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Unravelling Competing Oxidation Mechanisms in Single Cu Nanoparticles

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Abstract

Chemical reactions involving nanoparticles often follow complex processes. In this respect, real-time probing of single particles under reactive conditions is crucial for uncovering the mechanisms driving the reaction pathway. Here, we have captured *in situ* the oxidation of single Cu nanoparticles to unravel a sequential competitive activation of different mechanisms at temperatures 50 – 200 °C. Using environmental scanning transmission electron microscopy, we monitor the evolution of oxide formation with sub-nanometer spatial resolution and show how different mechanisms closely determine the morphology of the particles. Moreover, using *in situ* electron energy-loss spectroscopy, we probe the localized surface plasmons of individual particles during oxidation, and with the aid of finite-difference time-domain electrodynamic simulations, investigate the signature of each mechanism in their plasmonic response. Our results shed light on the intricate processes involved in the oxidation of metallic nanoparticles, valuable for applications in catalysis, electronics, nanomedicine and plasmonics.

Introduction

Understanding oxidation processes and the corresponding mechanisms involved is paramount for the design, synthesis and fabrication of technologically relevant metal nanostructures^{1,2}. Focusing on Cu, its nanoparticles both in metallic and oxide forms are attractive for applications within electronics^{3,4}, photonics^{5,6}, catalysis^{7,8} and nanomedicine⁸, owing to Cu's unique physical and chemical properties, and relatively high abundance. However, applications of metallic Cu particles are limited due to their chemical instability at ambient conditions. At the same time, oxide-covered Cu nanoparticles are highly interesting for catalysis^{9,10} and active plasmonics^{5,11,12}. Moreover, hollow oxide nanoparticles synthesized by exploiting the nanoscale Kirkendall (NK) effect^{13,14} can be advantageous in sensor technologies^{15,16} and in nanomedicine⁸, due to their geometry and high surface area. Since the seminal report of the NK effect in Co nanoparticles¹⁷, other metals including Cu¹⁸, Ni¹⁹ and Fe²⁰, have been shown to undergo the same transformation to hollow structures upon oxidation. This effect, caused essentially by the higher diffusion rate of cationic metal ions through the oxide compared to oxygen ions, is manifested initially as the nucleation of small vacancies, which then accumulate to form nanoscale voids^{18,21}. Other oxidation mechanisms, such as the Cabrera-Mott²² and Valensi-Carter²³ processes, have also been reported for nanoparticles and thin films^{24–26}, as well as the Johnson-Mehl-Avrami-Kolmogorov (JMAK) nucleation of oxide islands^{27,28} at the initial stages of thin film oxidation. Overall, a holistic and detailed understanding of the entire oxidation pathway of metal nanoparticles, and in particular of Cu nanoparticles, is, however, still lacking. In part, this is because the majority of the existing *in situ* studies are based on particle ensembles^{29–31} and thus, inherently suffer from averaging effects. The few existing *in situ* single particle studies using scanning transmission electron microscopy (STEM)³² and plasmonic nanospectroscopy³³ are limited in that the former was executed at very low oxygen pressures, and the latter is blind to morphological details. Here, we address these challenges by recording *in situ* the morphological and compositional evolution of single Cu nanoparticles using annular dark-field STEM (ADF STEM) imaging, and by simultaneously probing the evolution of their localized surface plasmon resonances (LSPR) using electron energy-loss spectroscopy (EELS)^{6,34–36} in an environmental TEM (ETEM)³⁷ (**Fig. S1**), in analogy to the bulk plasmon studies of hydride formation in Pd nanocrystals³⁸. Based on our direct observations, we are able to identify the active oxidation mechanisms involved, and thus, uncover the subsequent oxidation pathways at different temperatures. Moreover, by combining our EELS results with finite-difference time-domain (FDTD) electrodynamic simulations, we determine the signature of different oxidation mechanisms in the LSPR of the particles.

