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編號：030028

## 作品名稱

對平面結構的石墨烯修飾並應用於直接甲醇燃料電池

## 得獎獎項

大會獎：一等獎

美國正選代表：美國第 63 屆國際科技展覽會

作者姓名：王聖槐

就讀學校：臺北市立第一女子高級中學

指導教師：洪偉修、張釗哲

關鍵字：石墨烯、直接甲醇燃料電池、鉑

## 作者簡介



王聖槐，目前就讀北一女中數理資優班。在進入溫班之前就已決定要過一個快樂而難忘的高中生活，特別是專題研究課程。不像班上許多優秀的同學，我的國小和國中都在很平凡的環境下長大，到了高中才決定鼓起勇氣嘗試未知的領域，把自己燃燒在懸空著的夢。在專題研究這漫長而艱辛的路上，培養了自行閱讀和吸收的能力，也學習如何針對問題做解決，開拓了自我小小的視野，也讓自己更有信心地面對生活中大大小小、不停而來的挑戰。

## 摘要

此研究希望找到適當的材料和製備方式，提升直接甲醇燃料電池 (DMFC)的工作效能。

使用石墨烯為基材，將純度 99.999% 的石墨在高溫下以過錳酸鉀進行氧化，經剝離後得片狀級氧化石墨烯(GO)，然後以氯鉑酸( $\text{H}_2\text{PtCl}_6$ )提供正四價的鉑(Pt)，還原在此樣品上成零價鉑金屬做為催化劑的使用。使此樣品(G-Pt)於三電極系統下進行循環伏安法，分別對硫酸與甲醇進行催化量測此新型材料的氧化電位。對硫酸進行催化，可得氫的脫附面積；對甲醇進行催化，則是觀察此新型材料的運用成效之優劣。

本實驗進一步於氧化石墨烯(GO)加入苯甲醯氯(Benzoyl chloride)做修飾，合成經氧化修飾的石墨烯(GO-B)，同樣地還原觸媒鉑在此材料上(G-B-Pt)。經電化學分析後比較是否因修飾後接上苯甲醯氯而有比較好的性能表現。

結果發現，經苯甲醯氯修飾的材料，氫的脫附及甲醇的氧化電位數值表現上高於未修飾者，說明在三電極系統下，本實驗加入的修飾藥品有助於提升直接甲醇燃料電池的工作效能，將來可被運用於燃料電池上。

## Abstract

Due to the amount of petroleum is predicted to be used up in less than 50 years. It is very important to replace such an effective energy source. Direct methanol fuel cells(DMFCs) have drawn great attention recently due to its high density, low pollution emission and low operating temperature.

This experiment aims to enhance performance in DMFCs.

Graphene oxide (GO) was prepared by oxidizing graphite using potassium permanganate ( $\text{KMnO}_4$ ). Benzoyl Chloride was added to modify the surface which is called GO-B in order to compare with the one without being modified. Then hydrogen hexachlorplatinate ( $\text{H}_2\text{PtCl}_6$ ) was reduced to Pt on the surface, using sodium borohydride ( $\text{NaBH}_4$ ) to be as a catalyst. G-B-Pt and G-Pt are elements derived from the process where Go-B-Pt and Go-pt reduce  $\text{H}_2\text{PtCl}_6$  to Pt on the surface.

In the end, sulfuric acid( $\text{H}_2\text{SO}_4$ ) and methanol( $\text{CH}_3\text{OH}$ ) were to catalyze by the means of cyclic voltammetry (CV), and then it is obvious that the modified electrochemical performance of Graphene Oxide turned out to be superior.

The activity of methanol electro-oxidation of two samples in G-B-Pt was about  $600 \text{ mAcm}^{-2}$  while that of G-Pt was only about  $400 \text{ mAcm}^{-2}$ . The enhanced catalytic activity may be due to the unique interaction between Pt and graphene. Pt supported on GO-B can exhibit larger electrochemical active surface, which can offer more Pt activity sites for chemisorption of methanol. Also, the current value of G-B-Pt is more steady than G-Pt. Thus, the result shows that this report provides a new method of modifications of materials having energy-related application values which command great significance for references.

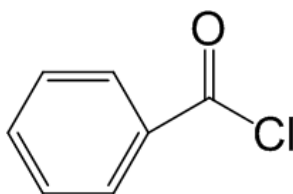
## 壹、前言

隨著科技的進步，人類對於能源產生極高的依賴性，加上地球人口以倍數成長，不可替代能源如石油等大量地被消耗，能源問題便顯得日益重要。如何發展價格合理、低污染、可穩定供應、乾淨的替代能源成為現世代很重要的課題。燃料電池具有低污染、發電效率高、無須充電、應用範圍廣等優點，而其中直接甲醇燃料電池（DMFC）被視為未來最具潛力的能量來源，因其無須氫重組等複雜的熱交換系統，可在低溫下進行反應，又攜帶方便、燃料容易補充。

目前燃料電池較常被使用的金屬觸媒是鉑，因其具有諸多項優點如化學穩定性高、高活性與高導電性等，但鉑為貴重金屬，欲實際應用就必須有效利用以降低成本，而增加鉑觸媒的表面積不失為一種好方法。

製備石墨烯方法有機械剝離法、化學氣相沉積法（CVD）、氧化剝離法等。本研究仿 1958 年 Hummers 的做法，經氧化剝離法，得氧化石墨烯為基材，再對表面進行修飾，並比較有無較好的電性表現。

此研究希望能找到適當的材料與方法，提升 DMFC 的工作效能。利用二維平面碳材料——石墨烯做為基材，在三電極系統之下，對 DMFC 進行催化，並探討有無修飾的表面對於其結果是否有正面的影響。加入的表面修飾藥品為苯甲醯氯（Benzoyl chloride）。



圖一 苯甲醯氯結構式

## 貳、研究設備及器材

### 一、實驗器材

1. 電子天平 (小數點以下四位)
2. 磁石攪拌加熱器
3. 分析篩 (BUNSEKIFURUI MESH NO270)
4. 離心機
5. 超音波振盪儀
6. pH 計
7. 自動吸管
8. 二次水

### 二、實驗試藥

1. 石墨烯(graphite(sp-1))，  
純度 99.999%；Bay Carbon, Inc.
2. 硫酸(sulfuric acid)， $\text{H}_2\text{SO}_4$ ：  
純度：96%； $M=98.07$ ； $d=1.84$ ；Acros
3. 硝酸鈉(sodium nitrate)， $\text{NaNO}_3$ ：  
純度:99+% ； $M=84.9947$ ； $d=2.26$ ；Acros
4. 過錳酸鉀(potassium permanganate)， $\text{KMnO}_4$ ：  
純度：99.5+%； $M=158.03$ ；Acros
5. 過氧化氫(hydrogen peroxide)， $\text{H}_2\text{O}_2$ ：  
純度：35wt%； $M=34.00$ ； $d=1.135$ ；Acros

6. 鹽酸(hydrochloric acid) ,  $\text{HCl}$  :  
純度 : 37 wt% ;  $M=36.55$  ;  $d=1.18$  ; Sigma Aldrich
7. 乙醇(ethanol) ,  $\text{C}_2\text{H}_5\text{OH}$  :  
純度 : 99.9% ;  $M=46.07$  ; J.T.Baker
8. 氯鉑酸(hydrogen hexachloroplatinate) ,  $\text{H}_2\text{PtCl}_6 \cdot x\text{H}_2\text{O}$  :  
 $M=409.82$  ; Acros
9. 氫氧化鈉(sodium hydroxide) ,  $\text{NaOH}$  :  
 $M=40.00$  ; Acros
10. 硼氫化鈉(Sodium borohydride) ,  $\text{NaBH}_4$  :  
純度 = 98+% ;  $M=37.83$  ; Acros
11. 苯甲醯氯(Benzoyl chloride) :  
純度 : 99+% ;  $M=140.57$  ; Alfa Aesar
12. 甲基甲醯胺(Dimethylformamide) ,  $(\text{CH}_3)_2\text{NC}(\text{O})\text{H}$  :  
 $M=73.09$  ;  $d=0.949$  ; Acros

### 三、實驗儀器

1. 掃描式電子顯微鏡—Scanning electron microscope (SEM)
2. 原子力顯微鏡—Atomic force microscope (AFM)
3. 粉末 X 光繞射儀—powder X-ray diffraction(XRD)
4. 拉曼光譜儀—Raman Spectroscopy
5. 感應耦合電漿質譜分析儀—Inductively Coupled Plasma Mass Spectrometry

## 參、研究方法或過程

### 一、製備 G-Pt

1. 將 sp-1(純度 99.999%)的石墨(graphite)進行氧化。
  - (1) 3 克石墨、1.5 克  $\text{NaNO}_3$  與 69 毫升飽和  $\text{H}_2\text{SO}_4$  在冰域中進行反應，控溫在  $0^\circ\text{C}$ 。
  - (2) 9 克  $\text{KMnO}_4$  緩緩加入，並保持溫度在  $20^\circ\text{C}$  下。
  - (3) 離開冰浴，利用油浴控溫在  $35^\circ\text{C}$ ，攪拌反應 30 分鐘。
  - (4) 加入 138 毫升  $\text{H}_2\text{O}$ ，此時溫度上升至  $98^\circ\text{C}$  並恆溫 15 分鐘。
  - (5) 利用冷水浴降溫至室溫 10 分鐘。
  - (6) 再加入 420 毫升  $\text{H}_2\text{O}$  與 3 毫升 30% 的  $\text{H}_2\text{O}_2$ ，進行再一次放熱，等待回到室溫。
  - (7) 利用  $270\mu\text{m}$  的篩網取濾液再離心，取部份固體並利用 200 毫升  $\text{H}_2\text{O}$  和 200 毫升 30% $\text{HCl}$  與 200 毫升乙醇混和液。清洗此樣品兩次。
  - (8) 進行過濾和真空抽乾，得到粉末固體樣品。
2. 將金屬鉑還原在此新型材料上
  - (1) 25mgGO 均勻地分散在水中，為時 1 小時。
  - (2) 加入 5 毫升 0.02M 的  $\text{H}_2\text{PtCl}_6$ 。
  - (3) 以 1M 的  $\text{NaOH}$  滴定至  $\text{pH}=10$ 。
  - (4) 以 1 克  $\text{NaBH}_4$  做為還原劑緩慢加入。
  - (5) 在室溫下攪拌 24 小時。



