

NaBH₄ 화학적 처리를 통한 백금화 카본 전극의 촉매반응 향상

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Enhanced Electrocatalytic Activity of Platinized Carbon Electrode via NaBH₄ Treatment

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Abstract

The effect of a chemical pretreatment on the surface carbon was investigated using a scanning electron microscope (SEM) and electrochemical methods. Primitive carbon has a reducing power likely due to incompletely oxidized functional groups on the surface. We aim to control this reducing power by chemical treatment and apply for the spontaneous deposition of nanoparticles (NPs). Highly ordered pyrolytic graphite (HOPG) was initially treated with a reducing agent, NaBH₄ or an oxidizing agent, KMnO₄, for 5 min. Subsequently, the pretreated carbon was immersed in a platinum (Pt) precursor. Unexpectedly, SEM images showed that the reducing agent increased spontaneous PtNPs deposition while the oxidizing agent decreased Pt loading more as compared to that of using bare carbon. However, the amount of Pt on the carbon obviously decreased by NaBH₄ treatment for 50 min. Secondly, spontaneous reduction on pretreated glassy carbon (GC) was investigated using the catalytic hydrogen evolution reaction (HER). GC electrode treated with NaBH₄ for a short and long time showed small (onset potential: -640 mV vs. MSE) and large overpotential for the HER, respectively. Although the mechanism is unclear, the electrochemistry results correspond to the optical data. As a proof-of-concept, these results demonstrate that chemical treatments can be used to design the shapes and amounts of deposited catalytic metal on carbon by controlling the surface state.

Keywords: Chemical treatment, Spontaneous reduction, Catalytic reaction

1. 서 론

Platinum (Pt) nanomaterials on carbon supporters have drawn considerable amounts of attention in various fields, including electrochemical sensors, fuel cells, and hydrogen production by water splitting[1-3]. Several previous approaches have been utilized to modify inert carbon electrodes with active platinum for specific redox reactions. First, colloidal Pt nanoparticles synthesized by wet chemistry were attached onto the surface of an inert carbon supporter by physisorption/chemisorption. This approach has been widely used to characterize the activity of synthesized nanomaterials. Organic species of either surfactants or linkers, however, may influence the surface-sensitive electrocatalytic activity[4]. Second, the direct electroplating/electroless deposition of Pt onto carbon electrodes has been conducted. Compared to the adsorption of pre-synthesized nanoparticles, this generates surfactant/

linker-free nanoparticles on the carbon electrodes[5,6]. Meanwhile, control of the size, shape and loading amount is cumbersome, though the pulsed electroplating technique reportedly can be used to fabricate nanowires[7]. Finally, Pt nanomaterials were formed spontaneously by simply dipping a carbon electrode into a solution containing Pt precursors[8]. This process can be realized by the reducing functional groups on the carbon electrode, such as carbonyl groups, indicating a surface-terminated reaction. In addition, defects on carbon electrodes, such as step edges and kinks, appear to affect the formation of nanoparticles because they act as nuclei for crystallization during the formation of solid particles[7,9]. Thus, this process is very sensitive to the surface state of the carbon electrode.

Highly ordered pyrolytic graphite (HOPG) provides a well-defined surface of the graphitic carbon allotrope. The surface functionality, structure of defects, and termination of defects of HOPG influence the spontaneous metal deposition on the HOPG[7]. Previously, Pt was spontaneously deposited preferentially onto edge defects of HOPG with irregular agglomerates[9-11]. Microparticles on both the terrace and edge were observed at longer immersion times. This trend indicates that the nucleation of the Pt seed begins at defects, followed by further

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growth to microparticles. In contrast to HOPG, glassy carbon (GC) is popular as a de facto working electrode in electrochemistry due to its low cost, good compatibility, high conductivity, simple pretreatment process, and inertness to chemical environments. Inspired by the spontaneous deposition of Pt on HOPG, the formation of Pt nanomaterials on GC was also investigated[8]. Polydisperse Pt nanoparticles were formed randomly on the entire surface of GC compared to the preferential generation of Pt at the edge sites on HOPG. At longer immersion times, dendritic Pt microstructures were observed[8]. The electrochemical response of Pt-modified GC shows the similar activity for the hydrogen evolution reaction (HER). These investigations of the spontaneous formation of Pt demonstrate the critical role of the surface state of the carbon electrode, whereas control of the surface state has not yet been reported to the best of our knowledge.

