ESI

Structural and Optical Characterization of Nanoalloys Mixing Gold or Silver With Aluminium or Indium: Evolution Under Various Reactive Environments

Élise CAMUS,[a] Michel PELLARIN,[a] Nicholas BLANCHARD,[a] Olivier BOISRON,[a] Matthias HILLENKAMP,[a] Lucian ROIBAN,[b] Pascal ANDREAZZA,[c] and Emmanuel COTTANCIN *[a]

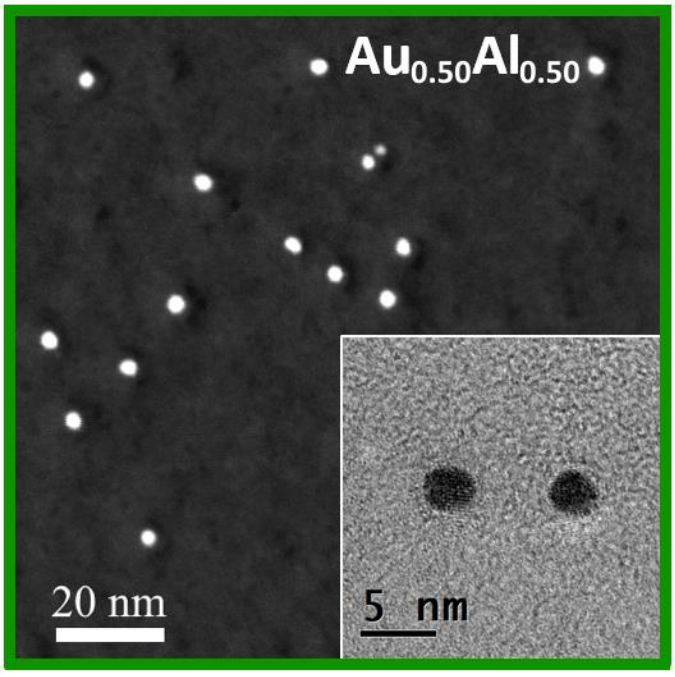
Received 00th January 20xx,

Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

Electronic Supplementary Information

TEM Characterization (complementary results)



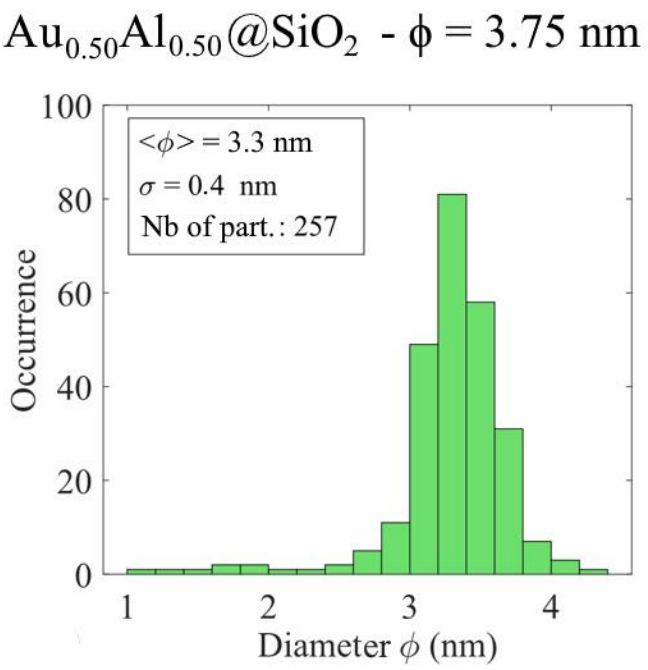


Fig. SI1: (left): size-selected $Au_{0.5}Al_{50}$ BNPs co-deposited in a silica matrix (∅=3.75 nm) and (right): corresponding size distribution. Insert of (left): bare $Au_{0.5}Al_{50}$ BNP of diameter 3.9 nm.

