

Supporting Information

Palladium Nanocrystals Bound by {110} or {100} Facets: From One Pot Synthesis to Electrochemistry

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1. Experimental Section

Synthesis of Pd RD NCs (Recipe I):

In a typical synthesis, 500 μ L aliquot of 10 mM H_2PdCl_4 solution and 50 μ L of 1 mM KI solution were added to 10 mL of 25.0 mM CTAB solution heated at 95 °C under stirring at 250 rpm. After 5 min, 80 μ L of freshly prepared 100 mM ascorbic acid (AA) solution was added, and the reaction was allowed to proceed for 30 min.

Synthesis of other Pd NCs (Recipe II):

The synthesis for Pd cubic NCs is similar to that for preparing Pd RD NCs excepted that 12.5 mM CTAB solution was used as the solvent and 25 μ L of 1 mM KI solution was added as the addictive. The other Pd NCs indicated in Fig. 2 were prepared in the same recipe but with minor adjustment of C_{CTAB} and C_{KI} .

Characterization:

The products were separately by centrifugation (10000 rpm, 10 min) and concentrated to 500 μ L for TEM measurement. The transmission electron microscopy (TEM) measurements were conducted on a JEOL JEM-2010 microscope. The UV-vis absorbance spectra were measured on a PerkinElmer LAMBDA 40 spectrometer.

Electrochemical measurement:

The NCs were precipitated in strong basic aqueous solution followed by washes with ultrapure water for 3–4 times according to the previous report¹ to finally achieve a suspension in 500 μ L water. Then 16 μ L of the suspension was pipetted onto a polished gold electrode and the solvent was allowed to evaporate in air. The catalyst-layer was rinsed thoroughly with Milli-Q water ($\geq 18.2 \text{ M}\Omega \text{ cm}$) and then served as the working electrode in subsequent electrochemical measurements with a Au foil as the counter electrode and a $\text{Hg}/\text{Hg}_2\text{SO}_4$ electrode or saturated calomel electrode (SCE) served as the reference electrode in acidic or alkaline electrolyte, respectively. However, all the reported potentials are referred to the SCE in the paper. A CHI 660B

electrochemistry workstation (CH Instruments, Shanghai) was employed for the potential control. Furthermore, before the electrochemical measurements, further cleaning process similar to that for bulk Pt single crystal electrodes, i.e., CO adsorption on Pd NCs at ca. 0.1 V followed by anodic potential scan to 0.8 V (SCE) to strip the CO adlayer on Pd with minimum disruption of surface Pd atom arrangement². This procedure was repeated for 2 or 3 times to attain the reasonable electrochemical responses of the Pd NCs.