In situ ADF STEM of single Cu nanoparticle oxidation at elevated temperatures

Polycrystalline Cu nanodisks with radius $R = 43 \pm 7$ nm and nominal 20 nm thickness were fabricated by hole-mask colloidal lithography³⁹ on TEM substrates with integrated resistive heaters. First, samples were annealed inside the ETEM for 60 minutes at 400 °C in 3 mbar H₂ to remove hydrocarbons and to recrystallize the disks into dome-shaped particles with few grains and

$R = 35 \pm 5.0$ nm. They were then oxidized in 3 mbar O_2 at 50 – 200 °C. Selected ADF STEM images recorded during oxidation are depicted in **Fig. 1a**.

Starting at 50 °C, we observe that oxide islands nucleate and grow on the particle surface (arrows in **Fig. 1b**, **Fig. S2.1**), consistent with previous observations for extended Cu surfaces at early stages of oxidation^{27,40}. The oxide islands subsequently coalesce into a complete layer (identified as mostly Cu_2O – see **SI Fig. S2.4**), which then grows homogeneously and reaches a self-limiting thickness of 5.5 ± 0.7 nm after 90 min of accumulated O_2 exposure. As a second key point, we observe a distinct gap of accumulated vacancies between the oxide shell and the metal core (**Fig. 1c**). At 100 °C, the nanoparticles initially undergo a similar sequence of events, including the nucleation of oxide islands on the surface, and their coalescence into a continuous oxide layer separated from the metal core by a vacancy gap (**Fig. 1a**). However, at this temperature, the oxide shell does not self-passivate but enters a new oxidation stage, where a Kirkendall void nucleates at the metal – vacancy gap interface, and expands inwards into the metal core. During this expansion, the void initially keeps an approximately planar growth front towards the shrinking Cu core (**Fig. 1d**). Interestingly, after the void has expanded approximately half-way across the particle, the growth front reorients and begins expanding angularly into the remaining half of the metal core (images at 60 and 90 min at 100 °C in **Fig. 1a**). Raising the temperature to 150 °C increases the oxidation rate and although the nanoparticles undergo very similar processes to 100 °C (**Fig. 1a**), we also notice important differences. One is the coarser morphology of the oxide shell, characterized by larger grains and increased surface roughness (**Fig. 1f**). The other interesting difference is the formation of a thin *inner* oxide shell, separated from the outer oxide shell by a vacancy gap (**Fig. 1e**). At 200 °C, the overall oxidation sequence and particle morphology is very similar to 150 °C but the process occurs at an even higher rate. An important aspect to emphasize is the growth of a single void for the majority of Cu nanoparticles with $R_0 < 40$ nm oxidized at 100, 150 and 200 °C (**Fig. S2.2**). Alternative scenarios, such as the nucleation of multiple voids, are rare but become more frequent for larger and more polycrystalline particles (**Fig. S2.3**).

Figure 1. ADF STEM of single Cu particle oxidation at different temperatures. (a) ADF STEM images acquired during the oxidation of Cu nanoparticles at 50, 100, 150 and 200 °C, in 3 mbar O₂, after different O₂ exposure times (indicated in the images). Scale bars are 50 nm. Specifically relevant features are highlighted: (b) the nucleation of oxide islands on the metallic surface at the initial stage of oxidation, (c) the formation of a homogeneous outer oxide shell after oxide island coalescence, and the vacancy gap layer between the outer shell and the metal core, (d) the typical NK void nucleation site at the metal – gap layer interface, (e) the inner oxide shell formed inside the particle and separated from the outer oxide shell by the vacancy gap layer, and (f) a comparison of the oxide morphology for oxidation at 50 °C (left) and 200 °C (right), revealing larger grain size and increased surface roughness at 200 °C.

