Sulfonation of graphene nanosheet-supported platinum via a simple thermal-treatment toward its oxygen reduction activity in acid medium

Tai-Feng Hung a, Bei Wang b, Chi-Wen Tsai a, Meng-Hsiu Tu a, Guo-Xiu Wang b, Ru-Shi Liu a,*, Din Ping Tsai c, Man-Yin Lo d, Der-Shiuh Shyu e, Xue-Kun Xing e

a Department of Chemistry, National Taiwan University, Taipei 106, Taiwan
b School of Chemistry and Forensic Science, University of Technology Sydney, Sydney, NSW 2007, Australia
c Department of Physics, National Taiwan University, Taipei 106, Taiwan
d Material and Chemical Research Laboratories, Industrial Technology Research Institute, Hsinchu 300, Taiwan
e SYNergy ScienTech Corp., Science Tech-based Industrial Park, Hsinchu 300, Taiwan

Article info
Article history:
Received 15 May 2012
Received in revised form 5 July 2012
Accepted 6 July 2012
Available online 26 July 2012

Keywords:
Sulfonation
Graphene
Platinum catalyst
In situ chemical reaction
Thermal treatment
Oxygen reduction reaction

Abstract
The sulfonated graphene nanosheet-supported platinum (s-Pt/GNS) catalyst synthesized via a simple thermal-treatment in the presence of concentrated sulfuric acid was reported in this study. Influence of sulfonation on its structural, surface, morphological and catalytic characteristics of as-prepared s-Pt/GNS was explored using X-ray diffractometer, Raman spectrometry, zeta potential analyzer, scanning and transmission electron microscopes, and cyclic voltammetry. For the oxygen reduction reaction, the current density generated from the s-Pt/GNS at 0.6 V was approximately 32.5 A g⁻¹ Pt, which was about 193% higher than that of original Pt/GNS.

1. Introduction
Graphene, a single layer of carbon atoms densely packed into a benzene-ring structure, was experimentally isolated for the first time from highly oriented pyrolytic graphite in 2004 [1]. In comparison with other carbon allotropes, graphene offered not only great specific surface area but also excellent mechanical, optical, thermal and electronic properties [2]. Owing to its fascinating features, it had attracted tremendous attention in a wide range of fields, especially as an alternative support for synthesizing various metal/graphene nanosheet (M/GNS) hybrids [3–14]. Among those developed techniques [15], utilizing an in situ chemical reduction to produce the M/GNS was recommended because of the metal precursor and graphite oxide (GO) were able to simultaneously reduce by sodium borohydride (NaBH₄) or hydrazine (N₂H₄). Moreover, metal nanoparticles (NPs) thus formed were homogenously deposited onto the GNS via the bottom-up route [16].

Recently, GNS-supported platinum (Pt/GNS) catalyst with remarkably enhanced catalytic activity for oxygen reduction
reaction (ORR) had been demonstrated [3–9,12–14]. The improved ORR activity was attributable to the GNS possessed great specific surface area for uniform dispersion of Pt NPs and superior electrical conductivity for fast electron transportations as well. Although the Pt/GNS exhibited impressive catalytic activity as described above, protons generated at the anode were significantly restricted by the so-called triple-phase boundaries (TPBs), resulting in the lower cell performance. Several efforts had verified that sulfonated carbon supported Pt (s-Pt/C) catalyst not only showed much better catalytic activity than the pristine one but also required less Nafion content within the catalytic layer [17–22]. It was probably due to the fact that the s-Pt/C served as a mixed electronic and protonic conductor, efficiently minimizing the drawback resulted from the TPBs. Nevertheless, most of the previous studies were focused on carbon black [17–21] or carbon nanotube [22] supports.

Instead of complicated compounds [17,18,20,22] or polymers [19,21,22], an inexpensive sulfuric acid was chosen as the sources of sulfonic groups in this study. The sulfonated Pt/GNS (s-Pt/GNS) was synthesized via a simple thermal treatment under nitrogen atmosphere. The as-prepared s-Pt/GNS was characterized by X-ray diffractometer (XRD), Raman spectrometry, thermogravimetric analyzer (TGA) and zeta potential analyzer. Additionally, morphological observations were carried out using field-emission scanning electron microscopy (FESEM) and high-resolution transmission electron microscopy (HRTEM). To evaluate the electrochemically active surface area (S_{CA}) and ORR activity, the hydrogen adsorption–desorption curve and linear sweep voltammogram were measured from cyclic voltammetry (CV) and linear sweep voltammetry (LSV), respectively.

