

Electronic Supplementary Information (ESI) for

## Controlled Synthesis of Tetrapod/Mitsubishi-like Palladium Nanocrystals

Hai Zhu, Gan Li, Yanxi Zhao, Hanfan Liu, Jinlin Li, Tao Huang\*

*Key Laboratory of Catalysis and Material Science of the State Ethnic Affairs Commission & Ministry of Education, Hubei Province, College of Chemistry and Materials Science, South-Central University for Nationalities, Wuhan 430074, China*

Email: huangt6628@yahoo.com.cn

### Experimental Details

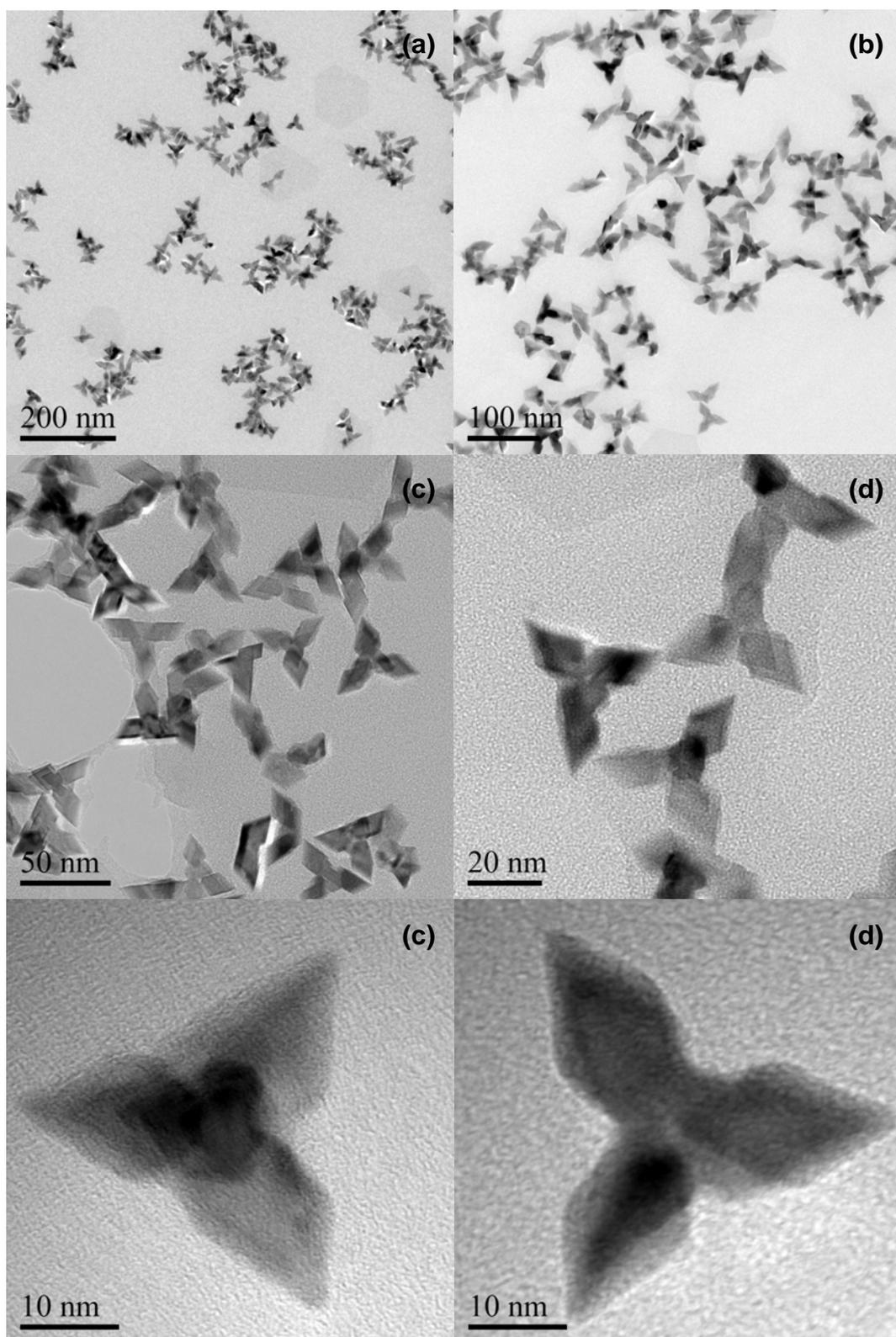
**Reagents:** palladium acetylacetonate, Pd(acac)<sub>2</sub> (99%) was purchased from Acros Chemicals, PVP (MW=30000, AR), sodium formate, sodium acetate, sodium propionate, sodium benzoate and DMF were purchased from Sinopharm Chemical Reagent Co., Ltd.(Shanghai, China). All reagents were used as received without further purification.

