Supplementary Information

In-Situ Liquid Cell Electron Microscopy of Ag-Au Galvanic Replacement Reactions

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Figure S1

Figure S1. TEM and HAADF-STEM images of the Ag-Au nanostructures formed immediately after immersion of the Ag nanoparticles in 100 μM aqueous NaAuCl4 solution. (a) Schematic rendering of a near-spherical polyhedral nanoparticle with small (100) and (111) facets. (b) TEM image showing side-by-side a polyhedral nanoparticle and nanocube immediately after immersion in NaAuCl4 solution; note the hollowing of the particle primarily at the location of the (100) facets while the cube has remained intact. (c) Schematic rendering of the nanocube bounded by large (100) facets. (d) Zoomed-out HAADF-STEM image, and (e) TEM image of the vicinity of the two particles shown in (b).
Figure S2: Au-Ag galvanic replacement reaction in aqueous Au salt solution with added sulfuric acid (pH 2.5). Sequence of HAADF-STEM images following the evolution of Ag nanocubes in 100 µM aqueous NaAuCl₄ solution with added 100 µM H₂SO₄ over 400 s of cycles of local focused electron beam exposure (cumulative exposure time indicated in the individual frames; beam current: 400 pA; probe size: 0.2 nm).
Figure S3. Hollowing out of Ag nanocubes in Au-containing solution. HAADF-STEM images and EDS maps of the Au-Ag nanostructures at the initial stages of observation of galvanic replacement reactions of Ag nanoparticles in 100 μM NaAuCl₄ aqueous solution at pH 2.5. The images and maps were recorded after the LCEM experiments and opening of the cell.
Figure S4

Figure S4: LCEM of Ag nanocubes in 100 μM aqueous NaAuCl$_4$ solution at pH 2.5 after addition of H$_2$SO$_4$. (a) Sequence of HAADF-STEM images following Au-Ag galvanic replacement reaction on a Ag nanocube in 100 μM aqueous NaAuCl$_4$ and 100 μM H$_2$SO$_4$, induced by cycles of local focused electron beam exposure (total exposure time indicated in the individual frames; beam current: 400 pA; probe size: 0.2 nm) at pH 2.5. STEM images electron dose rate: 14 e/Å$^2$·s; frame time: 4.2 s. Electron dose per image: 56 e/Å$^2$. (b) Line profile showing the changes in the HAADF-STEM intensity of the nanocube along the dashed line shown in (a). The line profile shows decrease in intensity with time related to the loss of Ag from the interior of the cube. In the later stages (after 125 s) the decrease in intensity is accompanied by shrinking of the cube size.

Figure S5

Figure S5. HAADF-STEM image and corresponding EDS spectrum of the Au-Ag nanostructures at the final stages of observation of galvanic replacement reactions of Ag nanoparticles in 100 μM NaAuCl$_4$ aqueous solution at pH 2.5. The image and spectrum were recorded in vacuum, after completion of the LCEM experiments and opening of the cell. Analysis of the XPS spectra of several nanostructures confirms a Au-Ag alloy with very high Au concentration (~ 92 at. %).