

Short Communication

## Application of Platinum Nanoparticles Decorated Three-Dimensional Graphene Modified Electrode for Methanol Electrooxidation

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A three-dimensional graphene (3DGR) was synthesized by electrodeposition directly on carbon ionic liquid electrode (CILE) with N-butylpyridinium hexafluorophosphate. Nanosized Pt catalyst was further electrodeposited onto 3DGR/CILE with its properties investigated through electron microscopy and electrochemistry. Electrocatalytic performances of the modified electrode (Pt/3DGR/CILE) to methanol oxidation were investigated. Experimental results demonstrated that an enhanced efficiency of Pt/3DGR nanohybrid on the electrode surface for methanol oxidation with the enhancement of the ratio of forward to backward peak current ( $I_f/I_b$ ), which was due to the large surface area of nanohybrid with 3D porous structure of GR and higher dispersion of Pt nanoparticles onto the electrode surface.

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**Keywords:** Three-dimensional graphene, Platinum nanoparticles, Carbon ionic liquid electrode, Methanol, Electrooxidation.

### 1. INTRODUCTION

Graphene (GR) nanosheet is a monolayer of  $sp^2$ -bonded carbon atoms that in a two-dimensional honeycomb lattice, which has aroused many attentions because of its large surface area, good conductivity, excellent electrocatalytic activities, fast mobility of charge carriers [1]. The specific electrochemical performances of GR make it suitable for applications in electrochemistry and electrochemical sensors [2]. Different procedures have been devised for GR productions [3]. Among them electrochemical reduction of graphene oxide (GO) is an efficient method, which is green, fast and

easy to control [4,5]. By optimizing the electroreduction conditions, the oxygenal groups on GO surface are reduced with GR film directly deposited on the electrode.

Compared with unsupported Pt nanocatalysts, nanosized Pt on different supporter has good spatial separation and exhibits excellent catalytic activity with long-term stability [6-8]. GR has superior electrical conductivity, electrochemical stability and large surface area, which is an excellent support of catalyst for electrocatalytic applications [9]. The hybrids of GR with other metal nanomaterials have synergistic effects and can be used in electrocatalytic applications with enhanced catalytic activity. Many papers have been reported to the synthesis of GR-supported Pt nanomaterials with various usages [10,11].

In this paper a three-dimensional GR (3DGR) was synthesized by electrodeposition method with an N-butylpyridinium hexafluorophosphate (HPPF<sub>6</sub>) based carbon ionic liquid electrode (CILE). CILE is fabricated with ionic liquids (ILs) as the modifier or the binder in the carbon paste electrode (CPE) [12]. ILs have many specific characteristics including high ionic conductivity, wide electrochemical windows, good electrochemical stability, CILE has shown the advantages such as high conductivity, good electrocatalytic ability and certain antifouling ability [13], which is often used as the basic working electrode. Nanostructured Pt is further electrodeposited on the surface of 3DGR/CILE and the modified electrode is named as Pt/3DGR/CILE. Electrocatalytic performance of this modified electrode towards methanol oxidation was carefully investigated with increased performances.

## 2. EXPERIMENTAL

### 2.1. Reagents

HPPF<sub>6</sub> (Lanzhou Yulu Fine Chem. Co., China), graphite powder (particle size 30 μm, Shanghai Colloid Chem. Co., China), graphene oxide (GO, Taiyuan Tanmei Co., China), H<sub>2</sub>PtCl<sub>6</sub>·6H<sub>2</sub>O (Sinopharm Chemical Reagent Ltd. Co., China) and lithium perchlorate anhydrous (LiClO<sub>4</sub>, Chengdu Kelong Co., China) were used as received. 0.1 M phosphate buffer solutions (PBS) were prepared and worked as supporting electrolyte. All the reagents were analytical grade and doubly distilled water was used.

### 2.2. Apparatus

Electrochemical experiments including cyclic voltammetry and electrochemical impedance spectroscopy (EIS) were performed on a CHI 660D electrochemical workstation (Shanghai CH Instrument, China) with three-electrode system. The fabricated Pt/3DGR/CILE was the working electrode, a platinum wire was the auxiliary electrode and a saturated calomel electrode (SCE) was the reference electrode. Scanning electron microscopy (SEM) was carried out on a JSM-7100F scanning electron microscope (Japan Electron Company, Japan).

### 2.3. Preparation of the modified electrode

CILE was prepared based on the reported method [14] with HPPF<sub>6</sub> as the modifier. Then it was polished to a mirror-like surface on weighing paper prior to use. 3DGR/CILE was prepared by potentiostatic electrodeposition [15]. In brief CILE was placed in a 0.1 mol L<sup>-1</sup> PBS solution containing 3.0 mg mL<sup>-1</sup> GO and 0.15 mol L<sup>-1</sup> LiClO<sub>4</sub>, which was magnetic stirring and N<sub>2</sub> bubbling. Electrodeposition was performed at -1.30 V for 300 s to get a stable electrochemical reduced 3DGR film (3DGR/CILE). After rinsed with water for three times, the electrode was dried in nitrogen atmosphere for the further modification.

