Polyol Syntheses of Palladium Decahedra and Icosahedra as Pure Samples by Maneuvering the Reaction Kinetics with Additives

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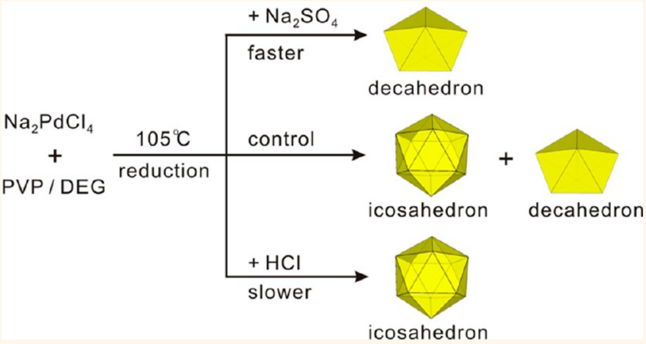
ABSTRACT This article reports a robust method based upon polyol reduction for the deterministic synthesis of Pd decahedra or icosahedra with tunable sizes and a purity approaching 100%. The success of such a selective synthesis relies on an ability to fine-tune the reaction kinetics through the addition of Na_2SO_4 and HCl for decahedra and icosahedra, respectively. In the absence of any additive, the product of a similar synthesis in diethylene glycol contained 10% decahedra and 90% icosahedra. By optimizing the amount of Na_2SO_4 (or HCl) added into the reaction solution, the percent of decahedra (or icosahedra) in the product could be increased up to 100%. The roles of Na_2SO_4 and HCl were also investigated in great detail, and two plausible mechanisms were proposed and validated through a set of experiments. In general, a faster reduction rate is needed for the synthesis of Pd decahedra when compared with what is needed for Pd icosahedra. This work not only offers a simple approach to the deterministic syntheses of Pd decahedra and icosahedra but also provides an in-depth understanding of the mechanisms involved in shape-controlled syntheses of noble-metal nanocrystals from the perspective of reaction kinetics. On the basis of the mechanistic understanding, we have also achieved successful synthesis of Pd decahedra as pure samples by adding a proper amount of NaOH into the system to speed up the reduction kinetics.



KEYWORDS: palladium · reaction kinetics · decahedron · icosahedron · polyol synthesis

Recently, Pd nanocrystals have attracted much attention owing to their great performance in an array of applications, including catalysis,[1−5] electrocatalysis,[6−8] plasmonics,[9−11] and sensing,[12] among others.[13,14] Like other noble metals such as Ag and Au, shape control has emerged as one of the most effective strategies for tailoring the properties of Pd nanocrystals and optimizing their performance in a specific application.[15] Thanks to the efforts from many groups, it has been a great success in preparing Pd nanocrystals with different shapes,[16] with notable examples including cuboctahedra,[17,18] cubes,[19−22] octahedra,[23−25] tetrahedra,[26] right bipyramids,[27] decahedra,[23,28] icosahedra,[23,28−35] bars/rods/wires,[36,37] and many others.[38−40] Among these Pd nanocrystals, decahedra and icosahedra are particularly attractive owing to their inclusion of a large number of twin defects. It was reported that these defects may play an important role in the shape evolution of nanocrystals due to symmetry breaking for the crystal lattice and thus formation of highly anisotropic nanostructures.[41] Furthermore, thanks to the disruption of the lattice caused by twin defects, these structures are expected to have enhanced performance in various applications. As reported in a prior study, for example, Pd icosahedra could absorb a much larger amount of hydrogen

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Received for review April 8, 2014 and accepted July 2, 2014.

10.1021/nn501919e

than single-crystal cubes.[42] It has also been shown that multiply twinned nanocrystals, such as icosahedra, were more active than their single-crystal counterparts when employed as electrocatalysts.[43,44]

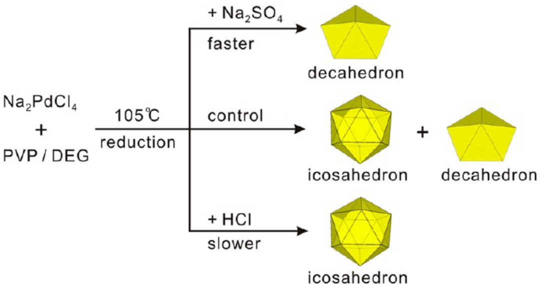
The internal lattice strain associated with a defect region also causes a higher total free energy for the system, making the decahedral and icosahedral structures thermodynamically favored only at relatively small particle sizes. As shown by computational studies conducted for a system in a vacuum, icosahedral nanocrystals of Pd could exist only at sizes by which the total number of atoms was fewer than 309.[45,46] When the size of a decahedral or icosahedral structure increases, the total free energy of the system will increase rapidly. As a result, one has to rely on kinetically controlled methods to generate decahedra and icosahedra relatively large in size. In light of these constraints, it is not hard to understand why much fewer syntheses have been reported in the literature for multiply twinned structures of Pd as compared to those with a single-crystal structure. In an early study, our group synthesized Pd decahedra and icosahedra by reducing Na_2PdCl_4 with citric acid (CA) in aqueous solution, with poly(vinylpyrrolidone) (PVP) serving as a colloidal stabilizer.[23] Although this synthesis was later optimized, the low purity (80%) and limited, nonuniform sizes prevent an extensive study or use of these nanocrystals. Li and co-workers reported the syntheses of Pd icosahedra as a pure sample and Pd decahedra as a mixture with tetrahedra in an organic solvent using a solvothermal method.[28] By varying the concentration of oleylamine (OAm) and introducing a purification step, they were able to obtain icosahedra, decahedra, tetrahedra, octahedra, and triangular plates. These authors also explained their results by developing a thermodynamic model to analyze the difference in surface free energy for these nanocrystals. Although they mentioned the possible role of coordination with OAm in changing the reduction rate of the Pd precursor, no discussion was made on the correlation between the twin structures of nanocrystals and the reaction kinetics. In addition, the complications associated with a pressurized system and postsynthesis separation will likely limit the production volume and popularity of this approach. In a most recent study, we demonstrated a polyol method based on ethylene glycol (EG) for the facile synthesis of Pd icosahedra as pure samples and with sizes controlled in the range 5−35 nm.[43] However, we failed to extend this polyol method based on EG to the synthesis of Pd decahedra.

