Observation of Surface Ligands-Controlled Etching of Palladium Nanocrystals

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Cite This: Nano Lett. 2021, 21, 6640–6647

ABSTRACT: Selective adsorption of ligands on nanocrystal surfaces can affect oxidative etching. Here, we report the etching of palladium nanocrystals imaged using liquid cell transmission electron microscopy. The adsorption of surface ligands (i.e., iron acetylacetonate and its derivatives) and their role as inhibitor molecules on the etching process were investigated. Our observations revealed that the etching was dominated by the interplay between palladium facets and ligands and that the etching exhibited different pathways at different concentrations of ligands. At a low concentration of iron acetylacetonate (0.1 mM), rapid etching primarily at {100} facets led to a concave structure. At a high concentration (1.0 mM), the etch rate was decreased owing to a protective film of iron acetylacetonate on the {100} facets and a round nanoparticle was achieved. Ab initio calculations showed that the differences in adsorption energy of inhibitor molecules on palladium facets were responsible for the etching behavior.

KEYWORDS: Liquid cell, in situ transmission electron microscopy, etching, surface adsorption, ligand, inhibitor molecules

The adsorption of ligand molecules on nanocrystal surfaces strongly influences the nanocrystal behavior in a variety of applications, including catalysis, self-assembly, synthesis, and etching. Oxidative etching has emerged as a feasible approach to manipulate the shape of nanocrystals. During the etching reactions, organic molecules or ions can be adsorbed on specific facets, which lead to facet-dependent etching and formation of nanocrystals with various morphologies. However, many specifics, such as the binding location of ligands and their effect on nanocrystal shape transformations, still warrant experimental observation.

The recent developments in liquid cell transmission electron microscopy (TEM) have enabled direct imaging of chemical reactions in liquids, including nucleation, growth, self-assembly of nanocrystals, and dynamic phenomena at electrode–electrolyte interfaces. Liquid cell TEM has been used to address some scientific issues regarding ligands, for example, surface ligands can impact the etching behavior, while the adsorption sites of ligands on specific nanoparticle facets as well as the correlated etching dynamics has not been revealed.

Herein, we investigated the etching of ~20 nm palladium (Pd) nanocrystals in an aqueous solution of FeCl₃ and iron(III) acetylacetonate (Fe(acac)₃). Typically, transition metal acetylacetonate is a promising candidate to inhibit etching, and consequently, Fe(acac)₃ was used as the inhibitor molecule to control the etching of Pd nanocrystals. By taking advantage of in situ liquid cell TEM, we directly observed the etching of Pd nanocrystals by tracking the facet evolution. It is worth noting that since Pd nanocrystals are widely used in catalysis and biosensing, the stability of Pd nanocrystals in various environments is of great interest.

An understanding of the etching behavior of Pd nanocrystals described in this study may facilitate further practical applications.

To prepare a liquid cell sample for our in situ TEM experiment, a droplet of ~2 μL reaction solution containing Pd nanocrystals, FeCl₃, and Fe(acac)₃ was encapsulated between two carbon films (Figure 1A, also see Methods). Note that the free Fe³⁺ from FeCl₃ acted as the primary etchant while the iron bonded in Fe(acac)₃ served as a coordination complex. Upon evaporating excess liquid, the liquid cell was sealed and subsequently transferred into the microscope for real-time imaging. We found that the Pd nanocrystals were uniformly distributed in the liquid cell (Figure 1B). The Pd nanocrystals...
had an average size of \( \sim 20 \) nm and exhibited a truncated cubic shape (Figure 1C, also see Figure S1) with exposed (100), (110), and (111) facets (Figure 1D). The three-dimensional view of the Pd nanocrystal was observed when it was rotating in the liquid cell (Figure S2).

Different etching phenomena were noticed at two different Fe(acac)\(_3\) concentrations. At 0.1 mM Fe(acac)\(_3\), a rapid etching of Pd nanocrystals was observed, as shown in Figure 1E. At this low concentration of Fe(acac)\(_3\), most of the Pd nanocrystals showed etch completion after 12 s. However, the etching was significantly suppressed under a high Fe(acac)\(_3\) (1.0 mM); no obvious shape change or little size change was observed after 20 s (Figure 1F). In both cases, some electron radiolysis species such as O\(_2\) and H\(_2\)O\(_2\) can promote the initial etching.\(^5\) It seems that there was moderate etching at the corners of Pd nanocrystals at the initial stage ("0 s" refers to the initial imaging time). Note that the electron dose rate (\( \sim 200 \) e\( \cdot \)Å\(^{-2} \)·s\(^{-1} \)) was controlled in the same manner in Figure 1E,F to incorporate the same electron beam effect in both concentrations. These results indicate that Fe(acac)\(_3\) molecules readily impacted the etching of Pd nanocrystals, leading to different etch rates and etching modes.

