In Situ Liquid Cell TEM Studies on Etching and Growth Mechanisms of Gold Nanoparticles at a Solid–Liquid–Gas Interface

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Etching and growth of gold nanoparticles at a solid–liquid–gas interface are investigated via in situ liquid cell transmission electron microscopy. For this purpose, the gold precursor tetrachloroauric acid is enclosed in the wells of a free-standing, locally thinned silicon nitride film covered by few-layer graphene. Etching of gold is attributed to hydroxide radicals generated by radiolysis and gaseous species which are located within a gas bubble. The etching mechanism comprises two distinct cases. In one case, the gas bubble is in direct contact with the gold particle, separated only by a thin liquid membrane. In the other case, the gold particle is thoroughly immersed in liquid in the vicinity of the particle. In the latter, etching molecules diffuse from the bubble through the liquid toward the surface of the nanoparticle and subsequently etch the gold platelet. During the particle etching process, concurrent nucleation and ripening of gold nanoparticles are observed. This growth is induced by local supersaturation of the solution with gold ions. Experimental results show that the growth process is limited by diffusion, even though the diffusivity of reactants is very low due to narrow-channel effects compared against the diffusivity of solvated ions in bulk liquids.

Understanding reaction pathways of etching and growth of nanoparticle systems is essential for tailoring new nanomaterials for catalysis,[11] plasmonics,[2] or biological[3] applications. The premier method which has been demonstrated for in situ characterization of reaction mechanisms on the atomic scale is liquid cell (transmission) electron microscopy (LCTEM).[4,5] This technique enables the direct observation of reactions at the nanoscale as well as monitoring of reaction kinetics. This has been demonstrated impressively in recent years for various material systems like gold,[6–8] platinum,[1,9] palladium,[10,11] silver,[12] iron oxide,[13] and even bimetallic nanostructures,[14,15] or anisotropic gold–silver core–shell nanoparticles.[12] Complex reaction mechanisms like oriented coalescence of nanoparticles,[16] dendrite growth,[17,18] aggregation[19] of nanoparticles, material deposition,[20] etching,[10] and corrosion[21] have all been investigated in liquid dispersions by direct observation at the nanoscale. To date, there are only a few studies documenting direct observation of reactions at interfaces, most of which are related to solid–liquid interfaces.[20,22,23] In situ liquid cell studies of reactions at the solid–liquid–gas interface, however, are few and far between even though a deep understanding of reaction mechanisms at these interfaces is essential for developing environmentally friendly industrial processes such as the leaching of noble metals in cyanide-free solutions using halides.[24,25] In a recent study, it was shown that gas bubbles can dramatically influence the dissolution behavior of gold nanoparticles in FeCl₃ solution.[26]

In this communication, we investigate into the etching of gold nanoparticles (AuNPs) at the solid–liquid–gas interface by in situ liquid cell transmission electron microscopy utilizing graphene-supported microwell liquid cells (GSMLC).[2,27] Furthermore, we examine a subsequent growth process of AuNPs in close proximity of both a liquid–gas and a solid–liquid interface. For this study, an aqueous solution of 10 mmol L⁻¹ tetrachloroauric acid (HAuCl₄) is investigated. The mechanisms of etching and growth of AuNPs are studied by analyzing dissolution and growth kinetics as well as particle motion.

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In order to investigate electron beam induced etching and growth processes of gold nanostructures at the solid–liquid–gas interface, an aqueous solution of HAuCl₄ is investigated by LCTEM. Figure 1 shows a series of bright-field TEM images of an etching process on a gold nanostructure at the solid–liquid–gas interface of a gas bubble. This gold nanostructure exhibits the threefold symmetry of an fcc-based platelet at $t_0$ which degrades during the course of the in situ observation. The nanoplatelet as well as the gas bubble was already present at the beginning of the experiment. The platelet might be either a result of electroless deposition [28] during sample preparation or caused by initial electron beam irradiation [29] during alignment. The bubble is believed to be a radiolysis product.

After the majority of the primary gold platelet is etched, growth of AuNPs is observed and monitored at the projected position of the gas bubble (Figure 1a frames 5–7). Additionally, condensation of a droplet inside the gas bubble [30] (Figure S4, Supporting Information) was observed which can be seen in frames 7 and 8 of Figure 1a.