**Synthesis of tetrapod/Mitsubishi-like palladium nanocrystals:** In a typical synthesis of tetrapod Pd nanocrystals, 50 mg of Pd(acac)<sub>2</sub>, 160 mg of PVP, 83 mg of anhydrous sodium acetate were dissolved in a mixed solvent of DMF (10 mL) and water (2 mL). After thorough mixing, the resulting homogeneous yellow solution was transferred to a glass three-necked flask. Under vigorously stirring, CO gas was bubbled continually into the solution at a flow rate of 0.3 mL·sec<sup>-1</sup>. Following the exclusion of air, the flask was heated at 100 °C for 3 h under atmospheric pressure. After being cooled to room temperature, the resulting black homogeneous Pd colloids were precipitated by acetone, separated by centrifugation and further purified by an isopropanol-acetone mixed solvent.

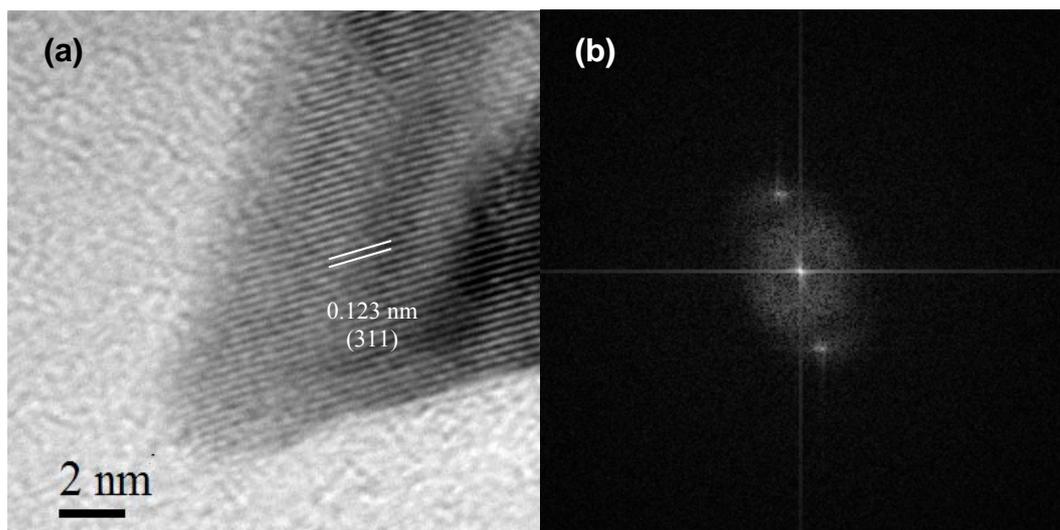
Under the same other conditions, the effects of carboxylates, CO flow rate, temperature and reaction time on morphological features were investigated, respectively.

**Characterization:** Transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) measurements were conducted on a FEI Tecnai G<sup>2</sup> 20 transmission electron microscopy operated at 200 kV. Diffractograms of HRTEM were obtained by fast Fourier transformation. The sample for TEM observation was prepared by placing a drop of the colloidal dispersion onto a copper grid coated with a perforated carbon film, followed by evaporating the solvent at ambient temperature. The average particle size was determined from the enlarged micrographs on the basis of the measurement of about 300 particles. Ultraviolet-visible (UV-vis) absorption spectra were measured with a Unicam SP1750 UV-visible spectrophotometer. X-ray powder diffraction (XRD) patterns were recorded on a Bruker D8 advance X-ray diffractometer employing Cu  $K\alpha$  radiation with 40 kV and 50 mA. X-ray photoelectron spectroscopy (XPS) was performed on a VG Multilab 2000 X-ray photoelectron spectrometer using Mg  $K\alpha$  radiation under a vacuum of  $8 \times 10^{-7}$  Pa. All binding energy values were determined with reference to carbon,  $C_{1s} = 284.6$  eV.