***In situ* EELS during oxidation at 50 °C**

To investigate the signature of the mechanistic evolution of Cu particles oxidized at 50 °C in their LSPR response, we employed *in situ* EELS (Fig. 2) in combination with FDTD simulations (Fig. 2d-e and SI Section S4.1-4.2) that explicitly take oxide island nucleation (cf. Fig. 1b), self-limiting oxide shell growth and vacancy gap formation stages (cf. Fig. 1c) into account. This way, we correlate the intricate morphological changes observed in the images with the LSPR from

single nanoparticles. **Figure 2** shows the time evolution of the LSPRs appearing in the EELS signal at two sets of perpendicular electron beam positions of a single Cu particle (ADF STEM images in **Fig. 2a**). At the general level, the two perpendicular LSPR modes follow very similar trends as the volume fraction of the metal converted to oxide, δ , increases, due to the maintained symmetry of the particle during oxidation, and they are in reasonable agreement with the corresponding FDTD simulations (**Fig. 2d-e**). The smaller change in the relative intensity of the peaks in the simulations compared to EELS is likely because the simulations concern absorption extracted in the far-field, whereas EELS is a near-field probe⁴¹. Moreover, slight geometrical differences between the experiment and the model, e.g. defects formed during oxidation, are not included in the simulations^{42,43}.

During the initial nucleation of oxide islands on the particle surface (at $\delta \approx 0 - 10 \%$), we observe either no change or a slight blue-shift of the LSPR in the EELS data. This is not reproduced in the simulations, which don't include changes in the surface electronic structure of Cu induced by oxygen adsorption and dissociation⁴⁴. Since the LSPR of the Cu particles overlaps with the interband transition edge, we speculate that the observed blue-shift is a consequence of an increasing interband transition edge energy, due to the downward shift of the d-band center in the surface atoms chemically bonded to oxygen. This pushes the interband transition edge away from the LSPRs and reduces their damping. The initial stage is followed by a second regime ($\delta = 10 - 15 \%$), characterized by rapid red-shift and intensity increase of the LSPR, which eventually slows down and ceases at $\delta \sim 20 \%$. These details are captured nicely by the FDTD model, and relate to the formation of the homogeneous oxide shell (dashed line in **Fig. 2d-e**) that induces spectral red-shift and intensification upon its further growth. This red-shift halts when the self-limiting oxide thickness is reached, which occurs at $\delta \sim 20 \%$. These results are in good agreement with plasmonic nanospectroscopy of a similar system³³ and signify how closely optical response and chemical and morphological properties of the particles are linked. For similar analysis of additional particles see **SI Fig. S2.5**.

Figure 2. In situ EELS of single Cu nanoparticle oxidation at 50 °C. (a) Selected ADF STEM images of a Cu nanoparticle oxidized at 50 °C (see Fig. 1 for additional images). (b, c) EELS signals from the particle recorded during oxidation with the electron beam positioned as specified in (a), revealing the LSPR signal of the particle. (d) The shift in the peak energy, ΔE_{peak} , and (e) the relative peak intensity, I/I_0 , of the LSPR response as functions of volume oxidation fraction, δ , (squares and circles) plotted together with the results of corresponding FDTD simulations for two perpendicular polarizations (triangles). The error bars in ΔE_{peak} , I/I_0 and δ correspond to the energy dispersion per pixel in the EELS measurements, the average uncertainty of the fitted peak intensity, and the average uncertainty of the image segmentation process, respectively. The dashed lines indicate transition from oxide island to homogeneous oxide shell growth.

