Electronic Supplementary Material (ESI) for Nanoscale.

Supporting Information

Length tunable penta-twinned palladium nanorods: seedless synthesis and electrooxidation of formic acid

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Experimental section

Materials. $PdCl_2$ (99.999%), $AgNO_3$ (≥99.0%), CuSO4 (≥99%), Bi(NO3)3 (99.999%), $PbCO_3$ (≥99.99%), CdO (≥99.99%), KI (≥99.0%), and CTAB(≥98%) were from Sigma-Aldrich. L-Ascorbic acid (AA) (99%) was from Acros Organics. HCl was from Fisher Scientific. Formic acid (88%) was purchased from Pharmco. All of the chemicals were used without further purification. A 10 mM H_2PdCl_4 was prepared by dissolving 0.0355g $PdCl_2$ in 20 mL of 0.02 M HCl solution. Water (18.2 MΩ·cm) purified by a Milli-Q system was used in all of the experiments.

1) **Synthesis of Pd nanorods.** In a typical synthesis of 100 nm Pd nanorods, 150 μL of 10 mM H2PdCl4 was added to 5 mL of 100 mM CTAB at 90 °C. After gently mixing the solution, 100 μL of 100 mM freshly prepared KI solution and 40 μL of 10 mM $AgNO_3$ were added in sequence. Five minutes later, 100 μL of 100 mM freshly prepared AA was added to the solution. The reaction was kept in 90 °C water bath for 1 hour, and the product was collected by centrifugation (6500 rpm, 10 min).

2) **Synthesis of Cubic Pd Nanocrystals.** Same as the nanorod synthesis, except that only 50 μL of KI solution was used and no $AgNO_3$ was added.

3) **Synthesis of 200 nm and 300 nm Pd nanorods.** In a typical synthesis of 200 nm and 300 nm Pd nanorods, a 150 μL of 10 mM H_2PdCl_4 was added to 5 mL of 100 mM CTAB at 90 °C. After gently mixing the solution, 100 μL of 100 mM fresh prepared KI solution and 10 μL of 10 mM $AgNO_3$ were added in sequence. 10 μL and 40 μL of 1 M HCl were added in the solution in order to form 200 nm and 300 nm Pd nanorods. Five minutes later, 100 μL of 100 mM freshly prepared AA was added to the solution. The solution pH is around 1.66 and 1.55, respectively. The reaction was kept at 90 °C in a water bath for 1 hour, and the products were collected by centrifugation (6500 rpm, 10 min).

4) **Synthesis of 400 nm and 500 nm Pd nanorods**. In a typical synthesis of 400 nm and 500 nm Pd nanorods, a 150 μL of 10 mM H_2PdCl_4 was added to 5 mL of 100 mM CTAB at 90 °C. After gently mixing the solution, 200 μL of 100 mM fresh prepared KI solution and 10 μL of 10 mM $AgNO_3$ were added in sequence. 80 μL and 120 μL of 1 M HCl were added in the solution in order to form 400 nm and 500 nm Pd nanorods. Five minutes later, 400 μL of 100 mM freshly prepared AA was added to the solution. The solution pH is around 1.45 and 1.36, respectively. The reaction was kept at 90 °C in a water bath for 1.5 hour, and the products were collected by centrifugation (6500 rpm, 10 min).

5) **Electrochemical measurement**. To study the electrochemical behaviors of these catalysts in formic acid oxidation, cyclic voltammograms (CVs) and chronoamperograms (CAs) were recorded in 0.5 M HCOOH + 0.1 M $HClO_4$ in a conventional two-compartment three-electrode cell. A Pt wire served as the counter electrode, and a KCl-saturated Ag/AgCl electrode was used as the reference electrode. All the potentials reported here were converted and respect to a reversible hydrogen electrode (RHE). For a typical measurement, the whole batch of Pd nanoparticles were further washed three times with warm water and re-dispersed in 100 μL ethanol before electrochemical measurement. 10 μL of Pd nanoparticles ethanol suspension was drop-coated on a glassy carbon (GC) disk electrode (geometric area: 0.196 cm^2) and used as the working electrode. The cell resistance was compensated with the iR

compensation function in the analyzer. Before any electrochemical measurements, the Pd particles were subject to an electrochemical cleaning process which entails electrochemical potential cycling between -1.2 to +0.6 V vs Ag/AgCl for 100 cycles at a scan rate of 0.5 V s^{-1} in CO-saturated 0.1 M $NaClO_4$ + 1 mM NaOH. The CO gas was kept purging in the solution during the cleaning process. Without this cleaning process, the particle surfaces are blocked, as shown by CVs in Figure S12 for Pd nanocubes obtained before and after the cleaning procedure. Adsorbed CO facilitates removal of surfactants and halides. The use of alkaline solution instead of more commonly used acidic solutions is to avoid hydrogen absorption at more negative potentials which are necessary for removing halides. The current density is obtained by normalizing the current to corresponding electrochemically active surface areas evaluated by using CO stripping charges (Figure S13), assuming the charge for the oxidation of a saturated CO adlayer is 320 $\mu C/cm^2$, which is the value for bulk Pd(100) surface.[1] Given that the major facets on Pd rods are {100} and Pd cubes are enclosed by {100}, this value is more accurate than the commonly used 420 $\mu C/cm^2$. Note that the morphology of nanoparticles does not change after these electrochemical measurements, as exemplified by TEM of 400 nm rods (Figure S14).

