

Quantitative Analysis of the Coverage Density of Br⁻ Ions on Pd{100} Facets and Its Role in Controlling the Shape of Pd Nanocrystals

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S Supporting Information

ABSTRACT: We report an approach based on a combination of inductively coupled plasma mass spectrometry and X-ray photoelectron spectroscopy for quantitative analysis of the role played by Br⁻ ions in the synthesis of Pd nanocrystals. The Br⁻ ions were found to adsorb onto Pd{100} facets selectively with a coverage density of ca. 0.8 ion per surface Pd atom. The chemisorbed Br⁻ ions could be removed via desorption at an elevated temperature under reductive conditions. They could also be gradually released from the surface when Pd cubic seeds grew into cuboctahedrons and then octahedrons. On the basis of the coverage density information, we were able to estimate the minimum concentration of Br⁻ ions needed for the formation of Pd nanocubes with a specific size. If the concentration of Br⁻ ions was below this minimum value, not all of the {100} facets could be stabilized by the capping agent, leading to the formation of nanocubes with truncated corners. The quantitative analysis developed in this study is potentially extendable to other systems involving chemisorbed capping agents.

Palladium nanocrystals with controlled shapes have received considerable interest in recent years because of their remarkable performance in various catalytic reactions, including alkene hydrogenation,¹ CO oxidation,² and various organic coupling reactions.³ It is well-known that the catalytic activity and selectivity of nanocrystals for a structure-sensitive reaction is strongly dependent on the type of facets exposed on the surface.⁴ Therefore, nanocrystals with a specific shape and thus the desired facets would be invaluable for various catalytic applications. Thanks to the efforts of many research groups, a large number of protocols for the synthesis of Pd nanocrystals with distinct shapes have been developed by identifying various capping agents as well as by developing strategies based on kinetic control.⁵ Typically, the function of a capping agent is to stabilize surface atoms with a specific arrangement through selective chemisorption. As a result, the growth rates of various types of facets can be altered, leading to the formation of nanocrystals with diversified shapes.⁶

Bromide ions have been widely used as a capping agent for the synthesis of Pd and Ag nanocrystals enclosed by {100} facets such as nanocubes and nanobars because they preferentially adsorb on the (100) surface.⁷ A typical protocol

for the synthesis of Pd nanocubes involves the reduction of a Pd(II) precursor by ascorbic acid in the presence of KBr or NaBr. The bromide is believed to serve as a capping agent for the Pd(100) surface, effectively altering the order of surface free energies and thus promoting the formation of Pd nanocrystals enclosed by {100} facets. Despite the full demonstration of its critical role in the formation of Pd nanocubes and nanobars, there is still no experimental evidence to support the proposed mechanism. As a result, a quantitative analysis of the role played by bromide ions in the synthesis of Pd nanocrystals would be critically important to both fundamental understanding and future development.

In this work, we quantitatively analyzed the role played by bromide ions in the synthesis of Pd nanocrystals using a combination of inductively coupled plasma mass spectrometry (ICP-MS) and X-ray photoelectron spectroscopy (XPS). Unlike other techniques for surface analysis such as scanning tunneling microscopy (STM), which usually requires the use of an extended surface and cannot easily generate chemical information,⁸ the combination of ICP-MS and XPS directly provides both elemental and surface chemical information about the nanocrystals. Thanks to the high sensitivity of ICP-MS, it is possible to measure directly the number of Br⁻ ions adsorbed on the surface of a specific number of Pd nanocubes. To achieve better statistics for the coverage density of Br⁻ ions on Pd(100), we used Pd nanocubes with three different edge lengths ($L = 7.5, 10.5, \text{ and } 18 \text{ nm}$). The samples were washed with deionized (DI) water four times to remove the excess capping agent. Table 1 lists the ratios of Br⁻ ions to Pd atoms for these samples as obtained from ICP-MS analysis. The ratio decreased from 0.11 to 0.09 to 0.05 as L increased from 7.5 to 10.5 to 18 nm. Because of the higher surface area to volume ratio for smaller nanocubes, the observation of such a negative correlation between the Br⁻/Pd ratio and the edge length

