Role of NH₃ in the Electron-Induced Reactions of Adsorbed and Solid Cisplatin

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ABSTRACT: The electron-induced decomposition of cisplatin (cis-Pt(NH₃)₂Cl₂) was investigated to reveal if ammine (NH₃) ligands have a favorable effect on the purity of deposits produced from metal-containing precursor molecules by focused electron beam induced deposition (FEBID). Scanning electron microscopy showed that cisplatin particles of different sizes react violently during electron irradiation. In particular, faceted particles of a few μm in size started to boil, became spherical and subsequently degraded. Energy-dispersive X-ray spectroscopy gave evidence for the formation of nearly pure platinum and a decrease of the chlorine content. Nitrogen, however, was not detected, pointing to an efficient and rapid removal of NH₃. In contrast, PtCl₂ particles do not degrade under comparable conditions, demonstrating that the ammine ligand plays an important role in the reduction of cisplatin to pure platinum. The fast release of NH₃ ligands under electron exposure was confirmed by high resolution electron energy loss spectroscopy, focusing in particular on low-energy electrons as produced in a transmission electron microscope. Finally, FEBID experiments using cisplatin adsorbed from the gas phase onto a surface were performed by high resolution electron energy loss spectroscopy, focusing in particular on low-energy electrons as produced in a transmission electron microscope. This chloride content reduced and were crystalline particles obtained. In conclusion, using NH₃ as ligand in metal containing FEBID precursors can favor the formation of pure metal deposits, but its effectiveness depends on the precise experimental conditions.

1. INTRODUCTION

Focused electron beam induced processing (FEBIP) is an advanced technique for nanofabrication with commercial applications, such as the repair of photolithography masks or the fabrication of tips for atomic force microscopy. Using FEBIP, material can be removed or added locally by irradiating a sample with an electron beam in the presence of a precursor gas. The precursor molecules transiently adsorb on the sample surface and dissociate as a result of the electron exposure. Material is etched away when the fragments react with the sample material to form gaseous products. In contrast, a deposit forms when the fragmentation of the precursor produces a solid residue. This latter technique is termed focused electron beam induced deposition (FEBID).

One of the main challenges for FEBID is to tune the chemical composition of the deposits. For instance, it is not uncommon that metal–organic precursors yield deposits in which the metal is not the dominant element. For many applications, such as nanoelectronics or plasmonics, metal contents of 20–50% are insufficient. Carbon has been identified as an important contaminant, typically originating from the ligands that are used to make the precursors volatile. Over the past decade, the mechanisms leading to the codeposition of carbon have been studied. Ideally, the
electrons would remove the ligands entirely, leaving no other residue than the intended material (e.g., Pt in the case of a Pt precursor). Therefore, the key to high-purity, carbon-free deposits lies in the use of precursor molecules with ligands that become volatile during electron irradiation. Another approach is to use carbon-free precursors. However, experiments show that ligand fragments may still remain in the deposit. For instance, the electron-induced dissociation of Pt(PF₃)₄ removes only one PF₃ ligand as such, while further exposure merely removes F from the remaining three PF₃ ligands. ₁₀ Also, while high purity deposits have been obtained using ClAuCO₁₁ and vapor pressure at temperatures around 165°C, this behavior might be the oxidation state of the central metal in such complexes. In addition to breaking the metal halogen bond, the metal center must be reduced to its neutral state.

In view of these difficulties, the search for better FEBID precursors is ongoing. ¹¹ Metal halides have been considered, as the halogen ligands are relatively easy to dissociate from the precursor. ¹² However, halogen ligands can also be incorporated into the deposit, as happens with, for example, PtPF₃, ¹³ SnCl₄, ¹⁵ TiCl₄, ¹⁶ and WCl₆. ¹⁷ A plausible explanation for this behavior might be the oxidation state of the central metal in such complexes. In addition to breaking the metal halogen bond, the metal center must be reduced to its neutral state. Incorporating a reducing agent into the deposition process or even in the precursor may lead to higher deposit purity. Unsatrated hydrocarbons, when exposed to low-energy electrons in the presence of NH₃, are efficiently reduced to saturated compounds. ¹⁸ This suggests that the reducing agent NH₃, incorporated as a ligand in FEBID precursors, can favor the complete removal of the ligands.

cis-Diamminedichloroplatinum(II) ([NH₃]₂ClPt, cisplatin) is an example of a neutral complex containing NH₃ ligands. Its vapor pressure at temperatures around 165°C is sufficient for gas phase experiments, enabling a study of dissociative electron attachment (DEA) to this compound. ¹⁹ FEBID using cisplatin appears feasible. Therefore, we study the decomposition of cisplatin under electron irradiation to investigate the effect of NH₃ ligands on the electron beam induced chemistry of precursor molecules.

