Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Supporting Information

Iodide-Induced Differential Control of Metal Ion Reduction Rates: Synthesis of Terraced Palladium-Copper Nanoparticles with Dilute Bimetallic Surfaces

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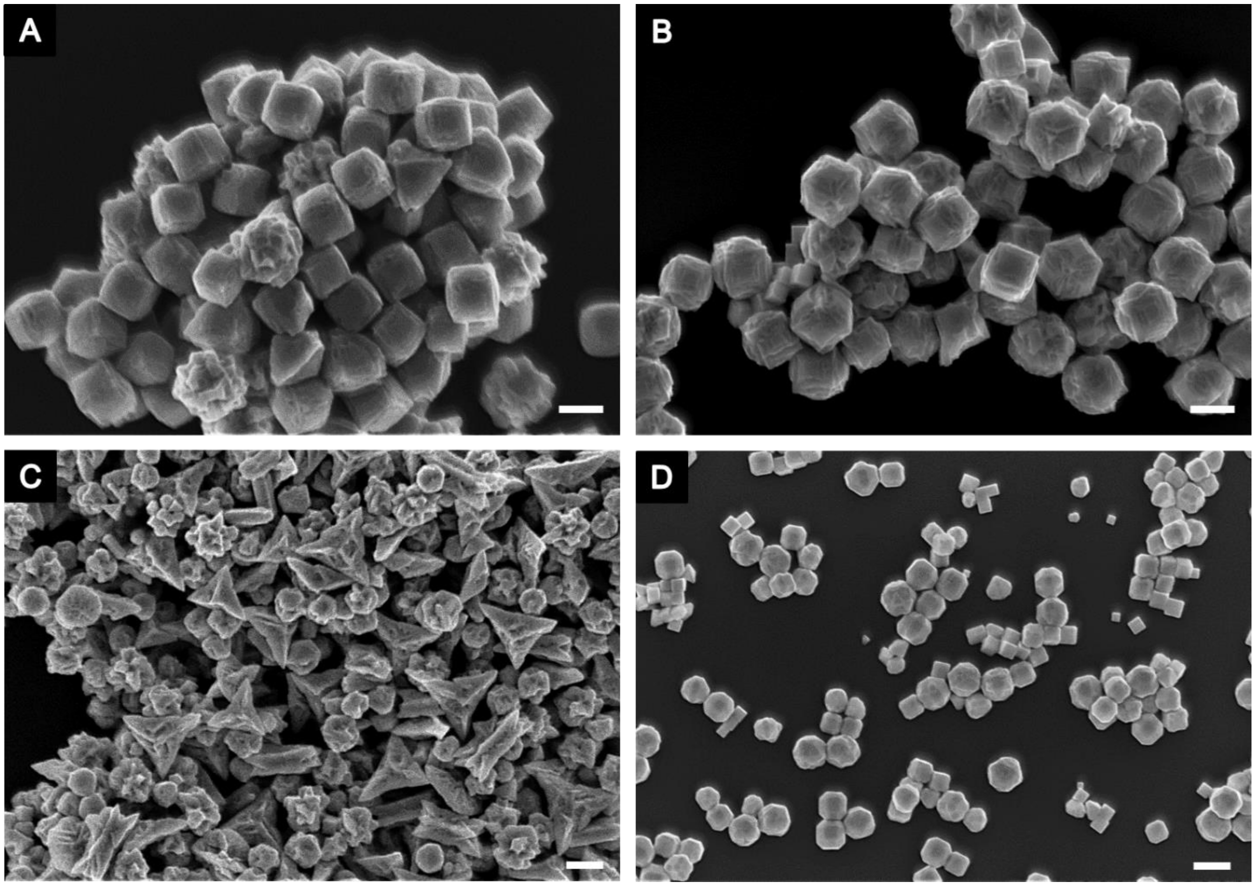

Figure S1. Large area SEM images of (A) terraced palladium-copper particles with 5 µM NaI and 20 µM $Cu(NO_3)_2$; (B) terraced palladium-copper particles with 5 µM NaI, 20 µM $Cu(NO_3)_2$, and 0.5 mM HNO_3; (C) tripods and dendritic palladium-copper particles with 20 µM $Cu(NO_3)_2$; and (D) rounded cubic palladium particles with 5 µM NaI. Scale bars: 200 nm.