2. Experimental details

2.1. Chemicals

All reagents including natural graphite powder (SP-1, Bay Carbon), hydrogen hexachloroplatinate (IV) hexahydrate (H₂PtCl₆·6H₂O, extra pure grade, Showa Chemicals Co., Ltd.), sodium borohydride (NaBH₄, 98+, %, Acros Organics), absolute ethanol (C₂H₅OH, ACS reagent, Sigma–Aldrich), concentrated sulfuric acid (H₂SO₄, reagent grade, Showa chemicals Co., Ltd.) and Nafion® solution (DE 2020, Du Pont) were used as received. The deionized (DI) water produced from a Milli-Q SP ultrapure-water purification system (Nihon Millipore Ltd.) was adopted throughout the experiments.

2.2. Preparation of sulfonated graphene nanosheet-supported platinum (s-Pt-GNS) catalyst

Scheme 1 illustrated a typical procedure for synthesizing the sulfonated graphene nanosheet-supported platinum (s-Pt/GNS) catalyst from graphite. First of all, graphite oxide (GO) was prepared from natural graphite powder using a modified Hummers method [23]. Due to the hydroxyl and epoxy groups were chemically attached onto graphite surface, the hydrophilic GO was obtained after step (a) [13]. As shown in Fig. S1, the d-spacing (layer to layer distance) was increased from 0.343 nm for pristine graphite to 0.978 nm for GO, which was ascribed to the bonds forming by the van der waals’ interactions between each graphite layer were significantly weakened after reacting with strong oxidizers. This hydrophilic GO was then exfoliated in DI water to form a 2 mg mL⁻¹ of graphene oxide nanosheet (GONS) solution by an ultrasonic processor under the amplitude of 40% (S450D, Brandson Digital Sonifer) for 1 h. Following the step (b), 90 mL of GONS solution was thoroughly mixed with 35.3 mL of Pt precursor solution in a round-bottomed flask under magnetic stirring. The resulting solution was refluxed at 110 °C for 3 h while 6 mg mL⁻¹ of the freshly prepared NaBH₄ solution was added. The black suspension was filtered after being cooled down to room temperature, whereas the residue was repeatedly washed with excess DI water and C₂H₅OH. The powdered sample was dried in a vacuum oven at 60 °C for 24 h to ensure the solvent was completely removed. To yield the s-Pt/GNS, the as-obtained Pt/GNS was further treated with concentrated H₂SO₄ under a nitrogen atmosphere at 160 °C for 24 h in step (c). Likewise, sulfonic groups were expected to be grafted onto GNS as other carbon materials [24]. Again, the s-Pt/GNS thus prepared was rinsed and dried by the same procedures used for the Pt/GNS.

2.3. Characterizations

Crystal structures of the as-synthesized Pt/GNS catalysts were identified using an X-ray diffractometer (XRD, PANanalytical PW3040-60 X’Pert pro) with a copper target (λ = 1.541 Å) that was excited at 45 kV and 40 mA. The corresponding patterns were recorded from 10° to 80° at a scanning rate of 0.04° min⁻¹. Their grain sizes of Pt nanoparticles were estimated by calculating the width of the Pt (1 1 1) peak according to the Scherrer equation [24].

Raman spectra were collected on a Jobin Yvon LabRam 300 system using a 632.8 nm He–Ne laser with its intensity of 6 mW. The pixel resolution was about 3 cm⁻¹, whereas the peak resolution was about 15 cm⁻¹ for the silicon wafer. Thermogravimetric analysis (TGA, Q500, TA instrument) was conducted to determine the amounts of Pt loaded onto the Pt/GNS from room temperature to 800 °C with a heating rate of 10 °C min⁻¹ under air flow of 60 mL min⁻¹ [17]. Due to this analysis was carried out under the air atmosphere, it was reasonable to expect that the Pt NPs were the sole residue at 800 °C. As plotted in Fig. S2, Pt contents were about 10±1 wt. %, in which the standard deviation was based on the measurements of three samples.

