

Cite this: *Chem. Commun.*, 2012, **48**, 543–545

www.rsc.org/chemcomm

COMMUNICATION

Multiply twinned Pt–Pd nanicosahedrons as highly active electrocatalysts for methanol oxidation†

An-Xiang Yin, Xiao-Quan Min, Wei Zhu, Hao-Shuai Wu, Ya-Wen Zhang* and Chun-Hua Yan*

Received 18th October 2011, Accepted 28th October 2011

DOI: 10.1039/c1cc16482a

Bimetallic Pt–Pd nanicosahedrons (NIs) with multiple {111} twins were obtained through a facile one-pot hydrothermal synthesis in a high shape selectivity of 82%. The {111}-enclosed NIs exhibited superior electrocatalytic activities to {111}-enclosed Pt–Pd nanotetrahedrons as well as commercial Pt catalysts (Pt black and Pt/C) for methanol oxidation.

Being of wide theoretical and practical interests, noble metal nanocrystals preserve plenty of morphology- and composition-dependent properties that can be realized through various controllable synthesis strategies.^{1,2} For example, anisotropic Au/Ag nanocrystals show distinct surface plasma resonance properties from spherical nanoparticles.^{3–6} The catalytic properties of Pt/Pd-based nanocrystals could be optimized through the tuning of their compositions and the exposing of specific facets, edges, corners, and defects.^{7–10} Notably, multiply twinned particles (MTPs) exhibit different properties from those of single-crystalline nanocrystals due to the existence of high-density of twinned-defects.^{11–13} For instance, the twinned-boundaries in Ag MTPs could act as diffusing channels for atoms.¹¹ The inter-lattice distances in a metal nanocrystal could be affected by the twin strain in the multiply twinned structure. As a result, the electronic structures and the catalytic properties of Pt-based nanocrystals could be further modulated by the formation of multiply twinned structures.^{14,15} Up to date, there have been several studies on the synthesis of twinned Pd decahedrons,^{16,17} icosahedrons,^{16–18} thin plates,^{17,19} bipyramids,²⁰ nanorods,^{20,21} and nanowires.²¹ However, it is very difficult to obtain Pt nanocrystals with twinned structures^{22,23} due to the large lattice strain in multiply twinned Pt nanostructures,²⁴ although the coreduction of Pt and Pd could help the formation of Pt–Pd alloy decahedrons or triangular nanoplates.²⁵

Herein, we report the synthesis of highly electrocatalytic active multiply twinned Pt–Pd NIs with a high shape selectivity under one-pot hydrothermal conditions, with poly(vinylpyrrolidone) (PVP) as a capping agent, Na₂C₂O₄ as a facet-selective agent, and HCHO as a reductant. The fine control of the reaction kinetics is crucial for the synthesis of noble metal MTPs,²⁵ as discussed below (see ESI† for experimental details).

In a typical synthesis, 0.015 mmol of K₂PtCl₄, 0.015 mmol of Na₂PdCl₄, 33 mg of PVP (*M*_w = 29000), 2.3 mmol of Na₂C₂O₄, 0.010 mL of HCHO (40 wt% aqueous solution) and 0.24 mL of HCl (1.0 M aqueous solution) were mixed and diluted to 15 mL with ultra-pure water and transferred into a 25 mL Teflon-lined stainless steel autoclave and sealed. The autoclave was then heated at 180 °C for 2 hours. The as-obtained black dispersions of nanocrystals were centrifuged, washed, and collected.

As shown in the transmission electron microscopy (TEM) images (Fig. 1a and b), Pt–Pd NIs were obtained with a size distribution of 11.2 ± 0.8 nm and a shape selectivity of 82%. The X-ray diffraction (XRD) pattern (Fig. S1, ESI†) confirmed that these NIs were of typical *fcc* structure and the broadened

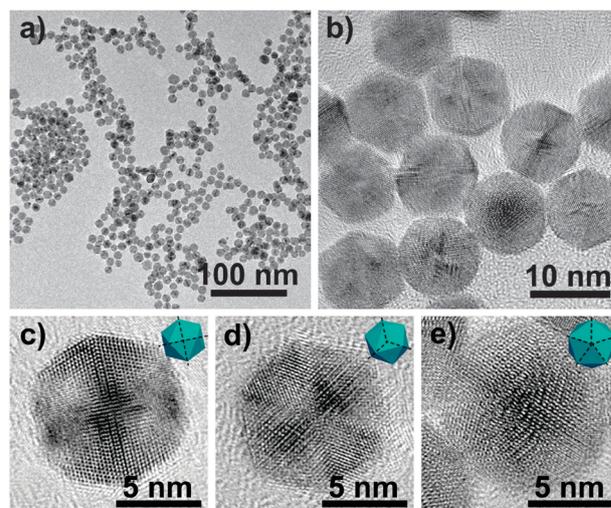


Fig. 1 TEM (a and b) and HRTEM (c–e) images of the Pt–Pd NIs. Panels b, c and e are the HRTEM images projected along the 2-, 3-, and 5-fold axis of the NIs, respectively. The tilting angle from panel c to panel d is about 20.5°.