6) **Instrumentation.** Scanning electron microscopy (SEM) images were performed on a Zeiss Supra35 scanning electron microscope at 5 kV. Regular transmission electron microscopy (TEM) images were obtained from a JEOL1200 transmission electron microscope at 120 kV. High-resolution TEM and selected-area electron diffraction (SAED) images were taken using a JEOL2100 transmission electron microscope operating at 200 kV. X-ray diffraction (XRD) measurements were performed on a Scintag X1 powder diffractometer equipped with a Cu Kα radiation (λ = 0.154 nm) operated at 40 kV and 25 mA in the range of 30°-90° by step scanning at 0.02°/5s. All the electrochemical measurements were performed on a CHI 700C electrochemical analyzer.

References

1. M. Hara, U. Linke and T. Wandlowski, *Electrochim. Acta*, 2007, **52**, 5733.

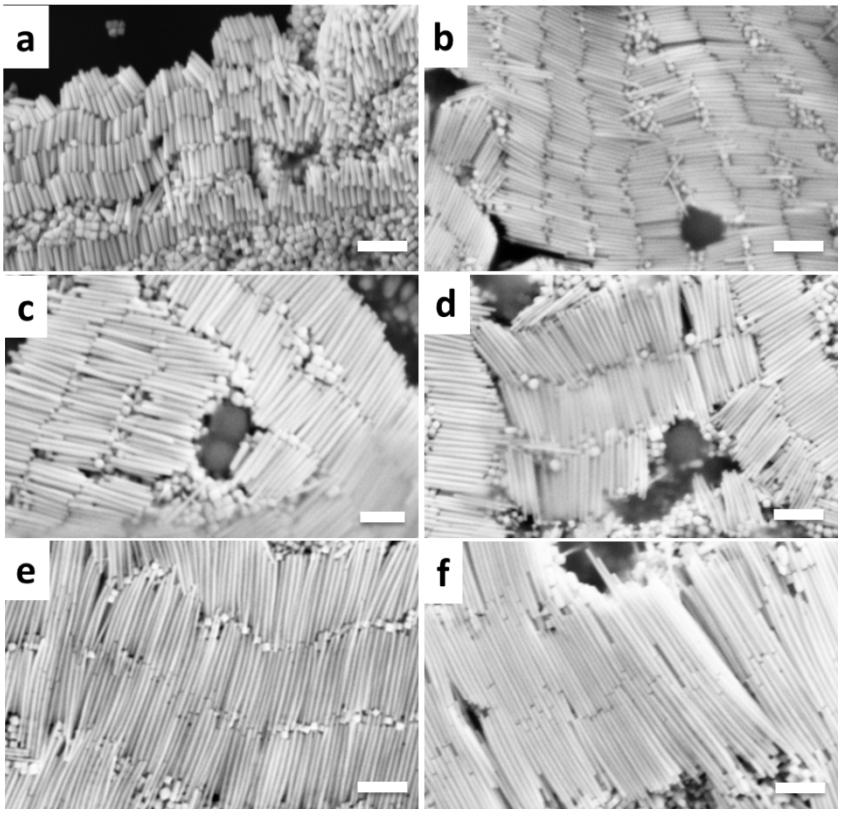

Figure S1. SEM images of Pd nanorods prepared by adding: a). 0 μL, b). 10 μL, c). 20 μL, d). 40 μL, e). 80 μL, and f). 120 μL of 1 M HCl. Scale bar: 200 nm.

