Supporting Information

Effects of side reactions on the kinetics of nanoporous gold formation revealed by real-time X-ray scattering during electrolytic dealloying

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Supporting Video Content

Supporting Videos 1-3 are attached.

- **Supporting Video 1.** This is a video of dealloying in HNO_3 in the stacked configuration (**Fig. S2g**) at 950 mV vs. Ag/AgCl**.** The dealloying current can be seen in **Fig. S3**, which is similar to that found in the side-by-side configuration**.** It is clear from the color change that the film is being dealloyed, which is also what we observed in the side-by-side configuration.
- **Supporting Video 2.** *In situ* dealloying data in HNO_3. One can see how the SAXS, WAXS, current, and charge evolve with respect to dealloying time. No new WAXS peaks appear during dealloying in HNO_3.
- **Supporting Video 3.** *In situ* dealloying data in $HClO_4$. One can see how the SAXS, WAXS, current, and charge evolve with respect to dealloying time. New WAXS peaks appear during dealloying in $HClO_4$, corresponding to AgCl growth as Ag is removed from the parent alloy.

Supporting Figures

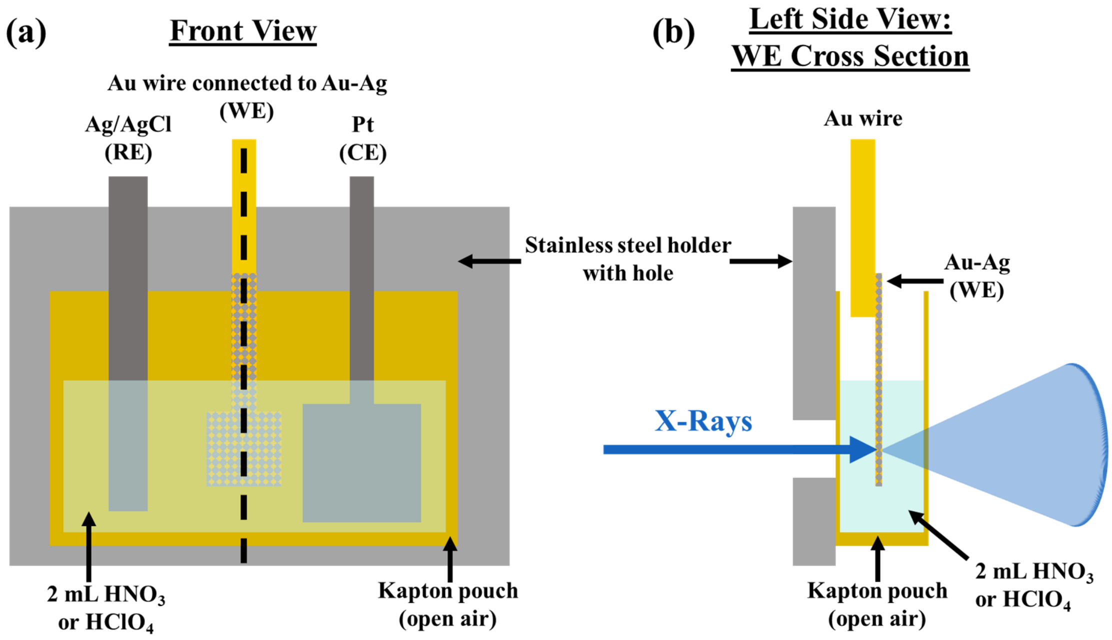

Fig. S1. Detailed diagram of side-by-side *in situ* configuration in **Fig. S2f**. (a) Front view. A Kapton pouch cell is filled with 2 mL of either electrolyte (HNO_3 or $HClO_4$), and three electrodes are placed inside. The Au-Ag working electrode (WE), the Pt counter electrode (CE), and the Ag/AgCl reference electrode (RE) are placed inside the electrolyte in a side-by-side configuration. The dashed black line through the WE in (a) is to show the cross section shown in (b), a left-side view of the *in situ* cell at the WE. X-rays (blue arrow) travel through a hole in the stainless-steel holder and interact with the Kapton pouch cell, the electrolyte, and the WE.