[a] *Univ. Lyon 1, CNRS, iLM, UMR 5306, F- 69622 Villeurbanne, France.*
[b] *Univ Lyon, INSA Lyon, UCBL, CNRS, MATEIS, UMR5510, F-69621 Villeurbanne, France*
[c] *Université d'Orléans, CNRS, ICMN, UMR7374, F-45071 Orléans, France.*
* E-mail: emmanuel.cottancin@univ-lyon1.fr
Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x

In-situ x-ray photoelectron spectroscopy (XPS)

In-situ x-ray photoelectron spectroscopy (XPS) was performed in order to infer the oxidation state of as-prepared BNPs. XPS measurements were performed with a VG CLAM IV spectrometer using Al kα radiation for AgAl and Mg kα radiation for $AuAl_2$. Wide scans and high resolution spectra were collected respectively with a constant pass energy of 50 and 20 eV, a step size of 1 and 0.1 eV. Collected XPS data were analysed using CASAXPS software, background was corrected using the Shirley model. Peak fitting was performed using Voigt shape functions with an asymmetric tail function for the metal-Al 2p peak. All the spectra were corrected for the position of the amorphous carbon at 284.4 eV.
Substrates were prepared by depositing an approximately 10 nm thick layer of amorphous carbon onto doped silicon substrates. Survey scans before nanoparticle deposition showed no other signal than carbon (see Fig. SI2).

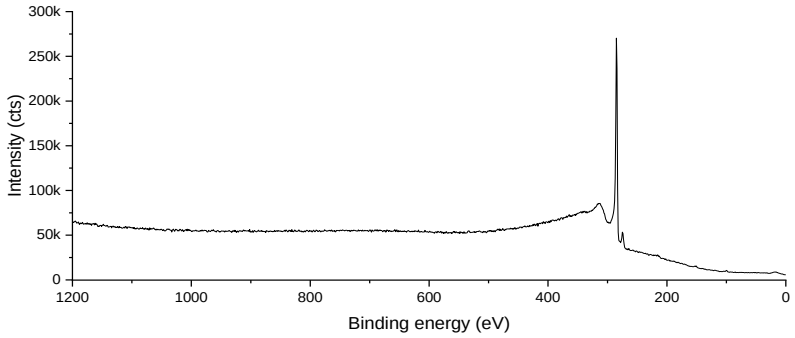


Fig. SI2: Overview spectrum of the carbon thin film substrate before nanoparticle deposition. No signals from spurious oxygen or the silicon substrate are visible.

Then, approximately 12 Å equivalent of non-size selected $Au_{0.37}Al_{0.67}$ BNPs (with an average diameter of about 4 nm) were deposited onto this film. The sample was then transferred at ~$\mathbf{10^{-9}}$ mbar pressure into the XPS chamber and analysed after ~25 minutes (Fig. SI3). The XPS spectra can be deconvoluted into metallic and oxidized Al fractions. The first spectrum shows approximately 83% of the aluminium in the metallic state, evolving to ~67% over several hours in ultra-high vacuum. From these spectra, we can deduce two observations. (1) Initially largely metallic BNPs oxidize even at ~$\mathbf{5.10^{-10}}$ mbar pressure at the scale of hours. This underlines the high reactivity of nanoscale aluminium and the necessity of proper protection. (2) The BNPs are not fully oxidized during fabrication and deposition, the 83% metallic percentage has to be seen as a lower limit. During co-deposition with the silica matrix the deposited BNPs are rapidly covered (of the order of seconds) and no longer exposed to oxygen traces in the carrier gas which could possibly oxidize BNPs after deposition. We furthermore judge oxidation by the silica matrix as minor as at least for pure Ag clusters no significant oxidation of the clusters by the matrix has been demonstrated, even down to smallest sizes (~20 atoms). [1]

