Dissolution and Persistence of Copper-Based Nanomaterials in Undersaturated Solutions with Respect to Cupric Solid Phases

Supporting Information

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This document contains 6 figures and 1 table in 16 pages.
**SEM images and AFM height distributions.** Scanning electron microscopy (SEM) images and AFM height distributions of Cu, Cu$_{ox}$, and Cu$_x$S NPs are shown in Figure S1. SEM images were taken with a LEO (Zeiss) 1550 Schottky field-emission SEM. Specimens were sputter coated with gold-palladium for 30 s prior to SEM imaging.

![SEM micrographs of A) Cu, B) Cu$_{ox}$, and C) Cu$_x$S NPs. D) Height distributions of Cu (blue), Cu$_{ox}$ (red), and Cu$_x$S (green) NPs measured by AFM.](image)

Figure S1. SEM micrographs of A) Cu, B) Cu$_{ox}$, and C) Cu$_x$S NPs. D) Height distributions of Cu (blue), Cu$_{ox}$ (red), and Cu$_x$S (green) NPs measured by AFM.

**XPS analysis.** XPS was used to investigate surface composition of Cu, Cu$_{ox}$, and Cu$_x$S NPs (Figure S2). Curve fitting to the Cu 2p$_{3/2}$ peak of Cu NPs found a primary peak at 932.7 eV and a shoulder at 933.8 eV. The primary peak is due to metallic copper, and the shoulder indicates the presence of cupric oxide.$^{1,2}$ The presence of cupric species is also evident from the characteristic shake-up bands that appear at 943 and 962 eV.$^{1,2}$ These results suggest that the Cu NPs have a thin cupric oxide shell around the metallic core. The much more pronounced shake-up bands of Cu$_{ox}$ NPs at 942.0 and 944.2 eV demonstrate that the ozonation process had strongly oxidized the
A strong peak at 934.9 eV demonstrates that Cu(OH)$_2$ was the dominant surface species of the Cu$_{ox}$ NPs. Unfortunately, the distribution between oxides and hydroxides could not be further elucidated by investigation of the O 1s region because of the dominant signal from the glass substrate. Finally, the main Cu 2p$_{3/2}$ peak shifted to 932.4 eV for the Cu$_x$S NPs, consistent with a conversion to the cuprous oxidation state present in copper sulfides such as chalcocite and covellite. Weak shake-up satellites and a shoulder at 933.7 eV demonstrate that some cupric species were also present. The S 2p doublet with peaks at 162.1 and 163.3 eV is attributable to sulfide species. The additional doublet at 168.4 eV is a clear sign that exposure to the atmosphere had caused oxidation to sulfate, which is also why the Cu(II) oxidation state is present in the Cu 2p region. Thus, a thin layer of copper sulfate appears to coexist with the more abundant cuprous sulfide species. XPS spectra for the C 1s binding region are shown in Figure S3. The prominent peak at 284.6 eV is due to adventitious carbon. The weaker peak at 288.4 eV indicates the presence of carbonate species. The carbonate peak is present in all three samples, although it is quite weak in the Cu$_x$S NP specimen.
Figure S2. XPS spectra of A) Cu, B) Cu$_{ox}$, and C) Cu$_x$S NPs in the Cu 2p region. D) XPS spectra of Cu$_x$S NPs in the S 2p region.
Figure S3. XPS spectra of the C 1s binding region.

EDS spectra. The EDS spectra for Cu, Cu$_{ox}$, and Cu$_{x}$S NPs are shown in Figure S4. The Cu and Cu$_{ox}$ NP samples were prepared on Si wafers attached to Ni aperture grids. The Si and Ni signals are from the grid and support. Unfortunately, the Cu$_{x}$S NPs could not be prepared on Si wafers. Due to poor adhesion, the Cu NPs would detach from the wafer during the sulfidation process. Instead, Cu$_{x}$S NPs were prepared on glass with a thin layer of titanium to promote adhesion. The glass was similarly mounted on a Ni aperture grid. The Si, O, Na, K, Ti, Ni, and C signals in the Cu$_{x}$S spectrum are all background.
Figure S4. EDS spectra of A) Cu NPs on silicon, B) Cu\textsubscript{ox} NPs on silicon, C) Cu\textsubscript{x}S NPs on glass, and D) the glass background for the Cu\textsubscript{x}S NP sample.

