Supporting Information

Resolving Single Cu Nanoparticle Oxidation and Kirkendall Void Formation with *In Situ* Plasmonic Nanospectroscopy and Electrodynamic Simulations

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S1: Size distribution of samples s1,2,3
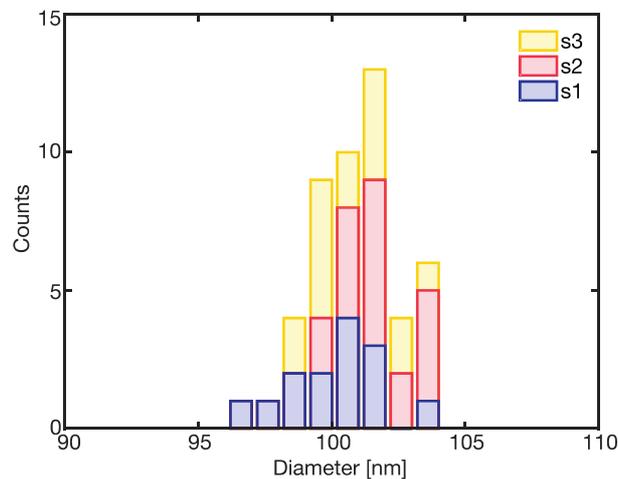
Figure S1: *Size distribution of 55 of the analyzed 110 particles from samples s1 (17 particles), s2 (20 particles) and s3 (19 particles). The diameters were extracted using Matlab by first finding the edge of the particle, by then setting a limit to the intensity gradient and thereafter fitting the edge pixels to a circle. The mean diameters are, s1: 102 ± 2.8 nm, s2: 102 ± 1.5 nm and s3: 102 ± 2.4 nm.*

S2: AFM of an annealed particle in the reduced metallic state
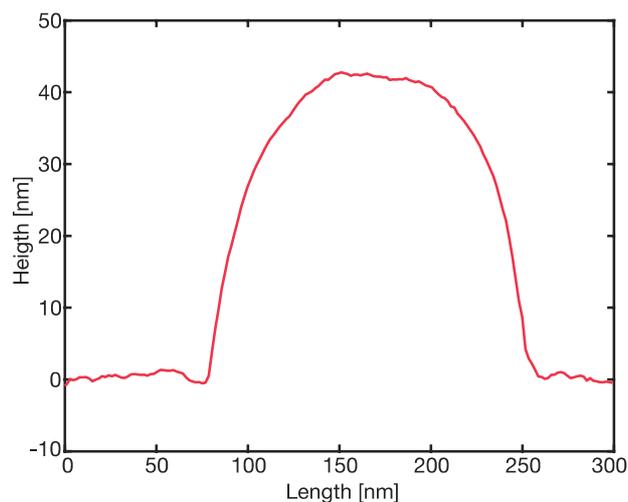
Figure S2: *AFM profile of reduced Cu particle after annealing for 24 h at 400°C in 4% H_2 in Ar carrier gas.*

S3: Shrinking core diameter due to oxide inwards growth
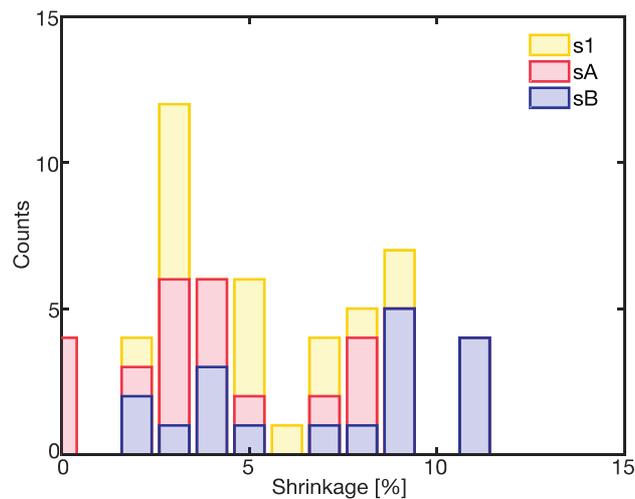
Figure S3: *Experimentally determined shrinkage of the core diameter due to oxide inward growth, as determined from TEM image analysis for 17, 18 or 19 particles of samples s1, sA and sB, respectively. Up until 30 minutes of oxidation at 150°C in 1% O_2 in Ar (approximate oxidation fraction 0.3-0.5), the maximum shrinkage is 9% (samples s1 and sA, respectively) and the mean shrinkage is 5.8 $\pm$ 2.2 % and 4.2 $\pm$ 2.7 % for s1 and sA, respectively. Upon oxidation for 60 minutes under the same conditions (sB), the maximum shrinkage is 11 % and corresponding mean shrinkage is 7.1 $\pm$ 3.8 %. The standard deviation is quite large, as it is hard to distinguish the oxide-core interface and the oxide surface has a large roughness, inducing a high uncertainty.*

