† Electronic Supplementrary Information

Fine-tuning the feature size of nanoporous silver

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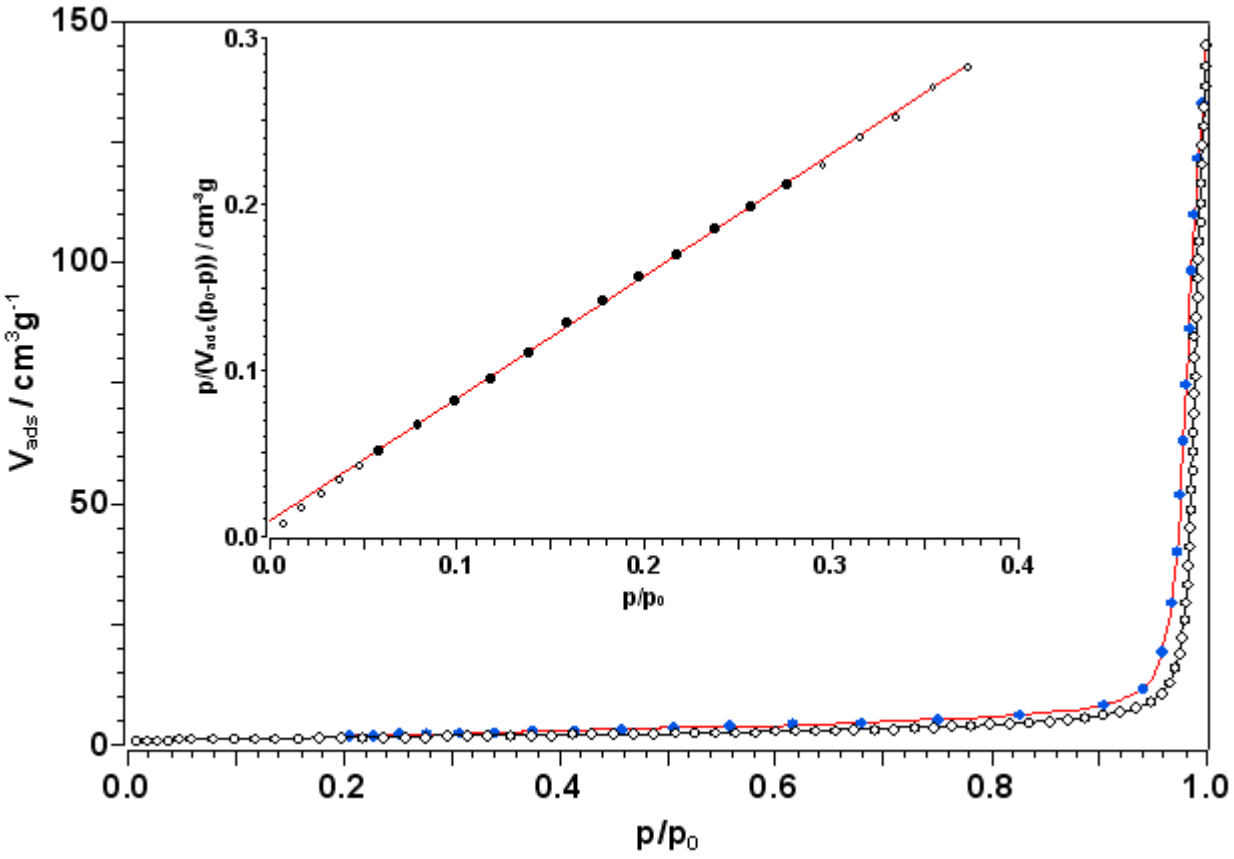
Microstructural characterization: The phases present in the Ag-Al alloy precursors and the corresponding nanoporous Ag were investigated by X-ray diffraction (XRD) in the 2θ range of 30 to 80 degrees using a Bruker X-ray diffractometer D8 with Cu-Kα_1 radiation (λ = 0.15406 nm). The chemical composition of the three types of alloy precursors ($Ag_{15}Al_{85}$, $Ag_{10}Al_{90}$ and Ag_5Al_{95}), the partially dealloyed structures (Fig. 2) and the fully dealloyed samples were investigated by energy dispersive X-ray spectroscopy (EDX) using an environmental scanning electron microscope (FEI XL30 ESEM-FEG). The fine porous microstructure achieved in nanoporous Ag was investigated using an ultra-high resolution scanning electron microscope (FEI XL30S SEM-FEG).