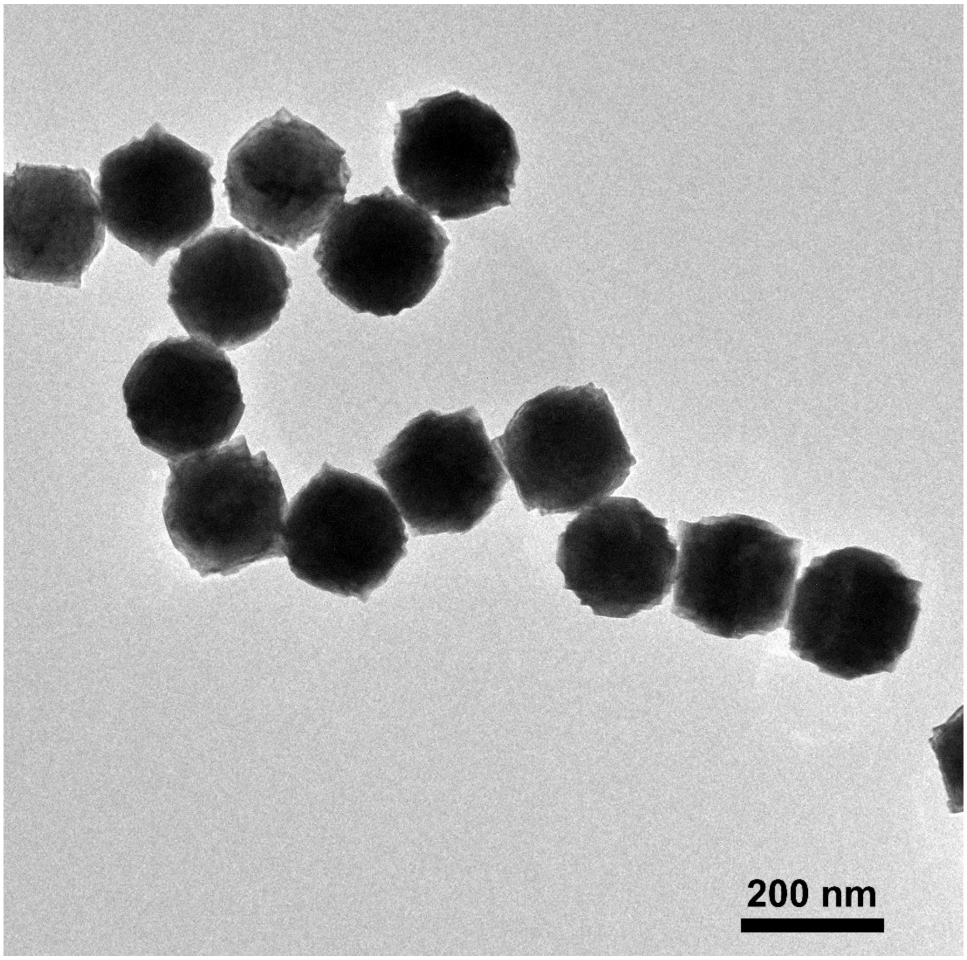

Figure S2. TEM image of the terraced palladium-copper particles synthesized under ideal conditions (with 5 µM NaI, 20 µM $Cu(NO_3)_2$, and 0.5 mM HNO_3). Scale bar: 200 nm.

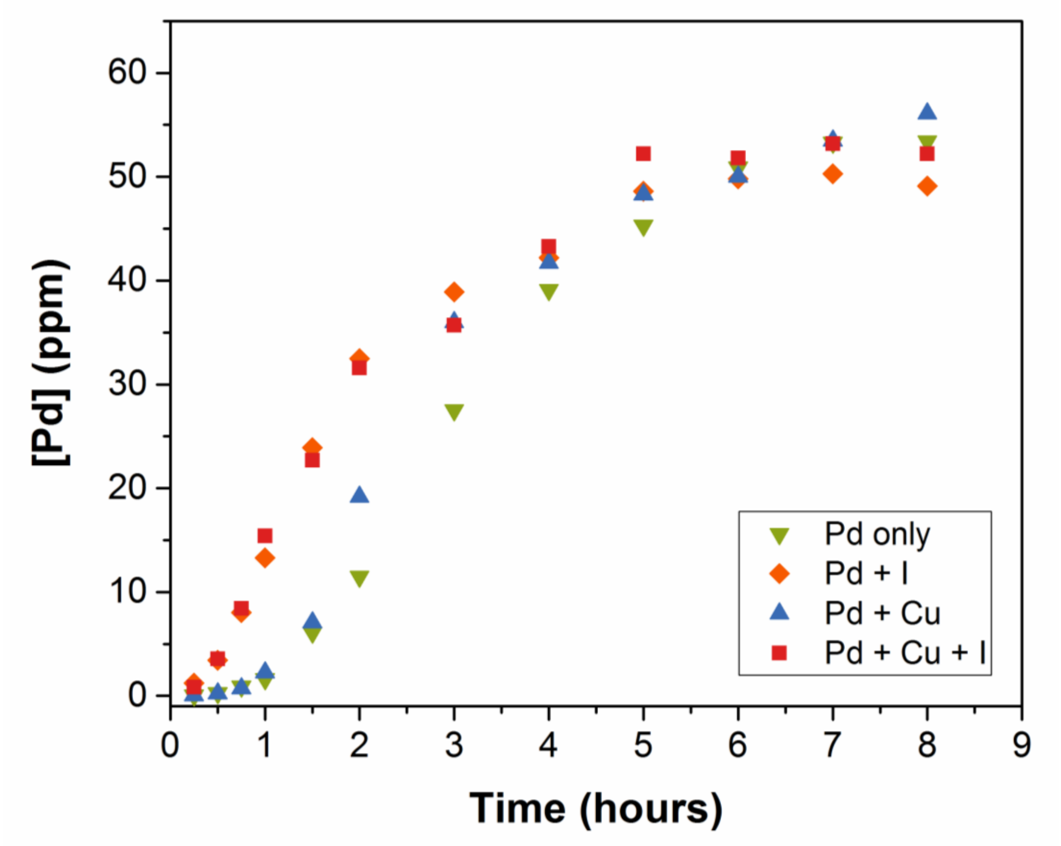

Figure S3. Graph of palladium incorporation during particle growth as determined by inductively coupled plasma mass spectrometry (ICP-MS) for palladium particles formed when no acid is present under different conditions: palladium only (green triangles); palladium and iodide (orange diamonds); palladium and copper (blue triangles); and palladium, copper, and iodide (red squares).

