Supporting Information

Synthesis of Pt dendritic nanocubes with enhanced catalytic properties

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Experimental Section

Chemicals and Materials: Oleylamine (OAm, >70%, Technical grade), $Pt(acac)_2$ and octadecene (ODE) were purchased from Alfa Aesar. High purity hydrogen and argon (Ar) were purchased from Suzhou Jinte High Purity Gas Co.,Ltd. (Suzhou, China). Oleic acid (OA), hexane and ethanol were purchased from Sinopharm Chemical Reagent Co., Ltd. All reagents were used as received without further purification.

Pt dendritic nanocubes synthesis: In a typical synthesis of Pt cubic dendrites, 0.1 g of $Pt(acac)_2$,15 mL of OAm were loaded into a 50 mL three-neck flask. A gentle Ar flow was bubbled to the system with a needle for 10 minutes and high purity hydrogen was then added to the flask. The magnetic stirring was started and the solution was heated to 90°C slowly and kept at this temperature for 2 h. The heating mantle was removed. When the reaction mixture was cooled to room temperature, ethanol was added to precipitate out the product via centrifugation at 4000 rpm for 10 min. The product was dispersed in hexane.

Pt nanoparticles (NPs) synthesis: In a typical synthesis of Pt NPs, 0.1g of $Pt(acac)_2$, 10 mL of ODE, 1 mL of OA and 1 mL of OAm were mixed and magnetic stirring under N_2.The mixture was heated to ca. 65°C to dissolve $Pt(acac)_2$ and the temperature was then raised to 180°C. About 10 uL in 100 mL ODE was quickly injected into the hot solution. The solution was further heated to 200°C and kept at this temperature for 1 hour before it was cooled down to room temperature. The above solution was washed and centrifuged for at least 3 times with ethanol. The final product was dispersed in 10 mL of hexane for further use.

Characterization: X-ray diffraction (XRD) characterization was carried out on a MERCURY CCD advanced diffractometer with Cu Kα radiation.TEM (including high-resolution transmission electron microscopy, HRTEM) studies were performed on a Tecnai G2 F20 S-TWIN high-resolution transmission electron microscopy operating at 200 kV. A drop of diluted nanocrystals was deposited on amorphous carbon coated copper grids.

Preparation of working electrode: The GC was polished successively with 1.0, 0.3, and 0.05 μm γ-Al_2O_3 in turn until the surface of GC was shiny and mirrorlike. The GC electrodes were allowed to dry at room temperature. Then, 5μL of the catalysts

ink (1mg/mL) was pipetted on the electrode and dried at ambient condition for at least 3h before electrochemical experiments.

Measurement of methanol oxidation reaction: The electrochemical measurements were performed in a standard three-electrode cell with CHI 600C potentiostat. The electrochemical active surface area (ECSA) of the catalysts was obtained by CV curves recorded from -0.25 V to 1.0 V in N_2-saturated 0.5 M H_2SO_4 aqueous solution. CV cures of methanol oxidation were carried out at the potential between 0.0 V to 1.0 V and Chronoamperometric curves were investigated at the constant potential of 0.5 V for 600 s in N_2-saturated 0.5 M H_2SO_4 + 0.5 M CH_3OH aqueous solution. Scan rate is 50 mV/s at room temperature.