There is only a very limited understanding of the driving force that leads to the formation of each type of multiply twinned structures. We suspect that the key to the formation of decahedral or icosahedral nanocrystals as pure samples lies in a better control of the reduction kinetics.[47] In general, the reaction has to be kept under kinetic control so the shape and structure of nanocrystals can be deviated from those favored by thermodynamics. It is highly desirable to create a set of rules to guide the selective syntheses of multiply twinned nanocrystals from the viewpoint of kinetic control. To our knowledge, there is still no report on the correlation between the reduction rates and the selectivity for nanocrystals with different twin structures.

In this article, we report the deterministic syntheses of Pd decahedra and icosahedra with a purity approaching 100% by introducing additives such as Na_2SO_4 and HCl into a polyol synthesis based on diethylene glycol (DEG). The switching from the more commonly used EG to DEG allowed us to control the reduction kinetics more precisely due to a weaker reducing power for DEG. The particle size could be readily tuned by terminating the reaction after different periods of time. For instance, Pd decahedra in the size range 5−15 nm and icosahedra in the size range 6−25 nm were all successfully prepared using this new method. Additionally, new insights into the mechanisms of the selective synthesis of multiply twinned structures were gained from the viewpoint of reaction kinetics. Our results showed that the formation of decahedra required a faster reaction rate when compared to the formation of icosahedra in the DEG system, which was also demonstrated by the results of a series of control experiments. The possible mechanisms for the impacts of Na_2SO_4 and HCl on the reaction kinetics were also elucidated in great detail. To our knowledge, this is the first report on the role of reaction kinetics in the selective formation of Pd decahedra and icosahedra. It not only provides a robust route to multiply twinned nanocrystals of Pd but also offers an in-depth understanding of kinetic control for the shape-controlled synthesis of nanocrystals.

RESULTS AND DISCUSSION

Syntheses and Characterizations of Pd Decahedra and Icosahedra. Scheme 1 shows the selective formation of Pd decahedra and icosahedra by introducing different additives into a polyol synthesis based on DEG. When no additive was introduced into the reaction solution, the product was a mixture of Pd decahedra and



Scheme 1. Schematic illustration of the synthetic pathways leading to the formation of Pd nanocrystals with two different twin structures.

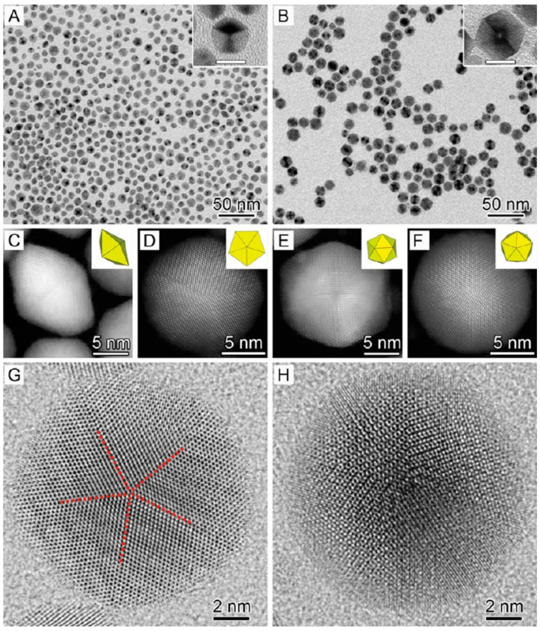


Figure 1. Structural characterizations for Pd decahedra and icosahedra prepared using the standard procedures. (A) TEM image, (C, D) HAADF-STEM images, and (G) HRTEM image of the Pd decahedra; (B) TEM image, (E, F) HAADF-STEM images, and (H) HRTEM image of the Pd icosahedron. The insets in (A) and (B) show higher magnification TEM images of an individual decahedron and icosahedron, respectively. The insets in (C, D) and (E, F) display the 3D models of the nanocrystals corresponding to the HAADF-STEM images. The scale bars in the insets of (A) and (B) are 10 nm.

