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Stability, Oxidation, and Shape Evolution of PVP-Capped Pd Nanocrystals

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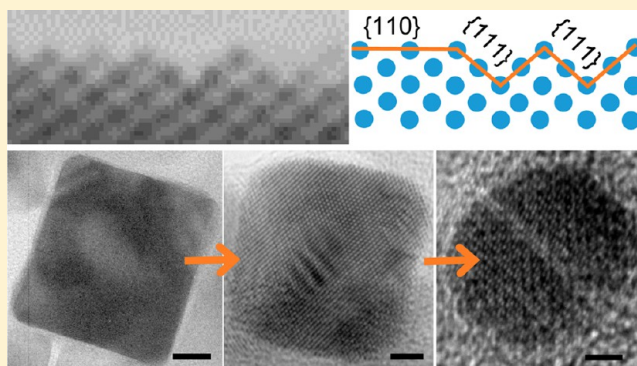
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S Supporting Information

ABSTRACT: A critical aspect in the practical applications and catalytic performance of shape-controlled nanocrystals is their stability and morphology retention under ambient conditions. Changes to the morphology of shape-controlled Pd nanocrystals capped by PVP are assessed by TEM, and surface oxidation was evaluated by X-ray photoelectron spectroscopy (XPS) over 12 months. Surface oxidation of PVP-capped Pd nanocrystals resulted in the loss of edge and corner sites and a transition to spherical morphologies. The shape stability of the nanocrystals was found to follow the trend cubic < cuboctahedra < octahedral ~ concave cubes. For low index planes, {111} surfaces were more resistant to oxidation compared to {100} facets, correlating with the surface free energy of the nanocrystals. Cubic and cuboctahedral nanocrystals transitioned to spherical particles while octahedral nanocrystals retained their morphology. The presence of high-energy {110} facets was observed in the cubic nanocrystals which undergo surface reconstruction. The presence of surface defects may also influence the rate of the structural changes. Concave cubic nanocrystals, which possess high index facets and surface energies, were consistently found to display excellent morphology retention. The concave cubic nanocrystals displayed superior shape stability and reduced oxidation compared to cubic and cuboctahedral nanocrystals. XPS analysis further determined that PVP capping ligands on different Pd surface facets strongly influenced the morphological consistency. The stability of the concave cubes can be attributed to the stronger chemisorption of PVP capping ligands to the high index planes, making them less susceptible to oxidation.



INTRODUCTION

Extensive developments in the controlled synthesis of noble metal nanocrystals (NCs), with specific morphologies, have allowed numerous shape-dependent properties to be determined.^{1–3} Altering the morphology of a NC exposes surface facets which display different atomic arrangements, leading to applications in selective catalysis; several hydrogenation^{4,5} and oxidation^{6,7} reactions demonstrate facet dependent reactivity. Nanocrystal shape can also influence the optical properties of plasmonic nanostructures, leading to enhanced sensing and biomedical applications.^{8,9} While early research efforts focused on synthesizing NCs enclosed by low index surface facets, such as {111} and {100} surfaces, there has been enormous progress recently in the growth of NCs enclosed by high index faces, achieved by manipulating growth kinetics.^{10,11} High-index facets are denoted by a set of Miller indices $\{hkl\}$ with at least one index being greater than one. The morphologies of such structures are often characterized by sharp corners giving rise to unique optical properties and improved surface enhanced Raman scattering.¹¹ High index surfaces having a

high density of low coordinated atoms located at step, edge, and kink sites thus have the potential for enhanced catalysis.¹² Improved catalytic and electrocatalytic performance of NCs terminated by high index facets has been demonstrated.^{13–16}

Pd is an important noble metal central to heterogeneous catalysis for chemical synthesis,¹⁷ fuel cells,¹⁸ and hydrogen storage.¹⁹ Recent developments in understanding the growth conditions and mechanisms that influence NC morphology have facilitated exceptional control over the solution synthesis of Pd NCs enclosed by well-defined facets. Shape control synthesis of Pd NCs has been reported using selective capping ligands,^{20–22} seeded growth,^{14,23–26} heteroexpitaxial growth,^{27–29} and electrochemical methods.^{16,30} The use of shape-controlled Pd NCs has been shown to enhance performance in catalysis^{14,27} and cancer therapy.⁶

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Many practical applications of NCs, such as catalysis, require the metal to be deposited on a support material. The stability of shape-defined Pd NCs on support materials over time has not been thoroughly evaluated and is of key importance in exploiting the structure-dependent properties of NCs. Loss of NC shape and changes in chemical state, due to surface oxidation, can have an impact on catalytic reactivity, molecular adsorption, and optical properties.