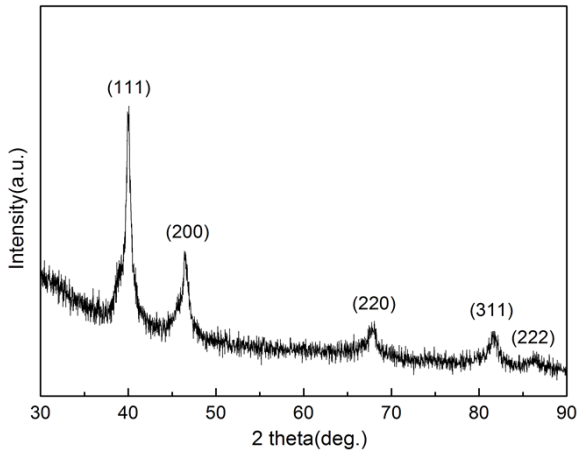
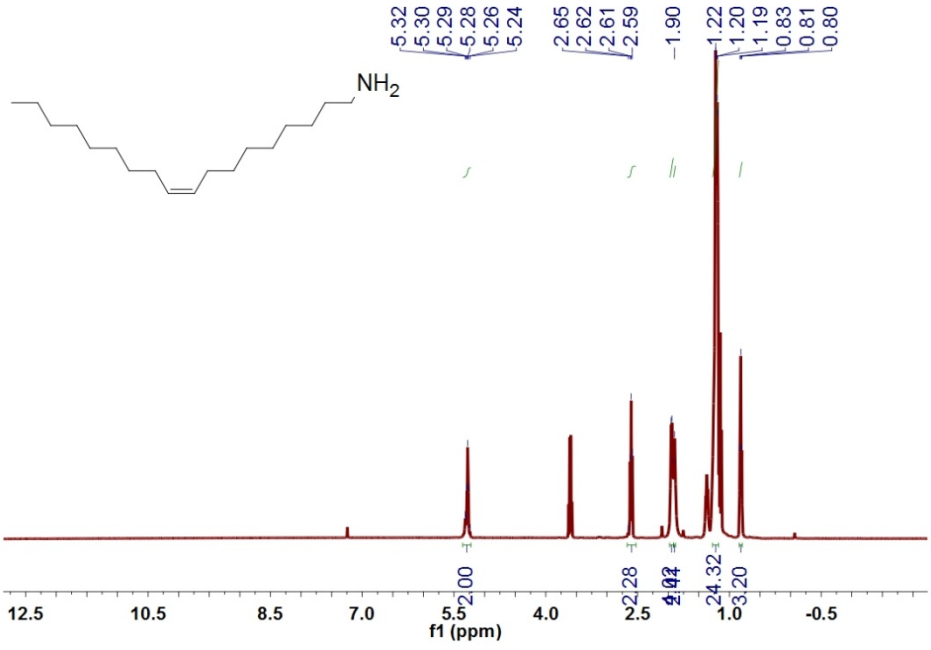
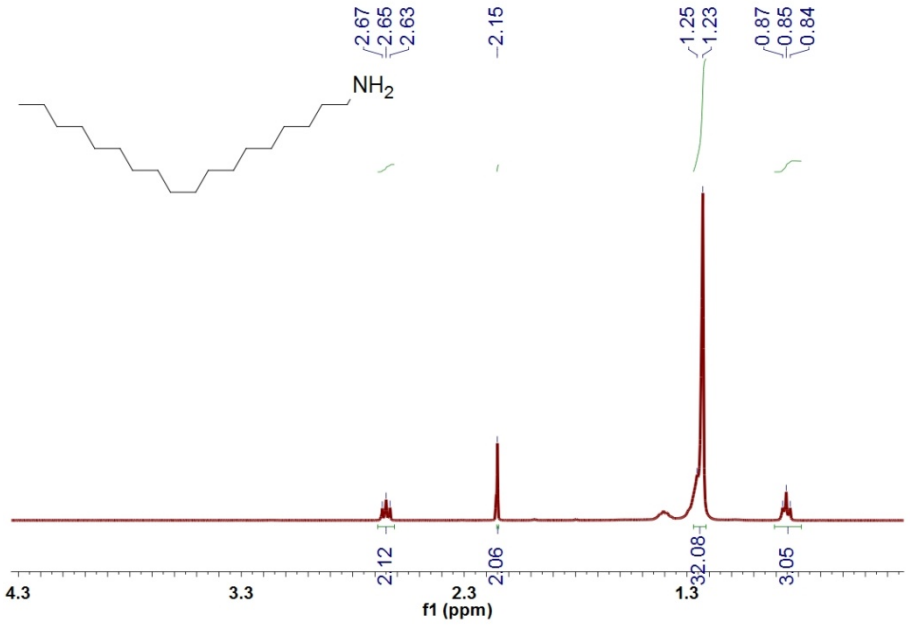