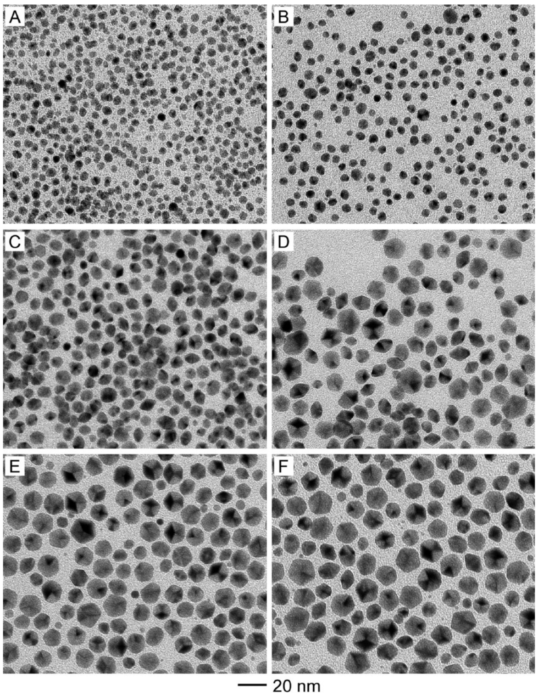


Figure 2. TEM images of Pd decahedra obtained using the standard procedure at different reaction times: (A) 0.5, (B) 1, (C) 2, (D) 4, (E) 6, and (F) 24 h, respectively.

icosahedra. When certain amounts of Na_2SO_4 and HCl were introduced, we obtained samples containing only Pd decahedra and icosahedra, respectively. Figure 1 shows structural characterizations of the Pd decahedra and icosahedra synthesized using the standard procedures. The TEM images at a relatively low magnification (Figure 1A and B) demonstrate the nearly 100% purity for the Pd decahedra with a size of 12.4 ± 1.6 nm and the icosahedra with a size of 15.9 ± 0.9 nm. In this paper, the "size" for a Pd decahedron or icosahedron refers to the dimension "*l*" shown in Figure S1. The insets show TEM images taken from an individual decahedron and icosahedron at a higher magnification. The pentagonal and hexagonal profiles correlate well with the decahedral and icosahedral structures, respectively. The corners of the decahedron were slightly truncated to reduce the surface free energies of these sites.[48] To better resolve the shapes and structures of these two types of nanocrystals, we took high-angle annular dark-field scanning-transmission electron microscopy (HAADF-STEM) and high-resolution TEM (HR-TEM) images from two of the decahedra and icosahedra with right orientations relative to the electron beam. The HAADF-STEM images are shown in Figure 1C–F together with the corresponding models in the insets. Figure 1G and H shows the high-resolution TEM images. As marked by the dashed red lines in Figure 1G, we can clearly resolve the five twin planes. Likewise, the multiply twinned structure of an icosahedron can also be resolved from the HR-TEM image in Figure 1H. The TEM image of Pd nanocrystals synthesized without introducing any additive is provided in Figure S2, showing that the product consisted of 10% decahedra and 90% icosahedra. These results indicate that the composition of the final products could be readily manipulated, shifting from a mixture of decahedra and icosahedra to pure decahedra or icosahedra, with the introduction of different additives at suitable amounts.

To gain insights into the mechanisms responsible for the formation of Pd decahedra and icosahedra, we analyzed the products sampled at different stages of a standard synthesis. Figure 2 shows the shape evolution process for Pd decahedra, while Figure S3A shows the size as a function of reaction time. Specifically, Pd decahedra with an average size of 5.1 nm were obtained at $t = 0.5$ h. These particles then grew to 6.5, 10.0, 13.9, 14.6, and 15.2 nm in size when the reaction time was extended to 1, 2, 4, 6, and 24 h, respectively. This result suggests that the sizes of the Pd decahedra could be readily controlled by simply terminating the synthesis after it had proceeded for different periods of times. This growth pattern could also be applied to the formation of Pd icosahedra, as demonstrated in Figure 3 and Figure S3B. A number of very small particles were also observed in the early stages (up to $t = 2$ h) of a standard synthesis of Pd icosahedra. Since it is very difficult to measure the sizes of such tiny

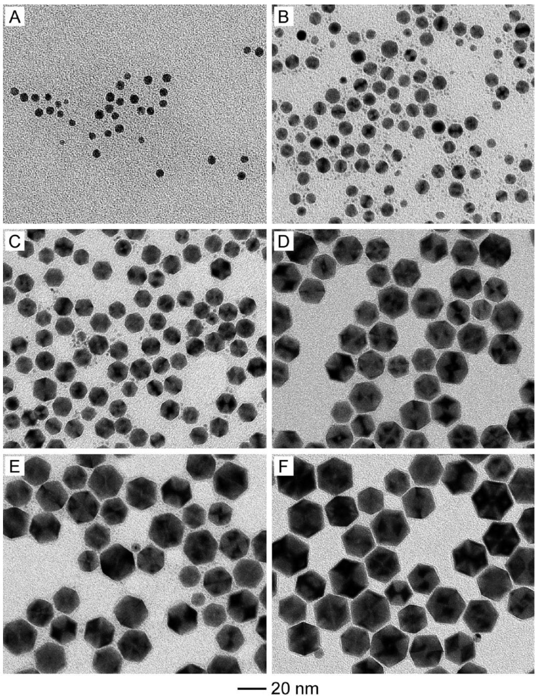


Figure 3. TEM images of Pd icosahedra prepared using the standard procedure at different reaction times: (A) 0.5, (B) 1, (C) 2, (D) 4, (E) 6, and (F) 24 h, respectively.

particles due to their aggregation, we excluded them from our counting when we calculated the average sizes of the Pd icosahedra. At $t = 0.5$ h, small icosahedra with an average size of 6.0 nm were obtained. The size of the icosahedra then increased to 25.0 nm as the reaction time was extended to 24 h. Taken together, we can conclude that the Pd decahedra and icosahedra both evolved from the multiply twinned seeds formed through homogeneous nucleation, which then grew into larger nanocrystals over time without changing their twin structure.

