hence, hinder the knowledge-driven optimization of TMO-NPs. Herein, we combine high-energy synchrotron X-ray absorption and X-ray total scattering experiments with atomistic multiscale simulations to investigate the self-restructuring of self-assembled Co-NPs from solution under dark or photocatalytic water oxidation conditions at distinct reaction times and atomic length-scales. Using the atomic range order as a descriptor, we reveal that dissolution of a Co-salt in BO_3 buffer leads to a self-optimization route forming disordered oxyborate Co_3BO_x-NPs unveiling a high oxygen yield due to the formation of surface oxo/hydroxo adsorbates. Those Co_3BO_x-NPs further self-restructure into distorted Co_3O_4-NPs and, lastly, into distorted CoOOH-NPs through a rate-limiting step integrating Co^{3+}-states during the course of a representative photocatalytic assay. Self-restructuring does not proceed from amorphous-to-ordered states but through stochastic fluctuations of atomic nanoclusters of ≈10 Å domain size. Our key insight into the structure-selection dynamics of TMO-NPs from solution offers a route for tuning their structure–function relationships for wide-ranging emergent technologies [1].

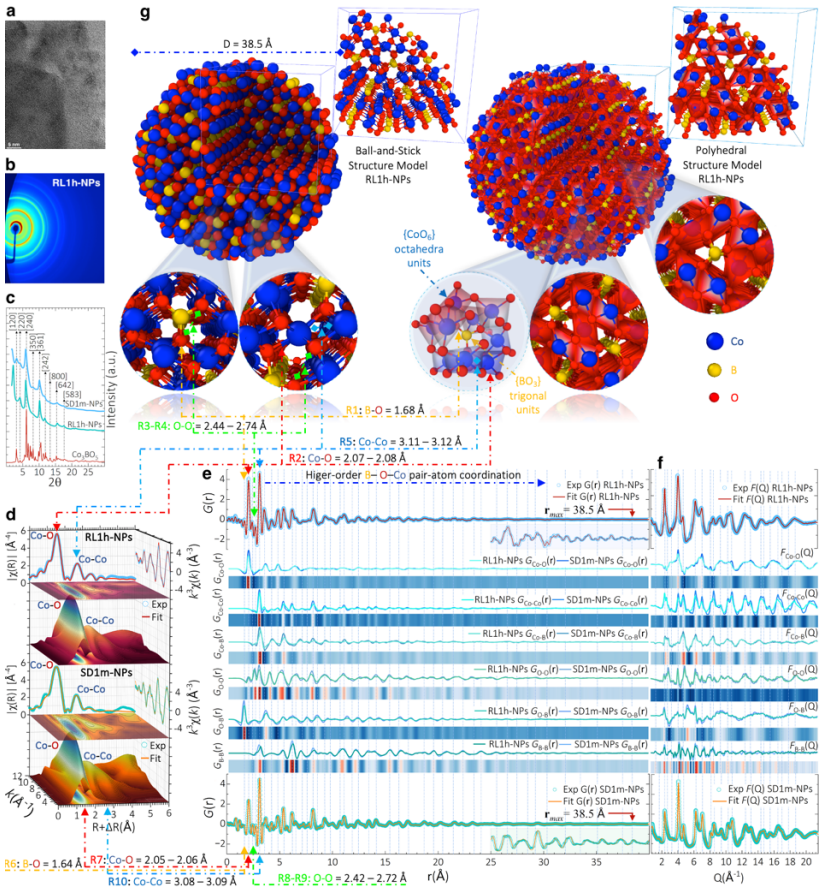


Figure 1. Atomic short-to-intermediate-range order of Co_3BO_x-NPs. ***a****) HR-TEM image.* ***b,c****) 2D-integrated I(2θ) pattern.* ***d****) Fitted FT\|k³χ(k)\| spectra and Wavelet-Transform (WT) of k³χ(k).* ***e,f****) RMC fitting of F(**Q**) and G(**r**) and partial $F_{i\text{-}j,k}$(**Q**) and $G_{i\text{-}j,k}$(**r**) functions of Co_3BO_x-NPs. The inset zooms the 25–40 Å region.* ***g****) The RMC simulated structure of Co_3BO_x-NPs.*

[1] Structure-selection dynamics of cobalt nanoparticles from solution synthesis and their impact on the oxygen evolution reaction. G.R. Patzke, F. Keller, M. Iannuzzi, L. Reith, K.P. Marshall, W. van Beek and Carlos A. Triana. *ACS Nano* 2024, **18**, 52, 35533–35549.