

## Dear Author

Here are the proofs of your article.

- You can submit your corrections **online**, via **e-mail** or by **fax**.
- For **online** submission please insert your corrections in the online correction form. Always indicate the line number to which the correction refers.
- You can also insert your corrections in the proof PDF and **email** the annotated PDF.
- For **fax** submission, please ensure that your corrections are clearly legible. Use a fine black pen and write the correction in the margin, not too close to the edge of the page.
- Remember to note the **journal title**, **article number**, and **your name** when sending your response via e-mail or fax.
- **Check** the metadata sheet to make sure that the header information, especially author names and the corresponding affiliations are correctly shown.
- **Check** the questions that may have arisen during copy editing and insert your answers/corrections.
- **Check** that the text is complete and that all figures, tables and their legends are included. Also check the accuracy of special characters, equations, and electronic supplementary material if applicable. If necessary refer to the *Edited manuscript*.
- The publication of inaccurate data such as dosages and units can have serious consequences. Please take particular care that all such details are correct.
- Please **do not** make changes that involve only matters of style. We have generally introduced forms that follow the journal's style.
- Substantial changes in content, e.g., new results, corrected values, title and authorship are not allowed without the approval of the responsible editor. In such a case, please contact the Editorial Office and return his/her consent together with the proof.
- If we do not receive your corrections **within 48 hours**, we will send you a reminder.
- Your article will be published **Online First** approximately one week after receipt of your corrected proofs. This is the **official first publication** citable with the DOI. **Further changes are, therefore, not possible.**
- The **printed version** will follow in a forthcoming issue.

### Please note

After online publication, subscribers (personal/institutional) to this journal will have access to the complete article via the DOI using the URL:

<http://dx.doi.org/10.1007/s10008-013-2325-7>

If you would like to know when your article has been published online, take advantage of our free alert service. For registration and further information, go to:

<http://www.springerlink.com>.

Due to the electronic nature of the procedure, the manuscript and the original figures will only be returned to you on special request. When you return your corrections, please inform us, if you would like to have these documents returned.

**Metadata of the article that will be visualized in OnlineFirst**

1	Article Title	<b>Preparation and electrochemical performance of graphene–Pt black nanocomposite for electrochemical methanol oxidation</b>	
2	Article Sub- Title		
3	Article Copyright - Year	<b>Springer-Verlag Berlin Heidelberg 2013 (This will be the copyright line in the final PDF)</b>	
4	Journal Name	Journal of Solid State Electrochemistry	
5		Family Name	<b>Chekin</b>
6		Particle	
7		Given Name	<b>Fereshteh</b>
8	Corresponding	Suffix	
9	Author	Organization	Islamic Azad University
10		Division	Department of Chemistry
11		Address	Ayatollah Amoli Branch, Amol, Iran
12		e-mail	fchekin@yahoo.com
13		Family Name	<b>Bagheri</b>
14		Particle	
15		Given Name	<b>Samira</b>
16		Suffix	
17	Author	Organization	University of Malaya
18		Division	Centre for Research in Nanotechnology & Catalysis (NANOCEN)
19		Address	IPS Building, Kuala Lumpur 50603, Malaysia
20		e-mail	
21		Family Name	<b>Hamid</b>
22		Particle	
23		Given Name	<b>Sharifah Bee Abd</b>
24		Suffix	
25	Author	Organization	University of Malaya
26		Division	Centre for Research in Nanotechnology & Catalysis (NANOCEN)
27		Address	IPS Building, Kuala Lumpur 50603, Malaysia
28		e-mail	
29	Schedule	Received	31 July 2013

30		Revised	5 November 2013
31		Accepted	7 November 2013
32	Abstract	<hr/> <p>This work reports the preparation, characterization, and electrocatalytic characteristics of a new metallic nanocatalyst. The catalyst, Pt black-graphene oxide (Pt-GO), was prepared by deposition of Pt black on the surface of graphene oxide nanosheet and characterized by transmission electron microscopy (TEM), energy-dispersive spectroscopy (EDS), and voltammetry. The Pt-graphene (Pt-GR) composite modified glassy carbon electrode (Pt-GR/GCE) was prepared with cyclic voltammetric scanning of Pt-GO/GCE in the potential range from <math>-1.5</math> to <math>0.2</math> in <math>0.1</math> M phosphate buffer solution at <math>50 \text{ mV}\cdot\text{s}^{-1}</math> for 5 cycles. The electrocatalytic properties of the Pt-GR/GCE for methanol (<math>\text{CH}_3\text{OH}</math>) oxidation have been investigated by cyclic voltammetry (CV); high electrocatalytic activity of the Pt-GR/GCE can be observed. This may be attributed to the high dispersion of Pt catalyst and the particular properties of GR support. The long-term stability of Pt-GR composite was investigated in <math>0.05</math> M <math>\text{CH}_3\text{OH}</math> in <math>0.1</math> M <math>\text{H}_2\text{SO}_4</math> solution. It can be observed that the peak current decreases gradually with the successive scans. The loss may result from the consumption of methanol during the CV scan. It also may be due to the poisoning organic compounds. The results imply that the Pt-GR composite has good potential applications in fuel cells.</p> <hr/>	
33	Keywords separated by ' - '	Platin black - Graphene - Methanol - Electrocatalysis - Catalyst	
34	Foot note information	<hr/>	

