Synthesis of Platinum Nanostructures Using Seeding Method

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We report Pt hexapod nanoparticles with 6.4 ~ 9.7 nm in size by a polyol process in the presence of PVP as a stabilizer and additive as a kinetic controller. The structure and morphology of Pt nanostructures are confirmed by field-emission transmission electron microscopy. The morphological control over platinum nanoparticles is achieved by varying the amount of seeds in the polyol process, where platinum precursor is reduced by ethylene glycol to form Pt nanoparticle at 150 °C. As volume ratio between precursor-solution and seed-solution is increased from 10 to 50, the shape of Pt nanostructures is evolved from small seeds to tripod and hexapod. In addition, the size-controlled platinum hexapod nanostructures are successfully obtained using seeding method.

Key Words: Platinum, Hexapod, Shape control, Seeding method

Introduction

Catalytic activity of platinum for energy conversion, especially, at low temperatures makes this metal electrocatalyst ideal for use as electrodes in direct alcohol fuel cells (DAFCs), dye sensitized solar cells (DSSC) and microbial fuel cells (MFCs).[1-4] Single crystalline platinum surfaces, such as low index (111), (100), and (110) structures, have been studied as idealized platforms for electrocatalytic reactions because the surface atomic arrangement affects the electrochemical properties. The exposed face of catalysts among them could be selected by modulating the growth rate of metal nanostructures.[5-8] It is most likely that a nanocrystal structure with a particular face is selectively formed by slow growth rate during the process with chemical environments. Especially, it has been reported that shapes of nanoparticles such as cube, octahedron, tetrahedron, cuboctahedron shows specific crystal planes such as {111} and/or {100}.[6,9-11]

In the Wulff facets argument or Gibbs-Curie-Wulff theorem, the shape of a crystal is determined by the relative specific surface energy of each face of the crystal. In the crystal structure, the equilibrium shape is the one that minimizes the surface Gibbs energy.[12-13] If surface energies are determined through various facets, the equilibrium shape can be expected. When this concept is translated into relative growth rates of the facets, the most stable facets would have lower growth rates and be the most developed ones in the overall equilibrium shape. Fast-growing facets will eventually disappear during growth in a chemical process, resulting in a crystal terminated by slower-growing facets. Once the facets form, fast-growing facets will persist, replacing the initial high-energy facet.

Herein, we report that morphology and size of Pt nanostructures could be controlled by means of polyol method. The shape of Pt nanoparticles was evolved from small seeds to tripod and hexapod as a function of volume ratio between precursor-solution and seed-solution. In addition, the size-controlled platinum hexapod nanostructures were formed using seeding method. The morphology, structure, and size distribution of the nanoparticles were elaborately characterized by field-emission transmission electron microscopy.

Experimental

One step method. A solution of 1 mM H_2PtCl_6, 10 μM $NaNO_3$, and 20 μM $FeCl_3$ was prepared in 50 mL of ethylene glycol (EG), to which we added 50 mg poly(vinyl pyrrolidone) (PVP, MW = 29,000). All chemicals used were of analytical grade. The change of color in the solution was observed as raised by 1 °C/min. At 180 °C, the solution became dark brown from yellow and was kept for 1 h until H_2PtCl_6 was completely reduced by EG. After the reaction for nanoparticle preparation, the colloid solution was cooled at room temperature, washed by acetone, and then precipitated using centrifuge.

Seeding method. To prepare seed colloid solution, 10 mM H_2PtCl_6, 100 μM $NaNO_3$, 100 mM PVP and 200 μM $FeCl_3$ were dissolved in 5 mL of EG. The solution was rapidly added to 45 mL of ethylene glycol at boiling temperature and then immediately cooled to room temperature resulting in a seed colloid solution. For seeding method, the seed colloid solution was mixed in a precursor-solution consisting of 1 mM H_2PtCl_6, 10 μM $NaNO_3$, 10 mM PVP and 20 μM $FeCl_3$ in the range of 2% to 10%. The seed-solutions were heated at 110 °C and 150 °C, respectively. The 2% seed-solution was heated at 110 °C for 24 h and then at 150 °C for 2 h. In addition, the 2, 6, and 10% seed-solutions were heated and reacted at 150 °C for 2 h. After the reaction, the seed-solutions were cooled at room temperature, washed by acetone, and then precipitated using centrifuge.

