Preparation of single-crystalline platinum nanowires with small diameters under mild conditions†

Zhongrong Shen, Mami Yamada and Mikio Miyake*

Received (in Cambridge, UK) 25th September 2006, Accepted 10th November 2006
First published as an Advance Article on the web 27th November 2006
DOI: 10.1039/b613895k

We report a convenient method to synthesize single-crystalline platinum nanowires with high aspect ratio of *ca.* 2.0 nm diameter by sophisticated and precise control of Pt(0) nuclei and their growth.

Studies on the preparation of highly-controlled Pt nanostructures have attracted intense interest because of their novel physical and chemical properties for a new generation of catalysts, electronics, and photonics.[1] Especially, the selective preparation of Pt nanowires with small diameter, high aspect ratio, and uniform orientation is hard to achieve, and is still a challenging subject in the field of nanomaterials.[2] The reported chemical preparations to synthesize nanowires include organization of nanocrystals,[3] template-directed preparation,[4] and growth-directed preparation.[5] Only polycrystalline nanowires have been fabricated by growth in flexible templates,[4] or by fusing nanoparticles into linear aggregation.[3] Although growth-directed preparation[6] produces single-crystalline nanowires, this method requires a long reaction time, over 16 hours. Xia and coworkers investigated a slow reduction process to induce Pt atoms into an anisotropic growth along the $\langle 111 \rangle$ direction in ethylene glycol.[5] However, the Pt nanowires can only be obtained under a very low Pt(II) precursor concentration. Difficulty in preparation of highly shape-controlled nanomaterials essentially originates from the series of several different steps, *viz.* formation of Pt(0) nuclei,[7] prevention of Pt(0) nuclei from aggregation into nanoparticles, and inducing Pt(0) nuclei to grow in a fixed direction with specific facets. Our new strategy is to control these key steps simultaneously, and strictly creates a single-crystal nanowire with high-aspect ratio and small diameter in a short period of time. We have demonstrated the importance of adsorbent (*e.g.*, NaI)[1b] on specific crystal face and solvent environment (*e.g.*, polarity)[8] to establish controlled shape or arrangement of metal nanoparticles, in addition to specific organic protective agents.[9] There are two critical strategies in the present preparation procedures. One is to stabilize Pt(0) nuclei by adsorption of sodium borohydride ($NaBH_4$)[10] on the Pt(0) surface in a less-polar solution, which is then further stabilized in the presence of alkaline triethylamine (TEA). Second, is to allow the directed growth of Pt(0) into nanowire by the plausible adsorption of *N*,*N*-dimethyl formamide (DMF) on Pt{111} facet after formation of naked Pt(0) by oxidation of $NaBH_4$ to $NaBO_2$. The preparation of Pt nanowire proceeds at room temperature and is completed within 3 hours. This idea to control multiple important steps by the aid of adsorbent and solvent control may be widely applicable to synthesize tailored shape-controlled nanomaterials for a variety of systems.

A typical reaction was conducted as follows: 2.5 ml aq. hexachloroplatinic acid (H_2PtCl_6, 10 mM), was reduced by 10 mg sodium borohydride ($NaBH_4$) (10 times to H_2PtCl_6 in molar ratio) in 20 ml DMF, and different amounts of toluene (0, 2.5, 7.5 and 12.5 ml). Precipitation occurred after stirring for 3 hours under air at room temperature. Centrifuged and washed with excess ethanol 3 times, the product dispersed easily into highly polar solution (water or methanol) by sonication.

The morphology of nanocrystals has been reported to be significantly affected by solvent polarity, which may change the degree of interaction between nanoparticles and protective agent.[11] We studied effects of solvent polarity by altering the volume ratio of mixed solution, water–DMF–toluene (R_{WDT}), from 1 : 8 : 0 to 1 : 8 : 5. Fig. 1 shows the TEM image of Pt nanocrystals. TEM samples were prepared by dropping methanol solution (2 droplets, ~0.05 ml) of Pt nanocrystal onto a carbon-supported copper grid, and drying naturally for 1 day. Only nanoparticles are obtained from highly polar solution with R_{WDT} = 1 : 8 : 0 (Fig. 1a) and 1 : 8 : 1 (Fig. 1b). On the other hand, due to a decrease in solvent polarity (R_{WDT} = 1 : 8 : 3, Fig. 1c), nanowires appear together with

