Highly Shape-Selective Synthesis of Monodispersed Fivefold Twinned Platinum Nanodecahedrons and Nanoicosahedrons

Wei Zhu, An-Xiang Yin, Ya-Wen Zhang,* and Chun-Hua Yan*^[a]

Shape controllable synthesis of colloidal inorganic nanocrystals (e.g., noble metals, II-VI and III-V group semiconductors, metal oxides) has drawn continually increasing interest because of their unique shape-dependent material properties and the perspective new applications.^[1] Wellshaped noble-metal nanocrystals are of scientific and technological significance in multidisciplinary fields of catalysis, optics, magnetics, electronics, plasmonics, photonics, biology and medicine, etc.^[1a,d,f,g] So far, various solution syntheses have been demonstrated as the robust approaches for manipulating the shape of single-crystalline and multiply twinned noble-metal nanocrystals (e.g., 1D wires and rods, 2D plates, regular and/or concave 3D polyhedrons and cubes with low or high Miller index facets) by virtue of their advantages both in finely tuning the reduction kinetics of the metal precursors and in readily controlling the subsequent nanocrystal growth regimes.^[1f] Amongst them, the uses of facet-selective chemical agents (e.g., coordinative molecules and foreign ions) and facet-predefined seeds, together with the mediated reducing rates of metal precursors are key factors for precisely defining the nanocrystal shapes.

Platinum-based catalysts are noteworthy for their wide uses in oil refinement, fine chemicals, and fuel cells, etc.^[2] Recently, much attention has been paid to shape controlled synthesis and catalytic reactivities of monodispersed Pt nanoparticles (NPs), which provide well-defined models for comprehending the relevance between morphology and catalytic properties (activity, selectivity and durability), for bridging the material gap between single crystal and industrial catalysis.^[2-4] So far, well-shaped Pt NPs with exposed basal facets, such as {111}, {100} and {110} (e.g., tetrahedron, octahedron, cube, cubo-octahedron)^[1a,5a,b,d,e,g] and high index facets, such as {730} and {411} (e.g., tetrahexahedrons and concave nanocrystals)^[5c,f,h] have been prepared by some solution methods, most of these NPs are single-crystalline. However, highly-strained Pt multiply twinned particles

[a] W. Zhu, A.-X. Yin, Prof. Dr. Y.-W. Zhang, Prof. Dr. C.-H. Yan Beijing National Laboratory for Molecular Sciences State Key Laboratory of Rare Earth Materials Chemistry and Applications, College of Chemistry and Molecular Engineering Peking University, Beijing, 100871 (P.R. China) Fax: (+86)10-6275-6787 E-mail: ywzhang@pku.edu.cn yan@pku.edu.cn

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/chem.201201099.

(MTPs) have been rarely synthesized;^[1f,6] the selective synthesis of Pt decahedrons and icosahedrons in fivefold twinned structures thus remains a challenging issue. Herein, we demonstrate a general and facile solid–liquid interface mediated reduction route towards highly shape-selective synthesis of monodispersed Pt nanodecahedrons (NDs) and nano-icosahedrons (NIs).

By the reduction of linear Pt^{II} complexes of Magnus' green salt (MGS, [Pt(NH₃)₄][PtCl₄]) and methylamine substituted Magnus' green salt (MSMGS, [Pt(CH₃NH₂)₄]-[PtCl₄]) (for characterization details see Figures S1–S3 in the Supporting Information) with strong metal-metal interactions in oleylamine (OAm), respectively, monodispersed Pt NDs and NIs were synthesized with high shape selectivities. As illustrated in transmission electron microscope (TEM) and high resolution transmission electron microscope (HRTEM) images (Figure 1 and Figure S4 in the Supporting Information) the Pt NDs obtained with a size of 17.0- (± 1.5) nm (333 particles were counted) and selectivity of 70% (after centrifugal separation, 877 particles were counted) were bounded with ten (111) facets. The Pt NIs with a size of $12.6(\pm 0.8)$ nm (318 particles were counted) and selectivity of 88% (after centrifugal separation, 1244 particles were counted) were bounded with twenty (111) facets. The distinctly observed twin boundaries and fast Fourier transform (FFT; Figure 1b, d, e, f) results confirmed that both of the structures were multiply twinned crystalline NPs. By comparing two-, three-, and fivefold symmetry HRTEM lattice fringes of the quasi-sphere Pt NPs (Figure 1 d, e, f) with previous HRTEM simulations of gold NIs with similar sizes, it was deduced that the geometry of these Pt NPs should have an icosahedral structure.^[7] Furthermore, high angle annular dark field-scanning transmission electron microscopy (HAADF-STEM; Figure S5 in the Supporting Information) affirmed the morphologies of Pt NDs and NIs. The contrast of HAADF-STEM images illustrated that the center of both Pt NDs and NIs was thicker than its edge. The contrast and profile of these Pt NPs fit well with the forecasted structures. Powder X-ray Diffraction (PXRD) results verified the purity and fcc structure of the Pt MTPs, and the broadened peaks confirmed the small sizes (Figure S6 in the Supporting Information).