(6) 以乙醇及二次水清洗並過濾。

(7) 最後真空抽乾，得到固體粉末 (G-Pt)。

## 二、製備 G-B-Pt

1. 將 sp-1(純度 99.999%)的石墨(graphite)進行氧化。(同製備 GO-Pt 步驟一)

(1) 3 克石墨、1.5 克  $\text{NaNO}_3$  與 69 毫升飽和  $\text{H}_2\text{SO}_4$  在冰域中進行反應，控溫在  $0^\circ\text{C}$ 。

(2) 9 克  $\text{KMnO}_4$  緩緩加入，並保持溫度在  $20^\circ\text{C}$  下。

(3) 離開冰浴，利用油浴控溫在  $35^\circ\text{C}$ ，攪拌反應 30 分鐘。

(4) 加入 138 毫升  $\text{H}_2\text{O}$ ，此時溫度上升至  $98^\circ\text{C}$  並恆溫 15 分鐘。

(5) 利用冷水浴降溫至室溫 10 分鐘。

(6) 再加入 420 毫升  $\text{H}_2\text{O}$  與 3 毫升 30% 的  $\text{H}_2\text{O}_2$ ，進行再一次放熱，等待到室溫。

(7) 利用  $300\mu\text{m}$  的篩網取濾液再離心，取部份固體並利用 200 毫升  $\text{H}_2\text{O}$  和 200 毫升 30%  $\text{HCl}$  與 200 毫升乙醇混和液。清洗此樣品兩次。

(8) 進行過濾和真空抽乾，得到粉末固體樣品。

2. 加入藥品苯甲醯氯(Benzoyl chloride)進行官能基的修飾。

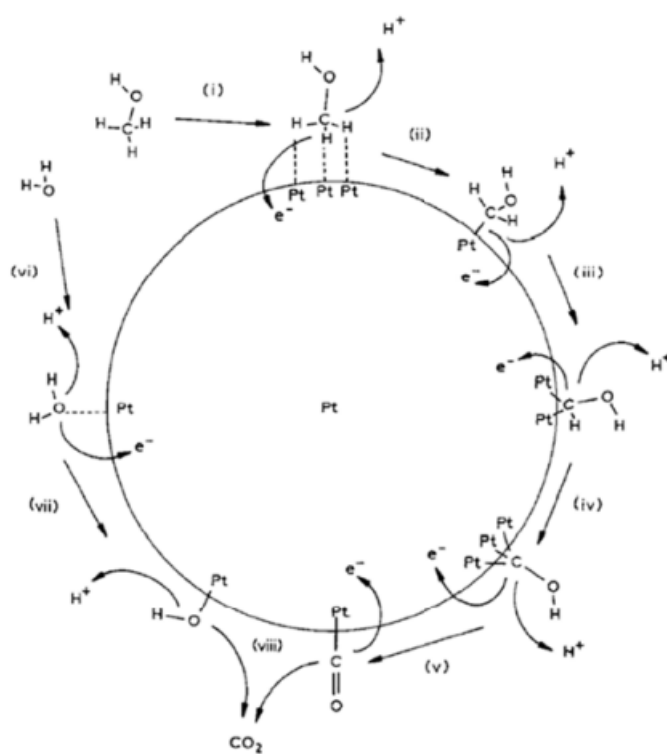
(1) 取 50 毫克 GO，在氬氣環境下加入 1mmol 的 Benzoyl chloride 和 50 毫升的甲基甲醯胺(Dimethylformamide)溶劑，反應兩天並控溫在  $50^\circ\text{C}$  至  $60^\circ\text{C}$ 。

(2) 進行過濾抽乾，得到固體粉末 (GO-B)。

3. 將金屬鉑還原在此新型材料上

(1) 25mgGO-B 均勻地分散在水中，為時 1 小時。

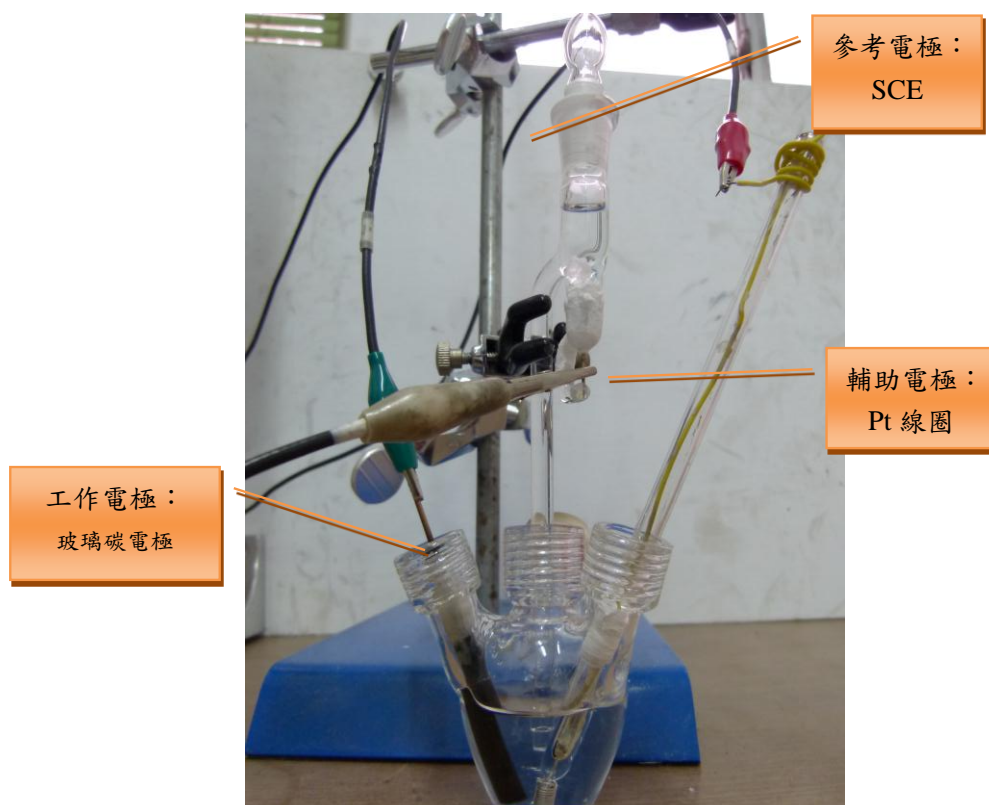
- (2) 加入 5 毫升 0.02M 的  $\text{H}_2\text{PtCl}_6$ 。
- (3) 以 1M 的 NaOH 滴定至  $\text{pH}=10$ 。
- (4) 以 1 克  $\text{NaBH}_4$  做為還原劑緩慢加入。
- (5) 在室溫下攪拌 24 小時。
- (6) 以乙醇及二次水清洗並過濾。
- (7) 真空抽乾，得到固體粉末 (G-B-Pt)



圖二 甲醇在鉑觸媒上的反應途徑

### 三、電化學量測

利用循環伏安法的三電極系統，量測甲醇的氧化電位，對於是否進行官能基修飾做比較。其中，三電極分別是：工作電極，即 Pt 還原在 GO/GO-B 上；參考電極，使用的是 SCE（飽和甘汞電極），內含 KCl 及  $\text{Hg}_2\text{Cl}_2$ ；輔助電極則是使用 Pt 線圈。以工作電極為負極，參考電極為正極進行甲醇電化學催化反應。