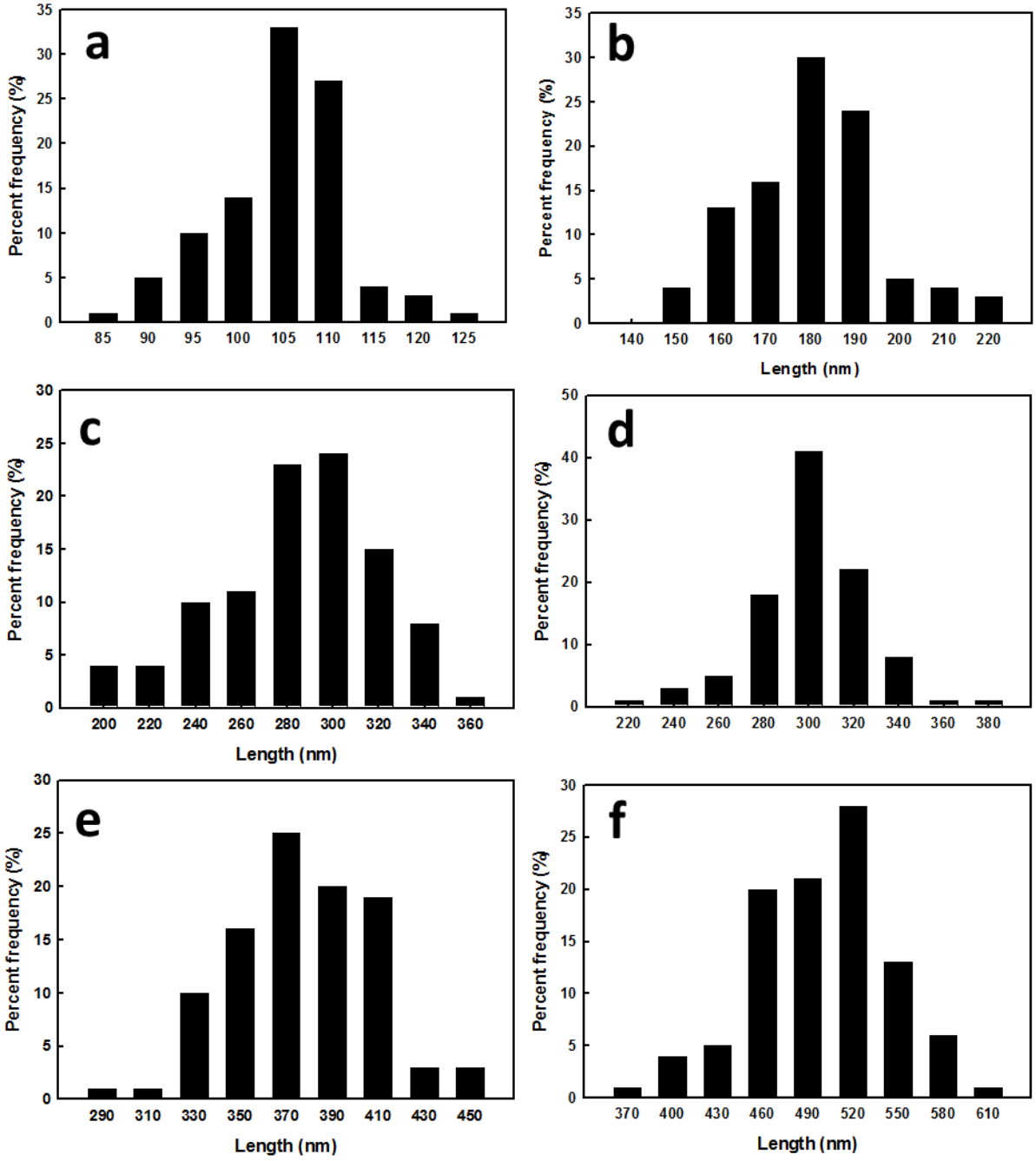

Figure S2. Length distribution histograms of samples shown in Figure S1

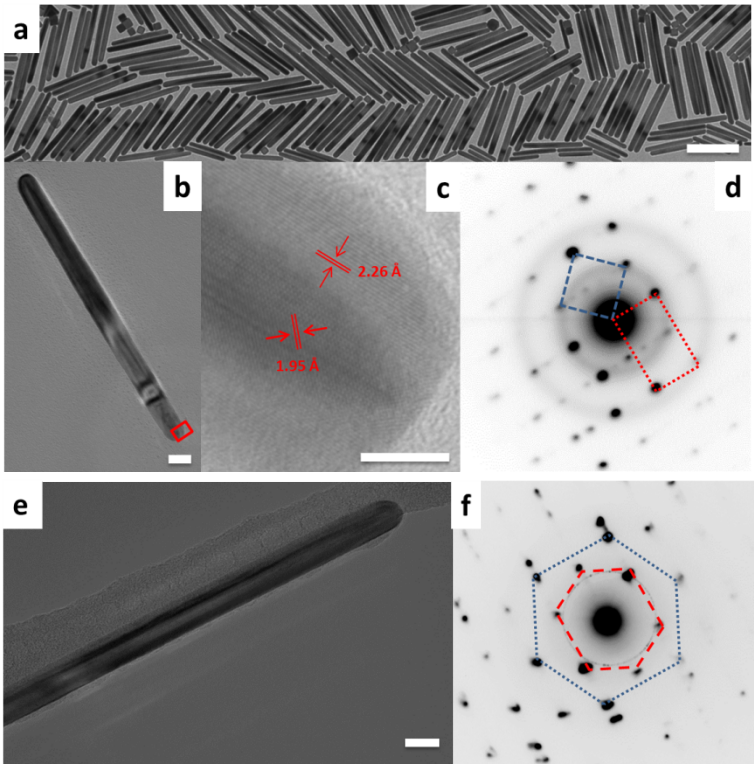

Figure S3. a). TEM image of ~300 nm Pd rods. Scale bar: 200 nm. b). higher magnification TEM image of a 280 nm Pd rod and c). High-resolution TEM image of the square region in b. The measured d spacing of 2.26 Å and 1.95 Å correspond to the (111) and (100) planes of Pd. Scale bar: 5 nm. d). corresponding SAED pattern of the Pd nanorod shown in b. The pattern shows an overlapping zone pattern of the square [100] (marked in blue) and rectangular [112] (marked in red) of a face-centered cubic structure and indicates that the nanorod grows along the [110] direction. e). TEM image of a 480 nm Pd nanorod. Scale bar: 20 nm. f). corresponding SAED pattern, which shows an overlapping zone pattern of the hexagon [111] (marked in blue) and elongated hexagon [110] (marked in red) of an fcc structure and indicates that the nanorod grows along the [110] direction.