The reactions were conducted in glass-made colorimetric cylinders (10 mL) with stoppers. Several milligrams of precursor (solid) and OAm (10 mL, liquid) were mixed in cylinders, and the products were formed at either 130 or 150 °C



Figure 1. TEM images of Pt: a) NDs, and c) NIs. b) HRTEM images of Pt NDs. d)-f) HRTEM images with incident direction on two-, three-, and fivefold axis, respectively, of Pt NIs. The insets of the HRTEM images are the corresponding FFT images and geometrical models.

after 7 days reaction. Pt NDs and NIs were obtained by the reduction of MGS and MSMGS with coexistence of precipitate, respectively. Because of their poor solubility in OAm, the precursors almost stayed at the bottom of the container during the reaction. The precursors maintained their green color until reduction occurred, indicating that the Pt^{II} chains had been preserved before they were reduced to Pt atoms. After that, the precursor turned black instantly as the reduction was initiated. Monodispersed Pt NDs and NIs evolved from week-long reactions. Hence, unlike previous homogeneous solution reduction mechanisms for the syntheses of Pt NPs,^[1f] the present synthesis ought to adopt a heterogeneous reduction route mediated by the solid–liquid interface formed by the insoluble precursor and OAm solvent.

To clarify the present synthesis mechanism, serial control experiments were carried out by considering the variants, such as types of precursors, solvents, amount of precursor added, temperature, and reaction time. At first, several Pt^{II} -based compounds were employed to uncover the role of precursors in the synthesis. With the same Pt content, 6.5 mg of $Pt(acac)_2$ (acac=acetylacetone), which is soluble in OAm, was taken instead of MGS. No typical MTPs but some branched NPs were observed after the mild reduction (Figure 2 a). Pt MTPs, therefore, could not simply be synthesized under conditions of mild reduction, low concentration

COMMUNICATION



Figure 2. TEM images of products from different experimental conditions: a) $6.5 \text{ mg Pt}(acac)_2$ reacted in 10 mL OAm at 130 °C for one week; b) 1 mg K₂PtCl₄ reacted in 10 mL OAm at 130 °C for one week; c) 5 mg MGS reacted in 10 mL OAm at 130 °C in air for one week; d) 5 mg MGS reduced in 10 mL OAm at 130 °C for 36 h. Inset: HRTEM image of sub-5 nm Pt NPs formed at the initial stages (taken from the area marked by the square).

of Pt(acac)₂, and prolonged reaction time. Insoluble precursor might result in an extremely low concentration of soluble Pt ions, and this would be beneficial for the formation of Pt MTPs. Hence, another OAm-insoluble precursor, K₂PtCl₄, was also applied in this synthesis. But only tripod NPs were obtained after optimization (Figure 2b). Further, when insoluble Magnus' pink salt (MPS) but without PtII chains (as one isomer of MGS) was used as the precursor, the reduction products contained low percentage of NDs or NIs (Figure S7 in the Supporting Information). This result indicated that factors other than solubility and species of ions affected the selectivity in morphology. If the precursor was reduced in the form of ions, the final products of MPS and MGS would be almost the same, whereas this was not the case. Consequently, the strong interaction between Pt^{II} ions nearby, which was the main structural dissimilarity between MGS to MPS (see the Experimental Section in in the Supporting Information), was considered to be the key factor for the formation of Pt MTPs. The reduction product (Pt NIs) of MSMGS with Pt^{II} chains also supported this speculation.