The morphology, structure, and size distribution of the nanostructures were characterized by field-emission transmission electron microscopy (FE-TEM) using a Philips F20 system operating at 200 kV. TEM samples were prepared by placing a drop of nanoparticle suspension dispersed in an ethanol on a carbon-coated copper grid.

Results and Discussion

Fig. 1 shows TEM image of Pt nanostructures obtained by means of one-step method. It was observed that almost all the Pt nanostructures consisted of hexapod shape (~ 95%) oriented along the <111> axis with the corners pointing toward the <100> directions. However, in the case of one-step method, the synthetic condition for the hexapod nanostructure should be elaborately controlled because of the experimental sensitivity in the chemical process.

Fig. 2A and B show Pt nano-seeds prepared by means of polyol process at boiling temperature of EG. The spherical nanoparticles of 3 ~ 4 nm in size were used as seeds for seeding method to synthesize Pt multipod nanostructures. Fig. 2C and D show TEM images of Pt nanostructures synthesized using seeding method in 2% seed-solution consisting of 1 mL seed colloid solution and 50 mL precursor-solution at 110 ^{o}C for 24 h. In the one-step method, as already shown in the Fig. 1, the Pt hexapod nanostructures were formed at 180 ^{o}C higher than 110 ^{o}C. However, in the case of seeding method, the formation of hexapod nanostructures was achieved at relatively lower temperature of 110 ^{o}C than 180 ^{o}C. This implies that heterogeneous nucleation for hexapod formation *via* seeding method is thermodynamically favourable compared to homogeneous nucleation *via* one-step method.[14] As shown in the Fig. 2C and D, the average size of hexapod nanostructures is ~ 10 nm. The nano-seeds seem to be partially grown into the hexapod nanoparticles. However, although the seeding method is systematically favourable, the spherical seeds seem to be partially grown into hexapod at 110 ^{o}C. For the complete reaction of 2% seeds-solution, the solution was reheated at 150 ^{o}C and kept for 2 h. As shown in Fig. 2E and F, small spherical seeds disappeared with overgrowth of hexapod nanostructures. Thus, it is considered that in the seeding method, the reaction at 150 ^{o}C is favourable for hexapod growth of nano-seeds.

Fig. 3 shows TEM images of Pt nanostructures synthesized by seeding method with different ratios between seeds-solution and precursor-solution (2, 6, and 10%) at 150 ^{o}C for 2 h. They clearly indicate complete reaction without any spherical seed. Fig. 3A shows TEM image of Pt nanostructures formed in 2% seeds-solution containing 1 mL seed colloid solution and 50 mL precursor-solution. In the case, the Pt nanostructures consist of ~ 95% hexapod with uniform average size of ~ 9.65 nm. It is found that the hexapod nanostructure shows octahedron shape grown to edge and corner. Fig. 3B shows TEM image of Pt nanostructures formed in 6% seeds-solution containing 3 mL seed colloid solution and 50 mL precursor-solution. In the case of 6% seeds-solution, the Pt nanostructures consist of 63% hexapod of ~ 7.25 nm and 37% tripod of ~ 10.58 nm. The hexapod structures became smaller in size compared to those synthesized in 2% seeds-solution. In particular, it is interesting that although no formation of tripod occurs at 2% seeds-solution, the tripod nanostructure is

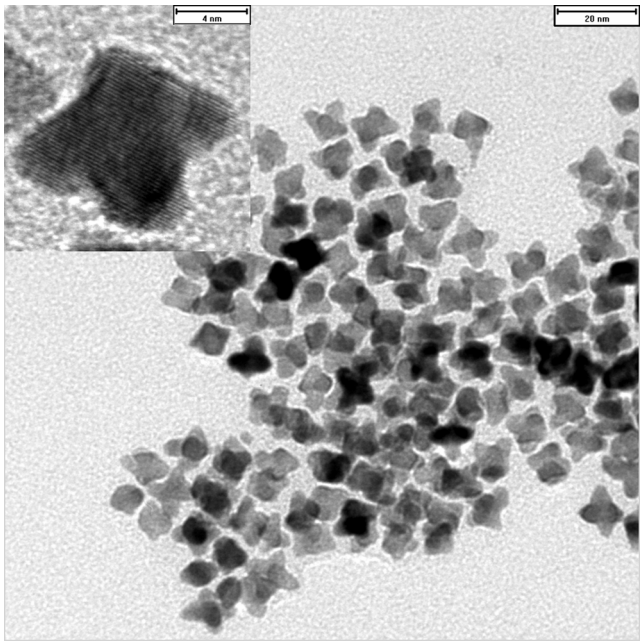


Figure 1. TEM image of Pt nanostructures obtained by one-step method at 180 ^{o}C.