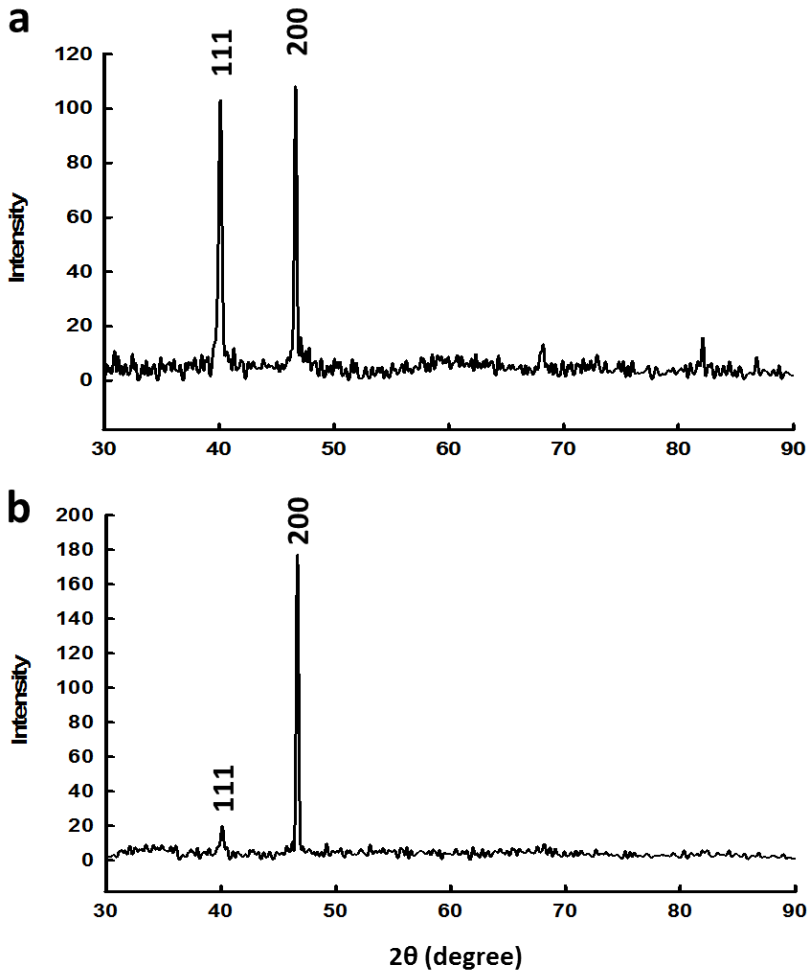

Figure S4. XRD patterns of (a) 372 nm Pd nanorods and (b). Pd nanocubes.

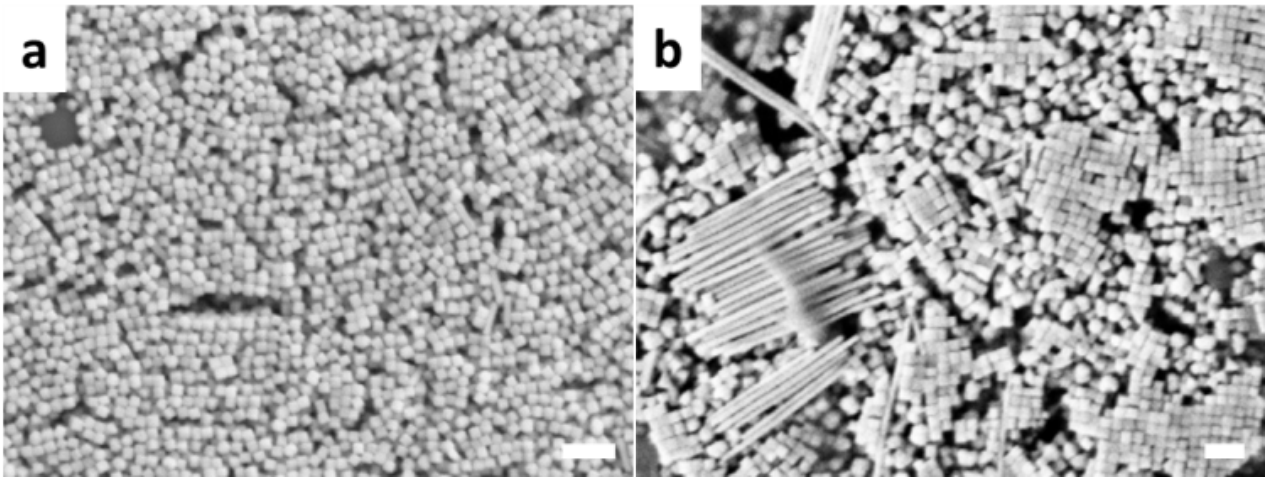

Figure S5. SEM images of Pd nanoparticles synthesized with (a) 20 μL $AgNO_3$ added (b) $AgNO_3$ was added after AA. Other ingredients are the same as making 105 nm (a) and 372 nm (b) rods in Table 1. Scale bar: 200 nm.