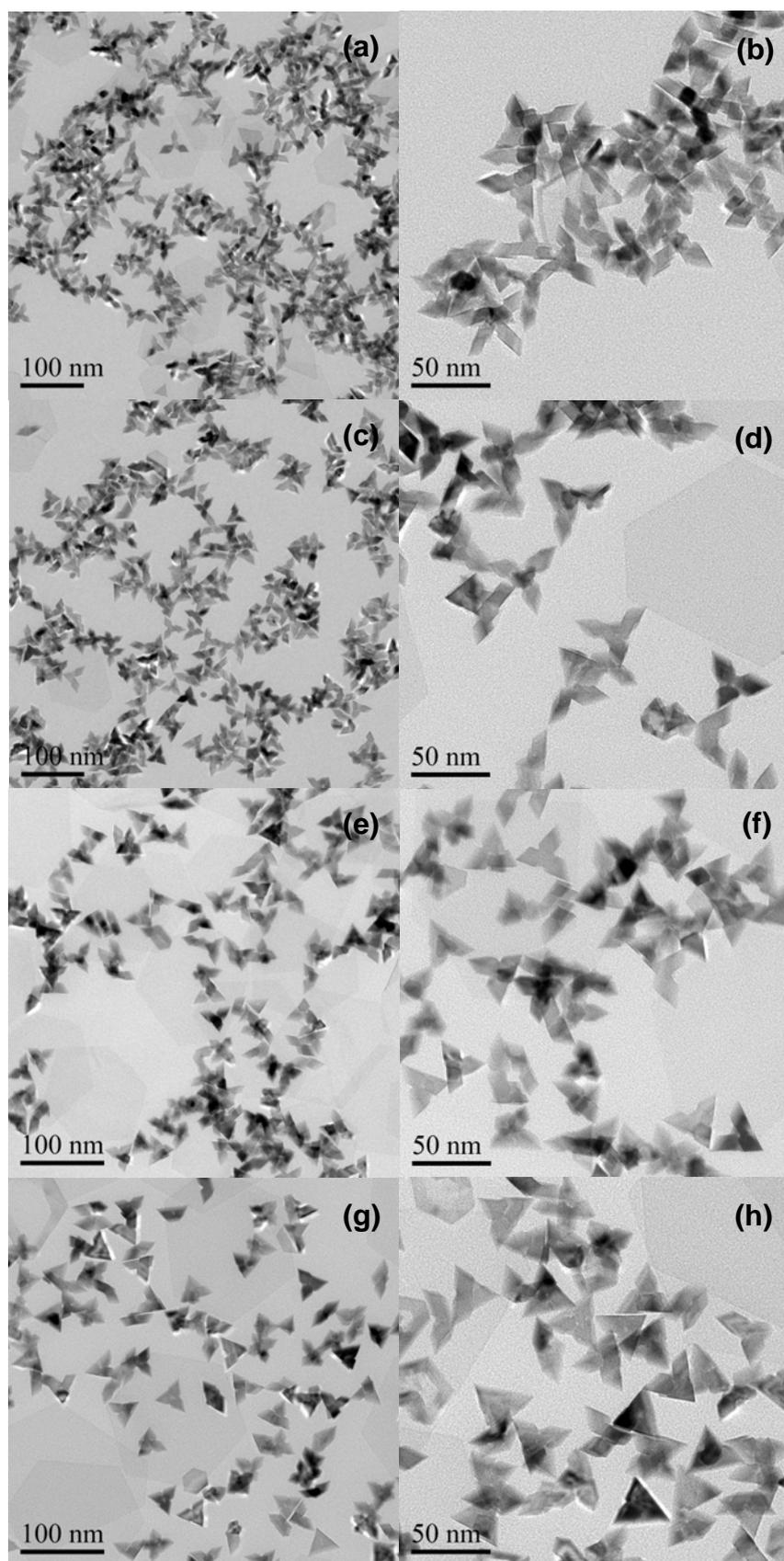
**Electrochemical Measurements:** Tetrapod Pd nanocrystals-modified working electrodes were fabricated by depositing ethanolic dispersion of purified tetrapod Pd nanocrystals onto a glassy carbon electrode followed by natural drying. A saturated calomel electrode (SCE) and a platinum foil were used as the reference and counter electrode, respectively. For the electrooxidation of formic acid, the cyclic voltammograms were recorded at a sweep rate of 50 mV/s in 0.5 M H<sub>2</sub>SO<sub>4</sub> + 0.5 M formic acid. Before cyclic voltammetry measurements, six cycles of potential sweeps between -0.2V and 1.2V at a sweep rate of 250 mV/s were applied in order to clean the Pd surface in-situ. Both positive and negative CV scans were performed on each sample. The arrows in the CV curves indicate the direction of the scan. The same electrochemical experiment was conducted for small Pd nanoparticles.