Understanding the Selective Formation of Pd Decahedra and Icosahedra. Two major steps are involved in the formation of metal nanocrystals.[47] The first step corresponds to the formation of seeds through a homogeneous nucleation process, which occurs as a means to reduce the total free energy of the system when the concentration of atoms (or clusters) from the reduction/decomposition of a precursor exceeds the level of supersaturation. Although the details of this process are still unclear, it is generally accepted that the type of seed produced is determined by both thermodynamic and kinetic parameters associated with the synthesis. The second step is the growth of the seeds into larger nanocrystals. During this process, the shape of the nanocrystals is largely determined by the growth rates of different facets. To this end, nanocubes could be obtained by retarding the growth rate of the {100} facets through selective surface capping.[22,47,49] Combined with the experimental observations described above, the selective formation of Pd decahedra or icosahedra should stem from the initial stage, namely, the formation of seeds. Additionally, considering that the same type of (111) plane is exposed on the surfaces of both decahedra and icosahedra, it is reasonable to rule out other effects such as facet-selective capping by an adsorbate. The hypothesis was also supported by the X-ray photoelectron spectroscopy (XPS) data collected from the as-obtained sample of Pd decahedra. As shown in Figure S4, no signal for the sulfur element was detected, suggesting the absence of SO_4^{2-} on the surface of the Pd decahedra. Therefore, we can focus on the effects of additives on the reaction kinetics.

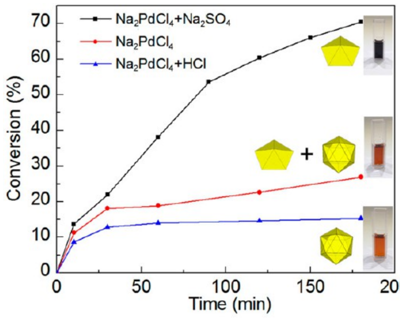


Figure 4. Plots showing the percent conversion of Na_2PdCl_4 into Pd atoms as a function of reaction time in the presence of different additives.

We also measured the percent conversion of $PdCl_4^{2-}$ into elemental Pd at different stages of a synthesis to qualitatively deduce the reduction kinetics responsible for the formation of Pd decahedra or icosahedra. As reported previously, the concentration of $PdCl_4^{2-}$ remaining in a reaction solution could be measured using UV–vis spectroscopy because the concentration of $PdCl_4^{2-}$ ions is directly proportional to the peak intensity at 279 nm.[50] Figure S5A shows the representative UV–vis spectra of the samples obtained at different stages of a standard synthesis of Pd decahedra. To evaluate the possible interferences from other substances in the reaction solution, a UV–vis spectrum (Figure S5B) was also taken from a control sample that was prepared using the same standard procedure (with $t = 180$ min) for the synthesis of Pd decahedra, except that no Na_2PdCl_4 was introduced. Since the Pd particles were removed from the solution by centrifugation prior to UV–vis measurement, we do not have to worry about the possible interference coming from their surface plasmon resonances. The results indicate that it was reliable and feasible to calculate the percent conversions of $PdCl_4^{2-}$ as a function of reaction time based upon the absorbance at 279 nm. Using this method, the percent conversions as a function of reaction time for the standard syntheses of Pd decahedra and icosahedra, as well as for a mixture of these two species, were obtained and are shown in Figure 4. At $t = 10$ min, the conversions were 13.7%, 11.3%, and 8.7% for the cases of decahedra, a mixture of decahedra and icosahedra, and icosahedra, respectively. At $t = 180$ min, the corresponding conversions became 70.4%, 26.9%, and 15.3%, respectively. Since Figure 4 was used only for a qualitative understanding of the correlation between the shape of nanocrystals and the reduction kinetics, we conducted only one single UV−vis measurement for each data point. From these data, it can be concluded that the reduction rate of the precursor followed the trend of decahedron $\gg$ decahedron + icosahedron > icosahedra. Our visual observations of the solutions were in good agreement with this trend. The pictures of the reaction solutions at t = 180 min are shown as insets next to the corresponding conversion curves. The color of the solution for the synthesis of decahedra was black, while the color of the solutions for the syntheses of icosahedra and the mixture were still brown due to high concentrations of $PdCl_4^{2-}$ ions. This finding further supports the argument that the reduction rate for the formation of decahedra must be much faster when compared to that for the formation of icosahedra.

To verify the effects of reaction kinetics on the synthesis of Pd decahedra, a set of control experiments were conducted. Since the reducing power of a polyol system can be enhanced at higher pH values, different amounts of NaOH were introduced into the DEG solution to adjust the reduction kinetics.[51,52] Figure S6 shows TEM images of the Pd nanocrystals obtained by adding different amounts of NaOH into the reaction system. As the amount of NaOH was increased from 0.1 to 1.0 mg, the products shifted from a mixture of decahedra and icosahedra to pure decahedra, as shown in Figure S6A and B. By increasing the amount of NaOH to 5.0 mg, a number of small particles with irregular shapes started to appear (Figure S6C). In this case, the reduction rate was extremely fast, resulting in the formation of a huge number of nuclei. These experiments further confirmed the need of a faster reaction rate for the preparation of decahedra relative to what was required for icosahedra. Significantly, the different requirements on the reaction kinetics for the two different types of multiply twinned structures allow us to selectively generate Pd decahedra and icosahedra as pure samples by controlling various experimental parameters.

