Real-Time Plasmon Spectroscopy Study of the Solid-State Oxidation and Kirkendall Void Formation in Copper Nanoparticles

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**Figure S1.** Phase diagram ($P$ vs. $T$) for the Cu-Cu$_2$O-CuO system in thin films, reproduced from Honjo, G. (*J. Phys. Soc. Jpn.* **1949**, 4, 330). Predominant phases are displayed in color.

**Figure S2.** Transmission UV-Vis spectra of (A) quartz and Au-seeded quartz substrates, and (B) FTO substrate. Air was taken as background.
Figure S3. *In-situ* transmission UV-vis spectra and *ex-situ* photographs (insets) of ca. 90 nm diameter Cu NPs on glass slides oxidized at different temperatures (indicated). Spectra were recorded at characteristic stages of the oxidation as in Figure 3. The sample oxidized at 110 °C does not reach full oxidation.

Figure S4. Transmission UV-Vis spectra of (A) oxidation of ca. 90 nm diameter Cu NPs on FTO substrate at 140 °C, and (B) FTO substrate. Air was taken as background.
Figure S5. *In-situ* kinetics of the normalized extinction and the wavelength of the SP band, presented as a function of time (A, B) and normalized time (C, D) at different temperatures (indicated). The SP extinction and the time $\tau$ corresponding to point $b$ (Figure 3) at each temperature were used for normalization of the respective set of spectra. Cu NP diameter: *ca.* 55 nm.

Figure S6. Grazing-incidence X-ray diffraction (GIXRD) of *ca.* 90 nm diameter Cu NPs annealed at 110 °C. Spectra $a – d$ correspond to samples at different stages of the oxidation (Figure S3). As the oxidation reaction proceeds, diffraction peaks corresponding to Cu decrease in intensity, while those corresponding to Cu$_2$O increase in intensity.
Figure S7. Top: HRSEM images of samples a – d (Figure S3), oxidized at 110 °C. Bottom: Respective NP size distributions, obtained by analysis of HRSEM images (ImageJ, >500 NPs).

Figure S8. HRSEM image of bare FTO. Image size: 500 nm².

Figure S9. HRSEM images (In-lens detector) of Cu NPs on FTO, annealed at 140 °C. Samples were removed from the furnace after reaching spectral features equivalent to those marked a – d in Figure S4. Note the increase in NP size and change of texture with oxidation, in agreement with Figures 6 and S7.
Figure S10. Top: TEM images of samples a – c (Figure S3), oxidized at 110ºC. Bottom: SAED patterns of respective NP ensembles; Cu (black) and Cu₂O (green) reflections are indicated.