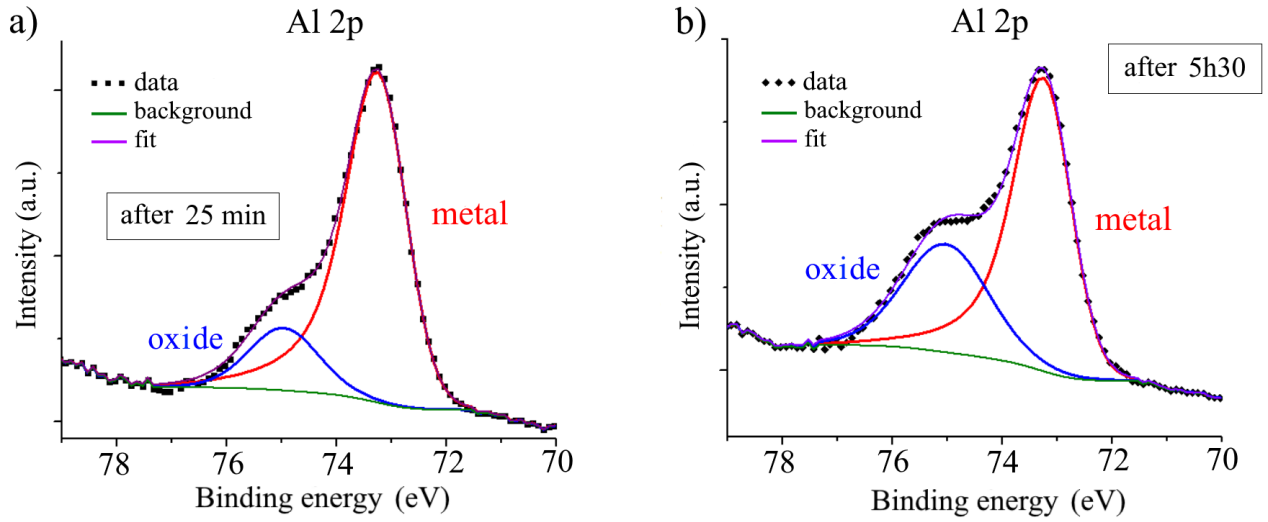
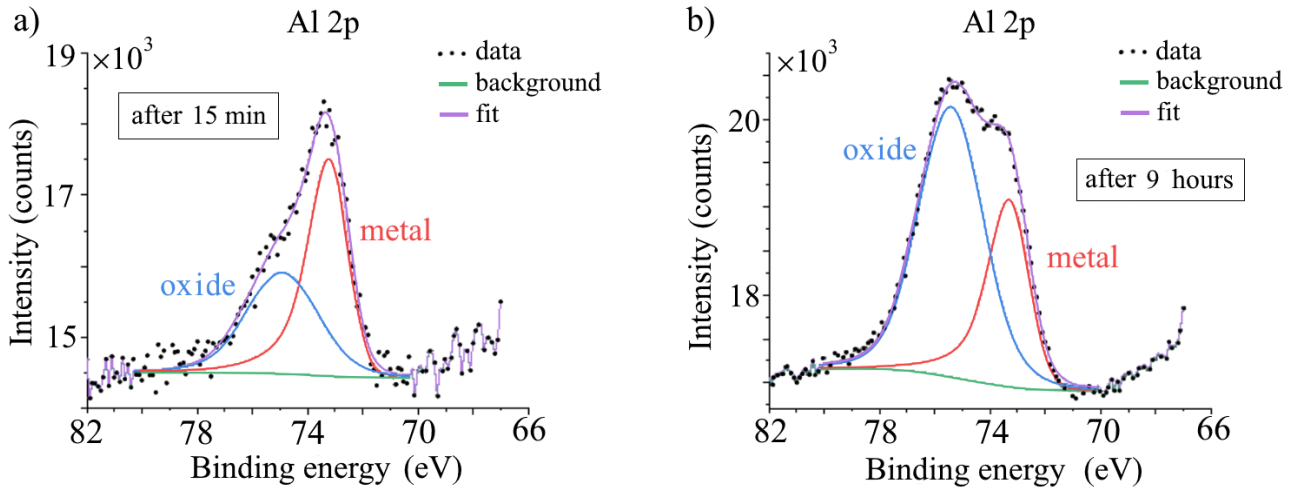


Fig. SI3: XPS response at the Al 2p transition for $AuAl_2$ BNPs. a) 25 minutes after the deposition, b) after 5h30 in UHV.