Ethylene glycol is most commonly used in the polyol syntheses of noble-metal nanocrystals.[53−55] When applied to Pd, the products were typically single-crystal species such as cubes, bars, and cuboctahedra, primarily due to the fast reduction kinetics associated with EG.[9,17,19,36] According to simulations, multiply twinned structures are favorable only under slow reduction kinetics.[47] In a recent study, we successfully synthesized Pd icosahedra in EG by introducing HCl to slow the reaction kinetics.[43] We also noticed that Pd decahedra started to appear in the products (with a percentage below 5%) when the amount of HCl added into the reaction solution was reduced. However, it was very difficult to increase the purity of decahedra by accessing the proper kinetics due to the strong reducing power of EG.

To verify the stronger reducing power of EG relative to DEG, a series of experiments were conducted using experimental parameters similar to the standard synthesis of Pd decahedra or icosahedra except for the substitution of DEG by EG. The reaction kinetics was monitored. As shown in Figure S7 and Figure 4, the reducing power of EG is much stronger than that of DEG, which could be attributed to the shorter hydrocarbon chain of EG.[56] The TEM images of Pd nanocrystals obtained in EG solution with different additives are shown in Figure S8. When Na_2SO_4 was introduced into the reaction solution, very tiny octahedral nanocrystals were obtained. With no additives, a mixture of decahedra and tiny octahedra was produced. When HCl was added, icosahedra could be synthesized in high purity. Taken together, it is clear that DEG played an important role in the standard syntheses due to its capability to access the right kinetics for either decahedra or icosahedra by increasing or decreasing the reduction rate through the addition of different additives.

The effects of other parameters, such as the amounts of PVP and salt precursor, were also studied from the perspective of reaction kinetics. Figure S9A and B show TEM images of Pd nanocrystals obtained by changing the amount of PVP to 30.0 and 200.0 mg, respectively, while keeping all other experimental conditions the same as in the standard procedure. The percentage of decahedral structures obtained by adding 30.0 mg of PVP dropped to 50%, and further to 35% when 200.0 mg of PVP was introduced. The results indicate that the amount of PVP in the system has a significant impact on the purity of Pd decahedra. Generally speaking, PVP, a common stabilizer in the polyol syntheses of noble-metal nanocrystals, serves two roles in determining the reaction kinetics: (i) PVP can coordinate with Na_2PdCl_4 to form PVP-$PdCl_4^{2-}$, which is more difficult to reduce,[31] and (ii) PVP can act as a reducing agent in a synthesis due to the hydroxyl group present in PVP.[57,58] The former effect can slow the reduction rate, whereas the latter can speed up the reduction. Therefore, there must be an optimum amount of PVP needed to produce Pd decahedra as a pure sample. This is in good agreement with our observations since we found that pure Pd decahedra could be produced by introducing 80.0 mg of PVP. TEM images of the products prepared by altering the amount of Na_2PdCl_4 added are shown in Figure S9C and D. A mixture of Pd decahedra and icosahedra with smaller sizes was obtained when decreasing the amount of Na_2PdCl_4 to 3.1 mg. On the other hand, when the amount of Na_2PdCl_4 was increased to 31.0 mg, Pd decahedra were obtained with high purity, >95%. Since the reaction rate typically increases with increasing the concentration of the precursor, we can once again conclude that fast reaction kinetics is necessary for the production of Pd decahedra in high purity.

How Does an Additive Affect the Reaction Kinetics: HCl *vs* Na_2SO_4. In general, two types of additives can be explored to tune the reduction kinetics of a nanocrystal synthesis. The first type of additive can adjust the reduction rate by coordinating with the precursor to form a more stable complex. For example, KBr has been widely used to tune the kinetics of Pd nanocrystal synthesis because Br^- has a stronger binding energy with Pd^{2+} than Cl^- and thus could form a more stable $[PdBr_4]^{2-}$ complex.[22,25] The second type of additive can control the reduction rate *via* regulation of the pH of a solution, such as NaOH or KOH in the polyol synthesis of Pd nanocrystals.[33,51,52]

To a standard synthesis of Pd icosahedra, 10.0 μL of HCl (3.0 M) was also added into the DEG solution. As shown in Figure 4, the reduction kinetics was slowed when HCl was introduced into the system. Two mechanisms are responsible for this change: (i) decreasing the pH of the solution upon the addition of HCl, which has an impact opposite what was observed for the addition of NaOH,[33,51,52] and (ii) increasing the concentration of Cl^-, thus making the $PdCl_4{}^{2-}$ more difficult to reduce due to the shift in chemical equilibrium and consequently slowing the reduction kinetics.[26,31]

In contrast to HCl, it was found that Na_2SO_4 could substantially speed up the reduction rate, as indicated by the increased conversion of $PdCl_4{}^{2-}$ to Pd atoms (see Figure 4). To elucidate the effect of Na_2SO_4 on the reaction kinetics, a set of experiments were designed. First, K_2SO_4 and $MgSO_4$, with equal molar concentrations were used to substitute Na_2SO_4 while keeping all other parameters fixed. The TEM images of the products obtained by adding K_2SO_4 and $MgSO_4$ both demonstrated the formation of Pd decahedra in high purity, as shown in Figure 5. This result reveals that the $SO_4{}^{2-}$ ions play a crucial role in regulating the reduction rate during the synthesis and thus increase the yield of the decahedra in the product.