The individual Pd nanocrystal was traced with high resolution to quantify the nanocrystal shape evolution during etching. At 0.1 mM Fe(acac)\(_3\), a rapid etching of Pd nanocrystals was observed, as shown in Figure 1E. At this low concentration of Fe(acac)\(_3\), most of the Pd nanocrystals showed etch completion after 12 s. However, the etching was significantly suppressed under a high Fe(acac)\(_3\) (1.0 mM); no obvious shape change or little size change was observed after 20 s (Figure 1F). In both cases, some electron radiolysis species such as O\(_2\) and H\(_2\)O\(_2\) can promote the initial etching.\(^5\) It seems that there was moderate etching at the corners of Pd nanocrystals at the initial stage ("0 s" refers to the initial imaging time). Note that the electron dose rate (\( \sim 200 \) e\( \cdot \)Å\(^{-2} \)·s\(^{-1} \)) was controlled in the same manner in Figure 1E,F to incorporate the same electron beam effect in both concentrations. These results indicate that Fe(acac)\(_3\) molecules readily impacted the etching of Pd nanocrystals, leading to different etch rates and etching modes.

The individual Pd nanocrystal was traced with high resolution to quantify the nanocrystal shape evolution during etching. At the low Fe(acac)\(_3\) concentration (0.1 mM), the etching reactions initiated at the \{100\} facets and proceeded rapidly along the \langle 100 \rangle directions (Figure 2A). In this scenario, the fast etching along the \langle 100 \rangle directions led to transforming the truncated Pd nanocube into a concave nanoparticle within 10 s. Meanwhile, we observed moderate etching at the corners. With continuous etching primarily along the \langle 100 \rangle directions, the concave cube split into small fragments. Most Pd nanocrystals were dissolved after 16 s.
To better understand the spatiotemporal details of the reaction, we constructed time-domain contour plots showing the dynamic shape evolution of the Pd nanocrystal, colored based on the local curvature. As shown in Figure 2B for the case of the low concentrated Fe(acac)₃ (0.1 mM), it reveals a unique etching mode dominated by the {100} facets with low curvature values. This is different from the commonly reported cases without inhibitor molecules in which etching initiates in the location with high curvature due to the high surface energy at the low coordinated sites. Our results can be attributed to the capping effect of inhibitor molecules on certain facets so that the selective oxidation of {100} facets leads to the formation of a concave structure. We classified the etching of the Pd nanocrystal into three stages based on the projected area etch rate, as shown in Figure 2C. Etching in the initial period was mild at the rate of ∼6 nm²/s, followed by a steady etching period at ∼18 nm²/s through etching of the {100} facets. The accelerated etching after ∼4 s can be attributed to the increase of specific surface area with more low-coordinated atoms exposed because of the formation of concave structure. Finally, an acceleration period was noticed at a rate of ∼22 nm²/s once the concave structure collapsed.

Etching of the Pd nanocrystal exhibited symmetrical characteristics concerning the evolution of center-to-face distance of the equivalent facets, such as the {100} and {110}, is similar (Figure 2D). This is governed by the geometry of Pd nanocube, and it is consistent with the shape evolution as shown in Figure 2B.

At high Fe(acac)₃ concentration (1.0 mM), the etching of Pd was significantly mitigated by the presence of the ligands at the nanocrystal surfaces. Sequential TEM images and the contour maps show that the truncated Pd nanocube evolved into nearly a spherical nanoparticle after 8 s of etching (Figure 3A,B). A crystalline thin film on the nanocrystal surface was observed. The thin film hindered the etching of the Pd nanocrystal, especially the {100} facets. This layered structure was further determined to be Fe(acac)₃ based on the crystal structure imaged by high-resolution TEM and chemical EDS mapping (see more details in Figure 4 and Figure S5). In contrast to the initial etching at low Fe(acac)₃ concentration where etching starts from {100} facets, the {110} and {111} facets are active and etched in this case since they are mostly exposed to the etchant solution without the protecting film. Thus, the etching leads to the transition of the truncated Pd nanocube into a nearly spherical shape.

