Residual Silver in Nanoporous Gold prepared by Alloy Corrosion

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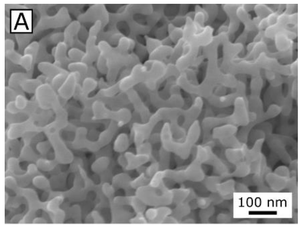
Fabrication of NPG



SEM image of the cross-section of a NPG sample

Nanoporous gold (NPG) is an unsupported bulk material with a bicontinuous pore and ligament structure. The high surface to volume ratio, high chemical flexibility and tunability as well as high electrical and thermal conductivity makes it interesting as a prototype for a rational design of catalysts.
When NPG is prepared by alloy corrosion of a Ag-Au alloy, residual Ag remains in the otherwise pure gold structure.[1]
Because Ag has an influence on the catalytic activity and stability of the NPG catalyst[2] and Ag tends to segregate to the surface due to its lower free surface energy,[3] XPS with different photon energies was used to determine the distribution of residual Ag in the near-surface regions of NPG.

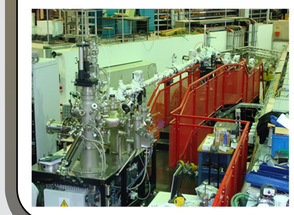
Alloy corrosion or dealloying is the selective leaching of the less noble metal from an alloy, e.g. Ag-Au. In this work, NPG was dealloyed in a multistep potential program with increasing dealloying potentials to avoid cracking of the ligaments.

Investigated Nanoporous Gold Samples

Several different NPG samples were investigated towards their distribution of residual Ag.
Methanol electrooxidation was chosen as a model electrocatalytic reaction.

Sample	Sample geometry	Treatment	L_B / nm
NPG_C_M	cylindrical without support	100 CV cycles in a solution of 1 M MeOH + 1 M KOH between -0.5 V and 1.3 V	34.2 ± 8.3
NPG_C_0	cylindrical without support	100 CV cycles in a solution of 1 M KOH between -0.5 V and 1.3 V	34.9 ± 8.9
NPG_A_M	cylindrical without support	5 min at 0.55 V vs. Hg/HgO in 1 M MeOH + 1 M KOH	42.3 ± 12.0
NPG_A_0	cylindrical without support	5 min at 0.55 V vs. Hg/HgO in 1 M KOH	36.1 ± 9.2
NPG_T	cylindrical without support	thermal annealing at 300 °C for 10 min	481.6 ± 120.1
NPG_P	cylindrical without support	partial dealloying, stopped at $\chi_{Ag,bulk}$ = 30 at. %	8.0 ± 1.7
NPG_F	thin film on glass support	as dealloyed	10.2 ± 2.0
NPG_F_T	thin film on glass support	thermal annealing at 300 °C for 5 min	12.3 ± 2.6

HESGM beamline of BESSY II

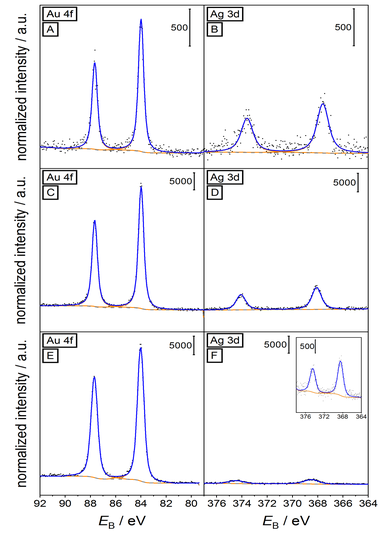


Instrument data (table)

Monochromator	SGM
Experiment in vacuum	Yes
Temperature range	50 - 1200 K (for T > 1200 K contact Station Manager)
Detector	XPS: Scienta R3000, NEXAFS: channel-plate-based electron detector (for use a fluorescence detector contact Station Manager)
Scattering Geometry	Horizontal
Angular range	-45° - 135° in respect to direct beam direction
standard sample size	10 mm x 10 mm (in a case of other sizes contact Station Manager)
azimuthal sample rotation	Yes
Software	SES for XPS, LabView-based and EMP2 for NEXAFS
Instrument responsible	Dr. Alexei Nefedov: 0721-608-23551, alexei.nefedov@kit.edu

[1] L. V. Moskaleva, S. Röhe, A. Wittstock, V. Zielasek, T. Klüner, K. M. Neyman, M. Bäumer, *Phys. Chem. Chem. Phys.* **2011**, *13*, 4529.
[2] T. Krekeler, A. V. Straßer, M. Graf, K. Wang, C. Hartig, M. Ritter, J. Weissmüller, *Mater. Res. Lett.* **2017**, *5*, 314.
[3] R. A. Manzhos, A. G. Krivenko, S. V. Doronin, M. A. Choba, V. A. Safonov, *J. Electroanal. Chem.* **2013**, *704*, 175.

XP spectra of NPG at different photon energies



E_{kin} of the emitted photoelectrons:

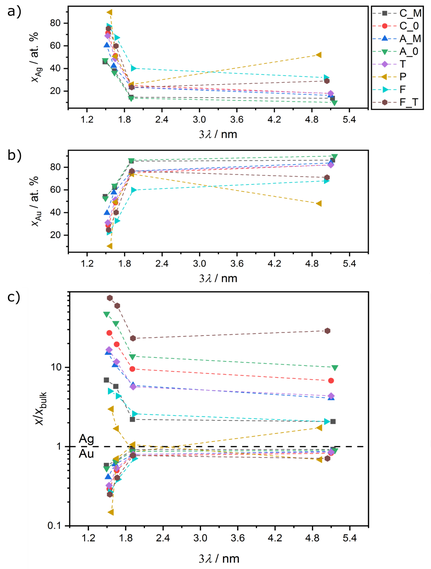
A and B: E_{kin} = 145 eV, Information depth at E_{kin}:
3 λ = 1.41 nm (Au), 1.59 nm (Ag)

C and D: E_{kin} = 211 eV, 3 λ = 1.60 nm (Au), 1.71 nm (Ag)

E and F: E_{kin} = 311 eV, 3 λ = 1.89 nm (Au), 2.01 nm (Ag)

Investigation of residual Ag by X-ray photoelectron spectroscopy

The elemental fractions of Ag and Au were determined for all samples and plotted vs. the information depth (3λ) of the analysis.



Elemental fraction of Ag (a) and Au (b) in surface-near regions of NPG and elemental fraction normalized by the bulk fraction as determined by EDX. Values > 1 indicate surface enrichment (Ag) and values < 1 indicate surface depletion (Au).

All NPG samples regardless of their treatment show an enrichment of Ag at the surface. The behavior is less pronounced for high values of bulk residual Ag as in the partially dealloyed sample.

In conclusion, fractions of residual as determined by EDX or XPS with Al K_α radiation are much lower than actually present at the surface of NPG.