Effect of alloy composition and sample thickness on the ligament size: Starting with the case of nanoporous Au obtained by selective dissolution of Ag from the Au-Ag alloys, it has been found that the higher the Ag content in the alloy precursor, the smaller the ligament size in the corresponding nanoporous Au. We used that approach in ref. 25 to achieve small ligament sizes in nanoporous Au by varying the composition of the alloy precursor from $Au_{25}Ag_{75}$ to $Au_{10}Ag_{90}$. The decrease in the ligament size of Au with increasing Ag content in the starting alloy can be explained by the corresponding dealloying time: unpublished experimental data (manuscript in preparation) show that a 2x1x1 mm^3 alloy with composition $Au_{10}Ag_{90}$ (at. %) is fully dealloyed by free corrosion in concentrated nitric acid within ~9 h, whereas a 2x1x1 mm^3 alloy with composition $Au_{30}Ag_{70}$ (at. %) is fully dealloyed after ~48 h under similar experimental conditions. Keeping the sample for a long time in acid contributes to the coarsening of the ligaments as mentioned in ref. 20. This explains why the Au-Ag sample dealloyed in 9 h has a smaller ligaments size compared to the one dealloyed in 48 h. Returning to the current work, we have observed a similar trend in the case of nanoporous Ag: by varying the alloy composition from $Ag_{15}Al_{85}$ to Ag_5Al_{95}, the ligament size of nanoporous Ag can be tuned from ~50 nm down to ~30 nm. However, other parameters such as the acid concentration and the thickness of the starting alloy were observed to significantly influence the dealloying time and subsequently the ligament size. For instance nanoporous Ag with ligament size ~30 nm instead of ~50 nm is obtained by reducing the thickness of the cold-rolled $Ag_{15}Al_{85}$ alloy precursor from ~0.8 mm down to ~ 0.1 mm.

BET specific surface area: For reliable BET analysis, a relatively large amount of sample (at least 200 mg) is required. Therefore 334 mg of nanoporous Ag was synthesized by dealloying 3 alloy precursors with composition $Ag_{15}Al_{85}$ (at. %) and having a total mass of 807 mg. The characteristic ligament size in the dealloyed material was found to vary between 50-60 nm. The specific surface area of the synthesized nanoporous Ag was measured by nitrogen adsorption following the BET method. Nitrogen adsorption/desorption isotherm was determined on a Sorptomatic 1990 Thermo Finningen at -196°C. Before the BET measurement, the sample was outgassed at 110°C for 18h as an effective way for water/solvent and contaminant removal. The BET specific surface area (S_{BET}) as well as the BET constant (C_{BET}) were calculated from the linear part of the nitrogen adsorption isotherms (0.05 <p/p0< 0.35).

Fig. S1 represents the N_2 adsorption/desorption isotherm curve obtained from the 334 mg nanoporous Ag. This curve is characterized by two regions: (i) at high relative pressures, a hysteresis loop associated with capillary condensation according to the Type IV isotherm with respect to the IUPAC classification; (ii) at low relative pressures, a linear behavior associated to the monolayer adsorption (See also inset Fig. S1). The quantity of N_2 adsorbed in that linear region was used to evaluate the specific surface area according to the BET method. The BET surface area S_{BET} (5.82±0.06 m^2g^{-1}) and the BET constant C_{BET} (80) can be deduced from the slope (0.73886541 ± 0.00483898) and the offset (0.00929689 ± 0.00087546) of that linear part of the adsorption isotherm (0.05 < p/p0 < 0.35).

Fig. S1: Nitrogen adsorption (open/white makers) and desorption (solid/blue markers) isotherm curve obtained for nanoporous Ag. The red line in the inset represents the linear fit used to evaluate the BET specific surface area.



Bimodal pore size distribution in nanoporous Ag: Alloy precursors with high Al content (i.e. Ag_5Al_{95}) were observed to undergo a full and explosive fragmentation in concentrated acid as a consequence of the high amount of energy released during dealloying. Full fragmentation is avoided by reducing the acid concentration below to ~10 wt%. However the corresponding nanoporous Ag displays a bimodal pore size distribution as shown in *Fig. S2:* (i) micropores with average diameter ~10-15 μm (*Fig. S2a and b in ESI*) and nanopores with average diameter ~30 nm (*Fig. S2c and d in ESI*).

Fig. S2: Scanning electron micrographs showing the bimodal pore size distribution in nanoporous Ag at different magnifications.