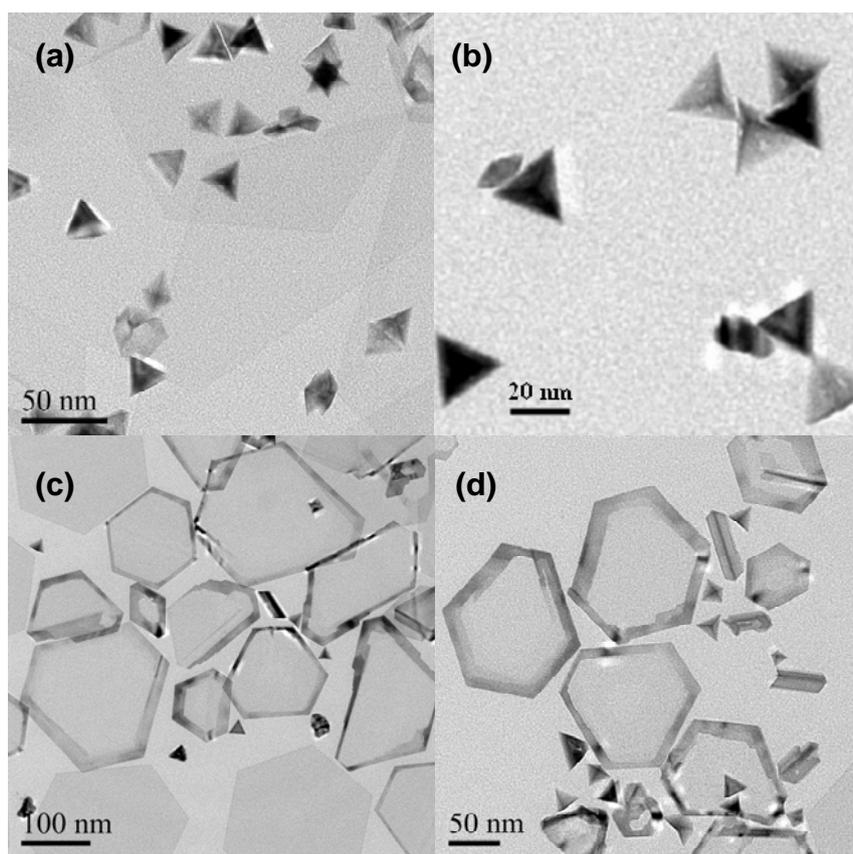
**Figure S1.** TEM images of the as-prepared tetrapod/*Mitsubishi*-like nanocrystals in the typical synthesis. CO gas flow rate was  $0.3 \text{ mL} \cdot \text{sec}^{-1}$ . Reaction at  $100 \text{ }^\circ\text{C}$  for 3 h.



