

# **CHEMISTRY**

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### Supporting Information

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#### **Highly Shape-Selective Synthesis of Monodispersed Fivefold Twinned Platinum Nanodecahedrons and Nanododecahedrons**

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## Experimental Sections

**Chemicals:** Oleylamine (OAm, >80%; Acros), octadecylamine (ODA, >90%; Acros), hexadecylamine (HDA, >92%; Merck-Schuchardt), dodecylamine (DDA; Sinopharm Chemical Reagent Co. Ltd, China),  $[\text{Pt}(\text{NH}_3)_4][\text{PtCl}_4]$  (Magnus green salt: MGS, >97%; Aldrich),  $\text{K}_2\text{PtCl}_4$  (AR; Shenyang Research Institute of Nonferrous Metal, China),  $\text{NH}_3\cdot\text{H}_2\text{O}$  (AR; Beijing Chemical Works, China),  $\text{CH}_3\text{NH}_2$  ethanol solution (CP; Sinopharm Chemical Reagent Co. Ltd, China), ethanol (AR; Beijing Chemical Works, China), cyclohexane (AR; Beijing Chemical Works, China),  $\text{Pt}(\text{acac})_2$  (Pt wt. %>48.0%; Alfa Aesar). The water used in the synthesis was ultrapure (Millipore, 18.2 M).

**Synthesis of methylamine substituted Magnus' Green Salt (MSMGS,  $[\text{Pt}(\text{CH}_3\text{NH}_2)_4][\text{PtCl}_4]$ ):** A few modifications were done to reported synthetic method (Ref S1). 250 mg  $\text{K}_2\text{PtCl}_4$  was dispersed in 10 mL of water in a flask. Then  $\text{K}_2\text{PtCl}_4$  solution was heated to 60 °C, and 4 mL  $\text{CH}_3\text{NH}_2$  ethanol solution (27%-32%  $\text{CH}_3\text{NH}_2$  was contained) was added. The jacinth solution turned to light yellow in a few minutes. The solution was heated to reflux at 90 °C for 1 h. After the solution cooled down (if certain precipitate appeared in the solution, a filtration procedure was needed), another 170 mg of  $\text{K}_2\text{PtCl}_4$  was dissolved in 10 mL of water and was added into the colorless solution. A green precipitate was formed immediately as solutions were mixed. The precipitate was separated by vacuum filtration and washed by water and ethanol for several times. Then the green precipitate was recrystallized in 50 mL of 0.1 mol·L<sup>-1</sup> HCl solution. During the recrystallization process, the solution turned orange as precipitate was completely dissolved. Green needle-like crystals were formed, when the solution cooled down naturally. Powdery MSMGS could be acquired, if the stock solution underwent a sudden cold procedure. The green crystal was separated with vacuum filtration and washed by water and ethanol. After that, the product was dried at 110 °C for 10 h.

**Synthesis of Magnus' Pink Salt (MPS,  $[\text{Pt}(\text{NH}_3)_4][\text{PtCl}_4]$ ):** As referred to previous method (Ref S2), 110 mg of  $\text{K}_2\text{PtCl}_4$  was dissolved in 10 mL of water and heated to 60 °C. After a few minutes, the solution became colorless. Then the solution was heated to reflux at 100 °C for 1 h. After it cooled down (if certain precipitate appeared in the solution, a filtration procedure was needed), another 92 mg of  $\text{K}_2\text{PtCl}_4$  was added into 10 mL of water and mixed with the solution at 0 °C. Pink precipitate immediately appeared. It was filtered under vacuum as soon as possible and washed by cold water. Then the pink salt was dried at 110 °C for 10 h.

The precursors, Magnus' Green Salt (MGS,  $[\text{Pt}(\text{NH}_3)_4][\text{PtCl}_4]$ ) and methylamine substituted Magnus Green' Salt (MSMGS,  $[\text{Pt}(\text{CH}_3\text{NH}_2)_4][\text{PtCl}_4]$ ), both were insoluble microrod-shaped green compounds with linear Pt(II) chains possessing strong Pt-Pt interactions as illustrated in Figure S1 (Ref. S3). In Pt(II) ion chains, the distance between two Pt ions nearby was about 3 Å which was much shorter than that of other common Pt precursors. It was the reason for its special colour and insolubility (Ref. S4). Magnus' Pink Salt (MPS) was an isomer of MGS, with the same cations and anions as MGS. The distance between two nearby Pt ions was more than 5 Å in MPS, much longer than that of MGS (Ref. S5). Powder X-ray diffraction (PXRD) (Figure S2) and thermogravimetry (TG) (Figure S3) results of self-prepared MSMGS and MPS fit well with the reported data.