# Preparation and electrochemical performance of graphene–Pt black nanocomposite for electrochemical methanol oxidation

Fereshteh Chekin · Samira Bagheri ·  
Sharifah Bee Abd Hamid

Received: 31 July 2013 / Revised: 5 November 2013 / Accepted: 7 November 2013  
© Springer-Verlag Berlin Heidelberg 2013

**Abstract** This work reports the preparation, characterization, and electrocatalytic characteristics of a new metallic nanocatalyst. The catalyst, Pt black–graphene oxide (Pt-GO), was prepared by deposition of Pt black on the surface of graphene oxide nanosheet and characterized by transmission electron microscopy (TEM), energy-dispersive spectroscopy (EDS), and voltammetry. The Pt-graphene (Pt-GR) composite modified glassy carbon electrode (Pt-GR/GCE) was prepared with cyclic voltammetric scanning of Pt-GO/GCE in the potential range from  $-1.5$  to  $0.2$  in  $0.1$  M phosphate buffer solution at  $50 \text{ mV}\cdot\text{s}^{-1}$  for 5 cycles. The electrocatalytic properties of the Pt-GR/GCE for methanol ( $\text{CH}_3\text{OH}$ ) oxidation have been investigated by cyclic voltammetry (CV); high electrocatalytic activity of the Pt-GR/GCE can be observed. This may be attributed to the high dispersion of Pt catalyst and the particular properties of GR support. The long-term stability of Pt-GR composite was investigated in  $0.05$  M  $\text{CH}_3\text{OH}$  in  $0.1$  M  $\text{H}_2\text{SO}_4$  solution. It can be observed that the peak current decreases gradually with the successive scans. The loss may result from the consumption of methanol during the CV scan. It also may be due to the poisoning organic compounds. The results imply that the Pt-GR composite has good potential applications in fuel cells.

**Keywords** Platin black · Graphene · Methanol ·  
Electrocatalysis · Catalyst

F. Chekin (✉)  
Department of Chemistry, Islamic Azad University, Ayatollah Amoli  
Branch, Amol, Iran  
e-mail: fchekin@yahoo.com

S. Bagheri · S. B. A. Hamid  
Centre for Research in Nanotechnology & Catalysis (NANOCEN),  
University of Malaya, IPS Building, 50603 Kuala Lumpur, Malaysia

## Introduction

Among the different types of supports used in heterogeneous catalysis, carbon materials attract a growing interest due to their specific characteristics [1]. It is observed that the structures and properties of carbon support, such as surface function groups [2], graphitization structure [3, 4], and surface area [5] have a large effect on the activity of the catalyst, so they attracted numerous interests in recent years in many fields, such as capacitor, catalyst or fuel cells, and batteries [6]. Various carbon allotropes, including graphite, diamond, fullerenes, and carbon nanotubes (CNTs), have very different electrochemical properties from each other [7]. Graphene was the missing allotrope of pure carbon materials. Graphene, a basic building block in all graphitic materials, is a single layer of carbon atoms arranged in a hexagonal lattice [8]. Graphene exhibits unique structure-dependent electronic, mechanical, and chemical properties and has a high surface area ( $2,630\text{--}2,965 \text{ m}^2\cdot\text{g}^{-1}$ ) [9–11]. Especially, graphene has a potential application as a heterogeneous catalyst support in direct methanol fuel cells [12–15].

Direct methanol fuel cells (DMFCs) have been considered the ideal fuel cell system for fuel cell-based mobile power supply systems. Indeed, there are certain advantages to be found in the use of methanol as fuel, not the least of which is its high energy density and the fact that it stays in liquid state at room temperature [16]. However, there are some unsolved technical problems involved in the commercialization of DMFCs: the high loading of noble metal electrocatalysts, the slow kinetics of electrode reaction, the crossover of methanol through the membrane, etc. [17, 18].

Several materials have been tested as electrocatalysts for small organic molecules, such as Pt, its alloys Pt–M ( $M = \text{Sn}, \text{Rh}, \text{Ru}$ ) in binary or ternary form [19–23] and even different methods to prepare Pt thin-film electrodes [24]. Pt-based catalysts are recognized as the best electrocatalysts for low-temperature fuel cells. The slow dissociative adsorption (dehydrogenation) of methanol results in the formation of

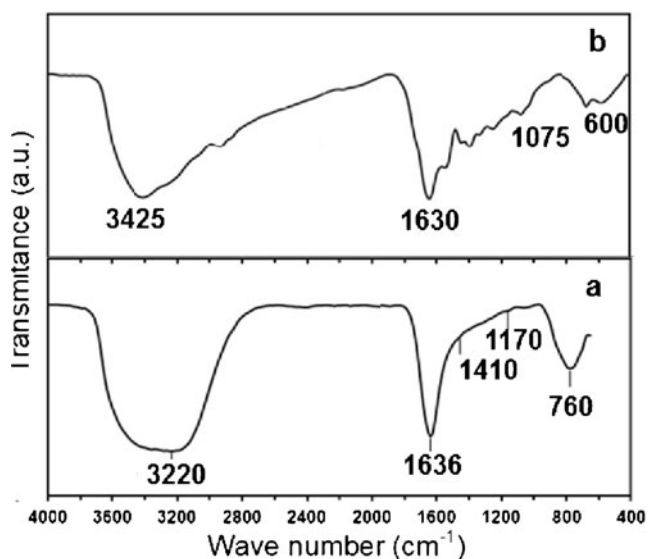


Fig. 1 FT-IR spectra of a GO and b Pt-GO

77 CO<sub>ad</sub> species [25], which poisons the Pt catalyst by blocking  
 78 the surface. To date, efforts have been focused on the develop-  
 79 ment of techniques to produce Pt catalyst with high surface area  
 80 [26]. The carbon-supported Pt-based catalysts were widely  
 81 used with improved long-term resistance and poison tolerance.