***In situ* EELS during oxidation at 100 – 200 °C**

To map the evolution of the LSPR modes in single Cu nanoparticles oxidized at 100, 150 and 200 °C, we performed identical *in situ* measurements to those described in the previous section. At these higher temperatures, beyond an initial oxide shell nucleation and growth, NK voids form and expand inside the particles. This is characterized by two subsequent phases of linear and angular void expansion, as introduced earlier (cf. **Fig. 1** and **Fig. S2.2**). Analyzing the evolution of the EELS spectra recorded parallel and perpendicular to the linear NK void growth front reveals a more complex LSPR response compared to oxidation at 50 °C (**Fig. 3b-c** and **Fig. S2.7**). For $\delta < 20\%$, the two LSPR modes behave similarly to the 50 °C case, and increase alike in intensity and red-shift. This is the consequence of the symmetric profile of the Cu core during this stage of oxidation. At $\delta \approx 20 - 25\%$, this trend ends and instead the LSPR modes split into two peaks, accompanied by a distinct drop in intensity (**Fig. 3d-e**). The corresponding ADF STEM images (**Fig. 3a** and cf. **Fig. 1**) reveal that mode splitting signifies transition to the NK regime, upon which the circular symmetry of the Cu core breaks. Overall, the evolution of the LSPRs with oxidation is in good agreement with our FDTD simulations, and *in situ* optical plasmonic nanospectroscopy³³. Small differences could stem from the thin inner oxide shell, which is not included in the FDTD model (**Fig. 3d-e**; details in **SI Section S4.3**). During the linear phase of void growth ($\sim 20\% < \delta < \sim 60\%$), the two modes diverge, as the aspect ratio of the remaining metallic core increases, resulting in continuous red-shift of the low energy longitudinal mode. This trend reverses as the void growth transitions to the angular phase, and the aspect ratio of the core decreases. Consequently, the longitudinal LSPR mode begins to blue-shift (**Fig. 3d**). This is reflected in the results, as the spectral position of the longitudinal LSPR mode of Cu particle reaching a minimum at $\delta \sim 50 - 60\%$ during oxidation.

Figure 3. In situ EELS of Cu nanoparticle oxidation at 100 °C. (a) Selected ADF STEM images of a Cu nanoparticle oxidized at 100 °C in 3 mbar O₂, showing the expansion of the NK void following first a linear and later angular growth (see Fig. 1 for additional images and Fig. S2.7 for analysis of oxidation at 150 and 200 °C). The accumulated O₂ exposure time is indicated for each image. All scale bars are 20 nm. (b, c) EELS LSPR signals acquired during oxidation from

the set of positions indicated by the markers in (a). (d) Peak energy shift, ΔE_{peak} , and (e) relative peak intensity, I/I_0 , of the LSPR in (b, c) plotted as functions of the particle volume oxidized, δ . The markers (circles and squares) correspond to the positions in (a). Error bars are measured according to the same description in Fig. 2. The experimentally obtained data is plotted together with corresponding FDTD simulations carried out for equivalent excitation polarizations (gray markers). The dashed lines indicate transition between different stages indicated by the schematics: oxide island nucleation, homogeneous oxide shell growth, Kirkendall void formation and transition from linear to angular void expansion.

Unravelling competing oxidation mechanisms

Starting at 50 °C, the collected evidence suggests that Cu₂O oxide islands nucleate and grow on the particle surface until they coalesce into a homogeneous oxide shell at $\delta = 15 \pm 4$ % that corresponds to an *effective* shell thickness (the total projected oxide area distributed over the whole hemisphere circumference) of around 3 nm (**Fig. 4a-b**). This shell grows homogeneously until it reaches 5.5 ± 0.7 nm thickness (**Fig. 4c**). This stage of homogeneous shell growth and thickness self-limitation is consistent with the Cabrera-Mott mechanism, for which oxide growth is driven by the Mott potential, ϕ_{Mott} . This potential is induced across the oxide layer and decreases in strength upon increasing oxide thickness, thereby leading to self-limiting growth^{22,45,46}. Fitting the time evolution of the experimentally determined oxide shell thickness with the Cabrera-Mott model yields good agreement (**Fig. 4d**). Based on the data obtained from all the particles oxidized at 50 °C, we extract an average Mott potential of $\bar{\phi}_{Mott} = -3.5 \pm 1$ V and an average energy barrier for extraction and diffusion of cations across the oxide of $\bar{W} = 1.1 \pm 0.05$ eV (**Fig. 4d** and **SI Section S5.1**). Considering that the Mott potential can be written as $\phi_{Mott} = (\epsilon + E_{ads} - \phi_0)/e$, where E_{ads} is the O⁻ adsorption energy, ϕ_0 is the metal work function and ϵ is the electron affinity of O, and using corresponding literature values for Cu, $\epsilon = 1.46$ eV⁴⁷, $E_{ads} < 1$ eV⁴⁸ and 4.5 eV $< \phi_0 < 5$ eV⁴⁹⁻⁵¹, we estimate a Mott potential in the range -2 eV $< \phi_{Mott} < -3$ eV, which is close to our experimentally obtained value. Similarly, we find the experimentally determined activation barrier, $\bar{W}$, to be in reasonable agreement with the literature^{22,52}, which further corroborates a Cabrera-Mott oxidation process at these conditions. As a second important aspect, we note that the observed vacancy gap (**Fig. 4b**) is formed during the Cabrera-Mott oxidation regime, as Cu ions get preferentially extracted from the outer perimeter of the metallic particle in order to minimize lattice strain.

