General Solvothermal Synthesis Method for Complete Solubility Range of Bimetallic and High-Entropy Alloy Nanocatalysts.

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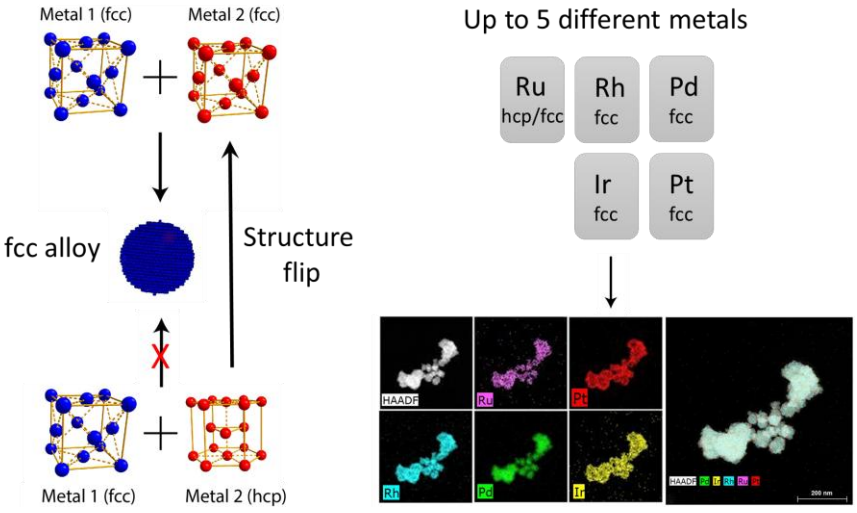
Bimetallic nanoalloys (NA) have excellent catalytic performance in a wide range of reactions and processes. They have unique structures and electronic properties, which may combine desirable properties from the individual metals. A particularly fascinating development is that NAs can be synthesized with at least 5 different metals simultaneously present, and these materials have been coined high-entropy Alloys. The NAs can be produced by many different methods, but common to all is the considerable complexity, lack of scalability and often harsh chemical or physical conditions. The catalytic properties hinge on a range of nanoparticle parameters such as crystallinity, particle size (surface area), morphology, crystal structure, and chemical composition (alloying or doping). Maximum catalytic activity often is achieved on certain crystal facets, and therefore there is an increasing focus on controlling not only size, but also morphology of NAs. In addition to morphology control, Fine-tuning of the electronic structure can be accomplished by alloying noble metals in solid solutions. This approach is limited for binary allloys with immiscibility gaps. As an example, the Pd_xRu_{1-x} system only forms a solid solution for $x < 0.16$ and $x > 0.82$ even for temperatures close to the melting point. Phase control for these systems is only possible for metals with identical bulk crystal structures, otherwise phase segregation occurs, as seen e.g. for Ru-containing Pd or Pt systems. Generally, no synthesis method has been identified which allows for preparation of both solid solutions and complete phase control for any combinations of noble metals, regardless of whether they have the same structure in the bulk phase.

Here we report[1] a general low-temperature solvothermal autoclave synthesis method at 200 °C with a reaction duration of 4-24h, to obtain phase-pure bimetallic and high entropy nano-alloys across the entire composition range. Tuning of solvent chemistry and precursors lead to six different bimetallic nanoalloys, PdxRu1-x, PtxRu1-x, IrxRu1-x, RhxRu1-x, Ir1-xPtx and Rh1-xPtx without immiscibility regions. All samples have face-centered-cubic (fcc) crystal structures, which is not previously observed for the ruthenium-based systems. Additionally, quaternary and quinary systems were produced demonstrating the ability to obtain medium and high-entropy nanoalloys. The method provides a simple, general production method of previously unknown solid solutions throughout their entire composition range potentially allowing for detailed tuning of nanocatalyst properties.



[1] Bondesgaard, M., Broge, N. L. N., Mamakhel, A., Bremholm, M., Iversen, B. B., General Solvothermal Synthesis Method for Complete Solubility Range Bimetallic and High-Entropy Alloy Nanocatalysts. *Adv. Funct. Mater.* 2019, 29, 1905933. https://doi.org/10.1002/adfm.201905933