**TEM analysis.** The EDS maps shown in Figure 1 illustrate that oxygen was strongly associated with copper following ozonation, and sulfur was strongly associated with copper following sulfidation. It also appears that a minor amount of oxygen was associated with the pristine Cu NPs; however, this could be an artifact attributable to the thickness of the particles. The measured atomic percentage of O in the Cu NP samples was only 3 ± 2%, and some fraction
of this percentage is due to background oxygen rather than oxygen in the structure of the Cu NPs. In contrast, the Cu:O ratio (as atomic percentages) in the ozonated samples was 0.9 ± 0.1 for the particles shown in Figure 2D, which is very near the 1:1 ratio expected for CuO. On the other hand, the Cu:O ratio measured from a similar set of nanoparticles on a separate TEM sample was 0.4 ± 0.1, which is closer to the 1:2 ratio expected for Cu(OH)₂. The average Cu:S ratio of the nanoparticles shown in Figure 2G was 1.4 ± 0.3, and the ratio ranged from 1.0 to 2.4. The average ratio matches spionkopite (Cu₁.₃₉S) well, but the high variability implies the presence of multiple CuₙS phases.

The brightest spots in the SAED patterns shown in Figure 2A and 2D are due to the underlying silicon substrate. These spots do not appear in the CuₙS samples, which were prepared on glass instead. The diffraction spots due to the particles themselves show up as rings in all three types of Cu-based NPs due to the polycrystalline nature of the particles. The polycrystallinity of the NPs is further illustrated in the STEM images shown in Figure S5. It is particularly evident from the variation in contrast in the annular dark field STEM image that individual Cu NPs consisted of multiple nanocrystallite domains with differing orientations. The d-spacings determined by SAED for Cu NPs were 2.09, 1.83, 1.27, and 1.09 Å, in good agreement with the reported values for the [111], [200], [220], and [311] crystal faces of metallic face-centered cubic Cu.² The two bright rings in the SAED pattern for the ozonated NPs are due to the two most intensely diffracting crystal faces of tenorite—the [-111] and [111] faces with measured d-spacings of 2.51 and 2.32 Å, respectively. The [110], [202], and [-113] faces of tenorite were also detected, with respective d-spacings of 2.75, 1.58, and 1.50 Å.² In contrast, the Cuₙox NPs located in the region where the Cu:O ratio was 0.4 had d-spacings of 2.78, 2.64, 2.48, 2.24, 2.07, and 1.77 Å. The two most intense peaks of tenorite were absent, and the remaining peaks closely match the [110],
[002], [111], [130], [131], and [060] faces of spertiniite. The SAED results corroborate the EDS data to confirm the presence of both tenorite and spertiniite in the ozonated samples. Thus, the Cu$_{ox}$ NP samples are a mixture of CuO and Cu(OH)$_2$ NPs. The SAED results for Cu$_3$S NPs also demonstrate a mixture of phases. Measured d-spacings of 3.09, 2.87, 2.77, and 1.93 Å match both spionkopite and yarrowite (Cu$_{1.12}$S) fairly well. On the other hand, measured d-spacings of 3.30, 3.23, and 2.82 Å match the [100], [101], and [103] faces of covellite. Ma et al. likewise found that sulfidation of Cu-based NPs results in a milieu of stable copper sulfide phases.

Figure S5. A) Bright field and B) annular dark field STEM images of a pristine Cu NP.

Discussion of model assumptions. The kinetic model used in this study assumes that the system is far from equilibrium so that the dissolved Cu species do not influence the reaction rate. To test this assumption, the dissolved Cu concentration within the AFM fluid cell was estimated by the mass balance model given in Equation 6. To represent conditions where dissolved Cu concentrations would be the highest, we assumed the initial Cu mass was 2 standard deviations above the average mass. The model assumes that complete mixing occurs within the flow cell, which is not correct because of the complex flow pattern caused by the presence of the oscillating cantilever. The AFM cantilever is connected to a base that covered at least 5-10% of
the sample during each experiment. Because the flow was restricted underneath the cantilever base, we observed that little or no dissolution occurred in the covered region. The initial mass parameter was reduced slightly to 300 ng to account for this effect. The model also assumes that all the dissolved Cu is in the divalent state. Some small fraction of the dissolved species will actually be cuprous ions, so this assumption overestimates the actual amount of dissolved cupric ion. Another model assumption is that the NPs do not form aggregates. The effect of aggregation would be to reduce the dissolution rate.

The model further assumes that the particles are hemispherical, so that the average height is equal to the radius. The initial Cu NPs are actually truncated tetrahedra that have triangular corners. The triangular corners dissolve more rapidly than other regions of the particles because of the high surface energy associated with the corners’ sharp curvature; thus, the contracting sphere rate law does not apply initially, and the model underestimates the actual copper release from an individual NP during the initial 1-2 h of the experiment. Because the corners dissolve rapidly, the initial shape is transient, and the particles rapidly convert to cylindrical nanodisks. As discussed in the following section, Equation 3 holds for cylindrical particles if we assume that the rate of change in nanoparticle height is equal to the rate of change of the radius. Based on our previous work with silver, this assumption is quite reasonable, so Equation 3 is valid in our system after the initial shape transition. The time series data reported herein and in our previous work show that the height of dissolving NSL-produced nanoparticles decrease at a constant rate, as predicted by Equation 3.