The etching kinetics was revealed in Figure 3C by showing that the projected area of Pd nanocrystal declined from 272 to 215 nm² while its circularity increased to 0.99 as a function of time. We calculated the circularity (C) using the formula: \[ C = \frac{4 \pi \cdot \text{area}}{\text{perimeter}^2} \]. The rise in circularity represents the Pd nanocrystal transformation from highly faceted to almost a sphere. Figure 3D indicates that the etching was symmetric in 1.0 mM Fe(acac)₃ and that the etch rates at different facets were almost the same and equal to 0.16 nm/s.

We observed that at high electron dose rate (∼2700 eÅ−²·s⁻¹), the surface protective layer of Fe(acac)₃ crystal can be damaged resulting in an etching mode that was similar to the mode of the low concentration Fe(acac)₃ (Figure S3). We also discovered that the etch rate was faster than if the protective layer remained intact by a factor of 2 from ∼0.9 to ∼3 nm²/s, at a higher electron dose rate of ∼2700 eÅ⁻²·s⁻¹ (Figure S4).

High-resolution images of the Fe(acac)₃ crystalline film on the Pd nanocrystals in a concentrated Fe(acac)₃ solution (1.0 mM) are shown in Figure 4A,B. The Fe(acac)₃ film shows a
layered structure with a 0.85 nm spacing, which corresponds to the (100) spacing of the Fe(acac)$_3$ crystal (Figure 4C). Our characterization of the Fe(acac)$_3$ film is consistent with the reported Fe(acac)$_3$ crystal structure$^{57}$ in which the Fe(acac)$_3$ molecular layers are assembled by van der Waals force. The chemical maps of the film derived from STEM EDS data can be found in Figure S5. The Fe(acac)$_3$ film is only located on the {100} facets of Pd nanocrystals, which means localized protection.

Fe(acac)$_3$ can transform into free Fe$^{3+}$ and acetylacetonate (acac) molecules and vice versa in an aqueous solution. We employed UV−vis spectroscopy to identify the transition states of Fe(acac)$_3$ at different concentrations. In Figure 4D, the peaks at $\sim$450 and $\sim$350 nm are assigned to the absorbance of the coordination bonds between Fe and acac molecules, while the peak at $\sim$300 nm originates from the conjugated C=C bonding$^{58}$. It shows that Fe(acac)$_3$ remains the coordination complex at 1.0 mM. However, Fe(acac)$_3$ dissociates into acac molecules at the concentration of 0.1 mM. This is consistent with the poor solubility of Fe(acac)$_3$ in water.$^{57}$

The state of Fe(acac)$_3$ is dependent on its concentration. As shown in Scheme 1A, at a high concentration (1 mM), the coordinated Fe(acac)$_3$ dominates while at a low concentration (0.1 mM), the abundant species are acac molecules and dissociated Fe$^{3+}$ ions. Accordingly, the free Fe$^{3+}$ ions can enhance the etching of Pd through oxidation reactions. At high concentration, the primary species in solution is Fe(acac)$_3$ molecules. The interaction between the Fe(acac)$_3$ molecule and Pd substrate is van der Waals force (Scheme 1B), which is regarded as “physisorption”.$^{59}$ We calculated the adsorption energies of Fe(acac)$_3$ on different Pd facets based on density functional theory (DFT). The results show that the differences in the absorption energy are minimal (Table 1). We consider that the Fe(acac)$_3$ molecules prefer to attach to the {100} facets because of the flat surface of the {100} facets and a good lattice match.$^{60}$ Both {100} facet of Fe(acac)$_3$ crystal and the {100} facet of Pd crystal share the orthogonal crystallographic symmetry, and similar d-spacings, which may facilitate the epitaxial growth of Fe(acac)$_3$ on Pd facets (Figure S6). These findings corroborate well with our experimental observations shown in Figure 4A.