Table 1. ICP-MS Analysis of the Coverage Density of Br⁻ Ions (ϕ) on the Surfaces of Pd Nanocubes with Different Edge Lengths (L)

L (nm)	Br ⁻ /all Pd	Br ⁻ /surface Pd	ϕ (ions/nm ²)
7.5	0.114	0.735	9.7 ± 0.3
10.5	0.087	0.779	10.3 ± 0.3
18.0	0.053	0.817	10.8 ± 0.6

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would be expected. On the basis of the crystal structure of Pd and the sizes of the nanocubes, we further calculated the ratio of Br⁻ ions to surface Pd atoms and then coverage densities of Br⁻ ions on these Pd nanocubes. As shown in Table 1, these two parameters were more or less the same for the three different nanocube samples. Considering the possible truncation at corners,⁹ a value of 0.8 for the Br⁻/surface Pd ratio indicated that the Br⁻ ions formed a monolayer on the {100} facets of the Pd nanocubes.

In general, there are two types of interactions between a capping agent and the metal surface: physisorption and chemisorption.¹⁰ To decipher which type of interaction is involved in the case of Br⁻ ions and Pd nanocubes, XPS experiments were conducted. First, we analyzed the surface chemical composition of a sample of Pd nanocubes (*L* = 18 nm) that had been washed different numbers of times with DI water. Surprisingly, in addition to Pd 3d peaks, N 1s, C 1s, and Br 3d peaks were also observed in the survey spectra (Figure S2 in the Supporting Information), indicating that the Br⁻ ions and poly(vinyl pyrrolidone) (PVP), a colloidal stabilizer, could not be removed by washing only. Since physisorbed Br⁻ ions should be removed during the washing process, this result suggested that chemisorption was likely the main interaction between Br⁻ ions and Pd(100). It was expected the chemisorbed Br⁻ ions could be removed only by desorption at a higher temperature. We demonstrated this concept by conducting another set of experiments in which aqueous or ethylene glycol (EG) suspensions containing PVP, citric acid, and the Pd nanocubes were aged at different temperatures for 18 h. The role of citric acid was to act as a mild reducing agent for the Pd²⁺ ions bound to the surface. Transmission electron microscopy (TEM) characterization showed that there was no significant change in the cubic shape of the nanocubes during the aging process (Figure S3).

Figure 1A shows high-resolution Pd 3d XPS spectra of the samples. The two peaks located at 340.4 and 335.1 eV can be assigned to elemental Pd 3d_{3/2} and Pd 3d_{5/2}, respectively. The shoulders at higher energies (342.2 eV for Pd 3d_{3/2} and 337.2 eV for Pd 3d_{5/2}), which are consistent with the reported values for Pd(II) samples,¹¹ confirmed the existence of Pd(II) species on the surface of the nanocubes due to chemisorption of Br⁻ ions. However, when the nanocubes were aged in the aqueous or EG solution containing a reducing agent at an elevated temperature, the shoulders gradually decreased in intensity and completely disappeared for the EG sample at 100 °C. The drop in intensity for the shoulder peaks indicates that some of the surface Pd(II) species were reduced to Pd(0) by citric acid during the aging process. Moreover, it is worth pointing out that the Pd(0) peak of the EG sample at 100 °C showed a slight shift to higher energy due to charge transfer from Pd to PVP, as reported in prior studies.¹²

The temperature dependence of the intensities of the shoulder peaks can be understood by the following argument: Increasing the temperature should accelerate the desorption of Br⁻ ions and increase the reducing power of citric acid. Synergistically, this would lead to reduction of Pd(II) to Pd(0) and removal of Br⁻ ions from the surface. This picture is supported by the ICP-MS data in Figure 1B, where the amount of Br⁻ ions remaining on the surface of the Pd nanocubes showed a similar trend after aging under different conditions. When the sample was treated in EG at 100 °C, the amount of Br⁻ ions dropped to only 12% of the original value. We analyzed the concentration of Pd(II) ions in the supernatant of