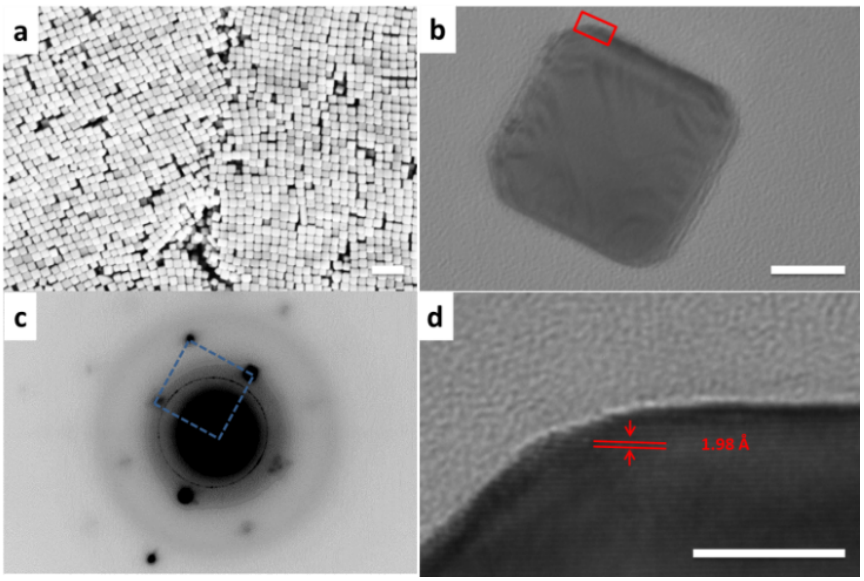

Figure S6. a). SEM image of Pd particles synthesized without addition of foreign ions. Scale bar: 200 nm. b). TEM image (scale bar: 20 nm) and c). corresponding SAED pattern of a Pd nanocube. d). High-resolution TEM image of the region indicated in b. Scale bar: 5 nm.

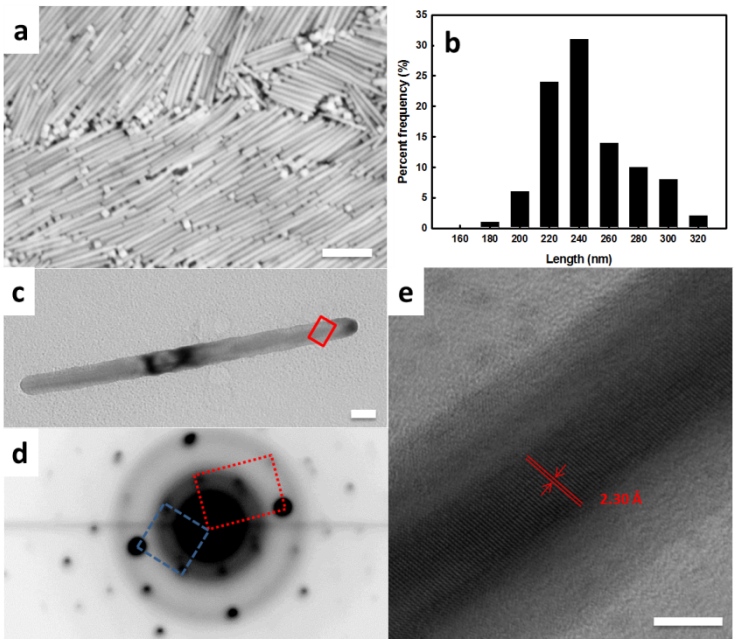

Figure S7. (a) SEM image of Pd nanorods prepared by adding 10 μL of 10 mM $CuSO_4$ instead of $AgNO_3$ to the reaction mixture. Other ingredients are the same as making 372 nm rods (Table 1). Scale bar: 200 nm. b). Corresponding length histogram for the sample in a. c). TEM image of a 260 nm Pd rod (scale bar: 20 nm) and d) its corresponding SAED pattern, showing an overlapping zone pattern of the square [100] (marked in blue) and rectangular [112] (marked in red) of a face-centered cubic structure. e) High-resolution TEM image of the square region in c. The measured d spacing of 2.30 Å corresponds to the (111) lattice planes of Pd. Scale bar: 5 nm

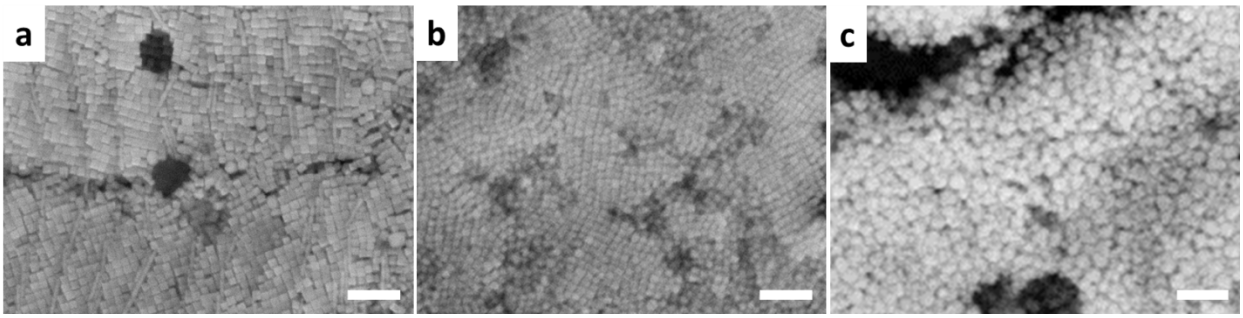

Figure S8. SEM images of Pd nanoparticles obtained with the addition of (a) 10 μL 10 mM CdO, (b) 10 μL 10 mM $PbCO_3$, (c) 10 μL 10 mM $Bi(NO_3)_3$. Other conditions are the same as making 295 nm rods (Table 1). Scale bar: 200 nm.