## Instrumentation

**PXRD:** The PXRD patterns of precursors and Pt MTPs were obtained on a Rigaku

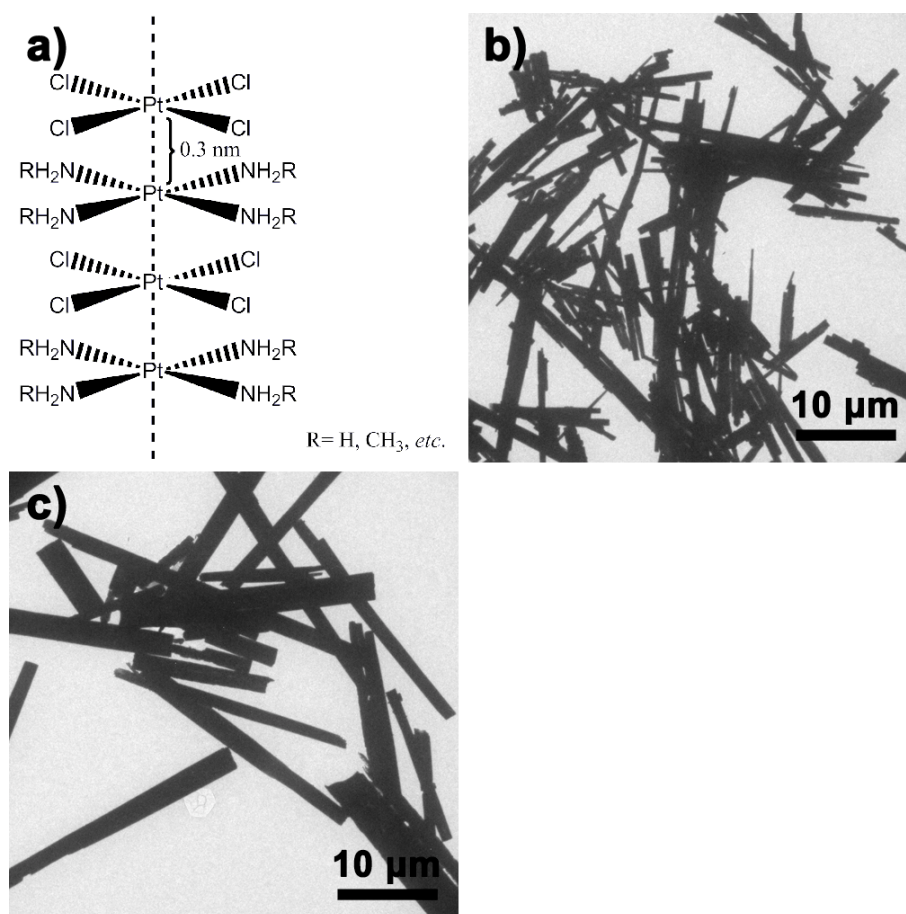
D/MAX-2000 diffractometer (Japan) with a slit of  $1/2^\circ$  at a scan rate of  $4^\circ \cdot \text{min}^{-1}$  under Cu  $K_\alpha$  radiation ( $\lambda = 1.5406 \text{ \AA}$ ). Pt NIs and Pt NDs dispersions in cyclohexane were previously dropped on glass slides for the preparation of PXRD measurement.

**TG:** Thermogravimetry measurement of Pt precursors (MSMGS and MPS) was performed on a Q600 SDT TGA-DSC-DTA instrument (U. S. A) in air with temperature programming (at rate of  $3^\circ \text{C} \cdot \text{min}^{-1}$  from RT to  $200^\circ \text{C}$ ,  $1^\circ \text{C} \cdot \text{min}^{-1}$  from  $200^\circ \text{C}$  to  $500^\circ \text{C}$ ,  $5^\circ \text{C} \cdot \text{min}^{-1}$  from  $500^\circ \text{C}$  to  $800^\circ \text{C}$ )

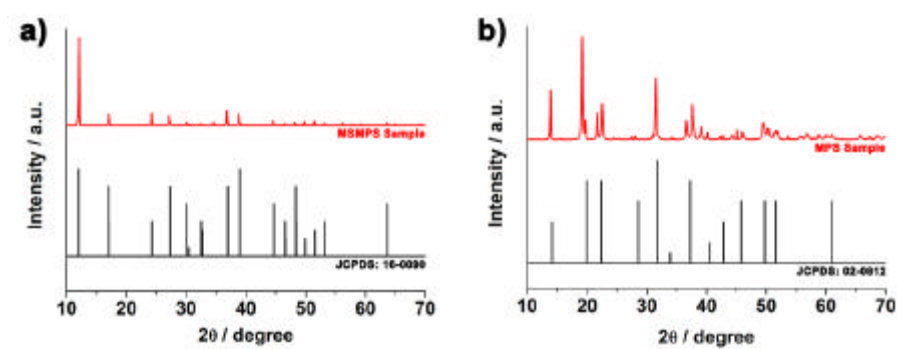
**TEM, HRTEM, and HAADF-STEM:** All obtained colloidal Pt samples were dispersed in cyclohexane under supersonic treatment. Then the colloidal solution was dropped onto a copper grid coated with amorphous carbon films. MGS and MSMGS samples were prepared by dispersing precursors in ethanol and transferring onto copper grids. TEM images of these samples were captured by a TEM (JEM-2100, JEOL, Japan) at an accelerating voltage of 200 kV. HRTEM and HAADF-STEM measurements were performed on a FEG-TEM (JEM-2100F, JEOL, Japan).