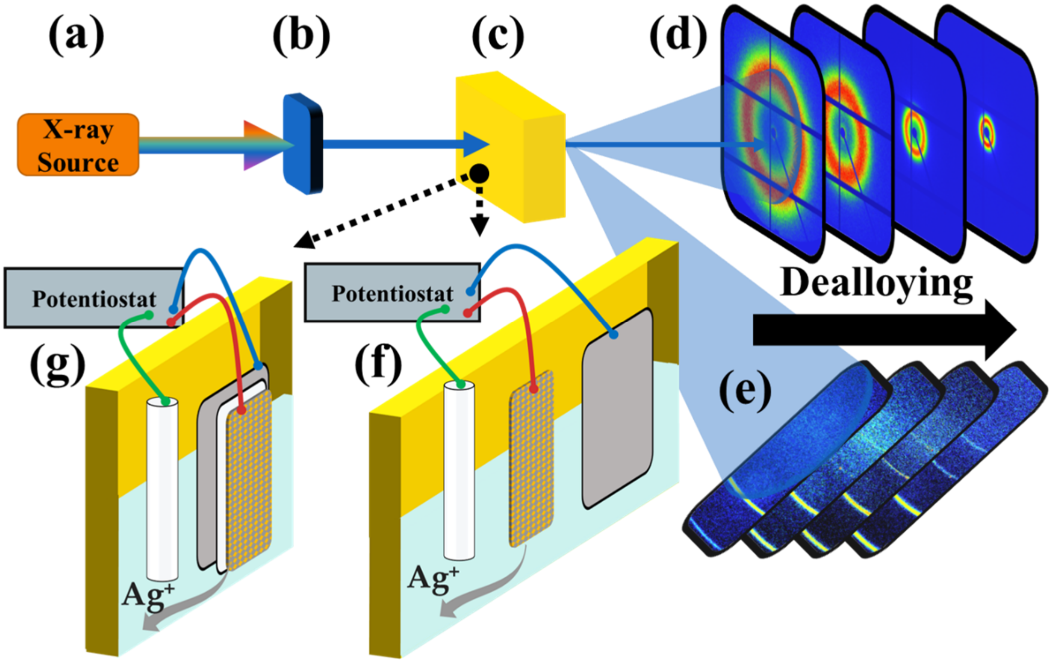

Fig. S2. X-ray scattering setup: (a) Multichromatic copper X-ray source. (b) Monochromation and collimation optics. (c) *In situ* pouch cell. (d) SAXS detector showing changes in microstructure during dealloying and (e) WAXS detector, showing changes in crystal structure during dealloying. (f) Side-by-side three-electrode *in situ* pouch cell configuration complete with Au-Ag parent alloy used as working electrode (red wire), Pt foil as the counter electrode (blue wire), and Ag/AgCl used as the reference electrode. This side-by-side configuration avoids unwanted scattering from the counter electrode and separator, as shown in the stacked configuration in (g).

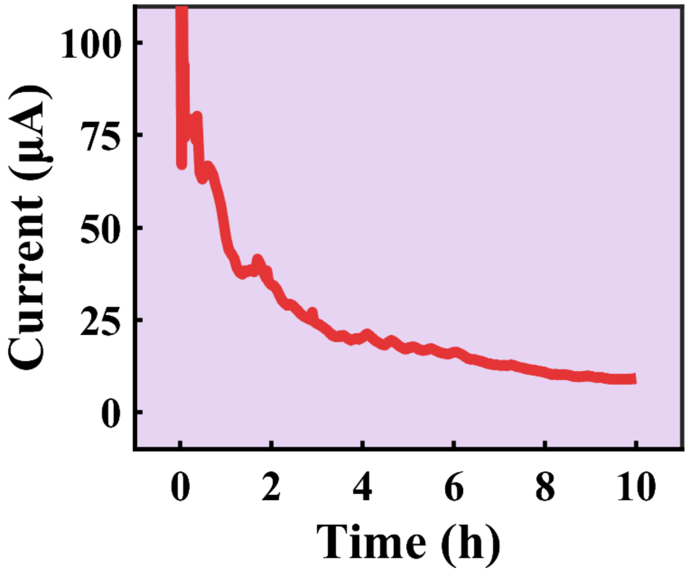

Fig. S3. *Ex situ* dealloying current for the stacked configuration found in **Fig. S2g** using 2 mL of 1 M HNO_3. An accompanying video is shown in **Supporting Video 1**, where one can see the obvious color change of the film, typical of dealloying.