Figure 4: Self-limited oxide growth at 50 °C. (a) A schematic drawing of the oxidation process at 50 °C including the formation of oxide islands followed by homogenous outer oxide shell separated from the metal core by a vacancy gap layer. (b) ADF STEM image of a particle oxidized at 50 °C in 3 mbar O₂ (same as in Fig. 2a). The outer oxide shell and the vacancy gap are marked. (c) The effective oxide shell thickness measured from ADF STEM images vs. the accumulated O₂ exposure time of 7 particles oxidized at 50 °C. (d) Time evolution of the effective oxide shell thickness of the particle in (b), with the error bars showing the uncertainty of the image segmentation process. The dashed line marks the transition from the oxide nucleation phase to a homogeneous oxide shell. The Cabrera-Mott model (solid line) is fitted to the data after the oxide nucleation phase (from 10 min) that yields the values for the Mott potential $\phi_{Mott} = -3.2 \text{ eV}$ and the barrier $W = 1.1 \text{ eV}$.

Moving to higher oxidation temperatures, as expected, the oxidation rate increases, accompanied by two distinct observations compared to oxidation at 50 °C (**Fig. 5**). The first is the aforementioned growth of two oxide shells, separated by a vacancy gap (**Fig. 5a-c, cf. Fig 1e**), where one oxide shell grows *outwards* from the surface of the original metallic particle, and a second one grows *inwards* (**Fig. 5b**). The location of these two oxide layers relative to the original Cu particle suggests that the outer oxide layer is the result of Cu diffusing out, while the inner layer must arise from oxygen diffusing in through the oxide according to the Valensi-Carter mechanism²³. This process is corroborated by EELS composition mapping (**Fig. 5c**), where the color map of the relative concentrations reveals the absence of Cu atoms in the vacancy gap. Furthermore, the analysis confirms that both oxide shells are mainly composed of Cu₂O (**Fig. S2.4b-c**), consistent with earlier investigations at similar conditions^{30,31,53}. Finally, examining the thickness evolution of the inner and outer oxide shells at 100, 150 and 200 °C confirms that the growth rate of both shells increases with temperature, but the outer shell grows faster than the inner shell at all temperatures (**Fig. 5e-g**).

The second important aspect is that the outward diffusion of Cu, responsible for the outer shell growth, is no longer limited by the Mott-field. Consequently, the oxide grows beyond the self-limiting thickness and the corresponding Cu extraction leads to a higher concentration of vacancies in the lattice, which introduces tensile strain. The strain magnitude increases with the number of vacancies up to a critical point when it becomes energetically unfavorable to accommodate the strain elastically. This prompts the rapid coalescence of the vacancies, seen as the nucleation of the NK void. From our experiments, we can deduce a critical $\delta = 0.22 \pm 0.04$ for NK void nucleation that is independent of particle size (**Fig. S2.6**). This is consistent with a strain-driven onset of NK void nucleation, where the vacancy density (rather than an absolute number) in the lattice sets the threshold for void formation. Important additional points are the non-uniform strain distribution in the nanoparticles due to the presence of the substrate, and that the inner oxide shell induces further tensile strain at the metal – oxide interface. Both these factors thus lead to the maximum lattice strain being situated at the metal – inner oxide interface, where NK voids thus are expected to nucleate, which is in excellent agreement with our observations (**Fig. 1, Fig. S2.2, S2.3**). As the final aspect, we highlight that the continued void growth is governed by minimizing the interfacial area between metal and inner oxide shell (**Fig. S3**), which leads to the experimentally observed transition from a linear to an angular void growth mode at $\delta = 60 \pm 10$ % (**Fig. 3 and Fig. S2.7**). In this final oxidation stage, the void continues to expand until the entire particle is consumed and a hollow oxide shell comprised of two layers separated by a vacancy gap is formed.