The most glaring assumption of the model is that the substrate is covered by a uniform distribution of NPs. The total mass of copper per unit area of substrate was found to be 143 ± 37 ng/mm². The average area of a single substrate was 1.3 ± 0.4 mm², so the average mass per
specimen was 186 ± 70 ng. This mass is greater than what would be expected for a substrate that was only covered by the nanoparticles of interest, which would only be about 48 ng, or 26% of the actual mass. For comparison, a copper thin film of equivalent thickness covering the entire substrate would have a mass of 677 ng. The difference between the measured and calculated mass of Cu NPs is due to defects in the initial lithographic mask of latex spheres. Irregular nanostructures caused by line defects in the mask can be seen in the SEM images of Figure S1. These nanostructures cover substrate area that would not be covered by the individual NPs. Other features on the substrates include Cu thin films where no latex spheres had been deposited and areas with no Cu whatsoever where a multilayer of spheres had been deposited. Because the Cu NPs cannot occupy the same substrate area as any of these defects, the nanoparticles themselves actually contribute significantly less than 26% to the total mass. The structures that resulted from defects in the lithographic mask have a lower surface area to mass ratio than the NPs; therefore, they release dissolved ions at a slower rate than the NPs and the model output represents an upper bound for the actual dissolved concentration. A lower bound can be estimated by assuming the other extreme; namely, that all the Cu mass is present as a thin film. This alternative assumption results in an estimated dissolved concentration that is about a factor of 3 smaller than the model assumption (see below).

**Contracting volume rate law for cylindrical nanoparticles.** As discussed above, nanoparticles produced by NSL initially have a truncated tetrahedral shape. The initial shape is transformed into a disk-like or cylindrical shape. This morphological change is caused by accelerated dissolution at the triangular corners where the surface energy is high. A contracting volume rate law can be derived for a cylinder. We assume a cylindrical volume of height $h$ and radius $r$. In our case, the particles are attached to a surface, so the height can only decrease from
the top down and not from the bottom up (i.e., the surface area on the bottom of the cylinders is unavailable for reaction). The volume, $V$, and available surface area, $A$, of the cylinder are given by Equations S1 and S2, respectively.

$$V = \pi r^2 h$$  \hspace{1cm} (S1)

$$A = 2\pi rh + \pi r^2$$  \hspace{1cm} (S2)

Differentiating Equation S1 by the chain rule yields Equation S3.

$$\frac{dV}{dt} = 2\pi rh \frac{dr}{dt} + \pi r^2 \frac{dh}{dt}$$  \hspace{1cm} (S3)

If we assume $dh/dt = dr/dt$, then Equation S3 can be factored to yield Equation S4:

$$\frac{dV}{dt} = (2\pi rh + \pi r^2) \frac{dr}{dt}$$  \hspace{1cm} (S4)

Substituting Equation S2 into Equation S4 gives Equation S5:

$$\frac{dV}{dt} = A \frac{dr}{dt}$$  \hspace{1cm} (S5)

Finally, by substituting Equation S5 into the contracting volume rate law given in Equation 1 and then dividing both sides by $A$, the result simplifies to Equation 3. Hence, the mathematical result for a cylinder is equivalent to the result for a sphere. Based on our previous work, the assumption of equality between the rates of change of height and radius is reasonable. The rate constants determined for NSL-produced Ag NPs dissolving in NaCl solutions were statistically the same for height and radius measurements, although the rate constants based on radius measurements were consistently lower than those based on height measurements. The statistical error between the two estimates was small enough to be of little practical significance, and it may have been due to a bias in the AFM measurements. AFM probes tend to become dull after repeated scans, and the effect of this dulling is to make the lateral dimensions of objects appear
larger. This source of error was not corrected for, so the time series of radius measurements would systematically underestimate the actual decrease in the particles’ lateral dimensions.

We now consider the effect of cylindrical geometry on Equation 5. First, assume that \( h = r \), which is a close approximation for the NPs in this study.\(^7\) Then Equation S1 can be simplified to a cubic function of \( r \) that is the same as the equation for the volume of a sphere without the leading factor of 4/3. Equation 5 is derived from Equation S6:

\[
\frac{[Cu^{z+}]}{[Cu^{z+}]_0} = 1 - \frac{[Cu^{z+}]_p}{[Cu^{z+}]_0}
\]  
(S6)

where \([Cu^{z+}]\) is the total dissolved Cu ion concentration, \([Cu^{z+}]_0\) is the initial Cu mass in the system expressed as an equivalent concentration, and \([Cu^{z+}]_p\) is the remaining Cu mass in the NPs expressed as an equivalent concentration. Both the numerator and the denominator of the second term on the right-hand side of the equation can be written in terms of the volume of a single particle. All the leading constants will cancel out by division; therefore, the result will be the same whether the volume of a sphere, a hemisphere, or a cylinder with \( h = r \) is substituted into the equation.

