Electronic Supplementary Information

High yield synthesis of catalytically active five-fold twinned Pt nanorods from a surfactant-ligated precursor

Jisun Yoon,[a] Nguyen Tien Khi,[a] Heonjo Kim,[a] Byeongyoon Kim,[a] Hionsuck Baik,[b] Seunghoon Back,[a] Sangmin Lee,[c] Sang-Won Lee,[a] Seong Jung Kwon,[c] Kwangyeol Lee[a*]*

[a] Department of Chemistry and Research Institute for Natural Sciences, Korea University, Seoul 136-701 (Korea)

[b] Korea Basic Science Institute (KBSI), Soul 136-713 (Korea)

[c] Department of Chemistry, Konkuk Uiversity, Seoul 143-701 (Korea)

E-mail: kylee1@korea.ac.kr (K. Lee), sjkwon@konkuk.ac.kr (S. J. Kwon)

Material Characterizations

Transmission electron microscopy (TEM) and high-resolution TEM were performed on a TECNAI G2 20 S-Twin operated at 200kV and TECNAI G2 F30 operated at 300 kV. The mass spectrometric data were obtained by using an electrospray ionization quadrupolar ion trap mass spectrometer (LCQ advantage, Thermo Finnigan, San Jose, CA, USA). X-ray photoelectron spectroscopy (XPS) was performed on ESCALAB250 X, Theta Probe XPS system.

Experimental Section

Preparation of Pt nanorods

A slurry of Pt(acac)$_2$ (0.05 mmol, Aldrich, 97%), 4.6 equiv 1,2-hexadecanediol (Aldrich, 90%), and octadecylamine (7.4mmol, Aldrich, 97%) was prepared in a two-neck round bottom flask (15 mL) with a magnetic stirring. The flask was placed in the oil bath heated to 80 °C and evacuated for 10 min with magnetic stirring, and then purged with Ar gas. After 4h aging under Ar at the same temperature, the yellowish solution was purged with CO gas. The flask was placed in an oil bath preheated to 160 °C and was heated for 1h under CO. Dark precipitates were obtained as products after introducing methanol into the cooled reaction mixture, centrifugation, and washing several times with methanol.

Preparation of Pt nanoparticles (polyhedrons, triangular plates, and fivefold twinned seastars)

A slurry of Pt(acac)$_2$ (0.05mmol, Aldrich, 97%), and octadecylamine (7.4mmol, Aldrich, 97%) was prepared in a two-neck round bottom flask (15 mL) with a magnetic stirring. (a) The flask was placed in the oil bath heated to 80 °C and evacuated for 10 min with magnetic stirring, and then purged with Ar gas. After 10 h aging step, the pale yellow solution was taken out and

cooled down to room temperature. Subsequently, 1,2-hexadecanediol (0.46 mmol, Aldrich, 90%) was introduced to the reaction mixture and repeated the (a) step. After 1 h aging step, the flask was placed in an oil bath preheated to 160 $^{\circ}$C and was heated for 1h under Ar. Dark precipitates were obtained as products after introducing methanol into the cooled reaction mixture, centrifugation, and washing several times with methanol.

Preparation of Pt nanodendrites from non-aged Pt(acac)$_2$

A slurry of Pt(acac)$_2$ (0.05mmol, Aldrich, 97%), and octadecylamine (7.4mmol, Aldrich, 97%) was prepared in a two-neck round bottom flask (15mL) with a magnetic stirring. The flask was placed in the first oil bath under vacuum at 80 $^{\circ}$C for 10min with stirring, and then purged with Ar gas. The flask was placed in an oil bath preheated to 160 $^{\circ}$C and was further heated for 1h under Ar. Dark precipitates were obtained as products after introducing methanol into the cooled reaction mixture, centrifugation, and washing several times with methanol.

Preparation of Pt nanocubes from non-aged Pt(acac)$_2$

A slurry of Pt(acac)$_2$ (0.05 mmol, Aldrich, 97%), 1,2-hexadecanediol (0.46 mmol, Aldrich, 90%), and octadecylamine (24 mmol, Aldrich, 97%)   was prepared in a two-neck round bottom flask (15 mL) with a magnetic stirring. The flask was placed in the oil bath heated to 90 $^{\circ}$C and evacuated for 10 min with magnetic stirring, and then purged with CO gas. The flask was placed in an oil bath preheated to 180 $^{\circ}$C and was heated for 50 min under CO. Dark precipitates were obtained as products after introducing methanol into the cooled reaction mixture, centrifugation, and washing several times with methanol.

Electrochemical measurements

Glassy carbon disk electrode (GCE) (dia. 3 mm, CH Instruments, Austin, TX) were used as support for Pt NPs. GCE were prepared by polishing with 1.0 and 0.3 μm alumina powder on a polishing cloth (Buehler) followed by sonication in water for 5 min. The electrodes were then rinsed with water and dried. 20 μL of 1/100 diluted nafion® perfluorinated resin solution (Aldrich,5 wt. % in lower aliphatic alcohols and water) was dropped on the cleaned GCE and dried for 30 min. The 5 mg of prepared Pt NP (rod or cube) were dispersed in 7 mL of methanol by 10 min of sonication. Then 20 μL of the Pt NP solution was dropped on the nafion coated GCE and dried for at least 1 h. The electrochemical experiment was performed using a CHI model 660d potentiostat (CH Instruments, Austin, TX). The three-electrode electrochemical cell consisted of a modified GC working electrode, an Au wire counter electrode, and a Hg/Hg$_2$SO$_4$, K$_2$SO$_4$(sat'd) reference electrode (0.64 V vs. NHE) was used. All the potential in this paper was reported vs. NHE

Fig. S1 (a) TEM image of Pt nanoparticles synthesized in the absence of CO. (b-d) HRTEM images of a truncated tetrahedron, a polyhedron, and a five-fold twinned seastar (Under e-beam, the sharp corners of a seastar are deformed). Corresponding FFT patterns of (e) a truncated tetrahedron with zone axis of <111>, (f) a polyhedron with zone axis of <01$\bar{1}$>, and (g) a five-fold twinned seastar with zone axis of <01$\bar{1}$>.
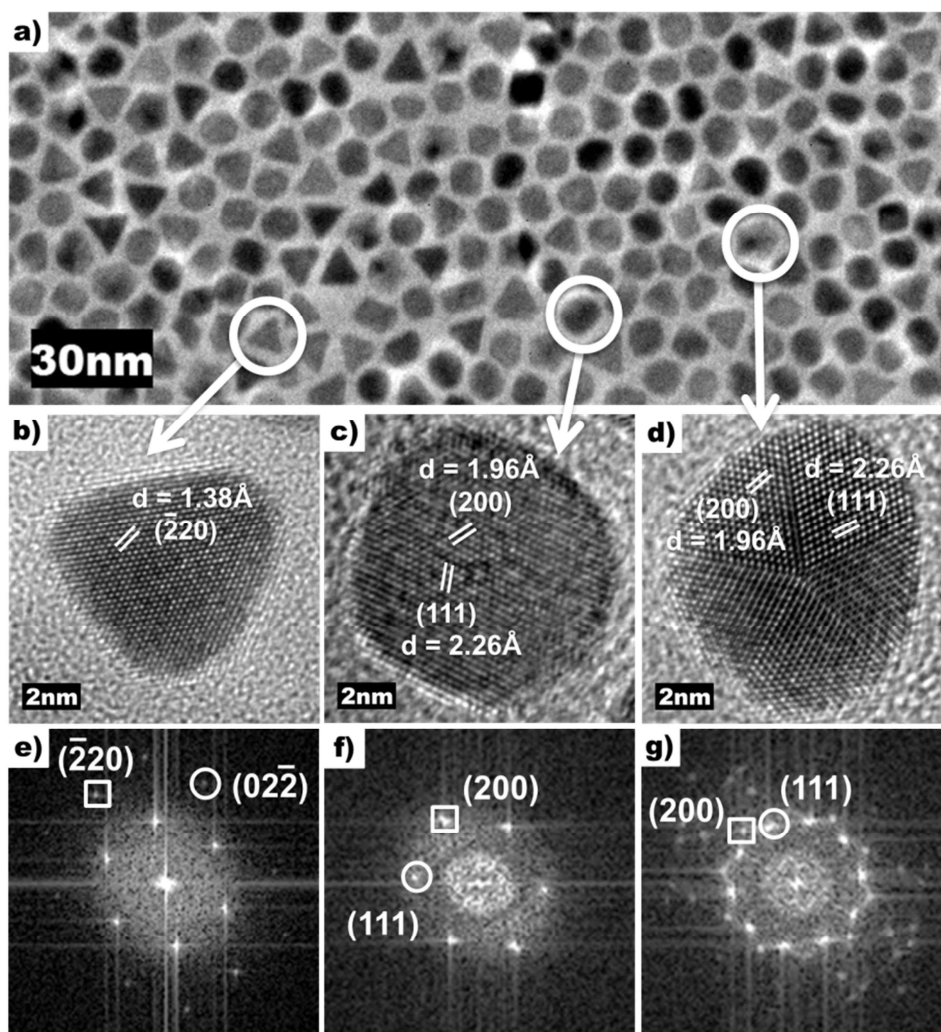
Fig. S2 Large-area TEM image of Pt nanoparticles synthesized under Ar from [Pt(acac)(NHR)]$_n$ (n= 2, 3; R= C$_{18}$H$_{37}$) (Fig. S1)**.**