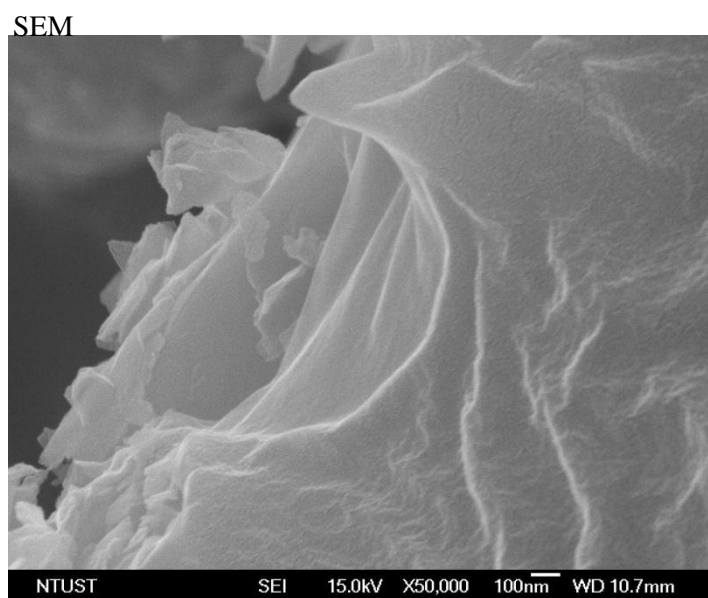


圖三 三電極系統

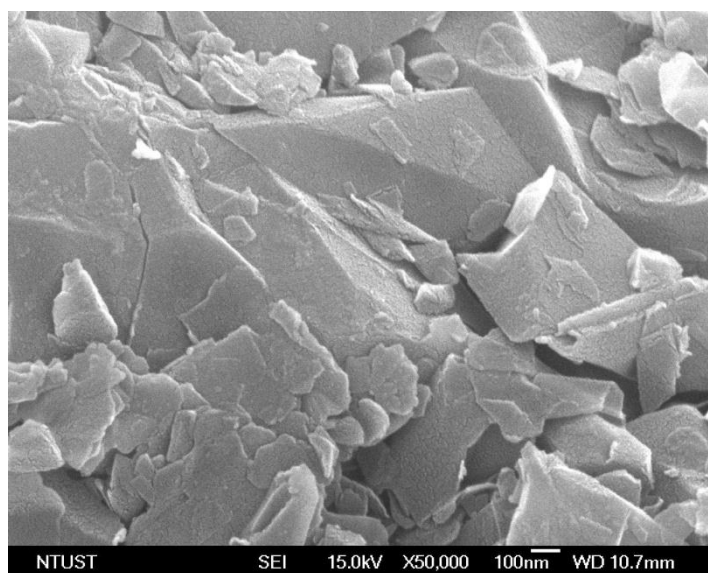
## 肆、研究結果與討論

### 一、石墨(graphite，簡稱 G)

以掃描式電子顯微鏡(SEM)觀察微觀下起始材料 sp-1 石墨(graphite)的構造。說明其結構為層狀(見圖四(a))，並且表面光滑(見圖四(b))。



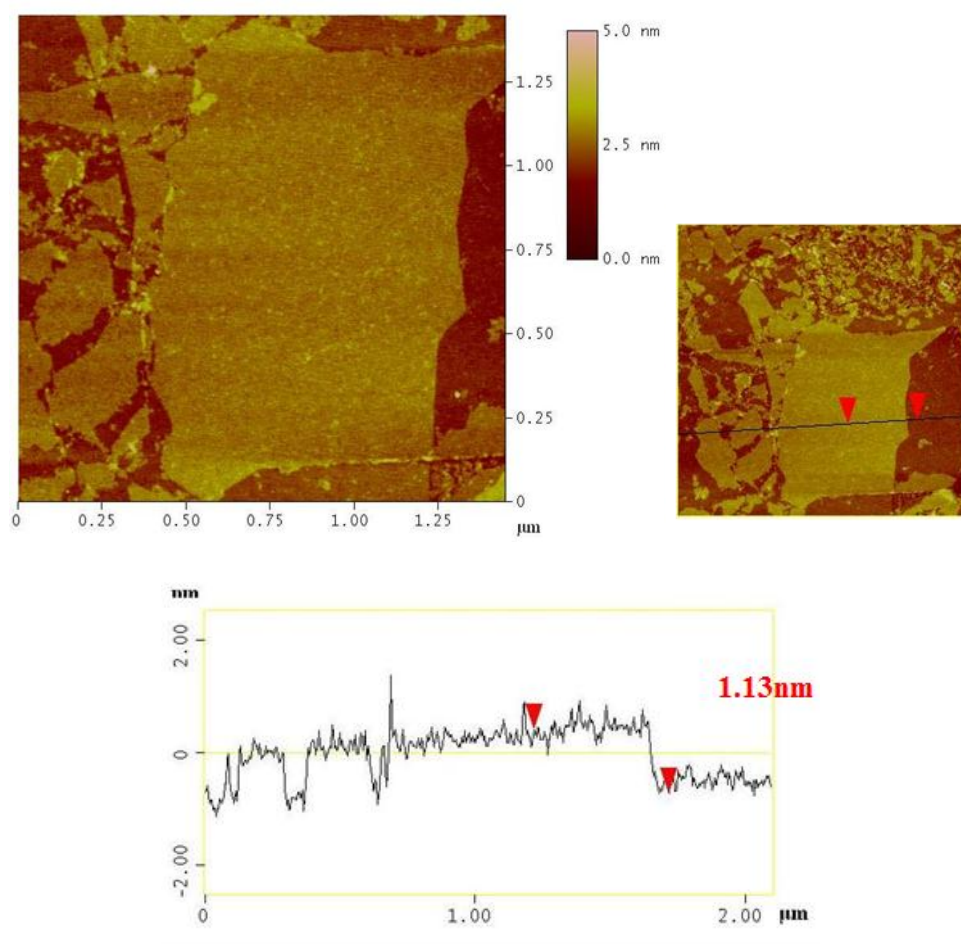
圖四(a)



圖四(b)

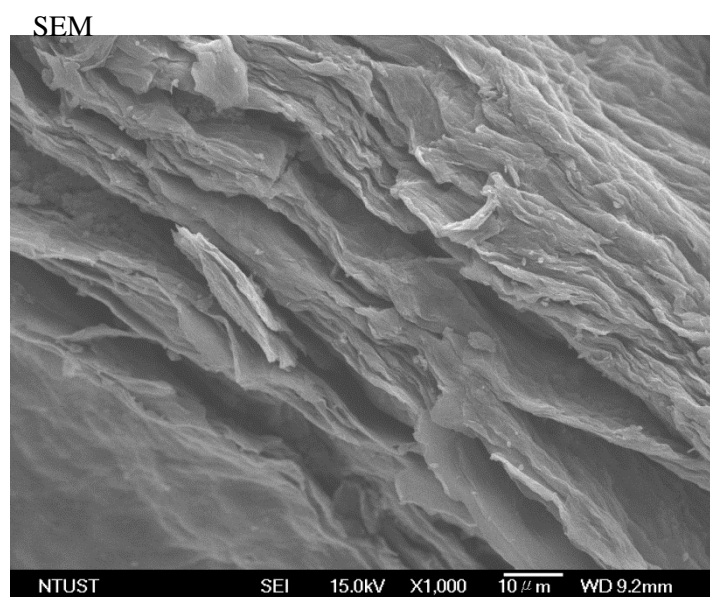
## 二、氧化石墨烯(graphene oxide，簡稱 GO)

在高溫下已過錳酸鉀將石墨進行氧化，得氧化石墨。再以原子力顯微鏡(AFM)鑑定厚度(見圖五)，得到數值為 1.13nm。說明所得到的樣品符合石墨烯的厚度，確認本實驗所進行反應的材料具有石墨烯的性質。

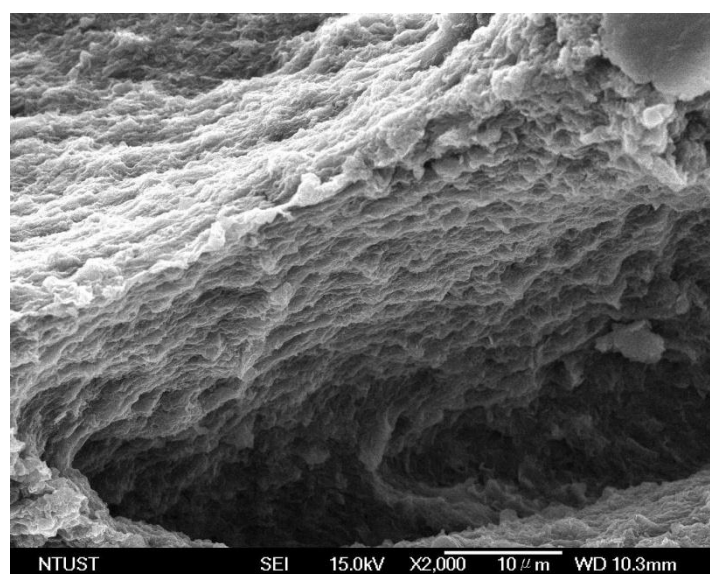


圖五 鑑定 GO 厚度。

以掃描式電子顯微鏡(SEM)觀察 GO 在微觀下的構造。發現 GO 的層狀結構依舊存在(見圖六(a))，但不同於石墨的是，GO 的表面更為粗糙(見圖六(b))，並且具有孔洞性質。



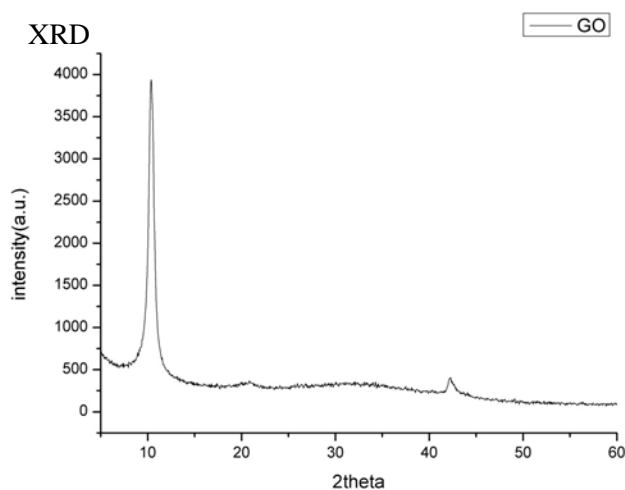
圖六(a)



圖六(b)

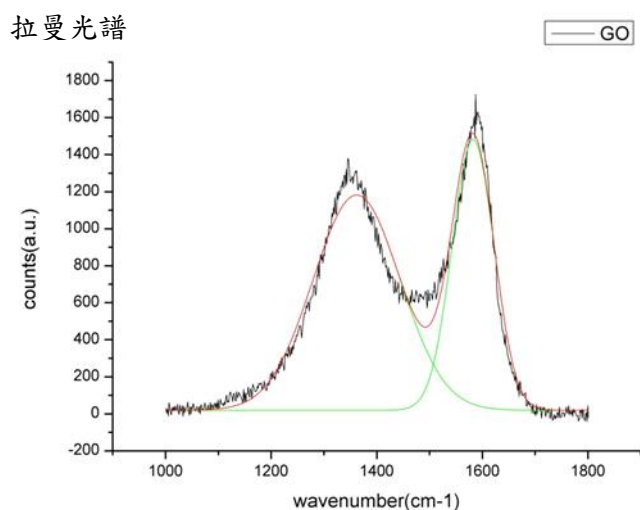
圖六(a)(b)為氧化後的石墨(GO)

以粉末 X 光繞射儀鑑定 GO。由布拉格公式： $n\lambda=2d\sin\theta$ ( $n$  為整數)。其中，左式波長為定植，經由  $n=1$  的單次繞射，故右式  $d$ ( $d$ -spacing)與  $\sin\theta$  成反比，經運算可得  $d$ 。得出特徵峰位在  $2\theta=10.29^\circ$ (見圖七)， $d$ -spacing 為 8.58(埃)。