Temperature was another important factor in this work, especially for the adjustment of the reaction rate. Below 100 °C, no obvious reaction took place in one week. For the synthesis of Pt NDs, 130 °C was the appropriate temperature. Due to the relatively slow reaction rate, a significant portion of branched structures appeared in the product below the appropriate temperature (Figure S8a in the Supporting Information). Shape selectivity was reduced with temperatures above 130 °C (Figure S8b and c in the Supporting Information). In this case, triangular, spherical, and icosahedral Pt NPs took over a high portion of the products; this probably resulted from the increased reduction rates of

www.chemeurj.org

precursors as well as overgrowth of Pt NDs. Similarly, as the temperature was increased to 150 °C, the shape selectivity of Pt NIs increased along with a decrease in branched structures (Figure S8d and e in the Supporting Information). No significant change in shape selectivity and size distribution took place at 160 °C (Figure S8 f in the Supporting Information).

Dodecylamine (DDA), hexadecylamine (HDA) and octadecylamine (ODA) were used instead of OAm as both solvent and reductant (Figure S9 in the Supporting Information). Notably, change of solvent in the reductions did alter the product morphologies. However, Pt NDs or Pt NIs still could be observed in the products from HDA (Figure S9b and e in the Supporting Information) and ODA (Figure S9c and f in the Supporting Information), with some Pt nanorods or branched structures, which might have been evolved from the preferential growth of multiply twinned seeds. When the solvent was changed to DDA, more branched structures existed in the products reduced from MGS or MSMGS (Figure S9a and d in the Supporting Information). Due to the distinct reduction capability and binding strength of solvents, product morphologies altered with the twinned structure retained. Therefore, OAm was an important requirement for highly selective synthesis of Pt MTPs. By altering the added amount of MGS from 1 to 10 mg, the optimum selectivity value was obtained at 5 mg (Figure S10a, b and Figure S4a in the Supporting Information). At low amounts of MGS, most of the products were branched structures; this possibly resulted from the relatively slow reduction rate of precursors together with few nuclei generated. However, when the added amount of MGS was 10 mg, a rather high reduction rate resulted in the overgrowth of Pt MTPs, and MTPs thus converted to stable NPs with larger sizes. In the case of MSMGS, no significant influence on shape selectivity and size distribution of Pt NIs was observed when the added amount of MSMGS was changed from 1 to 10 mg (Figure S4c, Figure S10c and d in the Supporting Information). Previously, it was reported that the etching of the O2/Cl- pair could effectively eliminate twinned seeds in the growth of metal NPs.^[8] However, in the present case, it is noted that concave and branched NDs in wide size distributions were acquired when the reaction was carried out in air (Figure 2c). Hence, the presence of the O_2/Cl^- pair in this synthesis could not remove the as-formed Pt twinned seeds, but affected the facet contour and size distribution of the Pt NDs during the nanocrystal growth.

TEM ex situ studies of temporal reactions revealed that MGS and MSMGS were mildly reduced in OAm (Figure 2d and Figures S4 and S11 in the Supporting Information). During the reduction of 5 mg MGS in 10 mL OAm, most of the green precursor sank on the bottom of the container. After 36 h, the precursor turned from green to black, indicating that reduction was initiated. After that, all the precursor was soon reduced to flower-like aggregates, polydispersed multiply twinned nuclei and branched MTPs (Figure 2d). Within the next few days, these structures gradually converted to Pt NDs. After 7 days reduction, products were

mainly monodispersed Pt NDs with certain coexisting branched aggregates (Figures S4a and S12a in the Supporting Information). Similarly, 4 mg of insoluble MSMGS started to reduce in 1 h at 150°C in 10 mL OAm. At the initial time of reduction, sub-5 nm Pt multiply twinned nuclei and flower-like aggregates were generated (Figure S11c in the Supporting Information). Then branched Pt NPs formed in 36 h (Figure S11 d in the Supporting Information). After several days growth, most NPs were well-defined Pt NIs with certain coexisting aggregates (Figures S11 e, S4c and S12b in the Supporting Information). Consequently, owing to the slow reduction rate of the linear precursors, the formation process of Pt MTPs was mapped. At the early stage of the reaction, multiply twinned nuclei transformed to kinetically favored branched or irregular MTPs. During prolonged growth over the next few days, thermodynamically favored Pt NDs or NIs were yielded due to either the induction of residual Pt ions or the drive of total energy minimization.[1f,9]