The most populated shape in this sample is the polyhedrons, followed by truncated tetrahedrons, and then by five-fold twinned
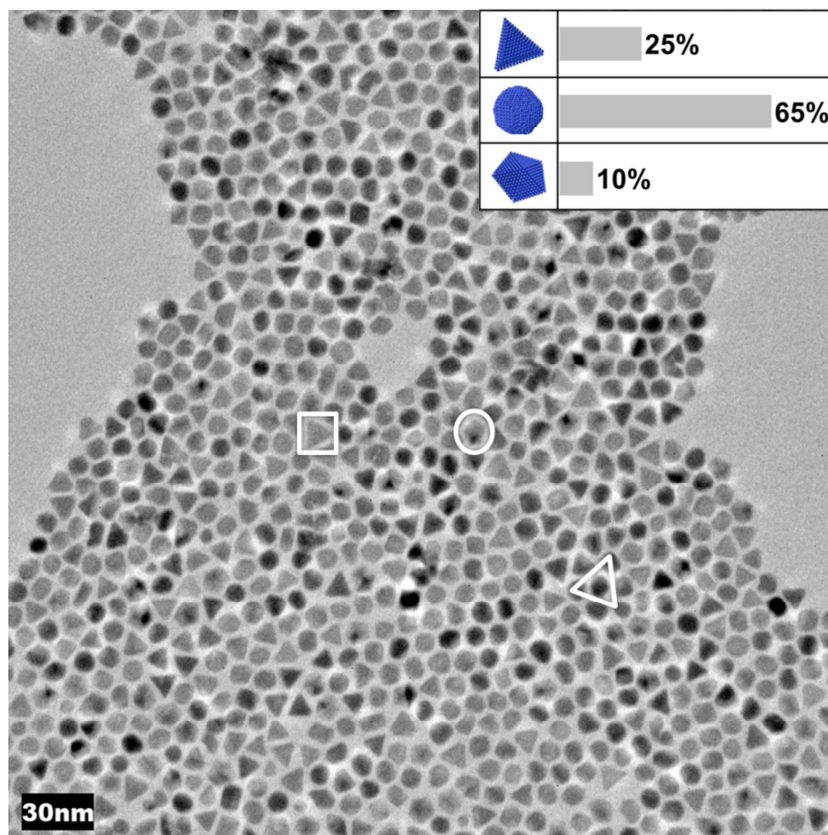
seastars.

Scheme. S1 Proposed growth of a five-fold twinned Pt nanorod along <110> direction from a five-fold twinned seastar-shaped

Pt seed.
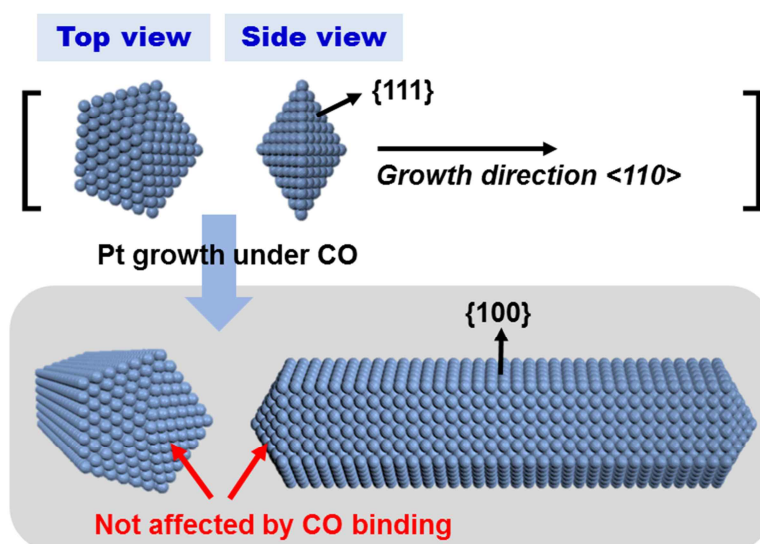
Fig. S3 (a) Mass spectrum of the $[Pt(acac)(NHR)]_n$ (n= 2, 3; R= $C_{18}H_{37}$) formed without 1,2-hexadecanediol and (b) with 1,2-hexadecanediol in the aging step. The mass spectroscopically identified species (m/z = 1271.73) was easily decomposed and combined to various m/z species under MS condition. The chemical formula (m/z = 1271.73) was determined to be $[Pt(C_5H_7O_2)(C_{18}H_{38}N)(CH_3OH)(C_2H_3N)]_2$. Methanol ($CH_3OH$) and Acetonitrile ($C_2H_3N$) have originated from the solvent used for MS measurement. (c) XPS spectrum of the new Pt precursor. The exprimental data (black line) exhibits the binding energy of Pt(II) (blue line).[1] Expanded view for the peaks at (d) m/z = 636.63, (e) 954.80, (f) 1271.73. The zoom scan was used for determining the charge states of corrosponding fragment ions. Zoom scan analysis of peak 636.63 and 954.80 showed a singly charged ion, while the analysis of the peak at m/z = 1271.73 showed a doubly charged state. (g) MS/MS data of m/z = 1271.73 indicating the presence of methanol and acetonitrile solvent molecules in the formula.
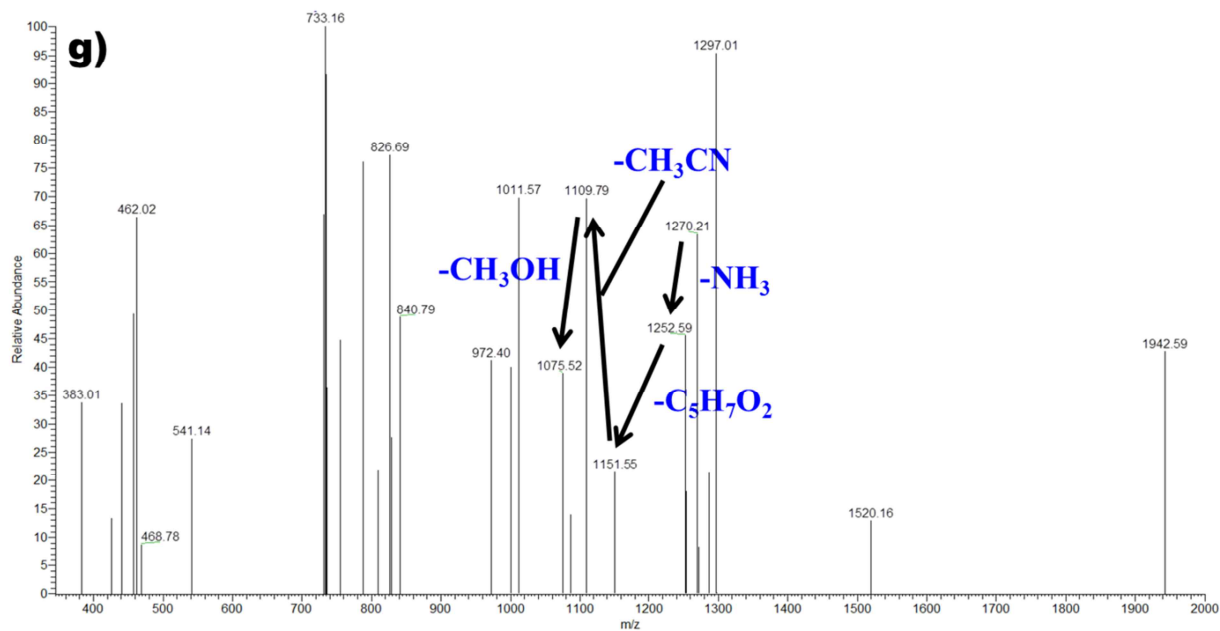
d) zoom scan : 636.63

