Facile Synthesis of Pt Nanoparticle and Graphene Composite Materials: Comparison of Electrocatalytic Activity with Analogous CNT Composite

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Here, we present a facile method to synthesize Pt nanoparticles (NPs) and graphene composite materials (Pt/G) via vacuum filtration. Anodic aluminum oxide (AAO) templates were used to separate Pt/G composite and liquid phase. This method can be used to easily tune the mass ratio of Pt NPs and graphene. Pt NPs, graphene, and carbon nanotubes (CNTs) as building blocks were characterized by a variety of techniques such as scanning electron microscopy, UV-Vis spectroscopy, and Raman spectroscopy. We compared the electrocatalytic activities of Pt/G with Pt NP and CNT films (Pt/CNT) by cyclic voltammetry (CV), CO oxidation, and methanol oxidation. Pt/G was much more stable than pure Pt films. Also, Pt/G had better electrochemical activity, CO tolerance and methanol oxidation than Pt/CNT loaded with the same amount of Pt NPs due to the better dispersion of Pt NPs on graphene flakes without aggregation. We further synthesized Au@Pt disk/G and Pt nanorods/G to determine if our synthetic method can be applied to other NP shapes such as nanodisks and nanorods, for further electrocatalysis studies.

Key Words : Platinum nanoparticle, Graphene, Vacuum filtration, Electrocatalytic activity, Methanol oxidation

Introduction

Pt has been widely used as an electrocatalyst in fuel cells, such as direct methanol fuel cells (DMFCs).1−8 In order to enhance the electrochemical surface area (ECSA) of Pt, there have been many research for the utilization of Pt, including Pt-Ru alloy,9−11 porous structure,12,13 bimetal,14−16 and core-shell nanoparticles (NPs).17−19 In recent years, there also have been several efforts to synthesize Pt NPs with different morphologies such as rod,13 flower-like,20 hollow nanostructures,21 and various others.22,23 However, one drawback of pure Pt is that it easily aggregates, leading to instable films. Not only to prevent aggregation but also to reduce the cost of fuel cells, Pt is usually loaded on supporting materials, the Pt surface was surrounded by residual reagent, such as Pt ion solution and a graphite dispersion. In these experiments, the Pt surface was surrounded by residual reagent, which usually caused low electrocatalytic activity, because using of reducing agents is inevitable for the chemical process. Meanwhile, Kakaei et al.24 fabricated Pt on graphene composites by an electrochemical method. In this case, however, controlling the ratio of Pt to graphene was not easy.

Herein, we synthesized Pt NPs and graphene hybrid materials (Pt/G) using a facile method. A 30 nm Pt NP and graphene solution were prepared separately, and Pt/G was deposited on anodic aluminum oxide (AAO) templates by filtration. By controlling the relative ratio of Pt NPs and graphene suspensions, the mass ratio of the final Pt/G composite could be controlled. We also fabricated Pt/G films with different shapes of Pt NPs and controlled the Pt NPs to graphene ratio. We further synthesized Pt NPs and CNT composites (Pt/CNT) by using an analogous method. To compare the electrochemical properties of Pt/G and Pt/CNT films, we used a cyclic voltammetry (CV) and confirmed their electrochemical activities by CO oxidation and methanol oxidation.

Experimental

Chemicals. Hydrogen hexachloroplatinate (IV) hydrate (H₂PtCl₆·nH₂O, n = 5.6) from Kojima, L(+)-ascorbic acid (C₆H₇O₆, 99.5%) from Kanto, and sodium citrate (Na₃C₆H₅O₇·2H₂O, 99.0%) from Yakury were used. Sodium hydroxide (NaOH, 98.0%) and dimethylformamide (CH₃NO, 99.8%) were purchased from Samchun and Sigma-Aldrich, respectively. The CNTs (CM-95, BET surface area ≈ 200 m²/g) were purchased from Iijin Nanotech Co. AAO templates (diameter = 25 nm, pore size = 200 nm, thickness = 60 μm) were purchased from Whatman International Ltd. All aqueous solutions were prepared with triply distilled deionized water (Millipore, >18.2 MΩ).
**Instrumentation.** Field-emission scanning electron microscopy (FE-SEM) images were obtained using a JEOL 7000F and a JEOL 7600F. Electrochemical experiments were performed by Autolab (PGSTAT12) equipped with a 3-electrode system [counter electrode, Pt mesh; reference electrode, Ag/AgCl (3 M KCl)]. UV-Vis spectra were taken using an S-3100 spectrophotometer (Scinco). Raman spectra were collected using WITEC Alpha300 system.