**Figure S2.** (a) HRTEM image of a pod branch of a single Pd tetrapod and (b) a fast Fourier Transform (FFT) pattern.

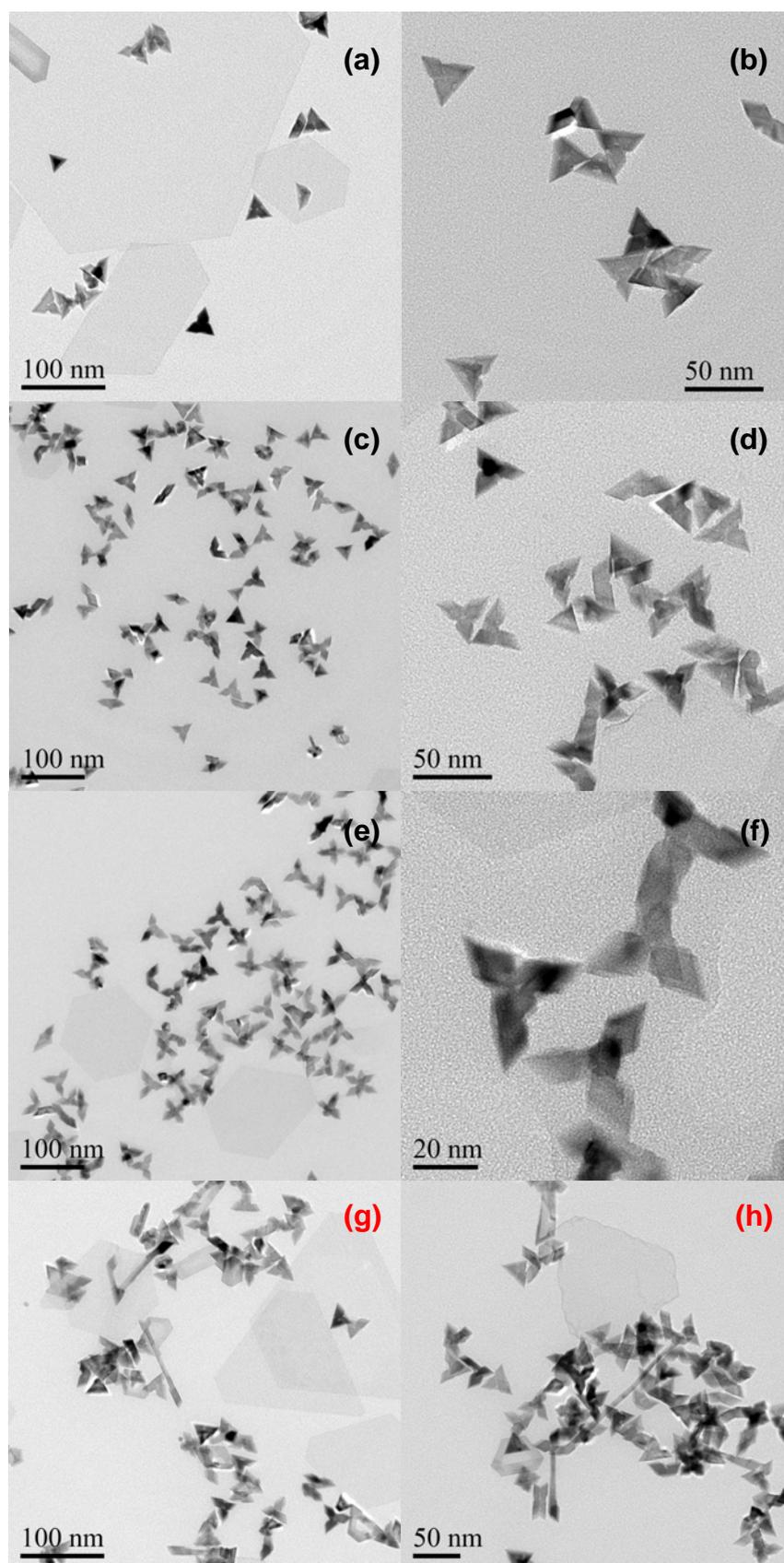


**Figure S3.** TEM images of the Pd nanocrystals prepared in the presence of different carboxylates. (a, b) sodium formate; (c, d) sodium acetate; (e, f) sodium propionate; (g, h) sodium benzoate. CO flow rate was  $0.3 \text{ mL} \cdot \text{sec}^{-1}$ .