e) zoom scan : 954.80

f) zoom scan : 1271.73
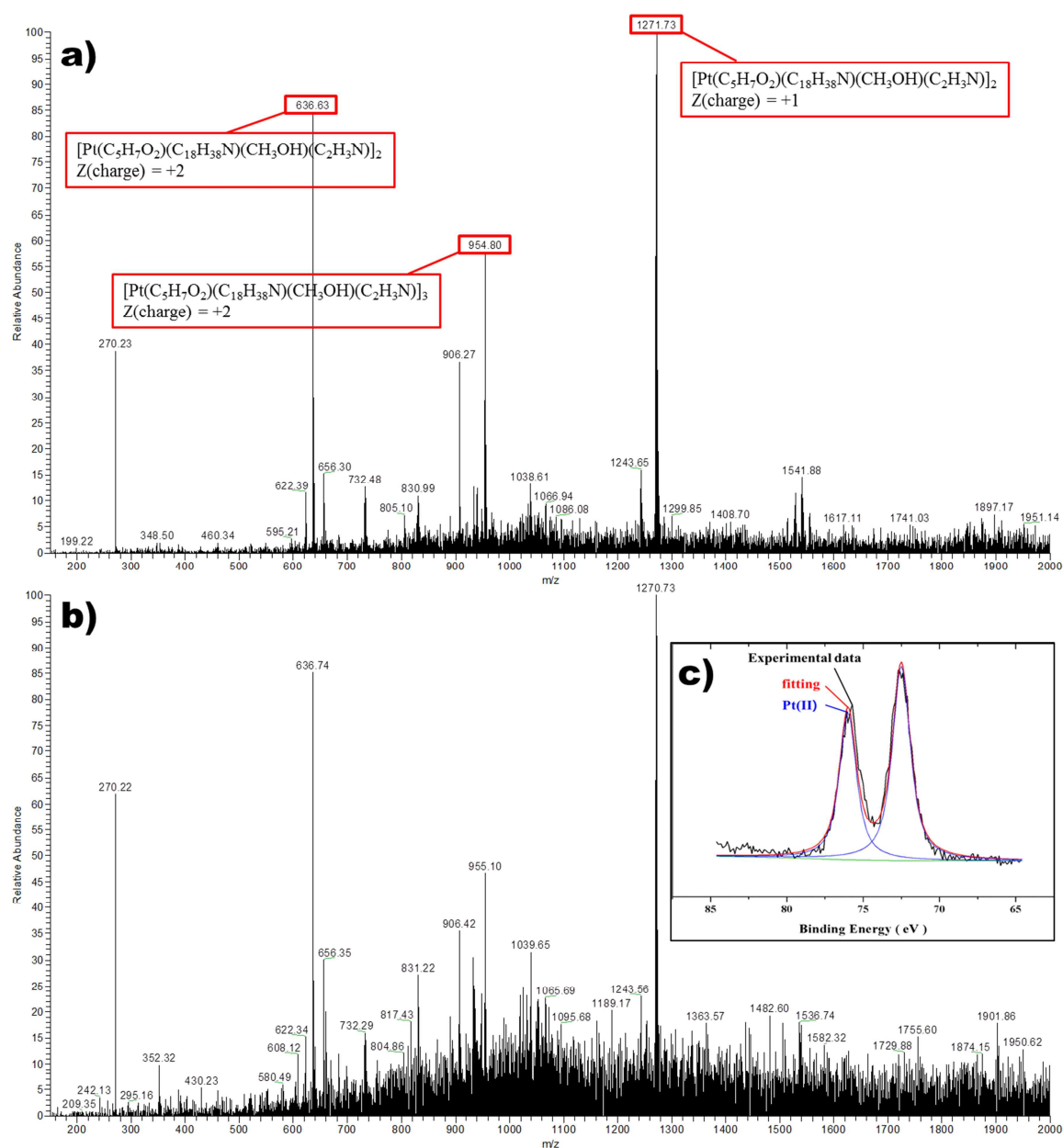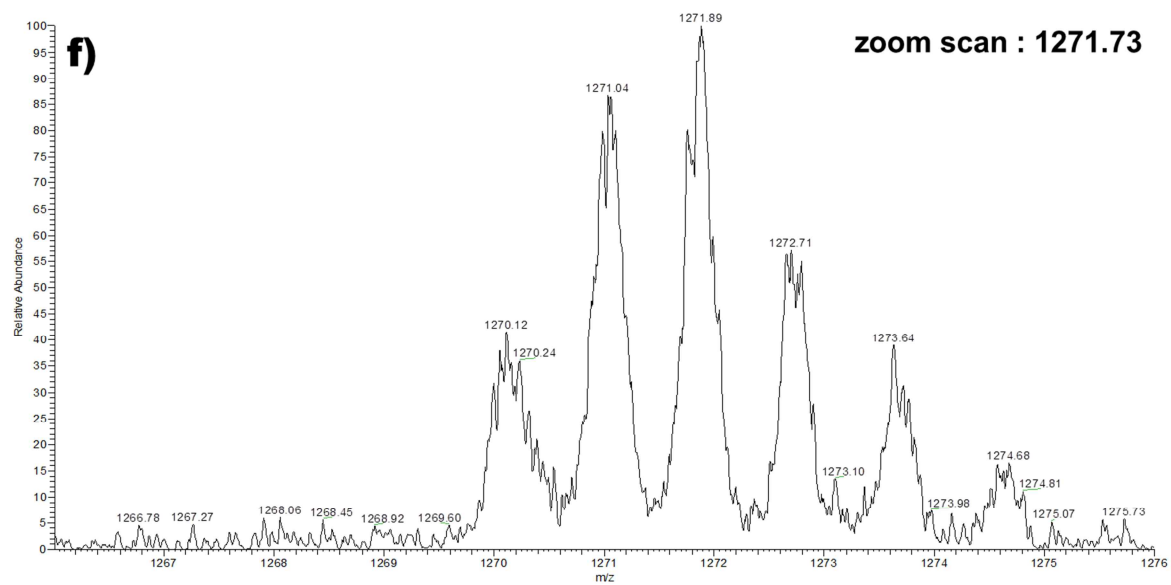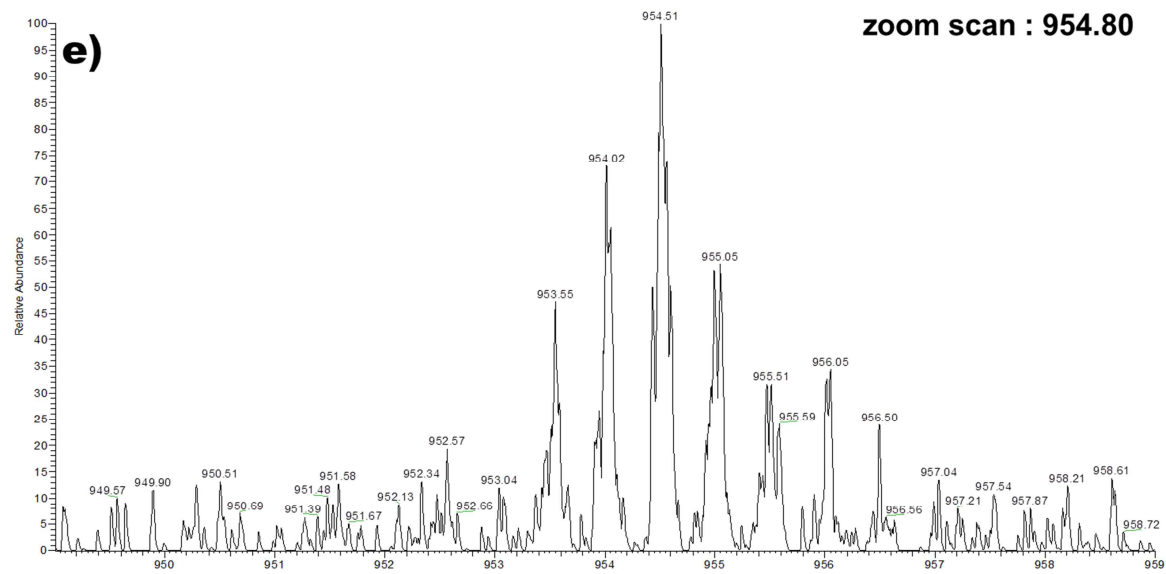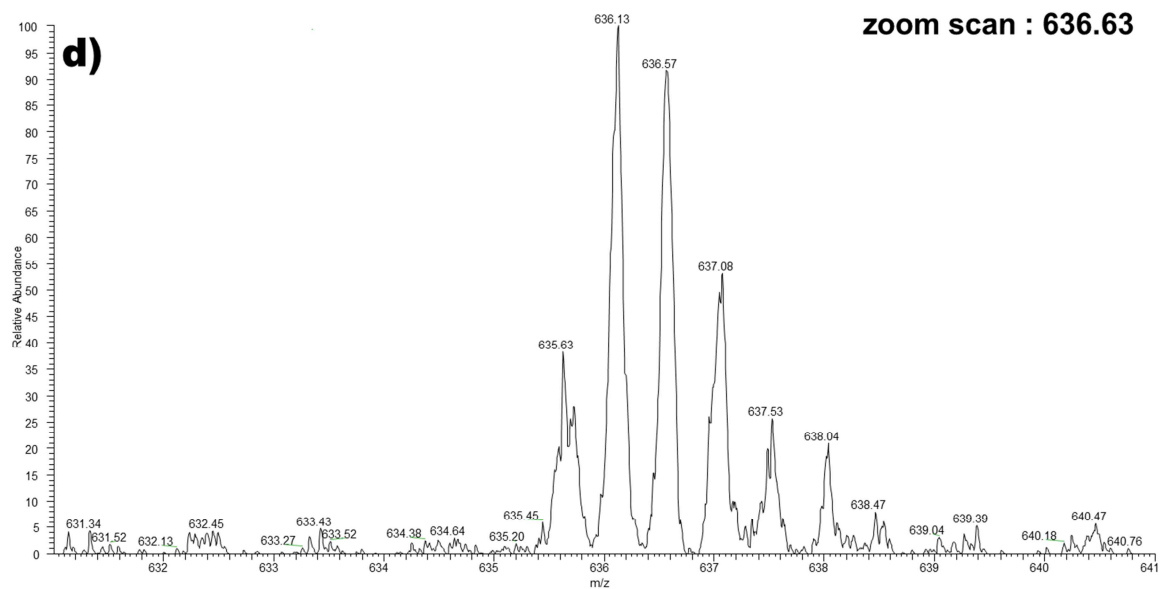
