Covalent Hybridization of Thiolated Graphene Sheet and Platinum Nanoparticles for Electrocatalytic Oxygen Reduction Reaction

Mohammad Shamsuddin Ahmed, Daekun Kim, Hyoung Soon Han, Haesang Jeong, and Seungwon Jeon*

Department of Chemistry and Institute of Basic Science, Chonnam National University, Gwangju 500-757, Korea

A covalently bonded thiolated graphene sheet-supported platinum electrocatalyst (GOS–Pt) has synthesized for electrochemical oxygen reduction reaction (ORR) in neutral media. The catalyst's structural features are characterized by transmission electron microscopy (TEM), energy dispersive X-ray (EDX), and X-ray photoelectron spectroscopy (XPS). Its activity towards the ORR has investigated by using cyclic voltammetry (CV), rotating disk electrode (RDE), and rotating ring disk electrode (RRDE) in 0.1 mol l\(^{-1}\) phosphate buffer solution (PBS) at pH 7, which is also used to assess the catalyst's kinetic parameters. On a glassy carbon electrode (GCE), the catalyst shows a significant catalytic activity, with its electrocatalysis of O\(_2\) reduction occurring via four-electron transfer reduction to H\(_2\)O with minimal generation of H\(_2\)O\(_2\).

Keywords: Covalent Bonding, Electrocatalyst, Oxygen Reduction Reaction, Thiolated Graphene Sheet, Phosphate Buffer Solution.

1. INTRODUCTION

Highly active catalysts for oxygen reduction reaction (ORR) in proton exchange membrane fuel cells (PEMFCs) is one of the great challenges in the field of electrochemical energy storage and conversion.\(^1\)\(^-\)\(^3\) Highly active Pt catalysts have used for many types of industrial reactions such as fuel cell reactions, CO oxidation in a catalytic converter, nitric acid production, and petroleum cracking, etc.\(^4\)\(^-\)\(^6\)

Graphene sheet is a two-dimensional flat lattice consisting of monolayers of carbon atoms in closely packed honeycombs. Since its discovery in 2004 by Geim et al.\(^7\) its excellent physical and chemical properties, such as high electrical conductivity,\(^8\)\(^,\)\(^9\) high surface area,\(^10\)\(^,\)\(^11\) and large amounts of edge-planes,\(^12\) have been explored for various electrochemical applications. Graphene sheet has been used in synthesizing nanocomposites\(^13\)\(^-\)\(^16\) and fabricating various microelectrical devices, such as cells,\(^17\) field-effect transistors,\(^18\) ultrasensitive sensors\(^19\) and electromechanical resonators\(^20\) due to its unique nanostructure and properties. Well separated, flat graphene sheets tend to form irreversible agglomerates or even restack to form graphite through strong π–π stacking and van der Waals interactions.\(^21\) Preventing aggregation is important because graphene’s most useful properties are strongly related to the individual sheets and has been achieved through it’s covalent modification.\(^22\)\(^-\)\(^24\)

Various noble metal nanoparticles (NPs) have been used to catalyze oxygen reduction reaction (ORR), such as platinum (Pt)\(^25\) palladium\(^26\) and gold,\(^27\) with Pt being the most popular and effective electrocatalyst for both the anode and the cathode reactions in fuel cells.\(^3\)\(^,\)\(^28\) Pt\(^25\) Pt based alloys\(^13\) and bimetallic, Pt–M\(^15\) are the most widely used and studied electrocatalysts, with there being numerous studies of the catalysis the ORR by graphene-based Pt.\(^13\)\(^,\)\(^15\)\(^,\)\(^25\)

The medium’s pH and the electrode’s composition affect the mechanism of O\(_2\) reduction. Catalysis using graphene sheet and graphene-based materials in acid and alkaline media have been reported,\(^13\)\(^,\)\(^15\)\(^,\)\(^25\) although both acid and alkali can be corrosive. Much less research has focused on catalysis in neutral media, such as phosphate buffer solution (PBS)\(^16\) or NaCl solution,\(^29\) possibly because of the poor catalytic onset potential and low current density.

