Preparation of Tetrahedral Pt Nanoparticles Having {111} Facet on Their Surface

Akane Miyazaki,* Shuichiro Yoshida, Yoshio Nakano, and Ioan Balint[†]
Department of Environmental Chemistry and Engineering, Interdisciplinary Graduate School of Science and Technology,
Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 226-8502
[†]*Institute of Physical Chemistry, Romanian Academy, Spl. Independentei 202, 77208 Bucharest, Romania*

{100} and {111} facets are typical for metal clusters having FCC structure. We have ever succeeded to obtain square Pt particles having {100} facet on their surface. However, there has not been an effective method to obtain Pt nanoparticles with the other facets, i.e., {111}. In this paper we report a novel preparation method of tetrahedral Pt nanoparticles, whose surface is controlled {111}, by using a thermosensitive capping polymer [poly(*N*-ethylacrylamide)].

Thermosensitive polymer is a group of polymers, which change their hydration state by ambient temperature. When the temperature is lower than the phase transition point, the polymer is hydrophilic and its aqueous solution is transparent. If the temperature increases above the critical point, the polymer chains become hydrophobic and start to shrink. The aqueous solution of the dehydrated polymer is opaque. It has been reported that the hydrophobicity of a thermosensitive polymer is an important factor governing the shape of the colloidal Pt nanoparticles resulted from the reduction of aqueous solution containing a complex precursor.[1] The morphology of the Pt nanoparticles obtained by using poly(*N*-isopropylacrylamide), poly-NIPA, was clearly related to the phase transition temperature (LCST, lower critical solution temperature). At T > LCST, around 68% of the resulted Pt nanoparticles were cubic shaped, whereas the geometry of the resulted Pt particles was less clear at T < LCTS. These results reveal the possibility to control the growth along a preferential direction through the interaction between the hydrophobic polymer and the surface of metal cluster. Therefore, it is expected that Pt nanocrystals with different morphologies (size and shape) can be synthesized by changing the nature of the capping polymer. This study describes for the first time the preparation of a Pt colloid statistically rich in tetrahedral nanoparticles by using a thermosensitive polymer, poly(*N*-ethylacrylamide) (poly-NEA).

The *N*-ethylacrylamide monomer was synthesized from ethylamine hydrochloride and acryloyl chloride in diethyl ether.[2] The substance obtained was identified as *N*-ethylacrylamide by ^{1}H and ^{13}C NMR. The poly-NEA was prepared by radical polymerization of the *N*-ethylacrylamide monomer in *tert*-buthanol.

The LCST of the poly-NEA was obtained from the change in absorbance of poly-NEA aqueous solution at 500 nm with increase in the ambient temperature. The sudden increase of the absorbance at 342.2 K, showed in Figure 1, corresponds to the phase transition temperature (LCST). This LCST value is close to that reported for poly-NEA (345.0 K).[2]

In order to obtain Pt nanoparticles, aqueous solution of 10^{-4} M K_2PtCl_4, which contained 10^{-2} M (as monomer unit) of poly-NEA, was bubbled by Ar gas and then H_2 gas. Then the reaction vessel was sealed tightly and kept in a water bath at a suitable temperature. At given reaction times, the vessel was opened and the samples for TEM were prepared by soaking a grid (carbon substrate, Oken) in the colloidal solution and then drying it in the air. The TEM (Hitachi H-8100) was operated at 200 kV.
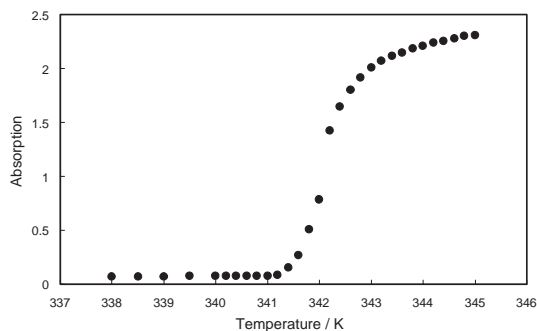

