

## Synthesis of Platinum Nanoparticles Using Electrostatic Stabilization and Cluster Duplication of Perfluorinated Ionomer

Pyoung-Chan Lee, Dong Ouk Kim, Tai-Hoon Han, Soo-Jung Kang, Lyong Sun Pu, and Jae-Do Nam\*

*Department of Polymer Science and Engineering, SAINT, Sungkyunkwan University, Suwon 440-746, Korea*

Byung Woo Kim

*Department of Chemical Engineering, Sungkyunkwan University, Suwon 440-746, Korea*

Jun-Ho Lee

*Polymer Technology Institute, Sungkyunkwan University, Suwon 440-746, Korea*

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**Abstract:** Platinum (Pt) nanoparticles were prepared by the liquid-phase reduction of tetraammineplatinum (II) chloride ( $[\text{Pt}(\text{NH}_3)_4]\text{Cl}_2$ ) using Nafion as a stabilizer under various conditions of the Nafion phase. This method is novel in its use of electrostatic interactions between the Pt complex ions and sulfonic groups in the hydrated Nafion molecules. The synthesized Pt nanoparticles of the recast film system had a cubic shape. In the case of the Nafion solution system, the Pt nanoparticles mainly had a spherical shape. The shapes and sizes of the Pt nanoparticles were strongly influenced by the Nafion phase.

**Keywords:** Nafion, cluster duplication, platinum nanoparticles.

### Introduction

Owing to their extremely small size, the characteristic of nanoparticles, which makes them different from macroscopic solids, is that they have a very large percentage of surface atoms. Because of this characteristic, nanoparticles possess many novel chemical and physical properties and have possible future application in ceramics, catalysis, optics, electronics, and magnetic storage.<sup>1-9</sup> In particular, platinum (Pt) nanoparticles are of great interest because of their excellent catalytic activity. Their catalytic activity depends on the size distribution and morphology of the particles and, therefore, the synthesis of particles with well-controlled sizes and morphology could be critical for these applications. To prepare stable Pt nanoparticles, polymer<sup>10</sup> and polyelectrolytes<sup>11-13</sup> have been used as protective matrixes. In particular, Sarathy *et al.*<sup>14</sup> prepared hexagonal Pt nanoparticles using a thiol as the protector and transferred them to a toluene phase. The size of the metal catalyst particles was able to be controlled by stabilizing them in a liquid phase using surfactants.<sup>15,16</sup> The stabilization mechanism of the surfactant can be explained on the basis of their electrostatic effect, where the hydrophobic part is assembled on the particle surface and the charged hydrophilic or lipophilic

group is pointed toward the other end, which causes electrostatic repulsion between the nanoparticles.

Since the development of Nafion<sup>®</sup> by DuPont, the exact structure of perfluorinated ionomers has been intensively investigated. However, the morphology of Nafion and the relationship between its structure and unique properties have not yet been clearly identified.<sup>17</sup> The sulfonated surface of the ionic clusters in Nafion has been reported to catalyze various reactions such as alkylation, condensation, and esterification, due to its strong acidity.<sup>18</sup> Therefore, the hydrated clusters may be used as a reactive vessel for other materials such as metals. Han *et al.*<sup>19</sup> showed that the hydrated Nafion clusters can act as a reactive vessel (or template) for the reduction of a cationic gold ligand in the liquid phase using a liquid-phase impregnation/reduction method. Gold nanoparticles and nanorods were successfully synthesized inside the Nafion film seemingly visualizing the replicated structure of the Nafion cluster network. Liu *et al.*<sup>20</sup> reported that Pt nanoparticles without a carbon support could be prepared by the alcohol reduction method using an anionic Pt complex.

In this study, we report a similar synthetic route to Pt nanoparticles with different shapes and sizes using the electrostatic interactions between a cationic Pt complex and the sulfonic groups in the hydrated Nafion molecules under various Nafion phase conditions. The particle size and mor-

\*Corresponding Author. E-mail: jdnam@skku.edu

phology were strongly influenced by the reduction conditions.

## Experimental

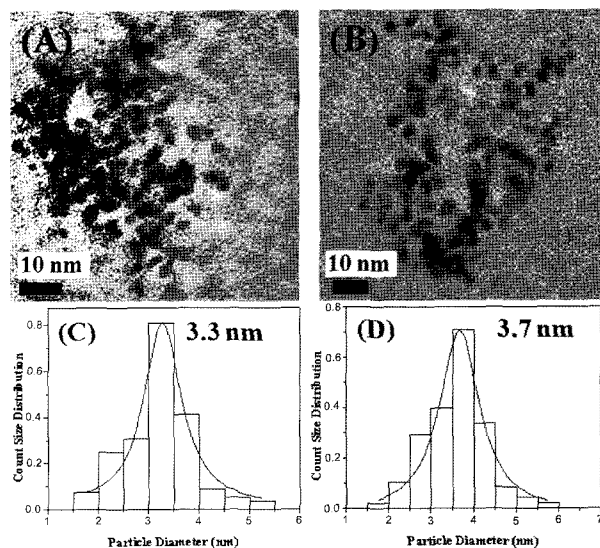
### Synthesis of the Pt Nanoparticles in the Nafion Solution.

