Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.


# Supporting Information: Near ambient pressure XPS study of subnanometer silver clusters on $Al_2O_3$ and $TiO_2$ ultrathin film supports

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## 1) APXPS Experiments on Ag foil

The APXPS experiments were performed at the bending-magnet beamline 9.3.2 of the Advanced Light Source, Lawrence Berkeley National Laboratory. Silver foil purchased from Alfa Aesar with 99.998% purity was used in this work. The silver foil was mounted on the sample holder along with a piece of gold foil for energy calibration. The sample was cleaned by repeating 3 cycles of Ar sputtering ($6.6\times10^{-6}$ mbar Ar, 1.5 kV acceleration voltage) for 30 min and annealing at 400 $^{o}$C for 3 min in UHV. After sputter-anneal cleaning, we collected the Ag 3d, C 1s, O 1s and Au 4f spectra at 770 eV photon energy. All the peak positions were calibrated with the Au $4f_{7/2}$ peak (binding energy (BE) = 84 eV). During the XPS measurement, the samples went through the atmospheres of UHV, 0.66 mbar $O_2$ and 0.66 mbar CO at various temperatures. The temperature was monitored by a k-type thermocouple. Two individual UHV leak valves were used to introduce $O_2$ (Air Gas, UHP) and CO (Air Gas, UHP) to the analysis chamber. A calibrated Baratron gauge was used to monitor the total pressure in the analysis chamber.

Ag 3d spectra of silver foil at 80 $^{o}$C under different atmospheres are shown in Figure S1a. An additional feature ($Ag^+$) appears with a BE shift ~ 0.5eV relative to the Ag metallic peak ($Ag^0$) upon oxygen exposure (0.66 mbar). An similar additional component also appears when the foil is exposed to 0.66 mbar of CO. In Figure 1b, we show the Ag 3d spectra taken at different temperatures under 0.66 mbar of oxygen. The $Ag^+$ component is observed under all three temperatures.

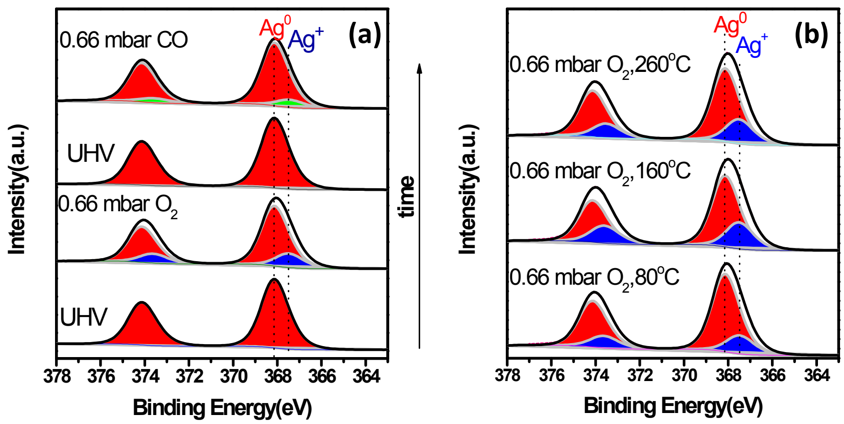


Fig.1 (a) Ag 3d spectra of silver foil at 80 °C under different conditions. (b) Ag 3d spectra of silver foil with different temperatures under 0.66 mbar of $O_2$ atmosphere.