Here, we report the stability and shape evolution of faceted Pd NCs supported on activated carbon. Activated carbon is one of the most commonly used support materials due to its high surface area, inertness, and low cost. In this article, the stability of shape-controlled Pd nanostructures including cubic, octahedral, and cuboctahedral NCs are assessed by TEM and XPS. In addition to low index NCs, the stability of concave cubes enclosed by high index surface facets is also investigated. The concave cubes displayed excellent stability after immobilization and superior oxidation resistance compared to cubic and cuboctahedral NCs. Structural features present in the as-synthesized NCs, such as surface faceting and defects, influence the stability of the NCs. XPS was utilized to probe the changes to the NC oxidation state and to understand the origin of the stability observed for high index surface facets. In this study, the chemisorption of PVP on the surface of Pd NCs enclosed by different surface facets was found to be important for NC stability and retention of their morphology.

EXPERIMENTAL SECTION

Pd NCs of different surface facets were prepared by the methods described by Xia and co-workers.²⁶ A variety of NC shapes and sizes were investigated including 10 and 20 nm Pd cubic, 28 nm cuboctahedra, and octahedral NCs with an edge length of 21 nm. High index facet concave cubes were prepared from 10 nm cubic seeds, measuring ~20 nm across in length and 35 nm from corner to corner.¹⁴ For the stability studies six batches of each NC were prepared. Pd NCs were immobilized on activated carbon by stirring at room temperature overnight and collected by filtration. Immobilization of the NCs on carbon was evident from the color change of the solution which changed from dark brown to near-colorless. The morphological stabilities of the carbon-supported NCs were carried out by preparing the samples on TEM grids. Samples for analysis were prepared in triplicate and were left in ambient conditions (air, ~20 °C).

Materials Characterization. Microscopy. Scanning electron microscopy (SEM) images were obtained using a FEI DualBeam Helios NanoLab 600i high-resolution SEM. Transmission electron microscopy (TEM) analysis was performed using a JEOL 2100 transmission electron microscope, operating at a voltage of 200 kV. Scanning transmission electron microscopy (STEM) was carried out on a FEI Titan TEM at an operating voltage of 300 kV.

X-ray Photoelectron Spectroscopy (XPS). XPS spectra were collected on a KRATOS-AXIS-165 using a monochromatic Al K α line (1486.6 eV) as the X-ray source. All spectra were collected at a takeoff angle (Θ) of 90° to the surface normal. Spectra were referenced to the C 1s at a binding energy 284.8 eV, and a Shirley background was applied. The C 1s spectra were fitted to Gaussian (70%)–Lorentzian (30%) profiles. The high-resolution Pd 3d scans were fitted with asymmetric Gaussian–Lorentzian profiles. The relative ratio of the Pd 3d doublet was fixed during the fitting, while the full width at half-

maximum (fwhm) and peak position were allowed to vary within a reasonable range to obtain the best fit.

RESULTS AND DISCUSSION

Structural Stability of Pd Nanocrystals. The as-synthesized cubic Pd cubes, shown in Figure 1a, are largely

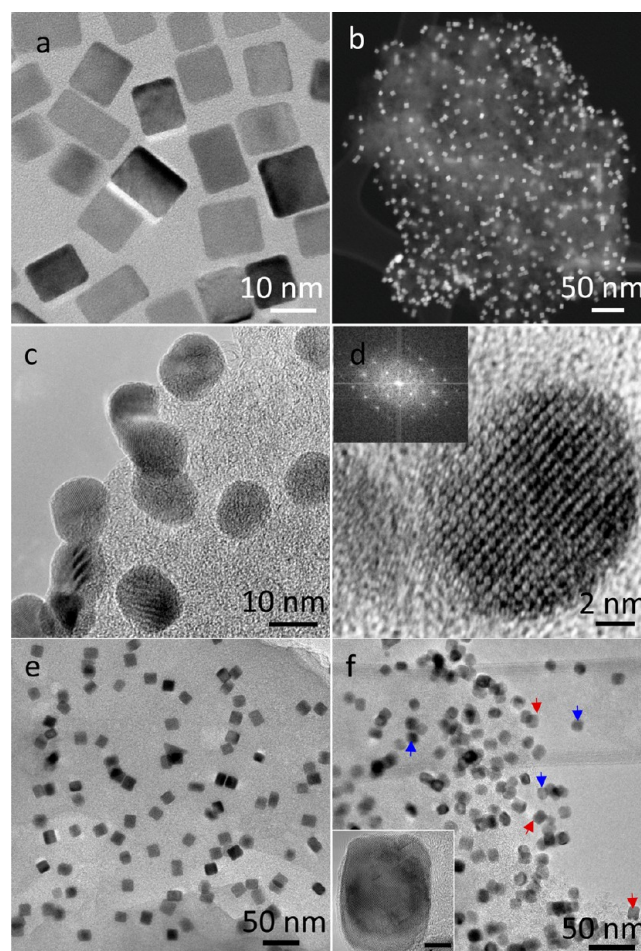


Figure 1. (a) TEM images of as-synthesized 10 nm PVP-capped cubic Pd NCs. (b) STEM image of 10 nm cubes deposited on activated carbon. (c) TEM image of 10 nm cubes 6 months after deposition onto carbon. (d) TEM image of cubic NC, aged for 12 months, (e) 20 nm cubic Pd NCs 1 week and (f) 6 months after deposition on activated carbon. The red arrows highlight NCs with well-maintained cubical morphologies, and the blue arrows highlight NCs evolved to truncated NCs. The inset in (f) shows typical 20 nm cubic Pd NC 12 month after ambient exposure (scale bar is 5 nm).

