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Short Communication

One-Step Synthesis of Hexapod Pt Nanoparticles Deposited on Carbon Black for Improved Methanol Electrooxidation

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We report hexapod Pt nanoparticles (Hexa-Pt/C) deposited on carbon black synthesized by means of polyol process in the presence of poly(vinyl pyrrolidone) and NO_3^- and Fe^{3+} as additives. The Hexa-Pt/C shows nanosized pods grown along {111} facets observed by transmission electron microscopy. For methanol electrooxidation, the Hexa-Pt/C exhibited much improved electrocatalytic activity and stability due to a particular surface exposure favorable for catalytic reaction in comparison with commercial polycrystalline Pt catalyst.

Keywords: Hexapod, Pt, Electrocatalyst, Methanol, Electrooxidation

1. INTRODUCTION

Direct methanol fuel cells (DMFCs) are considered to be a promising electrochemical device due to various merits such as low operating temperatures, ease of handling a liquid fuel, high energy density of methanol and applications to micro-sized fuel cells.[1,2] In the DMFCs, platinum (Pt) as an electrocatalyst of the anode has shown an excellent catalytic activity in acid electrolytes.[3] However, it is known that pure Pt is not efficient due to its high cost and low CO poisoning tolerance. To overcome the limitation of Pt, there have been various attempts such as Pt-based alloying, shape controlling and core-shell nanostructures.[4,5] In particular, it has been well-known that the catalytic properties of Pt nanoparticles (NPs) strongly depend on their shape, size and crystallinity.[6]

To enhance the catalytic activity of metallic nanostructure catalysts, there have been many efforts to manipulate structure and shape of NPs during synthetic process.[7] The structure or shape-controlled metallic catalysts have exhibited much improved catalytic performance due to a particular surface exposure favorable for catalytic reactions in comparison with typical polycrystalline metallic catalysts.[8] For shape-controlled metallic NPs, various synthetic approaches such as polyol process in aqueous[9] or organic[10] solutions and chemical[11], thermal[12] and photochemical[13] reduction have been suggested.

Herein, we synthesized Hexa-Pt NPs deposited on Vulcan XC-72R (Hexa-Pt/C) using the polyol process with ethylene glycol in the presence of poly(vinyl pyrrolidone) and NO_3^- and Fe^{3+} ions using a one-step process. The structural and electrochemical properties of the catalysts were characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM), and cyclic voltammetry (CV).

2. EXPERIMENTAL PART

2.1. Synthesis of Hexapod Pt nanoparticles deposited on carbon black

The Hexa-Pt/C was prepared by the modified polyol process using ethylene glycol (EG) as a reducing agent. A solution of 2 mM H_2PtCl_6, 10 mM $NaNO_3$, and 20 μM $FeCl_3$ was dissolved in 50 ml of EG with 50 mg poly (vinyl pyrrolidone) (PVP, MW = 29,000). The Vulcan XC-72R carbon used as the carbon support were added to the solution and mixed with continuous stirring at room temperature. All used chemicals were analytical grade. The solution was raised by 5 ^{o}C min^{-1} and was kept for 2 h at 250 ^{o}C until H_2PtCl_6 was completely reduced by EG. The resulting colloid solution was cooled at room temperature and washed with water and then with ethanol several times to remove ethylene glycol and excess PVP.

2.2. Structural analysis

XRD patterns of Pt samples were obtained using a D2 PHASE system (Bruker) with Cu K_a source (λ = 0.15406 nm) radiation at 30 kV and 10 mA in 2θ = 20° to 80°. The size and morphology of catalysts were analyzed by TEM using a Tecnai G2 F30 system (FEI) operating at 300 kV. TEM samples were prepared by placing drops of catalyst suspension dispersed in ethanol on a carbon-coated copper grid.