Herein, we report the spontaneous platinization of glassy carbon with a controlled size and loading level via a chemical pretreatment. Both HOPG and GC were pretreated with either a strong oxidizing agent (potassium permanganate, KMnO_4) or a reducing agent (sodium borohydride, NaBH_4) followed by immersion into a Pt-plating solution. The morphology of the deposited Pt on HOPG was investigated and the electrochemical behavior of the modified GC was confirmed through the HER. The results show that the chemical pretreatment provide a means by which to control the surface state of the carbon electrode to create desired shapes and loading amounts of PtNPs for better electrocatalysis. Namely, this method using oxidizing/reducing agents, which are frequently used for formation of graphene oxide[12], can simply modify reactivity of functional groups on the carbon surface without anodic current or acidic pretreatment[9,13].

2. 실험

2.1. Materials

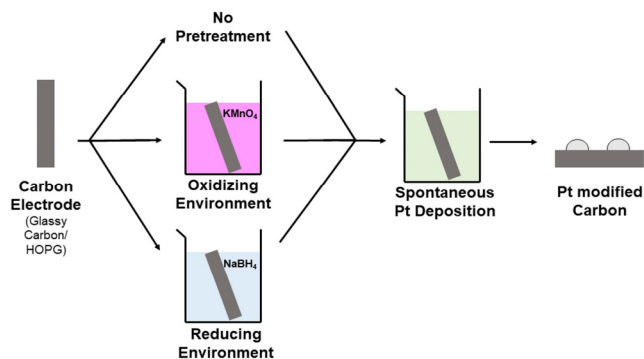
The 98% sodium borohydride (452882, NaBH_4), 99.99% potassium hexachloroplatinate(IV) (379589, K_2PtCl_6), 99.999% sulfuric acid (339741, H_2SO_4) were purchased from Sigma Aldrich. The 99.99% potassium permanganate (P1066, KMnO_4) was purchased from Samchun.

2.2. Scanning electron microscope (SEM) imaging

The Pt microstructures on the substrate were investigated with Inspect F50 SEM (FEI). The SPI-3 HOPG (SPI Supplies[®]) was used as a substrate for spontaneous platinization in that it can be easily held on the SEM. First, the outermost HOPG was exfoliated with a scotch tape for exposing a fresh plane. Second, the fresh plane of HOPG was treated with 10 mM NaBH_4 or KMnO_4 for 5 min and subsequently washing with ultrapure water. Third, a 10 mM K_2PtCl_6 aqueous solution was dropped on the pre-treated HOPG and maintained for 10 min. After washing with water, surface structure was studied by the SEM.

2.3. Electrochemistry

The cyclic voltammetry (CV) was obtained with a CHI 900B Potentiostat (CH Instruments Inc., Austin, TX) and three-electrode systems. The glassy carbon electrode (GC, 3 mm diameter, BASi), a Pt wire,



Scheme 1. Illustration of spontaneous Pt modification on the carbon electrodes with or without a chemical pretreatment.

and a mercury-mercurous sulfate electrode (MSE, sat'd K_2SO_4) were used as a working electrode, a counter electrode, and a reference electrode, respectively. The GC electrode was polished with 15, 6, 3, and 1 μm diamond powder on a polishing pad. After that, washing and sonication with water were performed. The GC electrode was chemically treated with 10 mM NaBH_4 for 5 min or 50 min, and then washed with water. A pre-treated electrode was immersed in the 10 mM K_2PtCl_6 aqueous solution for 10 min, and subsequently washing. The HER performance depending on treatment time was checked in 0.5 M H_2SO_4 electrolyte purged with Argon for 20 min. A Pt disk electrode (1.6 mm diameter, BASi) was used as a control experiment for HER. Scan rate was 100 mV/s.

3. 결과 및 고찰

Scheme 1 illustrated the procedure for spontaneous Pt formation on the carbon electrodes in the absence or presence of chemical pretreatment. Spontaneous reduction of Pt precursor requires the reducing agent existed on the surface of carbon as an oxidized functional group such as carbonyl group. These functional groups may have various oxidation number so that the control of both dispersion and coverage of the Pt is difficult. In order to adjust the number and the oxidation state of reducing functional groups, chemical pretreatment of either oxidizing or reducing environment is applied respectively. For oxidizing functional groups, KMnO_4 served as an oxidizing agent, which increase the coverage of reducing functional groups. The higher coverage of Pt was expected due to the more reducing power on the surface. On the other hand, the treatment of NaBH_4 can reduce the reducing function groups. The decrease/elimination of reducing groups on the surface may dramatically decrease the spontaneous Pt deposition. After spontaneous deposition of Pt in the solution containing Pt precursor, Pt modified carbon electrode was characterized. A bare carbon electrode without any chemical pretreatment acts as a control experiment.