A solid–liquid interface mediated reduction mechanism based on linear Pt^{II} complex precursors is illustrated in Scheme 1, so as to account for the formation of monodis-



Scheme 1. Probable growth mechanism of Pt NDs and NIs.

persed Pt NDs and NIs in this work. At first, the insoluble microrod-shaped (Figure S1 in the Supporting Information) linear precursors (solid) were solvated and dissolved by OAm (liquid), and gradually underwent a heterogeneous reduction reaction both at the solid-liquid interface and in the solution to form $(Pt)_m^{n+}$ nanoclusters under mild temperatures and stagnant environment. The gradual formation of the nanoclusters was confirmed by the dynamic light scattering (DLS) results (Figure S13 in the Supporting Information). Simultaneously, twinned Pt nuclei formed from the nanoclusters (Figure 2d and Figure S11c in the Supporting Information). As referred by previous investigations on the initial nucleation mechanisms of noble-metal clusters theoretically (Pt)^[10a] and experimentally (Au),^[10b] a non-zero valence intermediate with a metal-metal chain was probably formed by partial reduction and connection of several metal ions.^[1f,10] With this perspective, the solvated and partially reduced MGS and MSMGS with Pt-Pt chains in OAm could be considered as special intermediates of the nanoclusters for the twinned nuclei. In turn, more and more thermodynamically favored twinned Pt nuclei were continually evolved from the nanoclusters in the week-long reaction.

The formation of twined structures was probably due to the contraction of surface Pt atoms of the nuclei driven by high levels of external stress generated from depositing an overlayer of the incompletely reduced $(Pt)_m^{n+}$ nanoclusters with strong Pt-Pt interactions on the growing nuclei,^[9] under a rather slow supply of Pt⁰ monomers from the consecutive reduction of the dissolved species coming from the confined solvation and dissolution process at the solidliquid interface.^[1f] The twinned structures of the nuclei were rather stable and even resistant to the etching by the O2/Clpair in the week-long reaction in open air (Figure 2c). Under these conditions, branched Pt NPs were formed during the preferential growth on the active sites (e.g., defects, kinks, high energy facets) of the twinned nuclei at the initial stage.^[5d,11] After reaction over a sufficient time, the thermodynamically favored Pt MTPs with high selectivities were generated at the prolonged growth stage, and a few branched NPs also coexisted. On the other hand, it seemed that slow but continuous supply of Pt⁰ monomers through the growth stage contributed to the size focusing of the preformed twinned seeds, and the rather slow reaction rate hindered the Ostwald ripening process, even when the monomers were fully consumed. Therefore, monodispersed Pt MTPs were preferentially formed under the present mild reaction conditions.^[1e]

The preformed branched structures might convert to Pt MTPs or grow into branched aggregates in this process. Still a portion of branched aggregates existed in the final products (Figure S12 in the Supporting Information); this can possibly be ascribed to the inhomogeneity of the reaction media. In sum, a rather slow reduction rate of the linear precursors with Pt^{II} chains possessing strong metal-metal interactions at solid-liquid interface was concluded to play a key role in creating the present monodispersed Pt MTPs. However, the major difference between the reactions of these two precursors was that different MTP structures were acquired with this strategy. MSMGS tended to be more easily solvated in OAm due to the fact that it possesses hydrophobic methyl groups in the coordinating ligands when compared with MGS, and thus showed a relatively high reducing rate, which in turn generated more nuclei. Under these conditions, Pt NIs of small size (12.6 nm) formed with MSMGS, whereas Pt NDs of larger size (17.0 nm) formed for MGS. Moreover, Pt NIs with a smaller size of 7.5 nm (Figure S14 in the Supporting Information) were generated under the reduction of lowly crystallized MSMGS powder, which was obtained by allowing the stock solution to undergo a sudden cool procedure in ice water during the preparation of the MSMGS precursors, with somewhat enhanced solubility and an accelerated reaction rate in OAm. Nevertheless, the observed relevance between favored shape and size agrees with previous theoretical predications for fcc Pt.^[12]