Nanosized Pt particles were further electrodeposited with 3D/CILE as the substrate electrode by cyclic voltammetric method [16], which was performed in a 0.1 mol L<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub> solution with 0.01 mol L<sup>-1</sup> H<sub>2</sub>PtCl<sub>6</sub> and N<sub>2</sub> bubbling. After the potential was cycled between +1.0 and -0.1 V at a scan rate of 10 mV s<sup>-1</sup> for 25 cycles, the fabricated Pt/3DGR/CILE was rinsed with water and dried in N<sub>2</sub> atmosphere.

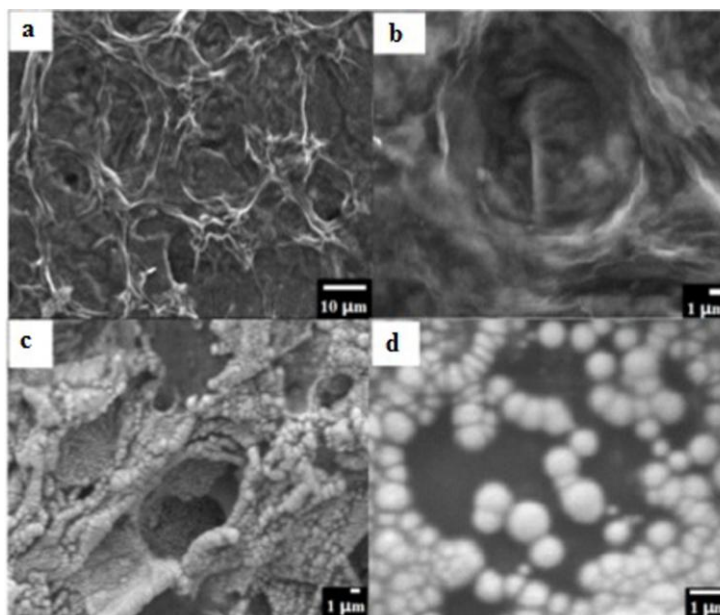
## 3. RESULT AND DISCUSSION

Figure 1 showed the SEM results of nanomaterials on the electrode with different enlarged multiple. As shown in Fig.1 (a, b), a 3D porous and cavity-like structures appeared with GR sheets connected together to form a macroscopic entirety. The pore sizes were in the range from several micrometers to more than 10 μm. Electroreduction of GO is a convenient method for the GR synthesis, the oxygenal groups on GO can be reduced with the recovery of GR structure [15]. This 3D structure can provide a largely exposed interface with the quantity of edges sites of GR increased, then higher conductivity could be achieved. In Fig.1 (c, d) large numbers of Pt nanoparticle with particle sizes bigger than 100 nm could be observed after deposition, which covered the whole surface of 3DGR. Electrodeposition is a convenient and green method to synthesis metal directly from the solution. By electroreduction the Pt nanoparticles was grown on the surface of 3DGR with a Pt/3DGR nanocomposite formed.

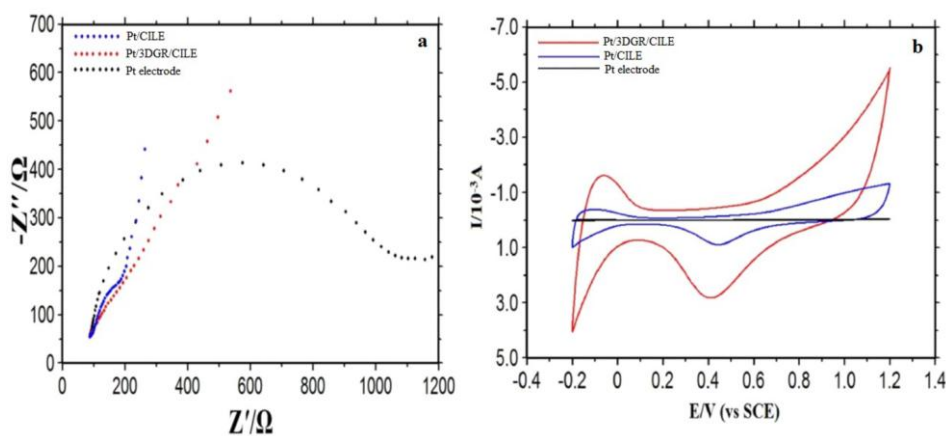
EIS can provide impedance information of modified electrodes, which is often used in electrochemistry. The semicircle diameter of Nyquist plot can reflect the electron transfer resistance ( $R_{et}$ ). As shown in Fig. 2a, the  $R_{et}$  value of Pt electrode was 1049.65 Ω and that of Pt/CILE was decreased to 75.00 Ω. Therefore Pt nanoparticles on the electrode surface decreased the interfacial resistance greatly. As for Pt/3DGR/CILE a straight line was observed, indicating that the  $R_{et}$  value was close to zero. So the presence of Pt/3DGR nanohybrid was beneficial for the faster electron transfer with the highest conductivity and the lowest interface resistance.