Beijing National Laboratory for Molecular Sciences, State Key Laboratory of Rare Earth Materials Chemistry and Applications, PKU-HKU Joint Laboratory in Rare Earth Materials and Biomorganic Chemistry, and College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, China.

E-mail: ywzhang@pku.edu.cn, yan@pku.edu.cn;

Fax: +86-10-62754179

† Electronic supplementary information (ESI) available: Synthesis details, more TEM images, instrumental characterizations, and electrocatalysis results. See DOI: 10.1039/c1cc16482a

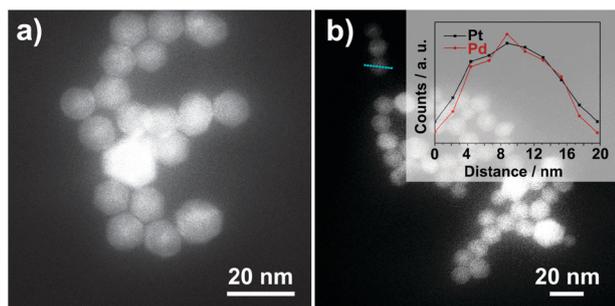
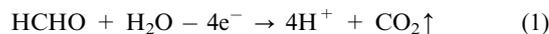


Fig. 2 HAADF-STEM image (a) and HAADF-STEM-EDS line-scan profile (b) of the Pt–Pd NIs.

diffraction peaks suggested the small particle sizes of these NIs. High-resolution TEM (HRTEM) images projected along the 2-, 3-, and 5-fold axis of the as-obtained Pt–Pd NIs were obtained to confirm their multiply twinned structure (Fig. 1c–e, respectively). As determined by both methods of the energy-dispersive X-ray spectroscopy (EDS) spectrum (Fig. S2b, ESI†) and inductively coupled plasma-atomic emission spectrometry (ICP-AES), these NIs were composed of Pt and Pd with a molar ratio of Pt : Pd = 44 : 56, which was close to the calculated Pt/Pd ratio (1 : 1) from the starting metal precursors. High angle annular dark field scanning transmission electron microscopy (HAADF-STEM) images and HAADF-STEM-EDS line scan profiles further suggested that the bimetallic NIs might hold an alloy structure rather than a core–shell one (Fig. 2).

A series of control experiments were carried out to reveal the possible growth mechanism of these Pt–Pd bimetallic NIs. In principle, the relatively slow reducing rate would promote the formation of multiply twinned metal nanocrystals since the dedicated control over the reaction kinetics was crucial to the synthesis and stabilization of multiply twinned Pt–Pd NIs.²⁵ In practice, the amounts of $\text{Na}_2\text{C}_2\text{O}_4$ and HCHO used in the synthesis were important to the formation of monodisperse Pt–Pd NIs (Fig. S3 and S4, ESI†). When the amounts of $\text{Na}_2\text{C}_2\text{O}_4$ were increased from 0 to 2.3 mmol, the as-prepared nanocrystals turned from irregular polyhedrons with various sizes to monodisperse NIs with a shape selectivity of above 80% (Fig. S3a–e, ESI†). But much fewer nanocrystals could be obtained with the amount of $\text{Na}_2\text{C}_2\text{O}_4$ further increased to 3.0 mmol (Fig. S3f, ESI†). The much slower reducing rate could be ascribed to the coordination effects of $\text{C}_2\text{O}_4^{2-}$ to $\text{Pt}^{2+}/\text{Pd}^{2+}$ ions. These results suggested that the use of an appropriate amount of $\text{Na}_2\text{C}_2\text{O}_4$ would not only stabilize the {111} facets of the as-prepared Pt–Pd nanocrystals,²⁶ but also manipulate the reducing kinetics to form the multiply twinned NIs. Meanwhile, with the amounts of HCHO solution (40 wt%) increased from 0 to 0.005 and 0.010 mL, the reducing rate was accelerated and much more Pt–Pd nanocrystals could be obtained with the shape selectivity of NIs maintained above 80% (Fig. S4a–c, ESI†). However, when the amounts of HCHO solution (40 wt%) were further increased to 0.020, 0.050, 0.10 and 0.20 mL, the obtained nanocrystals would gradually turn from MTPs to single-crystalline ones with much smaller sizes (Fig. S4d–f, ESI†). Especially, with 0.20 mL of HCHO solution (40 wt%) employed in synthesis, *ca.* 5 nm large Pt–Pd nanotetrahedrons (NTs) with a shape selectivity of above 80% could be obtained (Fig. S4f, ESI†), similar to our previous results.²⁶