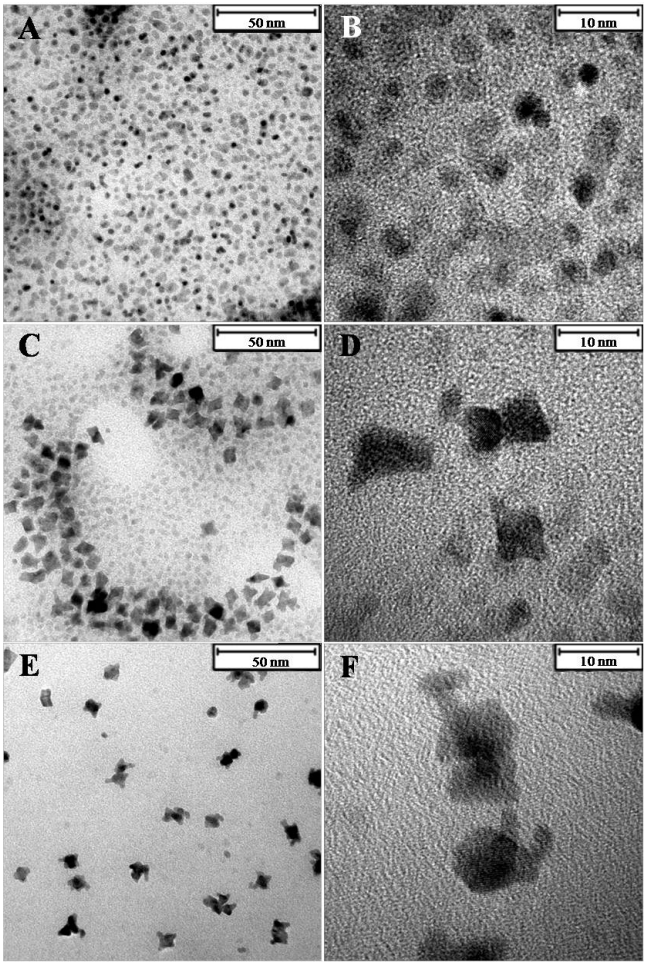


Figure 2. TEM images of Pt nano-seeds prepared by means of polyol process at boiling temperature of EG (A & B), Pt nanostructures synthesized using seeding method in 2% seeds-solution at 110 ^{o}C for 24 h (C & D), and Pt nanostructures reheated at 150 ^{o}C for 2 h (E & F).

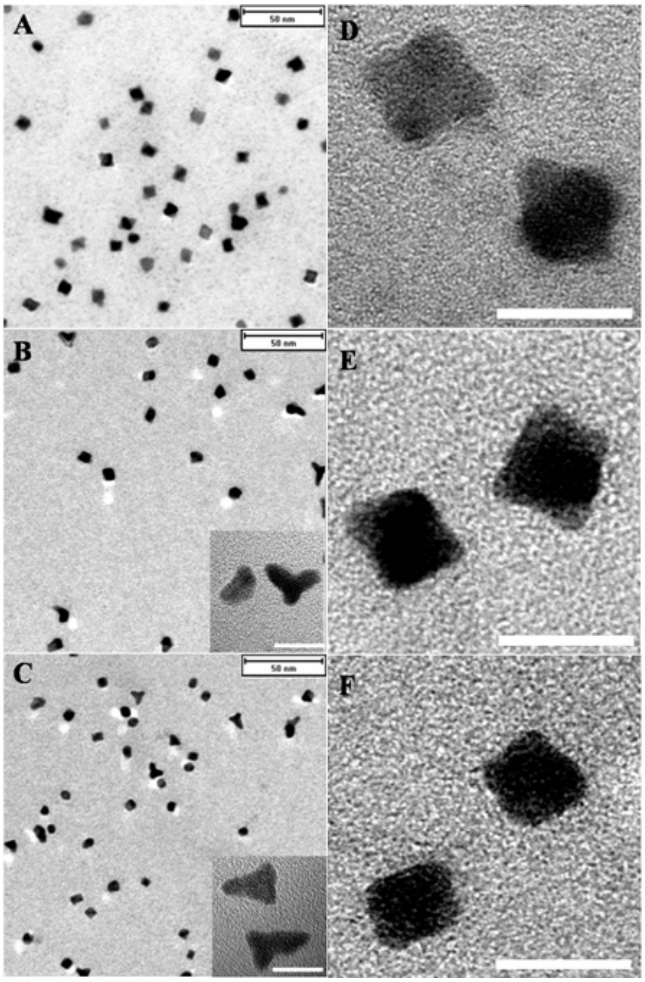


Figure 3. TEM images of Pt nanostructures synthesized by seeding method with (A) 2%; (B) 6%; (C) 10% seeds-solution at 150 °C for 2 h. High-resolution TEM images Pt nanostructures synthesized through (D) 2%; (E) 6%; (F) 10% seeds-solution (D ~ F, Scale bar = 10 nm).