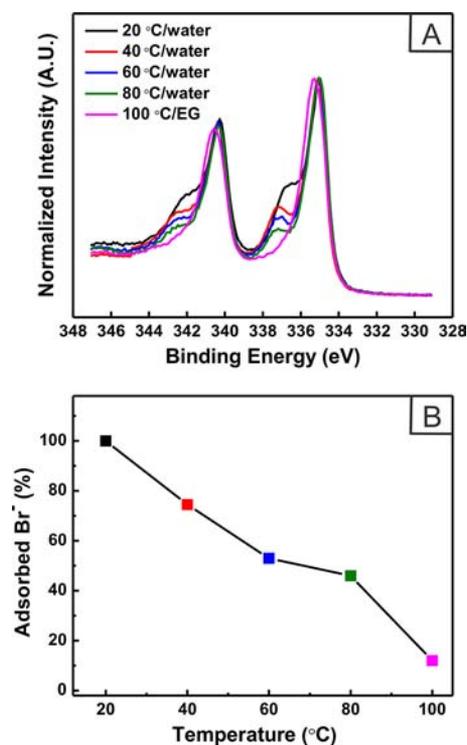


Figure 1. (A) Pd 3d XPS spectra and (B) ICP-MS analysis of residual Br⁻ ions for Pd nanocubes subjected to aging in water or ethylene glycol (EG) at different temperatures for 18 h.

the reaction solution using ICP-MS and found essentially no detectable amount of Pd(II), excluding the possibility of the replacement of Pd–Br complexes with citrate. Combining the XPS and ICP-MS results, we can conclude that the desorption of Br⁻ ions from the {100} facets of Pd nanocubes can be described by the following half-reaction:



Interestingly, when the Br⁻-free nanocubes were aged in an aqueous KBr solution (10 mM) under air, the Br⁻ ions were found to adsorb onto the surface of Pd nanocubes again. In contrast, there were no detectable Br⁻ ions on the surface of the nanocubes when the aging was conducted under a N₂ atmosphere (Figure S4). These results suggest that the Br⁻ ions could bind to Pd{100} facets only in the presence of O₂, which could drive the half-reaction shown in eq 1 in the reverse direction.

The role played by bromide ions in the nanocube synthesis is generally considered to involve selective adsorption onto the Pd{100} facets, thus stabilizing these facets. The slower growth rate along [100] eventually leads to the formation of cubes enclosed by {100} facets. To validate this mechanism, another set of experiments were conducted according to our previously established protocol,¹³ in which the Pd nanocubes with *L* = 18 nm were used as seeds for further growth of Pd in the presence of formaldehyde. By varying the amount of Pd precursor, we obtained nanocrystals with different proportions of {100} and {111} facets, including truncated cubes, cuboctahedrons, truncated octahedrons, and octahedrons. As illustrated in Figure 2A, the proportion of {100} facets gradually decreased during the overgrowth. For example, the proportion of {100} facets for cuboctahedrons is only 50% of that for the cubic seeds. At the stage of a perfect octahedron, which would be