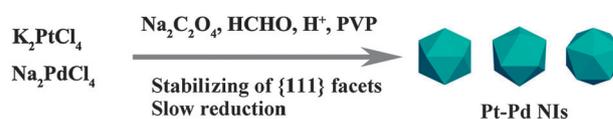
Another way to manipulate the reducing kinetics was to modulate the pH values of the reaction solutions. As revealed by the half reaction of the HCHO oxidation:



High concentration of H^+ in solution would hamper the reducing capability of HCHO molecules and thus slow down the reducing rate in synthesis. In experiment, a proper amount of HCl solution was needed for the preparation of Pt–Pd NIs (Fig. S5, ESI†). Without HCl added, no multi-twinned NIs but single-crystalline Pt–Pd NTs would be obtained (Fig. S5a, ESI†). With excess HCl used, the reducing rate would be too slow that only a small amount of nanocrystals with broad size-distributions could be obtained (Fig. S5d and e, ESI†).

Temperature-controlled experiments revealed that with the reaction temperature raised from 150 °C to 180 °C, more metal nanocrystals could be prepared with the shape-selectivity of NIs increased at the same time (Fig. S6, ESI†), indicating that a proper range of reaction temperature was necessary for the synthesis of Pt–Pd NIs. Time-sequential experiments showed that after 1 h, the as-obtained NIs would not have any significant variation in shape and size (Fig. S7, ESI†), suggesting the hydrothermal stability of these NIs. In addition, molar ratios of the K_2PtCl_4 and Na_2PdCl_4 precursors were also important to the preparation of NIs (Fig. S8, ESI†). No pure Pt NIs could be formed without the addition of Pd precursors (Fig. S8a, ESI†). With the increase in the Pd/Pt ratio in precursors, the shape selectivity of NIs would be significantly enhanced. Especially, uniform Pd NIs (*ca.* 20 nm) with a selectivity of 90% could be obtained when Na_2PdCl_4 was used as the only metal precursor (Fig. S8d, ESI†).

Based on these experimental facts, we suggest a plausible growth mechanism for the Pt–Pd bimetallic NIs, as shown in Scheme 1. Proper amounts of reductive HCHO were needed to modulate the reaction kinetics for the preparation of Pt–Pd NIs. As shown in eqn (1), the reducing rate could be also finely tuned by the pH value of the reaction solution. Under this condition, the use of $\text{Na}_2\text{C}_2\text{O}_4$ would not only reduce the surface energy of the {111}-facets of the icosahedrons by binding strongly to them and thus stabilize the multiply twinned NIs, but also modulate the reaction kinetics to ensure a slow reducing rate for the generation of multiply twinned NIs in high selectivity in 1 hour (Fig. S7, ESI†), due to the fact that $\text{C}_2\text{O}_4^{2-}$ anions showed both high coordinative capability to Pt(II) and Pd(II) species and strong adsorption on the surfaces of Pt–Pd nanocrystals.²⁶ In addition, the strong surface adsorption of $\text{C}_2\text{O}_4^{2-}$ species would also prevent the possible O_2/Cl^- etching effect, which would etch these multiply twinned nanocrystals and lead to the formation of single-crystalline ones.¹⁶ Thus, the fine control over the reaction kinetics, the thermodynamic stabilization of {111} facets, and the protection of the multiply twinned NIs from etching effects were necessary for the preparation of monodisperse Pt–Pd NIs.



Scheme 1 One-pot hydrothermal synthesis of Pt–Pd NIs.

