SYNTHESIS THIN FILM ELECTRODES GRAPHENE VIA NOVEL 3D PRINTALBE TECHNIQUE AND DETERMINE PROPERTY ELECTROCHEMICAL

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Abstract: *Graphene film electrodes have many important applications, but the fabriacion of these electrodes is difficult dues to the poor processing of graphene. This article describes the preliminary results of using 3D printing technology to fabricate thin-film electrodes from graphene oxide inks. Graphene oxide ink is synthesized by chemical method. The graphene oxide (GO) and reduction graphene oxide (r GO) thin film were chacracterized by filed scanning electron microscopy (FESEM) and Energy-dispersive X-ray spectrocopy (EDX spectrocopy) to make sure the morphological and optical characteristics of the thin film. In addition, the electrochemical aera active studies were also determined by cyclic voltametry (CV) curves. The r GO thin film displays higher electrochemical area active in comparison with GO, which is 2.56 cm^2 compare to 0.31 cm^2, indicating the best result for the superior conductivity of thin film electrode.*

Keywords: 3D inks; Electrodes; Graphene oxide; Composite.

1. INTRODUCTION

Graphene is studied worldwide due to its distinctive properties of high thermal conductivity, enhanced surface area, zero band gap, permeability to gases and outstanding electron mobility at room temperature. Currently, graphene is considered a miracle material because of its unique thermal, electronic, optical and mechanical properties, and it has received lots of attention. Graphene family, notably pristine graphene sheets, multilayered graphene flakes and graphene based composites offer an array of unique features that can be innovative made use of for biomedical applications, electronics, energy storage and catalysis [1]. Nowadays, graphene material is the most noticeable due to significant advantages of easy fabricating and low cost. Graphene thin film electrodes have much important application, and they are usually synthesized by solution method using spin-coating, drop casting, Langmuir-Blodgett, self-assembly techniques.

In recent years, 3D printing technology has strongly developed because of the fabrication of thin film electrode much easier, more precise and more rapid [2]. 3D printing technology, also known as additive manufacturing technology, has received extensive attenting from many researchers around the world. It is also considered vital for the advent of the third industrial revolution. 3D printing is computer-mediated form of additive or subtractive manufacturing of three-dimension constructs. Additive manufacture refers to the procedure of materials assembling in a layer-by-layer fashion to make a tridimensional construct in accordance to a model data. On the other hand, the subtraction approach make use of a bulk material that is further shaped in compliance with a computed design, at lower cost with limited margins for innovation. Compared with other traditional manufacturing technology, 3D printing has the advantages of designable shaping, low manufacturing cost, rapid prototyping and environmental friendliness. It has been widely used in manufacturing, biomedical, aerospace, construction industry, electronics and other fields. A 3D printer can create objects directly from the model on a computer with highly precision. Among of a 3D printing

technology, direct ink writing is easily operable and conveniently create shapes. It is very suitable for printing mixed systems of various materials, including structural materials, electrical materials, biological materials [3]. Almost 3D printing graphene-based inks started out from graphene oxide (GO) form due to its good water-dispersibility and production possibility on an industrial scale. After printing, GO will be reduced to r GO by different physical or chemical methods.

In this work, GO was synthesized via chemical oxidation route from commercial graphite and used for the preparation of 3D printing ink.The electrode was continuously reduced in Ar gases at different temperatures to improve them conductivity. The electrochemical properties of prepared 3D-printed rGO thin films have been characterized by cyclic voltammetry method with potassium ferricyanide/ferrocyanide redox couple. The electrochemical area activity of these electrodes were also calculated.

2. EXPERIMENT

2.1. Materials

Sulfuric acid (H_2SO_4, 98%), phosphoric acid (H_3PO_4, 85%), nitric acid (HNO_3, 63%), Kalipemanganate ($KMnO_4$), were purchased from Sigma-Aldich. Potassium ferricyanide/ferrocyanide couple redox solution were prepared by mixing solutions of 10 mM $K_3Fe(CN)_6$ and 10 mM $K_4Fe(CN)_6$. Graphene oxide was synthesis by Tour method. The graphite papers were provided by Xiamen TOB New Energy Technology.

2.2. Apparatus and Equipment

The graphene oxide electrodes were fabricated by 3D-printing machine of electronic laboratory of Institute of Tropical Technology.