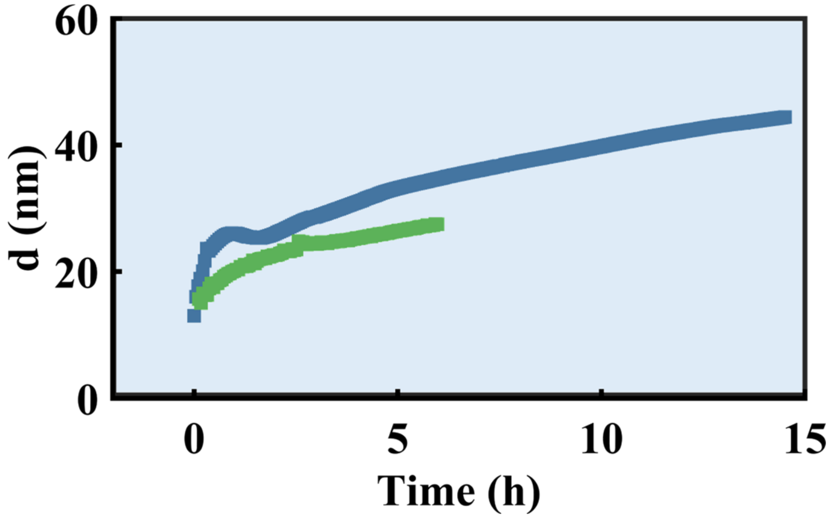

Fig. S4. *d* vs. time curves for two *in situ* dealloying experiments performed in $HClO_4$. The blue curve is the *d* vs. time curve shown in the manuscript, and the green curve is from another, shorter dealloying experiment not shown in the manuscript.

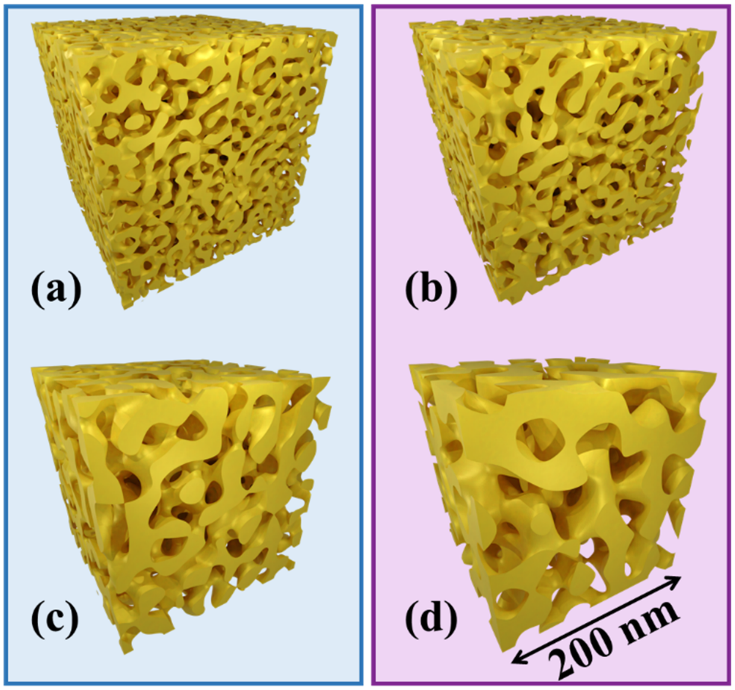

Fig. S5. Gaussian Random Field[1–3] models generated at various points during dealloying using the experimental data found in **Fig. 3e** in the main manuscript. We have reported how to create these structures in a previous work.[4] At the beginning stages of dealloying in $HClO_4$ (a) and HNO_3 (b), the structure size is similar: ~13 and ~16 nm, respectively. By 2 hours of dealloying time, the structure size of the $HClO_4$ (c) is smaller than that of HNO_3 (d): ~26 and ~40 nm, respectively. The side lengths of the simulated cubes are all 200 nm.