The process of dissolution starts with the development of a gas bubble which forms prior to the first micrograph of Figure 1a. It is accepted from various experiments as well as radiolytic simulations (see Figure S1 in the Supporting Information) that dissolved hydrogen and oxygen gas forms during LCTEM [29,31]. These molecules can precipitate into gas bubbles when the local solubility is strongly exceeded. When the gas bubble comes into contact with the Au platelet, the platelet dissolves at the area of contact. This indicates that gaseous species are present in the bubble which supports etching of the gold platelet. Possible candidates supporting the etching of gold are strongly limited since the precursor solution contains only hydrogen, oxygen, gold, and chlorine. Reactions involving molecular oxygen are assumed to be unlikely and hydrogen bubbles have been shown to inhibit gold etching processes [26]. Accordingly, it is proposed that distinct chlorine-containing gases like molecular chlorine (Cl₂) or hydrochloric acid (HCl) are involved in the dissolution process. This is also justified since halides are known to play an important role during dissolution of noble metals. In chloride leaching solutions, noble metals are dissolved by an oxidation to metal ions and a consecutive complex formation of these ions with chloride ions [24,25]. During the dissolution of gold by chloride leaching, two reaction steps are known to strongly influence the reaction rate: i) the mass transfer of the oxidant to the surface of the noble metal and ii) the etching reaction at the surface [24,25]. This is also possible with different halide ions as was investigated by Jiang et al. [10] for the case of palladium nanocrystals in bromine-containing solution. The authors concluded that palladium...
was etched by a complex formation with bromide ions during electron bombardment.

In the present case, we hypothesize the underlying reaction mechanism depicted in Figure 1b. Hydroxide radicals are formed as primary products of radiolysis during electron beam irradiation of the specimen solution. These hydroxide radicals are a strong oxidant which may be able to oxidize gold atoms into ions (most likely Au\(^{+}\)). The latter are dissolved by complex formation with chloride ions assumed to originate from gaseous molecular chlorine and hydrochloric acid in the gas bubble. These suggestions are supported by radiolytic simulations of the solution chemistry conducted by Schneider et al.,\(^ {31}\) predicting that both oxidative and reductive species emerge during LCTEM. Depending on the electron dose rate, these species can induce chemical reactions in both directions. Furthermore, it is known from radiolytic simulations by Park et al.,\(^ {32}\) that distinct chlorine-containing species form during LCTEM of aqueous solutions of HAuCl\(_4\). The stated reaction list, however, might not be complete. For example, it is known from combustion chemistry that chlorine radicals react with hydrogen and oxygen radicals.\(^ {32}\) Although there are no high temperatures inside the liquid cell, many radicals are generated by radiolysis, which are known to be capable of forming HCl and Cl\(_2\). Both species, HCl and Cl\(_2\), can be easily split up into H\(^{+}\) and Cl\(^{-}\) (deprotonation of HCl in solution) and chlorine radicals (homolytic fission of Cl\(_2\)), respectively and thus provide reactants for complex formation with gold ions.