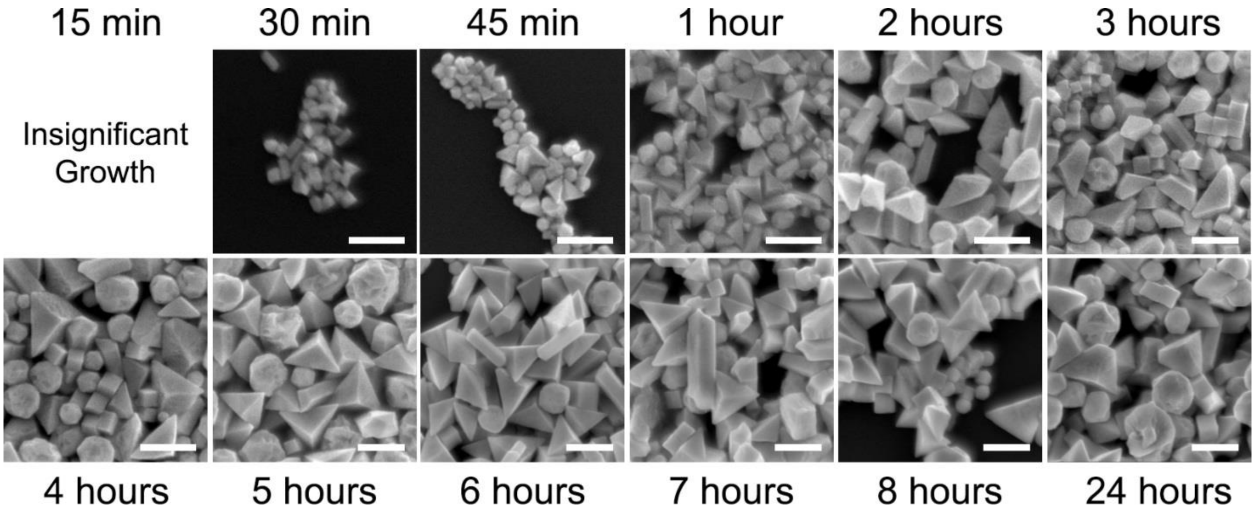

Figure S4. SEM images showing the evolution over time of the {100} multiply twinned structures formed when only palladium is present (ie. in the absence of copper and iodide). Scale bars: 200 nm.

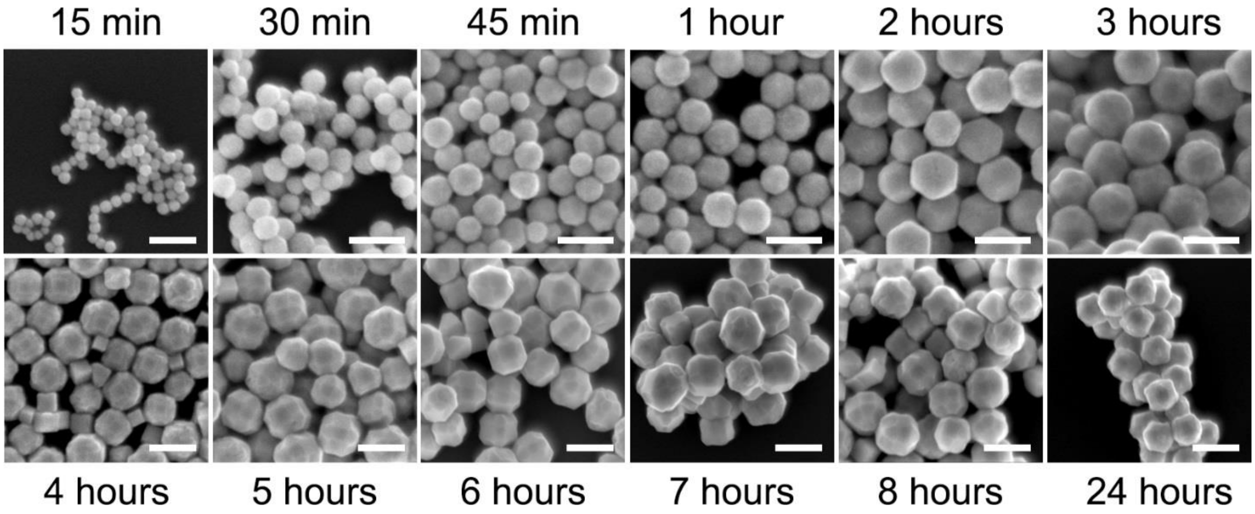

Figure S5. SEM images showing the evolution over time of the rounded cubic particles that form in the presence of 5 μM NaI. Scale bars: 200 nm.