82 In this work, a different method was proposed for the  
 83 preparation of Pt/graphene oxide composite where graphene  
 84 oxide was synthesized from graphite using the simplified  
 85 Hummers' method and Pt black was deposited on graphene  
 86 oxide sheets and their electrocatalytic activity for methanol  
 87 oxidation was investigated. Several experiments such as effect  
 88 of methanol oxidation, effect of scan rate, chronoamperometry  
 89 (CA), and long-term stability were carried out.

## 90 Experimental

### 91 Chemicals and apparatus

92 Graphite flakes were purchased from Asbury Graphite Mills,  
 93 Inc (Asbury, NJ). Sulfuric acid (H<sub>2</sub>SO<sub>4</sub>, 98 %) and methanol

Fig. 2 TEM images of a GO and b Pt-GO

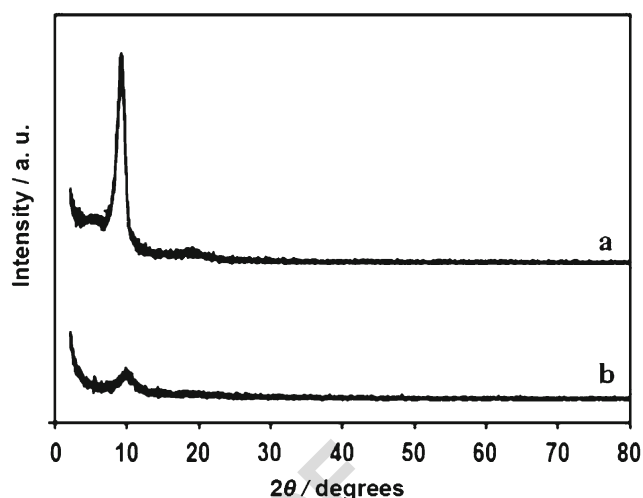
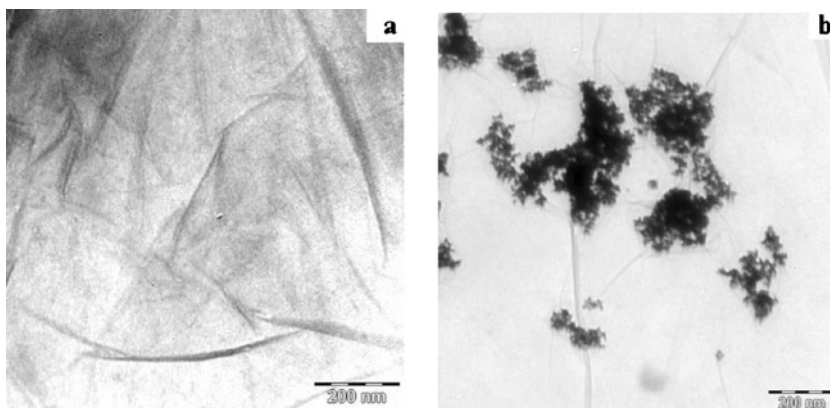


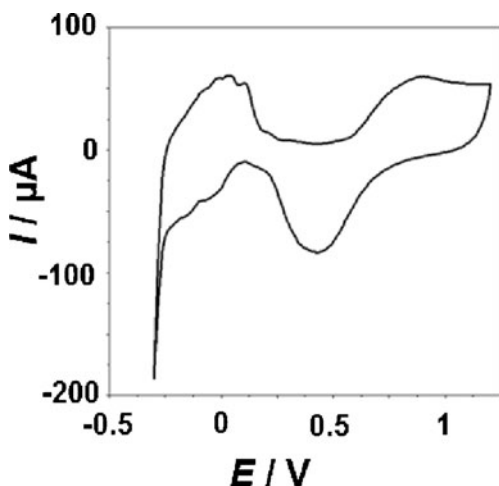
Fig. 3 XRD images of a GO and b Pt-GO

(CH<sub>3</sub>OH, 99.8 %) were from Sigma Aldrich. All other  
 94 chemicals were analytical grade and were used as purchased.  
 95

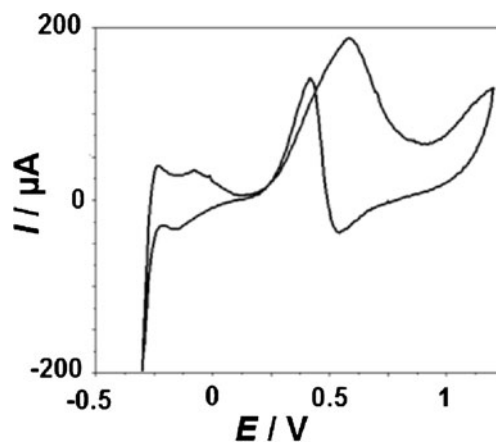
96 Electrochemical measurements were performed with an  
 97 Autolab Potentiostat/Galvanostat (Netherlands). The three-  
 98 electrode system, which consists of a Pt-GR/GCE as working  
 99 electrode and Ag|AgCl|KCl<sub>3M</sub> as the reference electrode, and  
 100 a platinum wire as an auxiliary electrode (Metrohm), was used  
 101 in all voltammetric experiments. The LEO-Libra 120 micro-  
 102 scope was employed for GO and Pt-GO transmission electron  
 103 microscopy (TEM) images.