**DLS.** The DLS size distribution characterizations of the as-formed Pt nanoclusters (at reaction for 24 h and 48 h in OAm at  $150^\circ \text{C}$ , with using MSMGS as the precursor) dispersions in cyclohexane were performed on a Horiba SZ-100 nano-particle analyzer (Horiba, Japan).

## Supplementary Data

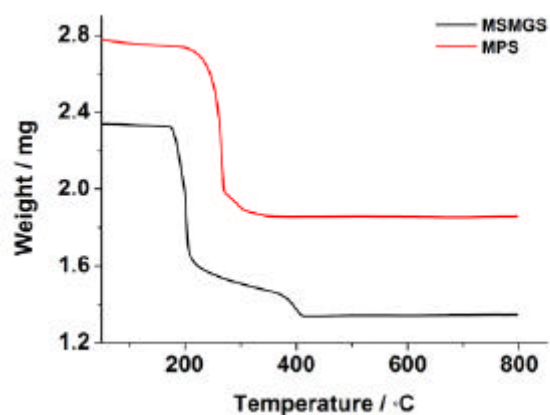


**Figure S1.** a) Molecular structure scheme of MGS and MSMGS; TEM images of microrod-shaped b) MGS and c) MSMGS precursors.

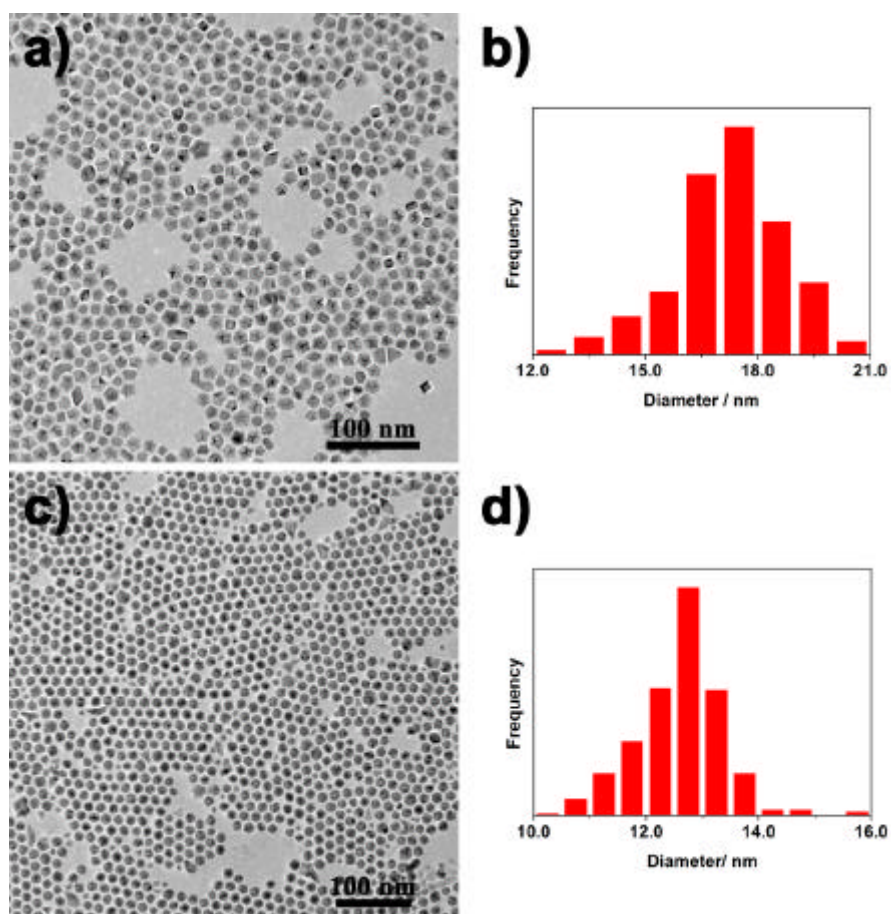


**Figure S2.** PXRD patterns of home-made a) MSMPS and b) MPS, compared with standard XRD data of MSMPS (JCPDS: 16-0090) and MPS (JCPDS: 02-0812).

