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Thermal Stability Study of Ni-Co Core-Shell Nanoparticles by *in situ* TEM

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Bimetallic nanoalloys have been shown to have tunable chemical and physical properties by varying the composition, atomic ordering and size of clusters [1]. In fact, the surface structure, composition and segregation properties [2,3] of nanoalloys are crucial in determining chemical reactivity and activity [4,5]. A core-shell structure results from the chemical ordering of an atom forming a shell that covers a core of another atom. The viability of these nanostructures for industrial applications such as catalysis depends on the material's structural stability. Unfortunately, nanoalloys are unstable even at temperatures far below the melting temperature in the bulk [6]. Despite the large number of studies reported in the literature, understanding the driving forces for thermal instability of nanoalloys is still limited.

Ni-Co core-shell nanoparticles with diameter of 25 nm were dispersed in hexane and drop-casted on the Aduro MEMS heating device. Thermal annealing of the particles was performed using a Protochips Aduro heating holder inserted in a FEI Titan transmission electron microscope with a ChemiSTEM energy-dispersive x-ray spectroscopy (EDS) system. The particles were annealed to temperatures from 80°C to 600°C while microstructural changes were observed by Z contrast imaging. EDS maps were subsequently acquired providing elemental and quantitative distribution of Ni and Co within the particle. Figure 1 shows a TEM image of the core-shell nanoparticles (Figure 1a) with the corresponding EDS map (Figure 1b) and spectra (Figure 1c) at room temperature showing presence of surface oxide. During the annealing experiment, concentration of oxide was observed to significantly decrease at 440°C to 550°C [7]. By 600°C, the core-shell structure of the particles was disrupted with Ni and Co evenly distributed throughout the particle (Figure 2).

From these results, we conclude that core-shell reconfiguration occurred in the stepwise process of oxide removal starting at 440°C followed by Ni segregation at 600°C driven by the increasing temperature and reducing environments inside the TEM. At 600°C, Ni diffusion into Co was induced [8] resulting in segregation of Ni out of the core to the shell. Furthermore, the observed segregation of Ni correlates with the results of an x-ray photoelectron spectroscopy (XPS) study after two oxidation-reduction cycles of the same nanoparticles [7]. Environmental TEM (ETEM) studies with similar experimental conditions than the XPS study are underway to further investigate the observed reconstruction of the core-shell structure [9].

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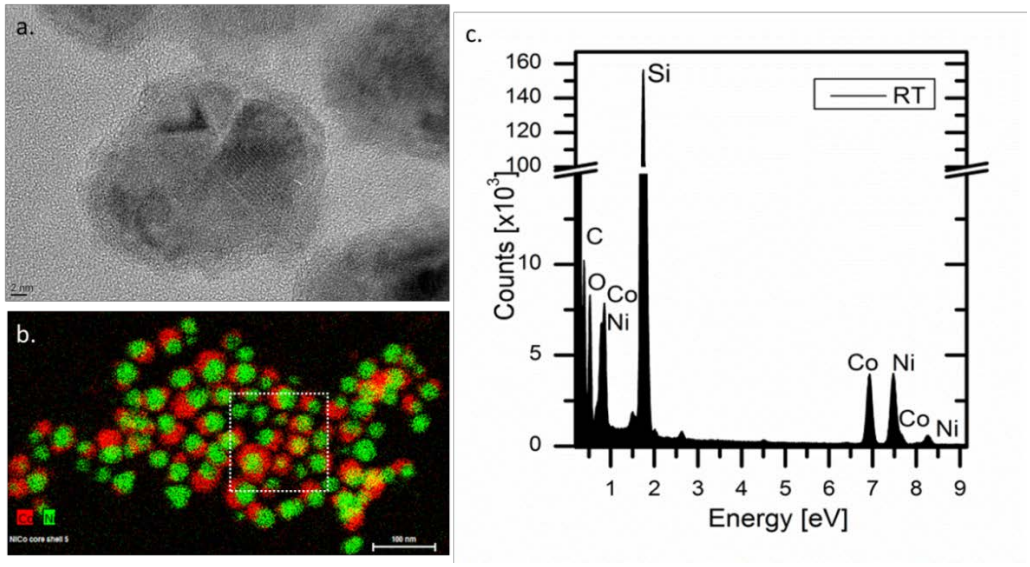

Figure 1. TEM image **(a)** and EDS elemental map **(b)** of the Ni-Co core-shell nanoparticle at room temperature. Green and red colors in the EDS map **(b)** correspond to Ni and Co, respectively. **c** shows the EDS spectra acquired from the boxed area in **(b).**

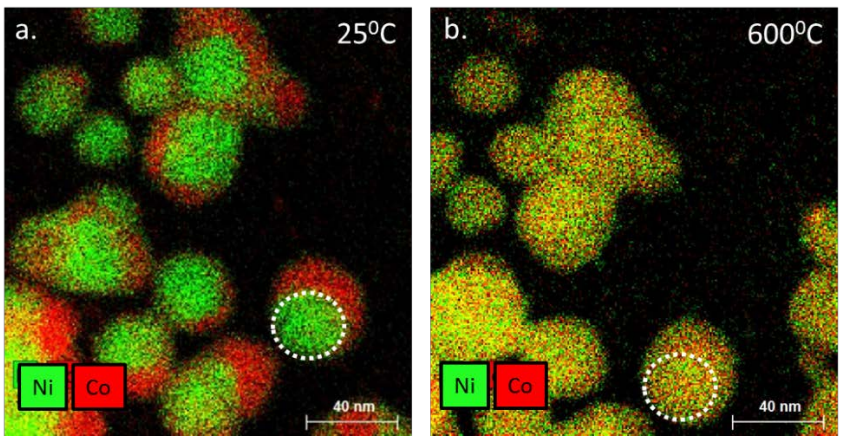

Figure 2. EDS maps of the Ni-Co core-shell nanoparticle before annealing at 25°C **(a)** and 600°C **(b).** The core of the nanoparticle is circled in **a** and **b** to show the segregation of Ni from the core to the shell occurring at 600 °C.

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