The field emission scanning electron microscopy (FESEM) images were taken by S-4800 field emission SEM (Hitachi, Japan). The distribution of materials on the 3D electrodes was analyzed by the element mapping method using SEM (Joel JSM-6510LV) with energy dispersive x-ray (EDX) mapping. Cyclic voltammetric experiments were performed with a multichannel potentiostat/galvanostat (Biologic VSP-3000) using a three-electrode configuration with a standard calomel electrode as a reference electrode (RE), a Pt electrode as a counter-electrode, and the modified 3D printed GO electrodes as working electrodes (WE).

2.3. Fabrication of working electrode

2.3.1. Preparation of graphene oxide inks

Graphene oxide was synthesized by Tour's method acroding to the paper has been reported. Taking accurately the mixute of 90 ml of concentrated acid H_2SO_4 and 10 ml of concentrated acid H_3PO_4 (9:1 (v/v) ratio). Then, the mixture was poured in to the flask that placed on an ice tray. Next, adding 1 grams of graphite powder into the acid mixture, continuous stirring gently until the graphite was dispersed througly, then cooled the mixture with ice so that the system of temperature was not exceed 10 ^oC. When the temperature of the solution reaches 10 ^oC, adding slowly 6 grams of $KMnO_4$ to this mixture, continuing stirred about 10 minutes to ensure that the graphite powder and $KMnO_4$ were evenly dispersed. The solution was heated to 70 - 80 ^oC for 4 hours. Afterward, these mixture was cooled to room temperature. After that, 10 ml of H_2O_2

10% was added slowly and stirred about 15 minutes until the bubbles occurred and a bright yellow color was observed. Then, the solution was distluted with distilled water in a 2 liter beaker. The solution was centrifuged several times with 5% HCl solution to remove the residues after the reaction. Then, the washing process was carried out repeatedly with distilled water until the solution reaches a neutral medium. In the last of three washing times, the product and water are put into the ultrasonic device for 20 minutes, then obtained the GO gel product.

2.3.2. 3D direct writing fabrication electrode materials

In this paper, GO thin film electrodes were fabricated using direct ink writing method on the 3D printer. The composite ink was loaded into a 5 cm^3 syringe and extruded from a 0.3 mm diameter nozzle directly onto a graphite paper, which was placed on a heating aluminum table of the printer, to to form written patterns with dimension 10 mm x 20 mm. In this research, the electrode samples were designed using Solidworks software, and the printing parameters were set up as follows: printing speed is 2 $mm.s^{-1}$, the thickness of each layer is 0.2 mm; the width of print line is 0.25 mm and the temperature of the sample table is 80 ^oC. After formation, the electrodes were dried at 100 ^oC for 30 minutes in an oven.

a *b* *c*

Figure 1. *(a): A 3D printer machine, (b): Grapheme oxide inks and (c): Printed electrode.*

2.3.3. Reduction GO thin film

Graphene oxide thin film electrodes were thermally treated in Ar atmosphere. For both groups (300 ^oC and 600 ^oC), annealed heating time was 15 min, pressure and flow rate of Ar were 55 Pa and 50 sccm, heating rate was 10 ^oC/minutes.

2.3.4. Electrochemical properties

Electrochemical properties of prepared electrodes were studied by cyclic voltammetric (CV) method in 5 mM K3[Fe(CN)6]/K4[Fe(CN)6] (1:1) redox system. CV experiments were performed with a multichannel potentiostat/galvanostat (Biologic VSP-300), using three cell electrode system in which graphene thin film printed on graphite paper is taken as working electrode (WE), while saturated calomel electrode (SCE) and platinum grid acted as reference and counter electrode, respectively. All CV measurements are performed at room temperature (~25 ^oC), scanning potential from -0.4 V to +1.0 V, area of working electrode is 1 cm^2.

The electrochemical surface area of the electrode was calculated by the RAndles-Sevick equation; area was investigated utilizing cyclic voltametric (CV) technique. In

CV, the Randles-Sevcik equation is used to describe the effect of the scan rate on the peak current i_p. The significant parameters of cyclic voltammograms are the enormities of the anodic peak current (i_{pa}) and cathodic peak current (i_{pc}), the anodic peak potential (E_{pa}) and the cathodic peak potential (E_{pc}). The peak current for a reversible system is described by the Randles-Sevcik equation for the forward sweep first cycle:

$I_p = (2.69 \times 10^5)n^{3/2} AD^{1/2}C\upsilon^{1/2}$

Where i_p is the peak current (A)

n is the electron transfer (n =1 with couple redox solution $[e(CN)_6^3]^-/[Fe(CN)_6^4]$

A is the electrode area (cm^2)