Electrochemical behaviors of different electrodes were further explored in a nitrogen saturated 0.5 mol L<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub> solution by cyclic voltammetric experiments. The potential window was in the range from -0.2 V to +1.2 V and the scan rate was set as 50 mV s<sup>-1</sup>. As seen from Fig. 2b, the largest double-layer capacitance appeared on Pt/3DGR/CILE as compared with Pt electrode and Pt/CILE, indicating that the electrochemically active area of Pt/3DGR/CILE was larger than that of Pt/CILE and

Pt electrode. Therefore Pt/3DGR/CILE exhibited the highest electrochemically activity in which hydrogen adsorption characteristics could be clearly observed.



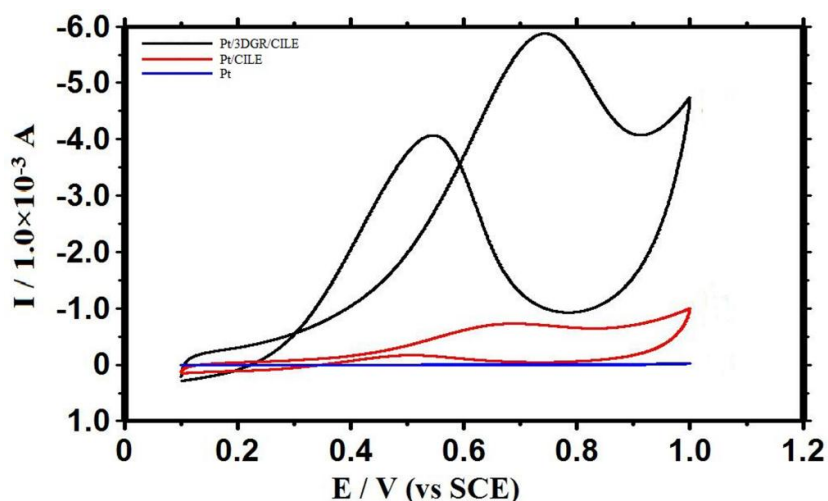
**Figure 1.** SEM of 3DGR/CILE (a, b) and Pt/3DGR/CILE (c, d) at different enlarged multiple



**Figure 2.** (a) EIS of different electrodes in a 5.0 mmol L<sup>-1</sup> [Fe(CN)<sub>6</sub>]<sup>3-/4-</sup> and 0.1 mol L<sup>-1</sup> KCl mixture solution with the frequencies ranging from 10<sup>5</sup> to 10<sup>-1</sup> Hz. (b) Cyclic voltammograms of different electrodes in N<sub>2</sub> saturated 0.5 mol L<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub> solution at a scan rate of 50 mV s<sup>-1</sup>

To check the electrocatalysis of Pt/3DGR/CILE towards electrooxidation of methanol, cyclic voltammograms were recorded in a nitrogen purged solution containing 0.5 mol L<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub> and 0.5 mol L<sup>-1</sup> CH<sub>3</sub>OH. As seen from Fig. 3, methanol electrooxidation on Pt/3DGR/CILE was greatly enhanced with the appearance of the biggest redox peak currents as compared with that of Pt/CILE and Pt electrode. Therefore 3D structured GR was benefit for the dispersion of Pt nanocatalyst, which resulted in the highest electrocatalytic activity of Pt/3DGR/CILE. The ratio of the forward peak current

( $I_f$ ) to the backward peak current ( $I_b$ ), which was used to evaluate the catalyst tolerance of Pt catalyst to the intermediate carbonaceous species that adsorbed on the electrode surface [17], was calculated as 1.56. This value was higher than the values of 1.17, 1.21, 1.26 and 1.47 that reported in previous works [18-21]. The higher  $I_f/I_b$  value suggested that 3DGR supported Pt nanocomposite could result in a more efficient oxidation process for methanol to carbon dioxide with increased tolerance to intermediate carbon species [22]. The 3DGR can provide a unique network as the pathway for the transfer of electron, and more Pt catalyst can also be deposited in the porous 3D structure of GR. The high porosity of Pt/3DGR nanocomposite is beneficial for the mass transfer of methanol to the electrode surface with more contact chances with Pt catalyst. Therefore the electrocatalytic oxidation of methanol could be greatly enhanced on Pt/3DGR/CILE.



**Figure 3.** Cyclic voltammograms of Pt/3DGR/CILE, Pt/CILE and Pt electrode in nitrogen saturated  $0.5 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$  solution containing  $0.5 \text{ mol L}^{-1} \text{ CH}_3\text{OH}$  at a scan rate of  $50 \text{ mV s}^{-1}$

#### 4. CONCLUSION

A nanosized Pt decorated 3DGR decorated CILE was prepared by electrodeposition and used for electrocatalytic oxidation of methanol, which exhibited better catalytic performances due to its larger surface area, higher conductivity and more contact interface for the utilization of Pt catalyst. Therefore Pt/3DGR nanohybrid could be used as the promising catalyst in electrochemical applications.

#### ACKNOWLEDGEMENTS

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