Rotating ring disk electrodes (RRDE),\(^26\) has been developed for measuring the amount of H\(_2\)O\(_2\). This technique involves H\(_2\)O\(_2\) generated at the generator electrode being carried towards the detector electrode by forced convection.
This work reports the chemical synthesis of covalently bonded thiolated graphene oxide (GOS) based Pt NPs (GOS–Pt) catalysts supported on GCEs and their use in 0.1 mol \( \text{L}^{-1} \) PBS. ORR was characterized using cyclic voltammetry (CV), rotating disk electrode (RDE), and RRDE. The GOS–Pt was characterized by transmission electron microscopy (TEM), energy dispersive X-ray (EDX) and X-ray photoelectron spectroscopy (XPS). Its electrochemical behavior, transferred electron number \( (n) \) during oxygen reduction was analyzed using RRDE. The modified electrodes’ kinetic and electrocatalytic activities towards the ORR were also analyzed through Koutecky–Levich and Tafel plots.

2. EXPERIMENTAL DETAILS

2.1. Instruments

A three-electrode potentiostat [CHI 700C electrochemical workstation (USA)] in a grounded Faraday cage was used for voltammetric measurements. Platinum wire, auxiliary electrode, and a calibrated Ag/AgCl electrode from Bioanalytical Systems Inc. (BAS) in 3.0 M NaCl solution for voltammetric measurements. Platinum wire auxiliary electrode and a calibrated Ag/AgCl electrode from Bioanalytical Systems Inc. (BAS) in 3.0 M NaCl solution. An EG and GPARC Model 636 RRDE system and a CHI 700C electrochemical workstation bipotentiostat were used for hydrodynamic voltammetry. TEM and EDX were undertaken on a TECNAI model FI-20 (FEI, Netherlands). XPS was carried out using a Multilab 2000 (Thermo Electron Corporation, England) with a 14.9 keV Al Kα X-ray source.

2.2. Chemicals

Graphite Powder-325 mesh, NaSH, \( \text{H}_2\text{PtCl}_6 \), \( \text{NaBH}_4 \), and tetrahydrofuran (THF) were from Aldrich. \( \text{H}_2\text{SO}_4 \) and \( \text{H}_3\text{PO}_4 \) were from DC Chemical Co. Ltd. (Korea) and were used as received. All other reagents were of analytical grade. High-purity argon and \( \text{O}_2 \) were used for (30 min purging) deaeration. Doubly distilled water (DW) was used to prepare all aqueous solutions. Aqueous 0.1 mol \( \text{L}^{-1} \) \( \text{Na}_2\text{S}_2\text{O}_3 \cdot 2\text{H}_2\text{O} \) PBS was used as the supporting electrolyte. The pH of PBS (pH 7.0) was adjusted with 0.1 M \( \text{H}_3\text{PO}_4 \) and 0.1 M NaOH.

2.3. Preparation of GOS–Pt

Graphene oxide (GO) was obtained by oxidizing graphite using improved Hummers method.\(^{30} \) Briefly, the mixture of concentrated \( \text{H}_2\text{SO}_4/\text{H}_3\text{PO}_4 \) (9:1) was added to a mixture of graphite/KMnO\(_4\) (1:6) at 50 °C and stirred for 12 h. The reaction was cooled to RT and transferred onto ice with 30% \( \text{H}_2\text{O}_2 \). The obtained solution was centrifuged, and then filtered. The solid material was then washed with water, and finally washed with 30% HCl.

Thiolated graphene oxide (GOS) was obtained by thiolation to GO.\(^{31} \) A 30 mg of GO powder was dispersed into 50 mL of water with 10 min ultrasound, then 5 mmol of \( \text{Na}_2\text{S} \cdot 9\text{H}_2\text{O} \) was added to the aqueous solution under stirring. The mixture was then heated at 95 °C under stirring for 3 h. After that, it was filtrated, and the obtained solid was washed with deionized water for several times. The as-prepared GOS was vacuum-dried at 40 °C for 24 h.

