Electronic Supplementary Information

Close insights into the growth pattern of palladium nanocubes with controllable sizes

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Calculation of Electrochemical Details for Typical Synthesis Procedure. The conditional reduction potential $E'_{AA}$ for AA in equation 3 can be described as follows (modified from reference 35):

$$E'_{AA} = 0.553 - \frac{RT}{F} \text{pH} + \frac{RT}{F} \ln \left[ \frac{[AAO]}{[AR]} \right] + \frac{RT}{2F} \ln \frac{K_O}{K_R} - \frac{RT}{2F} \ln \frac{K_O + [H^+]}{K_R + [H^+]}$$

(S1)

where $[AAO]$ and $[AR]$ indicate the equilibrium concentrations of AA in oxidative and reductive states, respectively. $K_O$ and $K_R$ are the first dissociation constants of the oxidized and reduced AA, respectively. Because of its weak acidity, AA with the oxidative form can be considered as a monovalent acid, and the values of $pK_O$ and $pK_R$ are given as 9.0 and 4.17. Considering the dosage of AA and ignoring the influence of other ions, the initial pH of the reaction system is 2.82.

Under typical synthesis procedure, when the reduction process is complete, the equilibrium concentrations of $[\text{PdCl}_4]^{2-}$, $\text{Cl}^-$, $[AAO]^{-}$, and $[AR]^{-}$ are calculated to be $1.00 \times 10^{-6}$, $8.00 \times 10^{-2}$, $2.00 \times 10^{-2}$, and $1.41 \times 10^{-2}$ mol/L, respectively. Hence, the value of $E'_{AA}$ is 0.306 V, and the conditional reduction potential for $[\text{PdCl}_4]^{2-}/\text{Pd}$ is 0.534 V.

Calculation of the Mole Fraction of Br in a Pd Nanocube. Because of the close values of the size of $\text{Br}^{-}$ ($r_{Br}$) and the distance of Pd (200) faces (0.5 $a$), we define $2r_{Br}$ to be equal to $a$ for simplification. Hence, the value for lattice constant of Pd is $a$. For a Pd nanocube with edge length of $n$, the number of atoms on surfaces is $N$, and the total amount of Pd atoms in the cube is $N_{Pd}$

$$N = 2 \times 6 \times \left( \frac{n}{a} \right)^2 = \frac{12n^2}{a^2}$$

(S2)
\[ N_{\text{Pd}} = 4 \times \left( \frac{n}{a} \right)^3 = \frac{4n^3}{a^3} \]  

(S3)

According to Scheme 2, every two Pd atoms possess one \( \text{Br}^- \), and the number of \( \text{Br}^- \) on cubic surface is \( N_{\text{Br}} \).

\[ N_{\text{Br}} = \frac{1}{2} N = \frac{6n^2}{a^2} \]  

(S4)

Consequently, the mole fraction \( \text{Br}^- \) in Pd cube is \( \chi \).

\[ \chi = \frac{N_{\text{Br}}}{N_{\text{Pd}}} = \frac{3a}{2n} \]  

(DS4)

**DFT Calculations.** To analysis the properties of different Pd low-index facets, First-principle DFT calculations were employed with the pseudo-potential plane-wave method. Three different facets with 5 layer atomic thickness, namely \{100\}, \{110\} and \{111\}, were cleaved and covered by a vacuum slab of 10 Å. The geometries are full optimized via generalized gradient approximation (GGA) with Perdew-Burke-Ernzerhof (PBE) approximation\(^1\). The \( k \)-point was defined at \( 2 \times 2 \times 1 \). The calculations of electron density maps (Scheme S1) were performed with CASTEP\(^2\).

To study the physical adsorption behavior of \( \text{Br}^- \) onto the top layer of Pd \{100\} facet, classical grand canonical Monte Carlo (GCMC) simulations were applied through Adsorption Locator module\(^3\), \(^4\). The simulations were performed with the standard universal force field (UFF) in the temperature range of 300–500 K. The \( \text{Br}^- \) was adsorbed onto the octahedral cavity (Scheme S2) with adsorption energy of -0.8863 kcal/mol.
Fig. S1. HRTEM images of twinned crystals generated while preparing Pd nanocubes: (A) decahedron, (B) icosahedron, (C) triangular bipyramid and (D) pentagonal rod. Images inserted indicate the corresponding FFT pattern of each structure.
Fig. S2. TEM images of Pd nanocrystals reacted for (A) 3, (B) 7 and (C) 10 h under typical synthesis procedure. Scale bar: 50 nm.
Fig. S3. TEM images of Pd nanocrystals prepared under typical synthesis procedure where KBr was replaced by same concentrations of (A) KI or (B) KCl, or same amount of (C) K$_2$PdBr$_4$ was occupied instead of K$_2$PdCl$_4$. Scale bar: 50 nm.
Fig. S4. TEM images of Pd nanostructures obtained with different concentrations of KBr (mmol/L):

(A) 630, (B) 315, (C) 158, (D) 78.8 to (E) 0. Scale bar: 20 nm. (Width: the mean width of nanostructures; Avg. $L/W$: the average aspect ratio.)
Fig. S5. TEM image and size distribution of Pd nanocubes gained with the concentration of KBr at 1.26 mol/L.
Fig. S6. TEM images of as-synthesized Pd nanoparticles based on the concentrations of reagents in Table S1 with AA as reducing agent and KBr as capping agent. Scale bar: 50 nm.
Table S1. Reagent concentrations for each reaction.

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<thead>
<tr>
<th>Items</th>
<th>Dosage of KBr / mmol/L</th>
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<tr>
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<td>22.7</td>
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Scheme S1. Electron density map of (A) {100}, (B) {111} and (C) {110} Pd facets gained through primary DFT calculation.

Scheme S2. Schematic illustration of one Br⁻ adsorbed onto Pd {100} facet.
REFERENCES