In order to verify our hypothesis, a quantitative analysis of the emerging particle volumes during the process is performed by measuring the projected areas of the particles involved as well as by tracking their motion. Figure 2a shows the evolution of the respective volumes of the primary Au platelet, the cumulative volume of the growing nanoparticles as well as the cumulative volume of all particles involved. The volume of the Au platelet is estimated by measuring its projected area with a side length of 9 nm and further assuming a thickness of 1.44 nm which is derived from previously observed Au platelet geometries.\(^ {7}\) The volumes of the AuNPs are determined by measuring their projected area and assuming a spherical shape. The first noteworthy observation is that the initial volume of the platelet is remarkably close to the cumulative volume of the growing particles in the end of the process. Conservation of mass may indicate a quasi-closed system where only few gold ions diffuse out of the observed area. This can be attributed to the limited area in which the electron beam interacts with the specimen solution as well as the sterically hindered and significantly decelerated diffusivities of the gold ions when compared to bulk solution. Figure 2b depicts the etching process in more detail displaying the equivalent radius of the platelet plotted against time. The time spans in which the particle is in direct contact with the solid–liquid–gas interface are marked. As seen previously, dissolution is enhanced in the case of contact between bubble and nanoplatelet. This is a strong indication that the solvation of gold occurs due to species originating from the gas phase. According to Wagner, the correlation between the effective radius \(r\) of a particle derived from its volume to time \(t\) can be described by a power law of the form \(r \propto t^{\beta}\).\(^ {33}\) The absolute value of the corresponding kinetic exponent \(\beta\) quantifies the dissolution behavior. In case of the particle being surrounded by liquid (Figure 1bii), \(\beta\) corresponds to values above \(-1/3\), which, according to Hixson and Crowell, is typical for diffusion-limited etching.\(^ {34}\) This could be attributed to the high viscosity in the liquid cell, which has been reported to decelerate diffusion-limited reactions.\(^ {2,11,30}\) Furthermore, a strong decrease of \(\beta\) with decreasing radius up to \(-1.41 \pm 0.08\) has been measured. This might be caused by an increase in surface energy (due to the increase of surface-to-volume-ratio) of the particle, which in turn, significantly increases the etch rate as suggested by Ely et al.\(^ {34}\) In the case when the particle is located at the solid–liquid–gas interface (Figure 1bi), \(\beta\) increases even more, suggesting a different reaction mechanism. After the third contact of the gold nanoplatelet with the gas bubble, where most of the gold volume has been etched, growth of AuNPs begins. We attribute this to local supersaturation of gold ions, following the rapid etching in conjunction with the high viscosity of the liquid (see the discussion below). This drives the reaction into the growth regime, which is in accordance with the law of mass action. The dissolution is

![Figure 2](image-url)
assumed to be limited by the reaction rate if the particle is in contact with the gas bubble and by diffusion if the particle is surrounded by liquid.

A comparable process of material transport was studied by Shin et al.,[36] who presented the growth and shrinking of two adjacent gas bubbles during LCTEM. The study revealed that the growth of the bigger gas bubble proceeded much faster when both bubbles were in direct contact with one another, separated only by a thin membrane of liquid. This was compared to the case when both bubbles were separated from each other and surrounded completely by liquid. The authors concluded that for the former case, gaseous reactants can directly permeate the thin liquid membrane. This process was significantly faster than in the latter case, where gaseous species have to diffuse through the liquid until they encounter the liquid–gas interface of the second bubble. Additional processes such as condensation at the gas–liquid interface of the first bubble and evaporation at the liquid–gas interface of the second bubble further slow down the overall material transport. In the present case, the mechanism is assumed to proceed in a similar way. In the case where the particle is in direct contact with the gas bubble, gaseous species can directly react with the nanoparticle by permeating a thin liquid wetting layer whereas in the other case where the particle is surrounded by liquid, the gaseous species must diffuse and condense before reacting at the gold surface. Thus, in the former case the surface reaction at the particle is assumed to be the rate limiting factor, whereas in the latter case, diffusion of chlorine-containing species is the rate-limiting factor of the etching process. It is noteworthy that this particular etching process was neither observed at larger, nor at lower dose rates. Thus, we suppose that a specific equilibrium state is a prerequisite for etching of gold at solid–liquid–gas interfaces because passivation is known to occur at different redox potentials.[24]

Next, the growth of gold nanoparticles in the thin liquid layer between the membrane of the liquid cell and the gas bubble is discussed in more detail. After about 17 s (see Video S1 in the Supporting Information), particle growth occurs at the projected position of the gas bubble. Since the particles cannot be located inside the gas phase, they must be located within a thin liquid layer between the membrane of the liquid cell and the gas bubble (Figure 1a, frames 5–8). Motion of the individual particles indicates that liquid surrounds the particles and that they do not adhere to a surface. The particle growth is most likely caused by a local supersaturation of the specimen solution with gold ions in the thin liquid layer and a reduction of gold by radiolytic species generated by electron-beam irradiation. This supersaturation might be a result of the diffusion of gold-containing molecules which originate from the primary nanoplatelet due to concentration and viscosity gradients. Significant diffusion through ultrathin liquid layers, however, is unlikely due to the large viscosity that is expected (see the discussion below). Thus, diffusion might take place via the gas bubble itself. Possible gaseous species like AuClₓ are known to form at high temperatures under ambient conditions.[30] The specific conditions inside liquid cells, however, might enable the formation of gold-containing gaseous species even at lower temperatures. Thus, a homogeneous diffusion process from the gas phase into the liquid phase could lead to local supersaturation within the confined liquid volume between the membrane of the liquid cell and the bubble. This process is illustrated in Figure 1biii.