**Synthesis of Pt NP, Graphene and CNT Solution.** Pt seeds and Pt NPs were prepared according to Brown et al. and Bigall et al. The density of Pt NP solution was 100 mg/L. Graphene was synthesized using a reducing agent system. As-prepared graphene (0.1 g) was dispersed in 1 L of dimethylformamide by sonication for 2 h. Centrifugation was then used at 3000 rpm for 30 min to remove residual insoluble small graphene particles. A clean upper solution was extracted by a pipette without any precipitate. CNT (0.1 g) was dispersed in 1 L of dimethylformamide, and CNT solution was prepared as described above. Both the density of graphene and CNT solution were 16 mg/L.

**Fabrication of Pt/G, Pt/CNT Composites and Pt NP Films.** For Pt/G composites, a 30 nm Pt NP solution and graphene solution were deposited on AAO templates by syringe pumps at a constant speed (80 mL/h for Pt NPs and 80 mL/h for graphene), as shown Scheme 1. The left part represents schematic process of fabrication of films step by step and real optical images corresponding to each illustration, respectively. The right part exhibits the deposition of Pt/G films onto AAO template. The AAO templates were used to filter the mixed Pt NP and graphene dispersed solutions. To avoid the loss of Pt NPs through pore of AAO, we injected graphene solution a little before the introduction of Pt NPs. During pumping, a vacuum was helped by an aspirator connected to Erlenmeyer flask. After filtration, the mixture was dried on the AAO templates without a liquid phase. After removing the AAO templates by floating composition on 3 M NaOH for 30 minutes, Pt/G films were obtained. The Pt/G film was washed 3 times by deionized water. Pt/CNT, Au@Pt disks/G, and Pt NR/G films were obtained by an analogous method. For Pt NP film, a 30 nm Pt NP solution was deposited on AAO templates by syringe pumps at a constant speed (160 mL/h). Before removing the AAO, Poly(methyl methacrylate) (PMMA) was spin coated to avoid scattering of Pt NPs during AAO removal. The other details were followed by the similar process of the fabrication of Pt/G. After the films were transferred, PMMA was removed by acetone. An ITO glass slide was coated with 40 mM (3-mercaptopropyl)-trimethoxy-silane (MTPMS), which was used to attach the Pt NP film, the Pt/G and the Pt/G film to ITO glass. The MPTMS modification process was based on a technique employed in our previous research. After treatment of ITO, the films were transferred to ITO glasses.

**Synthesis of Au@Pt Disks and Pt nanorods.** Au@Pt disks were synthesized by wet-chemical method as reported previously. Pt nanorods (NRs) were synthesized by using an electrochemical method with a 3-electrode system. The details of the synthesis have been reported previously.

**Results and Discussion**

We first investigated the quality of each Pt NP (ca. 30 ± 3 nm), graphene, and CNT starting materials before mixing. Uniformly distributed Pt NPs, shown in Figure 1(a), indicate that our wet-chemical synthesis was successful for controlling the size and shape of Pt NPs uniform. A relatively smooth graphene surface and highly connected CNT network are also shown in Figure 1(b) and 1(c). UV-Vis spectroscopy was used to characterize optical NP properties and measure NP sizes. As shown in Figure 1(d), the absorption peak at 294 nm indicates that the NPs were approximately 30 nm, which is consistent with the FE-SEM images. Raman spectroscopy was used to characterize the quality of carbon-based materials, which had three typical Raman features: a D peak (~1350 cm$^{-1}$) related to defects, G peak (~1580 cm$^{-1}$) associated with the vibration of sp$^2$ carbon atoms, and 2D peak (~2700 cm$^{-1}$) of the double resonance process, further confirming our as-prepared starting materials.