圖七 以 XRD 鑑定 GO

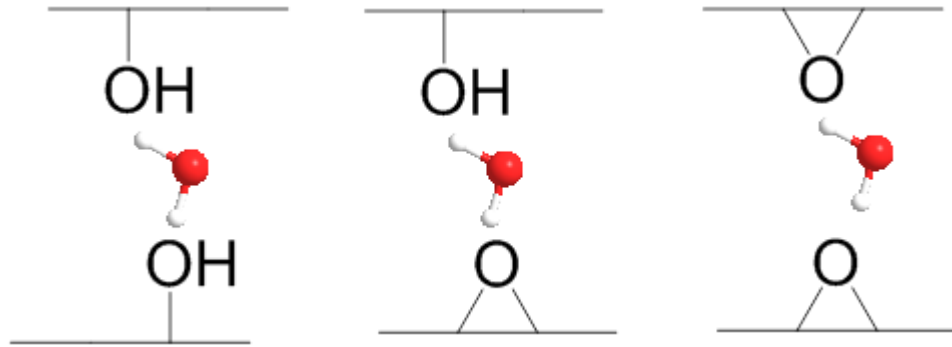
由文獻上顯示，D band 為石墨層的缺陷及  $sp^3$  的混層軌域所提供，其特徵峰  $1353\text{cm}^{-1}$ 。G band 為石墨層的層狀結構及  $sp^2$  的混層軌域所提供，其特徵峰在  $1587\text{cm}^{-1}$ 。經理論計算後，積分得  $I_D=240849(\text{cm}^2)$ ， $I_G=146158(\text{cm}^2)$ ， $I_D/I_G=1.648$ 。



圖八 以拉曼光譜鑑定 GO

## GO 結構

由參考資料顯示，經氧化過後的石墨，表面會產生-OH、-COOH、epoxy 等含氧官能基。其中，-COOH 會在石墨層的邊緣形成，而-OH 及 epoxy 會在石墨表層的碳中生成。



圖九 GO 結構示意圖

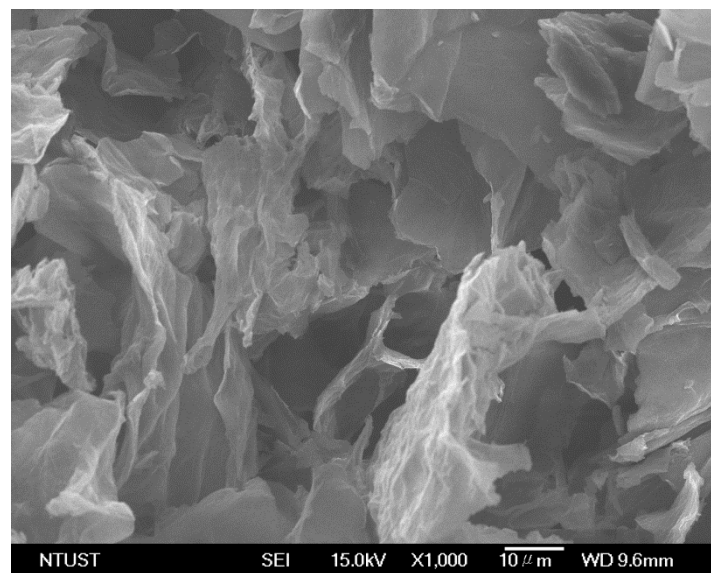


### 三、鑑定氧化後所得的 GO-B

經過苯甲醯氯修飾的表面，較 GO 更為粗糙(見圖十(a))，並且在剝離的現象更為明顯(見圖十(b))。



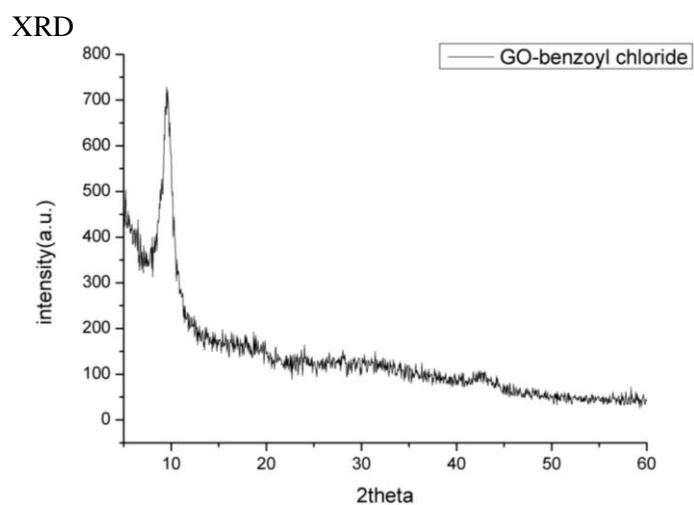
圖十(a)



圖十(b)

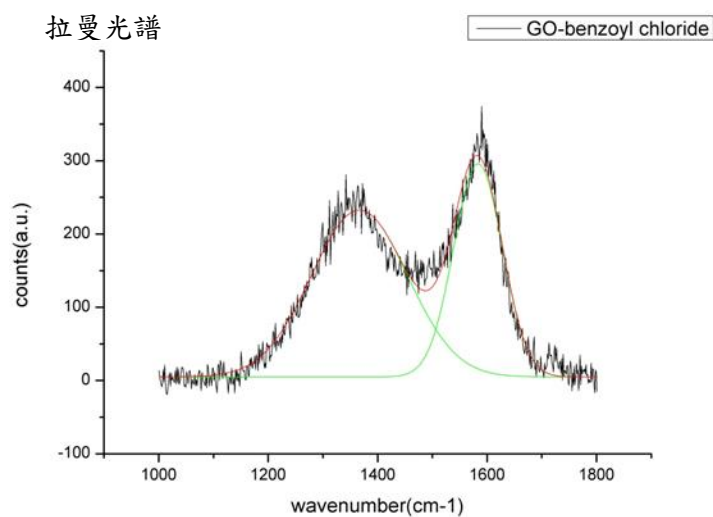
圖十(a)(b)為經修飾後的氧化石墨烯(GO-B)

和 GO 做比較，發現 d-spacing 被撐得更開，由原本 8.58 埃提升為 9.21 埃，說明修飾藥品苯甲醯氯有存在於樣品的表面。



圖十一 以 XRD 鑑定 GO-B

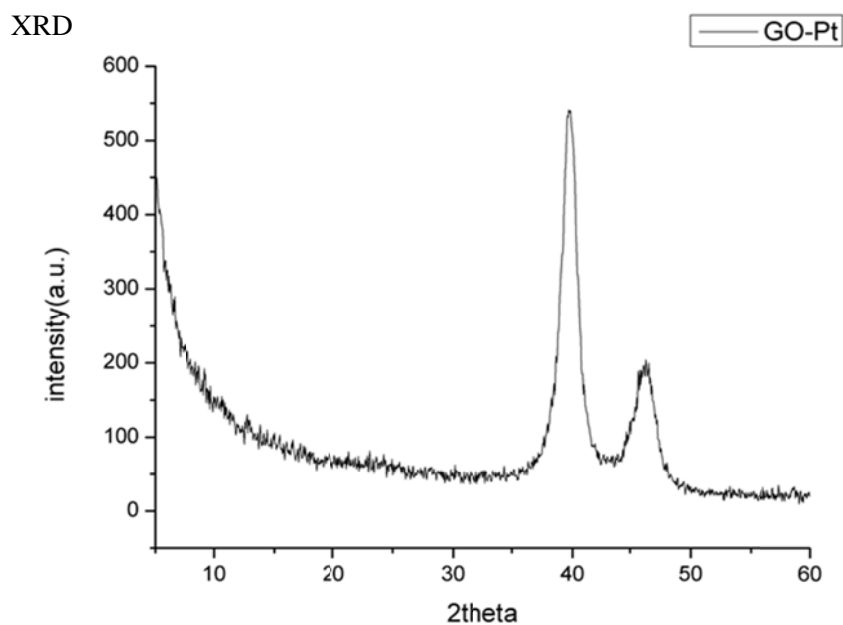
由理論計算得知 D-band 與 G-band 分別是  $50332(\text{cm}^2)$  以及  $32535(\text{cm}^2)$  相除之比值為  $I_D/I_G = 1.5470$ ，發現其值較 GO 小，得知推知所使用的藥品苯甲醯氯確實有被接上去。



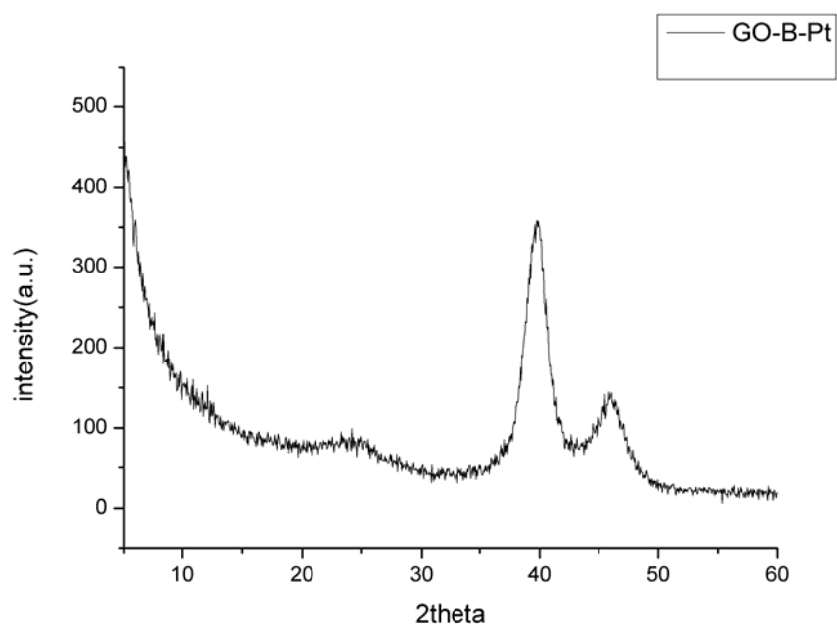
圖十二 以拉曼光譜鑑定 GO-B

#### 四、鑑定金屬鉑是否有還原在 GO 以及 GO-B 之上

以 XRD 鑑定樣品，發現圖十三(a)(b)表示金屬鉑分別在特徵峰  $39.8^\circ$  為(111)以及  $46.1^\circ$  為(200)。此訊號說明了在此 GO 以及 GO-B 上金屬鉑有被還原成零價。



