**Electronic Supplementary Information (ESI)** 

## 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<sub>2</sub>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  $^{\circ}$ 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<sub>2</sub>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 nm<sup>2</sup>.



**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 110°C. Bottom: SAED patterns of respective NP ensembles; Cu (black) and Cu<sub>2</sub>O (green) reflections are indicated.