2. EXPERIMENTS

2.1. Electron Microscopy. Cisplatin particles were studied using a Philips XL30 environmental scanning electron microscope (SEM, 20 keV) equipped with a field emission gun and an EDAX EDX detector for energy-dispersive X-ray spectroscopy (EDX). Videos of decomposing cisplatin particles were recorded on a Tescan Lyra-XM dual beam microscope, equipped with a field emission gun. Elemental analysis and diffraction experiments on cisplatin particles were performed on a JEOL 2010F transmission electron microscope (TEM) with a field-emission gun. The TEM was operated at 200 kV and has a Bruker EDX detector and a Gatan system for electron energy loss spectroscopy (EELS). TEM experiments on FEBID deposits were performed on a JEOL-2200FS which was operated at 200 kV.

The electron exposures applied to the samples varied between these different microscopic and microanalytic experiments. During acquisition of a single SEM image obtained within 0.3 s with an electron beam current of about 3 pA, exposures of about 10⁻⁶ C/cm² were applied to the scanned area. During EDX measurements in the SEM, the current was increased to about 200 pA and subsequent EDX spectra were acquired over time intervals of 30 s. The total exposure during an EDX measurement was therefore on the order of magnitude of 10 nC. Because of focusing on the particles, we estimate the number of electrons that effect changes in the area irradiated during EDX to be more than 4 orders of magnitude higher than during imaging. During diffraction pattern measurements in the TEM as described in section 3.3, a widely spread parallel electron beam with a current density of 10⁻² A/cm² was applied for 30 min on the sample leading to a total exposure on the order of 100 nC to the irradiated area.

2.2. High Resolution Electron Energy Loss Spectroscopy (HREELS). The decomposition of cisplatin was investigated by HREELS using a spectrometer consisting of a rotatable cylindrical double pass monochromator and a single pass electron-energy analyzer mounted in a μ-metal-shielded UHV chamber. ²₀,²¹ The base pressure of the system reaches 10⁻¹⁰ mbar through the combined action of an ion pump and a titanium sublimation pump. The HREEL chamber is connected to a sample preparation chamber with a base pressure of about 2 × 10⁻¹¹ mbar where cisplatin was evaporated from an oven heated to 90°C and condensed onto a room temperature polycrystalline Pt substrate. The oven is mounted in a load lock chamber and can be transferred to the preparation chamber using a manipulator. It consists of a crucible made from quartz glass with a resistive heater (Ta wire) and a chromel–alumel (type K) thermocouple for temperature measurement. Prior to each deposition, the Pt substrate was cleaned by resistive heating to an orange glow. During a single deposition, the crucible was kept at the same position and no adjustment of the heating current was made. Cisplatin was then deposited until a desired signal-to-noise ratio was obtained in HREELS.

The samples were exposed to electrons at different incident energies (E₀) using a commercial flood gun (estimated resolution of 0.5–1 eV) which was located in the sample preparation chamber and which delivered at these E₀ currents of the order of a few tens of microamperes per square centimeter as measured at the sample (surface area is approximately 3.8 cm²). After deposition and after each exposure the cryostat carrying the sample was transferred to the HREEL chamber for data acquisition. The analyzer is fixed at 60° with respect to the normal of the sample. The monochromator was set at a near-specular angle which produced the highest attainable intensity for the elastic peak. All HREEL spectra were acquired at E₀ = 3 eV with a resolution of 12–15 meV (fwhm of the elastic peak) and currents of the order of 0.1–0.2 nA as measured on the Pt substrate. This E₀ was selected considering resonance energies reported previously. ²² When HREEL spectra were measured at E₀ = 5 eV, which is close to a known gas phase resonance, noticeable changes of the spectrum were observed during 3 h whereas no changes were observed for at least 16 h when spectra were acquired at E₀ = 3 eV. Recording of the HREEL spectra at 3 eV thus contributes only to a minor extent to the changes observed in the exposure experiments. For longer recording times, however, the effect of the HREELS beam may become visible. This limits the recording time and thus the signal-to-noise ratio of the present experiments.