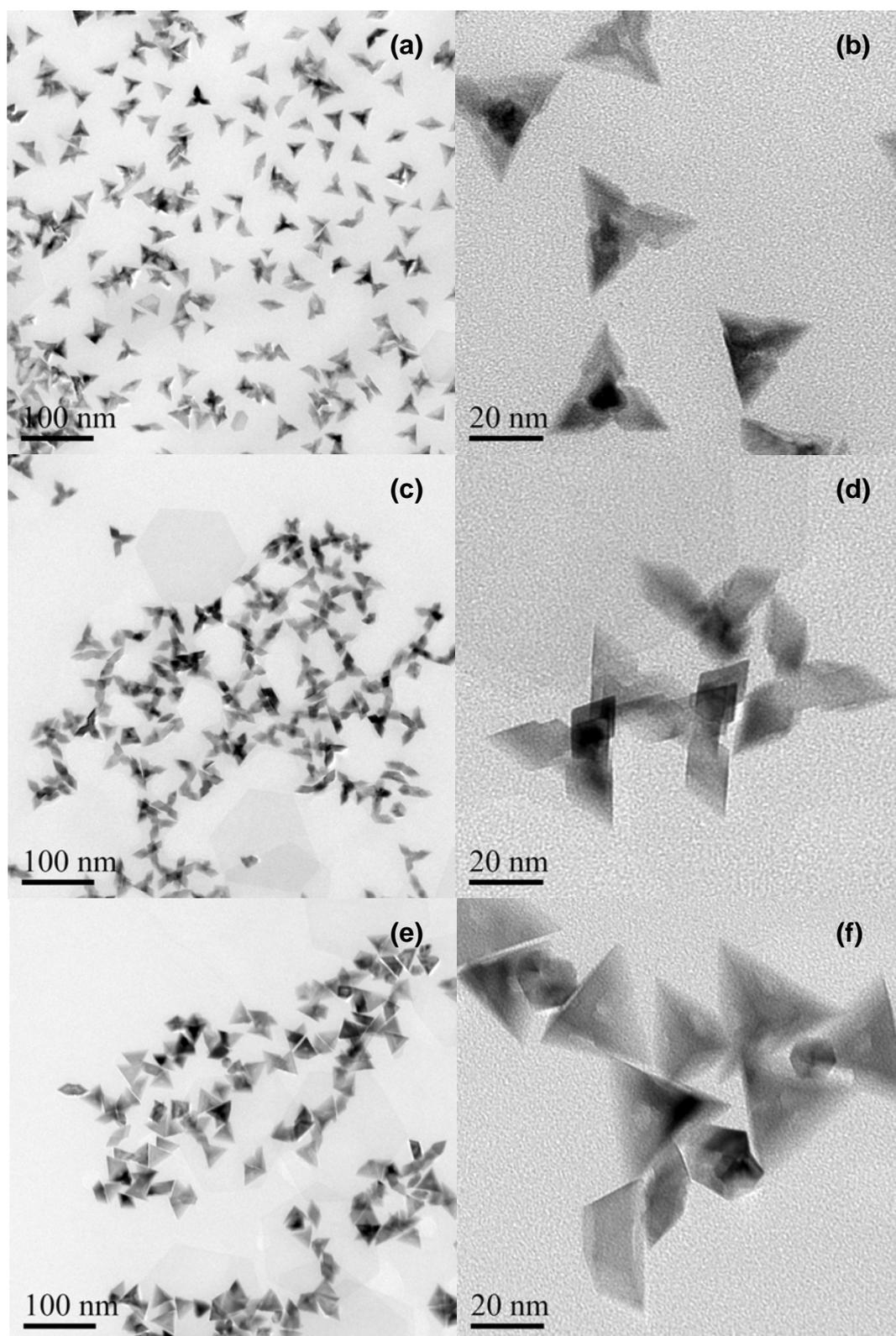


**Figure S4.** TEM images of the Pd nanocrystals prepared with addition of sodium nitrate (a, b) and without adding any carboxylate or other acid salt (c, d). CO flow rate was  $0.3 \text{ mL} \cdot \text{sec}^{-1}$ .

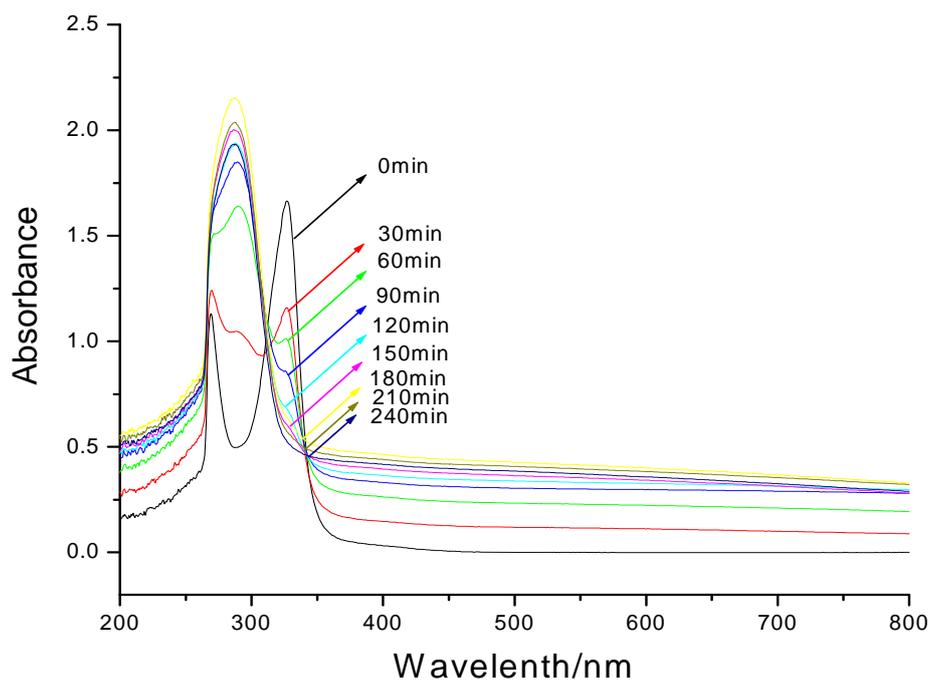
Reaction conducted at  $100 \text{ }^\circ\text{C}$  for 3 h.