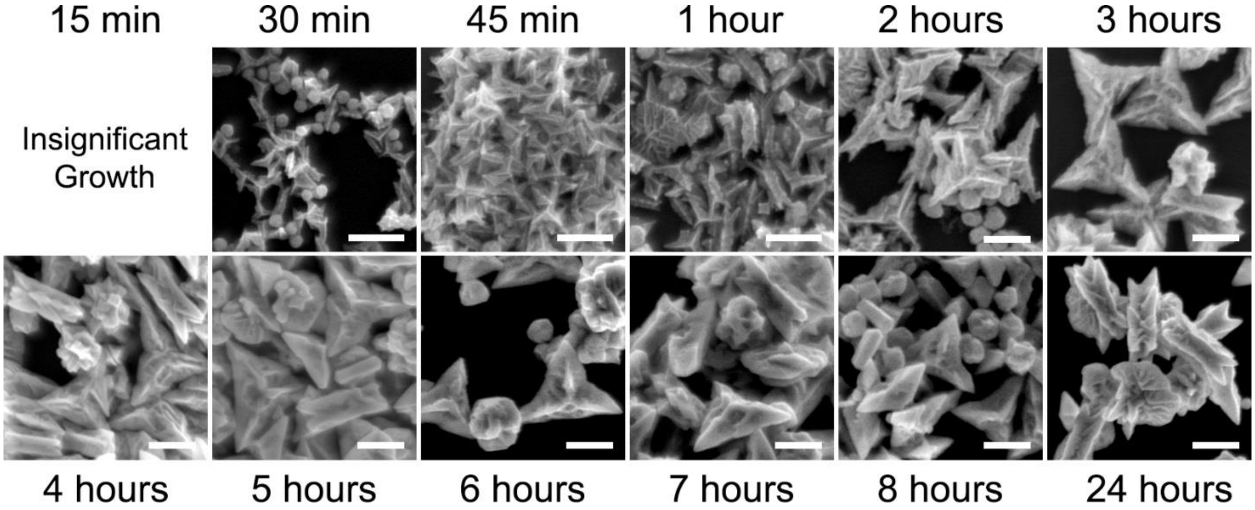

Figure S6. SEM images showing the evolution over time of the tripods, rods, and quasispherical dendritic structures that form in the presence of 20 µM $Cu(NO_3)_2$. Scale bars: 200 nm.

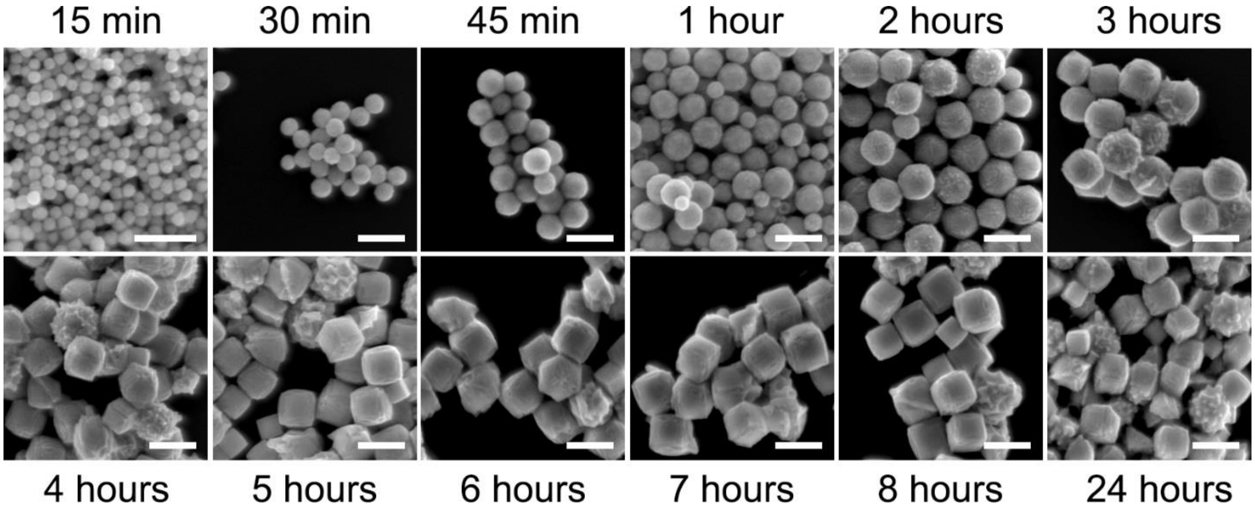

Figure S7. SEM images showing the progression of terraced palladium-copper particle growth with both 5 µM NaI and 20 µM $Cu(NO_3)_2$ in the growth solution. Scale bars: 200 nm.