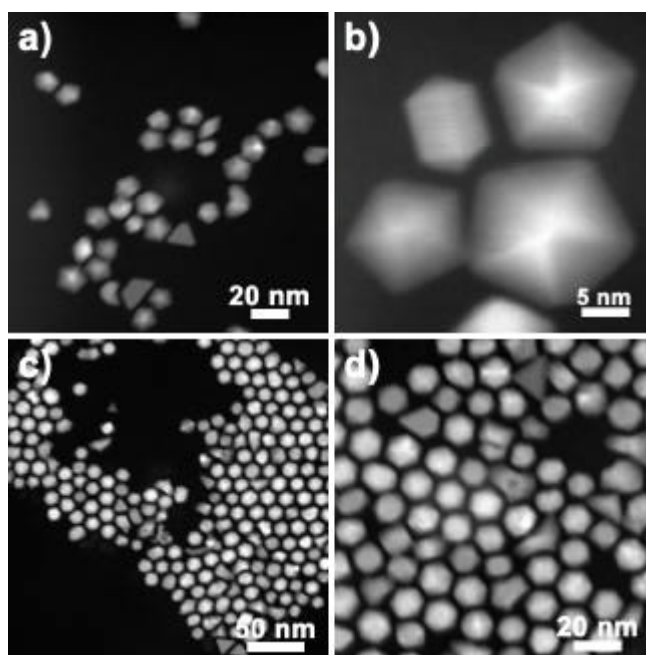




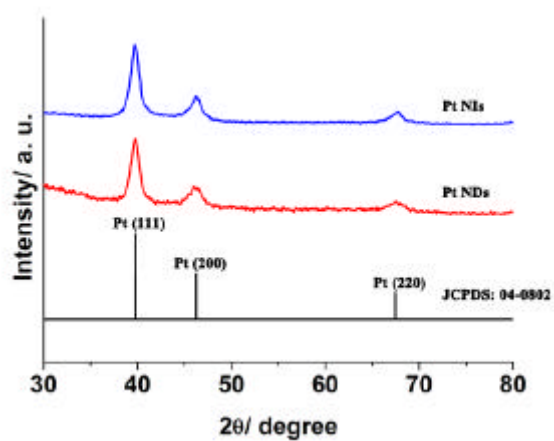
**Figure S3.** Thermogravimetry analysis curves of MSMGS and MPS at the range from room temperature to 800 °C in air. The weight losses were 42.4 % (residual mass: 57.6%) and 32.4% (residual mass: 67.6%) for MSMGS and MPS, respectively. The residual mass agrees with the nominal amount of platinum present in MSMGS and MPS, respectively.



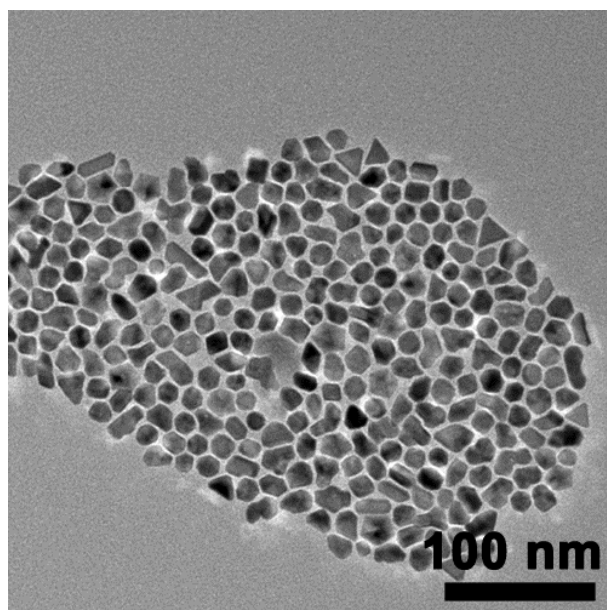
**Figure S4.** a) Low-magnification TEM image and b) size distribution of Pt NPs; c) low-magnification TEM image and d) size distribution of Pt NIs.