The HOPG served as a substrate to investigate the morphology of spontaneous Pt deposition after chemical pretreatment shown in Figure 1. In the absence of any chemical pretreatment, Pt particles were randomly form over entire HOPG surface and the distribution of size was ranging from hundreds of nanometer to a few micrometer shown in

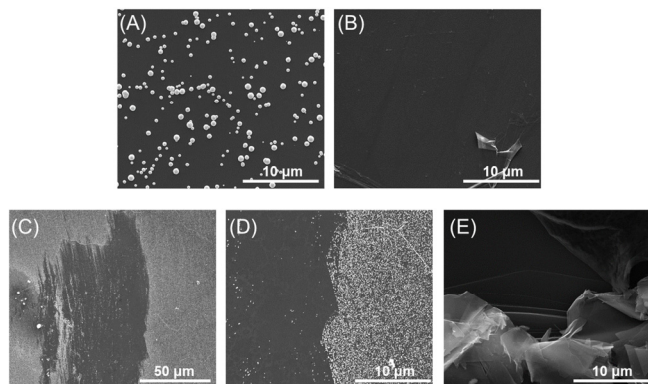


Figure 1. SEM images of the spontaneous Pt deposition on HOPG (A) without a chemical pretreatment, (B) with KMnO₄ for five minutes, and (C) and (D) with NaBH₄ for five minutes. A scratch during the mounting process served as a marker in (C) and (D). (E) HOPG surface treated with NaBH₄ for 50 minutes.

Figure 1(A), which is consistent with previous report at the similar deposition time[9,11]. At our experiment condition, preferential deposition of Pt was not observed. Pt particles generates random agglomerates entire surface. To adjust the number and the oxidation state of functional groups, HOPG was treated in KMnO₄ solution for 5 minutes before spontaneous Pt deposition. SEM image in Figure 1(B) shows the unexpected disappearance of spontaneous Pt deposition. Compared with Figure 1(A), the amount of Pt particles were negligibly small. Meanwhile, the pretreatment by reducing agent of NaBH₄ dramatically change the morphology of spontaneous Pt deposition. Figure 1(C) shows the higher coverage of smaller nanoparticles in contrast to Figure 1(A). Relatively monodisperse Pt nanoparticles with ca. 80 nm exists over entire HOPG surface as shown in Figure 1(D). These results were against a fact that the decrease of functional group will weaken the Pt deposition. Commonly, reducing functional groups for spontaneous Pt deposition will be generated by oxidizing agent and be consumed by reducing agent. Previously, NaBH₄ pretreatment on Au nanoparticle reduce Pt and Pd on Au surface[14,15]. They suggested the hydrogen formed by NaBH₄ served as a reducing agent. Although the detailed study on the mechanism is out of scope, similar hydrogen adsorption on carbon materials may change the morphology of spontaneous Pt deposition. When the time for pretreatment increased from 5 minutes to 50 minutes, Pt deposition does not occur in Figure 1E. We speculate that hydrogen on the surface at short treatment reduces Pt precursor while HOPG lost the reducing power by the reduction of reducing agent at longer treatment.

The electrochemical response for HER on Pt-modified carbon electrode was investigated by cyclic voltammetry (CV). Conventional glassy carbon served as a working electrode in order to confirm the similar trend observed in SEM images of HOPG. Figure 2(A) shows the well-known behavior of Pt. In cathodic region, two hydrogen underpotential deposition (UPD) followed by hydrogen evolution of split water were observed while the formation/reduction of platinum oxide was shown in anodic region. Mercury sulfate electrode (MSE) served as a reference electrode to prevent the effect of chloride anion for HER

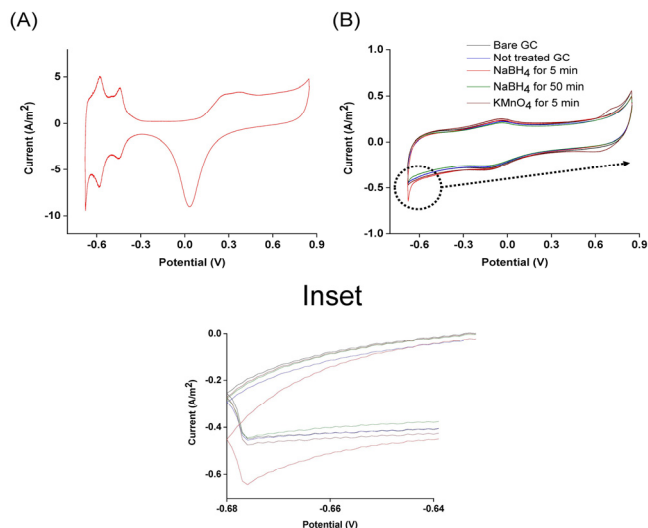
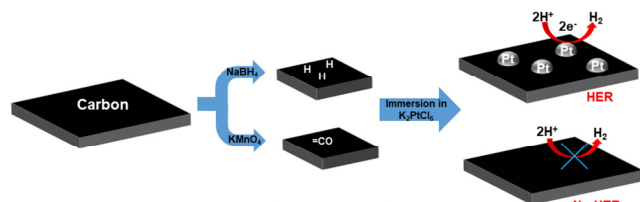