One benefit of our fabrication of Pt NPs and carbon-based materials over other methods is its ability to tune the Pt mass

![Scheme 1. The fabrication of Pt/G composites.](image-url)

![Figure 1. FE-SEM images of (a) 30 nm Pt NPs, (b) graphene, (c) CNT, (d) UV-Vis spectra of 30 nm Pt NPs; (e) Raman spectra of graphene and CNT.](image-url)
ratio with a uniform distribution. In both Pt/G and Pt/CNT, the amount of Pt NPs on the surfaces of graphene and CNT increased as we increased the mass ratio of Pt to graphene and CNT, respectively, as shown in Figure 2. The Pt/G ratios are (a) Pt$_{50}$G$_{16}$, (b) Pt$_{100}$G$_{16}$, and (c) Pt$_{200}$G$_{16}$, and Pt/CNT are (d) Pt$_{50}$CNT$_{16}$, (e) Pt$_{100}$CNT$_{16}$, (f) Pt$_{200}$CNT$_{16}$. (g) FE-SEM image of the large area of sample corresponding to (c), (h) large area of FE-SEM image corresponding to (f).

We performed CVs to investigate the electrochemical properties of as-prepared Pt/G, Pt/CNT, and pure Pt NP films. Figure 3(a)-(c) show CV data of Pt/G, Pt/CNT, and pure Pt NP films in nitrogen-saturated 0.1 M sulfuric acid at a scan rate of 50 mV/s, respectively. In the positive potential sweep, the Pt NPs are oxidized evident by a broad oxidation feature from 0.60 to 1.30 V. We observed a corresponding reduction peak at around 0.25-0.50 V in the negative potential sweep. H$^+$ was reduced and adsorbed onto the Pt surface with an increasing negative potential sweep from 0.08 to −0.20 V. With a further sweep in potential before H$_2$ evolution, the reduced H$^+$ is oxidized again, showing oxidation current peaks from −0.20 to 0.18 V, which describes the hydrogen desorption area used to measure the apparent exposed surface of Pt. In Figure 3(a)-(c), the current densities increased for all films as we gradually increased the amount of Pt NPs, as expected. For the detail analysis, the ECSA of each film was calculated by using the columbic charge for hydrogen adsorption and desorption. The hydrogen desorption area as a function of Pt mass for all of the investigated Pt films is plotted in Figure 3(d). For Pt/G, ECSA increases linearly with the Pt mass ratio, which indicates that the graphene effectively disperses Pt NPs without aggregation. Whereas, in case of the bare Pt NP films, the incremental amount of ECSA was reduced when the mass of Pt NP loading was higher than 100 µg. Obviously, the aggregation of Pt NPs can lead to the decrease of the exposed Pt surface to electrolyte.