In order to gain information about the reaction kinetics, the temporal evolution of the volume of individual gold nanoparticles is examined. The data evaluation was performed individually for each particle as suggested by Wang et al.[37] Figure 3a shows the advancement of the particle volume of five sample gold nanoparticles. In this case, two regimes are distinctly visible: i) growth of the particles followed by ii) a saturation regime, with drastically reduced growth rate that even drops to zero. The saturation regime indicates a lack of available precursor molecules that would be required for further growth. This supports the hypothesis that gold atoms forming the new nanoparticles originate mainly from the dissolved primary particle. The average of the growth exponents β was evaluated to be 0.20 ± 0.15 by determining the slope of a power law fit in the growth regimes. Figure 3a demonstrates the growth of five sample particles. Following the Lifshitz–Slyozov–Wagner (LSW) theory, a growth exponent β of 1/3 is expected for diffusion-limited growth and 1/2 for reaction-limited growth.[33] In our case, the measured growth exponent is consistent with diffusion-limited growth, albeit the peak value of the distribution is considerably lower than expected (see Figure 3b). This particularly retarded growth, however, was previously observed during various other LCTEM experiments.[2,12,38] It is worth mentioning that not all particles reach a stable state; some dissolve immediately before reaching a critical size, suggesting a critical radius of about 0.5 nm. This is shown for particle E in Figure 3a. The distribution of measured growth exponents for 50 particles is presented in Figure 3b. Although growth is limited by diffusion, the diffusivity of gold ions within the thin liquid layer is assumed to be strongly reduced compared to bulk solution by additional narrow-channel effects. These narrow-channel effects are mainly attributed to interactions of the liquid with the surface of the membrane of the liquid cell and the interface of the gas bubble which dramatically raise the viscosity of the liquid. In this case, the liquid layer between the membrane of the liquid cell and the gas bubble is expected to exceed the particle diameter only by a few nanometers. In order to estimate the viscosity of the surrounding liquid for AuNPs, the 2D Stokes–Einstein relation

\[ D = \frac{k_B T}{4 \pi \eta_{AuNP}} \]

with the diffusion coefficient D, Boltzmann constant \( k_B \), temperature \( T \), dynamic viscosity \( \eta \), and radius of the AuNPs \( r_{AuNP} \) can be evaluated.[5,39–42] First, the temporal evolution of the mean squared displacement (MSD) of all particles was measured by tracking their trajectories (Figure 3d), as shown in Figure 3c. A linear increase of the MSD suggests a normal diffusion regime. The diffusion coefficient D in the 2D case can be approximated via Equation (2) if the average particle radius remains constant.[42]

\[ \text{MSD} = 4Dt \]

This approximation is valid for our system as demonstrated in Figure S3b in the Supporting Information. When the radius of the particle is known, the viscosity can be calculated by
solving Equation (1) for $\eta$. Following this procedure, the viscosity was determined to be $1.44 \pm 0.04$ MPa s which is significantly larger than the expected bulk viscosity of water. Zheng et al., [5] however, revealed similar findings for viscosities of gold nanoparticles with a radius of 5–15 nm in a thin layer of an aqueous solution of 15% glycerol of roughly 30 nm in thickness. This supports our hypothesis that the thickness of the liquid layer between the membrane of the liquid cell and the gas bubble may be as thin as a few nanometers and, thus, diffusion of gold-precursor molecules takes place most likely between the gas phase and the liquid phase.

It is noteworthy that local contrast flickering adjacent to the gold platelet occurs in Figure 1a. This could be caused by mainly amorphous, cloud-like prenucleation states, indicating a large degree of gold ion saturation during the whole experiment. [43-45]

Another phenomenon which was observed during the growth process is the condensation of a droplet inside the gas bubble (Figure 1, frame 7) which might be an indicator of water vapor being present inside the gas bubble as well. This effect was investigated in more detail at a different position of the sample. The results are discussed in the Supporting Information (Figure S4, Supporting Information).