The Pt nanoparticle synthesis was performed in a three-neck round bottom flask with a magnetic stirrer and a reflux condenser. 10 g of Nafion solution (5 wt% solution in lower aliphatic alcohols/H<sub>2</sub>O mix, Aldrich) was first added to a mixture of 1-propanol, 2-propanol, methanol and de-ionized water (2 : 2 : 2 : 1, vol. ratio). Then, tetraammineplatinum (II) chloride ([Pt(NH<sub>3</sub>)<sub>4</sub>]Cl<sub>2</sub>, Aldrich) was added to the mixture at various concentrations to give Pt loadings of 1, 2, and 3 wt%. Subsequently, sodium borohydride solution was slowly added to this mixture under stirring at room temperature. The molar ratio between NaBH<sub>4</sub> and the Pt salt was 20 : 1, so as to reduce the metal ions completely. After stirring for several hours, the obtained solution was dried by the evaporation of the solvent under vacuum. The evaporation and drying were carried out at as low a temperature as possible to prevent any structural change to the nanoparticles. Then, the Nafion-Pt nanoparticles were dialyzed against de-ionized water several times to remove the excess NaBH<sub>4</sub> and other ions.

**Synthesis of the Pt Nanoparticles in the Recast Nafion Film.** In a typical synthesis,<sup>21</sup> 10 g of Nafion solution (5 wt% solution) was added to an alcoholic solvent at room temperature. Then, ([Pt(NH<sub>3</sub>)<sub>4</sub>]Cl<sub>2</sub>) was added to this mixture at various concentrations to give Pt loadings of 1, 2, and 3 wt%. Subsequently, the solution was cast and dried in a vacuum oven. The recast Nafion-Pt ions film was immersed in 0.1 L sodium borohydride solution at 60 °C for 4 h. After the complete reduction of the Pt ions to Pt, this film was washed with DI water several times to eliminate any other ions. The recast Nafion film was heated at 140 °C in a vacuum oven. The recast Nafion film containing Pt was washed again in DI-water after heat treatment for two nights. We considered that the sodium ions were completely removed from the films. The morphology of the Pt nanoparticle was observed by Energy-Filtering Transmission Electron Microscopy (Carl Zeiss, LIBRA120) and high-resolution transmission electron microscopy (HR-TEM: JEOL, JEM2100F) at an accelerating voltage of 200 kV. By tilting the samples in the TEM, we were able to determine the 3-dimensional shapes of the particles.

## Results and Discussion

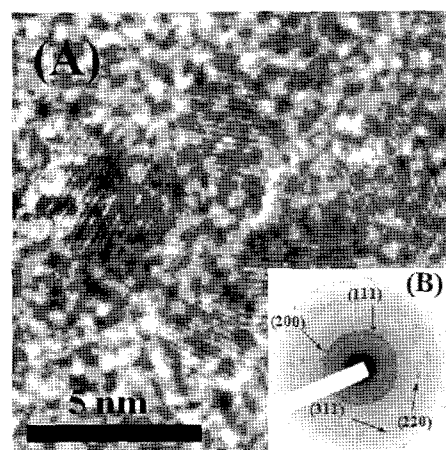
Figure 1 shows the TEM images of the Pt nanoparticles in the Nafion solution. In Figure 1(A and B), the Nafion/Pt solution predominately contained nanoparticles with a spherical shape. The stabilizing effect of the nonionic polymer in the formation of nanoparticles is generally referred to as steric stabilization,<sup>22-24</sup> owing to the hydrophobic and