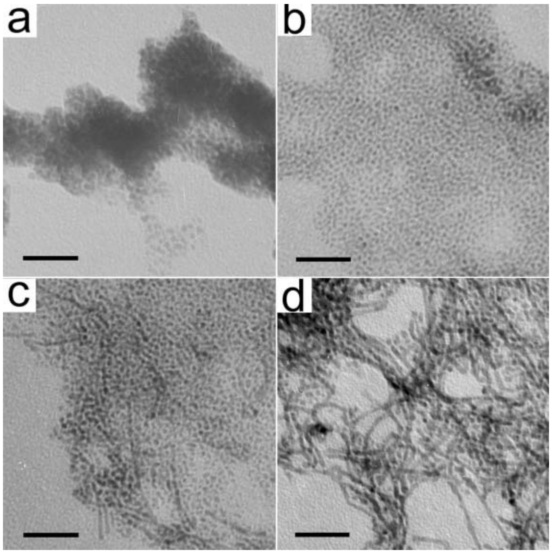

Fig. 1 TEM image of Pt nanocrystals prepared in mixed solution with varying ratios of water–DMF–toluene, specifically: (a) R_{WDT} = 1 : 8 : 0; (b) R_{WDT} = 1 : 8 : 1; (c) R_{WDT} = 1 : 8 : 3 and (d) R_{WDT} = 1 : 8 : 5. Scale bar is 25 nm.

School of Materials Science, Japan Advanced Institute of Science and Technology, 1-1, Asahidai, Nomi-shi, Ishikawa, Japan 923-1292.
E-mail: miyake@jaist.ac.jp; Fax: 0081-761-51-1149;
Tel: 0081-761-51-1540

† Electronic supplementary information (ESI) available: EDX spectrum of Pt nanowires. See DOI: 10.1039/b613895k

nanocrystals, and the amount of nanowire exceeds that of nanocrystal at R_{WDT} = 1 : 8 : 5 (Fig. 1d). Further information was obtained by using other solvents with different polarity index (P')[12] in place of toluene (P' = 2.4), such as methyl *tert*-butyl ether (MBE, P' = 2.5), benzene (P' = 2.7) and chloroform (P' = 4.1). Nanowires can be obtained from solution systems of MBE and benzene with P' values of less than 2.7, but cannot be obtained from a chloroform system with P' = 4.1. Therefore, solvent polarity plays a critical role in the formation of Pt nanowires.

We have changed the amount of $NaBH_4$, used as reducing agent, while maintaining other conditions constant with R_{WDT} = 1 : 8 : 5, since excess $NaBH_4$ has been reported to serve as a protective agent of nascent Pt nanoparticles.[10] No nanowires but only nanoparticles are observed with 2 and 4 times molar ratios of $NaBH_4$ to H_2PtCl_6 (2 × and 4 ×) (Fig. 2a and 2b, respectively), while nanowires appear when using the higher molar ratios of $NaBH_4$ (6 × and 8 ×) (Fig. 2c and 2d, respectively). Therefore, we deduce that Pt(0) nuclei are stabilized by excess $NaBH_4$ in this system, in a similar manner to results reported by Lee,[10] which indicated that Pt(0) nuclei were prevented from aggregation at the beginning of the reaction.

As is well known, $NaBH_4$ is stable in basic solution but is easily disassociated in acidic solution. Thus, an organic base, TEA, was added to the reaction system to stabilize $NaBH_4$-protected Pt(0) nuclei effectively. We added 2.5 ml TEA to the solvent system with R_{WDT} = 1 : 8 : 5, followed by reduction with 10 mg $NaBH_4$ (10 times the amount of H_2PtCl_6 in molar ratio). We monitored the formation of Pt nanowire by TEM after reduction for 10 min, 20 min and 3 h. As shown in Fig. 3a, Pt nanowires with length of *ca.* 50 nm appear even at 10 min After 20 min, nanowires grow to a length of 80–100 nm (Fig. 3b), and a network structure of nanowires is formed at 3 h (Fig. 3c). High resolution TEM (HRTEM) images indicate that almost all nanowires are in single-crystalline state (Fig 3d, 3e and 3f). Distribution of nanowire diameters is estimated in Fig. 4: average value is 2.0 ± 0.5 nm from over 200 measurements on Fig. 3c. The inset in Fig. 3d shows a selected-area electron diffraction (SAED) image with the five rings indexed to the {111}, {200}, {220}, {311} and {331} diffractions, respectively, which corresponds to a face-centered cubic (*fcc*) structure. The lattice spacing between the {111} planes, 0.23 nm, is also in agreement with that of bulk Pt crystal. Characteristic peaks of the powder X-ray diffraction (XRD) (Fig. 5) are identified by appropriate Miller indices. The peaks coincide with SAED data with *fcc* structure for Pt nanowires. The broad peak {111} indicates a narrow diameter of the Pt nanowires of 2.3 nm by the Scherrer formula, which value approximately coincides with the diameter of 2.0 nm estimated by TEM. Different from the growth along ⟨111⟩ direction reported by Xia