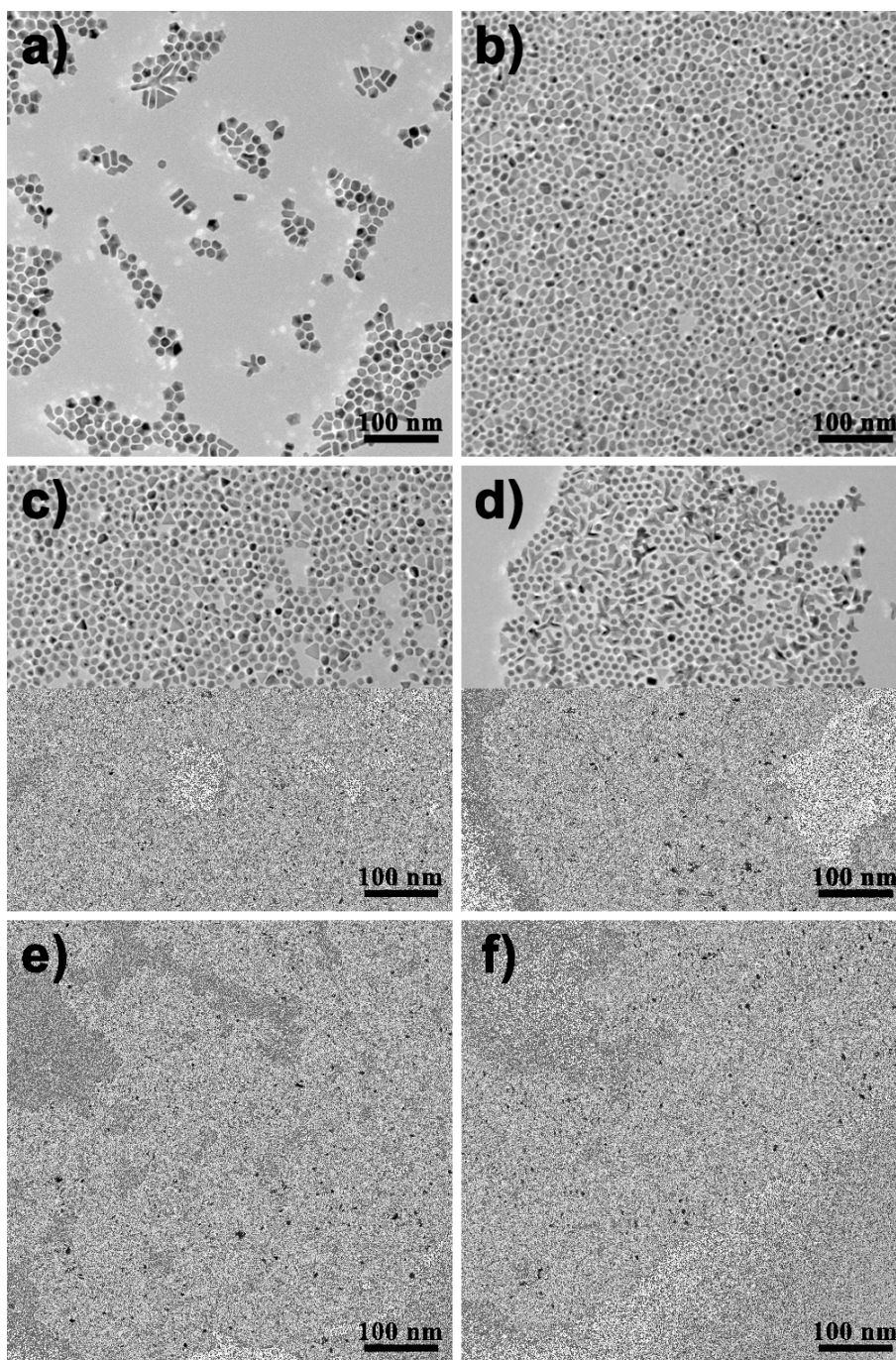
**Figure S5.** HAADF-STEM images of a, b) Pt NDs and c, d) NIs.



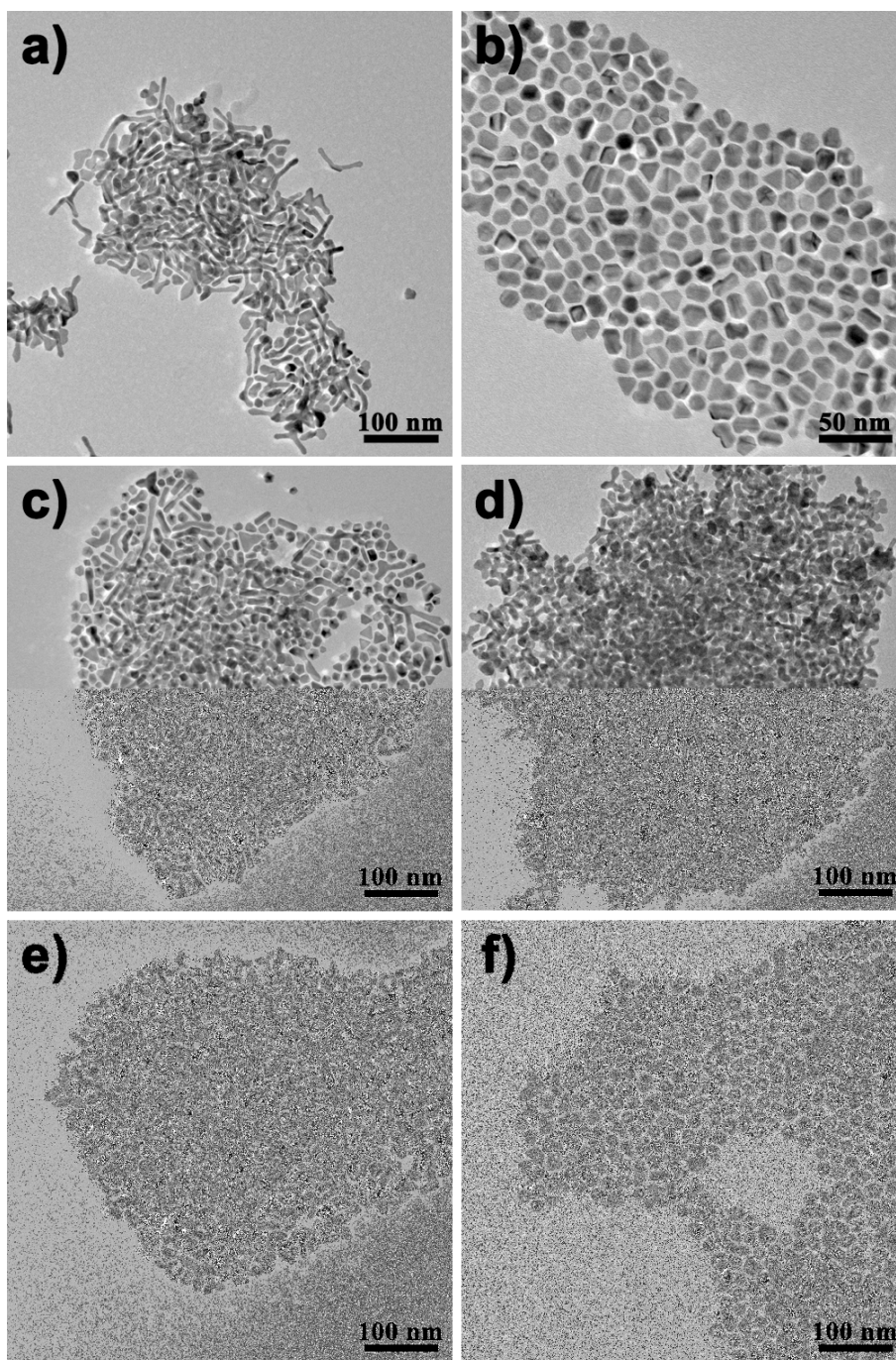
**Figure S6.** PXRD patterns of as-prepared Pt NDs and NIs, compared with standard XRD data of *fcc* structured Pt (JCPDS: 04-0802).