In summary, we have developed a robust solid-liquid interface mediated reduction method to synthesize monodispersed Pt NDs and NIs in high shape selectivities (>70%). The synthetic reactions seemed seriously affected by the interfacial dissolution and reduction process between solid linear Pt^{II} complex precursor and liquid oleylamine under mild conditions. Linear Pt^{II} chains of the insoluble precursors with strong metal-metal interactions and their weeklong confined reduction rate were demonstrated as two crucial factors in governing the formation of the Pt MTPs with fivefold symmetry. This work not only can guide the design of rational synthetic protocol for various metal MTPs, but also provide a new platform for Pt nanostructures of wide interest both in theoretical modeling and practical nanocatalysis.

Experimental Section

Synthesis of Pt nanodecahedrons (NDs): OAm used in all the reactions was previously purified under vacuum at 120 °C for 30 min. MGS (5 mg. powder) and purified OAm (10 mL) were mixed in a glass-made colorimetric cylinder (10 mL) with a stopper. After being stirred, the cylinder was sealed with a stopper and kept at 130 °C for one week. MGS sank to the bottom of the cylinder and turned black after about 36 h. After 7 days, black product adhered to the wall and bottom of the cylinder. The product could be washed down with several milliliters of cyclohexane. Ethanol (40 mL) was added to the mixture of reacted OAm solution and the above as-washed cyclohexane solution. After being centrifuged at $4800 \times g$ for 10 min, the supernatant was poured out. The precipitate was redispersed in cyclohexane, then washed with ethanol (40 mL), and centrifuged at $4800 \times g$ for 10 min. The product was washed with this method several times. Then the precipitate was dispersed in cyclohexane (10 mL), and the solution was subjected to supersonic treatment for 10 min. After that, the solution was centrifuged at $4800 \times g$ for 5 min to separate Pt NDs from branched aggregates. The Pt NDs were maintained in the dark brown supernatant.

Synthesis of Pt nanoicosahedrons (NIs): The synthesis of Pt NIs was similar to that of Pt NDs except that methylamine (4 mg) instead of Magnus' green salt (MSMGS, $[Pt(CH_3NH_2)_4][PtCl_4]$) was used as the metal precursor for a reaction at 150 °C for one week. For more details on the synthesis, instrumentation and characterizations of the obtained nanocrystals, please see the Experiment Section in the Supporting Information.

Acknowledgements

This work was supported by the NSFC (grant no. 21025101). Y.W.Z. particularly appreciates the financial aid of China National Funds for Distinguished Young Scientists from the NSFC.

Keywords: decahedra · icosahedra · nanostructures platinum · shape control

www.chemeurj.org

a) T. S. Ahmadi, Z. L. Wang, T. C. Green, A. Henglein, M. A. El-Sayed, *Science* **1996**, 272, 1924; b) X. Peng, L. Manna, W. Yang, J. Wickham, E. Scher, A. Kadavanich, A. P. Alivisatos, *Nature* **2000**, 404, 59; c) J. Park, K. J. An, Y. S. Hwang, J. G. Park, H. J. Noh, J. Y. Kim, J. H. Park, N. M. Hwang, T. Hyeon, *Nat. Mater.* **2004**, *3*, 891; d) S. E. Habas, H. Lee, V. Radmilovic, G. A. Somorjai, P. Yang, *Nat. Mater.* **2007**, *6*, 692; e) S. G. Kwon, T. Hyeon, *Acc. Chem. Res.* **2008**, 41, 1696; f) Y. N. Xia, Y. J. Xiong, B. Lim, S. E. Skrabalak, *Angew. Chem.* **2008**, 121, 62; *Angew. Chem. Int. Ed.* **2008**, 48, 60; g) C.-W.