### 104 Preparation of Pt-GR composite

105 Graphene oxide was fabricated based on the reported proce-  
 106 dure [27]. Prior to modification, the bare GCE was polished  
 107 on chamois leather with 0.05 μm alumina powder. Then it was  
 108 thoroughly sonicated in deionized water and absolute ethanol,  
 109 respectively. One milliliter of synthesized graphene oxide gel  
 110 and 1 mg of Pt black were dispersed in 5 mL water with the aid  
 111 of ultrasonic agitation. The cleaned GCE was coated by  
 112 casting 5 μL of the dispersed solution and dried at 50 °C in  
 113 an oven air to remove the solvent. The Pt-GR composite



**Fig. 4** Cyclic voltammograms of Pt-GR/GCE in 0.1 M H<sub>2</sub>SO<sub>4</sub> solution at scan rate 50 mV·s<sup>-1</sup>



**Fig. 6** Cyclic voltammograms of Pt-GR/GCE in 0.1 M H<sub>2</sub>SO<sub>4</sub> solution in the presence of 0.05 M methanol at scan rate 100 mV·s<sup>-1</sup>

114 modified glassy carbon electrode (Pt-GR/GCE) was prepared  
 115 with cyclic voltammetric scanning of Pt-GO/GCE in the po-  
 116 tential range from -1.5 to 0.2 in 0.1 M phosphate buffer  
 117 solution at 50 mV·s<sup>-1</sup> for 5 cycles [28, 29].

**Results and discussion**

FT-IR studies

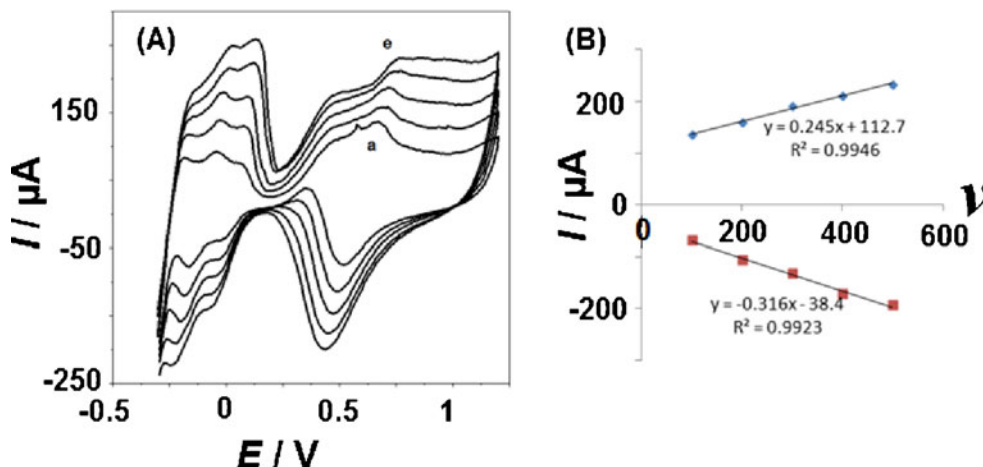
120 The Fourier transform infrared spectroscopy (FT-IR) spectra  
 121 of GO (Fig. 1a) shows a broad band at 3,320 cm<sup>-1</sup>, which was  
 122 related to the OH groups, and band at 1,637 cm<sup>-1</sup>, which is  
 123 typical of carboxyl and carbonyl groups. Besides, other C–O  
 124 functionalities such as C–OH (1,410 cm<sup>-1</sup>) and C–O–C  
 125 (1,170 cm<sup>-1</sup>) are also clearly visible. Furthermore, the band at  
 126 760 cm<sup>-1</sup> is because of epoxy symmetrical ring deformation.  
 127 These main characteristic peaks indicated that GO had been

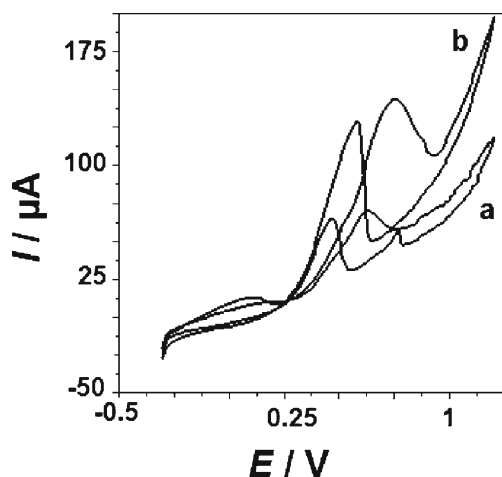
synthesized successfully. Also, the decoration of the surface  
 of the graphene oxide sheets by Pt was discussed by FT-IR spectroscopy. FT-IR spectrum (Fig. 1b) revealed that the resultant Pt-GO contained several functional groups like -OH (3,425 cm<sup>-1</sup>), C–O (1,075 cm<sup>-1</sup>) and C = O (1,630 cm<sup>-1</sup>). Therefore, it has a strong tendency to readily interact with Pt by hydroxyl and carboxyl groups. A peak at 600 cm<sup>-1</sup> was signified the formation of Pt–O bond.