In this communication, we report on the mediated dissolution of a gold nanoparticle at the solid–liquid–gas interface of a gas bubble. In accordance with the dissolution process of gold by chloride leaching, the underlying reaction mechanism is attributed to oxidation by hydroxide radicals generated by radiolysis of the specimen solution. This is followed by a complex formation of gold ions with chloride ions. These chloride ions originate from chlorine containing species like Cl$_2$ and HCl, which are assumed to be present in a gaseous state inside the gas bubble. The dissolution process was observed to proceed notably faster when the particle was in direct contact with the gas bubble. We attribute this phenomenon to different diffusion regimes for the reactive species to reach the particle surface. In close contact to the bubble, the reactants can directly permeate through a thin liquid membrane onto the surface of the gold particle. We assume that this reaction is limited primarily by the surface reaction. When the liquid layer between particle and gas shows a considerable thickness, the overall reaction is limited by the transport of oxidative species and complexing agents through the liquid toward the surface of the particle. The kinetic exponents of the dissolution process evolve from $-0.16 \pm 0.04$ until $-1 \pm 0.12$ in the contact case and from $-0.04 \pm 0.01$ until $-1.41 \pm 0.08$ for diffusion through liquid, respectively. The strong acceleration of volume loss in both cases is attributed to the increase of the surface energy as the particle size decreases. A subsequent growth of gold nanoparticles was observed and is assumed to be driven.
by a local supersaturation of the specimen solution with gold ions during the dissolution of the primary particle. Again, a diffusion-limited growth mechanism was revealed by the extraction of growth exponents. The particularly small mean growth exponent of $0.2 \pm 0.15$ is attributed to an extremely thin liquid layer accompanied by an extremely large viscosity which, in turn, slows down the diffusion-limited growth process. The exceptionally large viscosity was confirmed by tracking the particle motion yielding a value as large as $1.44 \pm 0.04 \text{ MPa s}$.

**Experimental Section**

**Preparation of the Specimen Solution:** For preparation of an aqueous solution of 10 mmol L$^{-1}$ HAuCl$_4$ 196.915 mg of HAuCl$_4$·3 H$_2$O crystals were dissolved in 50 mL deionized water.

**Loading and Sealing of the Liquid Cells:** 0.5 mL of the precursor solution were dispensed onto the microwell-containing silicon nitride-coated front side of the liquid cell templates utilizing a pipette. A R2/2 Quantifoil TEM grid covered with a few-layer (6–8 layers) graphene sheet purchased from ACS Material was placed on top of the microwell containing membrane with the graphene-covered side facing the liquid-cell template. The number of layers of graphene was determined by reflectance spectroscopy$^{[23]}$ using a specialized optical layer stack. This TEM grid was pressed down carefully while excess solution was removed by a filter tissue. After a short drying time of about 3 min, the graphene adheres at the silicon nitride surface, enclosing the liquid specimen within the microwells via a van der Waals interaction. The liquid cell architecture and the loading process is described in more detail in previous works.$^{[2,4]}

*In Situ Liquid Cell Transmission Electron Microscopy:* After sealing the precursor solution within the microstructures of the silicon nitride membrane, the liquid cell was placed into a conventional single-tile TEM specimen holder. This holder was subsequently loaded into a Philips CM 30 (S)TEM, operated at an acceleration voltage of 300 kV in TEM bright-field mode. The utilized electron dose rate was adjusted to $10^4$–$10^5$ e$^-$ nm$^{-2}$ s$^{-1}$.

**Image Analysis:** Image analysis was performed by image segmentation and particle tracking using FIJI$^{[49]}$ and TrackMate.$^{[49]}$ Data evaluation was conducted using a Python algorithm based on the SciPy ecosystem.$^{[50,51]}

**Supporting Information**

Supporting Information is available from the Wiley Online Library or from the author.

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**Conflict of Interest**

The authors declare no conflict of interest.

**Keywords**

etching, gold nanoparticles, graphene, liquid cell transmission electron microscopy, solid–liquid–gas interfaces

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