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Understanding the material formation of high-entropy alloy nanoparticles: in situ study using coupled X-ray diffraction/ absorption spectroscopy

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Abstract

High entropy alloy (HEA) catalysis has recently emerged as a new research topic.[1] So far, HEAs have been mainly used in engineering applications. It is, however, expected that these multi-metallic compounds also provide exciting new possibilities for catalysis.[2] This has often been cited as a paradigm shift from “using the materials we have” to “engineering the materials we need”.[2] Recent theoretical analyses predict a great potential for HEAs as new catalysts due to the almost unlimited number of unique surface sites.[3] By changing the alloy composition, the catalytic properties can be optimized to enable a new, statistical approach in materials design. From an experimental viewpoint, however, HEAs come with new challenges regarding their synthesis and characterization. While HEA nanoparticles are essential for catalysis to provide sufficiently large surfaces, their synthesis is only in its infancy. My work focuses on the formation mechanism of noble metal HEA particles, which is compared with the formation of binary alloys of the same noble metals (Pt, Ir, Os, Ru, Rh). Characterizing multi-metallic HEA particles is a challenge that requires novel approaches in material characterization techniques. In-situ crystallographic studies using advanced synchrotron-based techniques can provide new insights into the HEA material formation pathways. Coupled in situ powder X-ray diffraction/ X-ray absorption spectroscopy (XRD/XAS) [see Fig.1] is an analytical tool, which allows following both the crystallization processes as well as the changes in the oxidation state of the individual elements. In the in situ XRD/XAS reaction set-up, the precursor powder is placed in a capillary and heated in a reductive atmosphere, while diffraction pattern and absorption spectra are recorded quasi-simultaneously [see Fig. 2]. With this, we can directly track the alloy formation pathway of both the binary alloys and HEA nanoparticles. By understanding the material formation pathway in detail, we can deduce the parameters that determine the phase formation behaviour in the multi-metallic systems (single phase vs multiple phases). This gives new insights into alloy crystallization mechanisms and ultimately can provide guidelines for the design and synthesis of new multi-metallic alloy nanoparticles.

References

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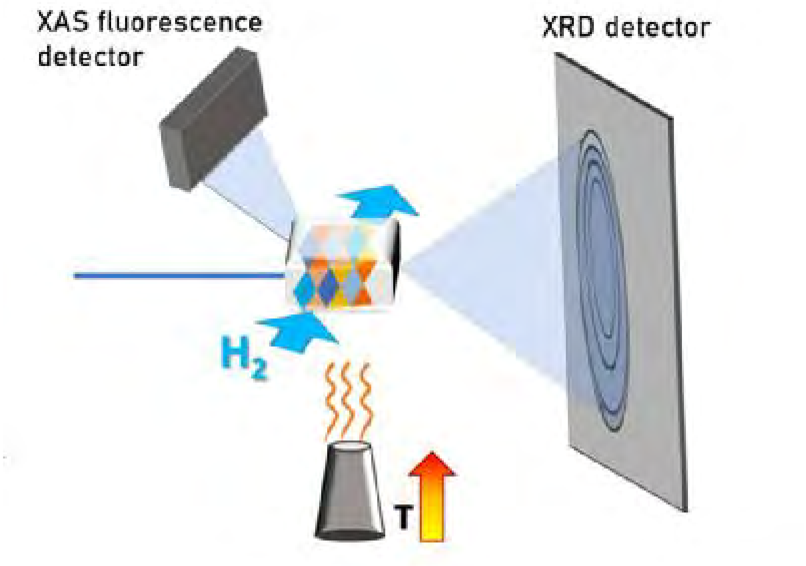
Schematic representation of the in situ setup



Following particle formation with XRD and XANES