TEM studies

As shown in Fig. 2a, it can be seen that GO was fully exfoliated into nanosheet with micrometer-long wrinkles by ultrasonic treatment, illustrating clearly the flake-like shapes of graphite oxide sheets. The typical TEM image of Pt-GO nanocomposite (Fig. 2b) illustrated that the Pt clusters were deposited on the basal planes and the edges of graphene. GOs are easily dispersed in water because of the oxygen-containing groups. Furthermore, these oxygenated functional groups, such as epoxy, hydroxyl (-OH), carboxyl (-COOH), and

**Q4 Fig. 5 a** Cyclic voltammograms of Pt-GR/GCE in 0.1 M H<sub>2</sub>SO<sub>4</sub> solution at different scan rates. The scan rates are (a) 100, (b) 200, (c) 300, (d) 400, and (e) 500 mV·s<sup>-1</sup>, respectively. **b** The plot of cathodic and anodic peak currents vs. scan rates





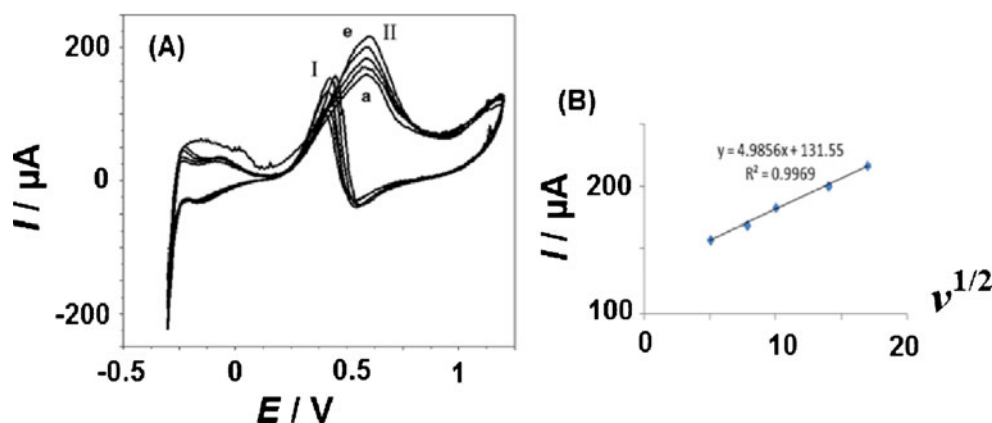
**Fig. 7** Cyclic voltammograms of **a** Pt-GO/GCE and **b** Pt-GR/GCE in 0.1 M H<sub>2</sub>SO<sub>4</sub> solution in the presence of 0.05 M methanol at scan rate 50 mV s<sup>-1</sup>

146 carbonyl (–C = O) groups attached on both sides and edges of  
 147 carbon sheets. These surface functional groups will subse-  
 148 quently act as anchoring sites for metal complexes [30].

149 XRD studies

150 Powder X-ray diffraction (XRD) is an effective method to  
 151 investigate the interlayer changes and the crystalline prop-  
 152 erties of synthesized samples. Figure 3 shows the XRD patterns  
 153 of synthesized GO and Pt-GO samples. As seen in Fig. 3a, the  
 154 GO shows a very sharp diffraction peak at 9.2° corresponding  
 155 to the (002) reflection. As compared to GO, Pt-GO (Fig. 3b)  
 156 shows a broader diffraction peak at 2θ = 10°. In addition, a  
 157 broad diffraction peak of Pt-GO implicates that the Pt can  
 158 influence the crystallization of sample. Also, the diffraction  
 159 peak of Pt-GO shifted towards higher 2θ values, we suspect  
 160 that the shift might be attributed to the functionalization of  
 161 graphene oxide sheets, where the Pt was intercalated into  
 162 interlayer spacing of GO. Pt phase has not been detected in  
 163 the XRD patterns of Pt-GO, possibly because the Pt content  
 164 on GO surface is not enough to clearly form crystalline.

**Fig. 8 a** Cyclic voltammograms of the Pt-GR/GCE in 0.1 M H<sub>2</sub>SO<sub>4</sub> solution in the presence of 0.05 M methanol at different scan rates: (a) 25, (b) 50, (c) 100, (d) 200, and (e) 400 mV·s<sup>-1</sup>, respectively. **b** The anodic peak current  $I_p$  vs.  $\nu^{1/2}$



Electrochemical activity of Pt-GR/GCE

165

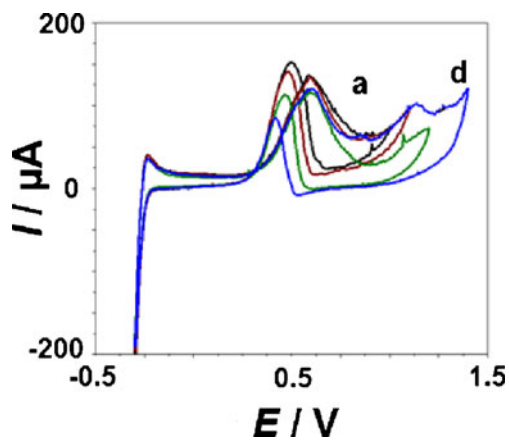
To evaluate the electrochemical activity of Pt-GR nanocom-  
 166 posite, cyclic voltammograms, experiments were tested within  
 167 a potential range from -0.3 to 1.2 V at a scanning rate of  
 168 50 mV·s<sup>-1</sup> in the solution of 0.1 M H<sub>2</sub>SO<sub>4</sub>. As seen from  
 169 Fig. 4, the Pt-GR film deposited on a glassy carbon electrode  
 170 was electrochemically active in which hydrogen adsorption  
 171 characteristics were presented. The electrochemically active  
 172 surface area (ECSA) was estimated by integrating the voltam-  
 173 mograms corresponding to hydrogen desorption from the  
 174 electrode surface [31]. The ECSA for the Pt/GR was estimated  
 175 to be 31.8 m<sup>2</sup>·g<sup>-1</sup> Pt, and the high ECSA was because of the  
 176 high theoretical specific surface area of graphene as a two-  
 177 dimensional (2D) nanomaterial that allows easy deposition of  
 178 the metal catalyst. This is due to the presence of 2D flat planes  
 179 and oxygen-containing groups.