**Solution to continuous flow kinetic model.** Equation 6 in the manuscript gives the mass balance on metal ions with the AFM liquid cell as the control volume, and it is reproduced here as Equation S7:

\[
\frac{d[Cu^{z+}]}{dt} = 3\frac{[Cu^{z+}]_0}{\tau_L}\left(1 - \frac{t}{\tau_L}\right)^2 \frac{[Cu^{z+}]}{\tau_R}
\]  
(S7)

where \( t \) is time, \( \tau_R \) is the residence time, and \( \tau_L \) is the particle lifetime. The initial condition is \([Cu^{z+}] = 0\). Equation S7 is a first-order, linear, ordinary differential equation, and it can be solved analytically by the use of an integrating factor. The solution for \( 0 \leq t \leq \tau_L \) is
The solution for $t > \tau_L$ is

$$[Cu^{z+}] = \frac{3[Cu^{z+}]_0\tau_R}{\tau_L} \left( 1 - \frac{t}{\tau_L} \right)^2 + \frac{2\tau_R}{\tau_L} \left( 1 - \frac{t}{\tau_L} \right) + 2 \left( \frac{\tau_R}{\tau_L} \right)^2 \left( 1 + \frac{2\tau_R}{\tau_L} + 2 \left( \frac{\tau_R}{\tau_L} \right)^2 \right) e^{-t/\tau_R}$$

(S8)

Concentrations calculated by Equations S8 and S9 for Cu and Cu$_{ox}$ NPs at the various pH values tested in this research are shown in Figure S6. Because the particle lifetime is much greater than the residence time, the maximum dissolved ion concentration is reached almost instantaneously, and then the ion concentration decreases smoothly until it is zero at about $t = \tau_L$. This decrease becomes more gradual at higher pH values.

**Figure S6.** Modeled concentrations of total dissolved Cu$^{2+}$ for A) Cu NPs and B) Cu$_{ox}$ NPs.

**Lower bound estimate of total dissolved Cu.** The model described above assumes that all the Cu mass on a substrate consists of uniformly sized NPs. As discussed above, these NPs actually account for less than 26% of the total Cu mass on the substrate. Because the other nanostructures
on the substrate dissolve more slowly than the NPs, the model overestimates the amount of dissolution and represents an upper bound. A lower bound can be estimated by assuming that the Cu mass consists entirely of a single thin film with thickness equivalent to the height of the NPs. Thin films have the lowest surface area to mass ratio, and, therefore, will dissolve more slowly than any of the other Cu structures on the substrate. We assume that the thin film dissolves according to a contracting volume rate law (Equation 1) and that the rate constant is the same as that measured for Cu-based NPs. The area for a thin film is essentially constant until the dissolution process is nearly complete and \( \tau_R \ll \tau_L \) in our system, so we assume that a steady state is achieved rapidly. The steady-state concentration is given by Equation S10:

\[
[Cu^{2+}] = \frac{[Cu^{2+}]_0 \tau_R}{\tau_L}
\]

(S10)

where all variables are as defined above. If we consider Equation S8, it will be noted that the leading multiplication factor is three times Equation S10. This leading factor in Equation S8 is also approximately equal to the maximum total dissolved Cu ion concentration because the terms in parentheses are nearly equal to 1 when \( t \) is small and \( \tau_R \ll \tau_L \). Thus, our lower bound estimate of the total dissolved Cu concentration is one third of our upper estimate.

**Comparison of calculated maximum total dissolved Cu concentrations with tenorite solubility.** The estimated maximum total dissolved Cu concentrations, which always occur within the first few seconds of the experiment because of the low residence time, are compared with tenorite solubility in Table S1. The maximum total dissolved Cu\(^{2+}\) concentration calculated by the model is at least an order of magnitude below the calculated solubility in every case.
**Table S1. Comparison of Dissolved Concentrations and Solubility**

<table>
<thead>
<tr>
<th>pH</th>
<th>Cu NPs (ng/L)</th>
<th>Cu&lt;sub&gt;ox&lt;/sub&gt; NPs (ng/L)</th>
<th>Tenorite Solubility (ng/L)</th>
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<td>4.8</td>
<td>1840</td>
<td>-</td>
<td>2.16 × 10⁹</td>
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<td>392</td>
<td>3096</td>
<td>4.49 × 10⁷</td>
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<td>47</td>
<td>151</td>
<td>1.27 × 10⁸</td>
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**References**