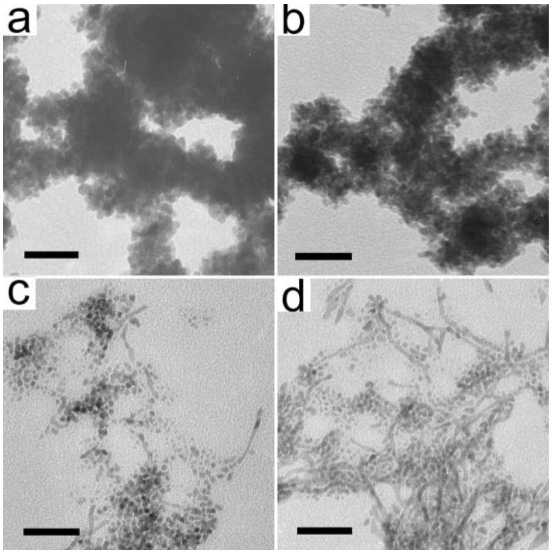

Fig. 2 TEM image of Pt nanocrystals prepared in R_{WDT} = 1 : 5 : 8 system with $NaBH_4$ levels of a) 2; b) 4; c) 6 and d) 8 times molar ratio to H_2PtCl_6. Scale bar is 25 nm.

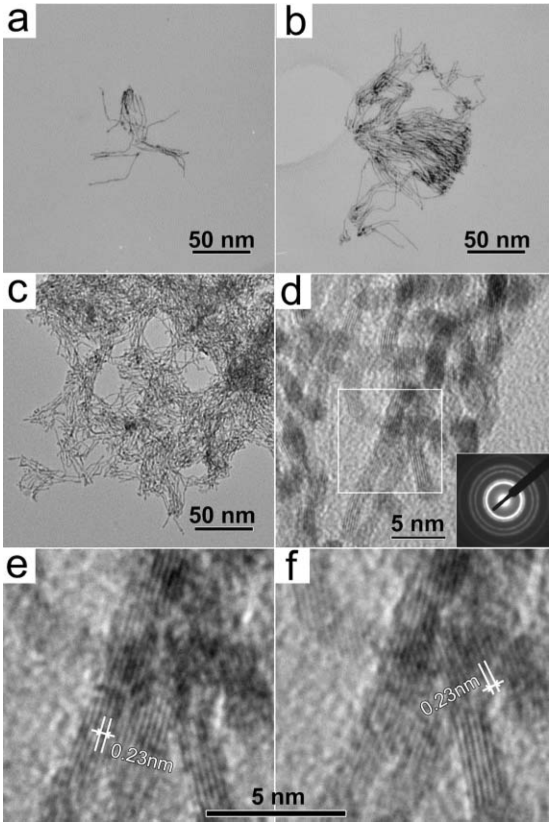

Fig. 3 TEM image of Pt nanowires after reduction for a) 10 min b) 20 min and c) 3 h respectively. d) High resolution TEM image of Pt nanowires in a single-crystalline state, inset shows the SAED pattern; (e) and (f) show the same enlarged nanowires (frame in d) under different focus, which shows the nanowires are single-crystal.

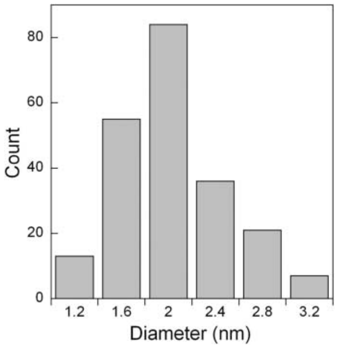

Fig. 4 Distribution diagram of Pt nanowires.