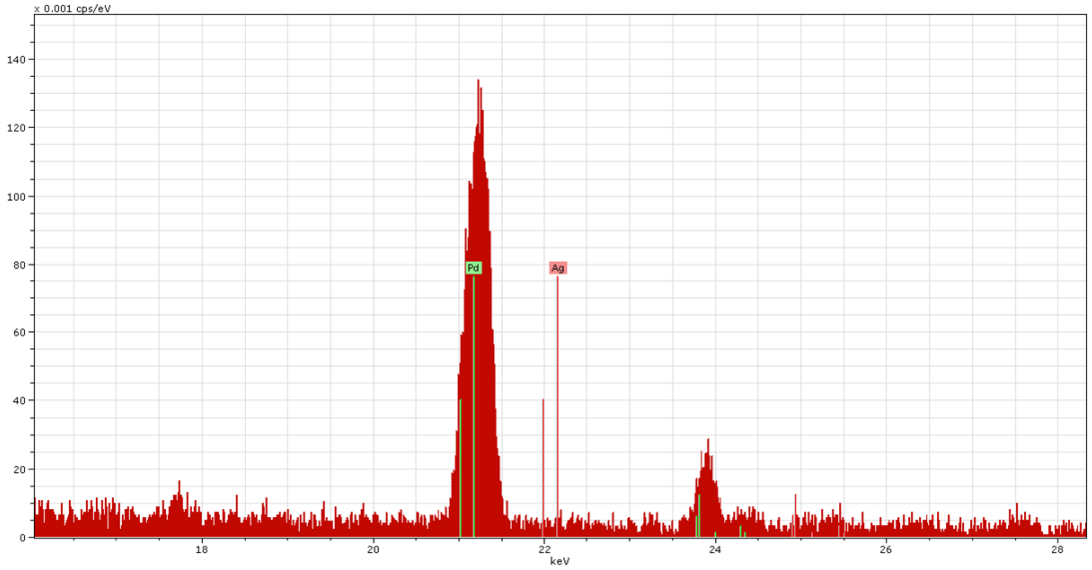

Figure S9. EDS spectrum from 295 nm Pd nanorods.

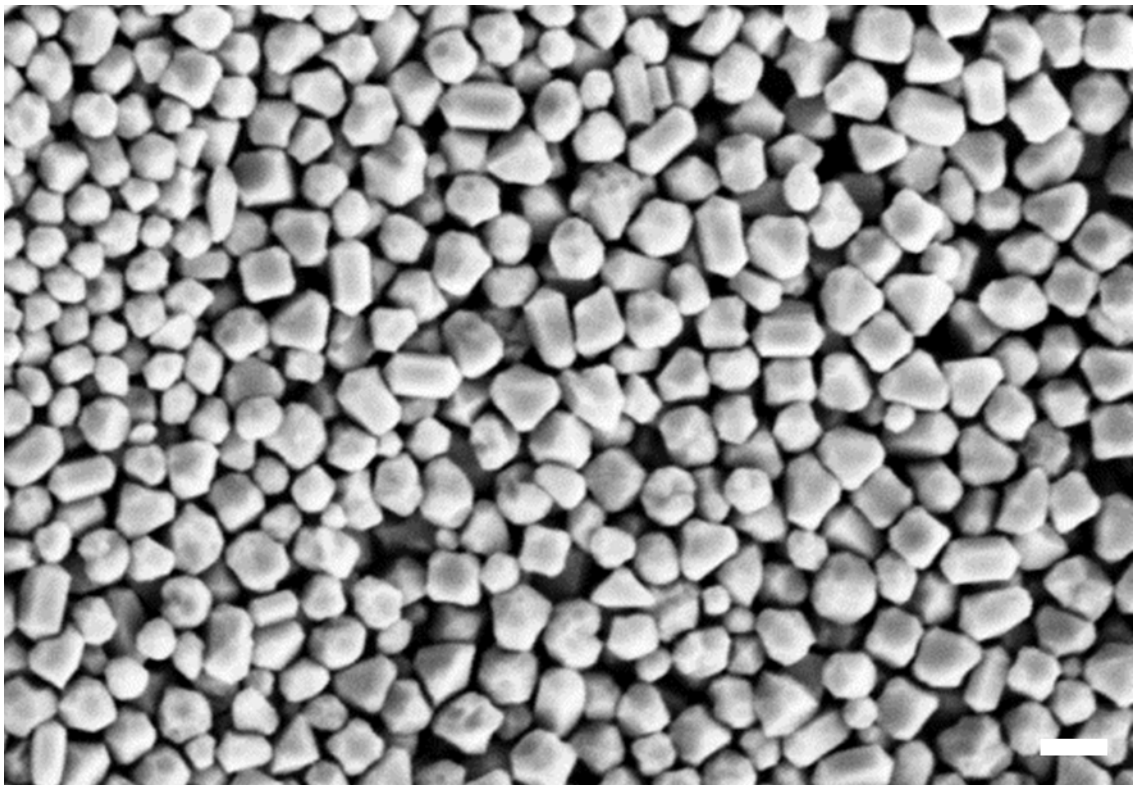

Figure S10. SEM image of Pd nanoparticles synthesized without using KI. Other conditions are the same as making 295 nm rods. Scale bar: 200 nm.

