Probing the Nucleation and Growth of High-Entropy Alloy Nanoparticles in Dropwise Synthesis by Small-Angle X-ray Scattering

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Understanding how multimetallic precursors evolve into high-entropy alloy (HEA) nanocrystals remains a central challenge in colloidal synthesis, particularly under dropwise addition where precursor reduction, nucleation, growth, and atomic mixing are closely coupled. Here, we use ex situ small-angle X-ray scattering (SAXS) to investigate the early-stage formation kinetics of PdPtRhIrRu HEA nanocrystals prepared by dropwise synthesis, with monometallic Pd nanoparticles as a benchmark. The SAXS profiles collected at different reaction times were analyzed using the Q invariant and the Avrami equation to follow the transformed fraction and extract kinetic signatures of nucleation and growth. Distinct two-stage kinetic behaviors were observed for the HEA and Pd systems, indicating that HEA nanocrystal formation follows a kinetically different pathway from that of monometallic Pd under the same synthetic conditions. This difference is consistent with the added complexity arising from the concurrent incorporation of multiple metal species during nucleation and growth. Direct comparison with the Pd system highlights that alloy formation in the HEA sample cannot be described as a simple extension of monometallic nanocrystal growth, but instead involves a more complex kinetic evolution during the early stages of synthesis. Electron microscopy further supported this interpretation, showing branched HEA nanocrystals in contrast to the more isotropic Pd nanoparticles. These results demonstrate that SAXS-based kinetic analysis provides a useful mechanistic framework for probing HEA nanocrystal formation and offers guidance for the rational design of multimetallic synthesis strategies with improved control over alloy nanostructure formation.

Keywords:
high-entropy alloy nanoparticles, small-angle X-ray scattering, nucleation and growth, dropwise synthesis, formation kinetics