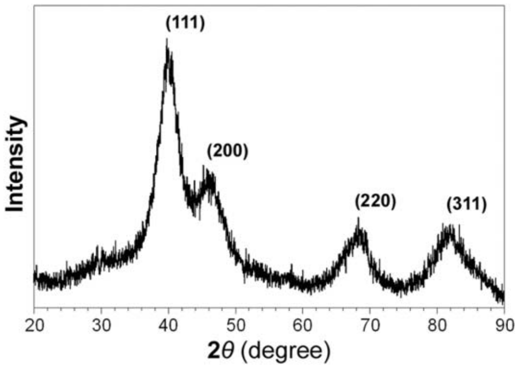

Fig. 5 Powder XRD spectrum of Pt nanowires.

et al.,[5] our Pt nanowires primarily grow perpendicular to the ⟨111⟩ direction. In order to grow to nanowires, Pt(0) nuclei should be naked by removal of the capping agent ($NaBH_4$). Oxidation of $NaBH_4$ by oxygen (air) to $NaBO_2$ is a compatible process to form naked Pt(0) nuclei. Such naked Pt(0) nuclei grow preferentially perpendicular to the ⟨111⟩ direction, presumably due to selective adsorption of DMF on Pt{111} facets. This idea is partially supported by ^1H NMR (300 MHz, CD_3OD) spectra of dried Pt nanowire samples measured after being re-dispersed in CD_3OD. The peaks are observed at 7.93, 3.02 and 2.86 ppm, which coincide well with those of DMF,[13] suggesting strong adsorption of DMF on Pt nanowires. Furthermore, no obvious peak can be detected for Na and Cl in the EDX spectrum (Fig. S1†). That is, there is very little Na and Cl left on the Pt nanowires. The yield of Pt nanowires is *ca.* 70 wt%, whose value is estimated by the ratio of recovered weight of Pt nanowires. Therefore, this is a convenient synthetic method of forming nanowires with high crystallinity, small diameter, and high aspect ratio. We believe that the process may be easily scaled up. There are some uncertain direction growth curves and junction shapes of nanowires from HRTEM observation (Fig. 3d), which may be attributed to the stirring system, although a more definite mechanism is under investigation. A plausible mechanism based on the present results is summarized in Fig. 6.

In conclusion, we have synthesized single-crystalline Pt nanowires with a high aspect ratio of *ca.* 2 nm diameter at room temperature in less than 3 h. We have controlled key steps such as stabilization of Pt(0) nuclei, as well as sophisticated growth into nanowires. We tune the solvent polarity and amount of $NaBH_4$ to prevent Pt(0) nuclei from aggregation in alkaline conditions (TEA). Single-crystalline Pt nanowires are produced after removing capping $NaBH_4$ by air oxidation with the aid of plausible adsorption of DMF on Pt{111} facetes. This method provides a clue for preparing a wide variety of shape-controlled metal nanocrystals, which may be useful in various fields, such as nanowire network electrodes, supracurrent devices, waveguides, hydrogen storage systems, nanosensors, biotransporters, *etc.*[14]

This work was partially supported by Grant-in-Aid for Scientific Research (Basic Research B, No. 17360385) from the Ministry of Culture, Education, Science and Sports, Japan and Technical Developments for PEFC Systems (No. 04003305-0) from NEDO, Japan.