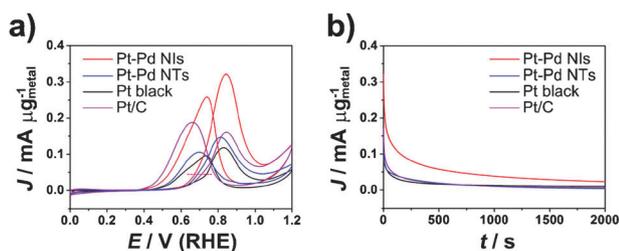


Fig. 3 Cyclic voltammetry (CV, scan rate: 50 mV s^{-1}) (a) and $I-t$ (b) curves of Pt–Pd NIs and NTs in $0.1 \text{ M HClO}_4 + 1 \text{ M CH}_3\text{OH}$. The mass activity of different catalysts was normalized in reference to the loading amount of metal (for NIs and NTs, both Pt and Pd were included).

To evaluate the effects of the multiply twinned structures of the as-prepared Pt–Pd NIs on their electro-catalytic properties, methanol oxidations on Pt–Pd NIs, NTs (*ca.* 4.9 nm in size; Fig. S9a, ESI[†]) and Pt black (Alfa Aesar, Fig. S9b, ESI[†]) were carried out with a three-electrode system in the electrolytes of 0.1 M HClO_4 and $1 \text{ M CH}_3\text{OH}$ protected by N_2 at room temperature (Fig. 3, Fig. S10 and S11, ESI[†]). The reduction peaks of the metal oxides on Pt–Pd NIs (0.71 V) and NTs (0.66 V) were negatively shifted relative to those of Pt black (0.76 V), showing their lower resistance to oxidation than that of Pt black. As shown in Fig. 3 and Fig. S11, the Pt–Pd NIs showed much higher activity to methanol oxidation than that of Pt–Pd NTs, Pt black and Pt/C catalysts, and the stability of the NIs and NTs was comparable to the references. Compared with the Pt–Pd NTs, the Pt–Pd NIs show a significant negative potential shift in CV curves, and the lowest potential for methanol oxidations at the same current density in the positive scan (Fig. 3a), indicating their much enhanced catalytic activity.²⁷ The mass activity of NIs (per unit weight of Pt and Pd) was about 2 times that of the NTs for methanol oxidations, although the electrochemical active surface areas of the NIs ($12 \text{ m}^2 \text{ g}_{\text{metal}}^{-1}$) were smaller than those of the NTs ($15.2 \text{ m}^2 \text{ g}_{\text{metal}}^{-1}$).

The above results suggest that the enhanced activity for methanol electro-oxidation obtained for Pt–Pd NIs (as compared with NTs) might be mainly ascribed to the difference in surface structures between multiply twinned NIs and single crystalline NTs, further considering that both of them had nearly the same compositions (Pt: Pd = 44:56 and 46:54 for NIs and NTs, respectively), and were enclosed by sole {111} facets. On the one hand, there would be plenty of multiply twinned defects on the surface of the NIs, which were much more active and would thus contribute to the significantly enhanced electrocatalytic activities.^{17,28} On the other hand, the distance between the nearby {111} lattice planes of the multiply twinned NIs would be smaller than those of single-crystalline NTs, and the adsorption behaviours of adsorbents on the {111} facets of NIs would be distinguished from that on the surface of NTs, resulting in the enhanced catalytic performance of the multi-twinned NIs.^{14,15}

In summary, we have demonstrated a highly shape-selective hydrothermal synthesis of multiply twinned Pt–Pd NIs. As a result of the fine control of the reaction kinetics using $\text{C}_2\text{O}_4^{2-}$ as the coordination agent, the slowed reducing rates of metal

ions in the synthesis promoted the formation of the multiply twinned Pt–Pd NIs. Because of their high density of twin-plane defects and high lattice strains, these multiply twinned NIs exhibit enhanced electro-catalytic activity to single-crystalline Pt–Pd NTs as well as commercial Pt catalysts (Pt black and Pt/C). The facile kinetic control strategy could be generalized to guide the further preparation of many other multiply twinned metal nanocrystals with enhanced properties.

This work was financially supported by the NSFC (Grant No. 21025101, 20871006, and 20821091). Y.W.Z. particularly appreciates the financial aid of China National Funds of Distinguished Young Scientists from the NSFC.

