Synthesis and Size Control of Pt Nanocubes with High Selectivity Using the Additive Effect of NaI

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The synthesis and size control of Pt nanocubes stabilized by polyacrylic acid sodium salt (PAA) were carried out by varying the reaction temperature and the growth rate between the {111} and {100} faces with the addition of NaI; the shape selectivity was about 70–80% and the cubic size was controllable between 7.5–10.5 nm.

Generally, fuel cells can be novel alternative energy resources in place of thermal power generation systems. Fuel cells possess very high energy conversion efficiency without emitting environmental pollutants and CO_2, and so can make an effective contribution in avoiding global warming. The polymer electrolyte fuel cell (PEFC) is expected to become the most widely used source in the general community because of its low operating temperature (below 100 °C). However, to enable its practical use in daily life, the cost of the Pt nanoparticles used as an electrode catalyst in PEFCs must be reduced. This can be done by developing Pt nanoparticles with higher catalytic activity.

The catalytic activity of Pt nanoparticles depends on their shape and size.[1] Cubic Pt nanoarticles exhibit higher catalytic activity compared to spherical particles, since cubic particles are composed of only (100) facets, with more defective and active sites accompanied by dissolution and surface reconstruction than (111) facets.[1] As for particle size, around 5 nm is thought to produce the most efficient catalytic performance.[2]

In this communication, we describe the novel preparation and size control of Pt nanocubes stabilized by a PAA ligand (PAA-Pt) with high selectivity (max 84%) by utilizing the additive effect of NaI and varying the reaction temperature. Many attempts have been made to control the shape and size of nanoparticles[3–6] about which we have also reported;[5,7] however, this is the first successful attempt to control "the size of precisely cubic" Pt nanoparticles while retaining high shape selectivity. Note that NaI was selected as an additive because I^- anions are widely known to adsorb onto a Pt crystal surface most strongly among the halogen anions,[8] and to act as a good controller for the growth rate between {100} and {111} faces of PAA-Pt. In addition to the reaction temperature, the influence of other experimental parameters, such as the concentration of NaI and the starting Pt complex and the anion effect, is also stated.

PAA-Pt was generally prepared as followings: NaI with a predefined molar ratio to K_2PtCl_4 was dissolved in 50 mL of x mM K_2PtCl_4 and PAA aqueous solution ($x = 0.1$, 0.5, and 1, K_2PtCl_4/PAA = 1). Ar gas was introduced through the solution for 20 min to exclude O_2. H_2 gas was bubbled for 5 min, and the vessel was then strictly sealed. The reaction mixture was left without stirring for 15 h under H_2. The solution color gradually turned brown when Pt ions were reduced to produce PAA-Pt. The reaction temperature was varied between 5 and 60 °C to investigate the dependence of the physical structure of PAA-Pt on temperature.

After the reaction finished, a small amount of the reaction mixture was cast onto a carbon-supported Cu grid for TEM. The shape and size distribution of PAA-Pt was determined by counting more than 200 particles in TEM images taken by a Hitachi H-7100. Water in the reaction mixture was removed by a rotary evaporator and dried overnight in vacuum to give PAA-Pt powders for the measurement of XRD on a Rigaku Rint 2000 with Cu Kα radiation.

Figures 1a and 1b show the TEM image of the prepared PAA-Pt with and without NaI. From these images, it is obvious that the shape of PAA-Pt tends to become cubic when NaI coexists in the reaction mixture. The XRD pattern of the obtained cubic PAA-Pt exhibits several peaks at 39.7, 46.2, and 67.4°, which correspond to (111), (200), and (220) of the fcc lattice.[5] The further investigation of the NaI effect on the physical structure (shape and size) of PAA-Pt was carried out by changing the molar ratio of NaI to K_2PtCl_4 in three K_2PtCl_4 concentrations (0.1, 0.5, and 1.0 mM), as summarized in Figure 1c.[9] It is noticeable that the cubic rate (the ratio of the cubic nanoparticles to all of the produced particles) and the average particle size tend to

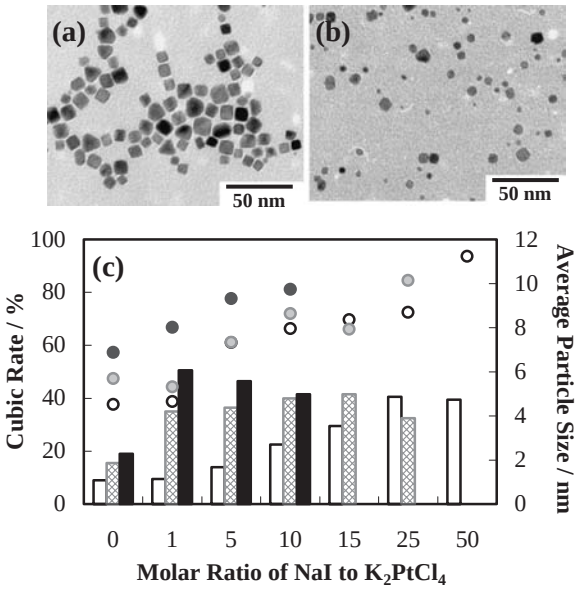

Figure 1. TEM image of PAA-Pt prepared under the reaction condition of NaI/K_2PtCl_4 = (a) 1.0 mM/1.0 mM and (b) 0 mM/1.0 mM. (c) Effect of the NaI molar ratio to K_2PtCl_4 on the average particle size (circles) and the cubic selectivity (bars) of the prepared PAA-Pt. The concentrations of K_2PtCl_4 were 0.1 (white), 0.5 (grey), and 1.0 mM (black), respectively.

increase with increasing NaI ratio and Pt concentration. This result indicates the formation mechanism of the cubic PAA-Pt: after a particle nucleus is generated at the first stage of the reaction, the particle grows gradually, accompanied by the different growth ratios between the {111} and {100} faces of PAA-Pt under the additive effect of NaI. As for cubic size, the particle is enlarged at high NaI concentrations since the ζ potential of PAA-Pt decreases with increasing electrolyte concentration in solution by the large interaction among particles.