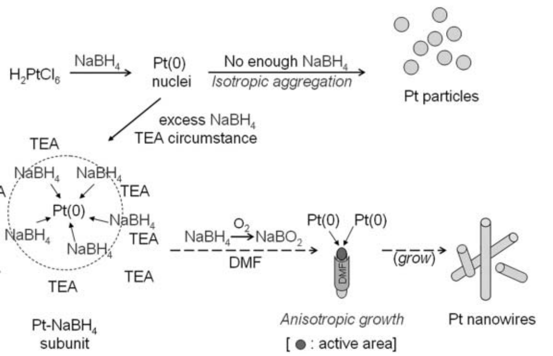

Fig. 6 Plausible mechanism for formation of Pt nanowires. The key factors are stabilization and destabilization of Pt(0) nuclei as well as presumable adsorption of DMF to produce sophisticated Pt nanowires. The first factor to stabilize Pt(0) nuclei is realized by excess $NaBH_4$, which can serve as a temporary ligand to Pt nuclei. At the same time, the hydrophobic interaction of less-polar solvent causes $NaBH_4$ to adsorb on the surface of Pt nuclei effectively. Moreover, the presence of TEA stabilizes $NaBH_4$, adsorbed on Pt nuclei. This prevents nuclei from aggregating into large nanoparticles without direction selectivity. After oxidation by oxygen, naked Pt(0) nuclei are released, and grow into single-crystalline nanowires with the aid of DMF adsorption on specific facet, Pt{111}.

Notes and references

1 (*a*) T. Teranishi, M. Hosoe, T. Tanaka and M. Miyake, *J. Phys. Chem. B*, 1999, **103**, 3818; (*b*) M. Yamada, S. Kon and M. Miyake, *Chem. Lett.*, 2004, **34**, 1050.
2 (*a*) J. D. Holmes, K. P. Johnston, R. C. Doty and B. A. Korgel, *Science*, 2000, **287**, 1471; (*b*) H. Shi, L. Qi, J. Ma and H. Cheng, *Chem. Commun.*, 2002, 1704.
3 (*a*) X. Fu, Y. Wang, N. Wu, L. Gui and Y. Tang, *Langmuir*, 2002, **18**, 4619; (*b*) X. Fu, Y. Wang, N. Wu, L. Gui and Y. Tang, *J. Mater. Chem.*, 2003, **13**, 1192.
4 (*a*) T. Kijima, T. Yoshimura, M. Uota, T. Ikeda, D. Fujikawa, S. Mouri and S. Uoyama, *Angew. Chem., Int. Ed.*, 2004, **43**, 228; (*b*) Y.-J. Han, J.-M. Kim and G. D. Stucky, *Chem. Mater.*, 2000, **12**, 2068; (*c*) Y. Sakamoto, A. Fukuoka, T. Higuchi, N. Shimomura, S. Inagaki and M. Ichikawa, *J. Phys. Chem. B*, 2004, **108**, 853; (*d*) A. Fukuoka, T. Higuchi, T. Ohtake, T. Oshio, J. Kimura, Y. Sakamoto, N. Shimomura, S. Inagaki and M. Ichikawa, *Chem. Mater.*, 2006, **18**, 337.
5 J. Chen, T. Herricks, M. Geissler and Y. Xia, *J. Am. Chem. Soc.*, 2004, **126**, 10854.
6 A. Gole and C. J. Murphy, *Chem. Mater.*, 2004, **16**, 3633.
7 J. M. Petroski, Z. L. Wang, T. C. Green and M. A. El-Sayed, *J. Phys. Chem. B*, 1998, **102**, 3316.
8 M. Yamada, Z. Shen and M. Miyake, *Chem. Commun.*, 2006, 2569.
9 T. Teranishi, M. Haga, Y. Shiozawa and M. Miyake, *J. Am. Chem. Soc.*, 2000, **122**, 4237.
10 J. Yang, J. Y. Lee, T. C. Deivaraj and H.-P. Too, *Langmuir*, 2003, **19**, 10361.
11 Z. Liu, Z. Hu, J. Liang, S. Li, Y. Yang, S. Peng and Y. Qian, *Langmuir*, 2004, **20**, 214.
12 L. R. Snyder, *J. Chromatogr. Sci.*, 1978, **16**, 223.
13 H. E. Gottlieb, V. Kotlyar and A. Nudelman, *J. Org. Chem.*, 1997, **62**, 7512.
14 For reviews see: (*a*) Y. Cui, Q. Wei, H. Park and C. M. Lieber, *Science*, 2001, **293**, 1289; (*b*) A. Rouxoux, J. Schulz and H. Patin, *Chem. Rev.*, 2002, **102**, 3757; (*c*) F. Patolsky, Y. Weizmann and I. Willner, *Nat. Mater.*, 2004, **3**, 692; (*d*) Q. Wan and T. H. Wang, *Chem. Commun.*, 2005, 3841; (*e*) D. Wang, R. Kou, M. P. Gil, H. P. Jakobson, J. Tang, D. Yu and Y. Lu, *J. Nanosci. Nanotechnol.*, 2005, **5**, 1904.