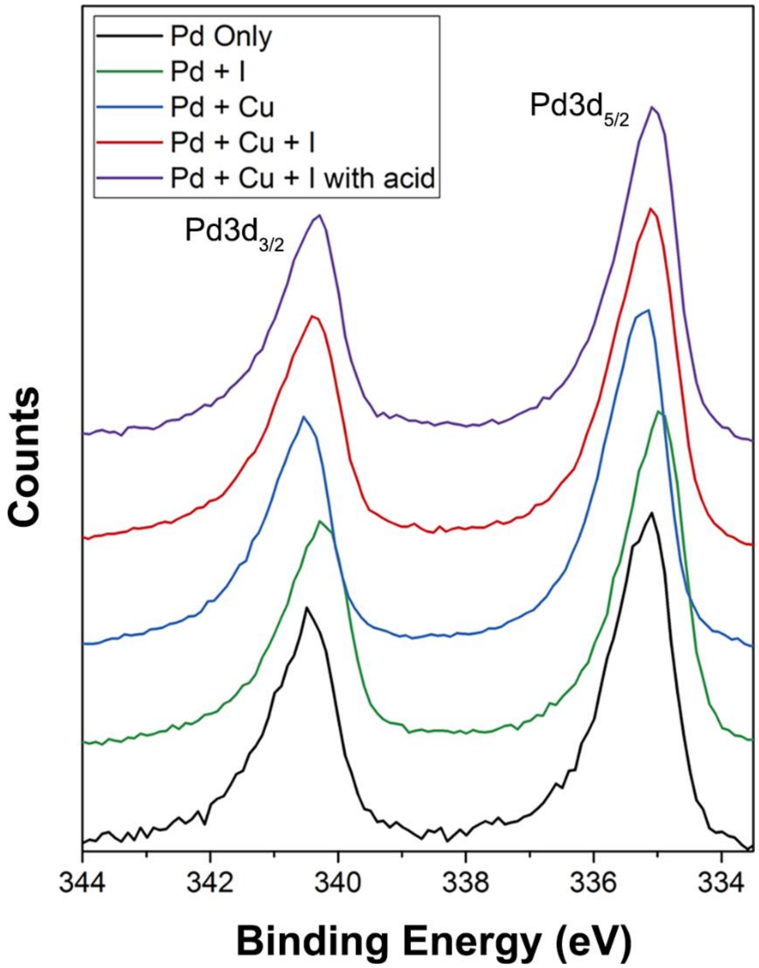

Figure S8. Normalized high-resolution XPS spectra of the palladium 3d region for palladium and palladium-copper particles formed in the presence and absence iodide. Particles were prepared for analysis after 6 hours of reaction, when particle growth is complete.

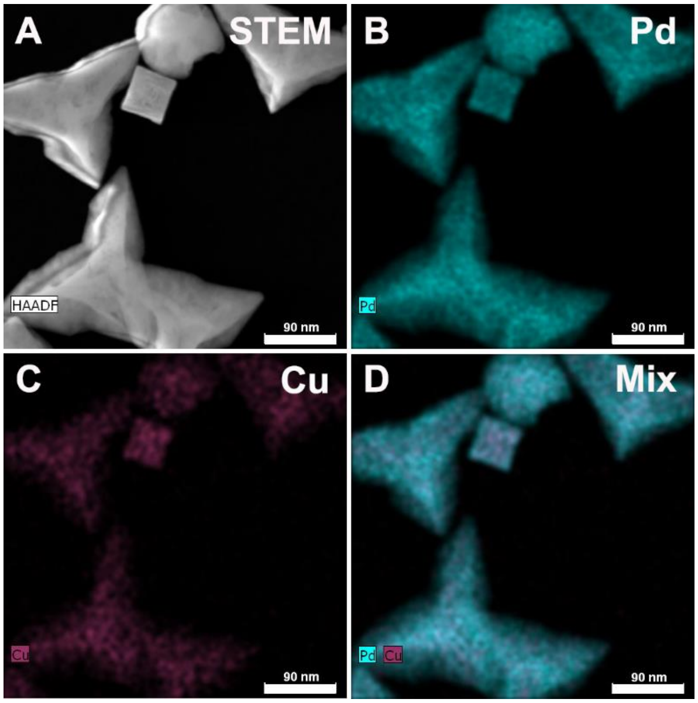

Figure S9. (A) HAADF-STEM image of palladium-copper tripods, (B) EDS map of palladium, (C) EDS map of copper, and (D) combined EDS map of palladium and copper. Scale bars: 90 nm.