2.3. Infrared Spectroscopy. The infrared spectrum of cisplatin was measured from a KBr pellet on an AVATAR 370 FT-IR spectrometer (ThermoNicolet).

2.4. Focused Electron Beam Induced Deposition (FEBID). FEBID was performed in a tungsten-emitter-equipped Hitachi S3600 scanning electron microscope. The cisplatin precursor was supplied by an internal gas injection system.
(GIS) which could be heated to 150 °C. Because of its use for low vapor pressure precursors, the GIS was designed with minimum needle length (smaller than 1 cm) and without valves to avoid undesired condensation and clogging in the needle. The precursor flow at the sample was manipulated by heating the GIS and positioning it close to the substrate, or by cooling and retracting the GIS. For FEBID, the GIS nozzle was positioned about 100 μm away from the substrate and the electron beam, with an angle of about 40° to the substrate surface. The substrate was a silicon wafer with a native oxide film and a resistivity in the milliohm range to avoid charging due to the electron beam. Typical FEBID parameters were 20 kV and 1 nA.

3. RESULTS AND DISCUSSION

3.1. Electron Irradiation of Cisplatin Particles. Figure 1a shows an SEM image of a cisplatin particle of several micrometers in size. The particle is very sensitive to the electron beam (20 keV, ~3 pA); the morphology changes almost immediately upon exposure. The faceted structure disappears and the particle becomes spherical (Figure 1b). Upon continued exposure the particle converts into a stable reaction product (Figure 1c). During the exposure of the particle the EDX signal was recorded over three selected intervals of 30 s each. Figure 2a shows the effect on the elemental composition of the particle. In the first interval (i.e., in the first 30 s of the exposure) the Pt and Cl signals are clearly observed (the Ni and Al signals originate from the supporting grid and sample holder). The N signal, normally easily detectable at 0.39 keV (see Supporting Information, Figure S4) is hardly observed, even during this first interval. After 60 s the Cl signal has dropped significantly and after 120 s almost no Cl is detected. The spectra have been normalized to the Pt peak to facilitate the qualitative analysis. The integrated Cl signal is plotted as a function of irradiation time in Figure 2b, normalized to the initial area. The signal decreases rapidly and saturates at about 6% of the initial value.

Figure 1. (a) SEM micrograph of a cisplatin particle on a lacy carbon membrane. (b) Same particle after irradiation with an electron beam (20 keV, ~3 pA). (c) Particle after complete decomposition.

Figure 2. (a) EDX spectra obtained during ongoing irradiation of the particle shown in Figure 1, integrated over 30 s intervals. All intensities were normalized to the Pt signal. Because of change of the sample composition, scattering of electrons and absorption of photons in the interaction volume changes. This effect is obvious here from the relative intensity change of Al and Ni (sample holder material). After an exposure of 210 s, the Cl signal has basically disappeared. (b) Integrated peak intensity of the Cl signal.

Figure 3. (a) TEM image of a decomposed cisplatin particle. Two positions for EELS analysis are marked, note that position 1 is over a lacy carbon support. (b) EEL spectra at the positions marked in part a. Cl and N edges are observed at neither position. (c) Diffraction pattern of the particle in part a, which clearly shows that polycrystalline Pt has formed.
Figure 4. (a) SEM image of PtCl₂ particles before extensive electron irradiation applied during EDX scans. (b) Several EDX scans revealing the relative Pt and Cl content. No significant change in composition is observed. Note that the platinum peak overlaps the carbon peak that originates from the target. This explains the small deviation from PtCl₂ stoichiometry. (c) Image after EDX analysis. (d) SEM image of an NH₄Cl particle before, (e) during, and (f) after a focused electron beam was applied at the position of the hole in the lower left of the picture and moved to the right. EDX of NH₄Cl is shown in the Supporting Information, section 4, Figure S4.

We have seen that the described effect is consistent for particles of similar sizes. Occasionally, the particles react to the electron beam in a dramatic fashion. After the change from the (original) faceted shape to the spherical shape, some particles appeared to boil, suggesting the release of gaseous reaction products. Videos recording this behavior are available in the Supporting Information (see also Supporting Information, section 2).

