# Independent control over residual silver content of nanoporous gold by galvanodynamically controlled dealloying

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#### **Supporting Information**

Residual Ag was determined for all samples by atomic absorption spectroscopy (AAS) after dissolution of npAu ( $x_{Ag,AAS}$ ). Residual Ag was determined for all samples by atomic absorption spectroscopy (AAS) after dissolution of npAu. Ag content is stated as mole fraction of silver ( $x_{Ag,AAS}$ ). For samples prepared by GCD and containing more 1 at% Ag, EDX measurements were performed at two positions A und B exposed after fracturing a disk-shaped macroscopic sample (Fig. S1) in order to check for the homogeneity of the residual silver content. Position A is close to the outer surface and position B is close to the centre of a macroscopic sample. EDX detection was not possible for all samples containing less than 1 at% Ag.

The ligament sizes were characterized by scanning electron microscopy (SEM) images, from which approximately 200 ligament sizes  $L_B$  were measured for each sample position A and B. From those values, an average ligament size  $L_{B,av}$  was determined.  $L_B$  distribution curves obtained for positions A ( $L_{B,A}$ ) and B ( $L_{B,B}$ ) in Figs. S2c, S3d, S10 and S11 are examples of a representative npAu samples to show the Gauss-distribution and uniformity of the samples and and within the sample. Shaded areas in the  $L_B$  distribution curves indicate the maxima of the mean ligament size.



**Fig. S1:** a) For SEM measurements for all obtained nanoporous gold monoliths and also EDX measurements of nanoporous gold monolith obtained by GCD, the monolith was fractured so that the cross section could be investigated close to the outer surface (position A shown in b)) and in the centre (position B shown in c)).



## ESI-1 Supplementary data for npAu obtained by free corrosion (FC)



### ESI-2 Supplementary data for npAu obtained by potentiostatically controlled dealloying (PCD)

During this dealloying technique the current response *I* allows to calculate the  $x_{Ag}$  in npAu ( $x_{Ag,calc}$ ). The geometric area  $A_{geom}$  was calculated with equation (S-1) assuming the alloy samples to be perfect cylinders.

$$A_{geom} = 2 \pi \left(\frac{d}{2}\right)^2 + 2 \pi \left(\frac{d}{2}\right) h \tag{1}$$

According S-1,  $A_{geom}$  amounted to 0.41-0.42 cm<sup>2</sup> for diameter d = 0.5 cm and height  $h = (0.015 \pm 0.005)$  cm.

 $A_{\text{geom}}$  allowed the calculation of the current density  $j_{\text{geom}} = I / A_{\text{geom}}$ .

The dealloyed Ag was calculated with equation (S-2):

$$x_{Ag} = \frac{\int_{t_0}^{t_x} (l \cdot t)}{F \cdot m_{alloy} \left(\frac{w_{Ag}}{M_{Ag}}\right)} = \frac{Q(t)}{F \cdot m_{alloy} \left(\frac{w_{Ag}}{M_{Ag}}\right)}$$

- I: current / A
- t: time ( $t_0$  = start of the dealloying;  $t_x$  = end of the dealloying) / s
- Q: electric charge / As
- *F*: Faraday constant (96 485 C/mol)
- $m_{\text{alloy}}$ : weight of the AuAg-alloy / g
- $w_{Ag}$ : mass fraction of Ag in AuAg-alloy
- $M_{Ag}$ : molar mass of Ag (107.87 g mol<sup>-1</sup>)

(2)



**Fig. S3**: Representative SEM images of npAu obtained by PCD in 5 M HNO<sub>3</sub> at +0.06 V vs. QRE from a)  $Au_{20}Ag_{80}$ , b)  $Au_{25}Ag_{75}$  and c)  $Au_{30}Ag_{70}$ ; and d) corresponding  $L_B$  distribution curves. e)-g) Corresponding histograms to the  $L_B$  distribution curves shown in d)



Fig. S4:Slow PCD of  $Au_{30}A_{70}$  at +0.06 V vs. QRE in 5 M HNO3 (black) and the calculated Ag<br/>residues  $x_{Ag,calc}$  (orange). The process could be stopped at a desired time. The times for<br/>termination yielding npAu with  $x_{Ag}$  of 5 and 10 at% are marked in inset.



**Fig. S5**: SEM images of npAu samples with  $x_{Ag,AAS}$  ( $x_{Ag,calc}$ ) of a) 2±1 (2), b) 5±1 (5), c) 7±1 (7) and d) 13±2 (10) at% from Au<sub>30</sub>Ag<sub>70</sub> prepared by PCD in 5 M HNO<sub>3</sub> at +0.06 mV vs. QRE terminating the dealloying process at the desired *Q* as shown in Fig. S4.



**Fig. S6**: Chronoamperograms for PCD of Au<sub>30</sub>A<sub>70</sub> (black), Au<sub>25</sub>A<sub>75</sub> (blue) and Au<sub>20</sub>A<sub>80</sub> (red) in 5 M HNO<sub>3</sub> at +0.06 V vs. a QRE. Note the zooms (right) of the colored areas in the left diagram.