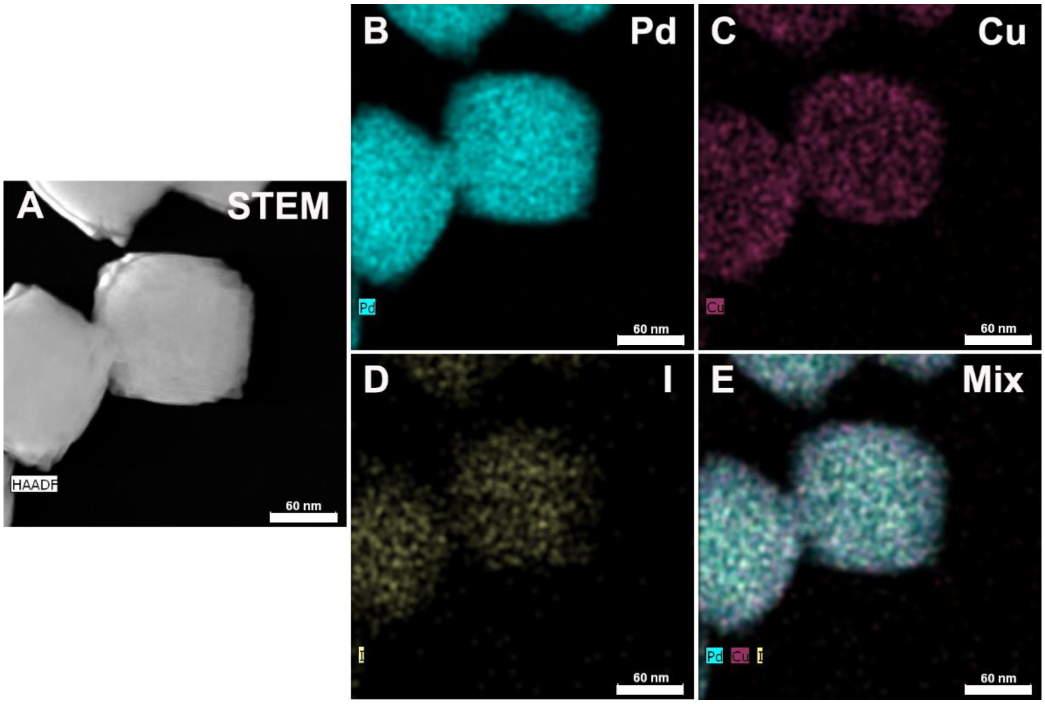

Figure S10. (A) HAADF-STEM image of terraced palladium-copper particles, (B) EDS map of palladium, (C) EDS map of copper, (D) EDS map of iodide, and (E) combined EDS map of palladium, copper, and iodide. Scale bars: 60 nm.

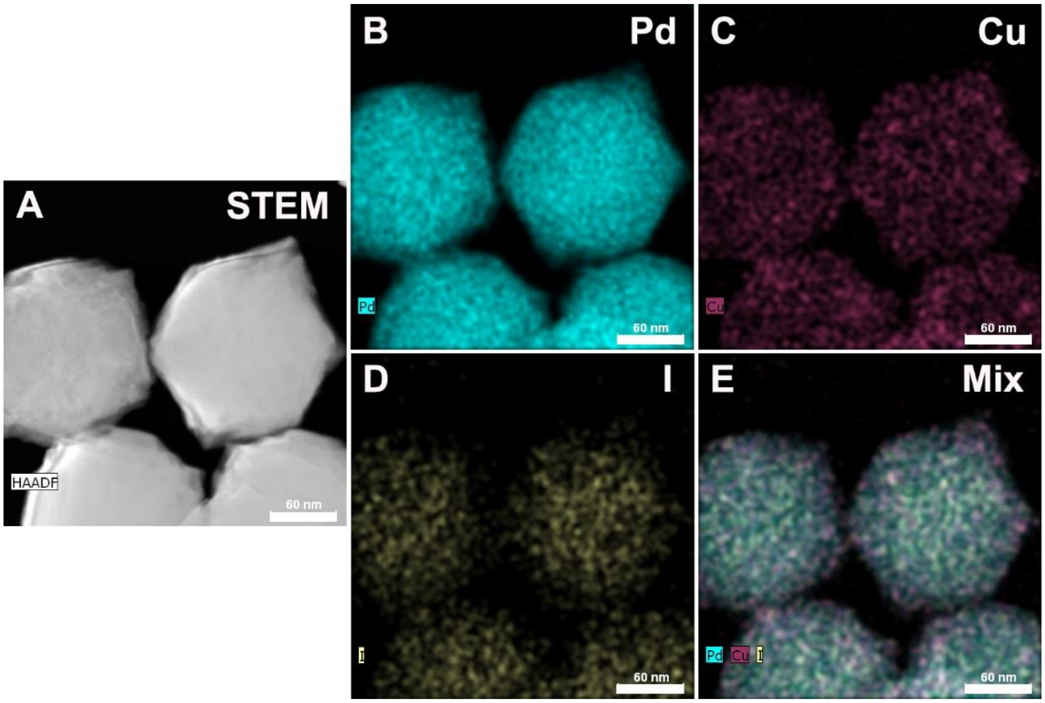

Figure S11. (A) HAADF-STEM image of terraced palladium-copper particles with added nitric acid to improve definition of the surface features, (B) EDS map of palladium, (C) EDS map of copper, (D) EDS map of iodide, and (E) combined EDS map of palladium, copper, and iodide. Scale bars: 60 nm.