The particles were studied in more detail in the TEM. Figure 3a shows a degraded cisplatin particle after exposure to a focused electron beam (200 keV). EELS measurements were done on two locations (Figure 3b). At location 1, the EELS spectrum in the range of C, N, and Cl edges only shows a C edge from the supporting amorphous carbon membrane. At location 2, no edges are visible in the selected energy window. These measurements demonstrate a complete absence of both Cl and N. Figure 3c shows a selected area diffraction pattern, taken on the edge of the degraded particle; the lattice spacing is consistent with polycrystalline Pt.

Please note that a complete analysis of the observed behavior is very complex. In the EDX measurements, the composition, the analyzed volume and the particle density change simultaneously and rapidly during the recording of the spectrum. This is for instance evident from the fact that the Ni and Al signals also change strongly during the exposure (Figure 2a), which indicates an extensive change in (among other parameters) the electron scattering behavior of the particle. We therefore do not attempt to quantify the composition.

The effect of irradiation on cisplatin particles appears to be size-dependent. Particles up to a size of about 10 μm react strongly to the electron beam (see Figure 1), while much larger particles do not show such a strong change in morphology. Instead, the electron beam can burn holes in larger particles (see Supporting Information, section 2, Figure S1). The center of a particle with length of about 17 μm was exposed to a focused electron beam of 20 keV (see Supporting Information, section 3, Figures S2, S3). A rough topology was observed within a radius of about 5 μm around the beam focus. After washing the sample in acetonitrile, the nonirradiated positions were partly washed away, leaving a rough skeletal structure that evidenced reactions at even larger distances away from the beam focus inside the particles. This experiment shows the spatial extent of the electron-induced reaction inside cisplatin particles.

Our results clearly demonstrate that cisplatin particles are very sensitive to the electron beam. The elemental analysis shows consistently that almost no N is detected even after short irradiation time and that the electron exposure removes the Cl during longer irradiation. The results therefore suggest that the NH₃ ligand is easily removed and that the majority of the Pt−N bonds break very rapidly.

We further investigate the potential role of the NH₃ ligand as a reducing agent in the electron-induced dissociation of cisplatin. If the ammine ligands are simply broken and desorb as NH₃ directly at the start of the exposure, PtCl₂ would be left behind. Therefore, we irradiated a particle of similar size from a commercial PtCl₂ sample in the SEM. Figure 4a shows the particle before extensive irradiation that was applied during recording of several EDX scans (Figure 4b). The electron beam did not significantly alter the composition. Also, the particle shifted slightly but did not lose its rough morphology according to the image recorded after the EDX analysis (Figure 4c). In contrast, NH₄Cl appears to be very sensitive to the electron beam. Parts d–f of Figure 4 show an NH₄Cl particle, of which large parts are easily etched away upon subsequent electron exposure. This behavior is consistent with earlier reports that NH₃ is efficiently degraded, yielding N₂ under electron irradiation.¹⁸,²³

In conclusion, the sensitivity of (NH₃)₂Cl₂Pt and NH₄Cl to electron irradiation on the one hand, and the insensitivity of PtCl₂ on the other hand, strongly suggests that the ammine ligands play an important role in the reduction of cisplatin to pure platinum. We hypothesize that hydrogen from the former ammine ligands is temporarily retained inside the cisplatin.
particle and may react with Cl ligands to form HCl during ongoing irradiation.

3.2. Low-Energy Electron Irradiation of Cisplatin Deposited from the Gas Phase. While the fate of the ammine ligands in cisplatin can only be deduced indirectly by SEM, high-resolution electron energy loss spectroscopy (HREELS) is capable of monitoring the evolution of NH3 content of the samples. At the same time, HREELS experiments enable us to link the electron-induced decomposition of solid cisplatin to results on DEA to gaseous cisplatin.19 In addition, recent studies on the FEBID precursors MeCpPtMe3,7 Pt(PF3)4,10 and Co(CO)3NO8 have shown that cross sections for DEA leading to dissociation of a ligand from the metal center can be very large at electron incident energies near 0 eV. These high cross sections suggest that such low-energy secondary electrons play an important role in FEBID. Therefore, we have further investigated the degradation of cisplatin by low-energy electrons.