圖十三(a) 金屬鉑還原在 GO 上

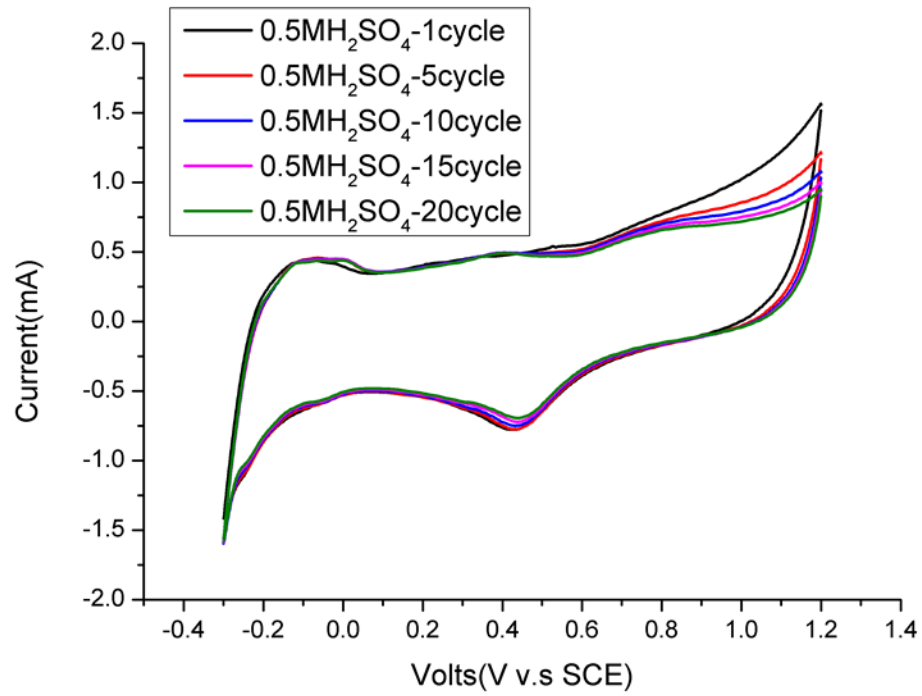


圖十三(b) 金屬鉑還原在 GO-B 上

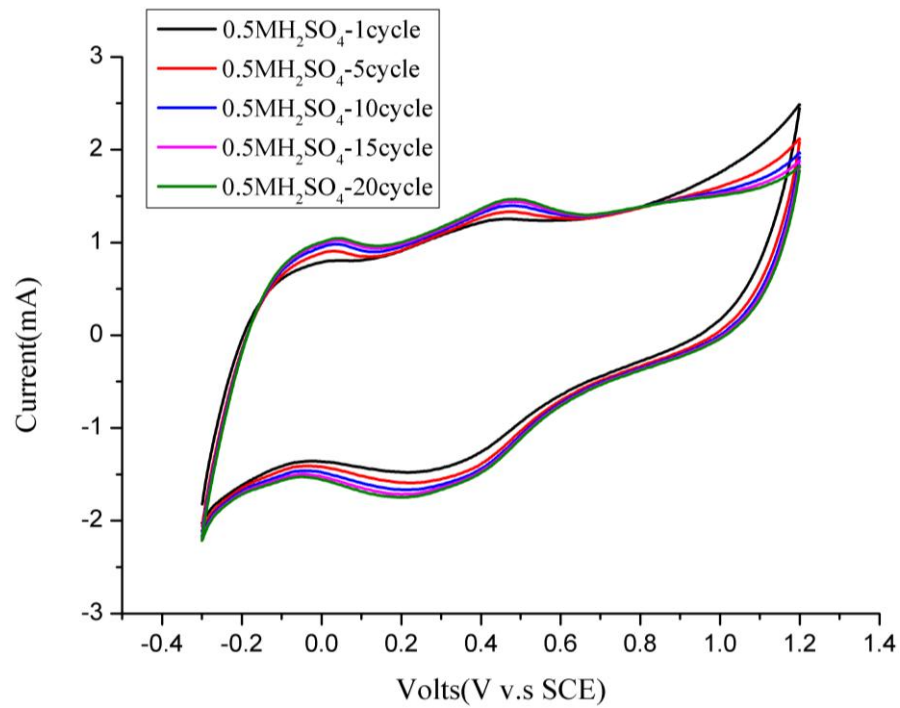
## 伍、結論與應用

就電化學的量測結果而言，首先是對硫酸進行催化，如圖十四(a)(b)。在  $0.5\text{MH}_2\text{SO}_4$  50mL，以  $20\text{mVs}^{-1}$  速度下做催化，經理論計算得氫的脫附面積，此積分出來的面積可視為金屬鉑的活性面積。未經修飾者(G-Pt)和經修飾者(G-B-Pt)兩者數值分別是  $0.0140(\text{cm}^2)$   $0.0278(\text{cm}^2)$ 。而比較兩者面積大小後發現，修飾者優於未經修飾者，說明 Pt 還原在 GO-B 之上的材料，較 Pt 氧化在 GO 之上的材料要好。

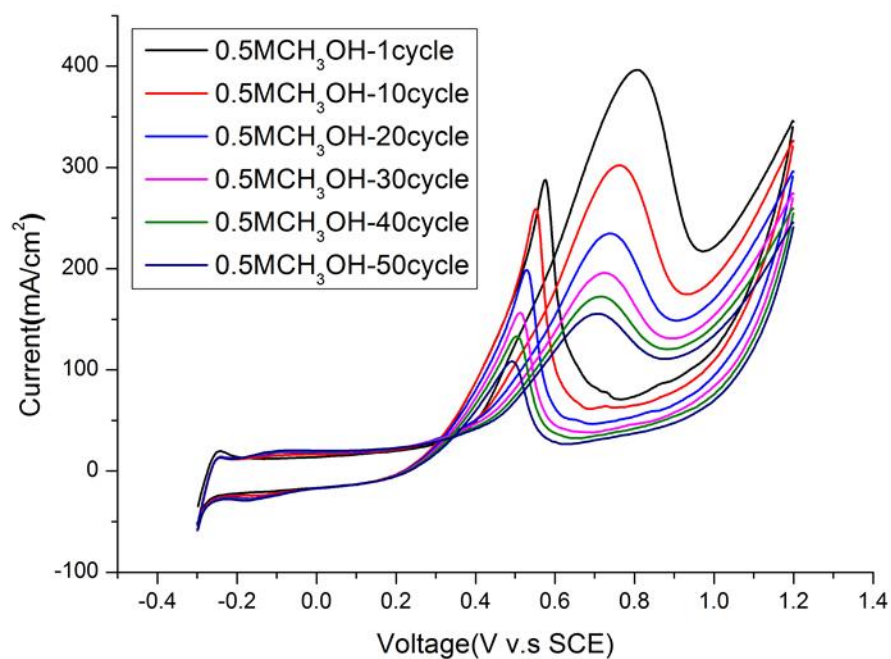
接著在原本 50mL 的  $0.5\text{MH}_2\text{SO}_4$  加入 50mL 0.5M 甲醇進行催化，同樣地以  $20\text{mVs}^{-1}$  做為掃描速度，如圖十四(c)(d)。此圖比較基材本身和電流值之間的關係。發現兩者有在 y 軸上的表現量 G-B-Pt 比 G-Pt 大約一點五倍；其次，由兩張圖的電流值比較，可發現在掃描圈數增多時，G-Pt 的電流值較不穩定，一下子就掉下來了；而 G-B-Pt 明顯有比較穩定的電流值；再者，就啟動電位而言，G-Pt 比 G-B-Pt 要來得高，說明 G-B-Pt 在較低的電位供應下就能啟動機制，而 G-Pt 則不然。



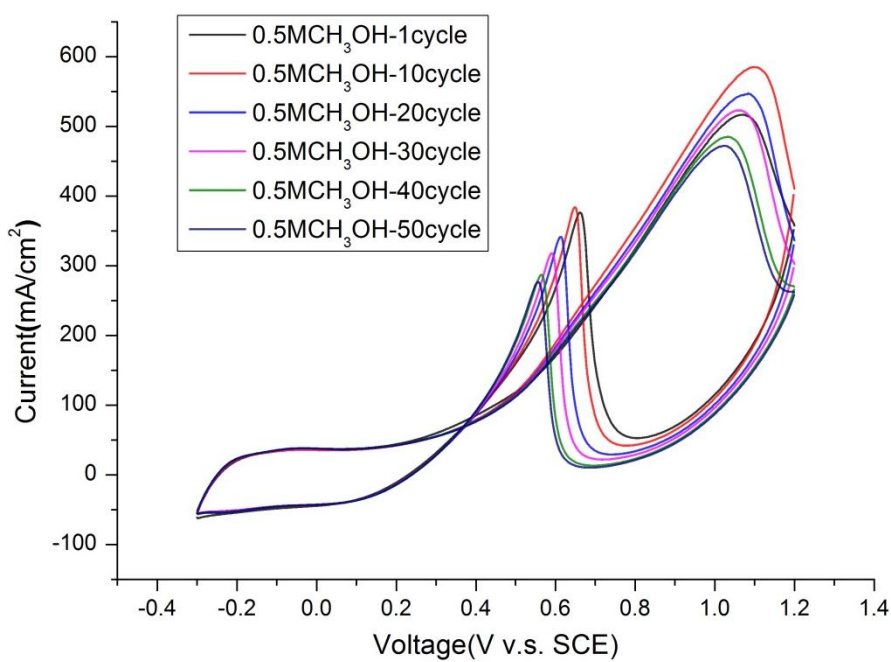
圖十四(a) GO-Pt 在 0.5M 硫酸催化下得到氫的吸脫附



圖十四(b) GO-B-Pt 在 0.5M 硫酸催化下得到氫的吸脫附



圖十四(c) GO-Pt 在 0.5M 甲醇催化下得到的氧化



圖十四(d) GO-B-Pt 在 0.5M 甲醇催化下得到氧化

## 陸、未來展望

本實驗選用的是單苯環接醯氯官能基，可嘗試接其他的官能基，如其他鹵素族元素；或是多苯環的藥物，探討其性質是否因苯環而具有較佳的穩定性，以利反應而提高鉑的裝載量；亦可嘗試長碳鏈做為撐開層與層之間距的方式，做為增強孔洞性的方式，同樣地希望提升觸媒的裝載量。