**Figure S7.** TEM image of Pt NPs reduced from 5 mg of MPS in 10 mL of OAm at 130 °C for one week.

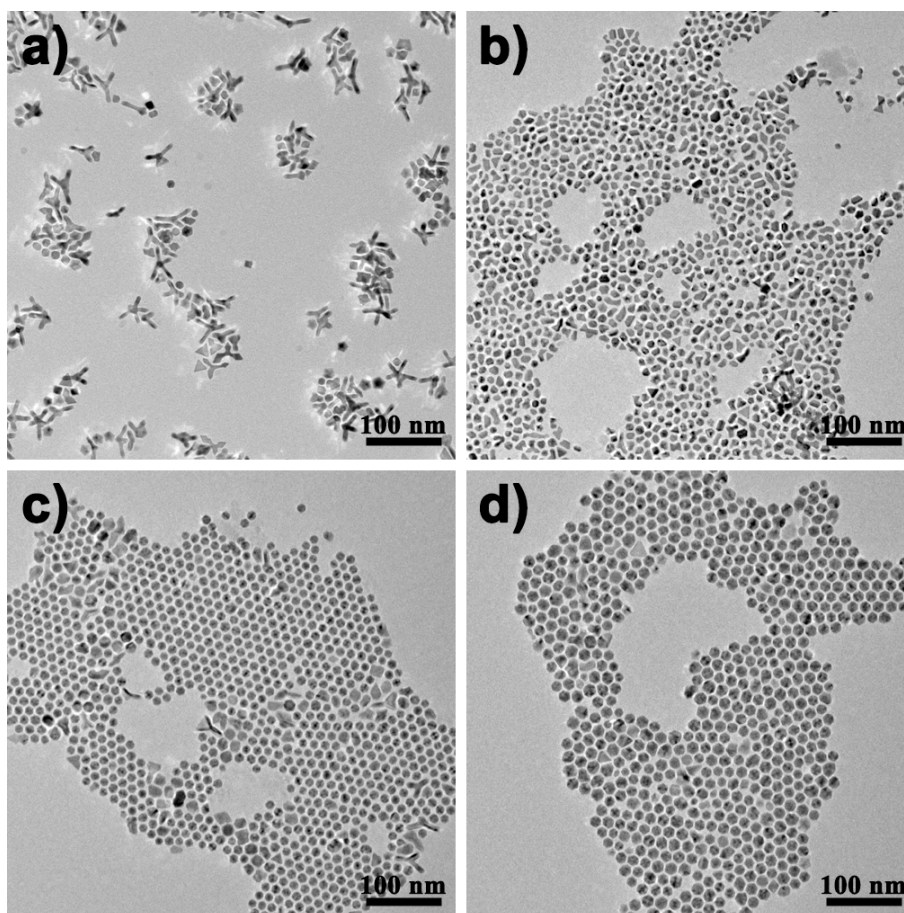


**Figure S8.** TEM images of products of temperature sequence reactions in the synthesis of Pt NDs and NIs: 5 mg of MGS reacted in 10 mL of OAm for one week at a) 125 °C, b) 140 °C and c) 150°C; 4 mg of MSMGS reacted in 10 mL of OAm for one week at d) 140 °C, e) 150 °C and f) 160°C.