Similar experiments were performed on $Ag_{0.5}$ $Al_{0.5}$ BNPs. Here a lower degree of initial metallicity was observed (~55%), with oxidation evolving more rapidly over time (see Fig. SI4).

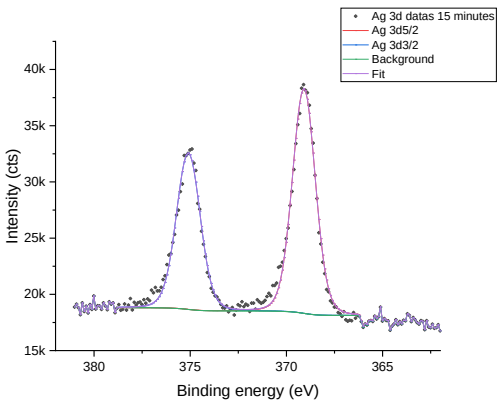


	position (eV)	FWHM (eV)	x_{mol} (%)
Al 2p metal	73.1	1.62	55.4 %
Al 2p oxide	74.9	3.06	44.6 %

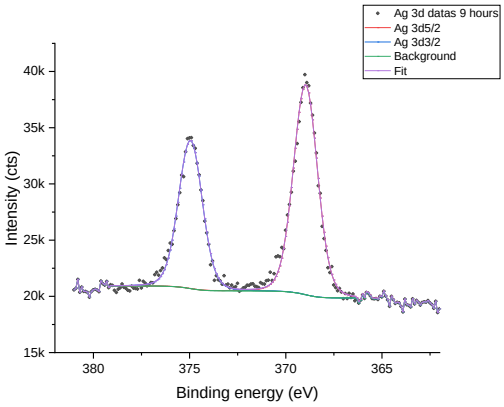
	position (eV)	FWHM (eV)	x_{mol} (%)
Al 2p metal	73.1	1.69	31.6 %
Al 2p oxide	75.4	2.78	68.4 %

Fig. SI4: XPS response at the Al 2p transition for $Ag_{0.5}$ $Al_{0.5}$ BNPs. a) 15 minutes after the deposition, b) after 9 hours in UHV.

The Ag lines did not show any sign of oxidation-induced shift over the same time period, under UHV conditions it is only Al which oxidises (see Fig. SI5).



a)



b)

	Position (eV)	FWHM (eV)
Ag $3d_{5/2}$	369.1	1.43 eV
Ag $3d_{3/2}$	375.1	1.43 eV

	Position (eV)	FWHM (eV)
Ag $3d_{5/2}$	369.0	1.47
Ag $3d_{3/2}$	375.0	1.45

Fig. SI5: XPS response at the Ag $3d_{5/2}$ and $3d_{3/2}$ transitions. a) 15 minutes after the deposition, b) after 9 hours in UHV.