characterized by six {100} surface facets. The cubic morphology was affected by the immobilization procedure onto activated carbon as shown by the STEM image in Figure 1b. Exposure of the immobilized cubes for 7 days revealed little change in the morphology of the NCs, while analysis of the same NCs after 3 months revealed that the morphology of the 10 nm cubes altered. Changes in shape were also observed to vary within a same sample, with some NCs becoming truncated while others displayed more pronounced changes, such as becoming spherical (Supporting Information Figure S1). After 6 months, the cubic NCs were almost entirely spherical in shape, as shown in Figure 1c. High-resolution TEM analysis of the NCs after 6 months revealed that many of the particles were defect-free

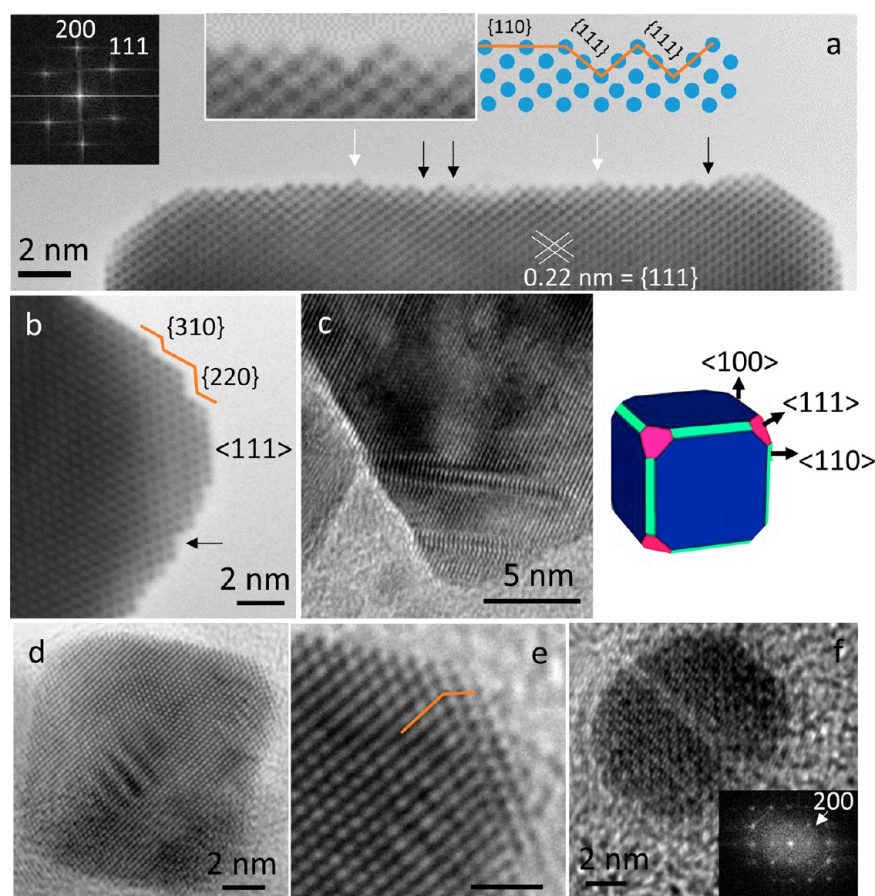


Figure 2. (a, b) HRTEM images of freshly synthesized cubic NC along the $[110]$ direction, (c) freshly prepared 20 nm cubic NC showing stacking faults, (d, e) 10 nm cubic NCs aged for 3 months, and (f) cubic NC aged for 6 months showing stacking fault along the particle.

single crystalline, while others contained stacking defects such as those shown Figure 1d. In contrast, the 20 nm diameter NCs showed a greater retention of their morphology over time, with a mixture of slightly and heavily truncated cubes observed as shown by comparison of the NCs 1 week and 6 months after deposition (Figure 1e,f). Cubic NCs stored under inert conditions (N_2 -filled glovebox) after immobilization also exhibited rounded corners, consistent with surface atom diffusion, but no transformation from a cubic to a spherical morphology was observed, indicating that interaction with O_2 influences NC stability. PVP-protected cubic NCs used in this study exhibited considerably greater stability compared to ethylene glycol protected NCs. Xiong et al.³¹ reported that dried 50 nm diameter Pd cubes capped with ethylene glycol formed a nanocrystalline PdO shell, readily observed by TEM after ~ 8 days of ambient exposure. Additionally, they reported an inverse relationship between NC size and stability with smaller (8 nm) cubes displaying superior stability (up to 90 days), compared to 50 nm cubes. This increased stability with decreasing size was not observed for the PVP-capped NCs used in this study, which clearly revealed that 10 nm cubes were less stable and lost their cubic morphology compared to the 20 nm cubes. Furthermore, TEM analysis on the aged cubes (after becoming spherical) did not show the presence of a crystalline oxide shell, suggesting a low degree of oxide formation due to a better surface passivation by bulkier PVP compared to ethylene glycol. The presence of the surrounding carbon matrix and polymeric capping ligands on the nanocrystals in this study obstructs direct imaging of ultrathin oxide layers by TEM.