2). **Grazing-incidence small-angle X-ray scattering (GISAXS) experiments on $Ag_3/Al_2O_3$ and $Ag_3/TiO_2$ samples.**

The GISAXS experiments were performed at the 12-ID-C beam line at the Advanced Photon Source of the Argonne National Laboratory using X-rays of 24.5 keV energy in an *in situ* GISAXS cell of our own design described for example in references [1-3] . The cell was sealed with mica windows and mounted on a computer controlled goniometer. The samples were positioned on a ceramic heater (Momentive Performance Materials Inc.) in a reaction cell having an internal volume of 25cm$^3$. The temperature was measured with a K-type thermocouple attached to the edge of the heater surface. The K-type thermocouple was attached to a temperature controller (Lakeshore model 340) which controlled the output of a KEPCO Power Supply (model ATE 55-5DM) for precise temperature regulation of the heater. The X-ray beam was scattered off the surface of the sample at near the critical angle ($\alpha_c$ = 0.18) of the substrate. A 1024x1024 pixel two-dimensional MarCCD detector was used for recording the GISAXS images from the sample. GISAXS data were collected as a function of reaction temperature .

The better sintering resistance of silver clusters on the titania support was confirmed by GISAXS, as illustrated in Figure S2 on the example of $Ag_3$ clusters. In the case of alumina supported clusters there is a change of the GISAXS pattern observed at 125 ºC, indicative of the onset of the sintering of the silver clusters. At 150 ºC a pronounced change in GISAXS pattern occurs, typical of scattering from small aggregates. This change is analogue to the one previously reported[1]. In the case of the titania-supported clusters, only a very small change in the GISAXS pattern is observed at 150 ºC, which indicates more stable clusters on titania. Thus, GISAXS confirms the findings from XPS that clusters sinter more easily (i.e. at lower temperature) on alumina than on titania.

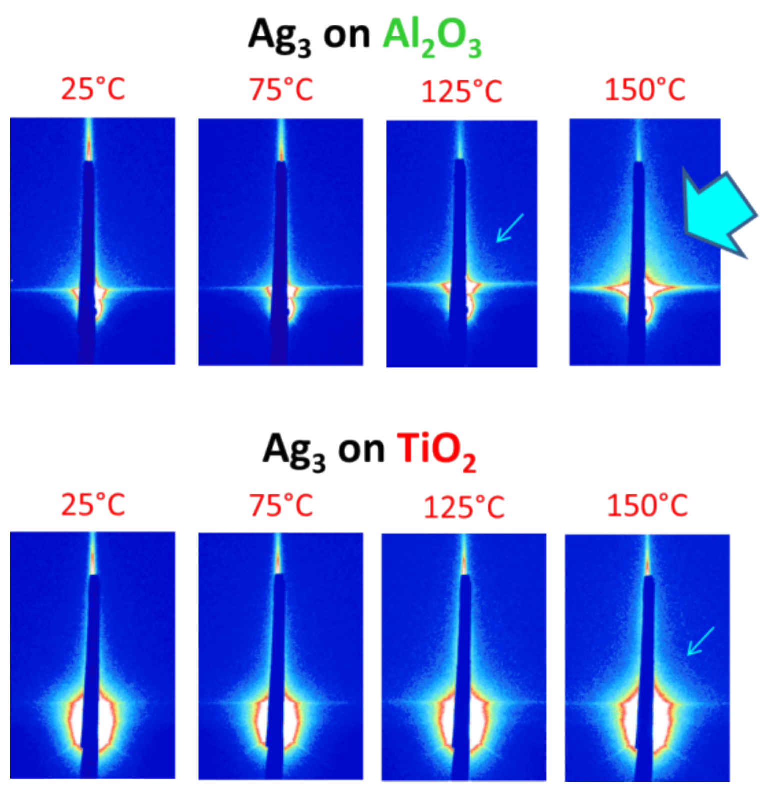

Figure S2. GISAXS images recorded on alumina- and titania-supported $Ag_3$ clusters at 25, 75, 125 and 150 ºC. The small arrow indicates a small change in the scattering pattern typical of the onset of particle agglomeration. The big arrow indicates significantly increased scattering from aggregates formed.

**Supplemenetal References**

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[2] S. Lee, B. Lee, S. Seifert, S. Vajda and R. E. Winans, *Nucl. Instr. and Meth. A,* 2011, **649**, 200-203.

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