Figure 5 compares an HREEL spectrum and an infrared (IR) spectrum of cisplatin. The most intense signals can be assigned to IR active vibrations of the NH3 ligand (see Table 1). An exception is the band at 360 meV that results from a hydrocarbon contamination due to a volatile compound that could not be removed from the evaporation source. In addition, several smaller peaks in the HREEL spectrum have no counterpart in the IR spectrum. The weak signal around 245 meV is considered to result from the adsorption of residual CO on the Pt substrate24 and the weak signal at 130 meV might relate to a C−C stretching frequency of the hydrocarbon contamination.25 In addition, some small signals are due to multiple scattering, e.g., 215 meV (187 + 30) and 320 meV (161 + 161). Finally, a high-intensity peak is observed around 30 meV energy loss. Two vibrations can potentially contribute to this signal, ν(Pt−Cl) at 39 meV and δ(N−Pt−N) at 28 meV. Because of the overlap with the large peak of the elastically scattered electrons, the exact position of this signal is difficult to read directly from the spectrum. We thus fitted a combination of Gaussian functions to the elastic peak of a background spectrum. This fit function was subtracted from the spectrum in Figure 5, to find a maximum at an energy loss of 30 ± 2 meV (see Supporting Information, section 5, Figure S5). We therefore conclude that the intensity of the signal is dominated by the δ(N−Pt−N) vibration.

![Figure 5](image-url)

**Table 1. Vibrational Band Positions of Cisplatin**

<table>
<thead>
<tr>
<th>Assignment</th>
<th>HREELS meV</th>
<th>FTIR cm⁻¹</th>
<th>IR cm⁻¹</th>
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</thead>
<tbody>
<tr>
<td>δ(N−Pt−N)</td>
<td>30</td>
<td>242</td>
<td>−</td>
</tr>
<tr>
<td>υ(Pt−Cl)</td>
<td>−</td>
<td>798</td>
<td>805</td>
</tr>
<tr>
<td>υ(C−C)</td>
<td>129</td>
<td>1040</td>
<td>−</td>
</tr>
<tr>
<td>δ(NH3)</td>
<td>161</td>
<td>1299</td>
<td>1298, 1313</td>
</tr>
<tr>
<td>δ(NH3)</td>
<td>187</td>
<td>1508</td>
<td>1537, 1624</td>
</tr>
<tr>
<td>δ(N−Pt−N)/υ(Pt−Cl) + δ(NH3)</td>
<td>215</td>
<td>1734</td>
<td>−</td>
</tr>
<tr>
<td>υ(C−O)</td>
<td>245</td>
<td>1960</td>
<td>−</td>
</tr>
<tr>
<td>υ(NH3) + δ(NH3)</td>
<td>273</td>
<td>2210</td>
<td>−</td>
</tr>
<tr>
<td>υ(NH3) + δ(NH3)</td>
<td>295</td>
<td>2380</td>
<td>−</td>
</tr>
<tr>
<td>2x δ(NH3)</td>
<td>318</td>
<td>2565</td>
<td>−</td>
</tr>
<tr>
<td>υ(C−H)</td>
<td>360</td>
<td>2904</td>
<td>−</td>
</tr>
<tr>
<td>υ(N−H)</td>
<td>411</td>
<td>3315</td>
<td>3203, 3200</td>
</tr>
<tr>
<td>υ(N−H)</td>
<td>411</td>
<td>3315</td>
<td>3284</td>
</tr>
<tr>
<td>2x δ(NH3)</td>
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<tr>
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<tr>
<td>ν(N−H)</td>
<td>411</td>
<td>3315</td>
<td>3297</td>
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*Present work. Residual gas adsorption (CO). Hydrocarbon contamination.*
The electron-induced decay of cisplatin was investigated by alternating measurements of HREEL spectra recorded at 3 eV (where reactions are not efficiently induced) and destructive irradiation using a flood gun at electron energies of 1, 5.5, and 10 eV. As an example, the changes in the spectra as a result of electron exposure at 10 eV are shown in Figure 6a. It is obvious that all signals of the NH₃ ligand lose intensity with ongoing irradiation. This clearly points to degradation of the Pt−NH₃ structure element. The observed intensity loss during irradiation might also be the result of a decreasing order in the surface structure. However, the intensity of the signal relating to the contamination does not change noticeably (see Figure 6) which would not be consistent with this explanation. The degradation seems to proceed with similar kinetics for electron energies of 10 and 5 eV (see Figure 6). At 1 eV only a few exposure cycles were possible due to very long irradiation times. While the data appear to point to a faster degradation at this energy, caution must be applied when drawing such conclusions because of the much longer exposure times at 1 eV, during which instrumental drift may contribute to the intensity changes.