30 mg GOS in 30 mL DW, 28 mg \( \text{H}_2\text{PtCl}_6 \) in 9 mL DW and 4 mL of 0.1% \( \text{NaBH}_4 \) were mixed together by continuous stirring for 24 h at 55 °C after 40 min ultrasonication to anchor Pt\(^{0} \) to the sulfur on GOS by covalent bonding. The final product GOS–Pt was washed three times with DW by vacuum-filtration (pore size 0.23 μm) after 20 min ultrasonication, and dried in a vacuum oven at 40 °C over night. To obtain an unfunctionalized GOS (mix-GOS/Pt), the above procedure (after thiolation) was adopted in the room temperature. It is only characterized by the electrochemical methods.

2.4. Preparation of Working Electrodes

RRDEs consisting of a GC disk and a Pt ring sealed in a polytetrafluoroethylene holder were polished with 0.05 μm alumina suspension on a polishing cloth (BAS, USA). After being polished to mirror surfaces, they were electropolished in aqueous 10% HCl at 1 mA cm\(^{-2} \) for 30 min to remove any Pt contamination. The solution was then replaced with 0.1 mol \( \text{L}^{-1} \) \( \text{H}_2\text{SO}_4 \); to evolved hydrogen at both the ring and the disk electrodes for 1 min. The ring collection efficiency \( (N = 0.18) \) was determined using ferrocene solution.

After cleaning, 2.0 mg GOS–Pt was dispersed in 1 mL DW to generate black solution, which was homogenized by ultrasonication for 60 min. A two 16 μL black solution (total Pt loading 5 × 10\(^{-5} \) g cm\(^{-2} \)) was casted onto GCE surfaces and the solvent was allowed to evaporate at RT. Electrochemical measurements of the electrocatalytic reduction of \( \text{O}_2 \) using the GOS–Pt modified electrodes were conducted in Ar and \( \text{O}_2 \)-saturated 0.1 mol \( \text{L}^{-1} \) PBS. To investigate the effect of the covalent bond between Pt NPs and GOS, mix-GOS/Pt was also casted onto GCE in the same protocol.

3. RESULTS AND DISCUSSION

3.1. Catalyst Characterization

3.1.1. Morphology of GOS–Pt Catalyst

The GOS supported Pt catalyst was characterized first by TEM (Fig. 1). The TEM images (Fig. 1(a)) illustrates a highly dispersed and remarkably uniform Pt on GOS.
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Fig. 1. The TEM image (a) and HRTEM image (b), Pt NPs size distribution with Gaussian curve and EDX spectrum (1(a) inset) for GOS–Pt synthesized catalyst.

All Pt NPs were considered to be spherical; the size distribution was uniform as well as a high surface coverage onto GOS. High-magnification (Fig. 1(b)) demonstrates that Pt NPs were set successfully onto GOS surface and the crystalline structure can be seen. The Pt lattice lines have shown clearly and the d-spacing between two lines is calculated as 0.22 nm. The Pt NPs particle size distribution obtained from 200 Pt spots. The histogram was fitted with a curve of a Gaussian shape to obtain the particle size distribution (Fig. 1(a) inset). The nanoparticles possess an average diameter of 4.7 nm. The GOS–Pt’s EDX spectra show signals from C, Pt and Cu (Fig. 1(a) inset) clearly reveals the presence of Pt besides the presence of Cu (due to the TEM Cu grid). The EDX spectrum reveals the GOS contains only Pt NPs.