Zeta potential was measured by a zetasizer analyzer (3000 HS, Malvern Instruments) to explore its surface property upon sulfonation. During the testing, the desired amount of catalyst was well-dispersed into DI water (pH = 5.3) under ultrasonication for 0.5 h. The well-suspended solution was slowly inlet into the electrophoresis cell, and the corresponding data was collected using its PCS software. The value was calculated with the standard deviations based on the measurements of three samples for each catalyst. For morphological observations, a field-emission scanning electron microscopy (FESEM, JSM-6700F, JEOL Ltd.) and a high-resolution transmission electron microscopy (HRTEM,
Philips Tecnai 20 microscope) equipped with an energy-dispersive X-ray (EDX) spectrometer were adopted.

2.4. Electrochemical measurements

The electrochemically active surface area \((S_{\text{EAS}})\) and oxygen reduction reaction (ORR) activity of each Pt catalyst were measured at room temperature by using a conventional three-electrode cell connected to an electrochemical analyzer (AUTOLAB PGST30, Eco Chemie). To prepare the catalyst ink, 2 mg of the powdered catalyst was homogenously dispersed in 5 mL of the 0.05 wt. % Nafion\(^{\oplus}\)/C\(_{210}\) solution by an ultrasonic processor \([14]\). The resulting suspension was carefully coated onto a glassy carbon (GC) electrode with a diameter of 5 mm (AFE3T050GC, PINE Instrument). The amounts of catalyst loaded onto each GC electrode were weighted by an analytic balance (XS204, Mettler-Toledo International Inc.) after the catalyst-coated GC electrode was completely dried. The Pt contents were then determined according to the composition of each catalyst ink and listed in inset of Fig. 5(a). The Pt crystal structures and grain sizes were not intrinsically affected after sulfonation in a high thermal-treating temperature \([24]\).

On the other hand, the weak and broad C (0 0 2) peak with a \(d\)-spacing of about 0.372 nm for Pt/GNS and 0.364 nm for s-Pt/GNS was detected in Fig. 1(a) and (b), respectively. These values were larger than that of pristine graphite (0.343 nm) as shown in Fig. S1(a). The increase in the \(d\)-spacing was attributed to the structural defects in some basal planes of the GNS \([26]\). However, we noticed a slight change in the shape and position of the C (0 0 2) peak for s-Pt/GNS in Fig. 1(b), implying that the crystallinity of GNS was different from that of the original Pt/GNS. This change in the crystallinity of the GNS upon sulfonation was further scrutinized by Raman spectroscopy.

Fig. 2 plotted their normalized Raman spectra of Pt/GNS and s-Pt/GNS catalysts. Two featured peaks corresponding to the D-band and the G-band were clearly appeared in both catalysts. The former was caused by the disorder of the graphite edges, whereas the latter was related with the in-

3. Results and discussion

3.1. XRD, Raman, TGA and zeta potential characterizations

Fig. 1 showed the XRD patterns of graphene nanosheet-supported platinum (Pt/GNS) and sulfonated Pt/GNS (s-Pt/GNS) catalysts. As can be seen, similar diffraction peaks assigned to (1 1 1), (2 0 0) and (2 2 0) planes of the face-centered cubic (fcc) Pt crystal (JCPDS 87–0646) were obviously observed for both catalysts in terms of peak position and intensity. These peaks were consistent with the results reported \([3–9,12–14,22,24,25]\), revealing that the Pt/GNS was successfully synthesized by an in situ chemical reduction. Most importantly, their Pt crystal structures and grain sizes were not intrinsically affected after sulfonation in a high thermal-treating temperature \([24]\).

On the other hand, the weak and broad C (0 0 2) peak with a \(d\)-spacing of about 0.372 nm for Pt/GNS and 0.364 nm for s-Pt/GNS was detected in Fig. 1(a) and (b), respectively. These values were larger than that of pristine graphite (0.343 nm) as shown in Fig. S1(a). The increase in the \(d\)-spacing was attributed to the structural defects in some basal planes of the GNS \([26]\). However, we noticed a slight change in the shape and position of the C (0 0 2) peak for s-Pt/GNS in Fig. 1(b), implying that the crystallinity of GNS was different from that of the original Pt/GNS. This change in the crystallinity of the GNS upon sulfonation was further scrutinized by Raman spectroscopy.

Fig. 2 plotted their normalized Raman spectra of Pt/GNS and s-Pt/GNS catalysts. Two featured peaks corresponding to the D-band and the G-band were clearly appeared in both catalysts. The former was caused by the disorder of the graphite edges, whereas the later was related with the in-

![](image1.png)

**Scheme 1** – Illustration of s-Pt/GNS synthesis from graphite: (a) modified Hummers method, (b) in situ chemical reduction and (c) sulfonation.