2.3 Electrochemical analysis

The electrocatalytic properties were measured in a three-electrode cell using a potentiostat (Eco Chemie, AUTOLAB) at room temperature with a scan rate of 50 mV s^{-1}. A Pt wire and Ag/AgCl (in saturated KCl) were used as a counter and reference electrode, respectively. The glassy carbon working electrode was coated with 5 μL of catalyst ink prepared by mixing catalyst, deionized water, isopropyl alcohol, and 5 wt% Nafion binder. After drying in 50 ^{o}C oven, the total loading of catalyst was 20 μg cm^{-2}. Cyclic voltammograms (CVs) of the catalysts were obtained in Ar-purged 0.1 M $HClO_4$ and 0.1 M $HClO_4$ + 2.0 M CH_3OH with a scan rate of 50 mV s^{-1} at room temperature. For comparison of electrocatalytic stability, the catalysts were kept at +0.5 V for 7200 sec in 0.1 M $HClO_4$

+ 2.0 M CH_3OH and then CVs were obtained in 0.1 M $HClO_4$ + 2.0 M CH_3OH.

3. RESULTS AND DISCUSSION

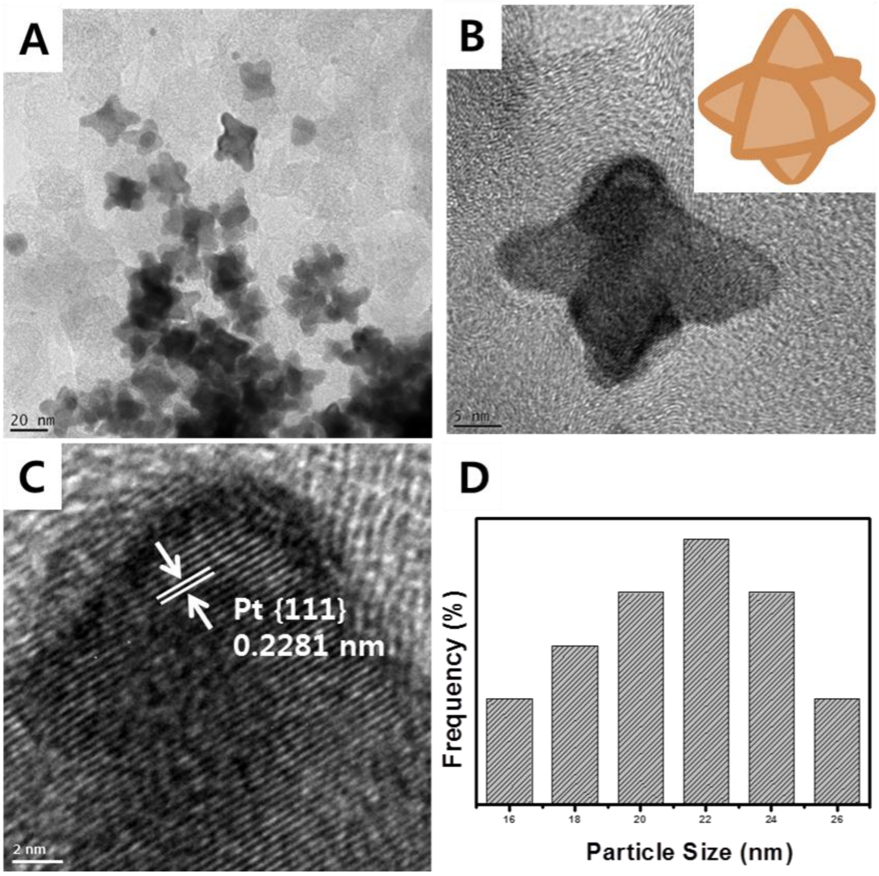

Figure 1. (A) TEM image of Hexa-Pt/C. (B) High-resolution TEM (HR-TEM) image of a Hexa-Pt NP. (C) HR-TEM image of a Hexa-Pt NP with {111} facet. (D) Size distribution of the Hexa-Pt NPs.

Fig. 1A shows TEM image of Pt NPs dispersed on carbon black (Hexa-Pt/C) representing that the Pt catalysts are deposited on carbon supports. As indicated in Fig. 1B, the Pt NP exhibits a hexapod shaped structure. In our synthesis process, PVP was used as a capping agent for forming {111} facets of Pt metallic nanostructures.[14] The NO_3^- and Fe^{3+} as additive ions could cause etching reaction of Pt nanostructure.[15] The additive ions could expose {111} facets of Hexa-Pt NPs by means of a different potential reaction and reducing rate. Accordingly, this suggests that the Hexa-Pt NPs formed by the present polyol process might have grown along {111} facets.[16] It can be clearly observed that a Hexa-Pt NP represents {111} facets with *d*-spacing of 0.2281 nm of Pt metallic phase (Fig. 1C of the high-resolution TEM image). The Hexa-Pt NPs exhibit a relatively large average particle size of ~22.15 nm (Fig. 1D) as compared to that of ~2.59 nm of commercial Pt NPs deposited on carbon black (E-TEK, Co.).