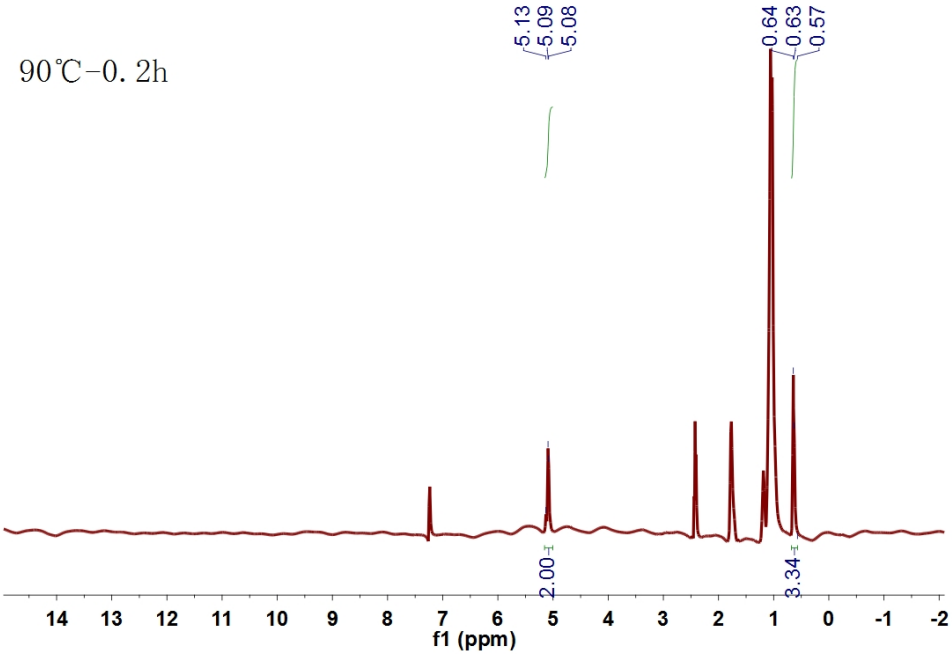
Figure S1. XRD pattern of Pt DNCs.

[1]HNMR spectra




2.67
2.65
2.63
2.15
1.25
1.23
0.87
0.85
0.84
NH2
2.12
2.06
32.08
3.05
4.3
3.3
2.3
1.3
f1 (ppm)

90℃-0. 2h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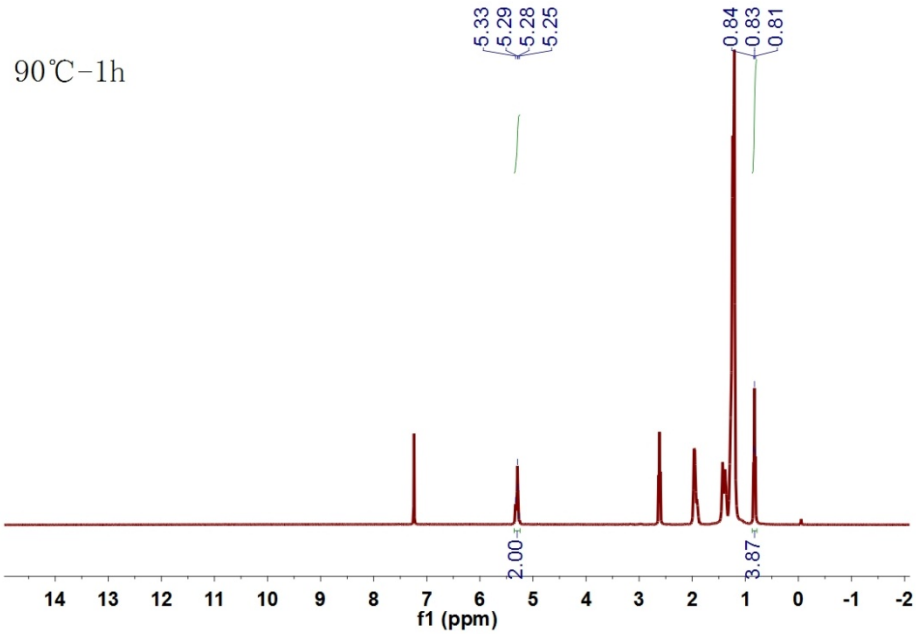
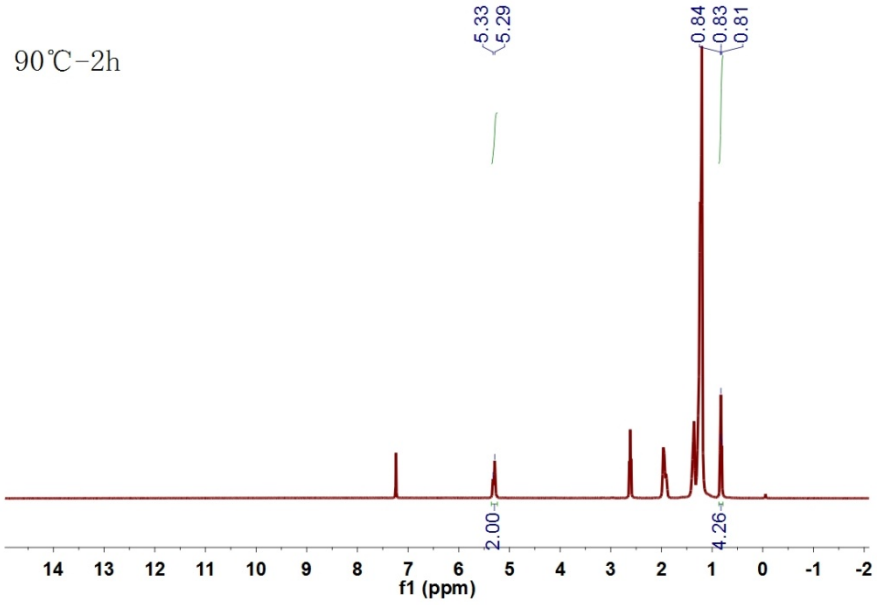
5.09
5.08
0.64
0.63
0.57
2.00
3.34
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
f1 (ppm)