Because the reduction rate is accelerated by the $SO_4{}^{2-}$ ions, it is reasonable to exclude the possibility of forming a complex between Pd^{2+} and $SO_4{}^{2-}$ ions. Such a complex, if formed, would be more difficult to reduce than $PdCl_4{}^{2-}$. Additionally, Na_2SO_4 is a salt of a strong acid and strong base, which should have no effect on the pH of the solution and, thus, no influence on the reaction kinetics through this route. These results suggest that the $SO_4{}^{2-}$ ions influence reaction kinetics through an interaction with the reducing agent. The $SO_4{}^{2-}$ ion consists of a central sulfur atom surrounded by four oxygen atoms in a tetrahedral arrangement, while the DEG is a mild reductant with two terminal hydroxyl groups. On the basis of a structural analysis, a possible mechanism can be proposed. As shown in Scheme 2, the oxygen atoms in $SO_4{}^{2-}$ can interact with the hydrogen atoms in the hydroxyl group of DEG to generate hydrogen bonds between $SO_4{}^{2-}$ and DEG. Previous reports have shown that the oxygen atoms in the $SO_4{}^{2-}$ ion could form hydrogen bonds with the hydrogen atoms in H_2O.[59] The newly formed hydrogen bonds make it easier for the hydroxyl groups to dehydrogenate.[60] In other words, DEG is more prone to be oxidized to aldehyde when $SO_4{}^{2-}$ is introduced into the solution. Since aldehyde is the actual reductant involved in a polyol reaction, more aldehyde means higher concentration of reductant and thus a faster reaction rate.[61]

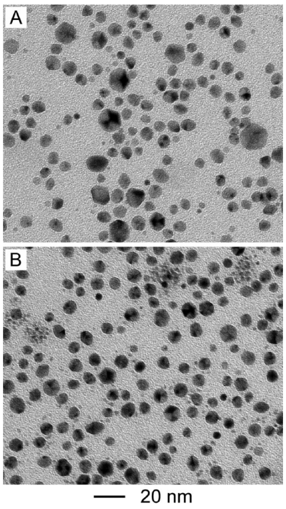
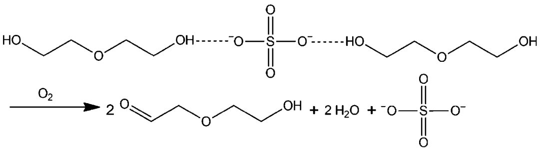


Figure 5. TEM images of Pd nanocrystals synthesized using the standard procedure for decahedra except for the substitution of Na_2SO_4 by (A) K_2SO_4 and (B) $MgSO_4$, respectively.



Scheme 2. Schematic illustration showing the interaction between $SO_4{}^{2-}$ and DEG molecule.

To verify the mechanism proposed for $SO_4{}^{2-}$ ions, we have also replaced it with $NaNO_3$, a salt with properties more or less similar to those of Na_2SO_4, in a standard synthesis of Pd decahedra. The percent conversion plot and TEM image of the products in Figure S10 indicate that $NaNO_3$ could also accelerate the reduction kinetics, leading to the formation of singly twinned particles, in addition to multiply twinned particles. A more detailed study is under way to elucidate the exact role of this additive in inducing the formation of Pd nanocrystals with a singly twinned structure. At the moment, it can be concluded that the $NO_3{}^-$ ions were able to accelerate the reduction kinetics, just like the $SO_4{}^{2-}$ ions.

The influence of the Na_2SO_4 concentration was further investigated by introducing different amounts

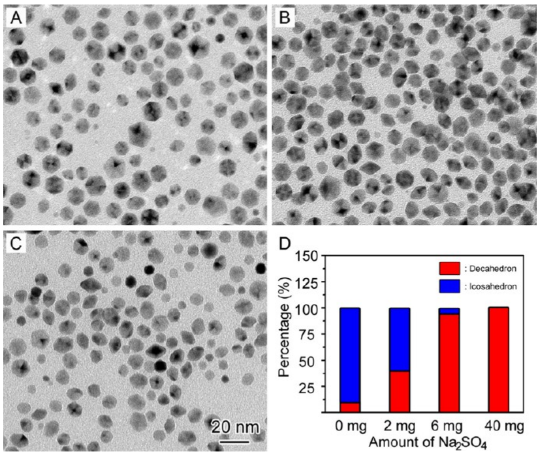


Figure 6. Effects of the concentration of Na_2SO_4 on the shape of Pd nanocrystals. TEM images of Pd nanocrystals obtained using the standard procedure for Pd decahedra except for the addition of Na_2SO_4 in different amounts: (A) 2.0, (B) 6.0, and (C) 80.0 mg. (D) Summary of the percentages of decahedral and icosahedral nanocrystals as a function of the amount of Na_2SO_4 introduced. The scale bar in (C) also applies to (A) and (B).