Figure 1. Absorbance of poly-NEA aqueous solution at 500 nm with increase in the ambient temperature.
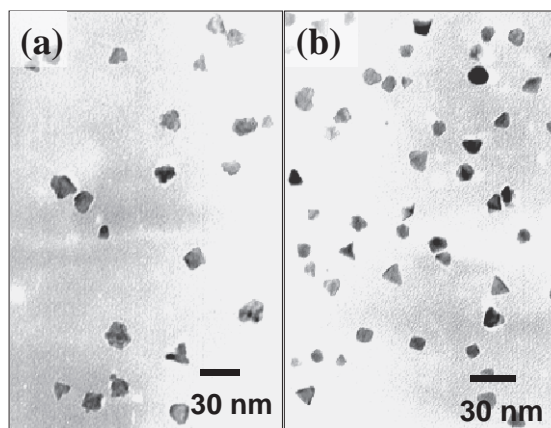

Figure 2. TEM images of Pt nanoparticles obtained by using poly-NEA as a capping material at (a) 313 K (below LCST) and (b) 353 K (above LCST).

Figure 2 shows the TEM images of the Pt nanoparticles obtained at 313 and 353 K, i.e., below and above LCST, respectively. Most of the Pt nanoparticles obtained at 313 K had irregular shapes. The highly defected surfaces of the large Pt particles are suggesting a formation mechanism involving the agglomeration of the very small particles in the early stages of the growth. On the other hand, the amount of well-faceted particles increased significantly at 353 K. As an interesting fact, a large fraction of triangular Pt particles was obtained at 353 K. The mean size of the particles obtained at 353 K was 7.3 nm. In order to evaluate the effect of temperature on the morphology of Pt nanoparti-
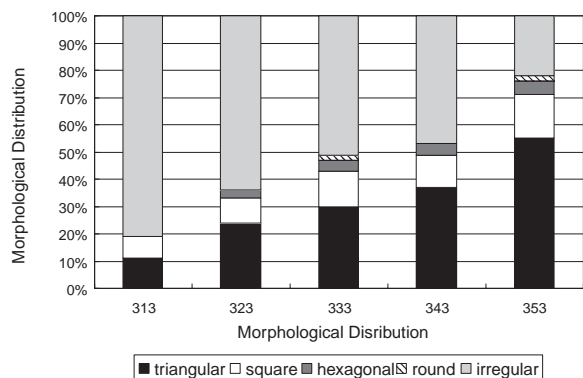
Figure 3. Morphological distribution of Pt nanoparticles obtained at different temperatures.

cles, we classified the shapes of platinum particles observed by TEM into five categories: hexagonal, square, triangular, round, and irregular. As for three dimensional structure, these shapes correspond to icosahedrons, cubes, tetrahedrons, polyhedrons, and agglomerate of small bodies, respectively.[3,4] For each samples, more than 100 particles was counted. Figure 3 shows the morphological distribution of the Pt particles obtained at different temperatures, after 12 h of growth. The increase of the triangular particle fraction with temperature was accompanied by a corresponding decrease in the amount of irregular particles. The formation of the small amounts of round, hexagonal, square-shaped particles was relatively independent on the synthesis temperature. The common feature of two thermosensitive capping polymers, poly-NIPA, and poly-NEA, is that they give a better morphological control at T > LCST. However, the contrast between the predominant morphologies obtained below and above the LCST was much stronger in the case of poly-NIPA.[1] The fraction of cubic particles increased dramatically from 30% (at 298 K) to 68% (at 313 K). In the case of poly-NEA, the fraction of the triangular particles is affected slightly by LCST (see Figure 3). The differences observed between the capping ability of the two polymers can be explained by their dehydration behavior with temperature. The increase of the poly-NEA absorbance with temperature (Figure 1) is less sharp than of the poly-NIPA.[1] This means that the poly-NEA chain is dehydrated in some extent even at T < LCST (342.2 K). Therefore, the structure-directing effect of the partially dehydrated poly-NEA made the effect of LCST less pronounced compared to poly-NIPA.