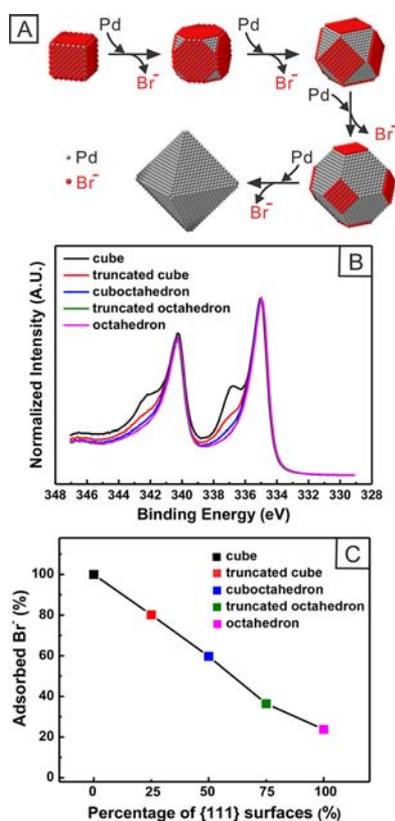


Figure 2. (A) Schematic illustration of bromide ion desorption along with Pd overgrowth on Pd{100} surfaces. (b) Pd 3d XPS spectra and (c) ICP-MS analysis of the residual bromide at different growth stages, showing that Br⁻ ions desorbed from the Pd {100} surfaces during the Pd overgrowth.

enclosed entirely by {111} facets, ideally there should be no {100} facets exposed on the surface. Figure 2B shows the Pd 3d XPS spectra of the Pd nanocrystals sampled at different stages of growth. The results reveal that the shoulder peaks diminished during the growth process and eventually disappeared in the Pd octahedrons. As discussed above, the shoulder peaks can be attributed to the chemisorption of bromide ions, so the drop in intensity for these peaks indicates that the Br⁻ ions gradually desorbed from the surface during the growth process. Furthermore, ICP-MS analysis also showed the same trend of decreasing Br⁻ ion concentration for the resultant nanocrystals during the shape evolution (Figure 2C). The amount of Br⁻ for cuboctahedrons was ca. 60% of that for the nanocubes, which is roughly consistent with the fraction of {100} surfaces obtained from the calculation based on models (50%). It is worth noting that the octahedrons still contained 20% of the Br⁻ ions initially adsorbed on the surface of the Pd cubic seeds. This could be attributed to slight truncation of the vertices of the octahedrons during the centrifugation process, which would create newly exposed {100} facets would trap some Br⁻ ions.

As we noted earlier, in a typical synthesis of Pd nanocrystals, the shape of the resultant nanocrystals can be controlled by introducing different capping agents. Because of the preferential adsorption of Br⁻ onto the Pd {100} facets, the introduction of Br⁻ ions would be expected to favor the formation of Pd nanocrystals enclosed mainly by {100} facets, such as truncated cubes and cubes, depending on the concentration of Br⁻ ions. However, the use of Br⁻ ions at a high concentration could lead

to an increase in the particle size due to the formation of a more stable [PdBr₄]²⁻ complex via ligand exchange between [PdCl₄]²⁻ and the excess Br⁻ ions. Since [PdBr₄]²⁻ has a higher stability constant,¹⁴ the reduction rate would be lower, and thus, the number of seeds generated in the initial stage would be decreased. As a result, the development of a protocol to control the shape while maintaining the size of the nanocrystals would be highly desired. On the basis of the coverage density of Br⁻ ions on Pd{100} facets acquired from ICP-MS, we designed a set of experiments to demonstrate the quantitative role of Br⁻ ions in controlling the evolution of Pd nanocrystals into nanocubes. Figure 3A schematically illustrates how to