Notes and references

- Z. L. Wang, *J. Phys. Chem. B*, 2000, **104**, 1153.
- T. K. Sau, A. L. Rogach, F. Jackel, T. A. Klar and J. Feldmann, *Adv. Mater.*, 2010, **22**, 1805.
- A. Tao, P. Sinsersuksakul and P. D. Yang, *Angew. Chem., Int. Ed.*, 2006, **45**, 4597.
- B. J. Wiley, Y. C. Chen, J. M. McLellan, Y. J. Xiong, Z. Y. Li, D. Ginger and Y. N. Xia, *Nano Lett.*, 2007, **7**, 1032.
- X. S. Kou, S. Z. Zhang, C. K. Tsung, Z. Yang, M. H. Yeung, G. D. Stucky, L. D. Sun, J. F. Wang and C. H. Yan, *Chem.–Eur. J.*, 2007, **13**, 2929.
- J. E. Millstone, W. Wei, M. R. Jones, H. J. Yoo and C. A. Mirkin, *Nano Lett.*, 2008, **8**, 2526.
- R. Narayanan and M. A. El-Sayed, *Nano Lett.*, 2004, **4**, 1343.
- K. M. Bratlie, H. Lee, K. Komvopoulos, P. D. Yang and G. A. Somorjai, *Nano Lett.*, 2007, **7**, 3097.
- N. Tian, Z. Y. Zhou, S. G. Sun, Y. Ding and Z. L. Wang, *Science*, 2007, **316**, 732.
- C. Wang, H. Daimon, T. Onodera, T. Koda and S. H. Sun, *Angew. Chem., Int. Ed.*, 2008, **47**, 3588.
- Y. Tang and M. Ouyang, *Nat. Mater.*, 2007, **6**, 754.
- K. C. Chen, W. W. Wu, C. N. Liao, L. J. Chen and K. N. Tu, *Science*, 2008, **321**, 1066.
- R. E. Algra, M. A. Verheijen, M. T. Borgstrom, L. F. Feiner, G. Immink, W. J. P. van Enkevort, E. Vlieg and E. P. A. M. Bakkers, *Nature*, 2008, **456**, 369.
- R. M. Wang, O. Dmitrieva, M. Farle, G. Dumpich, M. Acet, S. Mejia-Rosales, E. Perez-Tijerina, M. J. Yacaman and C. Kisielowski, *J. Phys. Chem. C*, 2009, **113**, 4395.
- P. Strasser, S. Koh, T. Anniyev, J. Greeley, K. More, C. F. Yu, Z. C. Liu, S. Kaya, D. Nordlund, H. Ogasawara, M. F. Toney and A. Nilsson, *Nat. Chem.*, 2010, **2**, 454.
- B. Lim, Y. J. Xiong and Y. N. Xia, *Angew. Chem., Int. Ed.*, 2007, **46**, 9279.
- Z. Q. Niu, Q. Peng, M. Gong, H. P. Rong and Y. D. Li, *Angew. Chem., Int. Ed.*, 2011, **50**, 6315.
- Y. J. Xiong, J. M. McLellan, Y. D. Yin and Y. N. Xia, *Angew. Chem., Int. Ed.*, 2007, **46**, 790.
- Y. J. Xiong, J. M. McLellan, J. Y. Chen, Y. D. Yin, Z. Y. Li and Y. N. Xia, *J. Am. Chem. Soc.*, 2005, **127**, 17118.
- Y. J. Xiong, H. G. Cai, Y. D. Yin and Y. N. Xia, *Chem. Phys. Lett.*, 2007, **440**, 273.
- X. Q. Huang and N. F. Zheng, *J. Am. Chem. Soc.*, 2009, **131**, 4602.
- J. Y. Chen, T. Herricks and Y. N. Xia, *Angew. Chem., Int. Ed.*, 2005, **44**, 2589.
- S. Maksimuk, X. W. Teng and H. Yang, *Phys. Chem. Chem. Phys.*, 2006, **8**, 4660.
- Y. N. Xia, Y. J. Xiong, B. Lim and S. E. Skrabalak, *Angew. Chem., Int. Ed.*, 2009, **48**, 60.
- B. Lim, J. G. Wang, P. H. C. Camargo, C. M. Copley, M. J. Kim and Y. N. Xia, *Angew. Chem., Int. Ed.*, 2009, **48**, 6304.
- A. X. Yin, X. Q. Min, Y. W. Zhang and C. H. Yan, *J. Am. Chem. Soc.*, 2011, **133**, 3816.
- S. J. Guo, S. Zhang, X. L. Sun and S. H. Sun, *J. Am. Chem. Soc.*, 2011, **133**, 15354.
- Y. Lee, A. Loew and S. H. Sun, *Chem. Mater.*, 2010, **22**, 755.