90℃-1h


5.33
5.29
5.28
5.25
0.84
0.83
0.81
2.00
3.87
14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2
f1 (ppm)

90℃-2h


5.33
5.29
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0.83
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2.00
4.26
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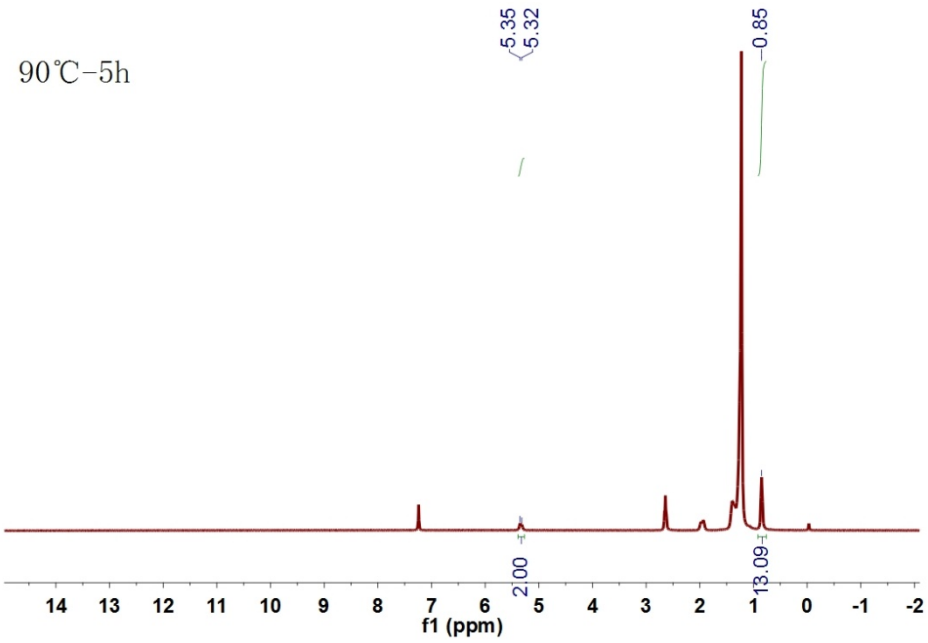
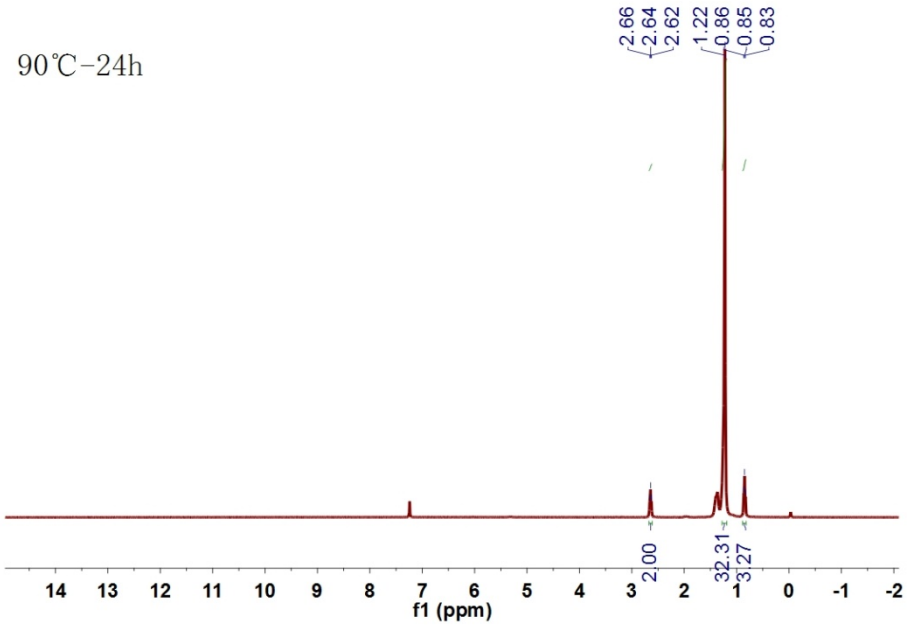
f1 (ppm)