The Pt NPs of Pt/CNT were better dispersed than bare Pt NP films, but the measured ECSA of Pt/CNT was less than that of Pt/G, demonstrating the ineffective dispersion of Pt NPs in CNT matrix. At 200 µg of Pt, the ECSAs of Pt/G, Pt/CNT, and Pt NP layers are typically 6.64, 4.90, and 3.95 mC/cm$^2$, respectively. To further compare the electrocatalytic activities of Pt/G and Pt/CNT toward CO electro-oxidation, we performed CV at a scan rate of 50 mV/s, by bubbling CO gas in 0.1 M sulfuric acid solution for 9 minutes (Figure 4(a), (b)). The magnitude of anodic current peaks indicates the degree of CO oxidation to CO$_2$. Both Pt/G and Pt/CNT exhibited higher electrocatalytic activity with an increasing mass ratio of Pt to carbon materials. The mass-normalized ECSA of the Pt/G and Pt/CNT composites, calculated from the amount of CO oxidation, are listed in Figure 4(c). The ECSA of the Pt/G remained constant, which indicates that Pt/G has high electrocatalytic CO oxidation capability. Pt/CNT, however, had 2.03-6.44 times lower values than Pt/G composites, which was probably due to the differences in the dimensionality of graphene and CNT. As expected, a 2-dimensional graphene sheet has a better contact region and larger exposed area for Pt loading than CNT. Since graphene is a flat sheet with an open structure, enabling the utilization
of both sides of graphene unlike CNT, which is a 1-dimensional rolled-up form of graphene. Similar results were observed in methanol electro-oxidation, which was performed in nitrogen-saturated 0.1 M sulfuric acid containing 0.05 M CH$_3$OH at a scan rate of 50 mV/s, as shown in Figure 4(d), (e). As the Pt mass ratio increased, higher methanol oxidation peaks occurred for both Pt/G and Pt/CNT. Figure 4(d), (e) present onset potentials for methanol oxidation on Pt/G of 92, 107 and 122 mV (vs. Ag/AgCl) at 50, 100 and 200 µg of Pt, respectively. Onset potentials of Pt/CNT were 107, 122 and 147 mV (vs. Ag/AgCl) at 50, 100 and 200 µg of Pt, respectively. The onset potential of Pt/G, which is related to electron transfer, was lower than that of Pt/CNT films, indicating that Pt NPs with graphene have better catalytic activity. The better electrical contact between Pt NPs and graphene might allow the better electron transfer from the reactant to the Pt/G composites. Panel F summarizes the oxidation current density versus Pt NP loading. Regardless of the Pt NP loading range, the Pt/G showed higher current density than the analogous Pt/CNT at a given mass of Pt loading. Obviously, the 2-dimensional graphene shows the better dispersion of Pt NPs in its matrix than the 1-dimensional CNT because there is lower possibility to be entangled with graphene. We compared charge density loss of Pt$_{200}$G$_{16}$ and Pt$_{200}$ NP films to determine the stability of Pt/G in 0.1 M H$_2$SO$_4$ at a scan rate of 50 mV/s, as shown in Figure 5. To clean and remove residual reagent from the Pt surface, cycling was performed 100 times at a scan rate of 500 mV/s. Compared to pure Pt films, charge density of Pt/G films remained almost constant after 1000 cycles (Figure 5(a)).
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Charge densities of 100th cycles are 518 μC/cm², 334 μC/ cm² for Pt/G, Pt film, respectively. After 700 cycles, charge density of pure Pt film was almost saturated and composite of Pt film was torn-out. After 1000 cycles, charge densities have decreased to 391 μC/cm² and 33 μC/cm² for Pt/G, Pt respectively. Figure 5(b), (c) show the enlargement of CV profiles in hydrogen desorption area for pure Pt film and Pt/G. Decrease of hydrogen desorption area in Pt is larger than spherical shape is under investigation and will be reported in near future.

The resulting composite materials showed the characteristic CV profiles of Pt NPs (panel C). The detailed comparison of electrocatalytic activity of Pt NPs on graphene other than spherical is lower possibility to be entangled with graphene. Furthermore, the suggested synthetic scheme allows the facile control of Pt NPs loading on graphene. Not only spherical NPs, but also various shapes of NPs can be immobilized on graphene without size or shape changes. Therefore, we believe that our synthetic route will provide a guided method to synthesize composite materials as electrocatalysts.

Acknowledgments. This work was supported by the National Research Foundation of Korea (National Leading Research Lab: 2012R1A2A1A03670370) and by the Human Resources Development program (No. 20124010203270) of the Korea Institute of Energy Technology Evaluation and Planning (KETEP) grant funded by the Korea government Ministry of Trade, Industry and Energy. This research was supported by Basic Science Research Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Education (2012R1A6A1040282).

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