The changes in the morphology of the Pd NCs from cubic to spherical are driven by energy minimization to the most thermodynamically favorable shape. To understand the factors contributing to the shape changes observed in the cubic NCs, high-resolution TEM was used to analyze the particles at different stages of aging. Figure 2a shows a TEM image of a freshly prepared cubic NC projected in the $[011]$ direction. A significant feature shown in Figure 2a is the presence of a $\{110\}$ facet, which is not often observed on nanostructures due to its lower stability compared to $\{111\}$ and $\{100\}$ facets. The schematic shown in Figure 2 illustrates the true structure of the cubic NCs showing the truncated corners with $\{111\}$ and $\{110\}$ facets in addition to the $\{100\}$ cubic faces.³² As shown in Figure 2a, these surfaces are relatively rough at the atomic scale and show missing-row reconstruction, characteristic of noble metal $\{110\}$ surfaces.³³ In some regions, rows of atoms are missing along the $[1-10]$ direction and give rise to a sawtooth configuration, as identified by black arrows in Figure 2a. The image is magnified in the inset of Figure 2a for clarity. Similar surface reconstruction has previously been observed on Au nanorods.³⁴ The presence of adatoms, shown by the white arrows in Figure 2a, is also observed. The driving force for this reconstruction is the formation of lower energy $\{111\}$ microfacets on the (110) surface giving an overall lower surface energy after reconstruction, as illustrated by the inset schematic in Figure 2a. No reconstruction was observed on the $\{100\}$ facets, and surface defects mainly consisted of single atom height terraces (Supporting Information Figure S2). A higher density of step sites was generally observed at the

corners as shown in Figure 2b. Here, the presence of high index $\{220\}$ and $\{310\}$ facets can be seen where the $\{100\}$ and $\{111\}$ facets meet. This observation is in excellent agreement with DFT calculations showing high index stepped surfaces being preferential to sharp corners at the boundaries between the (100) and (111) facets.³⁵ Additionally, as previously described, surface reconstruction of the $\{110\}$ facets is again seen in Figure 2b. As the NCs age, loss of the stepped surfaces, which are more prevalent at the corners, is observed, causing rounding of the corners (Figure 2c). The facets continue to reduce in size, eventually becoming spherical (Figure 2d). Such transformations are predicted by DFT calculations due to O_2 adsorption and surface oxide formation.³⁵ The presence of the $\{110\}$ facet on the cubic NCs is influential to the stability of the NCs due to the greater reactivity and lower stability associated with the surface. Nanostructures with high surface defect densities are less stable and more susceptible to oxidation, thereby affecting the rate of structural changes.^{36,37} Surface defects can also influence the coordination of capping ligands,³⁸ and a more defective surface may disrupt the packing or lower the coverage of the PVP capping layer, facilitating easier oxidation of the Pd NCs.

An additional structural feature of the cubic NCs which contributes to their variable shape evolution is the presence of stacking faults, as shown in Figure 2c. Stacking faults were found to be present in some of the resulting spherical nanoparticles as shown in Figure 2f. The exact origin of the defects is unclear and was not investigated in detail in this study. The as-synthesized NCs are single crystalline with a low defect density, although stacking defects can be observed as shown in Figure 2c. Defect formation has been shown to occur as a stress relieve mechanism.³⁹

The 20 nm cubic NCs display similar defect features to the 10 nm cubic NCs (Figure 1f inset). The larger size of the particles may hinder complete transformation to a spherical morphology as the effects of surface stress and interface stress are more pronounced for smaller particles.⁴⁰

Pd NCs with a cuboctahedral morphology are characterized by 6 square $\{100\}$ and 6 triangular $\{111\}$ facets, shown in Figure 3a. Similar to the cubic NCs, aging of cuboctahedral NCs results in a morphology change to the thermodynamically lowest energy spherical shape, as illustrated in Figure 3b. TEM also reveals that many of the NCs do not experience a uniform evolution of morphology. Figure 3c shows an aged octahedral NC with defined facets on one side of the NC and rounding on the opposite side of the NC, which was typical of many particles. The origin of the uneven rounding of surface facets is also attributed to the presence of surface defects as previous described for the cubic NCs. After 12 months many of the cuboctahedral NCs also became spherical (Supporting Information Figure S3).