- **Fig. S7**: Chronoamperograms for PCD of Au<sub>30</sub>A<sub>70</sub> in 5 M HNO<sub>3</sub> at +0.06, +0.12 and+ 0.30 V vs. a QRE demonstrating the effect of the applied potential on the Ag dissolution rate. Note the zooms (right) of the colored areas in the left diagram.
- ESI-3 Supplementary data for npAu obtained by galvanodynamically controlled dealloying (GCD)



**Fig. S8:** Representative SEM images of npAu obtained by GCD from  $Au_{30}Ag_{70}$  in 5 M HNO<sub>3</sub> at an initial current density of a) 5 mA/cm<sup>2</sup>, b) 25 mA/cm<sup>2</sup>, c) 50 mA/cm<sup>2</sup>, d) 100 mA/cm<sup>2</sup> and e) 125 mA/cm<sup>2</sup> showing how the macroscopic sample disintegrates into a powder after dealloying at to high  $j_{geom}$ .



**Fig. S9:** Critical potentials  $E_{crit}$  of different starting alloys in 5 M HNO<sub>3</sub> (red: Au<sub>20</sub>Ag<sub>80</sub>, blue: Au<sub>25</sub>Ag<sub>75</sub> and black: Au<sub>30</sub>Ag<sub>70</sub>).  $E_{crit}$  was determined from the polarization curves shown in Fig. 2c of the main manuscript.



Fig. S10: a) L<sub>B</sub> distribution curves of npAu from all AuAg-alloys prepared by GCD in 5 M HNO<sub>3</sub> with an initial current density of 5 mA/cm<sup>2</sup> corresponding to SEM images in Fig. 3 of the main manuscript. b) Representation of obtained ligament sizes of npAu samples using different preparation routes from Fig. S2c, Fig. S3d and Fig S10a. c)-e) Corresponding histograms to the L<sub>B</sub> distribution curves shown in a)

alloy	x <sub>Ag,calc</sub> [at%]	$x_{Ag,EDX,A}$ [at%]	$x_{Ag,EDX,B}$ [at%]
Au <sub>25</sub> Ag <sub>75</sub> (1)	1	$1.2 \pm 0.1$	$1.4 \pm 0.1$
Au <sub>30</sub> Ag <sub>70</sub> (2)	1	1.4 ± 0.2	1.4 ± 0.2
Au <sub>25</sub> Ag <sub>75</sub> (3)	2,5	2.3 ± 0.2	2.2 ± 0.2
Au <sub>30</sub> Ag <sub>70</sub> (4)	2,5	2.1 ± 0.2	2.9 ± 0.4
Au <sub>25</sub> Ag <sub>75</sub> (5)	5	4.6 ± 0.4	6.2 ± 0.4
Au <sub>30</sub> Ag <sub>70</sub> (6)	5	6.0 ± 0.4	5.3 ± 0.4
Au <sub>25</sub> Ag <sub>75</sub> (7)	7,5	7.4 ± 0.5	9.7 ± 0.6
Au <sub>25</sub> Ag <sub>75</sub> (8)	10	9.0 ± 0.6	14 ± 0.7

**Table S1:**Residual Ag content obtained by EDX at two different positions A and B shown in<br/>Fig. S1a. Only for higher Ag contents a gradient is determined.



**Fig. S11:**  $L_{\rm B}$  distribution curves (prepared as described and shown in Figs. S2, S3 and S10) of npAu samples described in Table S1 with different residual Ag content prepared by GCD in 5 M HNO<sub>3</sub> with initial current density of 5 mA/cm<sup>2</sup>. Within experimental uncertainty no clear correlation between residual  $x_{\rm Ag}$  and  $L_{\rm B}$  is observed.

#### ESI-4 Supplementary data for catalysis of partial alcohol oxidation over npAu

The formation of the coupling product methyl formate (MeFm) decrease strongly for npAu with  $x_{Ag} > 1$  at%. Additional measures such as increase of O<sub>2</sub> pressure and preptreatment could not enhance the MeFm production to a level that was achieved for npAu with  $x_{Ag} < 1$  at% in the main manuscript.



**Fig. S12:** Methyl formate (MeFm) production over npAu with  $x_{Ag}$  of 2-4 at%. a) Catalytic experiments were performed at 60 °C at different oxygen pressures for 24 h. Above 2 bar oxygen, saturation was observed for the MeFm production. b) Catalytic experiments were performed at 60 °C and 3 bar oxygen pressure for 24 h treating the catalyst differently before catalysis. Some npAu samples containing  $x_{Ag}$  of 2-4 at% were annealed at 200 °C in argon atmosphere, or at 200 °C and 400 °C under vacuum (100 mbar) for 2 h before catalysis to ensure the homogeneity of Ag distribution within npAu und to study temperature influences. Independent on the pretreatment atmosphere, no changes were observed at 200 °C. At 400 °C ligament coarsening occurred which caused a decrease in catalytic activity.