Whole-nanoparticle-ensemble refinements of compositionally complex systems from X-ray pair distribution function data *via* the Reverse Monte Carlo method

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Compositionally complex nanomaterials, which consist of multiple elements randomly mixed in a solid solution structure, have continued to attract interest as promising catalyst materials in recent years [1]. While their high-dimensional compositional space makes these materials prospect catalysts with tuneable properties, their multi-element nature also complicates comprehensive structural analysis through conventionally applied methods such as powder diffraction and X-ray absorption spectroscopy. Total scattering and pair distribution function (PDF) analysis has proven an excellent tool for structural characterisation of compositionally complex and nano-sized materials [2,3]. Regardless, PDF analysis has not been explored for identification of chemical short-range order (CSRO) and compositional inhomogeneities in nanoparticles. Such structural effects are difficult to describe through commonly employed small-box modelling methods. In contrast, large-box modelling offers a more holistic approach by including thousands of atoms in the structural model, thereby capturing both local and long-range structural effects. Nevertheless, large-box methods for nanoparticle systems are only just starting to emerge [4].

We present an approach for the investigation of chemical short-range order and elemental inhomogeneities in multimetallic nanoparticle systems through large-box modelling of X-ray PDF data. Specifically, we demonstrate a methodology for atomistic whole-nanoparticle-ensemble refinements of compositionally complex nanoparticles, with average particle sizes down to just 2.8 nm, through the Reverse Monte Carlo (RMC) method. We analyse a series of supported nanoparticle systems of increasing compositional complexity (Pt, PdPt, PdPtRh, PdPtRuRh and IrPdPtRuRh) to probe the robustness of the technique. The resulting RMC PDF refinements exhibit excellent fit quality, demonstrating that the employed atomic NP configurations accurately describe the experimental data. Refinements of NP ensembles with different compositional ordering, including core@shell, compositional gradient and fully random structures are compared to determine which model best describes the synthesised particles. Finally, by allowing atom-type swapping in the refinement algorithm, the presence of compositional ordering and CSRO is investigated. This large-box modelling approach enables identification of compositional inhomogeneities and chemical ordering effects that cannot be captured using conventional small-box modelling methods. The refinement results indicate the presence of few-atomic-layer-thick Pt-rich regions within the particles, a feature which is further investigated through state-of-the-art high-resolution electron microscopy and spectroscopy. Our work presents a new approach to the identification of CSRO and spatial compositional variations in nanoparticle systems through PDF analysis, revealing structural effects that elude conventional characterisation techniques. Furthermore, our results emphasise the challenges associated with comprehensive structural analysis of compositionally complex nanomaterials.

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