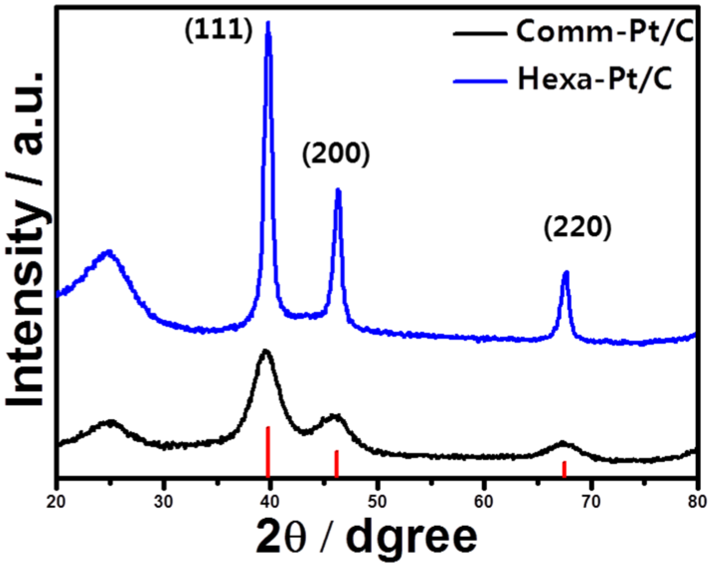

Figure 2. XRD patterns of Hexa-Pt/C and Comm-Pt/C compared to the reference pattern of metallic Pt (JCPDS #04-0802).

Fig. 2 shows XRD pattern of as-synthesized Hexa-Pt/C compared to that of commercial Pt/C (Comm-Pt/C). The diffraction peaks of the Hexa-Pt/C at 39.7°, 46.2°, and 67.4° correspond to (111), (200) and (220) plane, respectively, representing a face-centred-cubic crystal structure, which is exact agreement with those of the Comm-Pt/C. The broad peaks around 25° of the Hexa-Pt/C and Comm-Pt/C were associated with (002) plane of carbon black as a support.

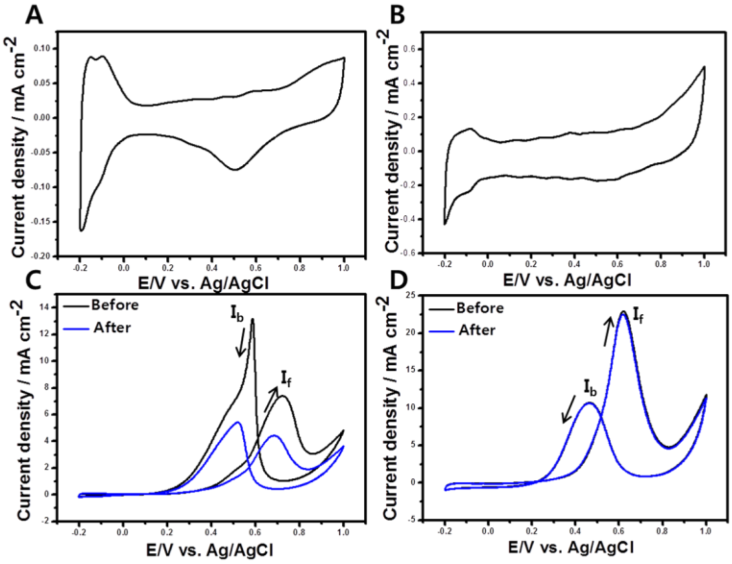

Figure 3. CVs of (A) Comm-Pt/C and (B) Hexa-Pt/C in 0.1 M $HClO_4$ with a scan rate of 50 mV s^{-1} at room temperature. CVs of (C) Comm-Pt/C and (D) Hexa-Pt/C before and after stability test for methanol electrooxidation in 0.1 M $HClO_4$ + 2 M CH_3OH with a scan rate of 50 mV s^{-1} at room temperature. The stability test of the catalysts was carried out at 0.5 V for 7200 sec in 0.1 M $HClO_4$ + 2.0 M CH_3OH.

