Supplementary Information

Modulating the Surface Chemistry of Gold Nanoparticles produced via laser ablation in liquids by favored oxidative processes in the presence of Br anions

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1 Secondary role of the counterion: the case of *S*3 sample

As described and discussed in the main manuscript for the *S*2 sample (NaBr salt used), similar conclusions arise from the *S*3 colloid (KBr salt used).

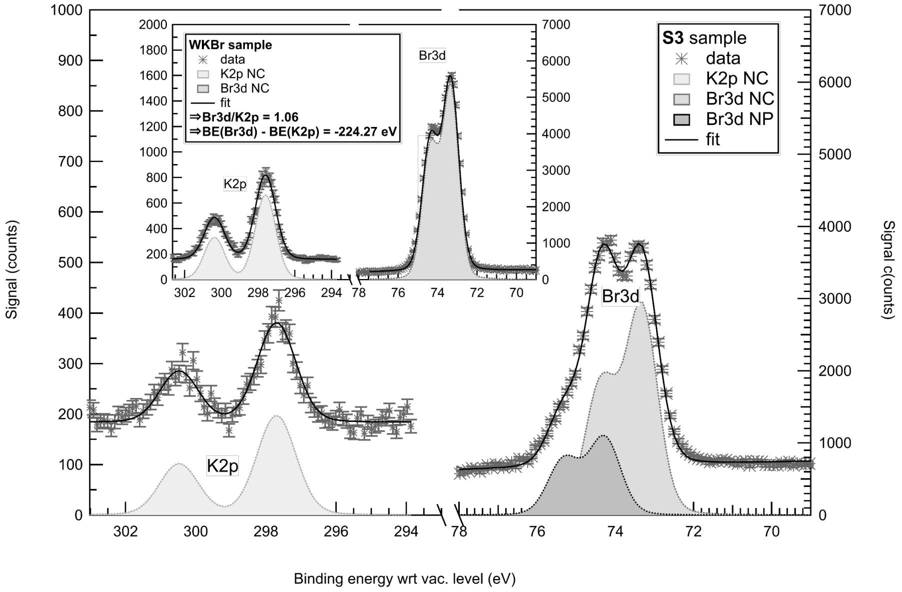

Fig. SI1 Br3d and K2p core levels recorded at 250 eV and 435 eV respectively on the *S*3 sample, along with the corresponding saline reference WKBr (inset). Photoelectron lines from nanoparticles and KBr nanocrystals are respectively denoted NP and NC. Associated fits are represented by solid lines and filled areas.

While two Br3d components are detected in the spectrum collected from the gold colloid, the counterion gives rise to a unique component in the K2p core level. The latter is attributed to KBr nanocrystals, as indicated by the WKBr reference spectrum. Once again, the absence of the counterion after the ADLS process is confirmed.

2 Adjustable halogen coverage: Au4f and Br3d spectra fitting

In Figure SI2, the extracted peak areas from the fitting procedure of the spectra recorded on each probed sample are presented. The Au4f core level includes both metallic and oxide components, while the Br3d core level peak encompasses contributions from halide nanocrystals (NC) and the surface of the gold nanoparticle (NP). The corresponding Au4f/Br3d

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ratio and Br coverage (σ_{Br} in nm^{-2}) are summarized in table S1, along with the sample characteristics such as pH and the saline concentration in NaBr or KBr (C_{XBr} in mM). Additionally, the signal percentage of the Au4f oxide component (Au4f^{n+}) is reported.