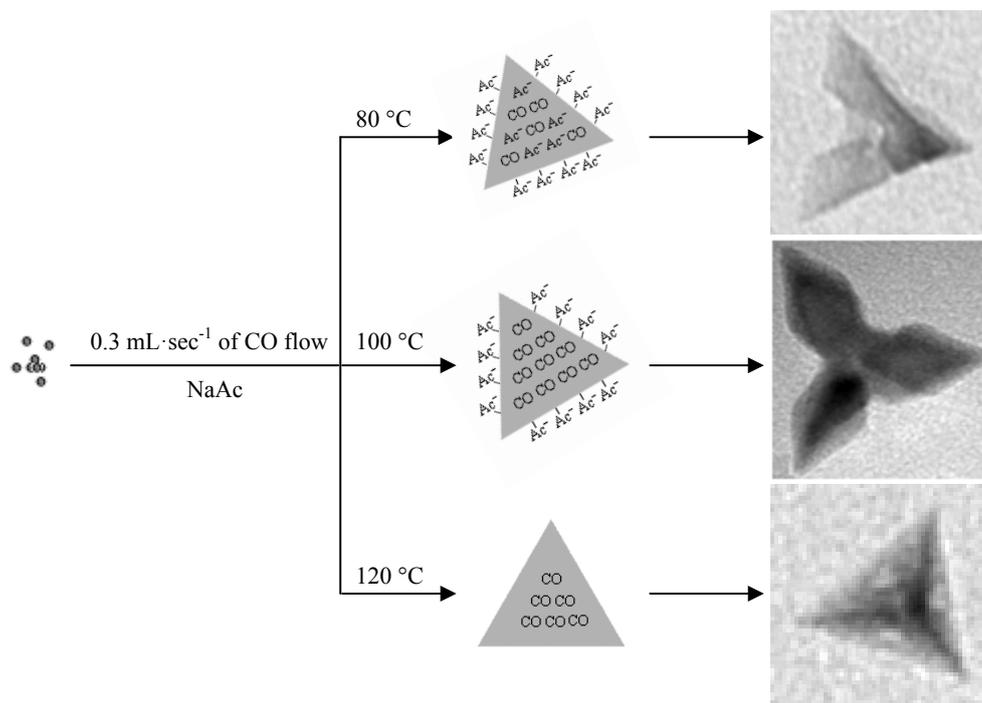
**Figure S5.** Effects of CO flow rates on the as-prepared Pd nanocrystals. (a, b)  $0.1 \text{ mL}\cdot\text{sec}^{-1}$ ; (c, d)  $0.2 \text{ mL}\cdot\text{sec}^{-1}$ ; (e, f)  $0.3 \text{ mL}\cdot\text{sec}^{-1}$ ; (g, h)  $0.4 \text{ mL}\cdot\text{sec}^{-1}$



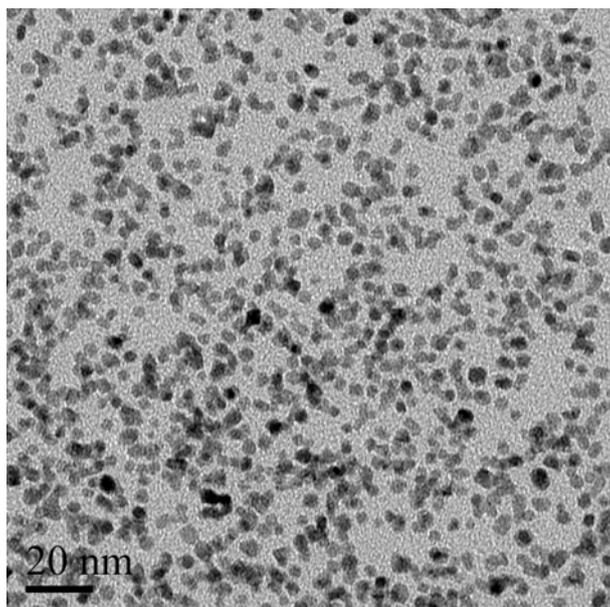
**Figure S6.** TEM images of Pd nanocrystals prepared at different temperatures. (a, b) 80°C; (c, d) 100°C; (e, f) 120°C. CO flow rate was 0.3 mL·sec<sup>-1</sup>.