Fig. S4 Large-area TEM image of Pt nanorods (Fig. 1a). The average length and diameter are 19 ± 4.5nm and 4.5 ± 0.7nm, respectively.
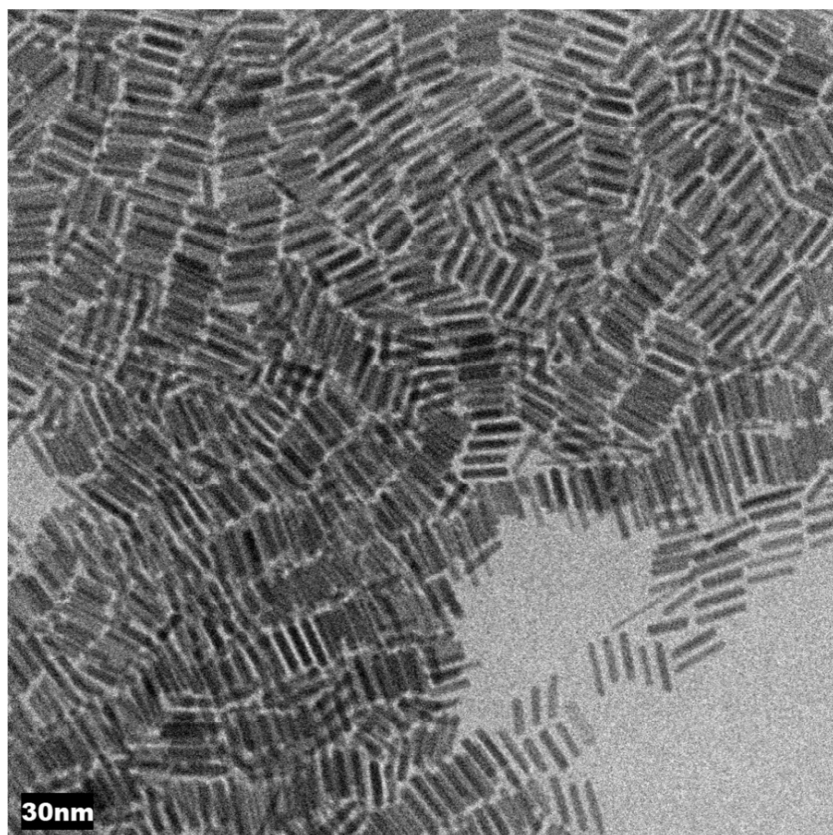

Fig. S5 Large-area TEM image of vertically aligned Pt nanorods (Fig. 1b)