Condition	$\delta_{5.25\text{-}5.35}$	$\delta_{0.81\text{-}0.85}$	$\delta_{0.81\text{-}0.85}/\delta_{5.25\text{-}5.35}$	Octadecylamine%
oleylamine	2	3.20	1.60	0
90°C-0.2h	2	3.34	1.67	0.04
90°C-1h	2	3.87	1.94	0.17
90°C-2h	2	4.26	2.13	0.25
90°C-5h	2	13.09	6.56	0.76
90°C-24h	0	3.27	/	100

Figure S2. [1]HNMR analysis with different reaction time

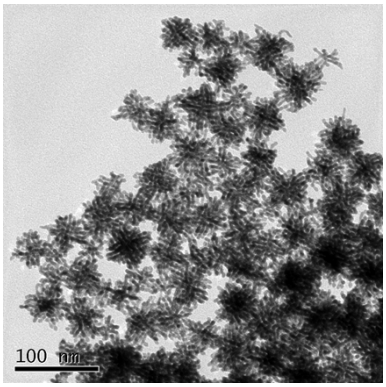


Figure S3. TEM image of Pt nanocrystals prepared in 24 h.

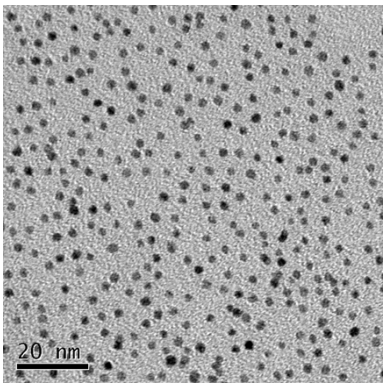


Figure S4. TEM image of Pt nanoparticles

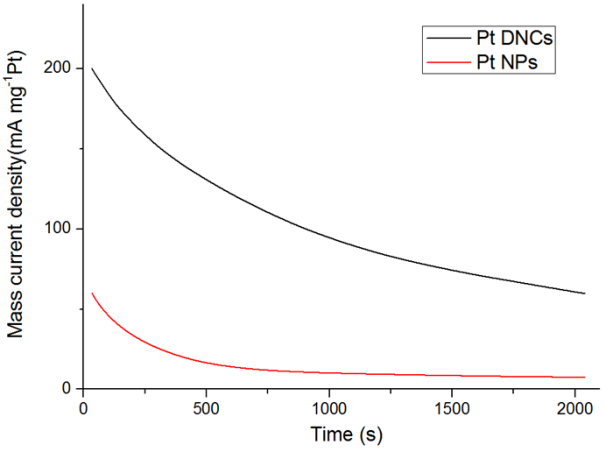


Figure S5. Chronoamperometric results of the methanol-oxidation reaction of Pt DNCs and Pt NPs

The Chronoamperometric results showed that the Pt DNCs maintained a high methanol oxidation current density.