The redox potential of the Pt-GR/GCE is scan rate depen-  
 181 dent. Figure 5a shows the cyclic voltammograms of the Pt-  
 182 GR/GCE in the solution of 0.1 M H<sub>2</sub>SO<sub>4</sub> at various scan rates.  
 183 It was observed that the values of  $E_{pa}$  and  $E_{pc}$  shift slightly to  
 184 the positive and negative directions, respectively, and  $\Delta E_p$   
 185 increases with increasing scan rate. The anodic and cathodic  
 186 peak currents are linearly proportional to scan rate (Fig. 5b),  
 187 suggesting that the reaction is not a diffusion-controlled pro-  
 188 cess but a surface-controlled one, as expected for immobilized  
 189 systems.

Electrocatalytic activity toward methanol oxidation

191

To evaluate the activity of the Pt-GR catalyst toward the  
 192 methanol electrooxidation, cyclic voltammogram experiments  
 193 were tested in the solution of 0.05 M CH<sub>3</sub>OH in 0.1 M H<sub>2</sub>SO<sub>4</sub>.  
 194 The cycling was repeated until a reproducible CV curve was  
 195 obtained before the measurement curves were recorded. As  
 196 seen from Fig. 6, a large methanol oxidation peak was ob-  
 197 served at +0.57 V and another peak of methanol oxidation was  
 198 seen at +0.43 V on the reverse scan. The peak current density  
 199 of Pt at the potential of 0.57 V was 58.83 mA·mg<sup>-1</sup> Pt which  
 200

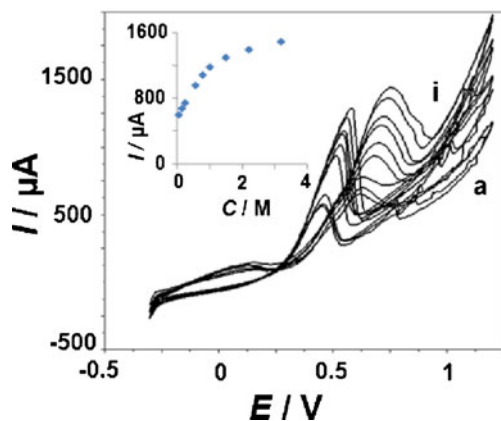


**Fig. 9** Cyclic voltammograms of the Pt-GR/GCE in 0.1 M H<sub>2</sub>SO<sub>4</sub> solution in the presence of 0.05 M methanol at different scan upper limits

201 indicates a high electrocatalytic activity in the methanol oxida-  
 202 tion reaction. This may be attributed to special frame and  
 203 properties of graphene can remove the intermediates poison-  
 204 ing in methanol oxidation. Also, the interaction between Pt  
 205 and GR may change the Gibbs energy of reaction products or  
 206 by-products [32]. A comparison electrocatalytic activity be-  
 207 tween Pt-GO/GCE and Pt-GR/GCE was carried out by cyclic  
 208 voltammetry in 0.05 M CH<sub>3</sub>OH+0.1 M H<sub>2</sub>SO<sub>4</sub> solution at  
 209 scan rate of 50 mV·s<sup>-1</sup> as shown in Fig. 7. The results indicate  
 210 that the Pt-GR/GCE substrate gives comparable electrochemi-  
 211 cal activity to Pt-GO/GCE.

212 Figure 8a shows the CVs of 0.05 M CH<sub>3</sub>OH in 0.1 M  
 213 H<sub>2</sub>SO<sub>4</sub> solution at various scan rates. The current of peak 2  
 214 was linearly proportional to the square root of scan rate within  
 215 some range (Fig. 8b), which indicates that oxidation may be  
 216 controlled by a diffusion process in a range of scan rates.  
 217 The diffusion coefficient of methanol in solution is calculated  
 218 6.4 × 10<sup>-6</sup> cm<sup>2</sup>·s<sup>-1</sup> using cyclic voltammetry.

219 CVs of 0.05 M CH<sub>3</sub>OH in 0.1 M H<sub>2</sub>SO<sub>4</sub> at Pt-GR/GCE  
 220 with different scan upper limits is shown in Fig. 9. It can be



**Fig. 10** Cyclic voltammograms of the Pt-GR/GCE in the presence of (a) 0.04, (b) 0.15, (c) 0.25, (d) 0.55, (e) 0.78, (f) 1.00, (g) 1.50, (h) 2.20, and (i) 3.20 M of methanol in 0.1 M H<sub>2</sub>SO<sub>4</sub> solution at a scan rate of 50 mV·s<sup>-1</sup>; Inset: plot of catalytic current vs. methanol concentration

**Table 1** Comparison of electrocatalytic activity of different electrode surfaces in 0.5 M CH<sub>3</sub>OH in 0.1 M H<sub>2</sub>SO<sub>4</sub> at a scan rate of 50 mV·s<sup>-1</sup>