formed in 6% seeds-solution. Fig. 3C shows TEM image of Pt nanostructures formed in 10% seeds-solution containing 5 mL seed colloid solution and 50 mL precursor-solution. In the case of 10% seeds-solution, the Pt nanostructures consist of 69% hexapod of ~ 6.39 nm and 31% tripod of ~ 7.51 nm. Maksimuk *et al*. also observed platinum tripod nanostructures with dominant {111} planes.[15] However, although the tripod nanostructures are relatively metastable in comparison with hexapod nanostructures, the increased amount of seeds could result in fast growth rate and thus formation of metastable tripod structures. In the case of 10% seeds-solution, the hexapod structures became smaller in size compared to those synthesized in 2% and 6% seeds-solutions. Thus, using seeding method as a function of ratio of seeds-solution to precursor-solution, we could obtain size-controlled dominant hexapod nanostructures, smaller than those previously reported.[16-17]

Conclusion

Platinum hexapod nanostructures were synthesized by means of polyol reaction in the presence of PVP and additives. The morphology of platinum nanostructures was controlled by varying the amount of seeds added to a polyol process. With increasing ratio of seeds-solution to precursor-solution, the shape of Pt nanostructures was dominantly evolved from sphere to hexapod. We could obtain size-controlled hexapod nanostructures as a function of ratio of seeds-solution to precursor-solution

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References

1. Larminie, J.; Dicks, A. *Fuel Cell Systems Explained* **2000**, 133.
2. Grätzel, M. *Nature* **2006**, *414*, 338.
3. Kim, S.-S.; Nah, Y.-C.; Noh, Y.-Y.; Jo, J.; Kim, D.-Y. *Electrochim. Acta* **2006**, *51*, 3814.
4. Markovic, N. M.; Gasteiger, H. A.; Ross, P. N. *J. Phys.* **1995**, *99*, 3411.
5. Seo, M.; Yun, Y.; Lee, J.; Tak, Y. *J. Power Sources* **2006**, *159*, 59.
6. Han, S.-B.; Song, Y.-J.; Lee, J.-M.; Kim, J.-Y.; Park, K.-W. *Electrochem. Commun.* **2008**, *10*, 1044.
7. Wang, C.; Dimon, H.; Lee, Y.; Kim, J.; Sun, S. *J. Am. Chem. Soc.* **2007**, *129*, 6974.
8. Ahmadi, T. S.; Wang, Z. L.; Green, T. C.; Henglein, A.; El-Sayed, M. A. *Science* **1996**, *272*, 1924.
9. Tao, A. R.; Sinsermsuksakul, P.; Yang, P. *Angew.Chem.* **2006**, *118*, 4713
10. Song, H.; Kim, F.; Connor, S.; Somorjai, G. A.; and Yang, P. J. *Phys. Chem. B* **2005**, *109*, 188.
11. Jun, Y.-W.; Choi, J.-S.; Cheon, J. *Angew. Chem.* **2006**, *118*, 3492.
12. Mullin, J. W. *Crystallization*, 4th ed.; Elsevier: Oxford, 2001; 216.
13. Wulff, G. Z. *Kristallogr.* **1901**, *34*, 449.
14. Fievet, F. J.; Lagier, P.; Blin, B.; Beaudoin, B.; Figlarz, M. *Solid State Ionics* **1989**, *198*, 32.
15. Maksimuk, S.; Teng, X.; Yang, H. *J. Phys. Chem. C* **2007**, *111*, 14312.
16. Herricks, T.; Chen, J.; Xia, Y. *Nano Letters* **2004**, *4*, 2367.
17. Song, H.; Kim, F.; Connor, S.; Somorjai, G. A.; Yang, P. *J. Phys. Chem. B* **2005**, *109*, 188.
18. Tao, A. R.; Habas, S.; Yang, P. *Small* **2008**, *4*, 310.