S4: 5 particles during the first stage of oxidation: the shell formation
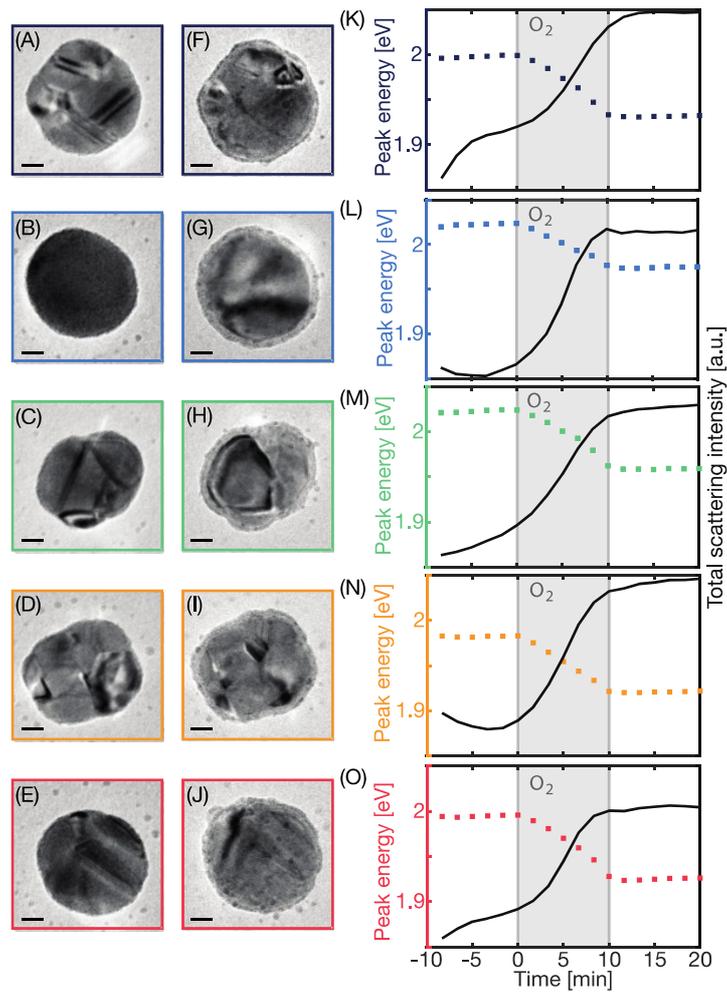
Figure S4: *5 particles from sample s0 (particles in A, B and E are particles s0p1, s0p2 and s0p3 in Fig. 6 in the main text), annealed at 300°C in 4% H_2 in Ar for 12h, and subsequently imaged in TEM (A-E). The particles are oxidized for 10 min in 1% O_2 at 150°C, such that an oxide shell has started growing but no void has formed yet. Corresponding TEM images after oxidation (F-J). The scale bars are 20 nm. The scattering peak energy collected during the in situ oxidation is plotted vs. time for these 5 particles (K-O), the peak shifts to lower photon energy (left axis) and increases in intensity (right axis); no peak split into two modes takes place, in agreement with our simulations and the assumption that the peak split signals void formation.*