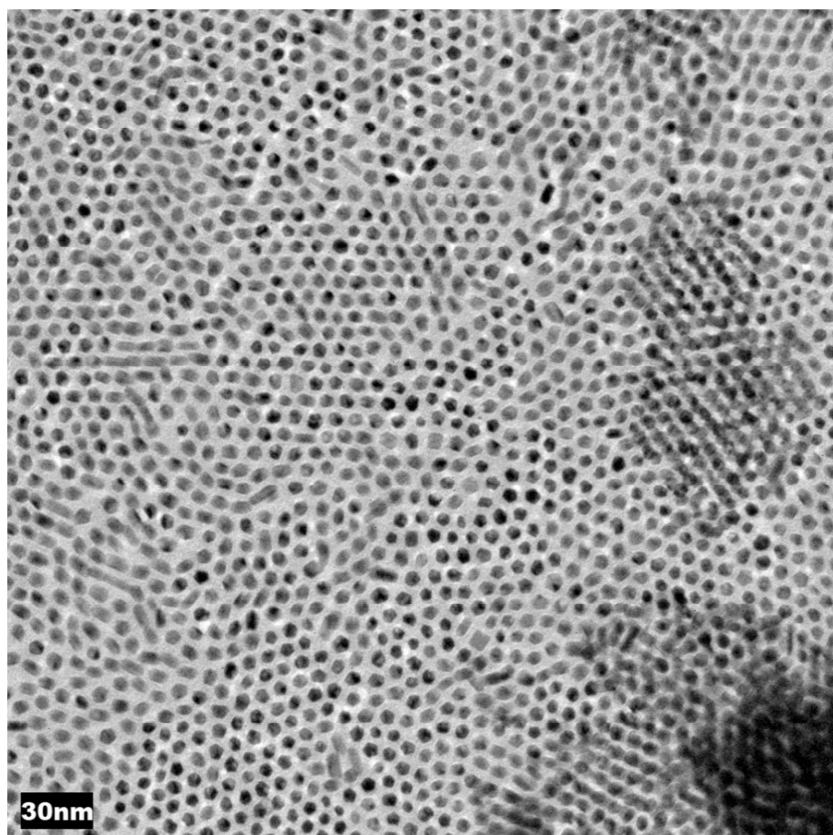**Fig. S6** TEM images of Pt nanorods synthesized at different temperatures from $[Pt(acac)(NHR)]_n$ ($n= 2, 3$; $R= C_{18}H_{37}$). The nanorod morphology was still obtained even at 300^oC
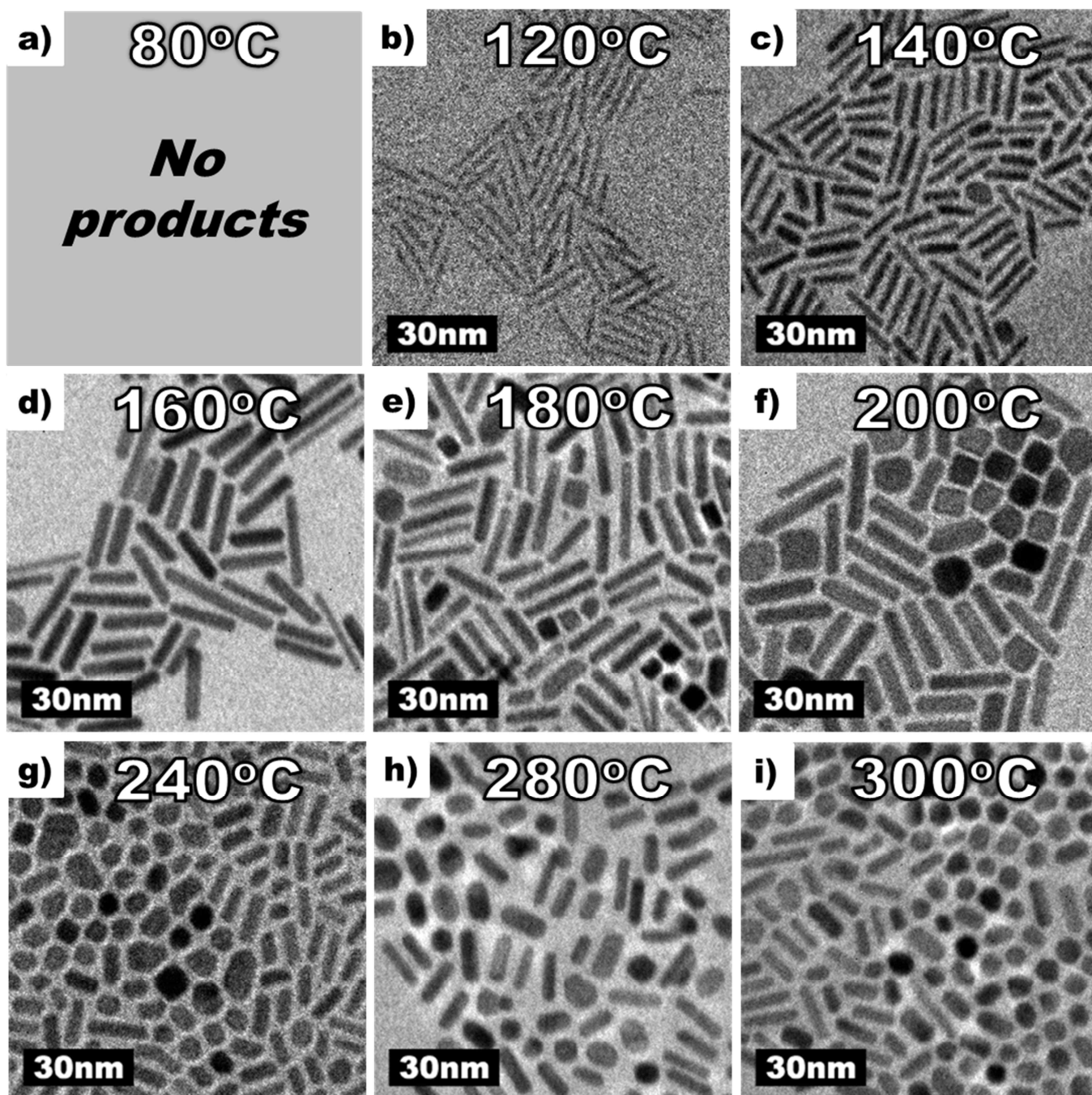
Fig. S7 TEM images of Pt nanorods. The aspect ratio correlates positively with the amount of 1,2-hexadecanediol used: (a) 0 equiv, (b) 1.5 equiv, (c) 3 equiv, (d) 6 equiv, (e) 9 equiv, and (f) 18 equiv.
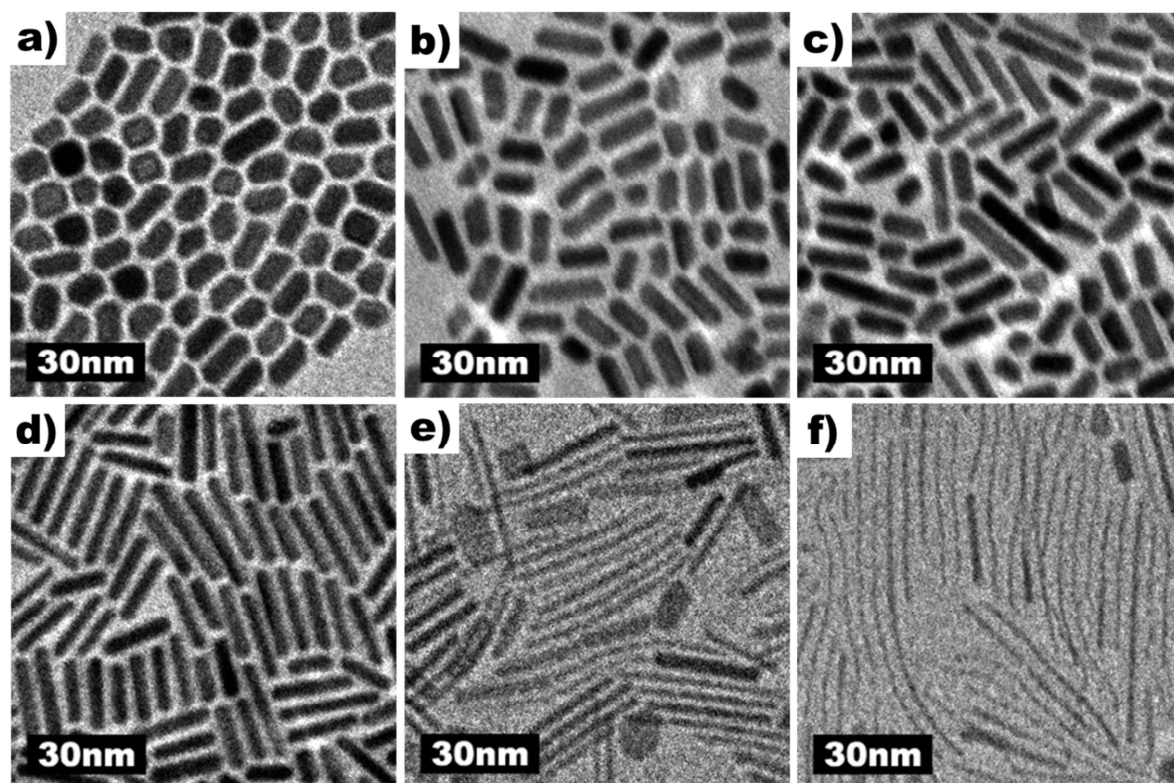