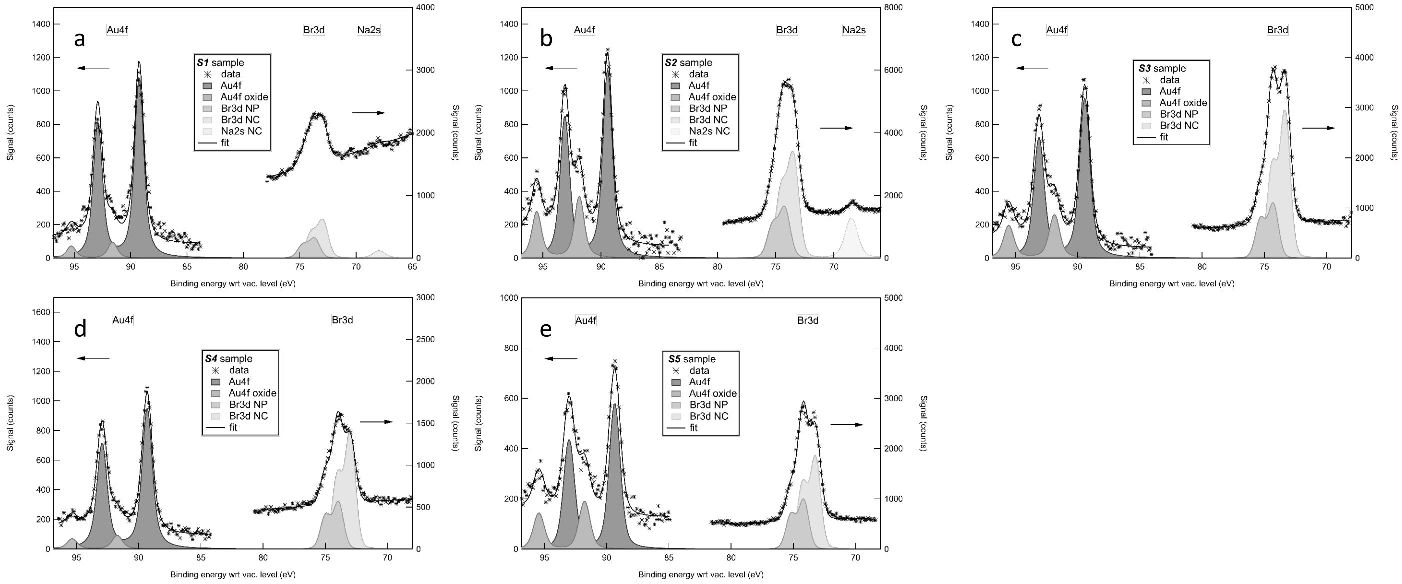

Fig. SI2 Au4f and Br3d core levels recorded at 250 eV on the all samples, namely: (a) $S1$; (b) $S2$; (c) $S3$; (d) $S4$; (e) $S5$ Associated fits are represented by solid lines and filled areas.

Table S1 All sample characteristics (pH and saline concentration C_{XBr} in NaBr or KBr) and results deduced from the fitting analysis (Au4f/Br3d ratio, Br nanoparticle surface coverage, σ_{Br}, and signal percentage of the Au4f oxide component, Au4f^{n+})

Sample	Figure	pH	C_{XBr} (mM)	Au4f/Br3d ratio	σ_{Br} (at/nm^2)	Au4f^{n+} (%)
S1	SI2.a	8.4	0.53	4.2 ± 0.7	2.8 ± 0.4	8 ± 1
S2	SI2.b	7.4	1.88	1.07 ± 0.05	8.5 ± 0.3	25 ± 2
S3	SI2.c	9.44	2.75	1.39 ± 0.10	6.9 ± 0.4	21 ± 1
S4	SI2.d	9.43	1.11	2.3 ± 0.2	4.6 ± 0.4	9 ± 2
S5	SI2.e	9.32	2.85	1.05 ± 0.05	8.6 ± 0.3	25 ± 2

3 Halogen-driven oxidation of the nanoparticle surface : percentage of adsorbed Br

In Figure SI3, the influence of the saline concentration of the percentage of adsorbed Br is reported. This percentage, denoted $\%_{Br}$, is defined as the proportion of adsorbed species with respect to the total amount present in the solution.

4 Attribution of the oxide Au4f component: oxygen or bromide induced oxidation

As discussed in the main article, attributing the oxide Au4f component using the ADLS setup is challenging, as this setup does not allow straightforward detection of the oxygen XPS signature. To address this limitation, we conducted an additional XPS characterization to resolve this critical issue.

This additional measurement was performed on sample $S6$, prepared under conditions comparable to samples $S3$ and $S5$ ([Br$^-$] = 2.75 mM, pH = 9.1) but with NaBr salt. The sample was prepared using a drop-casting method, where a droplet of the colloidal solution was dried on a Si wafer under ambient conditions. Subsequently, the sample was introduced into the UHV chamber (INSP laboratory), equipped with a monochromatized Al K_α x-ray source ($h\nu = 1486.6$ eV) and a hemispheric analyzer (PHOIBOS 100, SPECS). Under these conditions, we recorded Au4f, Br3d, and Na2s core-levels, with the spectra presented in Figure SI4. As in the PLEIADES experiment, we fitted the spectral lines, including two distinct components for the Br3d peak, corresponding to bromide adsorbed on the nanoparticle surface and NaBr crystals.