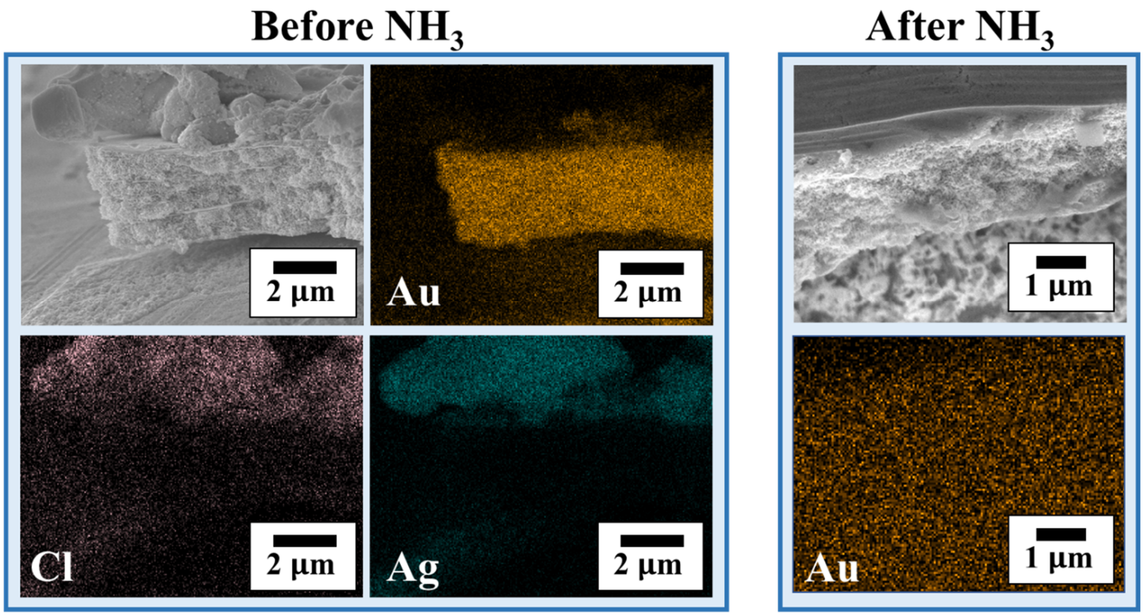

Fig. S6. EDX maps of nanoporous gold after *in situ* dealloying in $HClO_4$ (left), and the same sample washed in concentrated NH_3 (right). EDX shows that the dense film on the top of the NP-Au consists primarily of Ag and Cl (i.e. AgCl). After washing in NH_3, the sample is composed of Au, and the AgCl film at the surface has disappeared.