In comparison to cubic and cuboctahedral NCs, the octahedral NCs exhibited little change to their morphology over the same time period. Ideal octahedra are characterized by eight $\{111\}$ surface facets; however, many of the octahedra prepared by this seeded method employed were slightly truncated, exposing vertices capped with $\{100\}$ facets, as shown in the STEM image in Figure 3d. These NCs displayed excellent morphology retention as can be seen in Figure 3e, 6 months after deposition onto activated carbon. Even after 12 months the octahedral NCs displayed negligible changes to their morphology, and the particles retained well-defined facets (see Figure 3f). The overall stability trend of the polyhedra was

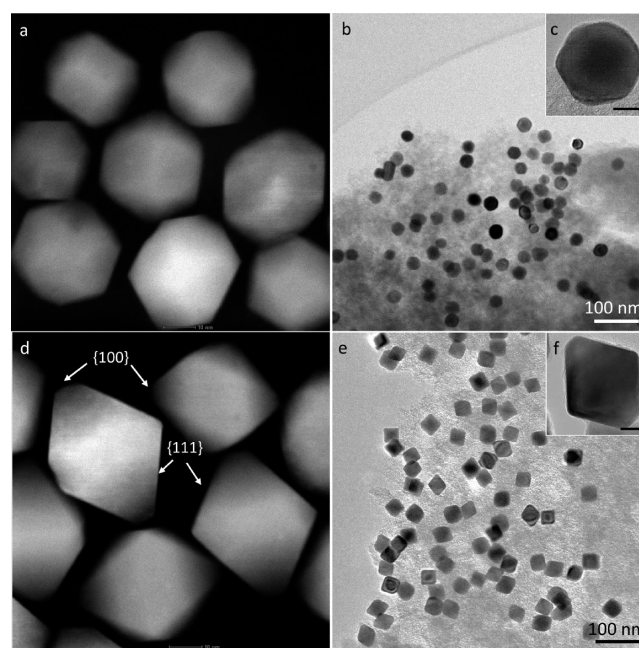


Figure 3. (a) STEM image of as-synthesized cuboctahedral NCs. (b, c) TEM images of cuboctahedral NCs 6 months after immobilization onto carbon. (d) STEM image of as-synthesized octahedral NCs. (e) Octahedral NCs 6 months and (f) 12 months after immobilization onto carbon. Scale bars in (a), (c), (d), and (f) are 10 nm.

found to be cubic < cuboctahedra < octahedral, which correlates with the surface free energy of face centered cubic metals, $\gamma_{\{111\}} < \gamma_{\{100\}} < \gamma_{\{110\}}$.⁴¹

High index surface facets are characterized by a high density of surface atoms with low coordination numbers. These open structures possess higher surface energies compared to close packed surfaces, typically $\gamma_{\{111\}} < \gamma_{\{100\}} < \gamma_{\{hkl\}}$ for fcc Pd. Figure 4a shows a TEM image of the as-synthesized concave Pd NCs. TEM analysis of the concave cubes 6 months after deposition on the carbon support revealed they exhibited excellent retention of morphology as shown in Figure 4b. In contrast to the cubic NCs, which lose their stepped facets on aging, HRTEM analysis of the concave cubes aged for 6 months (Figure 4c) showed the preservation of the high index faces, with most of the exposed facets belonging to the $\{730\}$ family planes, consistent with the as-synthesized NCs.¹⁴ The NCs still retained their concave shape 12 months after deposition onto activated carbon (Supporting Information Figure S4).

Oxidation and Interaction of PVP with Pd Nanocrystals. To further understand the stability of the shape-controlled NCs, XPS analysis was conducted to study the oxidation trends of the NCs as they aged and to probe the interaction of the PVP capping ligands with Pd. Figures 5a–c show the evolution of the Pd 3d core level spectra of the cubic Pd NCs over 24 h, 1 month, and 6 months, respectively, after immobilization on activated carbon. The Pd 3d spectra of the cubic NCs after 24 h showed the presence of mainly metallic Pd(0) at a binding energy of 335.4 eV, in good agreement with bulk Pd (335.2 eV).⁴² The slightly higher binding energy is typical of nanoparticles due to size and electronic effects.^{43,44} Notably, assignment of Pd oxidation states in the 3d core level varies somewhat in the literature. *In situ* XPS measurements of Pd(111) facets determined that peaks shifted to binding energies greater than +1.5 eV can be assigned to bulk oxide phases, while smaller shifts are attributed to surface oxide and

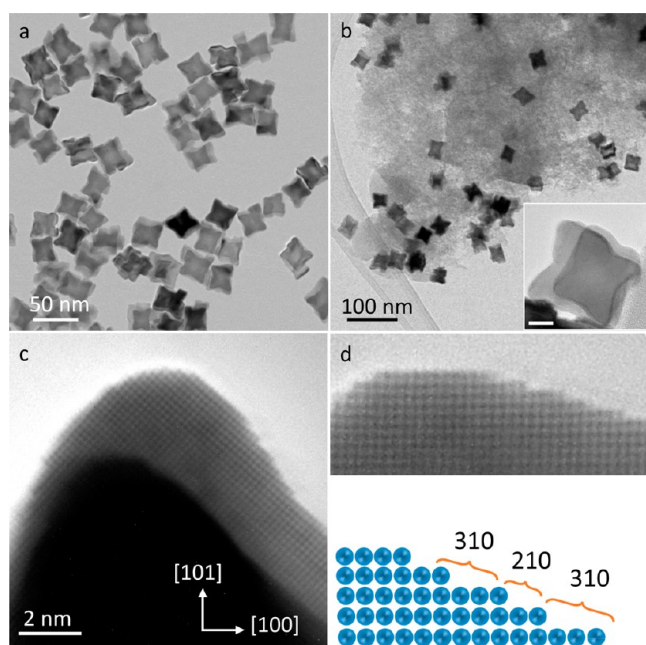


Figure 4. TEM image of (a) as-synthesized concave NCs and (b) 6 months after deposited onto activated carbon. (d) HRTEM image of concave NC with incident beam along the $[100]$ direction. The schematic illustrates the step configuration of the surface facet.