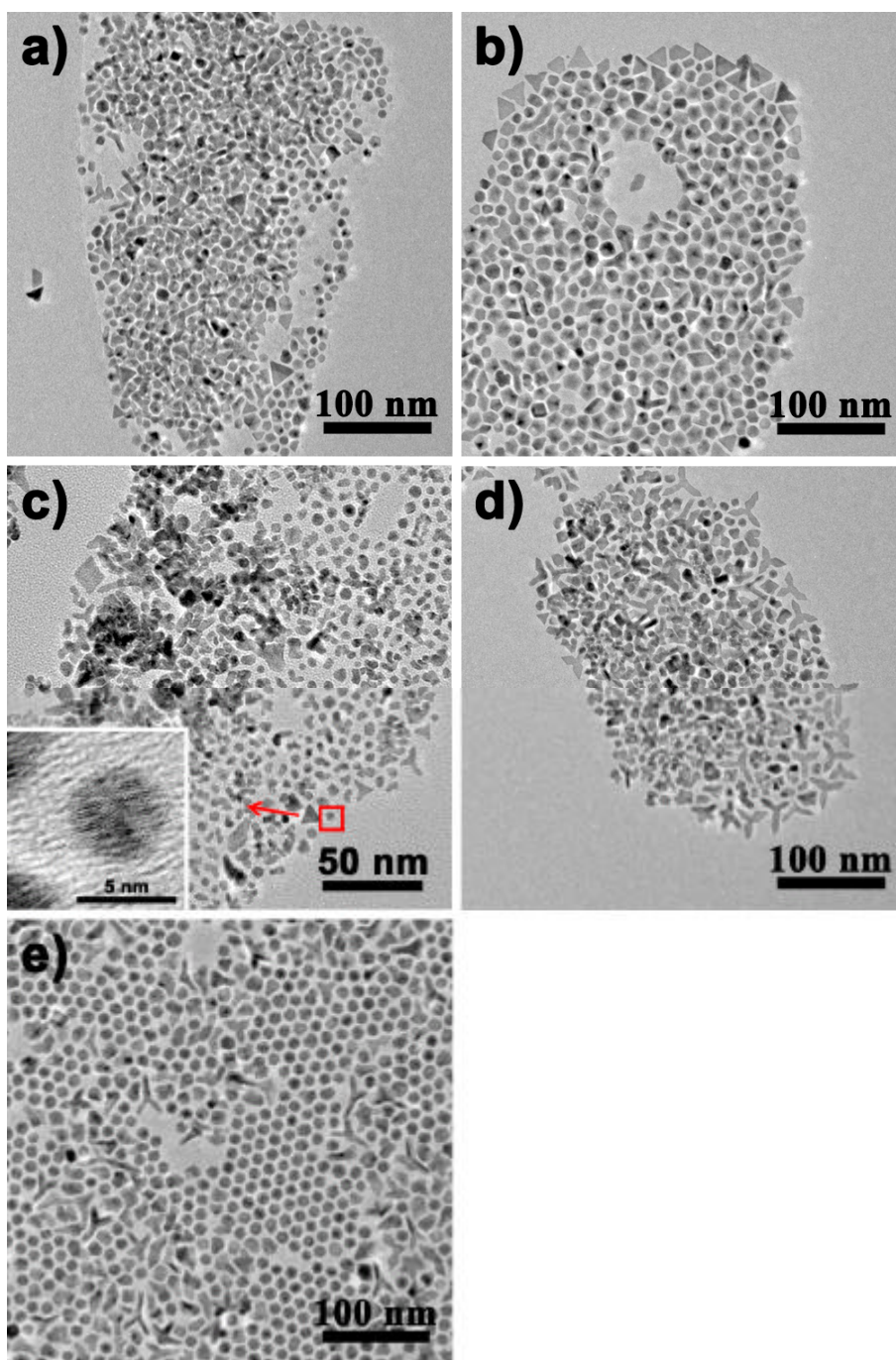


**Figure S9.** TEM images of Pt NPs reduced from 5 mg of MGS at 130 °C for one week in 10 mL of a) DDA, b) HDA and c) ODA, respectively; TEM images of Pt NPs reduced from 4 mg of MSMGS at 150 °C for one week in 10 mL of d) DDA, e) HDA and f) ODA, respectively.