Yang, K. Chanda, P.-H. Lin, Y. N. Wang, C.-W. Liao, M. H. Huang, J. Am. Chem. Soc. 2011, 133, 19993.

- [2] G. A. Somorjai, Y. Li, Introduction to Surface Chemistry and Catalysis, 2nd ed., Wiley, New York, 2010.
- [3] A. C. Chen, P. Holt-Hindle, Chem. Rev. 2010, 110, 3767.
- [4] a) N. M. Markovic, P. N. Ross, Surf. Sci. Rep. 2002, 45, 117; b) J. Solla-Gullón, F. J. Vidal-Iglesias, A. Lopez-Cudero, E. Garnier, J. M. Feliu, A. Aldaza, Phys. Chem. Chem. Phys. 2008, 10, 3689; c) G. A. Somorjai, H. Frei, J. Y. Park, J. Am. Chem. Soc. 2009, 131, 16589.
- [5] a) H. Lee, S. E. Habas, S. Kweskin, D. Butcher, G. A. Somorjai, P. D. Yang, Angew. Chem. 2006, 118, 7988; Angew. Chem. Int. Ed. 2006, 45, 7824; b) J. Ren, R. D. Tilley, Small 2007, 3, 1508; c) N. Tian, Z. Y. Zhou, S. G. Sun, Y. Ding, Z. L. Wang, Science 2007, 316, 732; d) J. T. Ren, R. D. Tilley, J. Am. Chem. Soc. 2007, 129, 3287; e) C. Wang, H. Daimon, T. Onodera, T. Koda, S. H. Sun, Angew. Chem. 2008, 120, 3644; Angew. Chem. Int. Ed. 2008, 47, 3588; f) X. H. Huang, Z. P. Zhao, J. M. Fan, Y. M. Tan, N. F. Zheng, J. Am. Chem. Soc. 2011, 133, 4718; g) C. Y. Chiu, Y. J. Li, L. Y. Ruan, X. C. Ye, C. B. Murray, Y. Huang, Nat. Chem. 2011, 3, 393; h) T. Yu, D. Y. Kim, H. Zhang, Y. N. Xia, Angew. Chem. 2011, 123, 2825; Angew. Chem. Int. Ed. 2011, 50, 2773.
- [6] a) S. Maksimuk, X. Teng, H. Yang, J. Phys. Chem. C 2007, 111, 14312; b) X. Gong, Y. Yang, S. Huang, Chem. Commun. 2011, 47, 1009.
- [7] J. M. Jose-Yacaman, J. Reyes-Gasga, S. Tehuacanero-Nunez, J. M. Montejano-Carrizales, X. X. Gao, *Top. Catal.* 2007, 46, 23.
- [8] B. Wiley, T. Herricks, Y. G. Sun, Y. N. Xia, Nano. Lett. 2004, 4, 1733.
- [9] D. L. Lu, K. Tanaka, Phys. Rev. B 1997, 55, 13865.
- [10] a) L. Colombi Ciacchi, W. Pompe, A. De Vita, J. Am. Chem. Soc. 2001, 123, 7371; b) T. Yao, Z. H. Sun, Y. Y. Li, Z. Y. Pan, H. Wei, Y. Xie, M. Nomura, Y. Niwa, W. S. Yan, Z. Y. Wu, Y. Jiang, Q. H. Liu, S. Q. Wei, J. Am. Chem. Soc. 2010, 132, 7696.
- [11] M. R. Axet, K. Philippot, B. Chaudret, M. Cabie, S. Giorgio, C. R. Henry, Small 2011, 7, 235.
- [12] a) F. Baletto, R. Ferrando, A. Fortunelli, F. Montalenti, C. Mottet, J. Chem. Phys. 2002, 116, 3856; b) F. Baletto, R. Ferrando, Rev. Mod. Phys. 2005, 77, 371; c) F. R. Negreiros, E. A. Soares, V. E. de Carvalho, Phys. Rev. B 2007, 76, 205429.

Received: March 31, 2012 Published online: August 21, 2012