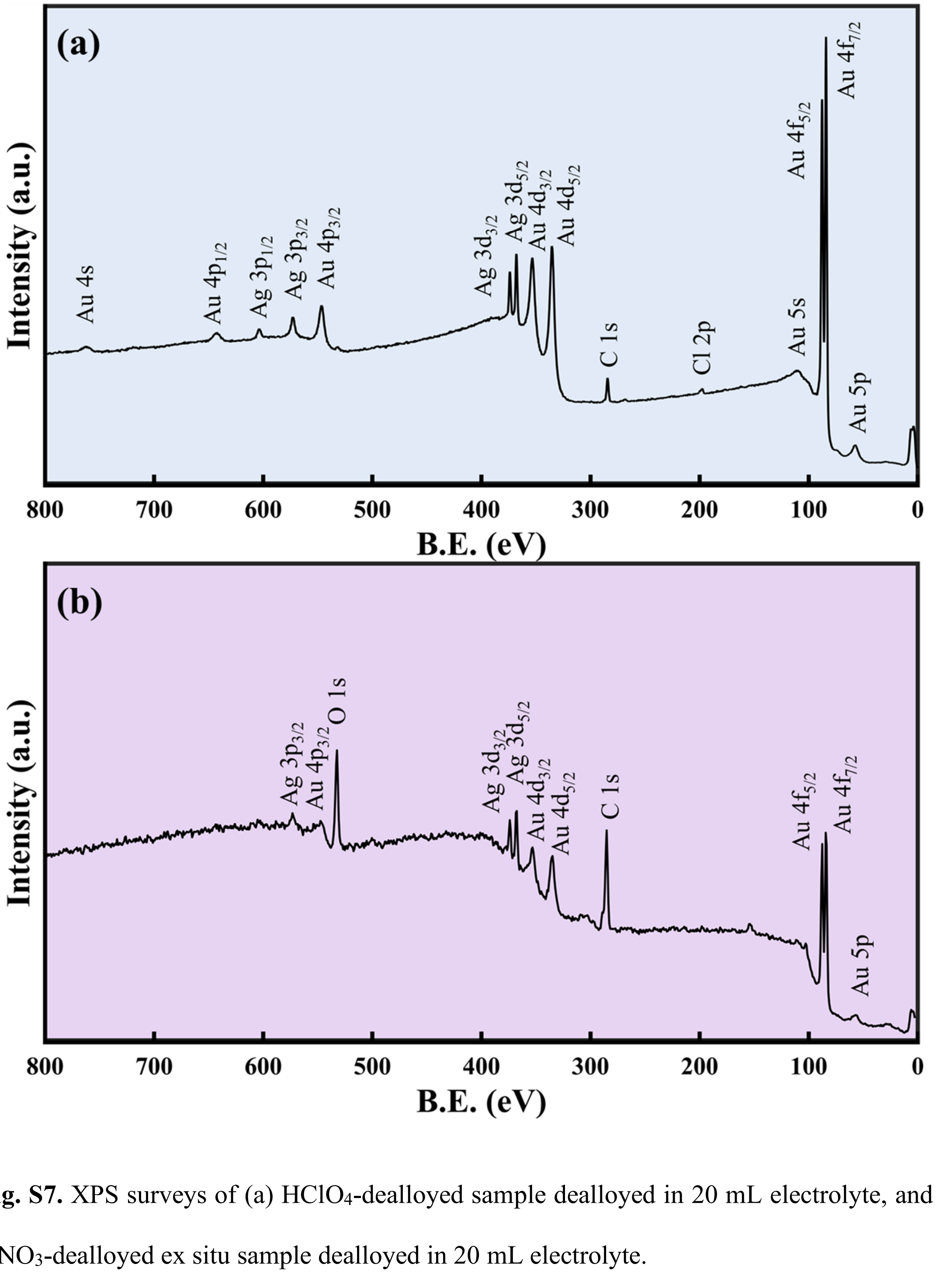

Fig. S7. XPS surveys of (a) $HClO_4$-dealloyed sample dealloyed in 20 mL electrolyte, and (b) HNO_3-dealloyed ex situ sample dealloyed in 20 mL electrolyte.

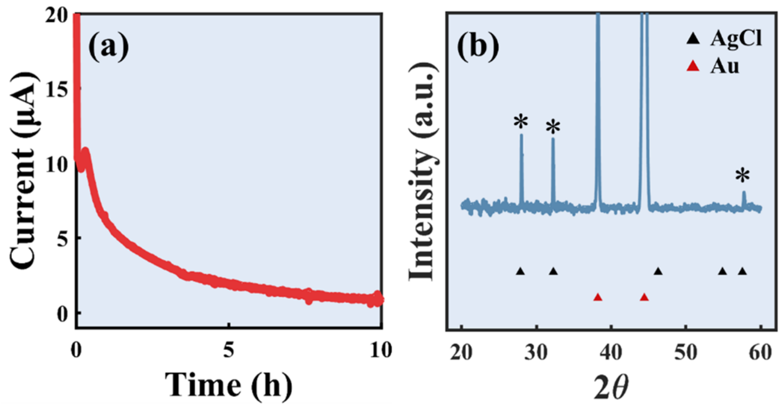

Fig. S8. (a) Current vs. time in an experiment using an Hg/Hg_2SO_4 reference electrode which does not contain Cl^- ions, and (b) X-ray diffraction pattern of the sample dealloyed in (a). AgCl peaks are shown in asterisks, and match with three of the peaks found in the black triangle pattern (PDF # 31-1238).

References

1 S. S. Welborn and E. Detsi, *Nanoscale Horizons*, 2020, **5**, 12–24.

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