For the Au4f spectrum, the oxide component was not observed in the fitting convergence. From the Au4f/Br3d NP intensity ratio, we calculated the Br surface coverage of sample $S6$ using SESSA simulations, which yielded $\sigma_{\mathrm{Br}} = 10.25$ at/nm², calibrated according to the SESSA simulation curve at $h\nu = 1486.6$ eV.

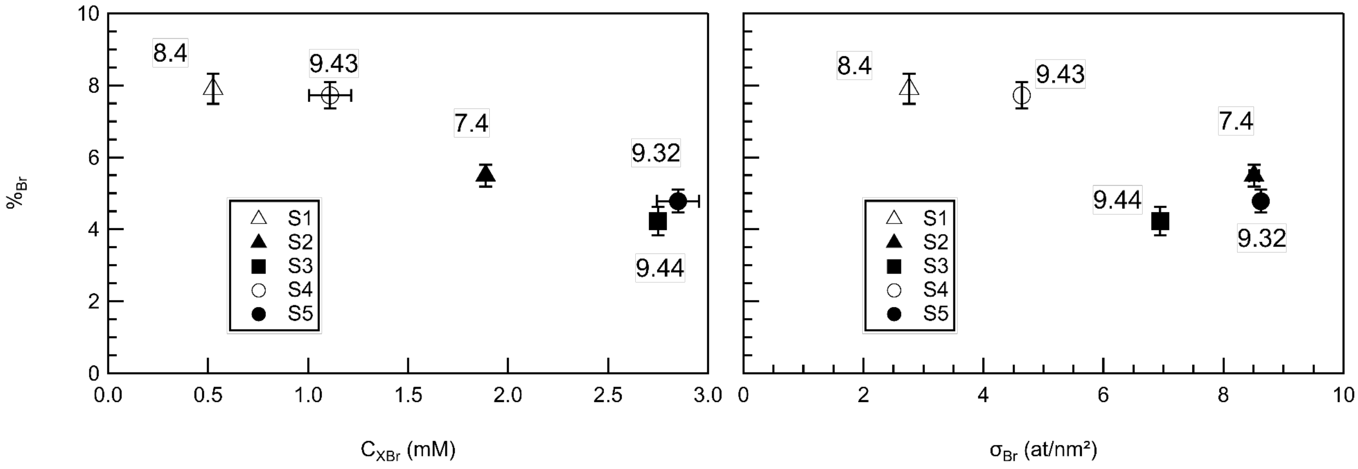

Fig. SI3 Evolution of the percentage of adsorbed Br ($\%_{Br}$) as a function of the saline concentration (left) and Br coverage (right). The pH of each sample is reported in the figure, adjacent to each marker.

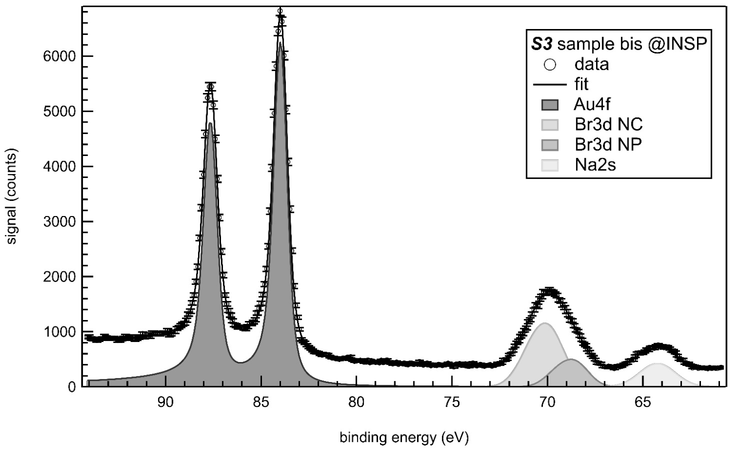

Fig. SI4 XPS spectrum recorded at INSP with an Al K_α source of $S6$ sample drop casted on a Si wafer.