In the low concentration case, the acac molecules are the primary products from Fe(acac)$_3$ dissociation. DFT calculations involving structure optimization show that covalent bonding between Pd adatom and the acac molecule is expected (Scheme 1C, also see Figure S7). The calculations suggest that the acac molecules are "chemisorbed" on the Pd surface in the 0.1 mM Fe(acac)$_3$. The adsorption energy of acac molecule on Pd {110} is much lower than the adsorption energy on the Pd {100} facets, which indicates the molecule interacts more strongly with Pd atoms on the Pd {110} than on the {100}. The adsorption of acac molecules stabilizes the surface Pd {110} by forming the Pd(acac)$_2$ complex, resulting in the modified surface energy landscape.$^{62}$

Dissociation occurs at both concentrations with acac molecules adsorbed on Pd facets. For example, at the high concentration of Fe(acac)$_3$, the adsorption of Fe(acac)$_3$ on the Pd facets is a dynamic process accommodated by the "physisorption" of Fe(acac)$_3$ and "chemisorption" of acac molecules simultaneously. This implies that the etching of Pd

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**Figure 3.** Mitigated etching of a Pd nanocrystal at 1.0 mM Fe(acac)$_3$. (A) Time series of in situ TEM images (Supplementary Video 2) with corresponding schematics during the shape evolution. The {100} facets are highlighted in blue. (B) Time-domain contour plots of the Pd nanocrystal. Contour lines are spaced in time by 2 s. The color of the curves shows the local curvature. (C) Projected area and circularity of the Pd nanocrystal as a function of time. (D) The average center-to-face distance as a function of time, extracted from contour plots in (B). The average etching rates were calculated based on different time ranges. Error bars, standard deviation from multiple measurements.
nanocrystals is mitigated by the physisorption of Fe(acac)$_3$ on the {100} facets and chemisorption of acac small molecules on the {110} facets. However, the protection by Fe(acac)$_3$ film is more effective with a thick layer up to $\sim 10$ nm. It is also noted that at the high concentration of Fe(acac)$_3$ (1 mM), the mitigation of etching can be dominated by the physical film protection of the {100} facets at the very beginning. If the Fe(acac)$_3$ film is destroyed by electron beam irradiation, the effects of acac molecules on the {110} facets are more prominent.

In summary, the nanoscale etching behavior of the Pd nanocrystals in the solution of Fe(acac)$_3$ was tracked in real-time using TEM imaging and UV-vis spectroscopy. The distinct adsorption modes of Fe(acac)$_3$ on Pd facets at different concentrations were also observed, as shown in Figure 4.

Scheme 1. States of Fe(acac)$_3$ at Different Concentrations

(A) Fe(acac)$_3$ can transform into free Fe$^{3+}$ and acetylacetonate (acac) molecules and vice versa, depending on the concentration. (B) The growth of Fe(acac)$_3$ molecular layers on the {100} facet at 1.0 mM Fe(acac)$_3$. (C) Adsorption of the acac molecule on the {110} facet at 0.1 mM Fe(acac)$_3$. 

Figure 4. Distinct adsorption modes of Fe(acac)$_3$ on Pd facets at different concentrations. (A) A TEM image of Fe(acac)$_3$ molecular layers grown on the Pd (100) facet in the liquid cell at 1.0 mM Fe(acac)$_3$. (B) A high-resolution TEM image of the layered Fe(acac)$_3$ with a 0.85 nm interlayer distance. (C) Atomic structure of Fe(acac)$_3$ molecular crystal with consistent spacing. (D) UV–vis spectra of Fe(acac)$_3$ in solution at different concentrations. Fe(acac)$_3$ dissociates into acac molecules at 0.1 mM.
Table 1. Adsorption Energy of Fe(acac)$_3$ and acac on Pd Facets

<table>
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<th>facet</th>
<th>Fe(acac)$_3$</th>
<th>acac</th>
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<td>(100)</td>
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<td>−0.54</td>
</tr>
<tr>
<td>(110)</td>
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<td>−0.72</td>
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<td>(111)</td>
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time through in situ liquid cell TEM. The facet-dependent etch rate, and the shape evolution of Pd nanocrystals were investigated at two different concentrations of Fe(acac)$_3$. At a low concentration of Fe(acac)$_3$ (0.1 mM), we found that the etching originated on the Pd {100} facets, while at a high concentration of Fe(acac)$_3$ (1.0 mM), the initial etching mostly occurs at the Pd {110} facets. At high concentrated Fe(acac)$_3$ (1.0 mM), an Fe(acac)$_3$ protective film was formed on the {100} facets, which significantly mitigated the etch rate of the {100} facets from 16 to 5 nm$^2$/s. In situ liquid cell TEM observation facilitates an opportunity to decipher nanoscale etching mechanisms and provides insights for designing corrosion-resistant nanomaterials by manipulating the interplay between inhibitor molecules and nanomaterials surfaces.