To identify electrochemical properties of the catalysts, CVs of the catalysts were obtained in 0.1M $HClO_4$ between -0.2 V and +1.0 V at 25 ^oC. The electrochemical active surface areas (EASAs) of the Comm-Pt/C (Fig. 3A) and Hexa-Pt/C (Fig. 3B) were measured using the following equation:

$$EASA[m^2 \cdot g^{-1}] = \frac{Q_H}{0.21 \times M_{Pt}} \quad [1]$$

where 0.21 mC cm^{-2} is the Coulombic charge (Q_H) associated with hydrogen adsorption and M_{Pt} is the Pt loading on the working electrodes. The EASAs of the Comm-Pt/C and Hexa-Pt/C are estimated to be ~62.4 and ~2.7 m^2 g^{-1}, respectively. The CVs of the Comm-Pt/C and Hexa-Pt/C for methanol oxidation are shown in Fig. 3C and 3D. Theoretically, methanol oxidation may proceed at 0.04 V vs NHE as follows:

$$CH_3OH + H_2O \rightarrow CO_2 + 6H^+ + 6e^- \quad [2]$$

Therefore, the lower onset potential indicates an evidence for superior electrocatalytic activity for methanol electrooxidation. The Hexa-Pt/C has lower onset potential (0.25 V) than the Comm-Pt/C (0.34 V) exhibited fairly good electrocatalytic activity of the Hexa-Pt/C toward methanol oxidation. Furthermore, the value for the Hexa-Pt/C of 0.26 mA·cm^{-2} at 0.35 V, near the kinetically controlled potential in the methanol reaction, exceeds that of 0.11 mA·cm^{-2} for the Comm-Pt/C. The Hexa-Pt/C despite the smaller EASA might have larger oxidation current density, i.e. excellent catalytic activity toward methanol electrooxidation compared with the Comm-Pt/C. In methanol electrooxidation reactions, the ratio the forward anodic peak current density (I_f) to the reverse anodic peak current density (I_b), i.e. I_f/I_b, can be used to describe the tolerance of catalyst to accumulation of carbonaceous species. A low I_f/I_b indicates a poor catalytic activity for methanol oxidation to carbon dioxide during the forward anodic scan and excessive accumulation of carbonaceous residues on the catalyst surface. On the other hand, a higher I_f/I_b indicates an excellent oxidation of methanol during the forward anodic scan and less accumulation of residues on the catalyst.[17,18] The higher I_f/I_b ratio of 2.13 for the Hexa-Pt/C than 0.57 for the Comm-Pt/C indicates less accumulation of residues on the catalyst during methanol oxidation, and thus an excellent catalytic activity.

To evaluate electrocatalytic stability of the catalysts, the catalysts were maintained at 0.5 V for 7200 sec in 0.1 M $HClO_4$ + 2.0 M CH_3OH. In the case of the Comm-Pt/C, oxidation current density after the stability test seriously decreases whereas the Hexa-Pt/C supports almost the same current density after the stability test suggesting much improved electrocatalytic stability of the Hexa-Pt/C for methanol electrooxidation. The shape and size of the catalysts after the stability test are compared as shown in Fig. 3C and 3D. In the case of the Hexa-Pt/C, the size and morphology of the catalysts still remain after the stability test resulting in much improved catalytic stability (Fig. 4A-C). On the other hand, the Comm-Pt/C shows agglomeration, increased average size, and wider size distribution after the stability test thus resulting in deteriorated catalytic activity (Fig. 4D-F). By combining electrochemical properties and structural analysis, we can conclude that the Hexa-Pt/C represent an alternative candidate for the DMFC anode catalysts.

4. CONCLUSIONS

The Hexa-Pt NPs on carbon black were successfully synthesized by means of polyol process with PVP and additive ions. The NO_3^- and Fe^{3+} as additive ions could expose {111} facets of Hexa-Pt NPs by means of a different potential reaction and reducing rate. The Hexa-Pt/C with controlled surface structure of {111} facets favorable for catalytic reaction could result in an excellent catalytic activity and stability for methanol electrooxidaion in comparision with the Comm-Pt/C. Thus, we suggest that the Hexa-Pt/C can be a promising anode catalyst for methanol electrooxidaion in acidic solution.

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