D is the diffusion coefficient (cm^2/s) (D = $6,7.10^{-6}$ cm^2/s)

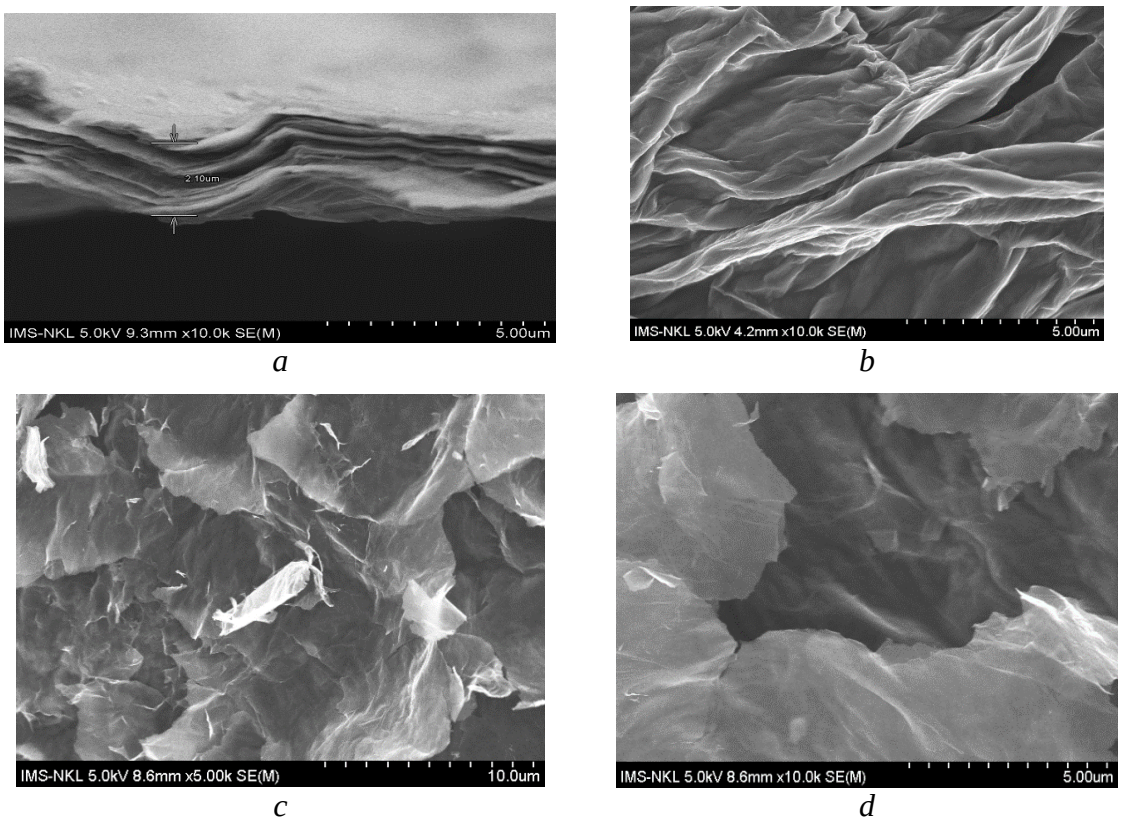
C is the concentration (mol/cm^3) (C = 5.10^{-6} mol/cm^3)

υ is the scan rate (V/s);

3. RESULT AND DISSCUSION

3.1. Structure and morphology of 3D printed thin film electrodes

Mophorlogical analysis



a *b*

c *d*

Figure 2. *(a): FESEM image of thin film graphene oxide electrode;*
(b): Thickness of thin film graphene oxide electrode,
(c): FESEM image of thin film graphene oxide electrode reduced at 300 ^oC,
(d): FESEM image of thin film graphene oxide electrode reduced at 600 ^oC.

Morphologyical analysis was carried out using field emission scanning electron microsopy (FESEM). The surface morphology of 3D printed GO and r GO thin film