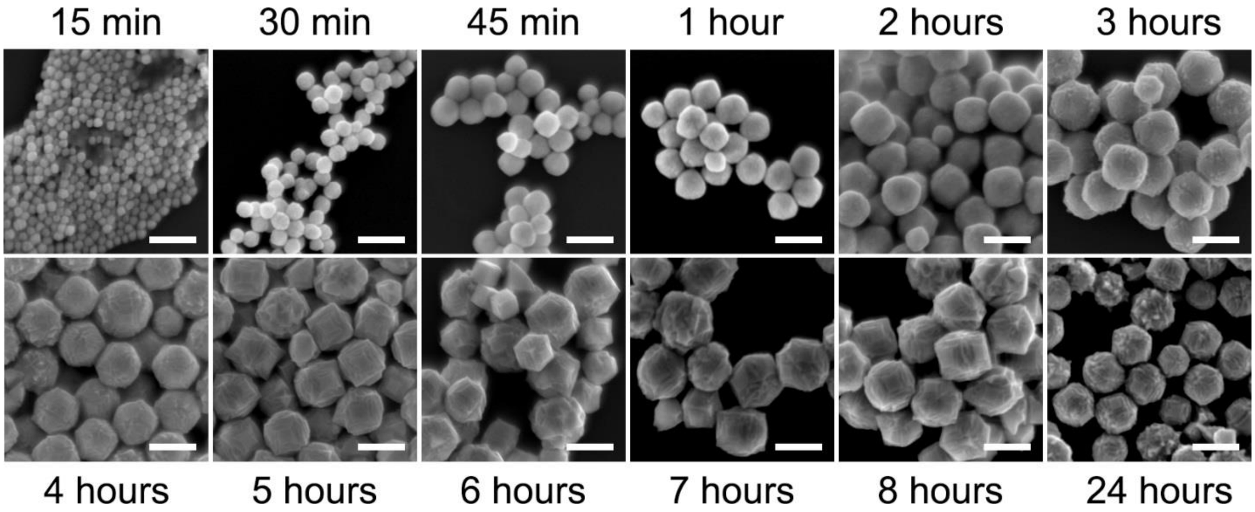

Figure S12. SEM images showing the evolution over time of terraced palladium-copper particles with sharper edge features formed in the presence of 0.5 mM HNO_3. Scale bars: 200 nm.

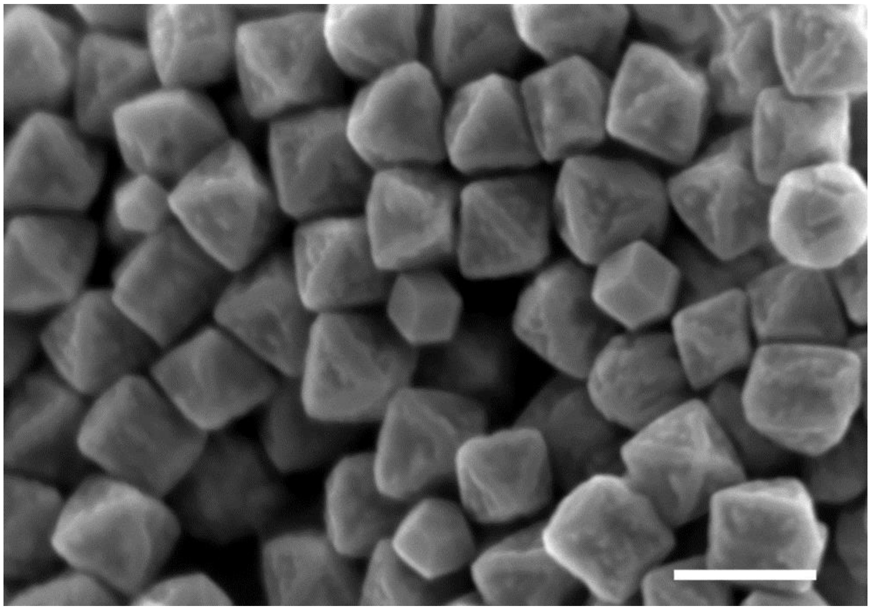

Figure S13. SEM image of concave octahedral palladium particles synthesized with 5 μM NaI, no copper, and 175 uL 100 mM nitric acid that are analogous in shape to those formed when 20 μM of copper is present under otherwise identical conditions. Scale bar: 200 nm.