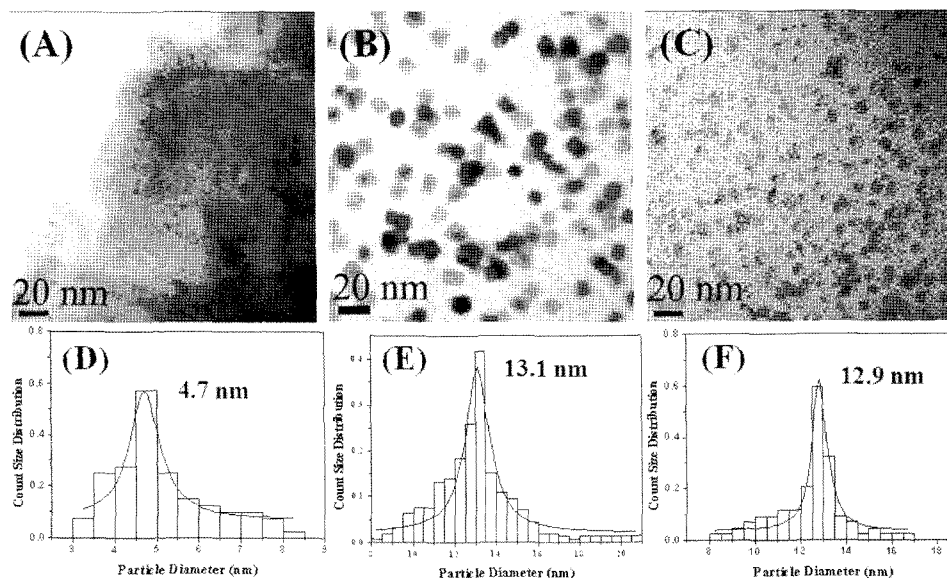
**Figure 1.** TEM image and particle size distribution of Pt nanoparticles in the Nafion solutions containing 1 wt% (A, C) and 2 wt% (B, D) of the Pt nanoparticles, where the particle size distribution of the Pt nanoparticles counted from the TEM image.

coordination interaction between the nonionic polymer and metal. As Nafion is an ionic polymer, the electrostatic stabilization could contribute to the stability of the Nafion-stabilized Pt nanoparticles (Scheme I). Therefore, the synthesized Pt nanoparticles are stable at a low loading of Pt (below 2 wt% in this study). Figures 1(C) and (D) show the particle size distribution of the Pt nanoparticles obtained from the TEM image. The size distribution is fairly narrow and the major peak is centered at 3.3 and 3.7 nm for Pt contents of 1 and 2 wt%, respectively.

As can be seen in Figure 2(A), the Pt nanoparticles exhibit crystalline structures that can be identified by their typical lattice fringes as  $\sim 0.2$  nm corresponding to the (2 0 0) lattice



**Figure 2.** HR-TEM images of Pt nanoparticles in the Nafion solution containing 2 wt% of Pt (A) and diffraction patterns of the selected area (B).

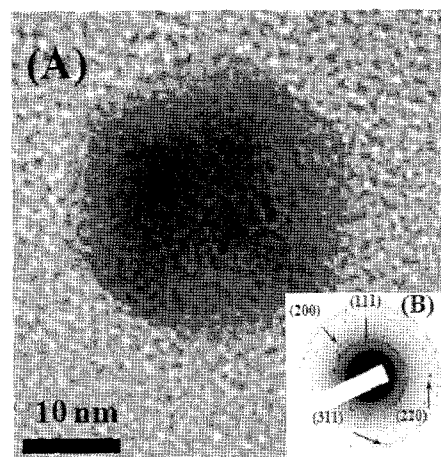


**Figure 3.** TEM image and particle size distribution of Pt nanoparticles in the recast Nafion films containing 1 wt% (A, D), 2 wt% (B, E), and 3 wt% (C, F) of Pt nanoparticles, where the particle size distribution of the Pt nanoparticles counted from the TEM image.

plane of Pt. The electron diffraction pattern in Figure 1(C) confirms the FCC (face-centered cubic) single crystalline structure of the synthesized Pt nanoparticles in the Nafion solution system. The diffraction patterns of the selected area could be indexed as the (1 1 1), (2 0 0), (2 2 0) and (3 1 1) planes of the FCC Pt structure.

At a high loading of Pt (over 3 wt% in this study), the Nafion stabilized Pt nanoparticles are unstable due to their agglomeration after a few days under laboratory conditions. It is reasonable to consider that Nafion may afford an insufficient steric and electrostatic stabilization effect to prevent the aggregation of the nanoparticles. There is a great possibility that the aggregation of the nanoparticles is related to the hydrophilic nature of the Nafion molecules.<sup>20</sup>