2. Particle size histogram of the Pd RD NCs

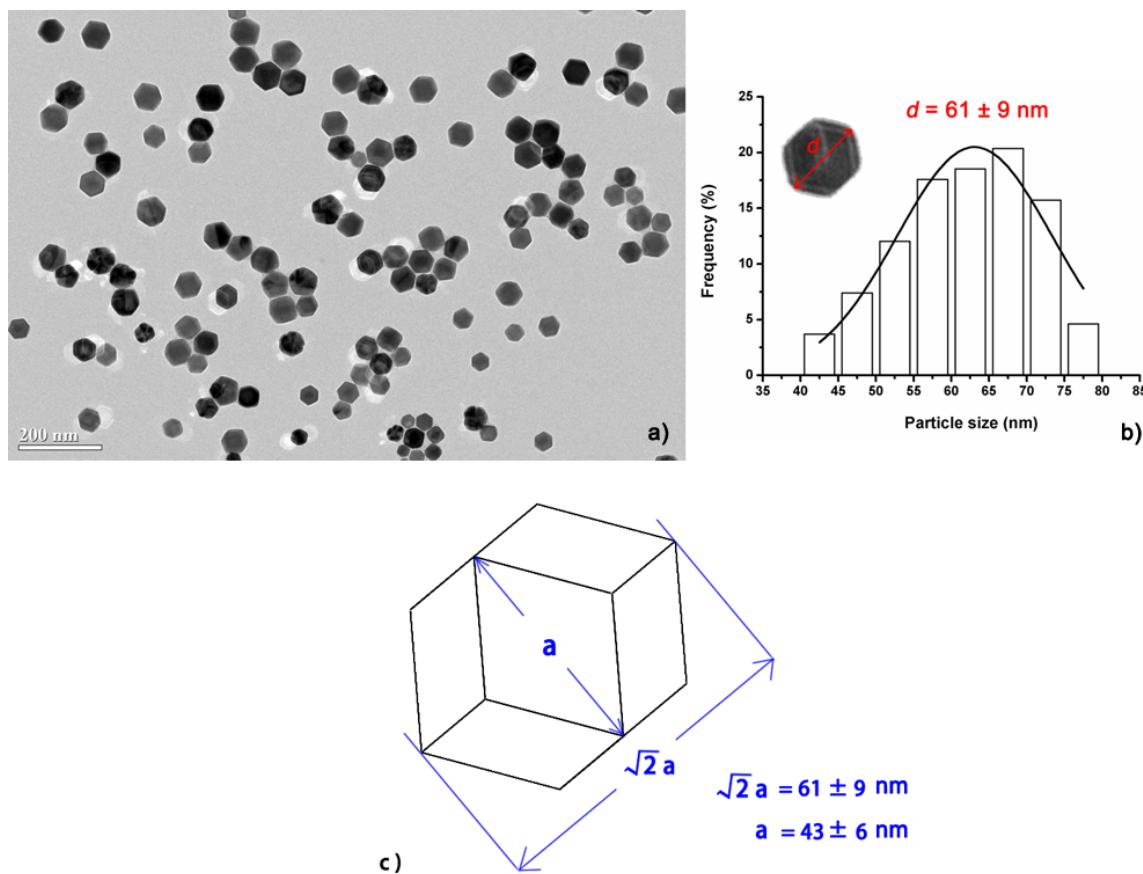


Fig. S1. a) Typical TEM image of Pd RD NCs for particle size statistics and b) the corresponding resulted histogram. c) The calculated relationship between vertex to vertex distance and plane to plane distance of a RD NCs. For the as-synthesized Pd RD NCs with the vertex to vertex of ca. 61 nm, the calculated plane to plane distance is around 43 nm, comparable to the size of obtained Pd cubic NCs.

3. TEM characterization of the Pd nanocubes

The obtained Pd cubic NCs are with the purity above 90 % with an average size (or edge length) of 48 ± 7 nm (see Fig. S2b). The image of a single RD Pd NC (Fig. S2c) and the corresponding SAED pattern (insert in Fig. S2c) demonstrates the well-shaped cubic structure and the single crystal nature, respectively. The HRTEM image (Fig. S2d) shows the exposed {100} facets with the d spacing of 2.08 Å for adjacent lattice fringes corresponding to that of the {100} plane of an *fcc* Pd crystal.