subsurface oxide species.^{42,45} Similar observations have been made for Pd(100) surfaces.^{46,47} Stable surface oxides can form on (111) and (100) surfaces but not on (110) facets.^{35,42} Furthermore, the structure of surface oxide species has been shown to be quite different from that of bulk PdO.⁴⁸ The second shoulder peak in Figure 5a, located at a binding energy of 337.1 eV, can be assigned to bulk PdO, which is in excellent agreement with the 1.7 eV difference reported for PdO and Pd(0).^{47,49} Exposure of 20 nm cubic NCs to ambient conditions for 1 month resulted in a similar Pd 3d spectra,

but with increased line broadening of the peaks and a shift of 0.15 eV to higher binding energies, consistent with previous studies.^{47,50} The first shoulder peak shown in Figure 5b occurs at a binding energy of 336.5 eV, typical of PdO reported for nanoparticles.⁵⁰ The second shoulder peak centered at a binding energy of 337.6 eV can typically be assigned to the presence of highly oxidized Pd species such as PdO₂ (reported in the range between 337.2 and 338.2 eV).^{51–53} As the cubic NCs age over 6 months, the PdO_x peak intensity increased, which can be seen from comparison of the Pd 3d spectra in Figure 5a–c. Figure 5d displays the Pd 3d spectra of concave cubes 4 weeks after immobilization onto activated carbon, showing the presence of predominately metallic Pd(0) at 335.2 eV and a surface PdO associated peak at 336.4 eV. Comparison of Figures 5c and 5e clearly shows that the concave cubes are considerably less oxidized than the cubic NCs after exposure to ambient conditions for 6 months, consistent with their shape retention. The total oxide signal for the concave cubes after 6 months was similar to that observed for $\{111\}$ enclosed octahedral NCs, as shown in Figures 5e and 5f.

The nature of the surface facets present in the NCs is important for understanding the oxidation behavior of faceted NCs. O₂ adsorption on Pd is spontaneous but absorption energies are facet-dependent; Pd atoms on (110) surfaces have higher adsorption energies (1.56 eV/O atom) compared to stepped or close packed (111) or (100) surfaces.³⁵ The ease of O₂ dissociation on Pd follows the trend $\{110\} > \{100\} > \{111\}$, which is the origin of the superior reactivity for oxidation-type reactions observed for Pd $\{110\}$ catalysts.^{6,54} Therefore, the $\{110\}$ facets only observed on the cubic NCs are more reactive and susceptible to oxidation compared to the $\{111\}$ and $\{100\}$ facets, consistent with XPS observations.

The intriguing observation of this study is the excellent stability and oxidation resistance of concave NCs with high index facets, when the open structure of such facets is typically associated with high reactivity. Analysis of oxide phases on high index Pd surfaces is lacking in the literature. However, atomically smooth $\{100\}$ and $\{111\}$ surfaces have been

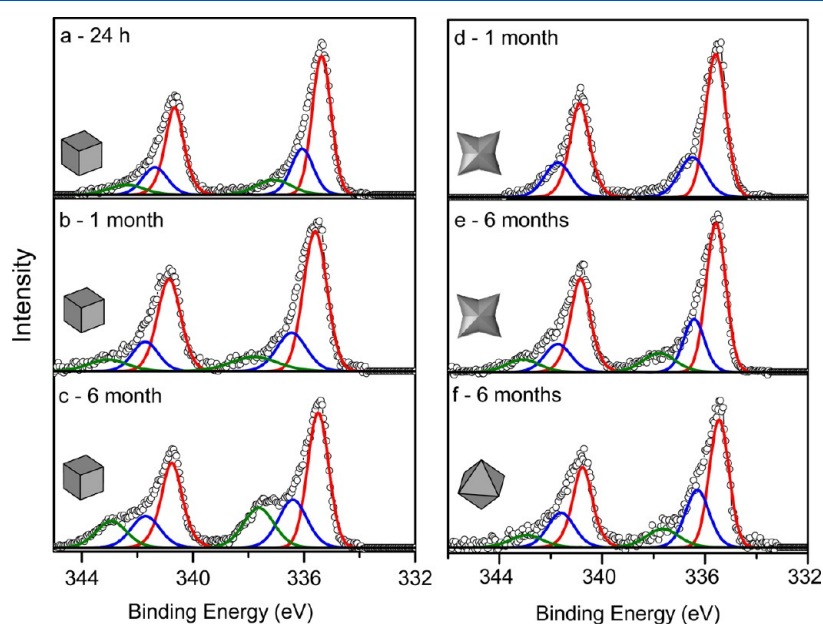


Figure 5. Background subtracted Pd 3d photoelectron emission spectra of carbon-supported Pd cubes after (a) 24 h, (b) 1 month, and (c) 6 months. Concave Pd cubes (d) 1 month and (e) 6 months and (f) octahedral NCs 6 months after ambient exposure.