of Na_2SO_4 into the reaction system while keeping all other parameters the same as in the standard procedure. As shown in Figure 6A, a mixture of decahedra (40%) and icosahedra (60%) was obtained when 2.0 mg of Na_2SO_4 was introduced into the solution. By increasing the amount of Na_2SO_4 to 6.0 mg, the decahedra were obtained in much higher purity (95%, Figure 6B). In our experiments, we found that the solubility of Na_2SO_4 in DEG was very limited (less than 3.3 mg/mL) by checking the bottom of the vial after the reaction. Thompson and coauthors reported that the weight percent of Na_2SO_4 in saturated EG solution was only 0.487%.[62] Because of the similarity between DEG and EG, we can conclude that Na_2SO_4 is likely not very soluble in DEG either. Furthermore, we found that the excellent quality of Pd decahedra was produced after the DEG solution was saturated with Na_2SO_4, as shown in Figure 1A. When 80.0 mg of Na_2SO_4 was introduced, pure decahedra could be readily produced (Figure 6C). As mentioned previously, a mixture of decahedra (*ca.* 10%) and icosahedra (*ca.* 90%) was obtained without the addition of Na_2SO_4 into the reaction solution (Figure S3). The percentages of the decahedral and icosahedral nanocrystals obtained by measuring 100 nanoparticles for each sample, as a function of the amount of Na_2SO_4 added, are presented in Figure 6D. The results indicate that the percent of decahedra in the products increased from 10% to nearly 100% with increasing the concentration of Na_2SO_4. This finding could be understood by our proposed mechanism. With more SO_4^{2-} ions dissolved in DEG, more hydrogen bonds could be formed and, thus, more conversion of DEG to aldehyde, which led to a faster reduction rate. Consequently, the yield of Pd decahedra could be tuned by changing the amount of Na_2SO_4 introduced into the reaction system.

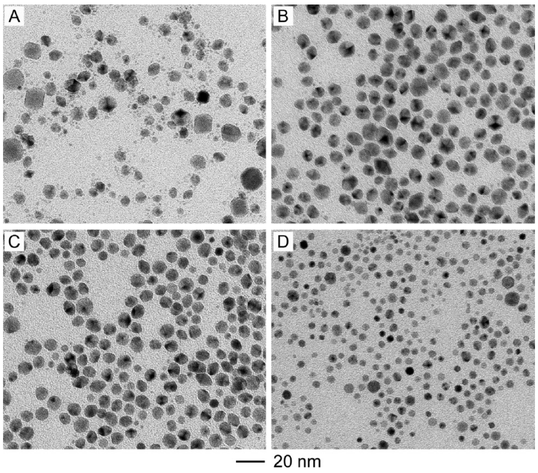


Figure 7. Effects of reaction temperature on the structures of Pd nanocrystals. TEM images of Pd nanocrystals synthesized using the standard procedure for Pd decahedra except for the use of different reaction temperatures: (A) 85, (B) 95, (C) 115, and (D) 125 °C.

Furthermore, the better control enabled by additives was markedly more significant when compared to the effects of other parameters. For example, owing to the positive exponential correlation between the reaction rate and temperature, based on the Arrhenius equation, the percentages of the twinned structures are likely sensitive to the temperature of the reaction. Further experiments were performed to study the temperature-related effects by using the standard amount of Na_2SO_4 (40.0 mg). The TEM images of Pd nanocrystals obtained at different reaction temperatures (from 85 to 125 °C) are shown in Figure 7. The product at 85 °C was a mix of decahedra and other morphologies, such as singly twinned structures and octahedra. To our surprise, decahedra were obtained in high purity in the temperature range from 95 to 115 °C. When the temperature was increased to 125 °C, single-crystal nanostructures with smaller sizes were obtained, owing to the faster reduction kinetics resulting from the high temperature. It seems contradictory that the pure decahedral nanocrystals could be produced in such a wide range of temperatures. Two possible reasons may be responsible for this result: with temperature rising, the strength of the hydrogen bonds is weakened, thus reducing the degree of DEG dehydrogenation; meanwhile, the rate of oxidation of DEG to aldehyde is increased. These two factors could balance the reaction kinetics into a reasonable region. Thus, the decahedral structure, a very tricky shape, could be synthesized in such a wide range of temperature, which also implies the excellent reproducibility of our synthetic approach based on the introduction of Na_2SO_4.

CONCLUSION

We have successfully synthesized Pd decahedra and icosahedra with tunable sizes of 5–15 nm and

6–25 nm, respectively, at nearly 100% purity using the same polyol system. The selective production of a specific twin structure was achieved through the introduction of a proper additive, namely, Na_2SO_4 for decahedra and HCl for icosahedra. Furthermore, we have found that the necessary reaction kinetics for the synthesis of decahedra was faster than that of icosahedra. According to this correlation, NaOH, another additive that can accelerate the reaction kinetics, was also shown to facilitate the production of Pd decahedra through the increase of pH in the system. Moreover, the effects of various additives were studied in detail. The results showed that HCl could slow the reaction rate by reducing the pH of the reaction solution and increasing the difficulty to reduce $[PdCl_4]^{2-}$ complexes. Additionally, it was found that Na_2SO_4 could speed up the reaction kinetics of the same polyol system. The formation of hydrogen bonds between oxygen atoms in SO_4^{2-} ions and hydrogen atoms in the hydroxyl groups of DEG allow the hydroxyl groups in DEG to easily oxidize into aldehyde groups, which is likely responsible for the faster reaction kinetics. The hypothesis was further supported by our observation on the role of NO_3^- ions in speeding up the reduction kinetics. Significantly, the percentage of decahedra could be tuned from 10% to nearly 100% by increasing the concentration of Na_2SO_4. With the use of Na_2SO_4, the range of reaction temperature suitable for the production of Pd decahedra could be as wide as 20 °C (from 95 to 115 °C). This further highlights the unique merits of Na_2SO_4, which possesses the ability to fine-tune the reaction kinetics. In conclusion, this work not only offers a facile and robust route to the selective syntheses of Pd decahedra and icosahedra as pure samples but also advances our understanding of shape-controlled syntheses of noble-metal nanocrystals.