## 柒、參考文獻

1. Xin, Y., J.-g. Liu, *et al* . **2011** , Preparation and characterization of Pt supported on graphene with enhanced electrocatalytic activity in fuel cell, *Journal of Power Sources* ,196(3) , 1012-1018.
2. Li, Y., L. Tang, *et al* , **2009** , Preparation and electrochemical performance for methanol oxidation of pt/graphene nanocomposites , *Electrochemistry Communications* 11(4) , 846-849.
3. Stankovich, S., R. Piner, *et al* , **2006** , Synthesis and exfoliation of isocyanate-treated graphene oxide nanoplatelets , *Carbon* 44(15) , 3342-3347.
4. Srinivas, G., J. W. Burrell, *et al* , **2011** , Porous graphene oxide frameworks: Synthesis and gas sorption properties , *Journal of Materials Chemistry* 21(30) , 11323-11329.
5. Hummers, W. S. and R. E. Offeman , **1958** , Preparation of Graphitic Oxide , *Journal of the American Chemical Society* 80(6) , 1339-1339.
6. Frelink, T., W. Visscher, *et al* , **1995** , Particle size effect of carbon-supported platinum catalysts for the electrooxidation of methanol , *Journal of Electroanalytical Chemistry* 382(1-2) , 65-72.
7. Stankovich, S., D. A. Dikin, *et al* , **2007** , Synthesis of graphene-based nanosheets via chemical reduction of exfoliated graphite oxide , *Carbon* 45(7) , 1558-1565.

## **Modification of Graphene with Enhanced Efficiency for Direct Methanol Fuel Cells**

### **Abstract**

The world's resources of easily accessible fossil fuels have been diminishing quickly over the last few decades. Thus, it has now become very important for people to increase the efficiency of fuel cells. Direct methanol fuel cells (DMFCs) have drawn great attention recently due to their high density, low pollution emission, and low operating temperatures.

Graphene is known as a 2D structure material, which has great conductivity when used as an electrode. Platinum nanoparticles are deposited onto graphene sheets via synchronous reduction of  $\text{H}_2\text{PtCl}_6$  and graphene oxide (GO) suspension using  $\text{NaBH}_4$ .

Furthermore, oxygen groups on the graphene oxide were removed to leave graphene. In order to enhance the electrochemical performance of DMFCs, this experiment also added modified material, benzoyl chloride and terephthaloyl chloride, to study the differences from the unmodified one. Samples were characterized by X-ray diffraction (XRD), raman spectroscopy, etc. The platinum metal surface area was evaluated by cyclic voltammetry (CV) on a thin porous coated disk electrode. It became clear that the modified electrochemical performance of graphene proved to be superior.



## Introduction

Due to the recent progress in development of gadgetry and technology, people are relying on portable energy resources much more. Additionally, irreplaceable resources such as petroleum and natural gas are more difficult to locate and more expensive to extract. Thus, it is very important for people to address the problem and find solutions.

Direct methanol fuel cells (DMFCs) is quite environmental friendly because it can utilize energy resources efficiently. Unlike fossil fuels, DMFCs can directly change chemical energy into electricity without heat loss. In order to lower the operating temperature, they need a catalyst to work on it. And catalyst needs to be deposited on substrate. Platinum is used as a catalyst while carbon materials are used as the substrate in industry.

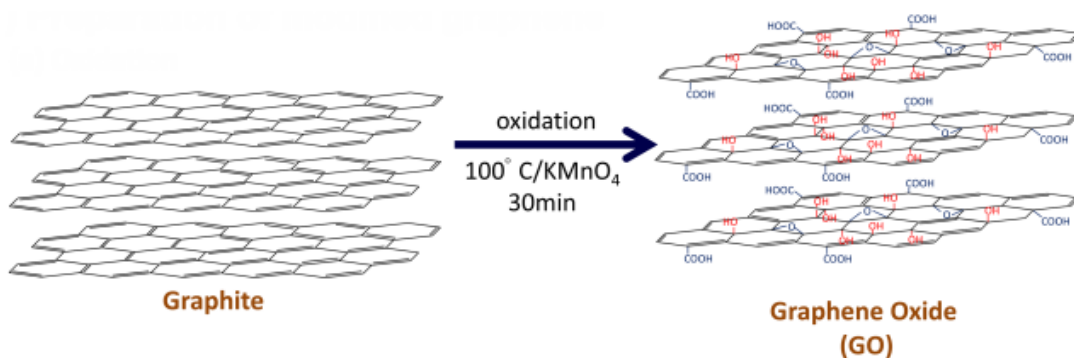
Graphene is known as a two dimensional (2D) structure carbon-based material which is very conductive and has high surface area. Many scientists have devoted themselves to finding different methods of preparing graphene by using such methods as mechanical exfoliating, chemical vapor deposition (CVD), and oxidation and reduction. This study chose the easiest way - oxidation and reduction to complete the study.

## Research Goals

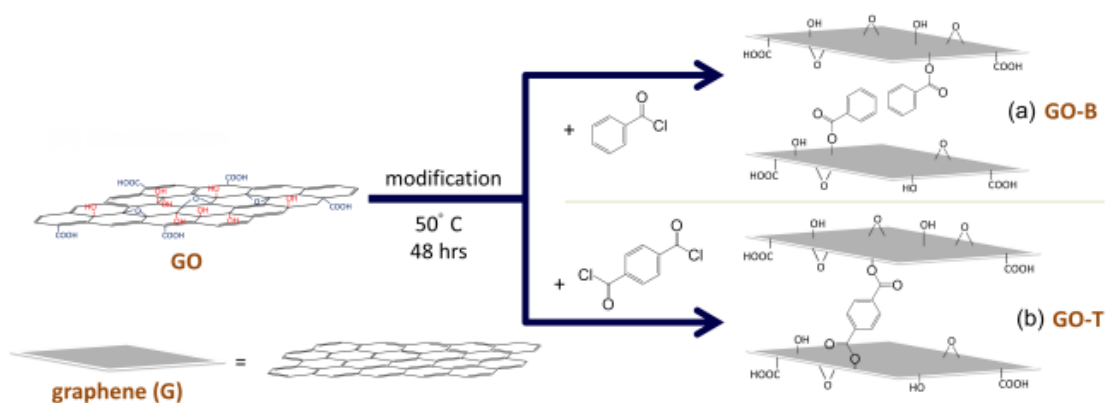
Enhance the efficiency for methanol oxidation by modification of graphene.

### (1) Preparation of modified grapheme

#### (a) Oxidation

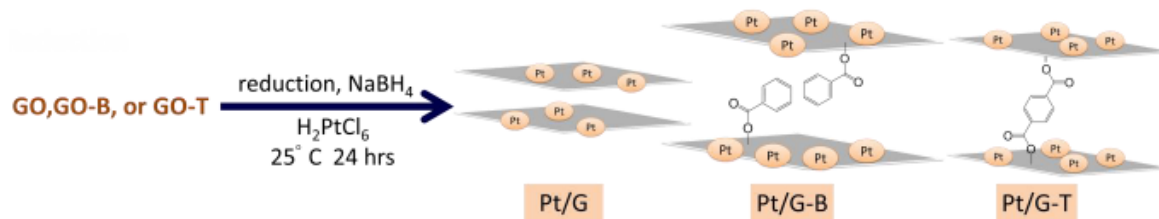


#### (b) Modification



### (2) Preparation of modified grapheme-based platinum electrode

Reduction



## Materials & Equipment

### Chemicals

graphite (sp-1), sulfuric acid, sodium nitrate, potassium permanganate,

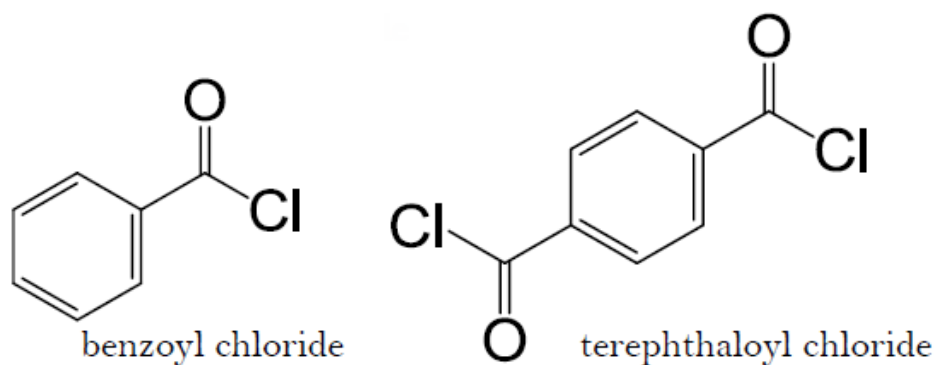
hydrogen peroxide, hydrochloric acid, ethanol, hydrogen

hexachloroplatinate, sodium hydroxide, sodium borohydride, benzoyl

chloride, terephthaloyl chloride, dimethylformamide

### Equipment

- (1) X-Ray Diffraction (XRD), (Bruker D8 advance) – interlayer separation, crystalline structure and size of Pt nanoparticles
- (2) Raman spectroscopy, (Jobin Yvon T64000) – sp<sup>2</sup> coupling strength
- (3) Inductivity Coupled Plasma Mass Spectrometry (ICP-MS), (Horiba JY 20002) – weight percentages of Pt
- (4) Cyclic Voltammetry (CV), (CH Instruments model 614B series electrochemical analyzer) – electrochemical properties of electrodes



## Methods

This work has tried to change the substrate of graphene, via modifying reagent. After modifying the structure, the spacing from layer to layer enlarged. Then, the catalyst coating on graphene oxide could work more efficiently to catalyze methanol.