The effect of NaI on the shape of PAA-Pt is to create the adsorption effect of I^- anions on the PAA-Pt surfaces during the reaction, not the electrostatic effect represented by the Hofmeister series: $SO_4^- > Cl^- > Br^- > I^- >$ without anion, where the solubility of organic ligands (here PAA) becomes lower on the left side of the series.[10] The additional experiment explains that the dependence of the cubic ratio on the Hofmeister series is not found when Na_2SO_4, NaCl, and NaBr are used in place of NaI. Thus, it is plausible that the adsorption of I^- anions onto the Pt particle surface triggers the faster growth ratio of the {111} faces than that of the {100} faces to produce the cubic PAA-Pt surrounded by 6 {100} faces.

Figures 2a–2d shows the TEM images of PAA-Pt synthesized at a different reaction temperature, *T*, from 5 to 60 °C. They demonstrate that the cubic PAA-Pt can be preferentially obtained between 20 and 60 °C with high selectivity ca. 70–80%, in addition, the cubic size was controllable between 7.5–10.5 nm by changing *T*. The temperature dependence on the physical structure of PAA-Pt was summarized in Figure 2e, indicating that the particle size first increased with rise of *T* until 20 °C, and then gradually decreases with increasing the cubic ratio of the particle shape. This finding is explained by the consideration that there are mainly two factors which determine the physical structure of the particle during the synthetic process; the ζ potential of the particle and the growth rate of the particle, and the electrostatic repulsion. The ζ potential becomes small and the growth rate of the particle is accelerated by increasing *T*, leading to the size increase. On the contrary, the electrostatic repulsion becomes larger by increasing *T*, resulting in the size decrease caused by the phenomenon that the number of the produced particle nuclei is enlarged. In this case, it is considered that the former factor is predominant from $T = 5$ to 20 °C, while the latter has an advantage from $T = 20$ to 60 °C. It should be mentioned that the difference of the surface growth ratio between {100} and {111} faces might become conspicuous by increasing *T*, since the value of the cubic ratio goes on increasing related to *T*. It is believable that the temperature is most effective parameter to control the cubic size of PAA-Pt under the additive effect of NaI.

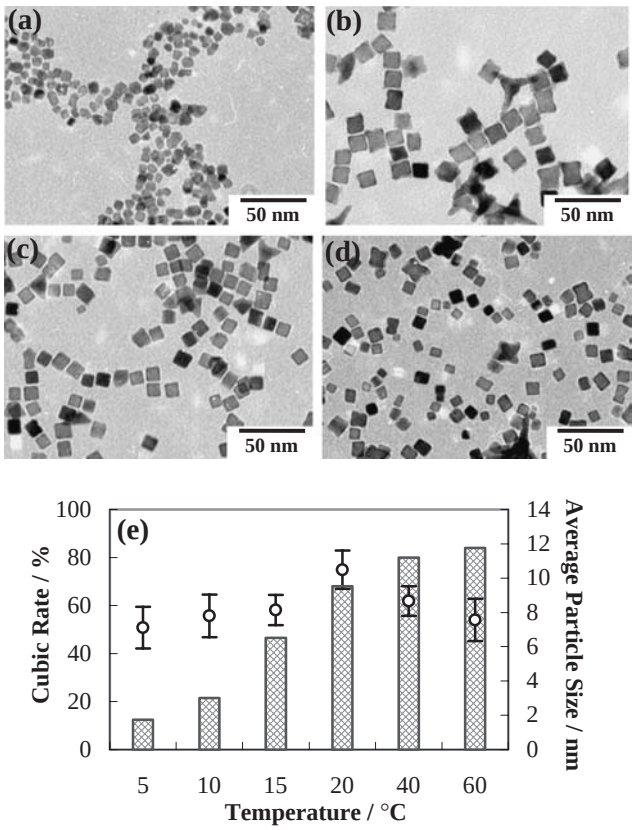

Figure 2. TEM image of PAA-Pt prepared with reaction temperatures = (a) 5, (b) 20, (c) 40, and (d) 60 °C. (e) Effect of reaction temperature on average particle size (circles) and cubic rate (bars) of the prepared PAA-Pt. The concentration of K_2PtCl_4 and NaI in solution was 1.0 mM.

In conclusion, we have presented the synthesis and size control of a cubic PAA-Pt nanoparticle, utilizing the additive effect of NaI during the particle growth process. The size and cubic ratio of PAA-Pt increased when the concentration of the starting Pt complex and NaI was increased before the particle aggregation phenomenon appeared. Especially, the cubic size of PAA-Pt could be changed by adjusting the reaction temperature between 20 and 60 °C, while retaining high shape selectivity. The catalytic activity of Pt nanocubes prepared in this manner is currently under investigation with the further goal of developing PEFCs with higher efficiency.

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