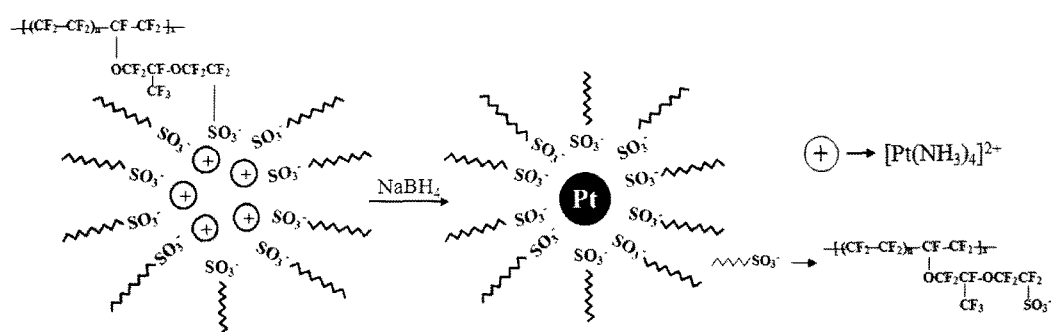
Figure 3 shows the TEM images of the Pt nanoparticles in the recast Nafion film. The thickness of the recast Nafion films was measured from the SEM images to be between 150 and 160  $\mu\text{m}$  in the dry state. As shown in Figure 3(A, B, and C), the Pt nanoparticles are well dispersed inside the recast Nafion film. The Pt nanoparticles show a square outline, which is found to be a cubic shape. The presence of clusters in recast Nafion films was confirmed in a previous study,<sup>25</sup> and these recast clusters have a larger size than those in the commercial films.<sup>26</sup> In the case of our study, the Pt complex ions interact with the  $\text{SO}_3^-$  groups in the Nafion molecules through an electrostatic interaction. When the cast film is dried, there is a significant possibility that the Pt complex ions disturb the formation of the Nafion clusters, since the Nafion polymer chains are solidified in the presence of the Pt complex ions.<sup>21</sup> Therefore, the Pt nanoparticles may very well be dispersed inside the recast



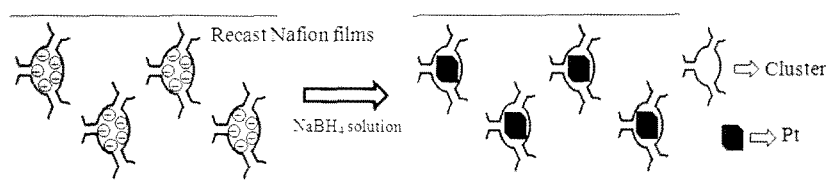
**Figure 4.** HR-TEM images of Pt nanoparticles in the Nafion recast membrane containing 2 wt% of Pt (A) and diffraction patterns of the selected area (B).

Nafion film after the reduction process. Figures 3(D), (E), and (F) show the particle size distribution of the Pt nanoparticles obtained from the TEM image. The size distribution is fairly narrow and the major peak is centered at 4.7, 13.1, and 12.9 nm for Pt contents of 1, 2, and 3 wt%, respectively.

Figure 4(A) shows that the Pt nanoparticles have a cubic shape. The fringe spacing observed in Figure 4(A) compares well with the literature results for Pt. In a previous study in which Nafion clusters were used as a template for duplicating metals, the metal nanoparticles were reported to reach a size of 5–6 nm, because gold is metallized in the confined structure of the Nafion clusters.<sup>19</sup> In our study, however, the recast clusters, which are larger than those of



**Scheme I.** Schematic representation of the synthesis of Nafion-stabilized Pt nanoparticles in the Nafion solution.



**Scheme II.** Schematic representation of ionic cluster in the recast Nafion film and the Pt reduction process that takes place therein.

the commercial films,<sup>26</sup> were used as a reactive vessel for synthesizing Pt and thus, larger nanoparticles are expected to be produced in the synthesis. For the Pt nanoparticles to grow larger, an additional ionic Pt source is needed, which in this case is provided by the neighboring clusters. In addition, the Pt nanoparticles are considered to grow in the soft and deformable structure of the hydrated Nafion clusters (whose modulus is 114 MPa at 23 °C) and, thus, the Pt particles may well grow to as large a size as 10 nm. As shown in Scheme II, the recast Nafion film, containing the Pt complex ions, is immersed in sodium borohydrate solution and Pt grows in the larger-sized clusters within it.<sup>21</sup> Figure 4(B) shows the selected-area electron diffraction patterns attributed to the (1 1 1), (2 0 0), (2 2 0), and (3 1 1) diffractions of the Pt FCC crystal structure. The Pt nanoparticle-incorporated Nafion film can be used for direct methanol fuel cells because the highly dispersed Pt nanoparticles reduce the amount of methanol crossover, leading to an increase in the cathode potential compared to that of the pristine Nafion.<sup>21,27</sup>

## Conclusions

Pt nanoparticles were successfully prepared by reducing a cationic Pt complex using NaBH<sub>4</sub> as the reducer in the presence of a perfluorinated ionomer. The size and morphology of the Pt nanoparticles were strongly influenced by the Nafion phase. In the case of the Nafion solution system, the Nafion/Pt solution contains nanoparticles with a spherical shape. On the other hand, in the case of the recast film system, the synthesized Pt nanoparticles were well dispersed inside the recast Nafion film and exhibited a cubic shape with a narrow size distribution.

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