Figure 5. Evidence of competing outer and inner oxide shell growth. (a) Schematics of the stages of oxide growth; the oxide island nucleation, homogenous oxide shell growth – both inner and outer oxide shells, and the formation of the NK void. (b) A particle before (top left) and after (bottom left) oxidation at 200 °C. The scale bar is 50 nm. To the right, the pre and post-oxidation images are overlaid to show the position of the inner and outer oxide shells relative to the perimeter of the pre-oxidation particle (in red). (c) Top row: EELS maps of the O and Cu signals from a section of an oxidized particle. Bottom row: ADF STEM image of the mapped region together with a map of the relative composition of Cu and O, confirming the lack of Cu at the vacancy gap between the outer and inner oxide shells. The effective inner (red triangles) and outer (blue squares) oxide shell thicknesses vs. O₂ exposure time as extracted from ADF STEM images for a number of single Cu particles oxidized at (d) 50 °C, (e) 100 °C, (f) 150 °C and (g) 200 °C.

Given our observations, it is apt to quantify the temperature dependence of the growth rates of these oxide shells by means of an Arrhenius analysis. Specifically, we apply the Johnson-Mehl-

Avrami-Kolmogorov²⁸ (JMAK) kinetic model for isothermal nucleation processes to δ (**Fig. 6a**), from which we obtain a rate constant, k , for each particle (for details see **SI Section S5.2**). Subsequently, we fit the rate constants to an Arrhenius equation of the form $k = k_0 \exp\left(-\frac{E_a}{k_B T}\right)$, where k_0 is the pre-exponential factor, E_a is the apparent activation energy and k_B is the Boltzmann constant (**Fig. 6b**), and extract $E_a = 0.37 \pm 0.1$ eV (for details see **SI Section S5.3**). This number is in the lower range of previously reported values for Cu nanoparticles (0.37 – 1.5 eV)^{30,31,54} and Cu thin films (0.3 – 1.0 eV)⁵⁵ under similar oxidation conditions. To discriminate between the E_a for the growth of the inner and outer oxide shells, the time to reach a specific effective oxide thickness, τ , is compared between the particles oxidized at 100, 150 and 200 °C. Here, our analysis yields $E_{out} = 0.30 \pm 0.1$ eV for the outer shell to reach 5 nm and $E_{in} = 0.45 \pm 0.1$ eV for the inner shell to reach 0.5 nm (**Fig. 6c-d** and **Fig. S5.8**). This is consistent with the lower diffusion coefficient of O₂⁵⁶ compared to that of Cu⁵⁷ through Cu₂O at these temperatures, which corroborates our experimental observations.

Figure 6. Kinetic analysis of Cu nanoparticle oxide growth. (a) The volume oxidation fractions vs. O_2 exposure times for three Cu particles oxidized at 100, 150 and 200 °C, respectively, obtained from ADF STEM images (error bars show the uncertainty of the image segmentation). The solid lines are fits to the Johnson-Mehl-Avrami-Kolmogorov (JMAK) model with the extracted numbers for parameter n and rate constant k indicated next to each fit. (b) Corresponding Arrhenius plot of $\log(k)$ extracted from JMAK model fits, yielding an overall oxidation $E_a = 0.37 \pm 0.1 \text{ eV}$. 21 particles were analyzed and correspond to the individual data points. (c, d) Arrhenius plots for the characteristic times to grow 5 nm thick outer oxide (c) and 0.5 nm inner oxide (d), from which the respective apparent activation energies are obtained, $E_{\text{out}} = 0.30 \pm 0.1 \text{ eV}$ and $E_{\text{in}} = 0.45 \pm 0.1 \text{ eV}$. The shaded areas show the 95 % confidence interval of each fit.

