

On the difficulty to form alloy nanoparticles by interaction of spark discharges with electrode surfaces in dielectric liquids.

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Using discharges in liquids to synthesize alloy nanoparticles (NPs) is very challenging, although several attempts led already to promising results (Panuthai *et al.*, 2010). The main advantage of this process is to be fast and low-cost. Furthermore, no surfactants are needed a priori in the physical approach whose up-scaling is easy.

Basically, the difficulty of producing alloy NPs by discharges in dielectric liquids comes from the main interaction processes occurring between the spark discharge and the electrodes.

Electrode erosion proceeds via several mechanisms among which evaporation plays a key role in the synthesis of the lowest size distribution of NPs (Hamdan *et al.*, 2013). Then, emission of metal vapours often proceeds sequentially depending on the melting point of the materials.

In a given alloy, metallic elements have specific melting points. For instance, in a brass alloy made of 63% copper and 37% zinc, zinc is expected to leave the electrodes far before copper, their respective melting points being close to 693 K and 1358 K respectively. On the other hand, in a $\text{Cu}_{28}\text{Ag}_{72}$ alloy, both elements have comparable melting points (silver melts around 1235 K) and are expected to be evaporated almost at the same time, which should favour the synthesis of alloy NPs.

Experiments were performed using nanosecond pulsed discharges created in liquid nitrogen between alloy pin electrodes. One important feature concerning this experimental method comes from air oxidation that occurs once liquid nitrogen is evaporated.

In the case of CuZn, no small NPs containing both copper and zinc could be found. Electron energy loss spectroscopy confirms also this conclusion by exhibiting typical CuO and ZnO spectra. As NPs are oxidized, the lack of alloy NPs might be due to air oxidation that would convert CuZn NPs into separate NPs of Cu_2O and ZnO (Figure 1). Indeed, according to Holse *et al.* (2015), upon oxidation in O_2 , the as-deposited metal clusters transform into a polycrystalline cluster consisting of separate CuO and ZnO nanocrystals. Specifically, the CuO is observed to segregate to the cluster surface and partially cover the ZnO nanocrystals. So, till now, the impossibility of synthesizing CuZn alloy NPs by discharges in liquids is still not proved.

In the case of CuAg, alloy NPs are clearly found after synthesis in liquid nitrogen and air exposure, demonstrating the possibility to form alloy NPs from alloys made of metal with similar melting points. Metallic CuAg particles are present, copper being not

oxidized but remaining at the metallic state. It is well known that in bimetallic nanoparticles, the two elements can be phase separated such as in core-shell structures, chemically ordered, or Janus structures, or the two species can be randomly mixed with complex segregation (Peng *et al.* 2015).

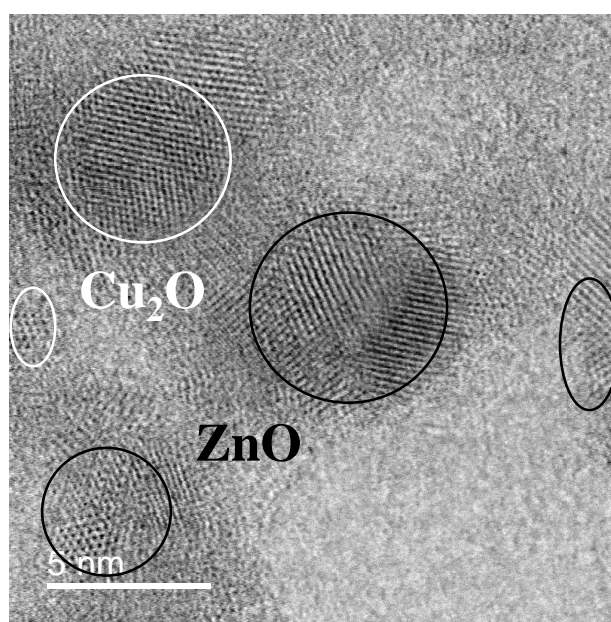


Figure 1. Separate Cu_2O and ZnO found after air oxidation of NPs produced by discharges in liquid nitrogen from $\text{Cu}_{63}\text{Zn}_{37}$ electrodes.

According to Nunez and Johnston (2010), in small alloy NPs sufficiently rich in silver, a spherical cap of silver would preserve a core of copper. Segregation would then explain the reason why copper can keep its metallic character, even after air oxidation.

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