suggested to allow oxygen diffusion into the lattice, thereby destroying the surface structure and NC shape.^{13,55} For low index surfaces, Pd(111) is more densely packed (1.53×10^{15} atoms cm^{-2}) compared to the Pd(100) surface (1.32×10^{15} atoms cm^{-2}) and Pd(110) surfaces (9.4×10^{14} atoms cm^{-2}). Consequently, oxide formation is the least favorable on Pd(111) as the higher surface atom density requires more lattice expansion to accommodate the formation of PdO_x .⁵⁶ Different factors may influence the oxidation of high index surfaces. In contrast to low index planes, on high index faces, O_2 atoms preferentially adsorb at step sites rather than diffuse into the lattice, helping to preserve the surface structure.¹³ The step structure of the high index facets may also better accommodate lattice strain induced by oxide formation, making them less susceptible to structural changes.

An important aspect in the stability of colloidal NCs is the presence of capping ligands at the particle surface. Passivating ligands can significantly alter surface free energy, thereby influencing the stability and oxidation resistance of surface facets.⁵⁷ XPS analysis was used to investigate the interaction of PVP capping ligands with the Pd surface. Figure 6 shows the N

nanoparticles can also break the N–C bond in the N–C=O group, with following hydrolysis gave $\text{CH}_2\text{--CH}_2\text{--NH}_2^+ \text{--} (\text{CH}_2)_3\text{--COO}^-$, as illustrated in Figure 6d. Their report is in excellent agreement with the N 1s binding energy of 401.2 eV, observed here, which is generally assigned to protonated amine species.⁵⁹ The peak contribution of charged N species is larger for the concave cubes compared to the low index polyhedral, suggesting greater chemisorption of the pyrrolidone N group on the high index surface facets. The atomically stepped surface is characterized by atoms with low coordination numbers which may facilitate a stronger interaction with the N groups. Bond cleavage is also considerably more favorable on stepped surfaces compared to atomically smooth surfaces which can lead to coordination of PVP, as illustrated in Figure 6d.⁶⁰

The C 1s spectrum of the cubic Pd NCs, shown in Figure 7a, contains three components at binding energies of 284.8 eV (C–C, C=C), 286 eV (C–N, C–O), and 287.6 eV (C=O);⁶¹ however, adventitious hydrocarbon will also contribute to the C–C and C–O peak intensities. The C 1s spectrum of the concave cubes contains an additional peak not observed for the cubic NCs at a binding energy of 288.9 eV, typically assigned to the O–C=O group. The presence of the carboxylate group, in addition of the C=O group, indicates that a portion of the chemisorbed PVP molecules undergo cleavage of the C–N bond and subsequent hydrolysis, consistent with the N 1s spectrum. The synthesis of cubic NCs in this study uses Br^- ions as selective capping agents to promote the formation of NCs enclosed by {100} facets. Analysis of the Br 3d core level spectrum of the cubic NCs shows that the Br^- species remain on the surface after immobilization onto activated carbon (Supporting Information Figure S5). The Pd(111) and high index facets were not observed to be capped with Br^- ions, which may facilitate stronger interactions with the PVP ligands compared to {100} facets. Furthermore, while Br^- ions have been shown to be chemisorbed to the surface, they can be displaced by ethylene glycol at 100 °C.⁶² Removal of PVP from noble metal surfaces generally requires more forcing conditions.⁶³

Several studies have shown that charge transfer and the coordination mode of PVP molecules with noble metal nanoparticles to be size dependent.^{64–66} The XPS data in this study also indicate that the interaction mode of PVP capping ligands is also dependent on the nature of the surface facet for Pd NCs. This finding is important for both shape selective NC synthesis with high-energy faceted surfaces, suggesting that the structure and electronic interaction of the ligand are important in preserving the long-term stability and structure of high-energy surfaces.

CONCLUSIONS

The stability, oxidation, and shape evolution of well-defined Pd NCs supported on activated carbon were assessed over 12 months. For low index surfaces, the octahedral NCs with {111} facets had greater stability compared to {100} facets due to the lower surface free energy. The presence of the relatively reactive and high-energy {110} facet on the cubic NCs increases the oxidation susceptibility of the NCs, making them the least stable shape studied. Surface defects influence the shape evolution of NCs, resulting in nonuniform changes in their structure. Concave Pd NCs characterized by high index surface facets displayed superior stability to cubic and cuboctahedral NCs. XPS analysis identified stronger chemisorption between the N groups of the PVP capping ligands on the high index