### 1. Synthesis of graphene oxide (GO)

3 g graphite, 1.5 g  $\text{NaNO}_3$  and saturated  $\text{H}_2\text{SO}_4$  were reacted in ice area. Then, 9 g  $\text{KMnO}_4$  was slowly added at  $20^\circ\text{C}$ . After adding oxidant, removed it from ice area, then kept at  $35^\circ\text{C}$  and stirred for 30 minutes. Next, 138 mL  $\text{H}_2\text{O}$  was added before heated to  $98^\circ\text{C}$  for 15 minutes. Sample was cooled down in ice area to room temperature for ten minutes. Next, added 420 mL  $\text{H}_2\text{O}$  and 3 mL 30%  $\text{H}_2\text{O}_2$ , then heat released to room temperature. The sample was coped with  $300\ \mu\text{m}$  sieving and centrifuged. In the end, filtered and washed the sample by using  $\text{H}_2\text{O}$ .

### 2. Preparation of modifying graphene oxide (GO-B, GO-T)

50 mg GO and 1mmol modifying material (benzoyl chloride or terephthaloyl chloride) were added into DMF solution at  $50^\circ\text{C}$  for 48 hours. Then sample was washed by water and filtered by pump.

### 3. Synthesis of Pt/G, Pt/G-B and Pt/G-T

GO, GO-B, or GO-T was dispersed in 120 mL water for an hour. 5 ml of 0.02M  $\text{H}_2\text{PtCl}_6$  was added to 25mg GO, GO-B or GO-T, and the pH of the solution was adjusted to pH=10 with 1M NaOH. One gram of  $\text{NaBH}_4$  was added into the reaction mixture, and the reaction was carried out at  $25^\circ\text{C}$  for 24hrs. In the end, sample was washed by water and filtered by pump.

## Results and Discussion

### 1. Characterization of substrate

#### (A) $sp^2$ coupling strength

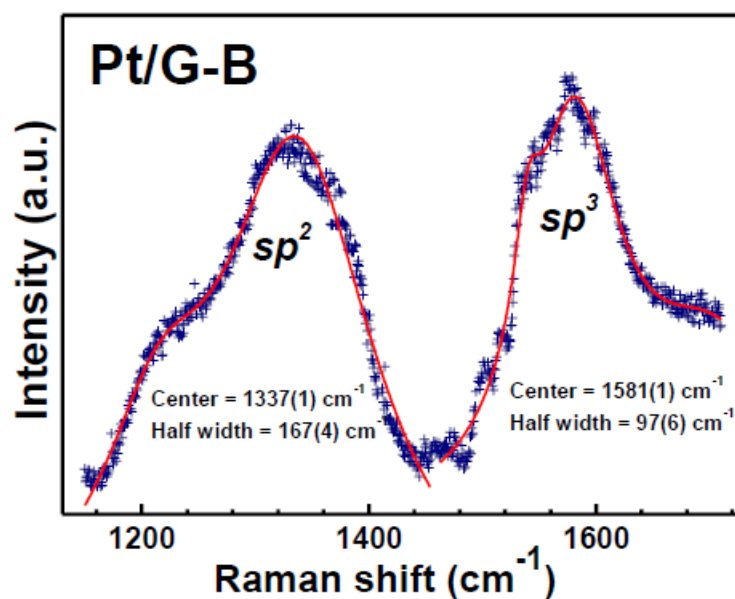


Fig. 2 Raman spectrum of Pt/G-B

Table 1  $sp^2$  coupling of the substrate

Sample	Pt/G	Pt/G-B	Pt/G-T
$sp^2$ Raman shift ( $\text{cm}^{-1}$ )	1300	1337	1345

The characteristic  $sp^2$  Raman lines of the modified substrates are found to be shifted to higher frequencies (1337, 1345 v.s 1300), showing that the strength of  $sp^2$  coupling is enhanced. The enhancement of higher frequencies shows that the binding of carbon and carbon is stronger. By stabilizing the structure of the substrate, it is expected to stabilize the efficiency.

(B) Number of graphene layers

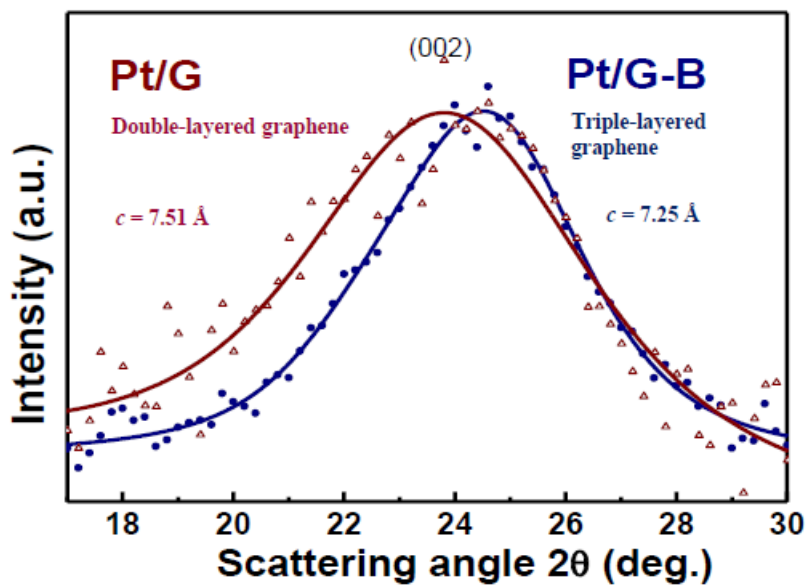


Fig. 3 Characteristic of graphene (002) XRD peak profile of Pt/G and Pt/G-B

Table 2 number of coupled layered

Sample	Pt/G	Pt/G-B	Pt/G-T
Number of coupled layers	2	3	3

The number of coupled graphene layer can be obtained from the width of the characteristic X-ray diffraction profiles. The result shows that the modified electrodes have 3 coupled layers whereas the non-modified electrode has 2 coupled layers.

## 2. Characterization of graphene-based Pt electrode

### (A) Size and relative surface area

The solid lines in plot indicate the fitted diffraction profile, which give a mean particle diameter of 2 nm in Pt/G-B.

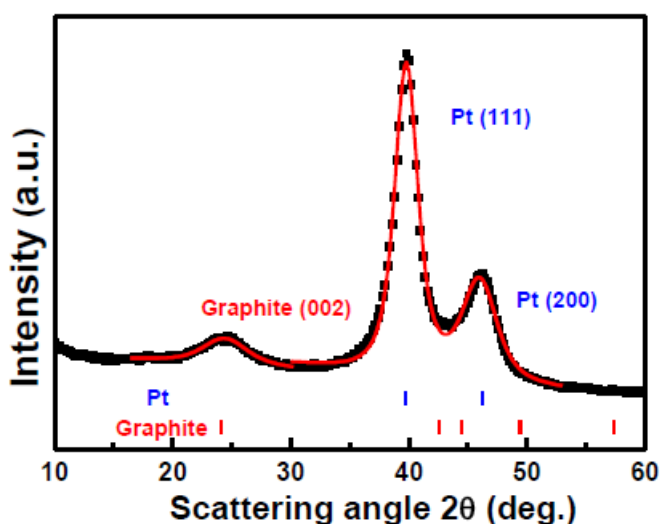


Fig. 4 XRD pattern of Pt/G-B

Table 3 Surface area of Pt nanoparticles deposited on substrate

Sample	Pt/G	Pt/G-B	Pt/G-T
Pt particle diameter (nm) (A)	4.1	2.0	1.5
Weight percentage of platinum (%) (B) measured by ICP-MS	6.80	6.00	3.94
Relative surface area (B/A)	1.65 (100%)	3.00 (198%)	2.63 (159%)

The particle size diameter of modified electrodes which is determined by XRD pattern are smaller than non-modified electrode. The relative surface area of modified electrode are higher than nonmodified electrodes. Among the three electrodes, Pt/G-B has the highest relative surface area which is about two times better than Pt/G.

(B) Active surface area

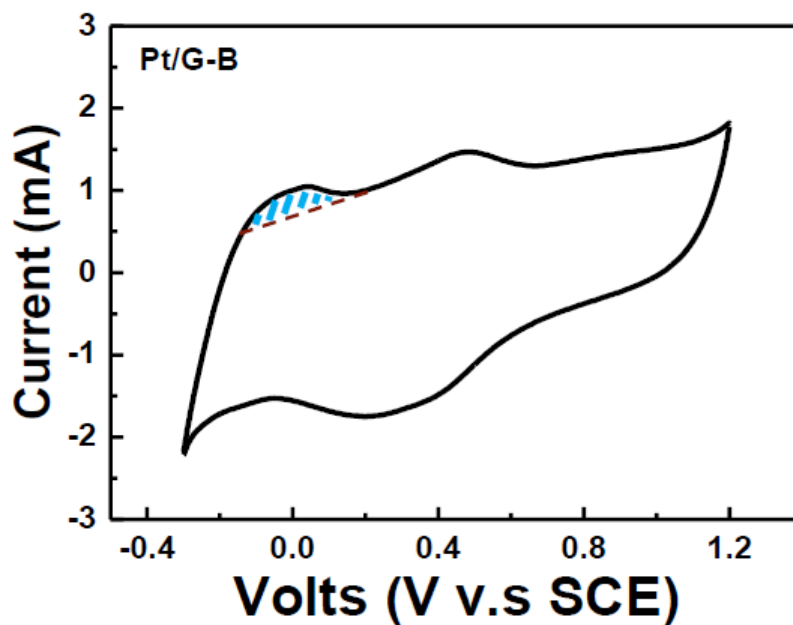


Fig. 5 Cyclic voltammograms of Pt/G-B in 0.5 M H<sub>2</sub>SO<sub>4</sub> at 25°C (5 mVs<sup>-1</sup>)

Table 4 Active Surface of Pt nanoparticles

Sample	Pt/G	Pt/G-B	Pt/G-T
Surface area (mg/mC)	9.8 (100%)	22.0 (224%)	15.7 (160%)

The H-desorption is directly proportional to the area of the Pt surface participating in the electrochemical process.