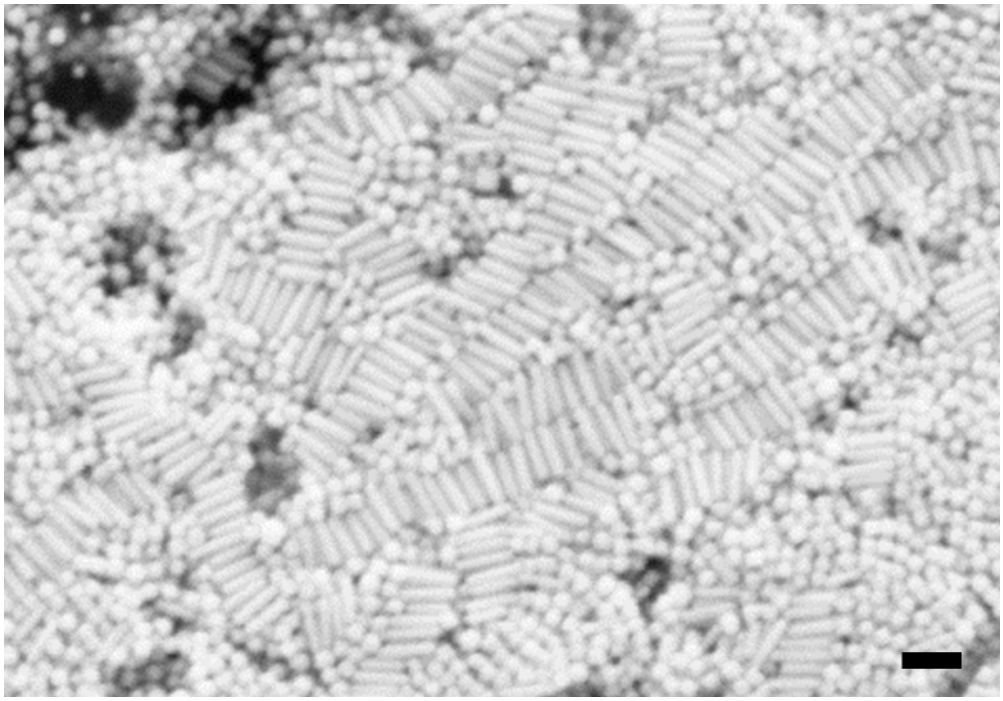

Figure S11. SEM image of Pd nanorods with 120 μL 1 M KCl added instead of HCl, other conditions are the same as making 489 nm rods. Scale bar: 100 nm

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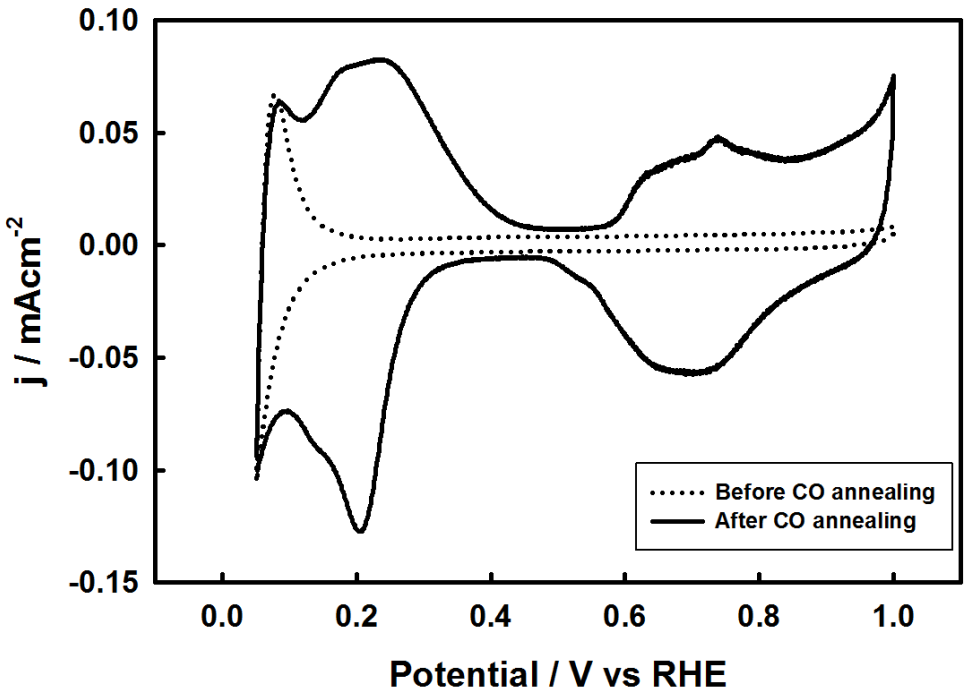

Figure S12. Cyclic voltammograms of Pd nanocubes obtained in 0.1 M $HClO_4$ before and after electrochemical cleaning in CO-saturated 0.1 M $NaClO_4$+ 1 mM NaOH. Scan rate: 0.1 V s^{-1}.

