Electron beam induced crystallization of co-sputtered amorphous high entropy alloy nanoparticles in ionic liquid

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Combinatorial co-sputtering from five elemental targets was used to synthetize high entropy alloy nanoparticles (Cr-Mn-Fe-Co-Ni) into ionic liquids. Multinary nanoparticles are of of general scientific interest and could be used in different applications ranging from catalysis and energy to medicine. Due to their low vapor pressure, ionic liquids[1] (salts with a melting point < 100°C) can be used as liquid substrates in sputter processes. Furthermore, the ionic liquid itself can act as an electronic as well as a steric stabilizer preventing particle growth and particle aggregation leading to the formation of extremely small nanoparticles with a strong effect on the morphology of the formed NPs[1].

Our research is based on the preparation and in-depth atomic-scale characterization of high entropy NPs systems. The main focus is set on the investigation of these alloy NPs by using various microscopy techniques, such as Cs corrected high-resolution transmission electron microscopy (HRTEM), (scanning) transmission electron microscopy ((S)TEM) and energy dispersive X-ray spectroscopy (EDS). With these techniques the size, shape, crystallinity, defects and chemical composition of the nanoparticles is deduced.

The fabricated high entropy alloy NPs appear amorphous after their synthesis. During illumination with a 300 keV electron beam structural changes occur. Up to 40 min the NP remain in the amorphous state. Above 40 min the illumination of the NP leads to a structural transformation to a crystalline state as visible in the lattice fringes observed in the HRTEM image and the corresponding reflection in the FFT. Similar observations have been reported by *Uematsu et al.* for Au NPs[2]. In order to verify our experiment, high entropy alloy NPs were heated to 100°C ex-situ for 10 h under similars vacuum conditions than in the TEM. After this annealing treatment, also crystalline alloy nanoparticles were obtained in accordance to the ones induced by electron beam illumination (Figure 1a). Further in-situ studies will be performed to study Ostwald ripening on the atomic scale and to investigate how the different diffusion constants of the various atomic species will affect the growth.

Finally, EDS elemental mapping of high entropy alloy NPs provides an effective way to study the chemical composition and the distribution of each element (Cr-Mn-Co-Fe-Ni) inside the nanoparticles as is shown in Figure 1.

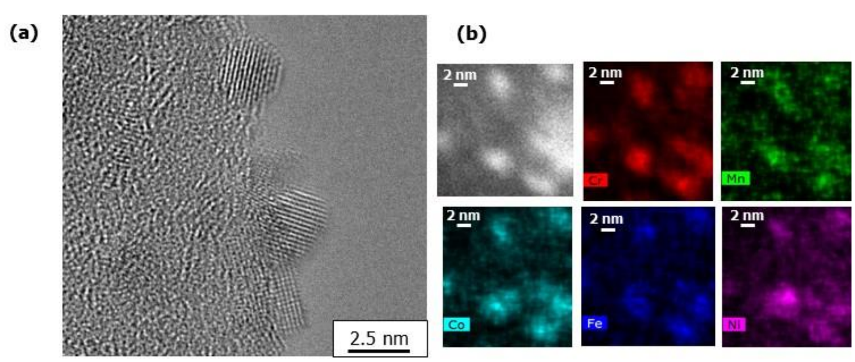

Figure 1: (a) Cs corrected high-resolution TEM image of high entropy alloy nanoparticles after their ex-situ crystallization (b) EDS elemental mapping for high entropy alloy nanoparticles after their in-situ TEM crystallization

1. König, D., Richter, K., Siegel, A., Mudring, A. V. & Ludwig, A. High-throughput fabrication of Au-Cu nanoparticle libraries by combinatorial sputtering in ionic liquids. *Adv. Funct. Mater.* **24,** 2049 - 2056 (2014).
2. Uematsu, T. *et al.* Atomic Resolution Imaging of Gold Nanoparticle Generation and Growth in Ionic Liquids Atomic. *J. Am. Chem. Soc*. **136**, 13789-13797 (2014).
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