## METHODS

**Palladium Nanocrystals.** Pd nanocrystals were synthesized according to the reported method.$^{43}$ STEM imaging and energy dispersive spectroscopy (EDS) elemental mapping of the nanocrystals are shown in Figure S1. The concentration of Pd nanocrystals in solution was $\approx 40$ µg/mL.

**In Situ TEM.** The TEM liquid cell was prepared by encapsulating liquid between two carbon film-supported copper grids. First, the Pd nanocrystal solution was dropcasted on the carbon support on the first copper grid and air-dried for $\approx 5$ min. Then, a droplet ($\approx 2$ µL) of the reaction solution (0.1 M FeCl$_3$, 0.2 mM HCl, and 0.1–1.0 mM Fe(acac)$_3$) was loaded onto the carbon support of the second copper grid and covered with the first grid. The liquid pockets were encapsulated between two carbon films supported on Cu grids due to van der Waals forces after evaporation of the excess liquid solution. Afterward, the liquid cell was loaded into an aberration-corrected transmission electron microscope for imaging. The in situ liquid cell experiments were performed on a Thermo Fisher Scientific ThemIS. The microscope was operated at 300 keV with a Super-X energy dispersive X-ray spectroscopy (EDS) detector, allowing for rapid chemical identification. The videos were recorded on a Ceta CMOS camera at 5 frames per second.

**UV–vis Spectroscopy.** The liquid-state UV–vis absorbance measurement was performed on Cary 5000 UV–vis-NIR spectrometer from 180 to 1000 nm with a step size of 1 nm.

**Density Functional Theory Calculations.** DFT calculations were performed by the Vienna Ab Initio Simulation Package (VASP).$^{64,65}$ The projector augmented wave (PAW) method$^{66,67}$ combined with the Perdew–Burke–Ernzerhof exchange$^{68}$ was used throughout the calculation. The plane-wave basis energy cutoff was set at 450 eV for high precision, and the related criteria were set 10$^{-6}$ eV for total energy change and 0.02 eV/Å for the force on each atom. The Monkhorst–Pack grids in the Brillouin zone of the primitive cells were set 5 × 5 × 1 for k-point sampling.

The Pd(100), Pd(110), and Pd(111) surfaces were all modeled by periodically repeated unit cells. For example, the Pd(100) surface was achieved by a 3 × 3 supercell. Each slab consists of four Pd atomic layers; the bottom two layers were fixed at their bulk lattice positions while the top two layers and the adsorbates were allowed to relax fully. Successive slabs were separated in the z-direction by a vacuum layer of 25 Å.

The adsorption energy calculation formula is given below

$$E_{\text{ads}} = E_{\text{adsorbate/surface}} - E_{\text{clean}} - E_{\text{adsorbate}}$$

where $E_{\text{adsorbate/surface}}, E_{\text{clean}}$, and $E_{\text{adsorbate}}$ represent the total energies of the adsorbate-slab, the clean slab, and the adsorbate species, respectively.

## ASSOCIATED CONTENT

**Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.nanolett.1c02104.

Supporting figures and discussions; EDS mapping of Pd nanocrystals and electron beam effect (PDF)

Video 1 shows rapid etching of a Pd nanocrystal at 0.1 mM Fe(acac)$_3$ (AVI)

Video 2 shows mitigated etching of a Pd nanocrystal at 1.0 mM Fe(acac)$_3$ (AVI)

Video 3 shows electron beam damages the surface ligands with a different etching mode at 1.0 mM Fe(acac)$_3$ (AVI)

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ACKNOWLEDGMENTS

This work was supported by the U.S. Department of Energy (DOE), Office of Science, Office of Basic Energy Sciences (BES), Materials Science and Engineering Division under Contract No. DE-AC02-05-CH11231 within the KC22ZH program. Work at the Molecular Foundry is supported by the Office of Science, Office of Basic Energy Sciences, of the U.S. Department of Energy under Contract No. DE-AC02-05CH11231. J.J. acknowledges the support from the National Natural Science Foundation of China (No. 51925903) and the National Key R&D Program of China (2018YFC0705401).

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