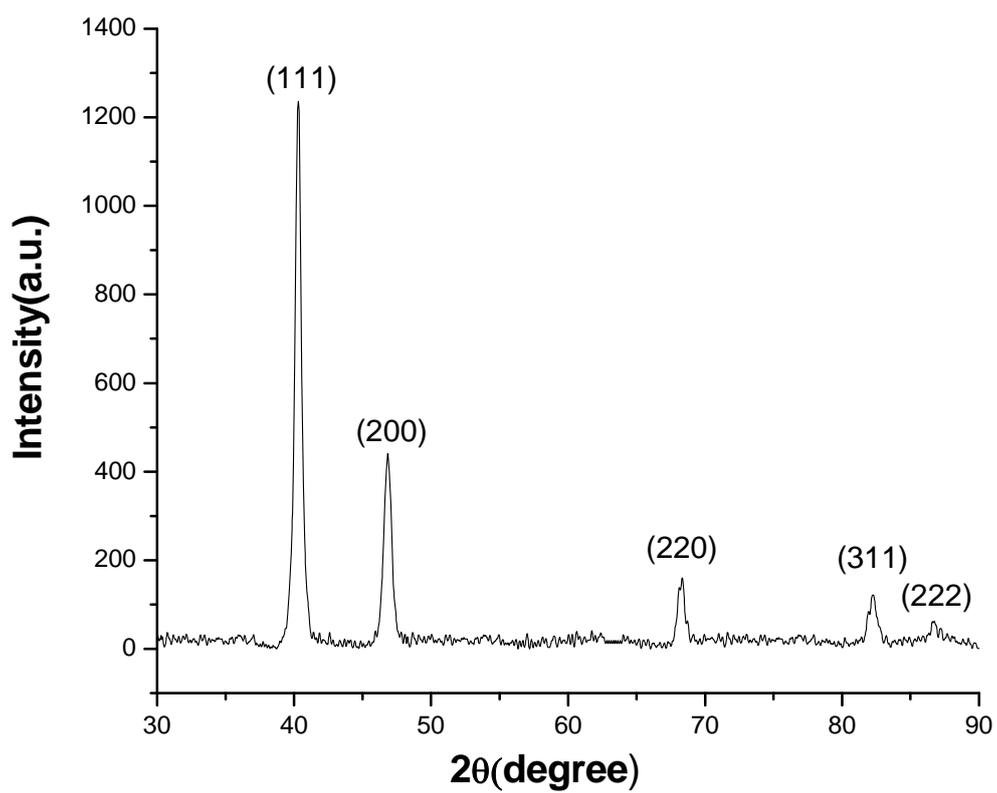
**Figure S7.** UV-vis absorption spectra of the reaction system at different stages.



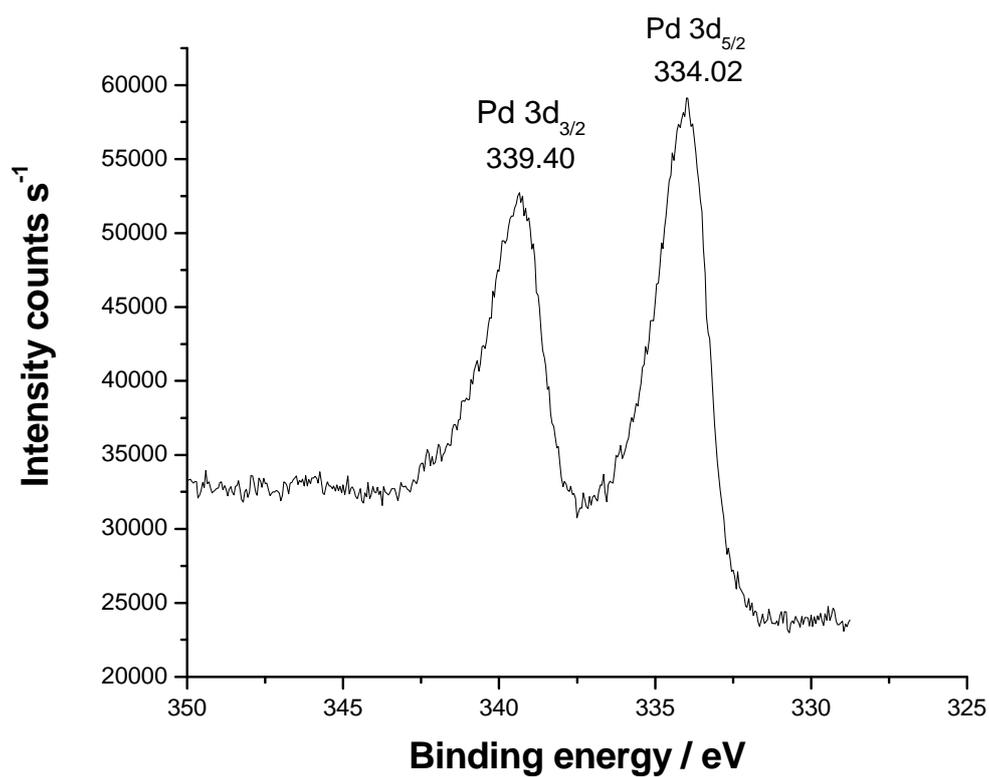
**Figure S8.** Schematic illustrations for the adsorption model of CO molecules and Ac<sup>-</sup> ions on one of the faces of the tetrahedral crystal seed in the growth process of Pd nanocrystals and the corresponding TEM images of the as-obtained nanocrystals. In all the cases, the CO flow rate was 0.3 mL·sec<sup>-1</sup> and the amount of NaAc was 83 mM.



**Figure S9.** TEM image of small Pd nanoparticles. The mean size was 4.5 nm.



**Figure S10.** XRD patterns of the typical tetrapod Pd nanocrystals.



**Figure S11.** XPS spectrogram of the typical tetrapod Pd nanocrystals.