Fig. S8 Temporal TEM images of the formation of Pt nanorods. After reaching a certain length of nanorods within a few minutes, the thickness of diameter increased without further length elongation.
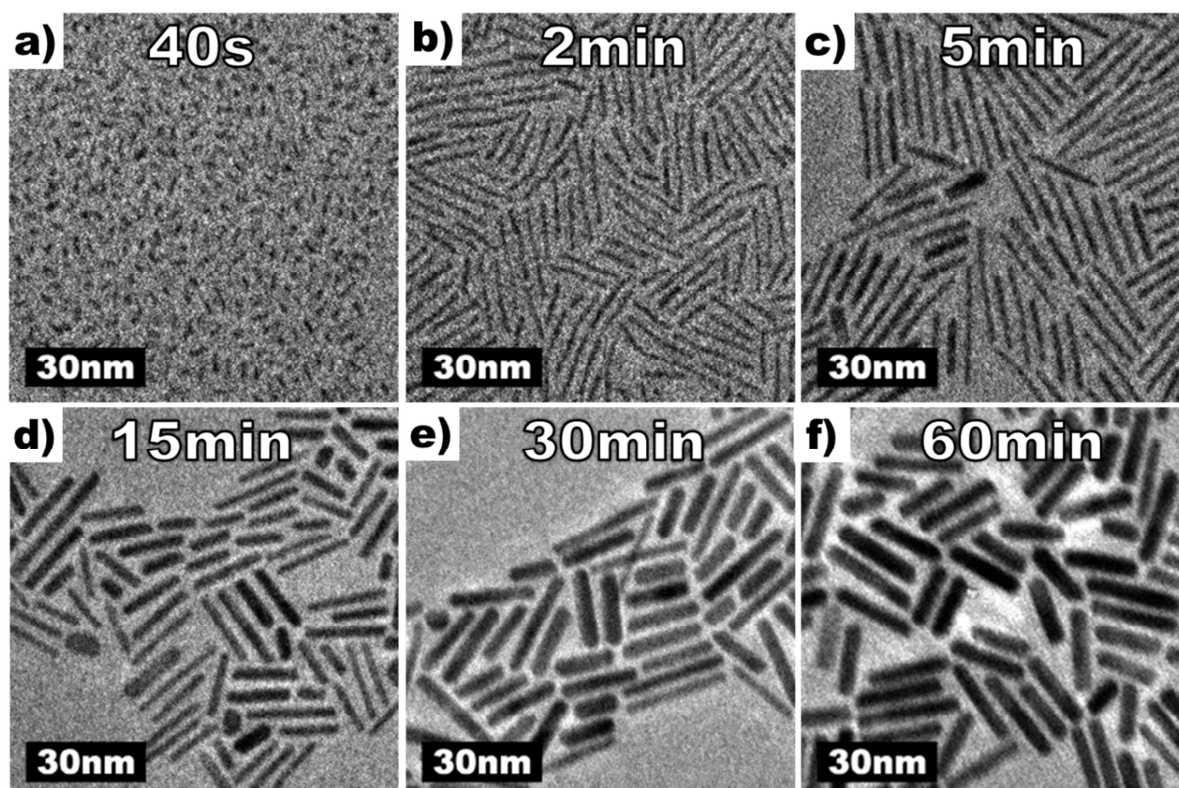
Fig. S9 TEM images of (a) Pt nanodendrites (under Ar) and (b) nanocubes (under CO) synthesized without the aging step of
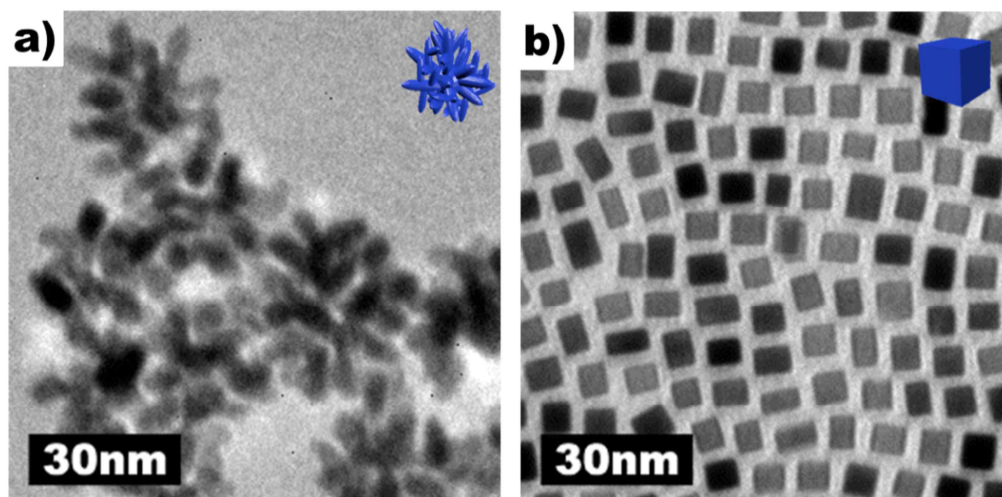
Pt(acac)$_2$.