**Fig. 1** – XRD patterns of (a) Pt/GNS and (b) s-Pt/GNS. Inset is its corresponding grain size of each catalyst calculated from the Scherrer equation.
phase vibration of the graphite lattice [27,28]. It was noticed that the Pt/GNS showed a significantly higher $I_D/I_G$ ratio ($\approx 1.50$) than the pristine graphite ($\approx 0.21$) in Fig. S3. This difference was attributed to the formation of individual GNS and the fact that the deposited Pt NPs served as the spacers to separate the GNS [3], leading to a more disordered structure in the Pt/GNS as evidenced in Fig. 1(a). However, the $I_D/I_G$ ratio of ca. 1.36 for s-Pt/GNS was slightly lower than the value from the Pt/GNS ($\approx 1.50$), reflecting a less disordered structure in the s-Pt/GNS. This probably caused by re-arrangement of the orientation of each GNS, which was induced by grafted sulfonic groups. Consequently, the results observed herein would be responded to the change in the XRD result for s-Pt/GNS (Fig. 1(b)).

Their surface properties of Pt/GNS and s-Pt/GNS were examined by the zeta potential analyzer, and the results were discussed as follows. It was found that the surface potential for original Pt/GNS was 5\textdegree/C6 1 mV, implying that the hydroxyl and epoxy groups grafted onto GO were successfully eliminated from the in situ chemical reduction. On the contrary, the value obtained for s-Pt/GNS was significantly shifted to $-54 \pm 3$ mV, which was ascribed to the dissociations of protons from sulfonic groups grafted onto the s-Pt/GNS. This result indicated that its surface property of Pt/GNS was obviously altered after sulfonation.

### 3.2. Morphological observations

FESEM micrographs of the original graphite and as-prepared graphite oxide (GO) were presented in Fig. S4. Following the chemical oxidation reaction, it was seen that the pristine graphite with flake-like morphologies (Fig. S4(a)) were transformed into the soft GO (Fig. S4(b)), meaning that the bonds forming by the van der waals’ interactions between each GNS were considerably weakened. Fig. 3(a) showed FESEM images of the Pt/GNS that was synthesized by an in situ chemical reduction of graphene oxide nanosheet (GONS) and Pt cations. The GNS exhibited a flower-like morphology, in which differed from the pristine graphite or the GO. Each GNS was formed by reduction of the GONS, whereas Pt NPs functioned as the spacers to separate the GNS, making the Pt/GNS with more flexible morphology. This result consisted with the XRD and Raman patterns illustrated in Figs. 1 and 2(a), respectively. Although the position and shape of the C (0 0 2) peak for s-Pt/GNS slightly changed upon sulfonation as shown in Fig. 1(b), the morphology in Fig. 3(b) was not significantly altered after sulfonation.

Fig. 4 displayed the HRTEM image and its selected area electron diffraction (SAED) pattern of the s-Pt/GNS. Flat GNS with wrinkles was identified in Fig. 4(a), revealing that GNS maintained its flexibility characteristic after sulfonation. Moreover, the magnified image in Fig. 4(b) demonstrated that the sizes of Pt NPs were smaller than 10 nm. The SAED pattern in the inset of Fig. 4(b) verified that s-Pt/GNS had a well-defined crystal structure, which was in a good agreement with the XRD pattern plotted in Fig. 1(b). In addition, the lattice-resolved TEM image in Fig. S5(a) indicated that the crystalline graphitic layers were in the (0 0 2) direction. The EDX spectrum in Fig. S5(b) revealed that the signals assigned to copper, Pt, sulfur, carbon and oxygen were detected, which were reflected from the copper grid and s-Pt/GNS, respectively. This finding confirmed that sulfonic groups were successfully grafted onto the s-Pt/GNS surface.

### 3.3. Electrochemical measurements

To investigate the influence of sulfonation on its catalytic activity of s-Pt/GNS, the electrochemically active surface area ($S_{\text{EAS}}$) and oxygen reduction reaction (ORR) activity were measured by cyclic voltammetry (CV) and linear sweep voltammetry (LSV), respectively. Fig. 5(a) presented the cyclic voltammogram (CV) for each catalyst recorded from $-0.2$ V to $0.2$ V.

