**Supporting information**

**Microstructure and electrochemical properties of nanoporous Gold produced by dealloying Au-based thin film nano-glass**

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Cyclic voltammetry (CV) cycles in 0.5 M KOH solution with a scan rate of 20 mV/s for samples A, B and C de-alloyed in 2 M HNO3 at 70 °C for 1 h.

Considering the elements present in the deposited thin film before de-alloying, the redox reactions potentially occurring over the tested potential range (-0.1 to 0.5 V vs Ag/AgCl) are the following:

* At -0.1 V the Au surface is covered by OH- groups, which are adsorbed on it. Then the Au-OHads are transformed to a monolayer oxide of the trivalent state of Au around 0.25 V. When reverting the potential the reduction of this state produces a negative current with a peak around 0.1 V vs Ag/AgCl [1–3].
* Cu atoms are oxidized to the CuII state from the beginning of the scan, and further oxidized to the CuIII state close to 0.5 V [4,5].
* Ag atoms are oxidized to Ag2O, giving a peak around 0.31 V vs Ag/AgCl, while the reduction of Ag2O to Ag gives a peak around 0.05 V [6,7].
* OH- chemisorbed species on Pd atoms are transformed into higher valence oxides such as PdO from the beginning of the scan and PdO2 from 0.3 to 0.5 V, while the reduction of PdO2 gives a broad reduction peak with a small current contribution from around 0.3 V to -0.1 V [8,9].

The difference in the CV scans reveals that each electrode contains a different amount of less noble elements. These elements are oxidized and reduced giving overlapping current contributions in addition to the redox reactions of Au. This effect is more pronounced for sample A and progressively less for B and C.

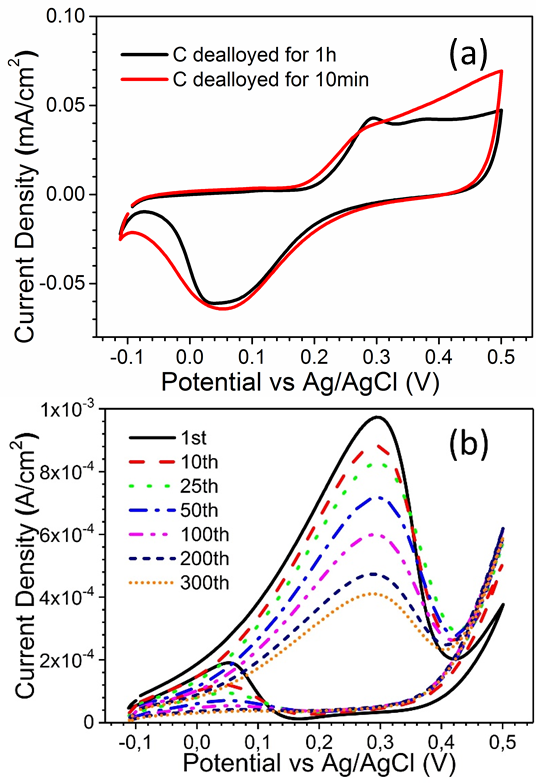


FIG. S1(a) CV Cycles of samples C de-alloyed in 2 M HNO3 at 70 °C for 10 min and 1 h in 0.5 M KOH solution with a scan rate of 20 mV/s. (b) Electro-catalytic performance of sample C de-alloyed in 2 M HNO3 at 70°C for 10 min tested for 300 cycles with a scan rate of 20 mV/s in 0.5 M KOH + 5 M CH3OH solution.

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FIG. S2 SEM images of samples C, de-alloyed for 10 min ((a) and (b)) and 1 h ((c) and (d)) in 2 M HNO3 at 70 °C, before((a) and (c)) and after ((b) and (d)) methanol electro-catalysis experiments. The size and morphology of the ligaments remain constant for the two tested samples.

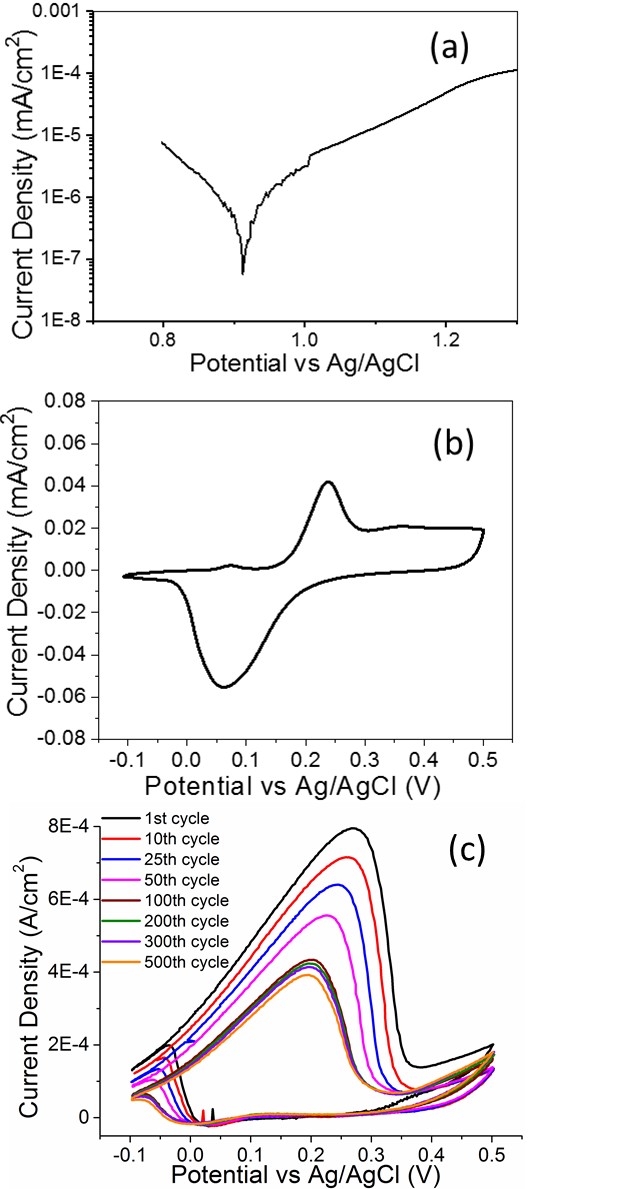


FIG. S3 (a) Potentiodynamic polarization curve of a Au standard obtained with a scan rate of 5 mV/s in a 1 M HNO3 aqueous solution at 70 °C. (b) Cyclic voltammetry (CV) cycles of a nanoporous Au standard in 0.5 M KOH solution with a scan rate of 20 mV/s. (c) CV cycles of nanoporous Au obtained from a Au-based ribbon dealloyed 8 h in 1 M HNO3 at 70 °C and at a potential of 1.05 V. The sample contained mostly Au at the end of the dealloying process. The sample was tested for 400 cycles with a scan rate of 20 mV/s in 0.5 M KOH+5 M CH3OH.

TABLE SI EDX measurements on the as-sputtered thin films. The nominal composition of the thin films is compared with the one of the target. The composition of the thin film varies in an acceptable range, considering the difficulty in determining it precisely in a thin film composed of multiple elements, whose EDX peaks tend to overlap each other.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
|  | Target | Sample A | Sample B | Sample C |
| Au | 40 | 42 | 44 | 43.4 |
| Cu | 28 | 29.2 | 26.5 | 25.3 |
| Pd | 5 | 5 | 5.5 | 4.9 |
| Ag | 7 | 6.2 | 6.9 | 6.3 |
| Si | 20 | 17.5 | 17.2 | 20.1 |

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