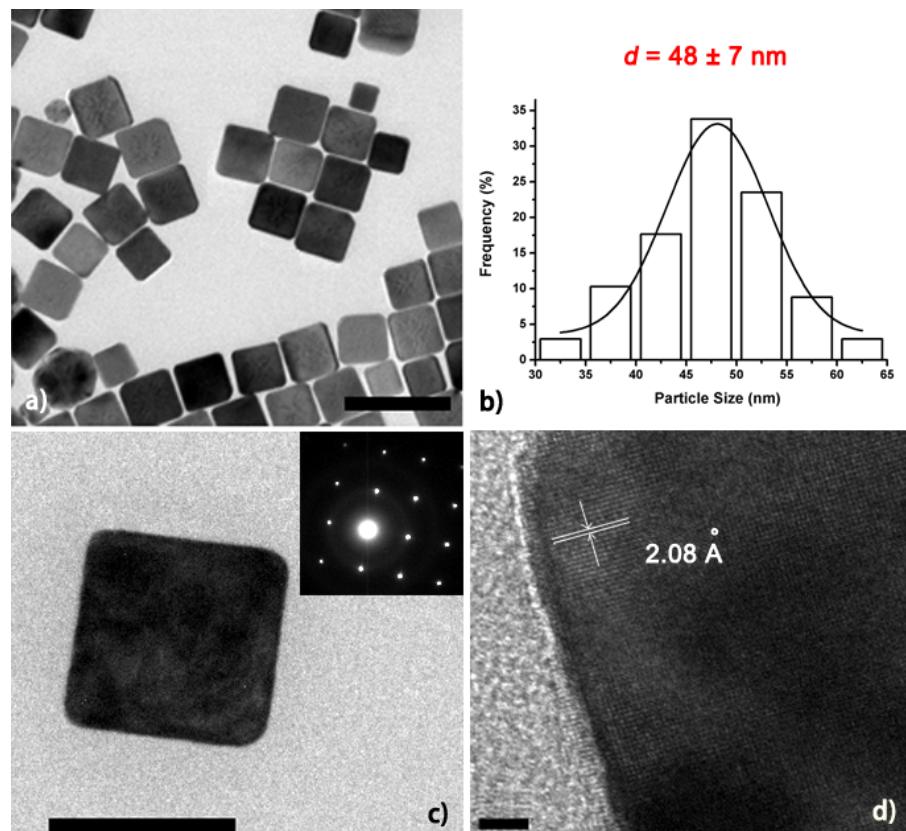


Fig. S2. a) TEM image of cubic Pd NCs (scale bar, 100 nm) and b) the corresponding resulted histogram. c) TEM image (scale bar, 50 nm) and corresponding SAED pattern (insert) and c) HRTEM image (scale bar, 2 nm) of a single cubic Pd NC.

4. Effect of Γ on the formation of Pd NCs

At a lower C_{CTAB} (see Fig. 2a and 2b), it was found that increasing C_{KI} not only increased the average particle size of the obtained cubic Pd NCs, but also improved the monodispersity. In their synthesis with an organic solution containing a high concentration of Γ (ca. 0.17 M), Huang et. al. reported that strong chemisorption of Γ on Pd(100) may passivate this facet leading to the formation of Pd nanocubes.³ In contrast, in their two-step seeds-mediated growth synthesis, Niu et. al. suggested that Γ used at the level of μM enhanced the deposition of Pd along the <100> directions,⁴ based on the visual observation of color change of the solution.

To reveal the effect of trace amount of Γ in the one-pot process, time-evolved UV-vis spectra of the precursor solutions related to Fig. 2a and 2b were recorded after the addition of the reductant AA. Shown in Fig. S3a and S3b, the main absorption peaks at 251 and 339 nm reflect the formation of different coordinated complexes $[\text{PdBr}_{4-n}]^{n-2}$ ($1 \leq n \leq 4$) in the precursor solutions, and the trace amount of the $[\text{PdBr}_m\text{I}_{4-m}]^{m-2}$ ($1 \leq m \leq 4$) complex might not have significant absorption given a total C_{KI} of 2.5 μM , as can be deduced from Fig. S3c. Notably, the main absorption bands for $[\text{PdBr}_{4-n}]^{n-2}$ species decreased much faster in the precursor solution containing 2.5 μM KI at the initial stage after AA was added. In addition, the 297-nm band owing to surface plasmon absorption of Pd NCs showed up earlier in the presence of KI as can be seen in Fig. S3b. These facts are indicative of a faster reduction rate with the addition of trace mount of KI, in support of the assumption made in previous report.⁴ It should be pointed out that the excess amount of CTAB can also stabilize the {100} facets.⁵ Therefore, different sizes and dispersions of the Pd nanocubes synthesized with 0 and 2.5 μM KI could be rationalized by assuming that a higher C_{KI} here may favor the instantaneous nucleation of Pd nuclei and faster growth rate, benefiting the monodispersity of the obtained NCs with a larger size.⁶

