

In situ environmental HRTEM study of the restructuring under reducing atmosphere of small oxidized silver-indium nanoparticles

J.Ramade¹, C. Langlois², M.Pellarin¹, L.Piccolo³ and E.Cottancin¹

¹ Institut Lumière Matière, UMR 5306 Université Lyon 1-CNRS, 69622 Villeurbanne Cedex, France

² MATEIS, UMR 5510 INSA, Université Lyon 1-CNRS, 69621 Villeurbanne Cedex, France

³ IRCELYON, UMR 5256, Université Lyon 1-CNRS, 2 avenue Albert Einstein, 69626 Villeurbanne Cedex, France

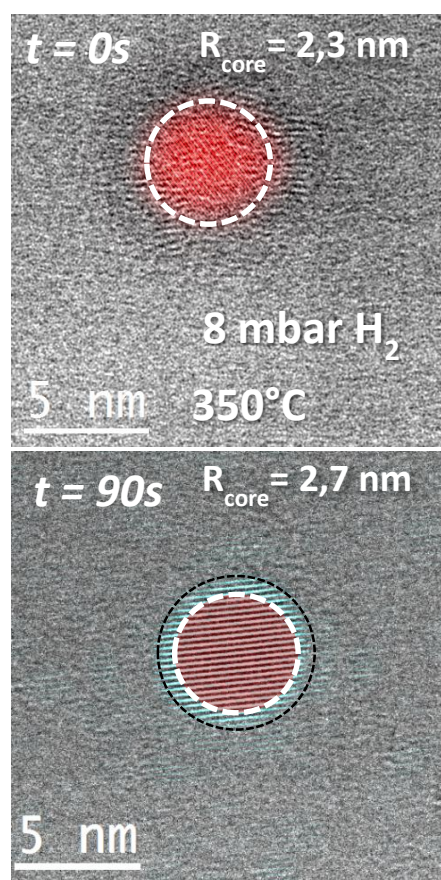


Figure 1 : Structure evolution of an $Ag_3In@In_2O_3$ NP exposed to reducing atmosphere

thickness during reduction. From these results, we constructed a (pressure, temperature) diagram highlighting the relationship between the temperature and H_2 pressure needed for activating the reduction. These results provide new insights in both physical and chemical processes involved during reduction of oxidized metal NPs at the atomic scale.

The behavior of small oxidized Ag-In nanoparticles (NPs) under reducing atmosphere has been followed through environmental TEM (ETEM). In a previous paper, we showed that these particles exhibit a reversible shift of their localized surface plasmon resonance (LSPR), after exposition to oxidizing (air, 25°C), and reducing (H_2+N_2 , 500°C) atmospheres¹. The particles were synthesized by Low Energy Cluster Beam Deposition (at PLYRA in Lyon), which allows an independent control of their size and composition. The microscope used was a FEI Titan ETEM operating at 300 kV, with a Cs corrector of the objective lens. HRTEM images and movies of the bimetallic NPs were recorded at up to 500°C and under 10 mbar H_2 ².

The starting chemical configuration of the particles is a core@shell structure, with an Ag or Ag-In alloyed core of 4-5 nm in diameter and a partially crystallized In_2O_3 shell of 1-2 nm thickness. The NPs were exposed in the ETEM to successive (H_2 pressure, temperature) couples, from (1 mbar H_2 , 25 °C) to (10 mbar H_2 , 500 °C). They were monitored both at the local (single NP tracking) and global (observations on large assemblies, under low magnification) scales. The structural changes observed at the atomic scale range from the almost complete extraction of the Ag-rich core from the In_2O_3 shell, leading to “Janus” NPs, to the complete reduction of the indium oxide shell. The latter occurs at higher temperature than the melting point of indium (156°C), which induces a competition between two phenomena: i) the melting or evaporation of reduced indium, and thus the decrease in the shell thickness until its complete disappearance; ii) the diffusion of reduced indium atoms from the shell to the core, leading to the core growth (figure 1). This last point may be closely related to the evolution of the shell

1. E. Cottancin, C. Langlois, J.Lermé, M.Broyer, M.A. Lebeault, M.Pellarin, Phys. Chem. Chem. Phys. 2014, **16**, 5763
2. J.R. Jinschek, Chem. Commun., 2014, **50**, 2696