A triangular Pt nanoparticle was observed by high resolution TEM (JEM-2010F), and the image shows a crystalline structure with clearly resolved lattice fringes (Figure 4). The orientation as well as the lattice spacing of 0.225 nm corresponds to [111] plane of the face-centered cubic modification of Pt metal. The TEM results prove that the triangular particles are in fact Pt nano-tetrahedrons bounded by Pt {111} crystalline facets, relatively free of surface defects. Since TEM image always display the projection of the atoms onto the observation plane, the trigonal prismatic shape cannot be completely excluded. Other crystallographic orientations as well as steps and edges are also possible at the slightly rounded corners of tetrahedrons.
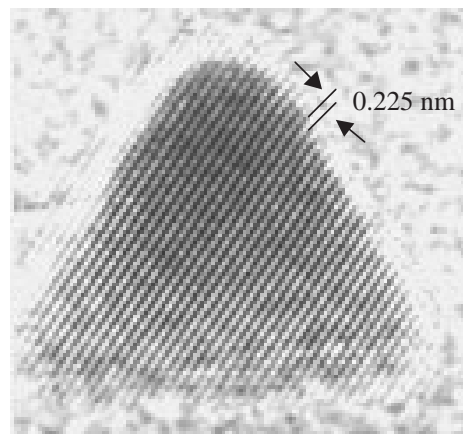

Figure 4. HR-TEM image of triangle Pt nanoparticles obtained by using poly-NEA.

Comparing the structure directing effect of poly-NEA and poly-NIPA,[1] it can be said that there are at least two factors which are controlling the final morphology of Pt nanoparticles: (i) hydrophobicity and (ii) nature of the functional groups. Hydrophobicity of polymers gives better morphological control, while the nature of the functional groups decides the direction of growth. By selecting adequate polymers and optimal reduction conditions, it is possible to control not only the size but also the shape (i.e., the dominant facet orientation) of the colloidal Pt nanoparticles. Either cubic Pt nanocrystals (with predominant {100} faces) or triangular Pt nanoparticle (rich in {111} faces) can be obtained by using poly-NIPA or poly-NEA, respectively. The synthesis of Pt nanocrystals with controlled morphology must have interesting applications in practice, since the catalytic activity for structure sensitive reactions depends on the orientation of the crystalline facets. Unique catalytic behavior of the cubic Pt nanoparticles was already reported for NO/CH_4[5] and $NO/O_2/C_3H_6$[6] reactions. Until recently, the structure sensitivity for a given reaction was mostly investigated on the clean surfaces (under high vacuum) of the single crystals. The structure sensitivity is difficult to be clearly evidenced over conventionally prepared catalysts because the ratio between different crystalline facets of the supported metal remains relatively unchanged regardless the preparation method. Therefore, the synthesis of well-defined metal nanocrystals, statistically rich in specific crystallographic orientation, is a promising tool to understand better mechanism of the structure sensitive reactions in real catalytic conditions.

References
1 A. Miyazaki and Y. Nakano, *Langmuir*, **16**, 7109 (2000).
2 S. Itoh and S. Fujishige, *Kenkyu Hokoku-Sen'i Kobunshi Zairyo Kenkyusho*, **167**, 5 (1991).
3 T. S. Ahmadi, Z. L. Wang, T. C. Green, A. Henglein, and M. A. El-Sayed, *Science*, **272**, 1924 (1996).
4 Z. L. Wang, *Adv. Mater.*, **10**, 13 (1998).
5 I. Balint, A. Miyazaki, and K. Aika, *Appl. Catal., B*, **37**, 217 (2002).
6 I. Balint, A. Miyazaki, and K. Aika, *Phys. Chem. Chem. Phys.*, **6**, 2000 (2004).