Supporting Information for: Nanoporous Gold for Electrocatalytic Methanol Oxidation

Matthias Graf,* Mareike Haensch, Jörg Carstens, Gunther Wittstock, and Jörg Weissmüller

E-mail: matthias.graf@tuhh.de

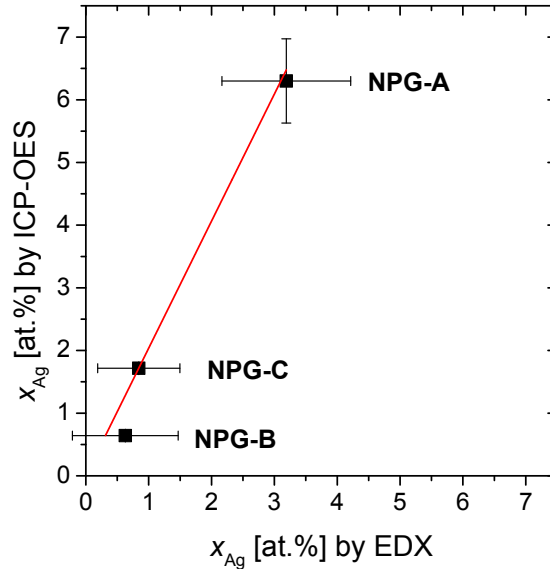# Ag contents as derived by EDX vs. ICP-OES

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_2CO_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.
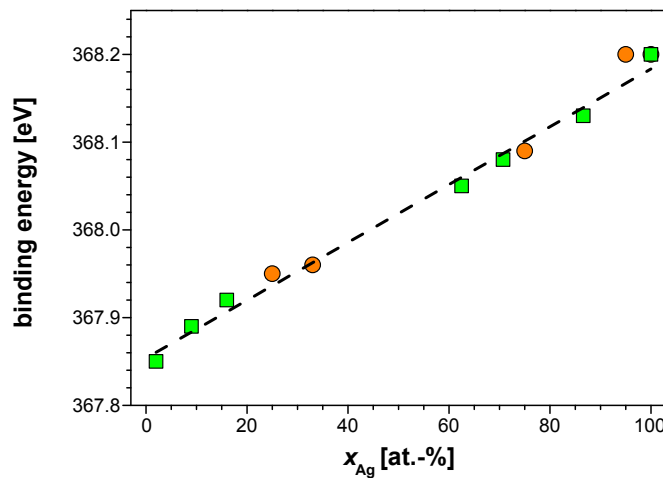

Figure 2: Reference samples of $Au_{1-x}Ag_x$ alloys of different compositions $x = 2 - 90$ at.% were prepared as well as a pure Ag sample and XP spectra were recorded. Ag $3d_{5/2}$ peak shift for the different alloy compositions (squares) are shown as well as values for binding energy shifts for Ag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

References

(1) Ji, C.; Searson, P. C. *Appl. Phys. Lett.* **2002**, *81*, 4437–4439.

(2) Tyson, C.; Bzowski, A.; Kristof, P.; Kuhn, M.; Sammynaiken, R.; Sham, T. *Phys. Rev. B* **1992**, *45*, 8924–8928.