It has been described before that gas phase DEA resonances exist at 1 and 5.5 eV. While the resonance at 5.5 eV exclusively leads to Pt−N bond cleavage and consequent NH₃(g) formation, chlorine abstraction was observed with high cross sections at 1 eV. However, no clear evidence exists for loss of the ammine ligand at electron energies of 1 eV in these gas phase experiments. In contrast, here we observed the loss of the NH₃ structure elements independent of the electron energy. We therefore conclude that the ammine ligands can in fact be efficiently abstracted by low energy electrons of 1 eV. The Pt−N bond dissociation energy lies in the range of about 1.7 eV and an electron affinity of 3.3 eV has recently been predicted for PtCl₂. On the basis of these values, electrons with energies near 0 eV should be capable of abstracting both ammine ligands via DEA according to

\[
\text{Pt(NH}_3)_2\text{Cl}_2 + e^- \rightarrow [\text{PtCl}_2]^- + 2\text{NH}_3
\]

The large gain in energy upon formation of [PtCl₂]⁻ from neutral PtCl₂ can make up for the major part of the energy required for dissociation of both NH₃ ligands from the complex, thus rationalizing the results so far.

In the HREELS experiments most of the NH₃ signal was lost after an electron exposure of 30 μC/cm². The typical beam current during EDX in the SEM is about 200 pA and the
particle size in Figure 1 is about 6 μm². This means that a primary electron exposure on the order of 100 mC/cm² was applied in the first 30 s, during which each primary electron generates many secondary electrons with energies similar to those applied during irradiation in HREELS experiments. This implies that the number of low energy electrons that were incident during the HREELS experiments is lower by orders of magnitude than the number of electrons that are produced in the sample during a single EDX measurement. The absence of a clear N signal in the EDX data is therefore consistent with the results from the HREELS experiments.

3.3. FEBID Using Molecular Films of Cisplatin. The results obtained from solid cisplatin particles (section 3.1) as well as the previous gas phase DEA results suggest that both the NH₃ and Cl ligands are removed efficiently under electron irradiation. Therefore, we explore the use of cisplatin as a precursor for FEBID. The reservoir containing the cisplatin precursor was heated to around 150 °C as the pressure readings indicated no significant gas flux at lower temperatures. Figure 7a shows three deposits that were formed under focused electron beam exposure while maintaining the gas flow. Deposit 1 resulted from writing a long and a short line, deposit 2 resulted from spot irradiation followed by writing two short lines, and deposit 3 was generated by writing a single line. EDX analysis on the deposits revealed a composition of about 50 at. % Pt and 50 at. % Cl, while nitrogen is again not observed (Figure 7c). We cannot exclude condensation of cisplatin as the substrate was not actively heated during FEBID. However, the chlorine content could not be decreased, even after further extensive irradiation of the deposited structures in the absence of the gas flux. This is in clear contrast to the cisplatin particles (see section 3.1) from which the chlorine was nearly completely removed. The sample shown in Figure 7a was exposed to solvents (acetonitrile, methanol, and water in an ultrasonic bath) to remove soluble residues such as remaining cisplatin. Figure 7b recorded after this washing step shows that the solvent has removed part of a thin layer (together with deposit 1) that was most likely formed by decomposition of condensed cisplatin during the acquisition of the first SEM image (Figure 7a). Other than this delamination, no changes occurred. The EDX spectrum of the deposits showed no evidence of further removal of Cl, as verified on various locations of the sample, and the deposits are stable in shape. The same composition was observed at different locations of the thin film between the deposits.

The formation of a Pt and Cl (1:1) containing FEBID deposit is in strong contrast to the experiments with particles which evidenced that electron-induced chemistry of bulk cisplatin does indeed reduce the compound to nearly pure platinum. Obviously, the irradiation of molecular films results in a different reaction product that contains considerable amounts of chlorine. This striking difference may result from different decay reactions of NH₃ in the particles and in thin layers. Possibly, NH₃ remains trapped in the particles for a sufficient time to be further decomposed yielding hydrogen which then reacts with the chlorine ligands to leave as HCl during ongoing irradiation. In contrast, NH₃ may easily desorb from thin molecular layers without reacting with a surrounding medium. This would result in a layer of partly degraded cisplatin that does not contain a sufficient amount of hydrogen to achieve a complete reduction of the material. This explains formation of a deposit that is different from PtCl₂ but still has a significant chlorine content.