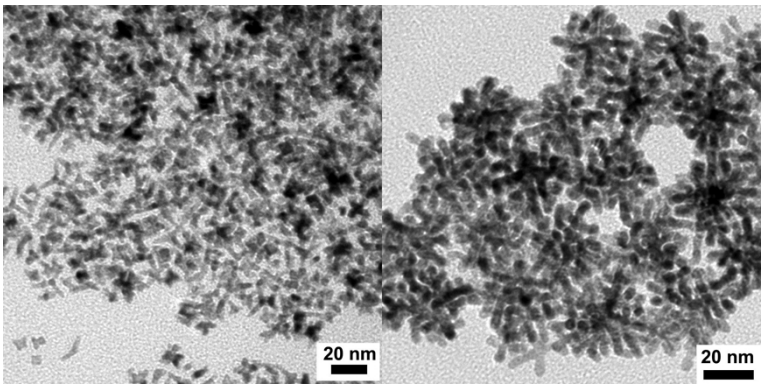


Figure S6. TEM image of Pt nanocrystals prepared at 60°C (left) and 120°C (right) in a hydrogen atmosphere.

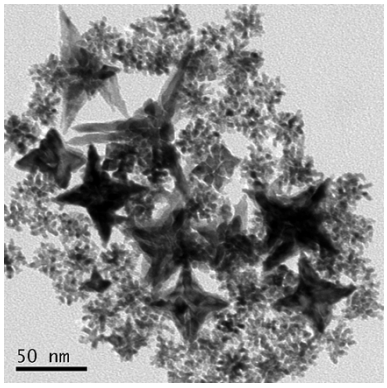
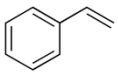
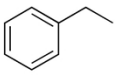
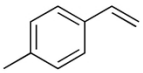
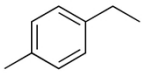
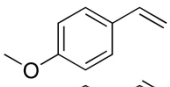
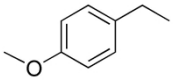
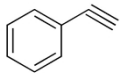
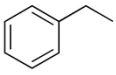
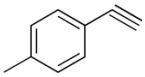
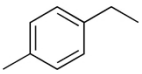
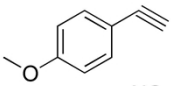
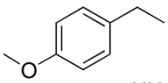
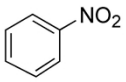
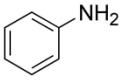
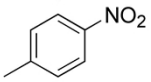
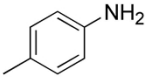
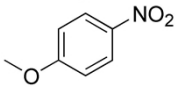
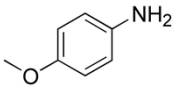


Figure S7. TEM image of Pt nanocrystals prepared at 2 atm hydrogen atmosphere.

Table S1. ECSA of Pt DNCs and Pt NPs catalysts

Catalysts	Electrode loading [g of Pt /cm^2]	Charge [QH, μC/cm^2]	ECSA [cm^2/g of Pt]	ECSA [m^2/g of Pt]
Pt DNCs	7.074×10^{-4}	56521.83	380504.04	38.05
Pt NPs	7.074×10^{-4}	27505.69	185167.89	18.52

Table S2. Hydrogenation of olefin, alkynes and nitrobenzene over Pt NPs[a]

Enter	Substrate	Product	Yield[b] (%)	time (h)
1			95	1
2			93	1
3			92	1
4			84	1
5			86	2
6			78	3
7			75	3
8			72	3
9			68	3

[a] All reactions were carried out with 1 mg Pt NPs, 1.0 mmol substrates and 2 mL methanol at 50°C in hydrogen balloon condition. [b]GC Yield.