Supporting Information for: Nanoporous Gold for Electrocatalytic Methanol Oxidation

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Ag contents as derived by EDX vs. ICP-OES

Figure 1: Residual Ag contents $x_{Ag}$ in samples of nanoporous gold obtained by three different dealloying routes and determined via energy-dispersive X-ray (EDX) spectroscopy inside a scanning electron microscope vs. $x_{Ag}$ as determined by inductively-coupled plasma optical emission spectroscopy (ICP-OES). Red line represents least-squares linear fit. Horizontal error bars from three repeated measurements at different sample spots of two different samples. Vertical error bars by two-fold repeated injection and two different samples.

Overall Ag concentration inside NPG samples was determined via inductively-coupled plasma optical emission spectroscopy (ICP-OES) using freshly prepared, cleaned (repeated rinsing in water) and dried (under vacuum) NPG samples (made as described in main text). After mass determination those were solubilized in *aqua regia* and diluted with water (NPG-A: 1:500, NPG-B and NPG-C: 1:100) to dissolve AgCl precipitates. After calibration each fusion was injected twice into an Optima 8300 DV ICP-OES instrument (Perkin Elmer) using Ar plasma excitation and Ag determination at 328.07 nm and each measurement replicated three times (standard deviation within one measurement below 4%). The error bars in Fig. 1 result from the averaging over two different samples from each dealloying route.
XPS shift of Ag(0) in Ag-Au alloys as a function of $x_{Ag}$

Shifts of the Ag 3d$_{5,2}$ peak due to alloy effects of Ag with Au were screened using electrodeposited Au$_{1-x}$Ag$_x$ alloy reference samples on sputtered Au substrates with $x = 2 – 87$ at.%. Electrodeposition (according to Ji et al.$^1$) was performed from $(100 - x)$ mM K[Au(CN)$_2$] + $x$ mM K[Ag(CN)$_2$] + 250 mM Na$_2$CO$_3$ at $-1200$ mV vs. Ag/AgCl RE and Au wire CE for 15 min to generate a closed alloy layer which was cleaned in water and dried under air subsequently. EDX confirmed the composition of the samples.

Figure 2: Reference samples of Au$_{1-x}$Ag$_x$ alloys of different compositions $x = 2 – 90$ at.% were prepared as well as a pure Ag sample and XP spectra were recorded. Ag 3d$_{5,2}$ peak shift for the different alloy compositions (squares) are shown as well as values for binding energy shifts for Ag 3d$_{5,2}$ peaks in different Ag-Au alloys from Ref.$^2$ (circles) are shown.

References