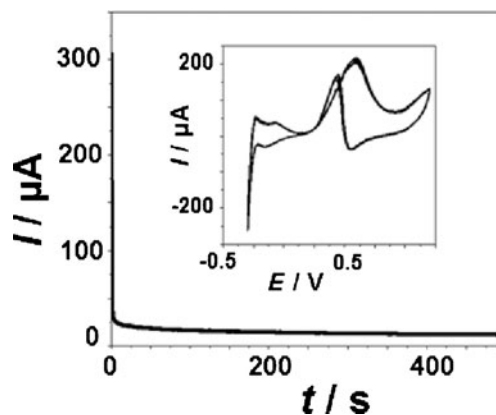
Electrode	<i>I</i> <sub>pa</sub> (mA/cm <sup>2</sup> )	<i>E</i> <sub>pa</sub> (mV)	Reference
Pt-MWNT/GC	3	700	[8]
Graphene/Pt/GC	45	652	[30]
Graphene/Pt/GC	19.1	650	[32]
Pt-Pd/GC	113	1,230	[34]
Pt-Ru/GC	108.4	1,119	[34]
Pt-Au-graphene/GC	4.8	600	[35]
Pt/RGO <sup>a</sup> /GC	9	700	[36]
Pt-G <sup>b</sup> /GC	7	570	[37]
Pt-GR/GC	58.8	610	This work

<sup>a</sup> Reduced graphene

<sup>b</sup> Oxide graphene sheets

221 observed that the potential of peak 1 shifts negatively with the  
 222 increasing scan upper limit while peak 2 almost remains the same;  
 223 this demonstrates that the oxidation of CH<sub>3</sub>OH be-  
 224 comes much easier to occur. So the oxidation of CH<sub>3</sub>OH is  
 225 through two approaches, the adsorptive productions and reac-  
 226 tion intermediates. With the positive shift of the scan upper  
 227 limit, the adsorptive by-products are oxidized sufficiently; this  
 228 can reduce the poisoning of catalysts. On the clean electrode  
 229 surface, the oxidation process through the intermediate be-  
 230 comes much easier, which can be seen from the negative shift  
 231 of peak 1.

232 Figure 10 shows the behavior of Pt-GR/GCE in the pres-  
 233 ence of different methanol concentrations of 0.04–3.2 M at the  
 234 scan rate of 50 mV·s<sup>-1</sup>, respectively. It is clearly observed that  
 235 the anodic current increases linearly with increasing methanol  
 236 concentration up to 1.0 M. The results indicated that the Pt-  
 237 GR composite can be an efficient catalyst for electrooxidation  
 238 of methanol. A comparison between the electrochemical activi-  
 239 ties toward methanol electrooxidation of Pt-GR/GCE to



**Fig. 11** Chronoamperometric curve for Pt-GR/GCE in 0.1 M H<sub>2</sub>SO<sub>4</sub> solution containing 0.05 M CH<sub>3</sub>OH at a fixed potential of 0.65 V. Inset: successive scans of Pt-GR/GCE in 0.1 M H<sub>2</sub>SO<sub>4</sub> solution containing 0.05 M CH<sub>3</sub>OH at a scan rate of 100 mV·s<sup>-1</sup>



240 some other surfaces used in other literatures is illustrated in  
 241 Table 1 [8, 32–37]. It is clear that the electrochemical activity  
 242 of our method is comparable with other results, which indicated  
 243 that the proposed method might be reliable and effective  
 244 in applications.

#### 245 Long-term stability of Pt-GR composite

246 The catalytic stability of the Pt-GR/GCE was examined using  
 247 chronoamperometry. Figure 11 shows the chronoamperometry  
 248 curve of 0.05 M CH<sub>3</sub>OH in 0.1 M H<sub>2</sub>SO<sub>4</sub> solution for the  
 249 Pt/GR catalyst modified electrode at a fixed potential of  
 250 0.65 V. For Pt/GR catalyst, the potentiostatic current decreased  
 251 rapidly at the initial stage, which might be due to the  
 252 formation of intermediate species, such as CO<sub>ads</sub>, CHO<sub>ads</sub>,  
 253 etc., during the methanol oxidation reaction [38]. Gradually,  
 254 the current decayed and a pseudo-steady state was achieved.  
 255 Also, the long-term stability of Pt-GR composite was investigated  
 256 in 0.05 M CH<sub>3</sub>OH in 0.1 M H<sub>2</sub>SO<sub>4</sub> solution by cyclic  
 257 voltammetry (Fig. 9, Inset). It can be observed that the peak  
 258 current decreases gradually with the successive scans. The  
 259 loss may result from the consumption of methanol during  
 260 the CV scan. It also may be due to the poisoning organic  
 261 compound.

#### 262 Conclusions

263 In the present work, Pt-GR catalyst was prepared by a typical  
 264 aqueous solution of Pt black on graphene oxide. TEM studies  
 265 show that well-dispersed, spherical particles were anchored  
 266 onto on the basal planes and the edges of graphene. The  
 267 electrocatalytic property of Pt-GR/GCE for methanol oxidation  
 268 has been investigated and high electrocatalytic activity is  
 269 observed. This may be attributed to the high dispersion of  
 270 platinum catalyst and the particular properties of graphene.