3.1.2. FT-IR Spectra Analysis

The reduction of GO and concomitant functionalization of the resultant GOS–Pt with GO and GOS were followed by FT-IR spectroscopic measurements. As shown in Figure 2, the FTIR spectrum of GO shows a strong peak at around 1631 cm⁻¹ attributable to aromatic C=C, along with peaks characteristic of C=O stretching (1730 cm⁻¹), and epoxy (1224 cm⁻¹). The reduction of GO to GOS is evidenced by the dramatic decrease in peak intensity at 1730, and 1224 cm⁻¹. Meanwhile, functionalization of GOS with Pt is reflected by the positive shifting of the peak at around 1033 cm⁻¹ to 1045 cm⁻¹ attributable to the GOS–Pt bond.

3.1.3. XPS Study

Details of the chemical changes during the thiolation of GO and addition of Pt NPs were further elucidated by XPS measurements. Figure 3(a) shows XPS survey spectra for GO, GOS, and GOS–Pt. As can be seen, a tiny S2p peak was observed upon thiolation and the O/C atomic ratio significantly decreased upon the Na₂S reduction. Subsequent Pt NPs caused further decrease in the O/C atomic ratio due to using of NaBH₄ as reducing agent, which was accompanied by the appearance of Pt 4f peak. The high-resolution C 1s XPS spectra for GO, GOS, and GOS–Pt shown in Figure 3(b). Compared with GO and the GOS or GOS–Pt samples showed a strong suppression for the oxygen-containing components of their C 1s XPS spectra and also a new peak for C—S observed at 286.7 eV. C 1s XPS spectra of GOS and GOS–Pt can be fitted with different components of functional groups: (i) SP² (nonoxygenated carbon) at 285 eV, (ii) carbon in C—O at 286.2 eV, (iii) carbon in C—S at 286.7 eV, and (iv) carbonyl carbon 289.3 eV.

The two peaks were attributed to Pt⁰ at 71.65 eV (4f⁷/2) and 74.85 eV (4f⁵/2) (Fig. 3(c)). Figure 3(d) shows the S 2p XPS spectra of the GOS and GOS–Pt. While the peak at 162.6 eV for the GOS is attributable to the S, its positively shift to a higher binding energy (163.7 eV) in GOS–Pt probably due to the electron transfer from GOS...
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Fig. 3. XPS survey spectra (a) and C 1S core level spectra (b) for GOS–Pt catalyst with GOS and GO; the Pt 4f spectra for GOS–Pt (c) and S 2p for GOS–Pt and GOS (d).

These results indicate efficient reduction of the oxygen-containing functional groups in GO by Na₂S as well as a successful thiolation had done and the Pt NPs attached to the graphene sheet via covalent bonding. The total numerical results of XPS quantitative microanalysis of the GOS–Pt is calculated as, C At.% of 76.65, O At.% of 20.53, Pt At.% 2.82; and their corresponding Wt.% are 51.17, 18.26, and 30.58, respectively.

3.2. Electrocatalytic O₂ Reduction on GO, GOS and GOS–Pt/GCE

3.2.1. CV Study

The electrocatalytic properties of GO, GOS and GOS–Pt for ORR were tested using a GC electrode. Figure 4

Fig. 4. CVs on GO, GOS and GOS–Pt at 100 mV/s in O₂ saturated PBS pH 7 neutral solution.
shows the CV curves in O₂-saturated aqueous solution of 0.1 mol ⁻¹ PBS in the potential range 0.5 V to 0.0 V at scan rate 100 mVs⁻¹. The clear ORR peak current density is highest at the GOS–Pt than that of GO and GOS, little increased after thiolation when compared to GO. These results are clearly demonstrated a significant ORR electrocatalytic activity has done by the GOS–Pt in respect to the GO and GOS CV graphs in O₂-saturated 0.1 mol ⁻¹ PBS.