Fig. S10 Overall reaction mechanism of the formation of Pt nanoparticles
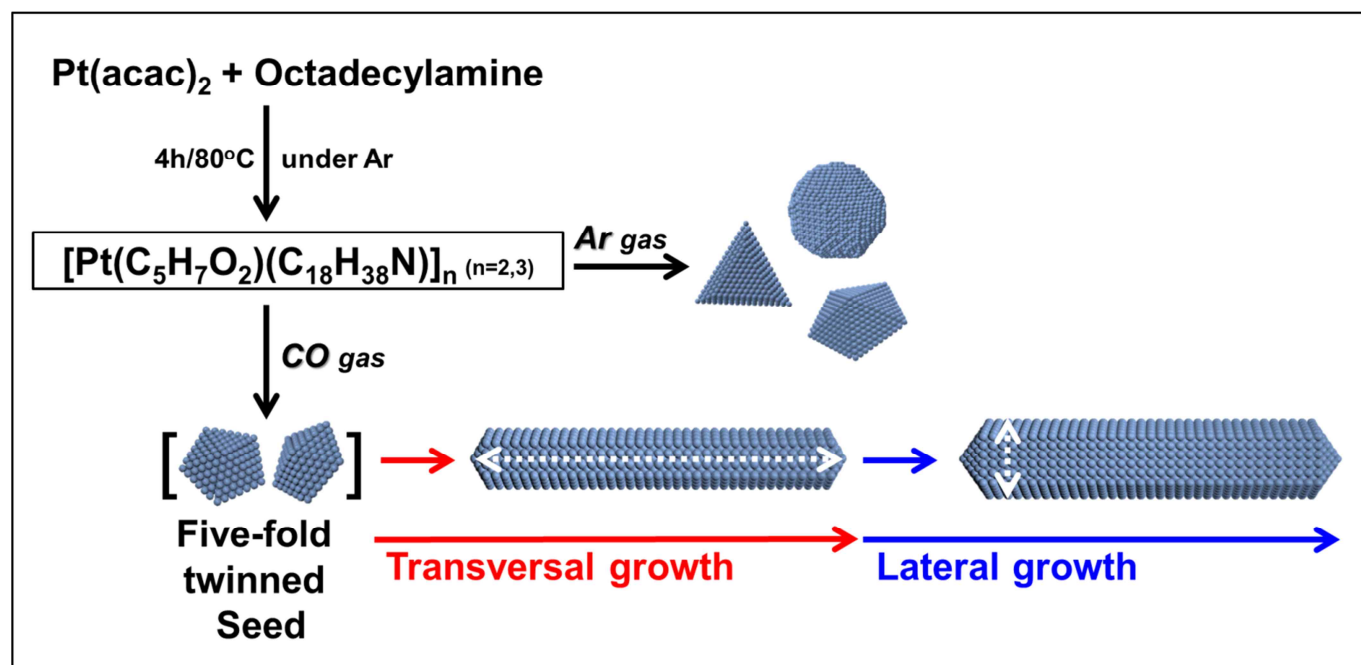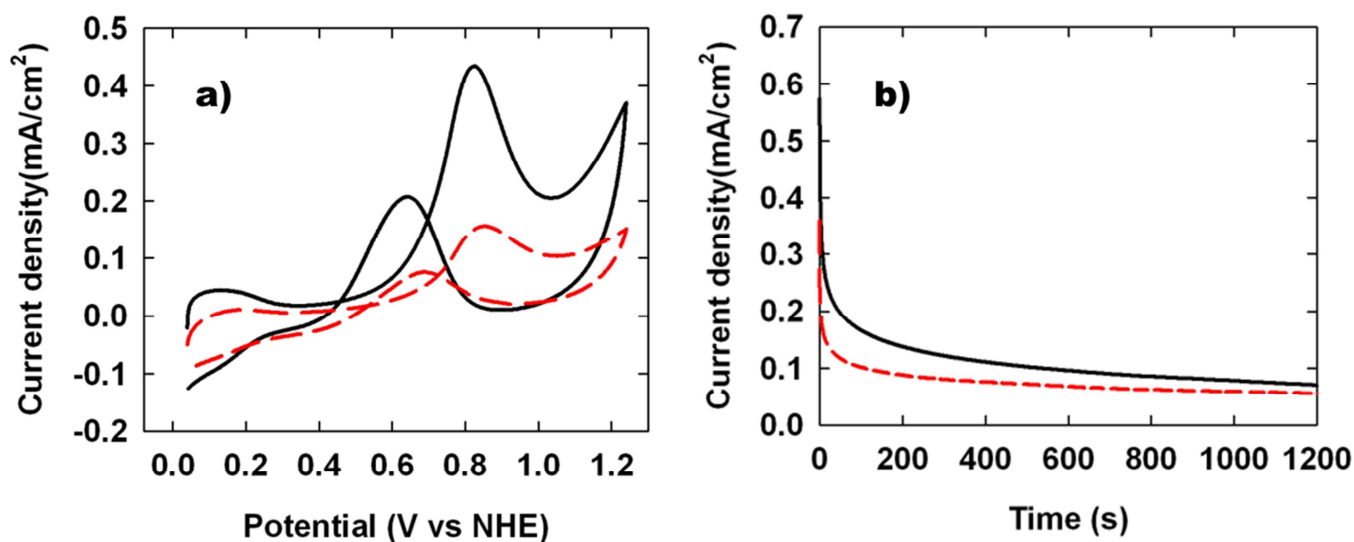
Fig. S11 (A) cyclic voltammograms and (B) chronoamperometry curves at 0.84 V (vs NHE) of Pt nanorod (black solid) and nanocubes (red dashed)modified GCE in 0.5 M MeOH + 0.5 M H_2SO_4 electrolyte solution. Scan rate was 50 mV/s.
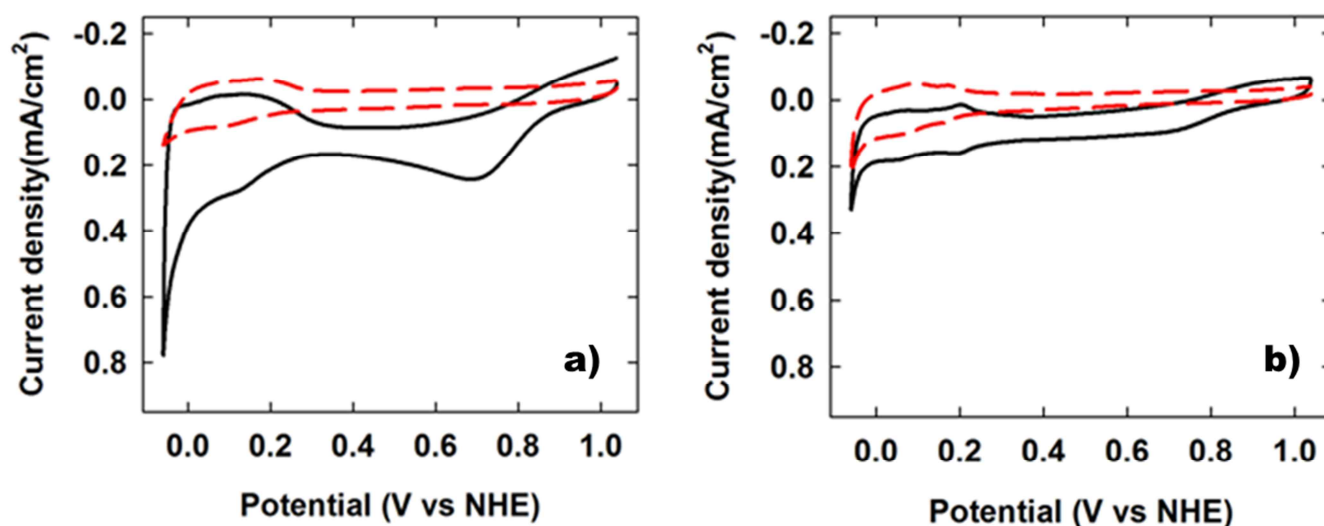

Electrocatalytic activity for methnaol oxidation reaction (MOR)

The electrocatalytic activity of the synthesized Pt NPs (nanorod and nanocubes) for the methanol oxidation reaction (MOR) characterized by cyclic voltammograms (CVs) and chronoamperometry (CA). Before the CVs were obtained, the electrodes were activated by scanning the potential between 0 V and 1.2 V several times in the same electrolyte solution (0.5 M MeOH and 0.5 M H_2SO_4). (a) shows the CVs of methanol oxidation which electrocatalyzed by Pt nanorod or nanocubes modified Glassy carbon electrodes (GCE). The voltammetric features are consistent with literature reports and are typical of the oxidation of methanol.[2] The methanol oxidation peaks for the Pt NP modified GCE developed at 0.80 V in the forward sweep and at 0.64 V in the backward sweep. The peak current densities associated with methanol oxidation in the forward scan were 4.34 mA/cm^2 for Pt nanorod and 1.55 mA/cm^2 for Pt nanocubes modified GCE. The electrochemically active surface area (ECSA) was obtained by calculation from the hydrogen desorption. The high activity of Pt nanorod modified GCE was 2.8 times bigger than the Pt nanocube modified GCE.