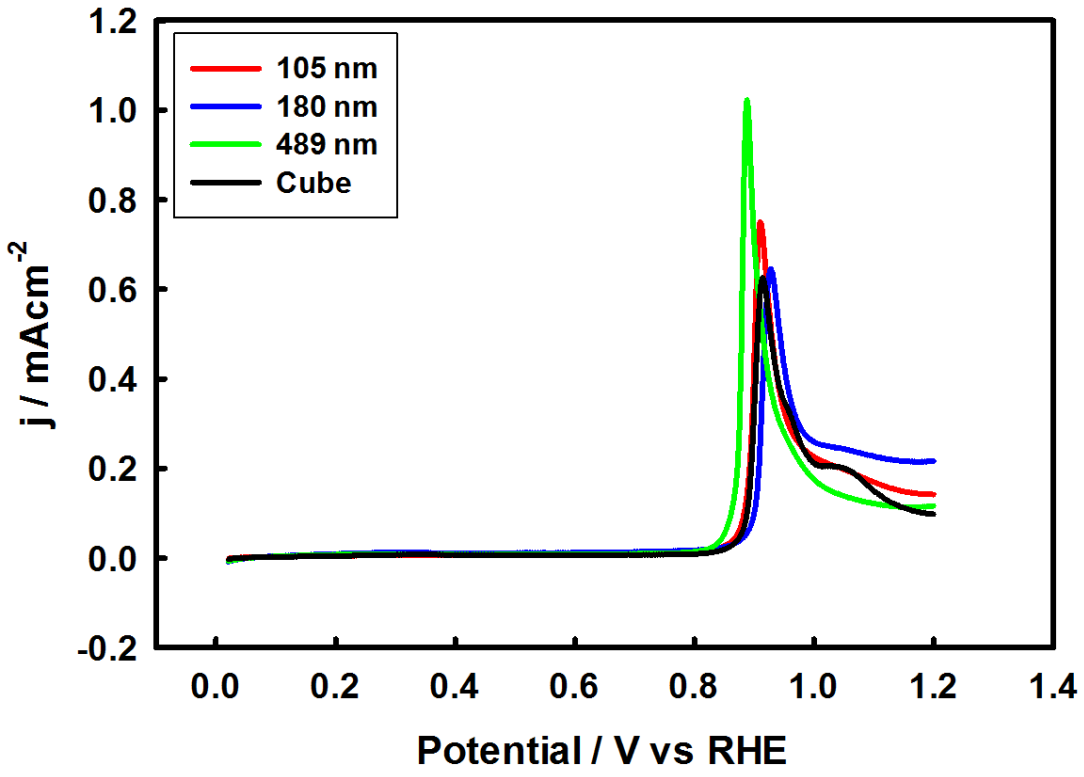

Figure S13. CO stripping voltammograms of Pd nanoparticles in 0.1 M $HClO_4$. Scan rate: 0.1 V s^{-1}.

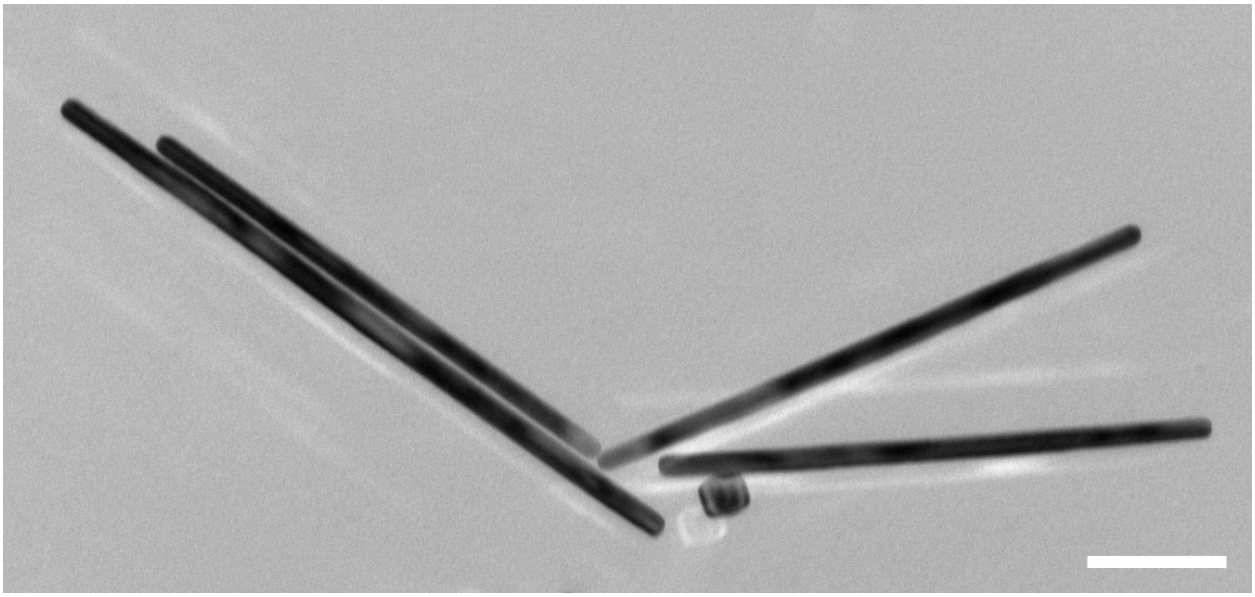

Figure S14. TEM image of 400 nm Pd nanorods after CO annealing and catalytic activity investigation. Scale bar: 100 nm.