The peak currents increase linearly (correlation coefficient 0.999) with the square root of the scan rates at GOS–Pt [Fig. 4 inset]. Indicates the electrocatalytic processes were controlled by O₂ diffusion at the GOS–Pt modified electrode.⁳³

### 3.2.2. Hydrodynamic Voltammetry Study

To further investigate the ORR performance, we carried out the linear sweep voltammetry (LSV) measurements on a rotating disk electrode (RDE) for GOS–Pt in O₂-saturated 0.1 mol ⁻¹ PBS at a scan rate of 20 mVs⁻¹ and a various rotation rate. As can be seen in Figure 5(a), the ORR at the GOS–Pt modified electrode commence around 0.3 V (onset potential), followed by a continuous increase in the current density with increasing rotation speed. The strongest limiting diffusion current with a wide current plateau has observed for ORR at the GOS–Pt modified electrode, most probably, the combined effects of the covalent bonding and the Pt NPs are responsible for the high ORR electrocatalytic activity. Thus, these results should be sufficiently promising to warrant further research efforts in developing catalysts through intermolecular charge transfer via covalent bonding.

The transferred electron numbers per O₂ involved in the oxygen reduction at GOS–Pt electrode was determined by the Koutecky–Levich equation as given below⁴⁸

\[
\frac{1}{i} = \frac{1}{i_k} + \frac{1}{B \omega^{1/2}} \quad (1)
\]

\[
B = 0.62nFCD^2/\nu^{1/6} \quad (2)
\]

\[
i_k = nFAC \quad (3)
\]

where \(i\) is the measured current (µA), \(i_k\) is the kinetic current, \(n\) is the number of electron transfer, \(F\) is the Faraday constant, \(A\) is the geometric area of working electrode (cm²), \(D\) is the diffusion coefficient of O₂ (1.9 × 10⁻⁵ cm²/s), \(\omega\) is the rotation rate (rad/s), \(\nu\) is the kinetic viscosity of the solution (1 × 10⁻⁵ cm²/s), and \(C\) is the concentration of dissolved O₂ in solution (1.2 × 10⁻³ M). The Koutecky–Levich plots at −0.1, −0.2, −0.3, −0.4, −0.5 and −0.6 V show a linear dependence at all potentials in Figure 5(b). The solid lines are plotted from the plateau current. The linearity and the parallelism of these plots are usually represented first order kinetics with respect to O₂. The dependence of transferred electrons (\(n\)) on the cathodic potential calculated from Eq. (1). The electron number during ORR on GOS–Pt estimated at −0.4 V is found to be around 3.8. According to the \(n\) value of the reaction, four electrons were involved. Hence, the Pt NPs are the active site so that the electron charge is transferred from Pt NPs to graphene.⁴⁰

In addition, RRDE was used to evaluate the ORR performance of the bulk Pt, GOS–Pt and mix-GOS/Pt electrodes. Figure 6 shows the disk and ring current densities for the bulk Pt, GOS–Pt and mix-GOS/Pt electrodes in 0.1 mol ⁻¹ PBS. The ring currents were measured to estimate the amount of generated hydrogen peroxide (H₂O₂) ions. At the disk electrode: a low catalytic reduction peak at the mix-GOS/Pt modified electrode was obtained in PBS. The onset potential \(E_{onset}\) observed at 0.1 V (vs. Ag/AgCl). Nevertheless, a highest catalytic reduction peak for the GOS–Pt modified electrode was recorded in same solvent system. The \(E_{onset}\) can be seen at 0.35 V (vs. Ag/AgCl) with highest current density compared to bulk Pt electrode. This result unambiguously indicates that the GOS has an important effect on ORR catalysis enhancement of Pt NPs. It seems that the close contact between \(p\) orbital of graphene sheet and \(d\) orbital of Pt NPs facilitates graphene sheet’s \(p\)-electron polarization via a covalent bonding, making the Pt NPs surface more easily accessible for O₂ adsorption and activation. Since H₂O₂ detected at the ring electrode, the GOS–Pt in PBS shows a significantly lower current density than that of other ring electrodes; indicating that 0.1 mol ⁻¹ PBS is...
suitable solvent system for GOS–Pt for ORR electrocatalysis with minimal H2O2 production. The transferred electron per O2 molecule during ORR on bulk Pt, GOS–Pt and mix-GOS/Pt were estimated from the ring and disk currents at various potentials.