---

**Fig. 2** — Normalized Raman spectra of (a) Pt/GNS and (b) s-Pt/GNS.

**Fig. 3** — FESEM micrographs of (a) Pt/GNS and (b) s-Pt/GNS, scale bar: 100 nm.

---

![Normalized Raman spectra of (a) Pt/GNS and (b) s-Pt/GNS.](image)

![FESEM micrographs of (a) Pt/GNS and (b) s-Pt/GNS, scale bar: 100 nm.](image)
1.2 V in N2-saturated 0.5 M H2SO4 solution. Their $S_{\text{EAS}}$ values were calculated with the recognized method based on the hydrogen adsorption–desorption curves by Eq. (1) [29,30]:

$$S_{\text{EAS}} = \frac{Q_H}{G \times 0.21}$$  \hspace{1cm} (1)

where $Q_H$ (mC) was the charge quantity calculated from integrated in CV for hydrogen adsorption–desorption, $G$ represented the loading of Pt metal (g m$^{-2}$) in the electrode, and 0.21 mC was the charge required to oxidize a monolayer of hydrogen on the Pt catalyst [29]. As listed in inset of Fig. 5(a), the $S_{\text{EAS}}$ value of s-Pt/GNS was calculated to be 42.7 m$^2$ g$^{-1}$, which was similar to the result reported elsewhere [5]. This value was about 24% and 53% higher than the Pt/GNS and 40 wt. % Pt/C, respectively.

Fig. 5(b) depicted the linear sweep voltammogram of each catalyst measured between 1.1 and 0.05 V in 0.5 M O2-rich H2SO4 solution. As indicated, the onset and half-wave potentials for s-Pt/GNS were 1.083 V and 0.734 V, respectively. These values were shifted to a more positive value as compared with Pt/GNS (1.078 V/0.687 V) and 40 wt. % Pt/C (1.039 V/0.543 V), implying that the ORR occurred easily in the presence of s-Pt/GNS. Furthermore, the Pt mass-normalized current density generated from s-Pt/GNS was 32,483 mA g$^{-1}$ Pt at 0.6 V, i.e., about 193% increase in the current density as compared with the original Pt/GNS (11,122 mA g$^{-1}$ Pt). The dramatic improvements in the electrochemical properties were attributed to the better compatibility of s-Pt/GNS in the Nafton solution as the inset of Fig. 5(b), because the sulfonic groups grafted onto the GNS surface [24]. Clearly, the presence of sulfonic groups greatly enhanced the active triple-phase boundaries [17–22].

4. Conclusions

This study reported a facile and cost-effective route to prepare an alternative sulfonated graphene nanosheet-supported platinum (s-Pt/GNS) catalyst with highly catalytic activity for the first time. XRD and Raman results indicated that sulfonation significantly changed the crystal structures of the GNS owing to the re-orientations of each GNS. Moreover, it also found that the surface property of s-Pt/GNS was noticeably altered as compared with the original Pt/GNS. The micrographs of FESEM and HRTEM clearly revealed that the sizes of Pt NPs were smaller than 10 nm and were well-distributed onto the GNS surface. Owing to its higher electrochemically active surface area, the s-Pt/GNS delivered remarkably enhanced catalytic activity for oxygen reduction reaction. As the results, the s-Pt/GNS thus prepared is anticipated to have potential application in fuel cell
because the triple-phase boundaries are able to efficiently minimize by the sulfonic groups grafted onto the s-Pt/GNS.

Acknowledgments

Financial support of the National Science Council of Taiwan (NSC 97-2113-M-002-012-MY3, 99-2811-M-002-093, 99-2120-M-002-012), the Ministry of Economic Affairs (101-EC-17-A-08-S1-183) and University of Technology, Sydney (UTS) is gratefully acknowledged. The help from the Precision Instrument Center at National Chiao Tung University in the HRTEM observation is also greatly appreciated.

Appendix A. Supplementary material

Supplementary material associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.ijhydene.2012.07.027.

REFERENCES


Appendix A. Supplementary material

Supplementary material associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.ijhydene.2012.07.027.

Acknowledgments

Financial support of the National Science Council of Taiwan (NSC 97-2113-M-002-012-MY3, 99-2811-M-002-093, 99-2120-M-002-012), the Ministry of Economic Affairs (101-EC-17-A-08-S1-183) and University of Technology, Sydney (UTS) is gratefully acknowledged. The help from the Precision Instrument Center at National Chiao Tung University in the HRTEM observation is also greatly appreciated.

Appendix A. Supplementary material

Supplementary material associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.ijhydene.2012.07.027.