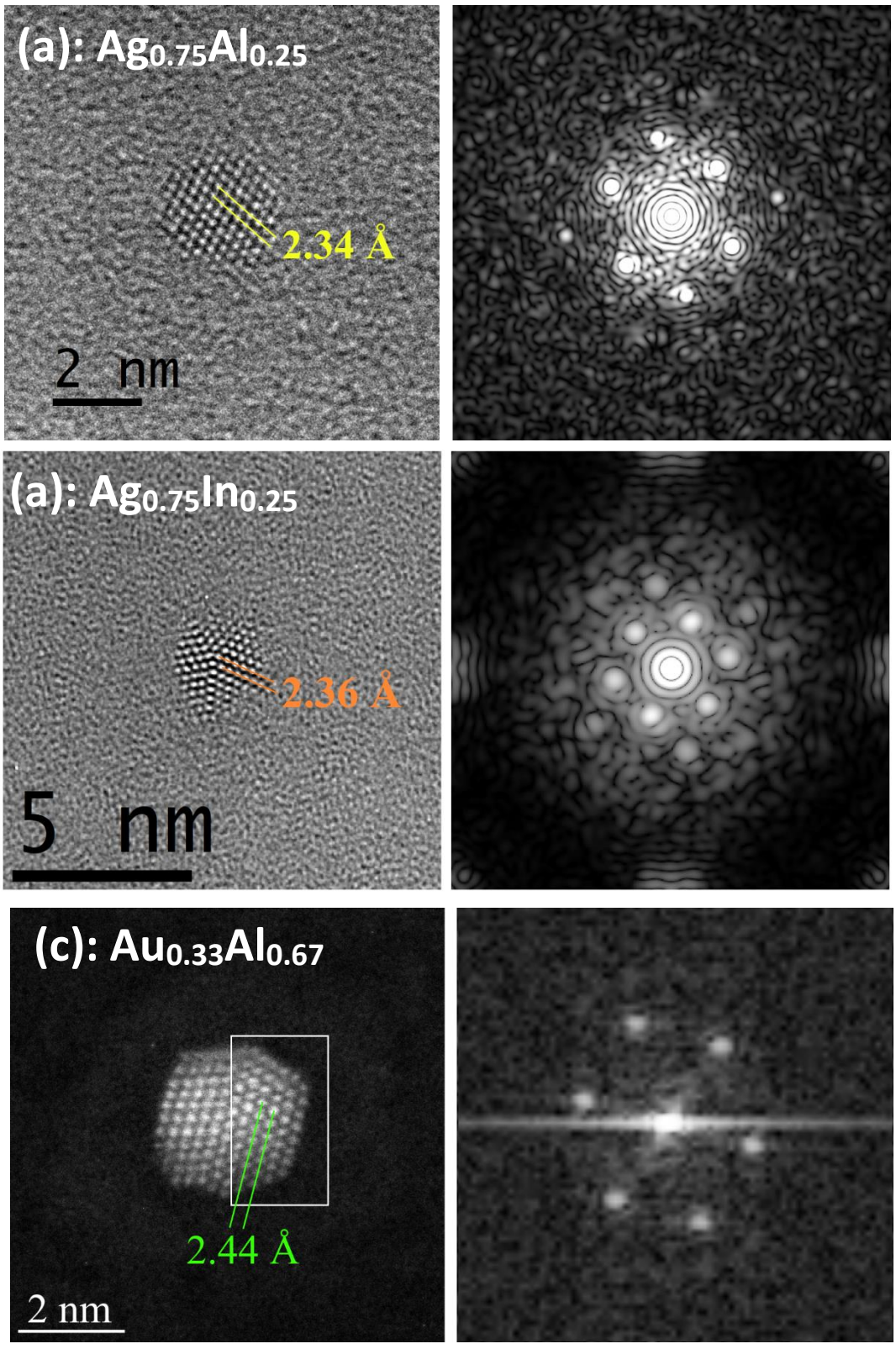


Fig. SI6: HR-TEM images (left) presented in Fig. 1 of the manuscript with the corresponding FFT patterns (right); d-spacing are noted on the left in the HR-TEM image. (a): $Ag_{0.75}Al_{0.25}$; (b): $Ag_{0.75}In_{0.25}$; (c): $Au_{0.33}Al_{0.67}$;

1. A. Campos, N. Troc, E. Cottancin, M. Pellarin, H.-C. Weissker, J. Lermé, M. Kociak and M. Hillenkamp, *Nature Physics*, 2019, **15**, 275-280.