S5: Rod analogy of the shrinking metal core
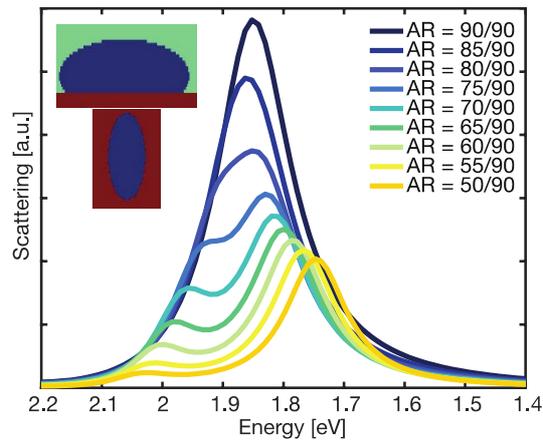
Figure S5: *A truncated Cu ellipsoid on a TEM membrane simulated for aspect ratios AR = 1 to 5/9. The length of the ellipsoid is 90 nm, and the height over the 25 nm thin SiN$_x$ TEM membrane is 30 nm. The insets show the geometry of the ellipsoid from a side and top-view.*

S6: Maxwell-Garnett mixing of the Cu core during initial stage of oxidation
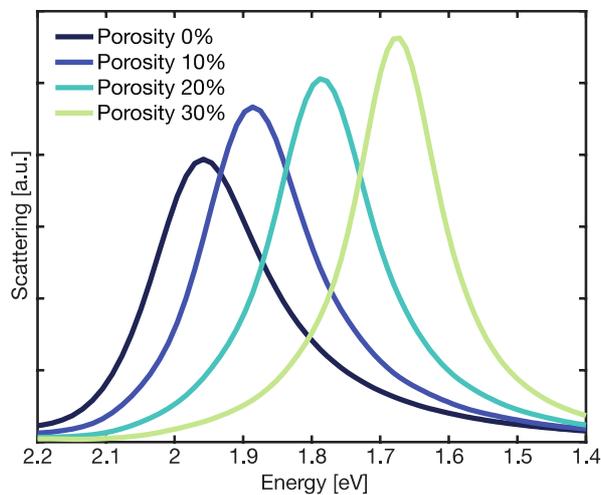
Figure S6: *Maxwell-Garnett mixing for simulating the scattering of Cu core porosity during the initial stage of oxidation. Mixing of the permittivities of metallic Cu with 0, 10, 20 and 30% vacuum, respectively, induces a shift of the LSPR peak to lower photon energies and an increase in scattering intensity due to the dilution of the free electron gas.*

S7: The raw post-oxidation spectra of the 12 particles displayed in Fig. 6
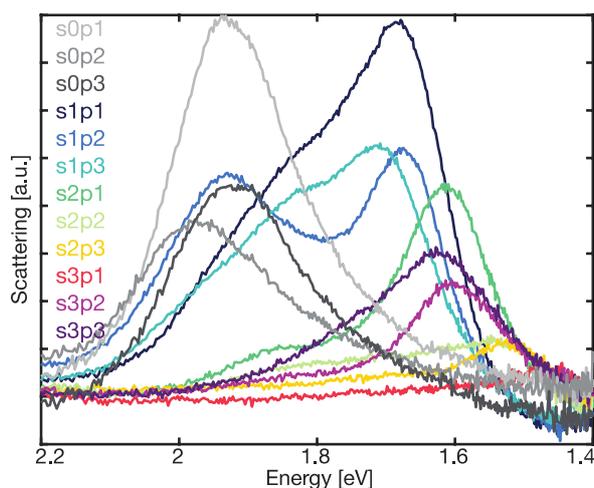
Figure S7: *The raw spectra for the 12 particles in Fig. 6 from which the peak positions are extracted by fitting to one or two Lorentzians. The spectra are collected directly after the oxidation reaction, thus showing the end state of the particles before TEM imaging. Particles in s0 have been oxidized for 10 minutes and don't show any peak split, s1 for 30 minutes, s2 for 45 minutes and s3 for 60 minutes, at 150°C in 1% O_2.*