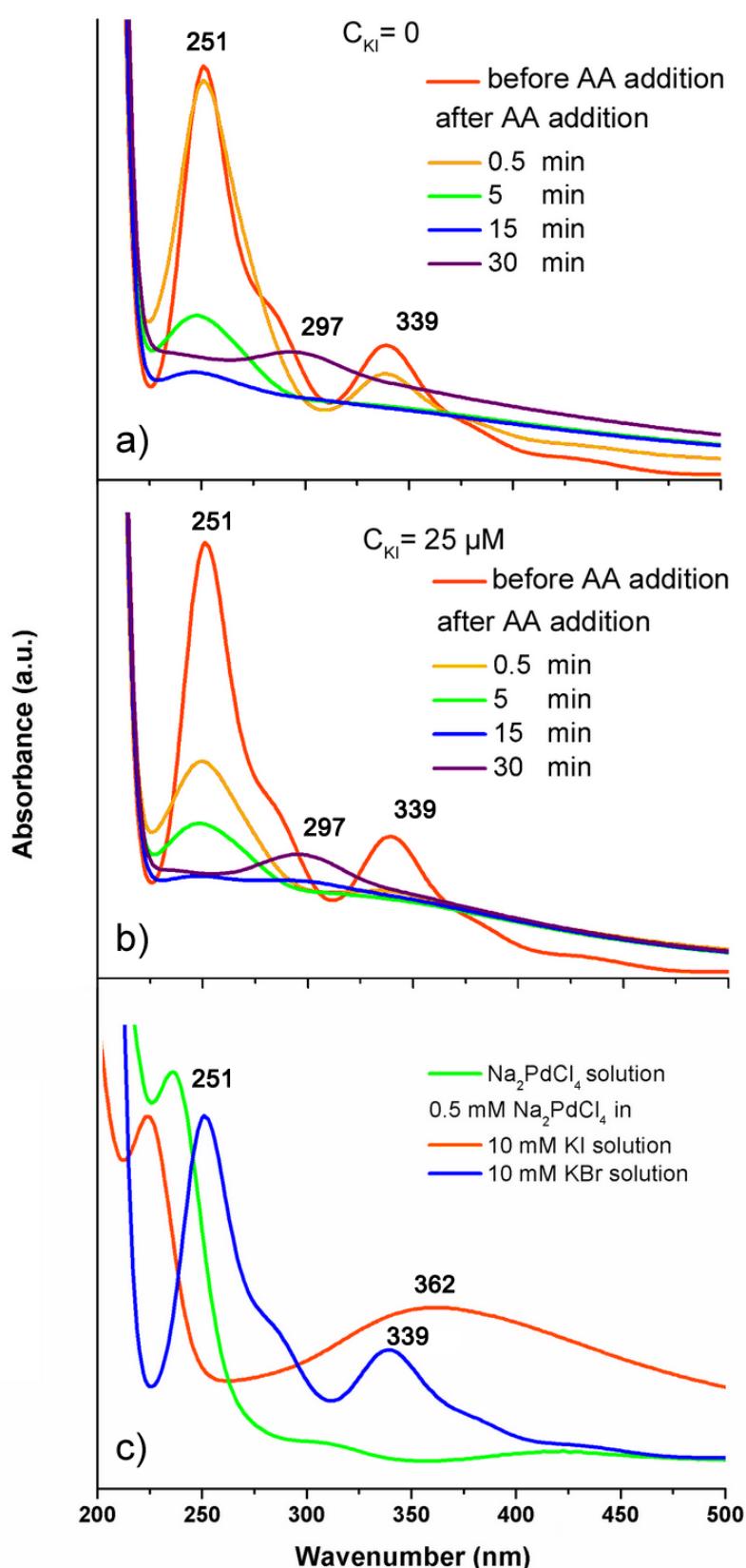


Fig. S3. Evolution of the UV-vis spectra of the precursor solutions a) with or b) without KI during the Pd NCs formation. c) UV-vis spectra of blank Na_2PdCl_4 and Na_2PdCl_4 in KI and KBr solutions.

