

High Entropy Nanoalloys

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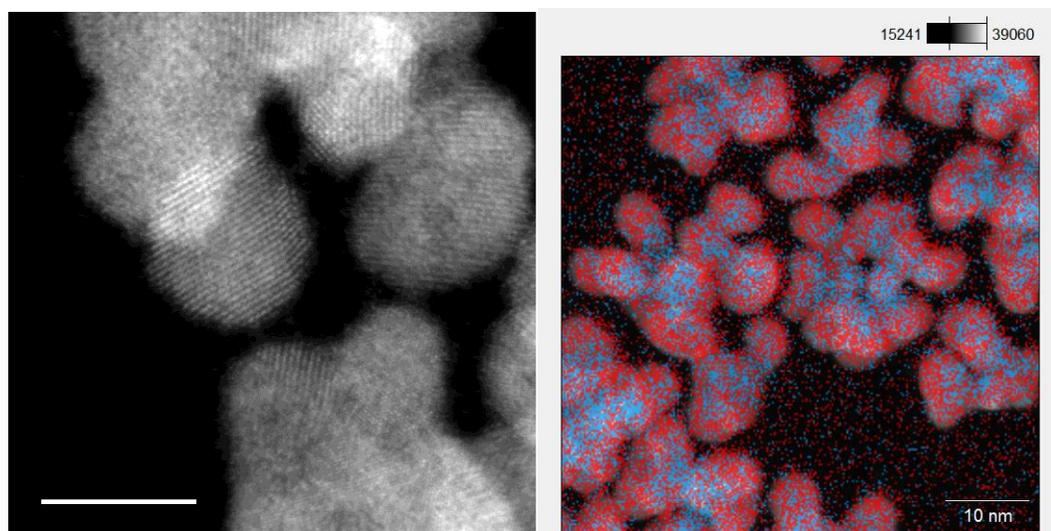
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High entropy alloys (HEAs) are single phase alloys typically containing five or more elements in near-equivalent molar proportions. Such alloys can offer novel properties which are unlike the properties of conventional alloys, which contain one predominant element with minor alloying elements. HEAs have been identified only recently¹; a large number of bulk alloys have been fabricated since then, by casting, powder metallurgy, milling etc. Relatively few HEA nanoparticles (NPs) have however been reported to date², despite the properties which they may offer. We have shown that multicomponent HEA NPs can be synthesized for catalyst production; we have characterised their structure and composition with a view to measuring their catalytic properties.

We have successfully synthesized nanolloys of platinum combined with other transition metals, via a chemical synthetic route (using oleic acid and octadecylamine as surfactants in a high boiling point solvent, 1-octadecene, at 200 C for 60 min): Pt-Ir-Rh-Ni-Cu, Pt-Ir-Rh-Ni-Fe, Pt-Ir-Rh-Ni-Cu-Fe and Pt-Ru-Co-Ni-Mo-Cr. X-ray diffraction shows that these nanoalloys are all face centred cubic; they are single phase and thus conform to the HEA definition. Scanning Transmission Electron Microscopy (STEM) was used to understand the compositional homogeneity using energy dispersive spectroscopy (EDS) and high angle annular dark field (HAADF) imaging to understand the structure and morphology.

The NPs are typically spherical with a diameter of 5-10 nm. Fig. 1(a) is a HAADF image of Pt-Ir-Rh-Ni-Fe which shows these NPs to be single crystals. Compositional mapping Fig. 1(b) identifies a core-shell microstructure, with quite marked compositional differences across the NPs. Concentration changes and differing diffusion rates during the growth process can result in compositionally modulated structures; such core-shell structures are frequently encountered in particles synthesized from multiple metal precursors in solution³. For catalytic purposes, core-shell structures offer particular advantages if a highly active metal (such as Pt) forms the surface.

Owing to the three dimensional nature of such core-shell particles it is not possible to determine the core composition without the shell contributing. In the case of Pt-Ir-Rh-Ni-Fe the largest compositional variations were in Rh and Pt, with the core being Rh-rich and the shell being Pt-rich (Table 1). The localisation of a high Pt content, along with some Ir, on the exterior of the particle is highly desirable from a catalysis perspective. Binary core-shell NPs of Pt combined with a non-noble component are prone to corrosion and shape change due to dealloying of the less noble component⁴. Here the use of a multicomponent high entropy alloy, which incorporates other noble and non-noble metals may offer enhanced stability and performance in catalysis applications. This work demonstrates that complex, multicomponent HEA NPs, with a narrow range of particle sizes, can be synthesised by a solution protocol. The core-shell compositional modulation and the overall composition has the potential to be controlled by varying the growth temperature and reactant concentrations. The relationship between catalytic performance and structural durability of these systems is currently under investigation.



(a) (b)

Fig. 1: Pt-Ir-Rh-Ni-Fe nanoparticles showing: (a) HAADF image demonstrating that the particles are single crystal; (b) STEM-EDS derived phase map, indicating a core-shell structure.

Table 1: Composition (at%) of the core and shell regions in Fig. 1(b) for Pt-Ir-Rh-Ni-Fe

	Pt	Ir	Rh	Ni	Fe
Core	23	6	48	18	5
Shell	54	13	1	23	9

References

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