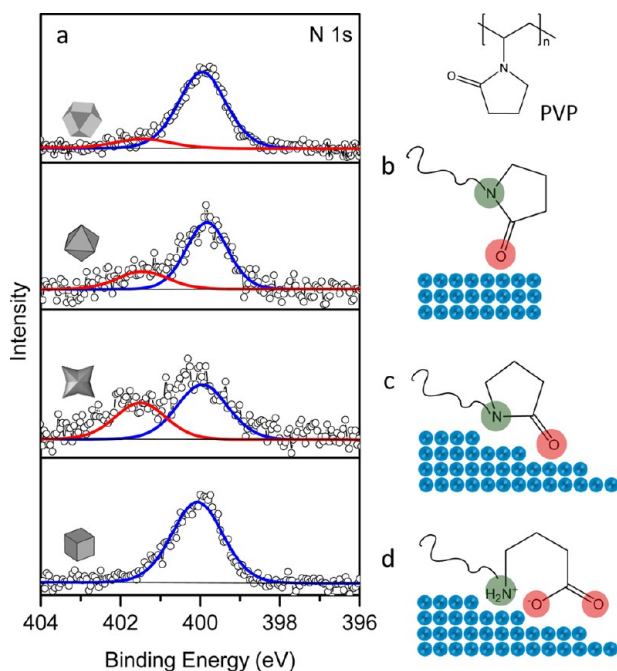


Figure 6. (a) N 1s spectra of Pd NCs immobilized on activated carbon. Schematic illustrating (b) the interaction of PVP through carbonyl O. (c) Coordination of PVP through both O and N groups. (d) Coordination of PVP with cleavage of the C–N bond.

1s spectra of the different polyhedra. The cubic NCs displayed a single peak at a binding energy of 399.8 eV, characteristic of the pyrrolidone N group.⁵⁸ The N 1s binding energy is similar to that of the free PVP, indicating that the N atoms are not involved in the coordination with the Pd surface on cubic NCs, as illustrated in Figure 6b. In contrast to the cubic NCs, all other Pd polyhedra displayed the presence of a peak at 401.6 eV, in addition to the peak at 399.8 eV. Shifts to a higher binding energy are associated with decreased electron density of the N group, indicating charge transfer from the PVP to the Pd, implying that the pyrrolidone N group is involved in the coordination with the surface, as illustrated in Figure 6c. Xian et al.⁵⁸ showed the chemisorption of PVP to spherical Pd

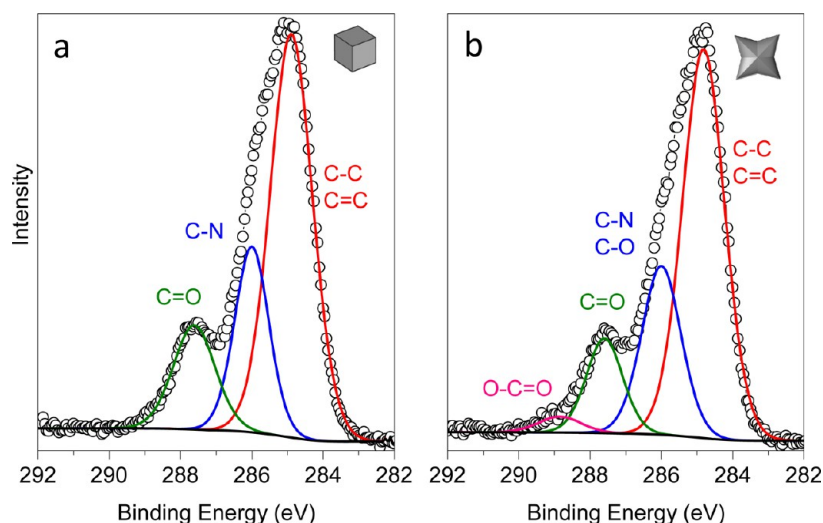


Figure 7. C 1s spectra of unsupported (deposited on glass substrate) (a) cubic Pd NCs and (b) concave cubic Pd NCs.

faces compared to the low index {100} facets. Controlling the interaction between the PVP capping ligands and the metal surface has been central in the synthesis of colloidal NCs. In particular, understanding the selective chemisorption of capping ligands onto certain crystal facets has been key to controlling the growth of NCs with specific morphologies. The work here highlights that these interactions also play a critical role in the long-term stability of NCs. Optimizing these interactions can facilitate the synthesis of NCs enclosed by well-defined surface facets with improved stability and oxidation resistance.

Structural evolution of nanoparticles is complex with several influencing factors. The stability trends observed in this study may not be general and nanoparticles prepared by alternative synthesis methods, with different capping ligands and support materials may display different stability trends. However, evaluating the stability of shape controlled nanocrystals is critical as morphological transformations, due to surface defects or surface oxidation, can influence their potential applications. The excellent stability of PVP-capped concaves cubes is promising as nanocrystals with high index facets have been shown to display enhanced reactivity in several catalytic applications.

■ ASSOCIATED CONTENT

■ Supporting Information

Additional TEM images of the cubic, cuboctahedral and concave cubic nanocrystals, and the Br 3d core level XPS spectra for cubic nanocrystals. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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