There is, to the best of our knowledge, no stable platinum(1) chloride. It might therefore be speculated that a mixture of platinum and PtCl₂ has formed. However, PtCl₂ is soluble in alcohols and should have been removed during treatment in the ultrasonic bath. To determine the nature of these deposits, FEBID using cisplatin was performed on holey carbon films so that the deposited material could be analyzed by TEM. EDX analysis in the TEM confirmed the 1:1 ratio of platinum and chlorine in the deposit (see Supporting Information, section 6, Figure S6). The diffraction pattern (Figure 8a) shows that the deposited material was amorphous, providing further evidence that the FEBID process does not yield a stable PtCl₂ phase as investigated in section 3.1. However, during the TEM imaging, the amorphous diffraction pattern changed in the time frame of minutes. During half an hour of irradiation, the clear diffraction pattern of crystalline platinum appeared (Figure 8b). EDX measurements show that the chlorine content has considerably decreased (see Supporting Information, Figure S6), but could not be removed completely even after this very extensive electron exposure. An image of the irradiated area (Figure 8c) shows small black dots on top of the amorphous matrix that were not observed before the extensive irradiation. We presume these to be small platinum particles. These results show that reducing the chlorine content in the deposit requires higher exposures in the absence of the ammine ligand, or of hydrogen released by the electron-induced decomposition of NH₃.

Figure 8. (a) Diffraction patterns of a FEBID deposit obtained from cisplatin at the beginning of the diffraction experiment, where the EDX composition was roughly Pt:Cl:N = 1:1:0. (b) Diffraction pattern after 30 min of irradiation showing appearance of pure platinum diffraction rings. (c) TEM image of the irradiated area after crystalline diffraction ring patterns had formed. Dark spots are due to Pt nanocrystals while the dark lines represent the underlying perforated carbon film.
4. CONCLUSIONS

We have investigated the electron-induced chemistry of solid and adsorbed cisplatin. Dramatic changes in morphology show that cisplatin particles are very sensitive to electron exposure. EDX measurements show that the chlorine can be nearly completely removed from the cisplatin particles. The fate of the NH₃ ligand is hard to monitor using EDX alone, because almost no nitrogen signal was detected even during the first EDX scan. HREELS measurements of thin cisplatin films show that the ammine ligands are lost after small electron exposures at very low electron energies. These results strongly suggest that the NH₃ ligand is cleaved off at very low electron exposures, both in the particles and in the thin film. The electron energies used during the HREELS experiments are typical of secondary electrons produced in copious amounts during irradiation in an electron microscope. The high sensitivity to electrons makes NH₃ thus in principle a promising ligand for FEBID precursors.

In addition, the results give evidence that NH₃ can act as a reducing agent. In contrast to cisplatin, PtCl₂ does not reduce the ammine ligands after small electron exposures, almost no nitrogen signal was detected even during the small electron exposures. These conditions are met in the bulk material, but not in the thin film. NH₃ is trapped inside the particles. In the absence of ammine ligands or the hydrogen atoms resulting from the electron-induced dissociation of NH₃, chlorine is then less easily removed from the deposit for FEBID experiments. Experimental parameters like process conditions on the electron-induced chemistry of cisplatin. We propose that the ammine ligands do not provide their full reducing power in the FEBID experiments, possibly because NH₃ desorbs readily from thin molecular layers while NH₃ is trapped inside the particles. In the absence of ammine ligands or the hydrogen atoms resulting from the electron-induced dissociation of NH₃, chlorine is then less efficiently removed from the sample.

In conclusion, NH₃ is a promising ligand that is easily removed under electron exposure. However, NH₃ acts as a reducing agent only under specific conditions, namely, when it remains in contact with the deposit for sufficient time to react. These conditions are met in the bulk material, but not in the present FEBID experiments. Experimental parameters like electron flux and conditions of cisplatin adsorption on the surface may be tuned to obtain deposits with higher platinum content.

ASSOCIATED CONTENT

Supporting Information

The following Supporting Information is available: . The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcc.5b12184.

Further SEM, EDX, and HREELS data (PDF)

SEM video showing the degradation of a small cisplatin particle (AVI)

SEM video showing the degradation of a larger cisplatin particle (AVI)

REFERENCES


**NOTE ADDED AFTER ISSUE PUBLICATION**

The name of one of the authors, Juraj Orszagh, was misspelled in the version published on February 15, 2016. The corrected version was published on the Web on May 23, 2016.