#### 271 References

- 273 1. Serp P, Corrias M, Kalck P (2003) *App Catal* 253:337–358
- 274 2. Xing YC, Li L, Chusuei CC, Hull RV (2005) *Langmuir* 21:4185–
- 275 4190
- 276 3. Bom D, Andrews R, Jacques D, Anthony J, Chen BL, Meieve MS,
- 277 Seleque JP (2002) *Nano Lett* 2:615–619

4. Stevens DA, Hicks MT, Haugen GM, Dahn JR, Stevens DA, Hicks 278  
 MT, Haugen GM, Dahn JR (2005) *J Electrochem* 152:2309–2315 279
5. Bong S, Jang B, Woo S, Piao Y (2013) *Int J Electrochem Sci* 8:7510– 280  
 7517 281
6. Tang L, Wang Y, Li Y, Feng H, Lu J, Li J (2009) *Adv Funct Mater* 19: 282  
 2782–2789 283
7. Peres NMR (2009) *Vacuum* 83:1248–1258 284
8. Li Y, Gao W, Ci L, Wang C, Ajayan PM (2010) *Carbon* 48:1124–1130 285
9. Geim AK, Novoselov KS (2007) *Nat Mater* 6:183–191 286
10. Zhu J (2008) *Nat Nanotechnol* 3:528–529 287
11. Li D, Kaner RB (2008) *Science* 320:1170–1171 288
12. Xu C, Wang X, Zhu JW (2008) *J Phys Chem C* 112:19841–19845 289
13. Si YC, Samulski ET (2008) *Chem Mater* 20:6792–6797 290
14. Seger B, Kamat PV (2009) *J Phys Chem C* 113:7990–7995 291
15. Yoo EJ, Okata T, Akita T, Kohyama M, Nakamura J, Honma I (2009) 292  
*Nano Lett* 9:2255–2259 293
16. Arico AS, Srinivasan S, Antonucci V (2001) *Fuel Cells* 1:133–161 294
17. Carrette L, Friedrich KA, Stimming U (2000) *Chem Phys Chem* 1: 295  
 162–193 296
18. Dillon R, Srinivasan S, Arico AS, Antonucci V (2004) *J Power 297*  
*Source* 127:112–126 298
19. Panja C, Saliba N, Koel BE (1998) *Surf Sci* 395:248–259 299
20. De Souza JPI, Queiroz SL, Bergamaski K, Gonzalez ER, Nart FC 300  
 (2002) *J Phys Chem B* 106:9825–9830 301
21. Freitas RG, Santos MC, Oliveira RTS, Bulhoes LOS, Pereira EC 302  
 (2006) *J Power Sources* 158:164–168 303
22. Freitas RG, Marchesi LF, Oliveira RTS, Mattos-Costa FI, Pereira EC, 304  
 Bulhoes LOS, Santos MC (2007) *J Power Sources* 171:373–375 305
23. Dubau L, Hahn F, Coutanceau C, Leger JM, Lamy C (2003) *J 306*  
*Electroanal Chem* 554:407–415 307
24. Freitas RG, Oliveira RTS, Santos MC, Bulhoes LOS, Pereira EC 308  
 (2006) *Mater Lett* 60:1906–1910 309
25. Freitas RG, Antunes EP, Pereira EC (2009) *Electrochim Acta* 54: 310  
 1999–2003 311
26. Bozzini B, De Gaudenzi GP, Busson B, Humbert C, Six C, Gayral A, 312  
 Tadjeddine A (2010) *J Power Sources* 195:4119–4123 313
27. Hummers WS, Offeman RE (1958) *J Am Chem Soc* 80:1339–1339 314
28. Basirun WJ, Sookhakian M, Baradaran S, Mahmoudian MR, Ebadi 315  
 M (2013) *Nanoscale Res Lett* 8:397 316
29. Mahmoudian MR, Alias Y, Basirun WJ (2012) *Electrochim Acta* 72: 317  
 53–60 318
30. Hsin YL, Hwang KC, Yeh CT (2007) *J Am Chem Soc* 129:9999– 319  
 10010 320
31. Søgaard M, Odgaard M, Skou EM (2001) *Solid State Ionics* 145:31–35 321
32. Li Y, Tang L, Li J (2009) *Electrochem Commun* 11:846–849 322
33. Dong L, Reddy R, Gari S, Li Z, Craig MM, Hou S (2010) *Carbon* 48: 323  
 781–787 324
34. Galal A, Atta NF, Hassan HK (2012) *Int J Electrochem Sci* 7:768– 325  
 784 326
35. Hu Y, Zhang H, Wu P, Zhang H, Zhou B, Cai C (2011) *Phys Chem 327*  
*Chem Phys* 13:4083–4094 328
36. Sharma S, Ganguly A, Papakonstantinou P, Miao X, Li M, Hutchison 329  
 JL, Delichatsios M, Ukleja S (2010) *J Phys Chem C* 114:19459– 330  
 19466 331
37. Mayavan S, Sim JB, Choi SM (2012) *J Mater Chem* 22:6953–6958 332
38. Kabbabi A, Faure R, Durand R, Beden B, Hahn F, Leger JM, Lamy C 333  
 (1998) *J Electroanal Chem* 444:41–53 334

## AUTHOR QUERIES

### **AUTHOR PLEASE ANSWER ALL QUERIES.**

- Q1. Please check if the affiliations are presented correctly.
- Q2. Sentence has been modified for clarity. Please check if the original thought is retained.
- Q3. For consistency 'peak II' was changed to 'peak 2'. Please check if correct.
- Q4. Figures 5 & 8 contains poor quality of text. Please provide replacement. Otherwise, please advise if okay to proceed with the figure/s as is.

UNCORRECTED PROOF