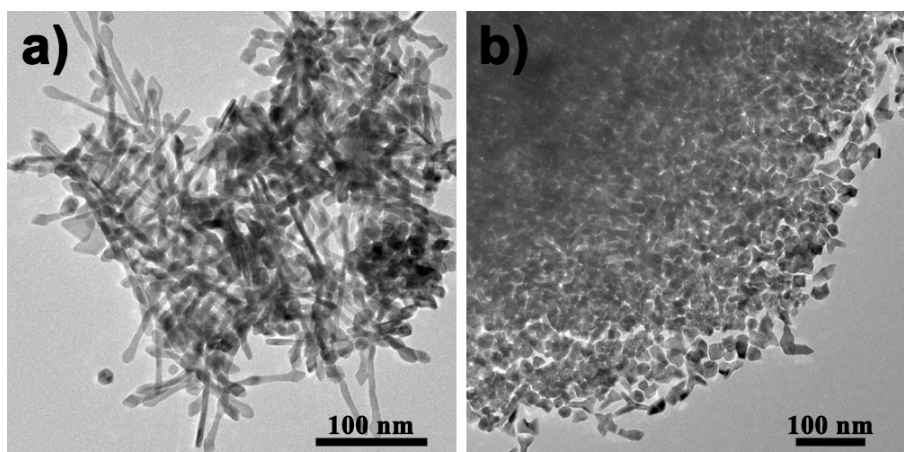




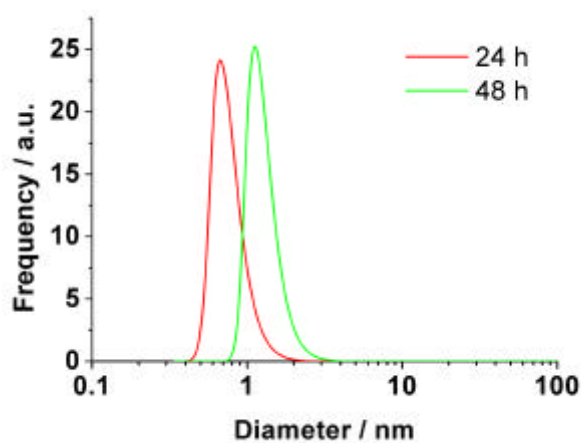
**Figure S10.** TEM images of products of reactions in 10 mL of OAm at 130 °C for one week with different amounts of MGS added in the synthesis: a) 1 mg and b) 10 mg; TEM images of products of reactions in 10 mL of OAm at 150 °C for one week with different amounts of MSMGS added in the synthesis: a) 1 mg and b) 10 mg.



**Figure S11.** TEM images of Pt NPs acquired from time sequence reactions: 5 mg MGS reduced in 10 mL of OAm at 130 °C for a) 60 h and b) 84 h, respectively; 4 mg of MSMGS reduced in 10 mL of OAm at 150 °C for c) 1.5 h, d) 24 h and e) 48 h, respectively. Inset in panel c) is the HRTEM image of sub-5 nm Pt nanoparticles formed at the initial stage, taken from the area marked by the red square.

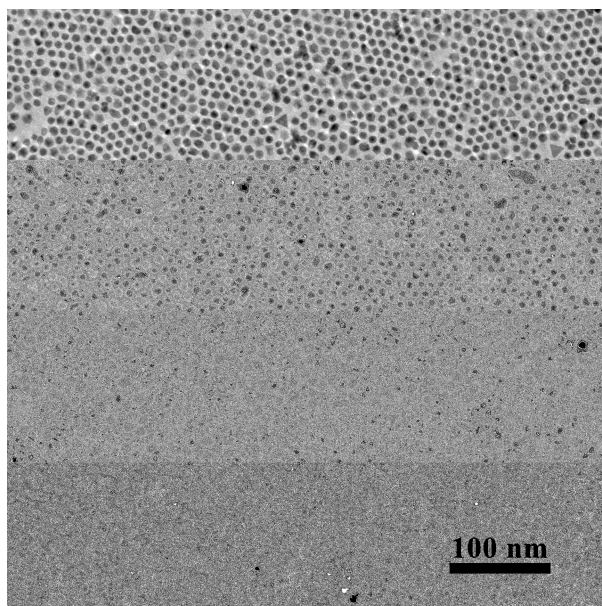


**Figure S12.** TEM images of precipitates separated from the products in the synthesis of a) Pt NDs and b) NIs by centrifugation.



**Figure S13.** DLS curves of the size distributions of the as-formed Pt nanoclusters (at reaction for 24 h and 48 h in OAm at 150 °C, with using MSMGS as the precursor) dispersions in cyclohexane. After reactions from 24 h to 48 h, the hydrodynamic diameter of the Pt nanoclusters increases from 0.7 nm up to 1.2 nm.





**Figure S14.** TEM image of 7.5 nm Pt NIs acquired from the reduction of MSMGS powders at 130 °C for 7 days.

**Ref. S1.** G. W. Watt, B. B. Hutchinson, D. S. Klett, *J. Am. Chem. Soc.* **1967**, *89*, 9.

**Ref. S2.** J. Breimi, D. Brovelli, W. Caseri, G. Hahner, P. Smith, T. Tervoort, *Chem. Mater.* **1999**, *11*, 977.

**Ref. S3.** J. Breimi, V. Gramlich, W. Caseri, P. Smith, *Inorg. Chim. Acta.* **2001**, 322, 23.

**Ref. S4.** J. R. Miller, *J. Chem. Soc.* **1965**, 713.

**Ref. S5.** W. Caseri, *Platin. Met. Rev.* **2004**, *48*, 91.