The integrated area (H-desorption) corresponding to desorption of H<sub>2</sub> indicates that metallic Pt nanoparticles on the Pt/G-B substrate have a larger active surface than those on Pt/G and Pt/GT substrates.



### 3. Catalytic Activity of Electrode

The peak current ( $I_p$ ) corresponds to the catalytic activity of the Pt-based catalysts

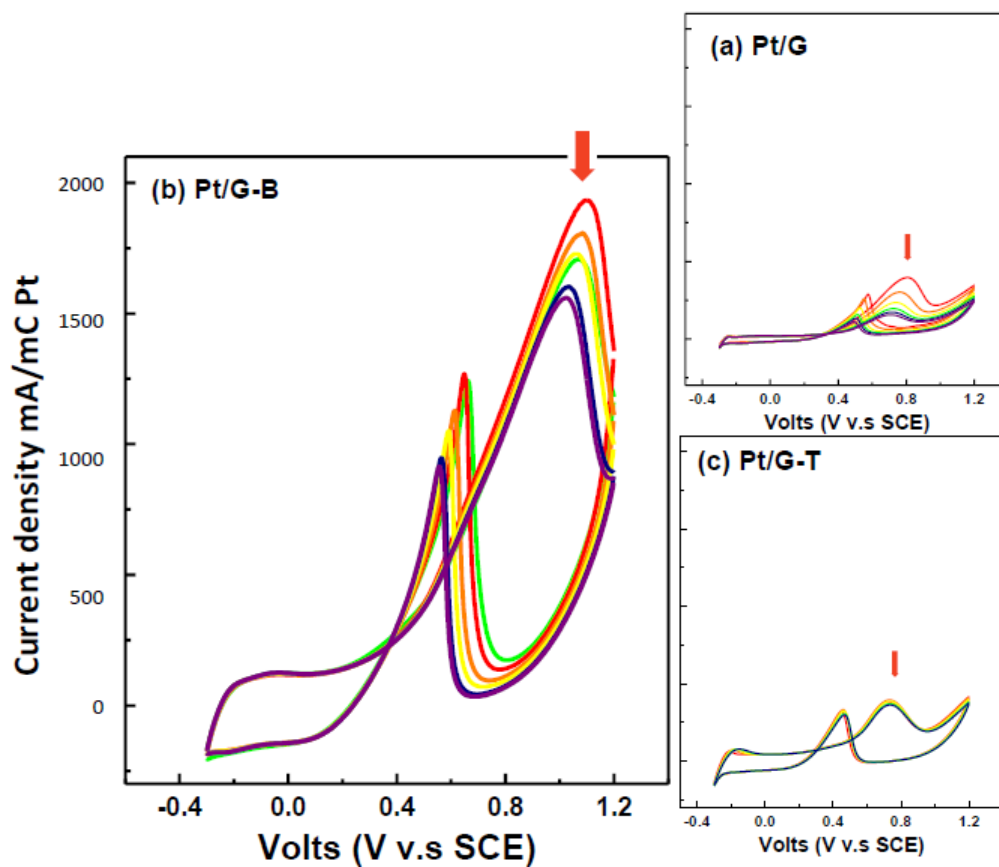


Fig. 6 Cyclic voltammograms ( $5 \text{ mVs}^{-1}$ ) of (a) Pt/G, (b) Pt/G-B, and (c) Pt/G-T vs. SCE in  $0.5 \text{ M H}_2\text{SO}_4 + 0.5 \text{ M CH}_3\text{OH}$  at  $25^\circ\text{C}$

- (1) Obviously, the electrocatalytic activity, known as y axis of current density, of the cell with a Pt/G-B substrate (2000) is significantly higher than these with Pt/G and Pt/G-T substrates ( $<400$ ).
- (2) The modified substrate (Pt/G-B, Pt/G-T) are more stable than non-modified electrode (Pt/G).

#### 4. Key parameters

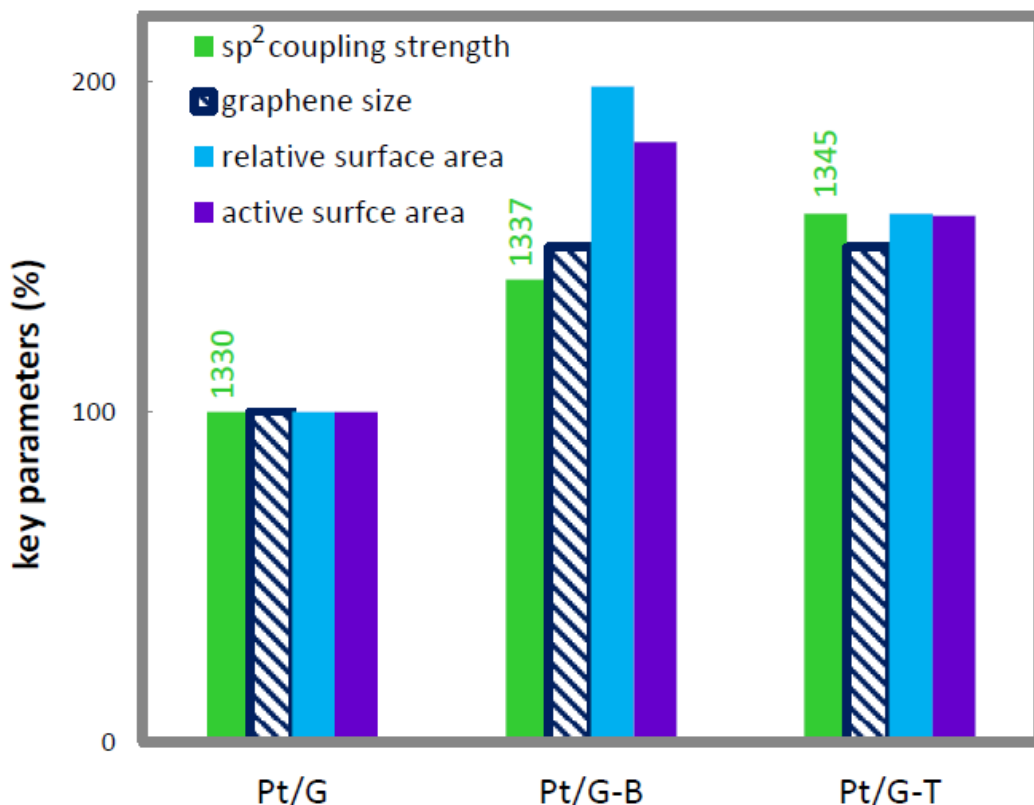


Fig. 7 Comparisons of the key parameters of the three graphene-based electrodes

- (1) The number of coupled graphene layers, active surface area, the catalytic Pt nanoparticle surface-area, the intra-layer sp<sup>2</sup> coupling of Pt/G-B are all considerably higher than those of Pt/G and Pt/G-T. The four parameters can effectively affect the electrical catalytic activity of the electrodes (Fig. 6(b)).
- (2) The interlayer bindings in Pt/G-B and Pt/G-T enhance the intra-layer sp<sup>2</sup> binding strength, which stabilizes the structure for a stable electrocatalytic activity through bias cycling (Fig. 6(b), 6(c)).

## Conclusions

1. The active surface area, the Pt particle size, the modified  $sp^2$  coupling strength, and the number of coupled graphene-layers are found to be the key parameters in catalytic activity of the electrode.
2. Modification does enhance the performance of the electrode. The modified electrode, Pt/G-B and Pt/G-T, are more stable than the non-modified electrode, Pt/G. More likely, due to the enhancement of the  $sp^2$  intralayer binding strength, the modified electrodes are more stable than non-modified electrode.
3. The modified electrode, Pt/G-B, provides better performance than Pt/G-T and the non-modified electrode, Pt/G. Among the modified electrodes, Pt/G-B has better catalytic performance than Pt/G-T.

## References

1. Xin, Y., J.-g. Liu, et al, 2011, Preparation and characterization of Pt supported on graphene with enhanced electrocatalytic activity in fuel cell, *Journal of Power Sources*, 196(3), 1012-1018.
2. Li, Y., L. Tang, et al, 2009, Preparation and electrochemical performance for methanol oxidation of pt/graphene nanocomposites, *Electrochemistry Communications* 11(4), 846-849.
3. Stankovich, S., R. Piner, et al, 2006, Synthesis and exfoliation of isocyanate-treated graphene oxide nanoplatelets, *Carbon* 44(15), 3342-3347.
4. Srinivas, G., J. W. Burrell, et al, 2011, Porous graphene oxide frameworks: Synthesis and gas sorption properties, *Journal of Materials Chemistry* 21(30), 11323-11329.
5. Hummers, W. S. and R. E. Offeman, 1958, Preparation of Graphitic Oxide, *Journal of the American Chemical Society* 80(6), 1339-1339.
6. Frelink, T., W. Visscher, et al, 1995, Particle size effect of carbon-supported platinum catalysts for the electrooxidation of methanol, *Journal of Electroanalytical Chemistry* 382(1-2), 65-72.
7. Stankovich, S., D. A. Dikin, et al, 2007, Synthesis of graphene-based nanosheets via chemical reduction of exfoliated graphite oxide, *Carbon* 45(7), 1558-1565.
8. Jiajun, W., Geping Y., et al, 2007, Effect of carbon black support corrosion on the durability of Pt/C catalyst, *Journal of Power Sources*, 171(2), 331–339.
9. Chang Hyeong Lee, Chi Woo Lee, et al, Electrooxidation of methanol on Pt–Ru catalysts supported by basal plane graphite in phosphoric acid solution, *Journal of Power Sources* 86(1-2), 478-481.

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## 評語

作者利用化學藥劑前修飾石墨烯，具含化學反應顯示對甲醇的反應比較未修飾的石墨烯優異。作者的觀念清晰，表達順暢，作品完整，值得獎勵。