5 Size distribution

Size distributions observed on samples $S1$ to $S4$ are reported in figure SI5. The number weighted size distributions are deduced from the analysis of TEM grid installed into the vacuum chamber on the line of sight of the nanoparticle beam onto the PLEIADES beamline. Nanoparticles collected on these TEM grids correspond to the nanoparticles probed by the x-ray beam. The number weighted size distributions are deduced from the analysis of TEM pictures using the ParticleSizer script in Fiji software (ellipse fitting mode). The surface equivalent diameter D of each nanoparticle is deduced from long axis length $2a$ and short axis length $2b$ ($D = \sqrt{4ab}$)

Notes and references

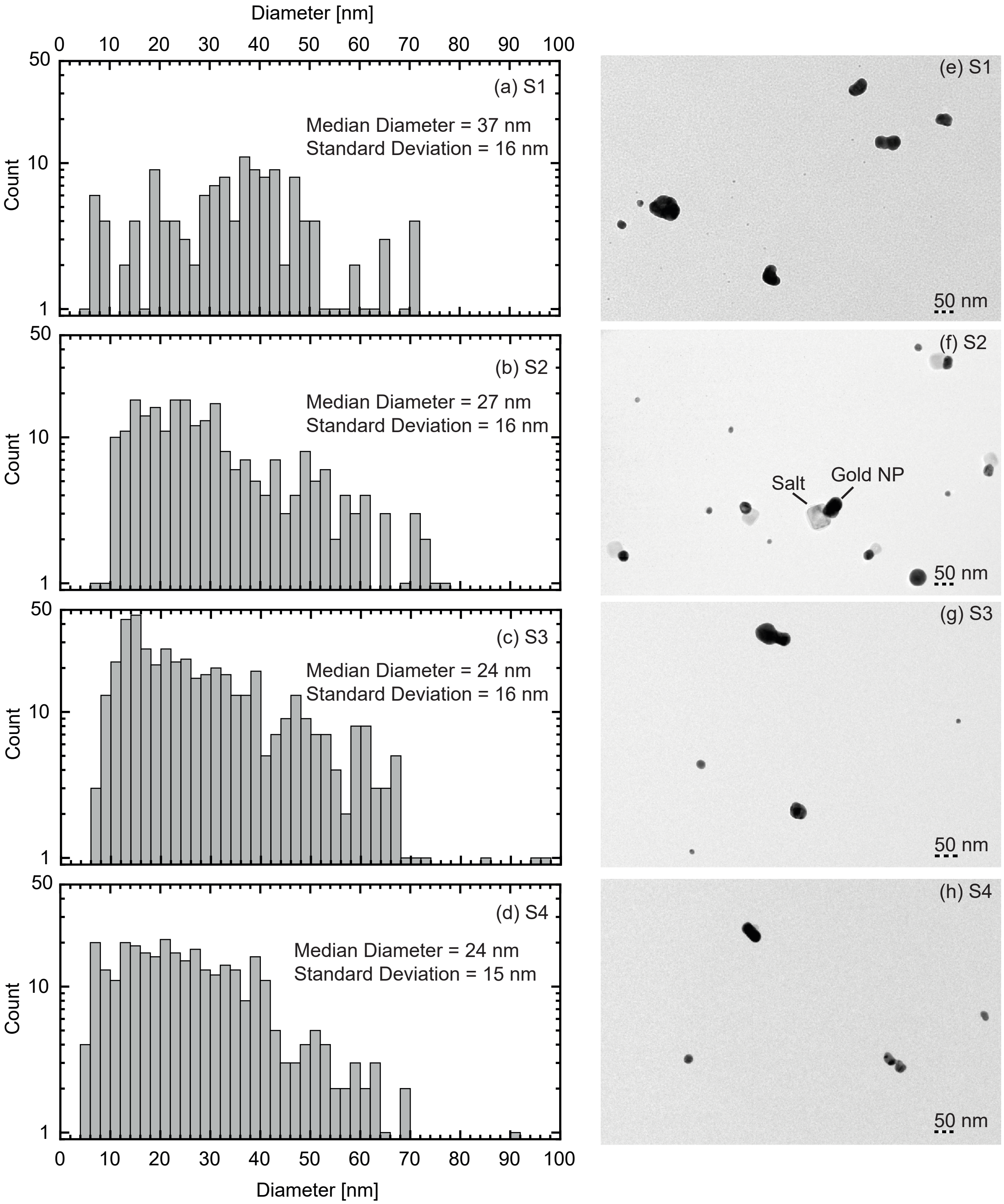

Fig. SI5 Size distributions observed on samples *S*1 (a), *S*2 (b), *S*3 (c), and *S*4 (d) and representative TEM pictures for *S*1 (e), *S*2 (f), *S*3 (g), and *S*4 (h) samples. On TEM picture for sample *S*2, salt crystals are observed in addition to the gold nanoparticles.