What dictates who, I$^-$ and Br$^-$, mediates the growth of cubic Pd nanocystals?

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**Figures and Captions**

**Fig. S1.** TEM image of CPNCs in the I$^-$-mediated case without the modification of pH.
Fig. S2. HRTEM image of Pd nanospheres at pH = 11.58
**Fig. S3.** TEM images of Pd particles in the $\Gamma$-mediated case by modifying the pH of the reaction system with KOH: (a) pH $\approx 11.71$ and (b) pH $\approx 11.90$.

**Fig. S4.** TEM images of Pd particles in the $\Gamma$-mediated case by modifying the pH of the reaction system with HClO$_4$: (a) pH $\approx 2.18$ and (b) pH $\approx 2.05$. 
Fig. S5. TEM images of Pd particles in the $\Gamma$-mediated case with pH = 2.37 modified by HNO$_3$ (a) and HCl (b).
Fig. S6. TEM images of as-formed products in the I\textsuperscript{−}-mediated case with pH = 10.67 after addition of KClO\textsubscript{4} or KCl: (a) $c_{\text{ClO}_4^{-}} = 2.4$ mmol/L, (b) $c_{\text{ClO}_4^{-}} = 4.8$ mmol/L, (c) $c_{\text{Cl}^{-}} = 2.4$ mmol/L, and (d) $c_{\text{Cl}^{-}} = 4.8$ mmol/L.

According to Fig. 1, S4 and S5, the anion of as-selected acid plays a certain role in the morphology control of Pd nanoparticles when pH < 2.72.

In the I\textsuperscript{−}-mediated case with pH = 2.37, when HClO\textsubscript{4} was used as the pH modifier ($c_{\text{ClO}_4^{-}} = 2.4$ mmol/L), CPNCs with a yield of ~90 % could be produced (Fig. 1f), but the side length increased and fluctuated between ~15 and ~21 nm; when HCl was used as the pH modifier ($c_{\text{Cl}^{-}} = 2.4$ mmol/L), the side length of as-formed CPNCs varied between ~9 and
~26 nm (Fig. S5b). Obviously, the introduction of anions caused CPNCs to lose size-uniformity, and the effect of Cl\(^{-}\) is more remarkable than ClO\(_4\)^{2-}.

To clarify the effect of anions on the growth of CPNCs when pH > 2.72, we choose the I\(^{-}\)-mediated case with pH = 10.67 as the reaction system (Fig. 1c) to investigate the effect of anions, for example, ClO\(_4\)^{-} and Cl\(^{-}\) ions. KClO\(_4\) or KCl was deliberately added into the reaction system, and the concentration of ClO\(_4\)^{-} or Cl\(^{-}\) was controlled as 2.4 mmol/L, just like the case of pH = 2.37.

ClO\(_4\)^{-} ions had a minor effect on the growth of CPNCs when c\(_{\text{ClO}_4}\) = 2.4 mmol/L (Fig. S6a): as-formed CPNCs were nearly the same as those obtained without addition of KClO\(_4\) (Fig. 1c). When c\(_{\text{ClO}_4}\) = 4.8 mmol/L (Fig. S6b), CPNCs still had uniform sizes, but the average side length is ~1 nm larger than that without addition of KClO\(_4\) or with c\(_{\text{ClO}_4}\) = 2.4 mmol/L. When KCl was added (c\(_{\text{Cl}}\) = 2.4 mmol/L), the morphology and size of as-formed CPNCs (Fig. S6c) nearly resemble those obtained without the addition of KCl (Fig. 1c) except for a few large irregular particles. When c\(_{\text{Cl}}\) = 4.8 mmol/L, more irregular particles appeared (Fig S6d).

The results above indicate that the effect of anions still exists when pH > 2.72. However, different anions exhibited different effects, depending on the adsorption strength of anions towards Pd species. Cl\(^{-}\) ions have much strong adsorption towards Pd species than ClO\(_4\)^{-}, and thus have a big impact on the growth of CPNCs, consistent with the case of pH < 2.72.
**Fig. S7.** TEM images of Pd particles in the Br\(^{-}\)-mediated case in the solution with different pH modified by HClO\(_4\): (a) pH = 1.47 and (b) pH = 0.71.

**Fig. S8.** TEM images of Pd particles in the Br\(^{-}\)-mediated case by modifying the pH of the reaction system with HNO\(_3\): (a) pH ≈ 2.18 and (b) pH ≈ 2.02.
Fig. S9. TEM images of Pd particles in the Br$^-$-mediated case by modifying the pH of the reaction system with HCl: (a and b) pH = 2.37, (c) pH = 2.12, (d and e) pH = 2.02 and (f) pH = 1.95.
**Fig. S10.** (a) UV-vis spectra of PdI$_4^{2-}$ of different concentrations in EG solution containing PVP identical to the reaction mixture used for the standard reduction process. (b) The linear dependence between the absorbance intensity at ~342 nm and the concentration of Pd$^{2+}$.

**Fig. S11.** (a) UV-vis spectra of PdBr$_4^{2-}$ of different concentrations in EG solution containing PVP identical to the reaction mixture used for the standard reduction process. (b) The linear dependence between the absorbance intensity at ~286 nm and the concentration of Pd$^{2+}$. 
Fig. S12. TEM images of Pd products obtained at different reaction times in the $\Gamma$-mediated case with pH = 2.72: (a) 15 min, (b) 20 min, (c) 25 min, (d) 30 min, (e) 35 min, and (f) 40 min.

Fig. S13. Side length-distribution histograms of CPNCs obtained at different times, as shown in Fig. S11(c-f): (a) 25 min, (b) 30 min, (c) 35 min and (d) 40 min. (e) Time-dependent relation between average side length and reaction time.
**Fig. S14.** Stabilization energies of Pd\(^{2+}\) complexes obtained at B3LYP/aug-cc-pVDZ level.

![Diagram of Pd\(^{2+}\) complexes energies](image)

\[
\begin{align*}
318.6 \text{ kcal/mol} & \quad \text{[Pd(H\(_2\)O)\(_6\)]}^{2+} \\
321.8 \text{ kcal/mol} & \quad \text{[Pd(H\(_2\)O)\(_4\)]} \cdot \text{E(O)}^{2+} \\
615.6 \text{ kcal/mol} & \quad \text{[Pd(I\(_2\)O)\(_4\)]} \cdot 2\text{I}^{2-} \\
624.6 \text{ kcal/mol} & \quad \text{[Pd(I\(_2\)O)\(_4\)]} \cdot 2\text{Br}^{2-} \\
695.6 \text{ kcal/mol} & \quad \text{[Pd(I\(_2\)O)\(_4\)]} \cdot 2\text{OH}^{2-}
\end{align*}
\]

**Fig. S15.** TEM images of Pd particles obtained in the Br\(^{-}\)-mediated original solutions (pH = 2.72) at 125 (a) and 110 °C (b).

![TEM images of Pd particles](image)

(100 nm)
Table S1. Solution and surface reduction rate constants of Pd$^{2+}$ at different pH in the $\Gamma$- or $\text{Br}^-$-mediated cases.

<table>
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<th>system</th>
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<th>surface reduction</th>
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<td></td>
<td>$k_1$/min$^{-1}$</td>
<td>$k_2$/mmol/L min$^{-1}$</td>
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<tr>
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