Conclusions

In summary, we have recorded the oxidation of single Cu nanoparticles with sub-nanometer spatial resolution at 50 – 200 °C using *in situ* ADF STEM and monitored the evolution of their LSPRs using EELS. Our *in situ* observations reveal the presence of multiple oxidation mechanisms at play, each with signatures that could be identified in both the morphology of the particles and their plasmonic response. We observe that initially, oxide islands nucleate on the particle surface and subsequently coalesce to form a homogeneous oxide layer separated from the metal core by a nanometer scale vacancy gap at all temperatures. At 50 °C, the Cabrera-Mott mechanism

dominates, as thermally driven diffusion through the oxide is negligible, which results in a self-limiting oxide shell thickness at this temperature. At temperatures 100 – 200 °C, concomitant with the outward oxide shell growth, an inner oxide shell grows according to the Valensi-Carter mechanism, arising from the thermally activated inward diffusion of oxygen ions. This inner shell is separated from the outer shell by the vacancy gap. Further on, thermally driven outward diffusion of Cu ions dominates the outer oxide shell growth and leads to NK void formation at a common oxidation fraction, regardless of particle size. The NK void expansion also follows a common trend across many particles, driven by metal - oxide interface minimization. The signature of these stages driven by their underlying oxidation mechanisms could be traced in the LSPR response of the particles. These insights on competing oxidation mechanisms of metallic nanoparticles are valuable for nanosensors⁵⁸, nanoelectronics⁵⁹ and catalysis^{60,61}. More generally, our *in situ* detection scheme provides opportunities to investigate the intricate details of chemical reactions involving nanoparticles in gaseous environments, and the resulting changes in their optical response.

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Competing interests

The authors declare no competing financial interests.

Methods

Sample fabrication. The Cu nanoparticles were nanofabricated by means of hole-mask colloidal lithography (HCL)³⁹ onto Wildfire chips from DENSsolutions in sparse quasi-random arrays. The steps of the HCL procedure were the following: 1) A thin film Poly(methyl methacrylate) – PMMA A4 – resist in Anisole (MicroChem Corporation) was spin coated at 1500 rpm for 60 s (acceleration 500 s^{-2}), followed by soft-baking on a hotplate at 170°C for 5 min. 2) 5 s O_2 plasma treatment (50 W, 10 sccm) to render the PMMA surface hydrophilic. 3) Drop-coating of poly(diallyldimethylammonium chloride) polyelectrolyte (Sigma Aldrich) diluted in water to 0.2 wt % and incubated for 40 s. 4) Drop-coating of aqueous sulfonate latex polystyrene (PS) bead suspension with approximate particle sizes of 100 nm, 120 nm and 150 nm, with subsequent 3 min incubation. 5) Evaporation of 15 nm Cr at a rate of 1 Å/s (Lesker PVD 225), followed by stroking a wet tissue over the substrates ~ 20 times to gently remove the PS beads and reveal the holes in the Cr mask without breaking the TEM membrane. 6) 5 min O_2 plasma (50 W, 10 sccm) dry etch of the PMMA layer through the holes in the Cr mask down to the substrate. 7) Evaporation of 20 nm Cu at 1 Å/s , followed by lift-off in acetone for approximately 24 h.

ADF STEM imaging and EELS measurements in environmental TEM. The *in-situ* STEM – EELS measurements were carried out in a 80 – 300 kV FEI Titan environmental TEM equipped with a field emission gun, monochromator and GIF Tridiem spectrometer. The ETEM instrument was operated at 300 kV in STEM mode with an electron probe convergence semi-angle of 10 mrad and with the monochromator excited, giving spatial and energy resolutions of $\sim 0.3 \text{ nm}$ and 0.1 eV, respectively. The fabricated samples were mounted on a DENS Wildfire holder to enable controlled heating of the particles inside the TEM. First, the Cu nanoparticles were thermally annealed for 60 minutes at 400°C in 3 mbar of H_2 atmosphere to remove hydrocarbons and to recrystallize into particles containing 1 - 8 grains prior to oxidation. Following annealing, the particles were heated to temperatures 50, 100, 150 and 200°C and oxidized in 3 mbar O_2 . The particles were exposed to O_2 a total time of 90 min at 50°C and 100°C , 50 min at 150°C and 6