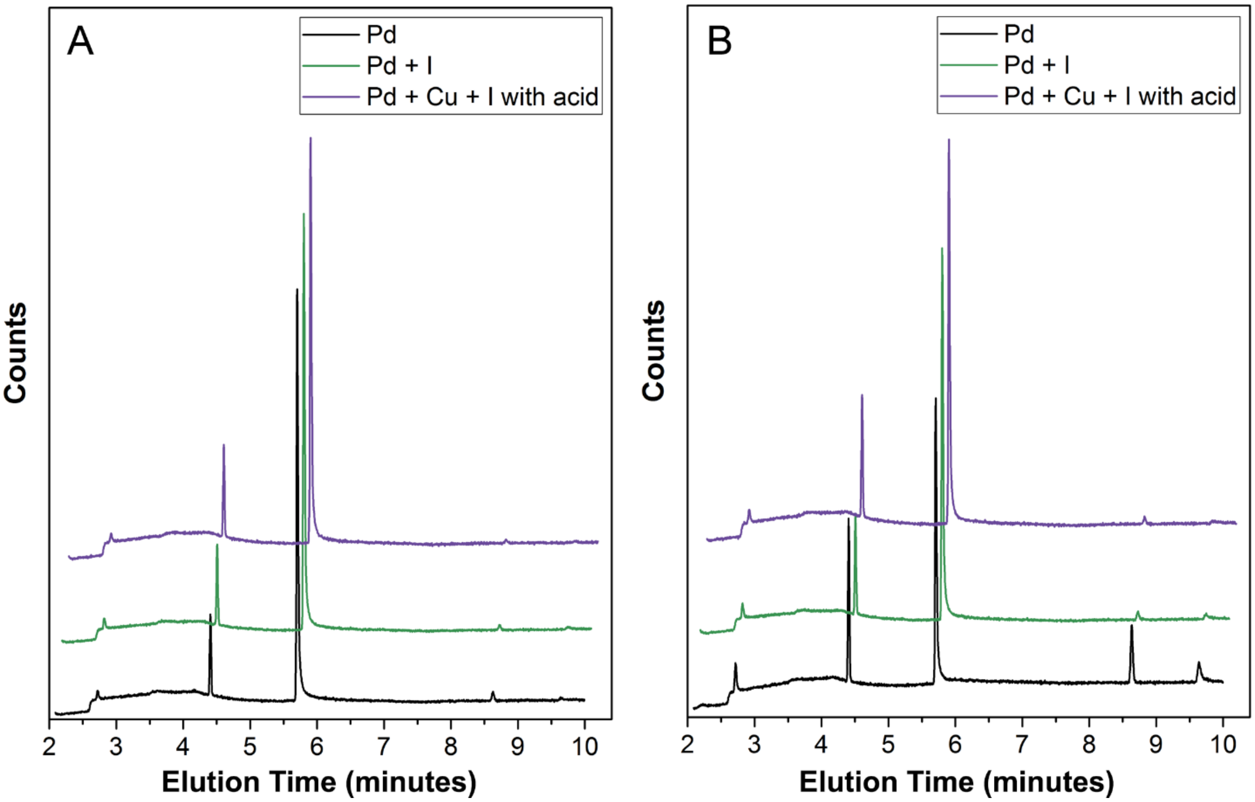

Figure S14. Gas chromatograms of the products of catalytic gas phase ethanol oxidation on nanoparticles formed under different conditions. Chromatograms are shown for (A) ~16.0% conversion and (B) the maximum conversion for each catalyst. Products and elution times are as follows: water, which is a byproduct of the oxidation reactions, (2.7 min); acetaldehyde (4.4 min); unreacted ethanol (5.7 min); ethyl acetate (8.6 min); and acetic acid (9.7 min). Chromatograms are offset slightly along the x-axis for clarity. Representative mass spectra for each peak are shown in Fig. S15. Reaction conditions: 5% ethanol and 20% O_2 in He (50 mL min^{-1}), 150 °C.

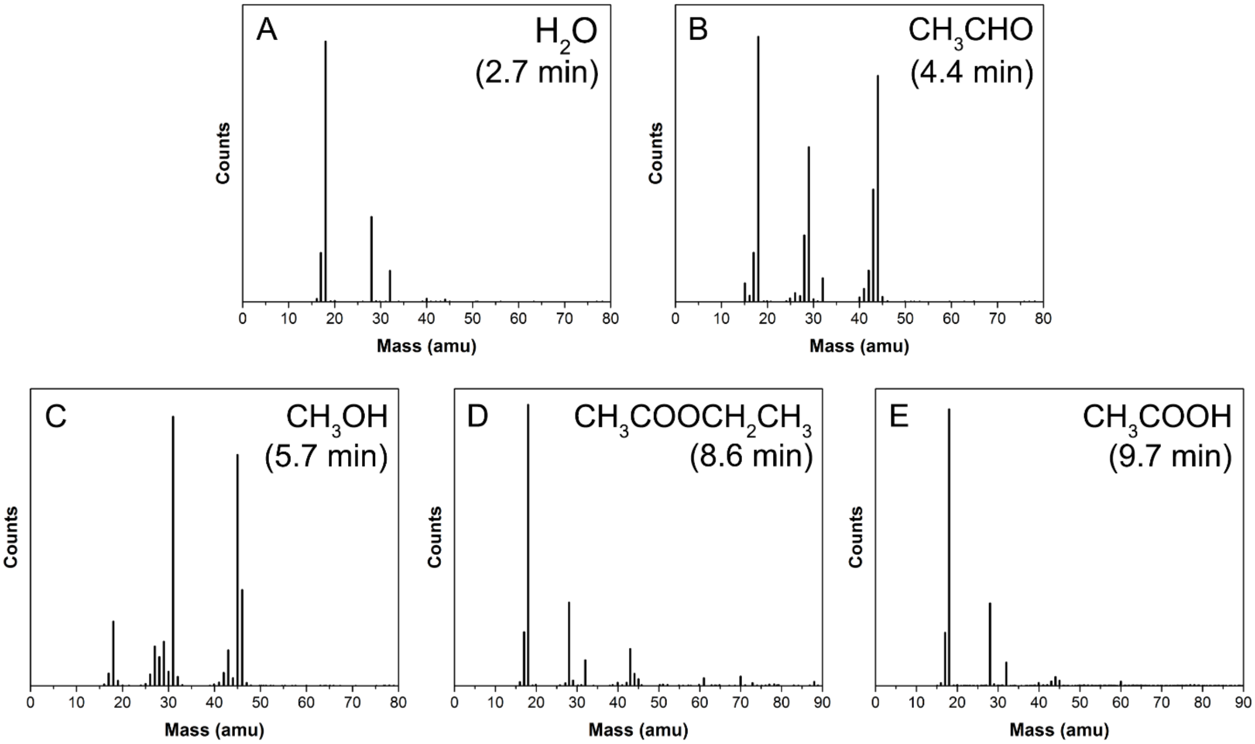

Figure S15. Representative mass spectra of the products of catalytic gas phase ethanol oxidation on nanoparticles formed under different conditions: (A) water; (B) acetaldehyde; (C) ethanol; (D) ethyl acetate; and (E) acetic acid. GC elution times are indicated.