To verify the \( n \) value during O2 reduction, the following equations has applied\(^4\)

\[
n = 4\frac{i_d}{i_r + (i_r/N)}
\]

where \( i_r \) is the current at the ring electrode, \( i_d \) is the current at the disk electrode, and \( N \) is the RRDE collection efficiency. Ring currents corresponding to the formation of H2O2. Figure 7(a) shows the number of transferred electrons (calculated by Eq. (4)).

Nevertheless, when \( i_r \) is close to 0, indicating the transferred electron number can be 4 and the ratio of \( i_r/Ni_d \) is 1, the transferred electron number can be 2.\(^4\) Figure 7(b) exhibits the variation of the ratio \( i_r/Ni_d \) versus the disk electrode potentials. According to Figure 7(b), the ratio of the \( i_r/Ni_d \) values are close to 1 at the bulk Pt and GOS–Pt as well as mix-GOS/Pt adjacent to 0. This evaluation also suggests a four-electron pathway has done at GOS–Pt.

### 3.3. Tafel Behavior

To additionally analyze the kinetics of the ORR, Tafel behavior in the mixed kinetic-diffusion control region was also examined using the conventional method of constructing Tafel plots on bulk Pt, GOS–Pt, and mix-GOS/Pt modified electrodes. The Tafel plots obtained from the kinetic current, \( i_k \) region (Fig. 7(c)). Generally, the slope of \(-118 \text{ mV} \) observed for bulk Pt at high current intensity, indicates the first electron transfer rate-determining step. The calculated values of Tafel slopes have shown in Table I. The data indicated that the rate-determining step for O2 reduction was identical at GOS–Pt modified electrode because the intrinsic slope for O2 reduction was very close to \(-118 \text{ mV} \); indicating that the first electron exchange is the rate-determining step on GOS–Pt. Moreover, the difference of the Tafel slopes among the electrocatalysts indicates the reaction mechanism (such as, \( n \) value) is not same.\(^26\) According to the Table I, the specific activity (SA) of GOS–Pt is much higher than mix-GOS/Pt at the respective kinetic regions, indicated a small size of Pt NPs and well attached to GOS–Pt surface.\(^4\)}
4. CONCLUSIONS

In summary, we have synthesized graphene sheet Pt metal hybrid using thiolated graphene as a support via a covalent bonding. The GOS–Pt NPs show much enhanced catalytic activity for ORR in neutral media due to covalent grafting. The covalently bonded GOS–Pt has higher ORR activity than that of the bulk Pt in 0.1 mol l⁻¹ PBS solution with minimal production of H₂O₂. This work demonstrates that graphene sheet (via covalent bonding) is indeed a promising support to improve NPs' activity for ORR through four-electron reduction.

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References and Notes

Table I. First-order transport corrected current density, SA, Tafel slopes, and the range of potentials over which the Tafel plots were linear for the modified GCE electrodes.

<table>
<thead>
<tr>
<th>Name</th>
<th>Disk current density at −0.3 V (mA/cm²)</th>
<th>SA at 0.1 V (m²/cm²)</th>
<th>Slope (mV)</th>
<th>R²</th>
<th>Range, E/V</th>
</tr>
</thead>
<tbody>
<tr>
<td>GOS–Pt</td>
<td>2.13</td>
<td>1.30</td>
<td>−149</td>
<td>0.998</td>
<td>0.3 to 0.05</td>
</tr>
<tr>
<td>Bulk Pt</td>
<td>1.21</td>
<td>0.91</td>
<td>−119</td>
<td>0.999</td>
<td>0.25 to 0.1</td>
</tr>
<tr>
<td>mix-GOS/Pt</td>
<td>0.41</td>
<td>0.26</td>
<td>−222</td>
<td>0.995</td>
<td>0.05 to −0.1</td>
</tr>
</tbody>
</table>