EXPERIMENTAL SECTION

Chemicals and Materials. Diethylene glycol (≥99.0%, lot no. BCBJ9740), sodium tetrachloropalladate(II) (Na_2PdCl_4, 99.998%), aqueous HCl solution (37%), sodium hydroxide (NaOH, 99.99%), sodium sulfate (Na_2SO_4, ≥99.0%), potassium sulfate (K_2SO_4, ≥99.0%), magnesium sulfate ($MgSO_4$, ≥99.5%), sodium nitrate ($NaNO_3$, ≥99.0%), and poly(vinylpyrrolidone) (PVP, $M_w \approx 55\,000$) were all obtained from Sigma-Aldrich. Ethylene glycol (lot no. K43B24) was purchased from J. T. Baker. All the chemicals were used as received. Deionized (DI) water of 18.2 MΩ·cm in resistivity was used throughout the experiments.

Syntheses of Pd Decahedra and Icosahedra in DEG. In a standard procedure for the synthesis of Pd decahedra, 80.0 mg of PVP and 40.0 mg of Na_2SO_4 were introduced into 2.0 mL of DEG hosted in a 20 mL vial, and the mixture was preheated in an oil bath at 105 °C for 20 min under magnetic stirring. Subsequently, 1.0 mL of DEG solution containing 15.5 mg of Na_2PdCl_4 was added using a pipet. After the reaction had proceeded for 3 h, it was quenched by immersing the vial in an ice–water bath. Finally, the product was collected by centrifugation and washed once with acetone and then twice with DI water to remove DEG and excess PVP. For the standard synthesis of Pd icosahedra, a similar procedure was used, except for the substitution of the Na_2SO_4 by 10.0 μL of aqueous HCl solution (3.0 M).

Measurements of Percent Conversions of the Precursor during the Syntheses of Pd Decahedra and Icosahedra. UV–vis spectroscopy was used to qualitatively analyze the reaction kinetics for the standard syntheses of Pd decahedra and icosahedra. Typically, an aliquot of 0.3 mL was sampled from the reaction solution at different stages using a pipet and immediately injected into 2.7 mL of aqueous HCl solution (0.1 M) to prevent the hydrolysis of $PdCl_4^{2-}$. The solution was then centrifuged at 55 000 rpm for 1 h to precipitate out the Pd nanoparticles. The supernatant was then collected and diluted with the same aqueous HCl solution for UV–vis measurement. The concentration of $PdCl_4^{2-}$ ions remaining in the solution at a specific reaction time could be calculated by comparing the absorbance at 279 nm with a calibration curve. The conversion of $PdCl_4^{2-}$ to Pd atoms can be derived from the concentrations of the initial and remaining $PdCl_4^{2-}$.

Instrumentation. Transmission electron microscopy images were obtained using a Hitachi HT-7700 microscope operated at 120 kV. HR-TEM and HAADF-STEM images were acquired with a JEOL JEM 2200FS STEM/TEM microscope equipped with a CEOS probe corrector (Heidelberg, Germany) to provide a nominal image resolution of 0.07 nm. UV–vis absorption spectra were recorded with a Lambda 750 spectrometer (PerkinElmer). The XPS data were recorded using a Thermo K-Alpha spectrometer with an Al Kα source (eV). An Eppendorf centrifuge (5430) was used for the centrifugation and washing of all samples.

Conflict of Interest: The authors declare no competing financial interest.

Acknowledgment. This work was supported in part by research grants from NSF (DMR, 1215034) and startup funds from Georgia Institute of Technology. As a visiting Ph.D. student from Zhejiang University, H.H. was also partially supported by a Fellowship from the China Scholarship Council. J.L. gratefully acknowledges the support by Arizona State University and the use of facilities in the John M. Cowley Center for High Resolution Electron Microscopy at Arizona State University.

Supporting Information Available: Definition of the size of a Pd decahedron and icosahedron; TEM image of Pd nanocrystals obtained using the standard procedure without adding additives; the average size of Pd decahedra and icosahedra synthesized using the standard procedure as a function of reaction time; XPS spectra collected from a typical sample of Pd decahedra; UV–vis absorption spectra recorded from a control sample and samples obtained at different stages of a standard synthesis of Pd decahedra; TEM images of Pd nanocrystals prepared by adding different amounts of NaOH; plots showing the percent conversion of Na_2PdCl_4 into Pd atoms in EG as a function of reaction time in the presence of different additives; TEM images of Pd nanocrystals obtained using EG with the addition of different additives; TEM images of Pd nanocrystals produced using the standard procedure for Pd decahedra with different amounts of PVP and Na_2PdCl_4 used; plots showing the percent conversion of Na_2PdCl_4 to elemental Pd as a function of reaction time in the presence and absence of $NaNO_3$, as well as the TEM image obtained in the presence of $NaNO_3$. This material is available free of charge *via* the Internet at http://pubs.acs.org.

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