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 Γ -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 I⁻-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 Γ -mediated case by modifying the pH of the reaction system with HClO₄: (a) pH \approx 2.18 and (b) pH \approx 2.05.



Fig. S5. TEM images of Pd particles in the I^- -mediated case with pH = 2.37 modified by HNO₃ (a) and HCl (b).



Fig. S6. TEM images of as-formed products in the I⁻-mediated case with pH = 10.67 after addition of KClO₄ or KCl: (a) $c_{ClO_{4}} = 2.4 \text{ mmol/L}$, (b) $c_{ClO_{4}} = 4.8 \text{ mmol/L}$, (c) $c_{Cl} = 2.4 \text{ mmol/L}$, and (d) $c_{Cl} = 4.8 \text{ mmol/L}$.

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⁻-mediated case with pH = 2.37, when HClO₄ was used as the pH modifier $(c_{ClO_{4}} = 2.4 \text{ mmol/L})$, 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 $(c_{Cl^{-}} = 2.4 \text{ mmol/L})$, 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 CI^- is more remarkable than CIO_4^- .

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, CIO_4^- and CI^- ions. $KCIO_4$ or KCI was deliberately added into the reaction system, and the concentration of CIO_4^- or CI^- was controlled as 2.4 mmol/L, just like the case of pH = 2.37.

 CIO_4^- ions had a minor effect on the growth of CPNCs when $c_{CIO_4^-} = 2.4 \text{ mmol/L}$ (Fig. S6a): as-formed CPNCs were nearly the same as those obtained without addition of KCIO₄ (Fig. 1c). When $c_{CIO_4^-} = 4.8 \text{ mmol/L}$ (Fig. S6b), CPNCs still had uniform sizes, but the average side length is ~1 nm larger than that without addition of KCIO₄ or with $c_{CIO_4^-} = 2.4 \text{ mmol/L}$. When KCI was added ($c_{CI^-} = 2.4 \text{ mmol/L}$), the morphology and size of as-formed CPNCs (Fig. S6c) nearly resemble those obtained without the addition of KCI (Fig. 1c) except for a few large irregular particles. When $c_{CI^-} = 4.8 \text{ mmol/L}$, 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 HNO₃: (a) pH \approx 2.18 and (b) pH \approx 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 Γ -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 Pd²⁺ complexes obtained at B3LYP/aug-cc-pVDZ level.



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

_	system	Modifier of pH	рН	rate constant	
				solution reduction	surface reduction
				$k_{1}/{\rm min}^{-1}$	k_2 /mmol/L min ⁻¹
	KI	HClO ₄	2.18	7.27×10^{-3}	3.08×10^{-2}
		КОН	11.45	9.94×10^{-3}	$2.07 imes 10^{-1}$
			11.90	4.06×10^{-1}	4.86×10^{-14}
	KBr	HClO ₄	1.01	4.06×10^{-2}	$4.48 imes 10^{-1}$
			1.67	9.90×10^{-2}	4.64×10^{-1}
		-	2.72	4.95×10^{-1}	2.72×10^{-16}

Table S1. Solution and surface reduction rate constants of Pd^{2+} at different pH in the I⁻ or Br⁻-mediated cases.