CA data were recorded at 0.84 V for 1200 s as a measure of the catalyst deactivation (b). We observed that the Pt nanorod modified GCE exhibited a slower current decay over time in comparison to the Pt nanocubes, indicating a larger catalytically active surface area and perhaps higher tolerance to CO-like intermediates.

Fig. S12 cyclic voltammograms of (A) Pt nanorod and (B) nanocubes modified GCE in O_2- (black solid), or Ar-(red dashed) saturated 0.5 M H_2SO_4 electrolyte solution. Scan rate was 50 mV/s.

Electrocatalytic activity for oxygen reduction reaction (ORR)

GCEs modified with Pt NPs (nanorod or nanocubes) were prepared as described in the experimental section, and their electrocatalytic properties for the oxygen reduction reaction (ORR) were also evaluated using cyclic voltammetry (CV). CVs were acquired in an O_2- or Ar-saturated aqueous electrolyte solution containing 0.5 M H_2SO_4. Before the CVs were obtained, the electrodes were activated by scanning the potential between 1.6 V and 0.0 V (vs. NHE) several times in the same electrolyte solution. Figure S12 shows the Pt NPs modified GCE exhibits a well-defined peak around 0.7 V that corresponds to the ORR. The onset potentials of ORR were around 0.84 V at both (a) Pt nanorod and (b) nanocubes modified GCE. The same onset potentials, in other word same overpotential of the Pt nanorod and nanocubes may represents that both Pt NPs are mostlyconsisted of same type of facets{100}. The current density difference between Pt nanorod and nanocubes modified GCE suggests that the Pt nanorod have enhanced electrocatalytic ORR activity. Even the exact   limiting current of ORR is difficult to tell using only CVs without the RDE system, the faradaic current after the peak of Pt nanorod modified GCE was at least 2 times bigger than the Pt nanocubes modified GCE.

  For electrocatalytic reactions, it is important to know ECSA of the catalyst. We determined this value experimentally using the hydrogen adsorption/desorption method .[4] The broad peaks between 0.30 V and -0.05 V shown in Figure S12 are characteristic of hydrogen adsorption and desorption. We calculated the active surface area of the Pt NP catalyst on the basis of the charge associated with the hydrogen desorption region (anodic current between -0.05 V and 0.3 V). After subtraction of the background charge, the total charge was 36.3 μC for Pt nanorod, and 33.3 μC for Pt nanocubes which corresponds respectively to 0.173 and 0.174 cm^2 of ECSA assuming that hydrogen desorption yields 210 μC/cm^2 of Pt surface area.[3]
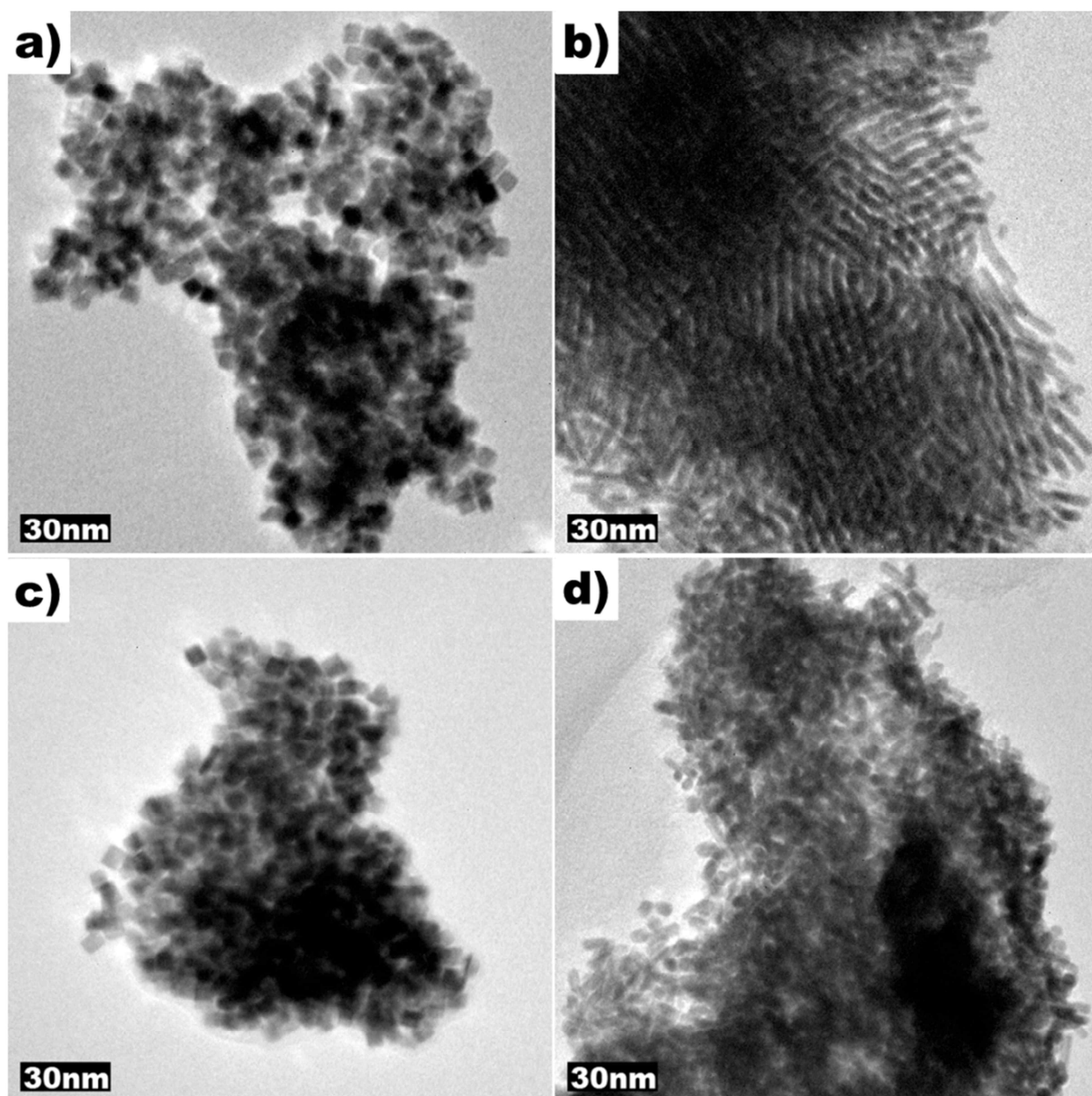
Fig. S13 (a, b) TEM image of Pt nanocubes and rods after removing surfactants and (c, d) after the electrochemical measurements.

Reference

1. G. C. Allen, P. M. Tucker, *J. Electroanal. Chem.* **1974**, *50,* 335
2. E. P. Lee, Z. Peng, W. Chen, H. Yang, Y. Xia, *ACS Nano* **2008**, *2,* 2167.
3. T. Biegler, D. A. J. Rand, R. Woods, *J. Electroanal. Chem*. **1971**, *29*, 269.