Structure and Composition of High-Entropy-Alloy Nanoparticle synthesized by Pulsed Laser Ablation in Liquid

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Background incl. aims
Recently, synthesis of colloidal alloy nanoparticles (NPs) by pulsed laser ablation in liquid (LAL) was successfully transferred to high entropy alloy (HEA) systems. HEA NPs are particularly interesting for heterogenous catalysis and form a simple solid solution structure despite their high chemical complexity. In this work the influence of the target composition, solvent and laser pulse duration on the structure as well the chemical composition of these NPs is investigated. Two HEA systems are chosen: CoCrFeMnNi (Cantor) and AgAuCuPdPt (Noble metal). While in preliminary work crystalline and amorphous NPs with oxide-shells were found, it is unclear to what extent the excess of one element in the base target leads to elemental segregation not dominated by oxidation.

Methods
The nanoparticles were synthesized by LAL in a circulating solvent (Acetone vs. Ethanol) and NIR-laser pulse durations (10 ps vs. 10 ns pulse duration) and characterized in (S)TEM. For chemical analysis methods like Z-contrast imaging and nanoprobe elemental mapping were applied, while the structural analysis was performed using methods like TEM-high-resolution phase-contrast imaging (-HR imaging) and selected area electron diffraction (SAED).

Results
All Cantor alloy systems show a pulse energy dependency of the phase structure with fcc solid solution with ps-lasers and amorphous NPs with ns-lasers, while additional core-shell and multi-core structured NPs driven by Mn and Cr oxidation are also found. Further, oxide-core-multi-shell NPs were observed where localized target oxidation could provide nuclei for their formation. Interestingly, a predominant fcc-structure without pronounced elemental segregation was found upon enrichment of Mn or Cr in the system synthesized with the ps-laser. Further, NPs synthesized by the ns- laser maintained their amorphous structure upon enrichment of either Cr or Mn however additional crystalline oxides were detectable.
The noble metal systems showed no segregation into core-shell or multi-core structured NPs. Instead, two solid solution NP fractions appear, which are Ag-rich and Pt-rich. Contrary to the Cantor alloy systems and verified by HR-imaging the noble metal NPs retain their crystalline structure when synthesized with ns-lasers, although some hints on amorphous structures in Cu-rich and Ag-rich NPs based on SAED warrant further examination.

Conclusion
In conclusion, the Cantor alloy system shows the possibility of amorphous and crystalline solid solution NPs controlled by the laser pulse duration. Segregation into core-shell, multi-core or even oxide-core-multi-shell NPs is dominated by oxidation. The noble metal system displays de-mixing tendencies between Ag and Pt resulting in two solid solution NPs fractions. This could hint towards different cooling rates during particle formation offering insights into the HEA formation mechanism by LAL.

Keywords:

High-entropy-alloy, nanoparticle, pulsed-laser-ablation

Reference:

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