min at 200 °C. ADF STEM images and EELS spectrum images were recorded approximately every 2.5 min at 50, 100 and 150 °C temperatures and every 1 min at 200 °C. EELS spectrum images were 10 x 10 pixels with a pixel size of ~ 10 nm. The beam was scanned within each pixel during the acquisitions. The relatively low resolution of the spectrum images was chosen in order to avoid excessive beam induced effects. Each spectrum had a dispersion per channel of 0.01 eV and acquisition time of 10 ms. Prior to each acquisition, the O₂ flow was temporarily stopped and the gas was pumped out in order to minimize further oxidation of the nanoparticles when exposed to the electron beam. The O₂ flow was resumed again after each acquisition. The data acquired from each particle at different times was combined into 3D image stacks (dimensions x, y and time), in the case of the ADF images, and 4D spectrum image series (dimensions x, y, energy and time). The spatial drift between different frames in each stack/series was corrected prior to analysis. The EELS spectra were analyzed after normalizing each spectrum with respect to the total area bound by it and the energy-loss axis, followed by removing the contribution from the zero-loss peak by fitting its tail with a power-law model. LSPRs at each time were fitted with Gaussian functions to determine their peak energy and intensity. The ADF STEM images were segmented using the image processing toolbox in MATLAB. The outer particle perimeter was detected automatically by morphological filtering (function *imopen*, structure element: disk, radius 5 pixels) to reduce noise close to the particle edge and the perimeter was detected using *bwboundaries*. A circle was fitted to the detected perimeter to calculate the particle radius *R*. The perimeters of the metallic Cu core, the void, the inner and outer oxide shells were drawn manually (function *drawassisted*) to measure the area of each phase. From the inner and outer oxide shell area, the effective oxide shell thicknesses were calculated. The oxidation volume fraction after NK void formation was calculated according to the formula for a spherical cap geometry during the linear phase and a spherical sector geometry during the angular phase of void expansion.

Finite-difference time-domain (FDTD) electrodynamic simulations. The Lumerical 2019b software (ANSYS) was used to perform the finite-difference time-domain electrodynamic simulations. The model geometry consisted of a rounded Cu hemisphere of radius 35 nm and an edge curvature of 5 nm. This particle was placed on a 25 nm thin silicon nitride film. Dielectric data for Cu from reference ⁶² and for Si₃N₄ from reference ⁶³ were used. The inner and outer Cu₂O oxide shells were simulated using the dielectric data from Tahir⁶⁴. The correct geometries were calculated at each δ to achieve the correct oxide volume using the Pilling-Bedworth expansion factor of 1.68²⁶. For $\delta = 0 - 10$ %, oxide islands were simulated with height from 2 to 3 nm, and the number of islands calculated based on the total oxide volume. The mesh overlay was 0.25 nm. For $\delta = 15 - 20$ %, homogenous oxide shell growth was simulated along with the vacancy gap (mesh overlay 0.25 nm). Until forming the vacancy shell, the core was shrunk accordingly from *R* = 35 nm to *R* = 33.2 nm, to account for the conversion of metal to oxide. From $\delta = 22$ %, a NK void was introduced in the model, and up to 60 %, the void grew with a linear front (mesh overlay 0.25 nm), between 60 and 65 %, the void was expanded angularly until full oxidation (mesh

overlay 0.5 nm). Illumination in the simulation was implemented by a total-field scattered-field source incoming from above the particle along the vertical axis, with two perpendicular polarizations that were simulated separately. The absorption cross-section was obtained by integrating the Poynting vector of the absorbed field. The peak(s) were fitted by one or two Lorentzian functions to obtain the peak energies and peak intensities.

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