Figure 2. CVs of (A) a Pt disk electrode and (B) a Pt-modified glassy carbon electrode with different pretreatments in 0.5 M H₂SO₄ electrolyte. The “bare GC (black)” sample was not treated with a chemical agent and a Pt precursor. The “Not treated GC (Blue)” sample was immersed only in the Pt precursor for 10 min without a chemical treatment. Both the red and green ones were immersed in a Pt solution after a NaBH₄ treatment. The brown one was immersed in a Pt solution after a KMnO₄ treatment. Scan rate: 100 mV/s.

and HER evolution starts at ca. -640 mV which is in good accordance with MSE vs. NHE. CVs on Pt-modified GC with different pretreatment were shown in Figure 2(B). Bare GC demonstrated the background current without hydrogen evolution reaction. After Pt was spontaneously deposited on bare GC without any pretreatment, CV changed slightly in anodic region but the activity for HER was still very low probably due to the very low coverage and large particle size. The platinized GC with a short NaBH₄ pretreatment, however, demonstrates the dramatic increase in HER activity indicated by the same onset potential (ca. -640 mV) to bare Pt electrode. In spite of high activity for HER, the features for the formation/reduction of platinum oxide were not obvious in this case. Small size of Pt may enhance the activity for HER even with small coverage. At longer pretreatment time with NaBH₄, HER activity disappeared completely. As shown in Figure 1E, HOPG lost its reducing power for Pt deposition at longer pretreatment with NaBH₄. Similarly, GC electrode do not have Pt particles after longer pretreatment of NaBH₄, resulting in no activity for HER. Compared with native GC, the surface state of GC itself seems to be changed in charging current of CV probably because of complete reduction of surface functional groups. The platinized GC with a short KMnO₄ treatment represents a low HER activity, corresponding to Figure 1(B). In addition, the redox peak in anodic region appears at around +600 mV. We speculate that the defects or functional groups on the carbon electrode is generated by chemical oxidation which are labile for oxidation than carbon on basal plane. As a summary, pretreatment of carbon materials with NaBH₄ with proper time induces the surface hydrogen while that with KMnO₄ oxidizes carbonyl functional groups. The former acts as the reducing agent and the latter cannot oxidized to higher



Scheme 2. Illustration of the effect of chemical pretreatment on the spontaneous Pt modification on the carbon electrodes and electrocatalytic activity for HER.

oxidation state in the subsequent immersion in the solution containing Pt precursor. The chemical pretreatment provide the successful way to control the size and coverage of spontaneous Pt deposition probably via surface hydrogen or prevent the spontaneous deposition of Pt by elimination of oxidizable functional group.

4. 결 론

We reported the spontaneous platinization of the carbon electrodes with controlled sizes and loading levels via a chemical pretreatment. Both HOPG and GC were pretreated with either a strong oxidizing agent (KMnO_4) or a reducing agent (NaBH_4) followed by immersion into a Pt precursor. The morphology of the deposited Pt on HOPG was investigated using SEM. The bare HOPG showed random Pt agglomerates on the entire surface, not at specific sites. Unexpectedly, the pretreatment of NaBH_4 or KMnO_4 for a short time led to relatively high coverage of monodisperse Pt particles or the disappearance of the spontaneous Pt deposition, respectively. Spontaneous Pt deposition on HOPG did not occur in the case of the long-term NaBH_4 treatment. The electrochemical behavior of the Pt-modified GC was investigated through the HER with a Pt catalyst. A bare GC showed background current without the HER current. After spontaneous Pt deposition without any chemical treatment, the CV changed slightly in the anodic region but the overpotential for the HER was still very high. Platinized GC after a NaBH_4 treatment for a short time demonstrated a dramatic increase in the HER activity. However, Platinized GC after a long-term treatment did not show HER activity. These results demonstrate that chemical treatments can be used to design the shapes and amounts of deposited Pt by controlling the surface state of carbon.

감 사

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