Direct measurement of the surface energy of bimetallic nanoparticles using in-situ heating TEM

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Surface energy is an important descriptor of metallic nanoparticles (NPs) as it drives, among others, their nucleation, growth, morphology and reactivity to different environments. Until now, experimental determination of absolute values of surface energy in metallic NPs has been limited to monometallic systems [1-4]. In case of bimetallic NPs, in which particle composition significantly affects surface properties, the experimental determination of surface energies is a challenging issue. In this contribution we present a direct and robust method to experimentally determine the absolute surface energy of bimetallic nanoalloys. Our approach relies on the real-time monitoring of the evaporation of bimetallic NPs in vacuum by *in situ* transmission electron microscopy and the extension of the Kelvin equation to two-component systems [5]. We determined the surface energy of supported Au, Cu and Cu-Au NPs prepared by pulsed laser deposition.

TEM *in situ* experiments were carried out in vacuum at temperatures above 700°C in an environmental gas-cell (Protochips, Inc.). Figures 1a and b show the evolution of an assembly of well-dispersed Cu-Au NPs with equiatomic composition when heated *in situ* at T = 700°C. Figure 1a shows the size and dispersion of the as-grown CuAu NPs on the SiN support of the environmental gas-cell (t = 0s). In figure 1b, a TEM image of the same area after t = 30 mins of heating is shown for comparison. Under heat stimulus, one observes the evolution of the crystalline state of the NPs, those with a radius smaller than 3 nm are all in the liquid state at T > 700 °C, as shown by their uniform image contrast and the absence of lattice fringes in their HRTEM images. Figure 1c shows the variation of the CuAu NPs radii with time. By adjusting the decreasing of the size of the NPs with a generalized Kelvin law to bimetallic compounds [5], the surface energy of the NPs could be extracted. The average surface energy is equal to 1.53 $J.m^{-2}$ for CuAu NPs. We also applied this method to determine the surface energy of pure gold and copper nanodroplets, as well as of $CuAu_3$ compound.

The determination of the absolute values of the surface energy of the monometallic and bimetallic NPs suggests that the surface energy for liquid Cu-Au nanoalloy follows a Vegard's law-like behaviour (inset of figure 1c). These experimental observations are confirmed by Monte Carlo simulations which bring additional insights into the structural stability and thermodynamic properties of Cu-Au NPs at high temperature.

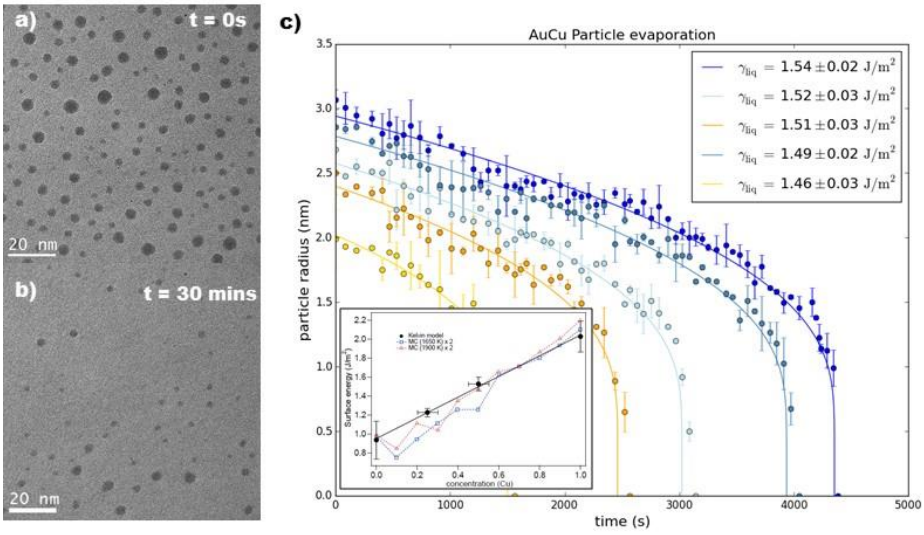

Figure1: TEM images of the evolution of CuAu NPs at 700 °C at t = 0 s (a) and t = 30 mins (b). Variation of the radii of six CuAu NPs with time c). Insets: corresponding extracted surface energies (right), variation of the surface energy of $Cu_{(1-x)}Au_x$ systems, blue-red lines are Monte Carlo simulations, the full black line is a linear fit of experimental data (left).

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