5. Chronoamperometry on formic acid and ethanol electrooxidations on Pd NCs

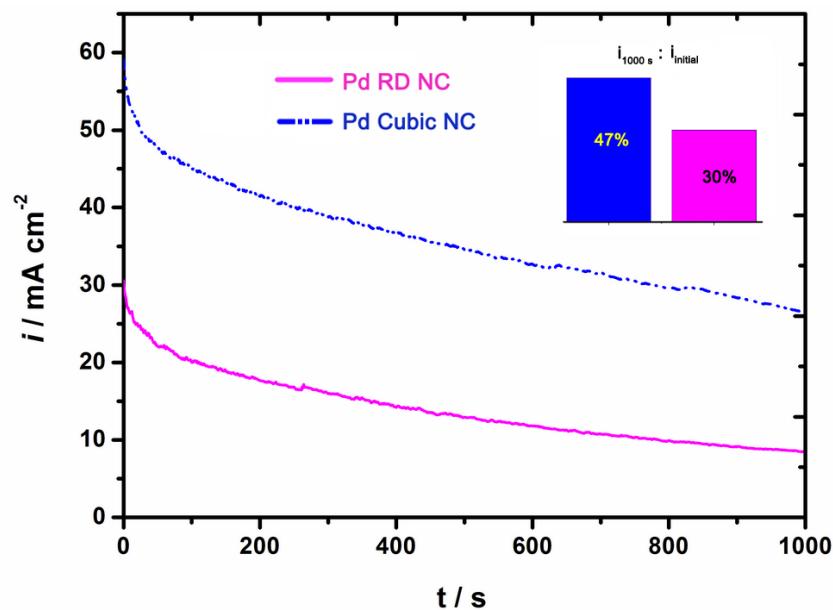


Fig. S4. Chronoamperometric curves for the Pd RD and cubic NCs coated-Au electrodes in 0.5 M H_2SO_4 + 0.5 M HCOOH solution at 0.2 V (SCE).

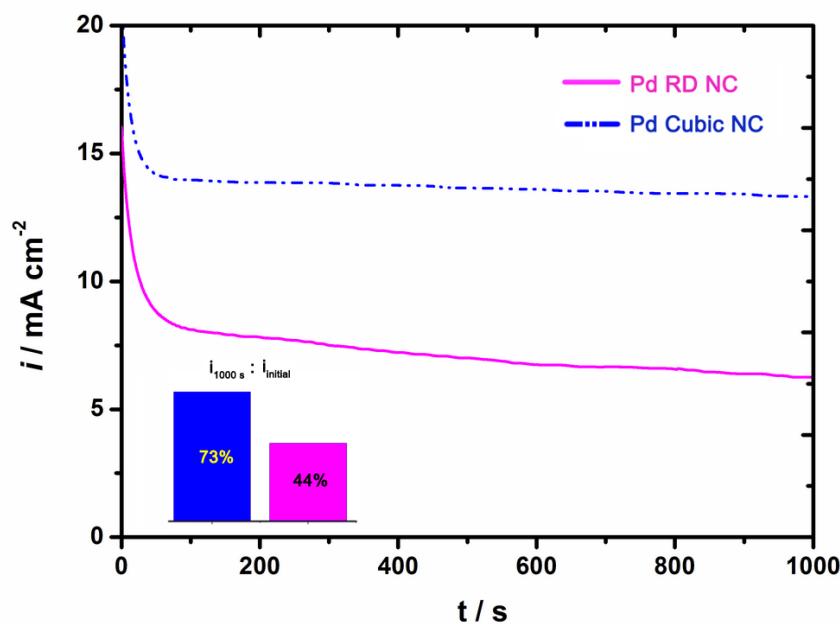


Fig. S5. Chronoamperometric curves for the Pd RD and cubic NCs coated-Au electrodes in 0.1 M NaOH + 1 M $\text{C}_2\text{H}_5\text{OH}$ solution at -0.2V (SCE).

References

- (1) Vidal-Iglesias, F. J.; Arán-Ais, R. M.; Solla-Gullón, J.; Herrero, E.; Feliu, J. M. *ACS Catal.* **2012**, 901.
- (2) Solla-Gullón, J.; Montiel, V.; Aldaz, A.; Clavilier, J. *J. Electroanal. Chem.* **2000**, *491*, 69.
- (3) Huang, X. Q.; Zhang, H. H.; Guo, C. Y.; Zhou, Z. Y.; Zheng, N. F. *Angew. Chem. Int. Ed.* **2009**, *48*, 4808.
- (4) Niu, W. X.; Zhang, L.; Xu, G. B. *ACS Nano* **2010**, *4*, 1987.
- (5) Lim, B.; Jiang, M. J.; Tao, J.; Camargo, P. H. C.; Zhu, Y. M.; Xia, Y. N. *Adv. Funct. Mater.* **2009**, *19*, 189.
- (6) Xia, Y.; Xiong, Y.; Lim, B.; Skrabalak, S. E. *Angew. Chem. Int. Ed.* **2009**, *48*, 60.