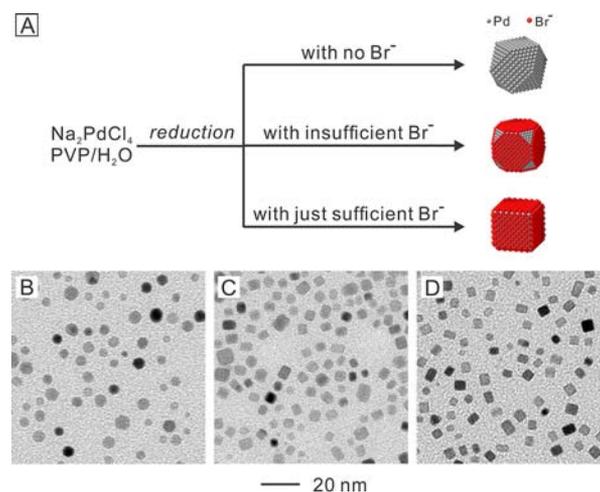


Figure 3. (A) Schematic showing how the shape of a Pd nanocrystal can be controlled by adding a specific amount of Br⁻ ions into the solution as a capping agent for the Pd{100} facets. (B–D) TEM images of Pd nanocrystals synthesized with different amounts of Br⁻ ions: (B) no added Br⁻; (C) in the presence of insufficient Br⁻; (D) with a sufficient amount of Br⁻ added. The shape evolution of Pd nanocrystals was clearly observed from (B) cuboctahedrons to (C) truncated cubes to (D) cubes.

control the shape of the Pd nanocrystals experimentally by controlling the amount of Br⁻ ions. First, a control synthesis was conducted in the absence of bromide ions. As expected, because of the lack of capping agent, Pd cuboctahedrons with a mean size of 5.7 nm were obtained (Figure 3B). Next, with information about the amount of Pd precursor, the yield of Pd, the ratio of Br⁻ ions adsorbed on the Pd{100} surface, and the resultant particle size, the critical amount of bromide needed to cover all of the Pd{100} facets can be estimated. When the amount of bromide introduced into the synthesis was less than the estimated critical value, the exposed Pd{100} surfaces could not be fully stabilized by the bromide ions, resulting in the formation of truncated cubes with some {111} facets on the surface (Figure 3C). When the amount of Br⁻ ions was further increased to exceed the critical value, we obtained perfect Pd nanocubes fully covered by {100} facets (Figure 3D). These results show that the degree of truncation of nanocubes can be tightly controlled by introducing a particular amount of Br⁻ ions into the synthesis. Moreover, it is worth noting that the average sizes of these three types of Pd nanocrystals were very close (5.7 nm for the cuboctahedrons, 6.0 nm for the truncated cubes, and 5.9 nm for the perfect nanocubes). The reason for this result was that the ratio of Br⁻ ions to Pd precursor in the last synthesis was ca. 0.15, just slightly higher than the critical

value. In comparison, the conventional protocol for nanocube synthesis involves the use of an excess amount of Br⁻ ions, with typical ratios in the range from 0.22 to 25.8.^{2b,7b} The relatively low concentration of Br⁻ ions involved in the new protocol effectively minimizes the kinetic effect caused by the ligand exchange, helping to keep the resultant particles at a similar size.

In summary, we have demonstrated a new strategy for quantitatively analyzing the role played by Br⁻ ions in the synthesis of Pd nanocrystals using a combination of XPS and ICP-MS. From the ratio of Br⁻ ions to Pd atoms obtained from ICP-MS analysis, the coverage density of Br⁻ ions on Pd{100} facets was found to be ca. 10 ions/nm² for Pd nanocubes of three different sizes. The chemisorbed Br⁻ ions could be removed from the surface through desorption at an elevated temperature under reducing conditions, as confirmed by the drop in XPS peak intensity for Pd(II) species. The adsorbed Br⁻ ions could also be released from the surface by decreasing the proportion of {100} facets during the growth of Pd nanocubes, which also confirmed the selective adsorption of Br⁻ ions on Pd{100} rather than {111} facets. Moreover, the quantitative information about the coverage density of Br⁻ ions allowed us to estimate the amount of Br⁻ ions needed to generate Pd nanocrystals with specific proportions of {100} and {111} facets. We believe that this approach based on a combination of XPS and ICP-MS can be extended to other systems for a systematic study of the explicit roles played by various capping agents in the shape-controlled synthesis of nanocrystals.

■ ASSOCIATED CONTENT

■ Supporting Information

Experimental section, characterization details, and calculation of the coverage density of Br⁻ ions on the {100} facets of Pd nanocubes. 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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