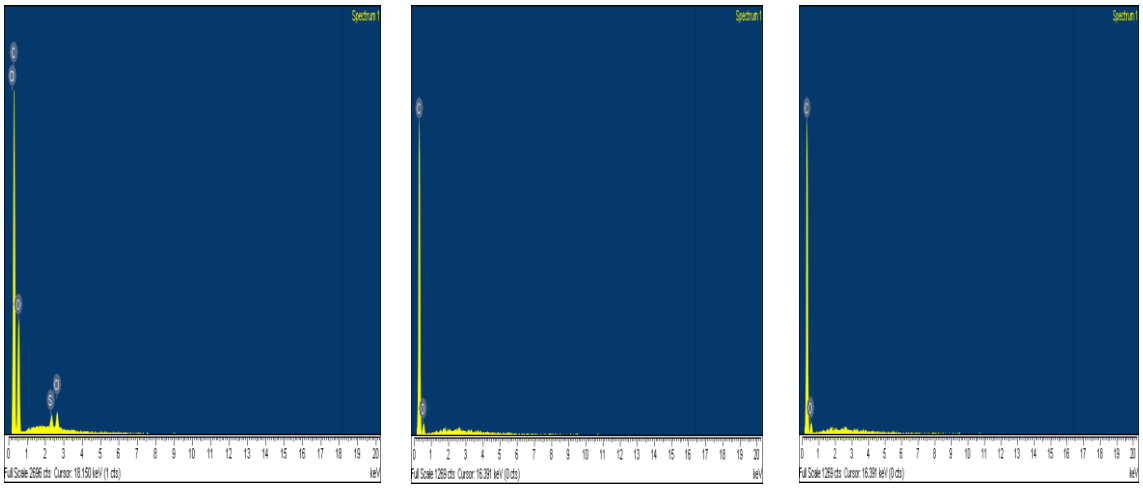
electrode are as shown on figure 2. As shown, figure (2a)(2b) illustrated the FESEM thickness and images of thin film graphene oxide electrode. Figure 2c reveals the layered structure of the GO flakes were exfoliated. The wrinkled or fold morphology can be observed in some areas. The thickness of graphene oxide printed after dried was about 2.1 µm. As can be seen that, with 3D printed-method, we can easily control the thickness of printed layer with a highly precise compare with other methods. This method also conveniently when preparing samples.

Figure 2(c) and 2(d) show the images of reduced graphene oxide at 300 ^{o}C and 600 ^{o}C (rGO 300 ^{o}C, rGO 600 ^{o}C), respectively, the folded and wrinkled structure has been observed. This folding structure can be found on both surface and the edge of rGO due to the losses of oxygen functional group. More folded and wrinkled structure is produce when the reduction stronger [4].

Energy Dispersive X-ray (EDX) spectra

EDX spectra is a powerful technique used to analysis all the elements in the samples.

We performed EDX elemental analysis of GO and r GO under the same condition. The results are show in figure 3.



(a) (b) (c)

Figure 3. *Energy Dispersive X-ray spectra of (a): GO; (b): rGO 300 ^{o}C; (c): rGO 600 ^{o}C.*

Table 1. *EDX elemental analysis of thin film graphene oxide and thin film graphene oxide reduction at 300, 600 ^{o}C.*

Atom weight precentage (%)	C	O	S	Ratio C/O
GO	67.60	27.85	4.54	2.42
rGO 300 ^{o}C	83.02	16.98	-	4.88
rGO 600 ^{o}C	88.53	11.33	0.14	7.81

The relative atomic weight ratios for the various samples are listed in table 1. The

carbon/oxygen (C/O) ratio is indicative of the degree of graphene oxidation, and assesses the nature of oxygen functionalities. The degree of oxidation of the graphene oxide can be estimated from C/O ratio. Optimally oxidized graphene oxide C/O atomic ratio lies between 2.1 to 2.9 [5]. The samples of GO prepared in this work exhibited a C/O atomic ratio of 2.42, consistent with the range reported for well-oxidized graphene.

Figure 3 b shows the atomic weight ratio C/O of GO increased from 2.42 to 4.88 after reducting at 300 ^{o}C in Ar gases. This result is evidence for some degree of reduction of the graphene oxide. This confirm the role of high temperature as a reducing agent. In addition, the r GO at 600 ^{o}C shows in figure 3 c, has a high value of C/O atomic ratio of 7,81, indicating low oxygen in the final product. This process was show to cause futher reduction of graphene oxide sheets. These data confirm that r GO sheets losses the oxygen groups compare to GO sheets.

3.2. Electrochemical properties of printed electrode

Cyclic voltammetry measurment

Cyclic voltammetry (CV) is an important technique used to investigate the electrochemical of different materials. The voltammetric results of GO and r GO electrodes have been compared using $[K_3Fe(CN)_6]/[K_4Fe(CN)_6]$ as a model redox system. Figure 4 displays the cyclic voltammograms of 5 mmol.L^{-1} $[K_3Fe(CN)_6]/[K_4Fe(CN)_6]$ recorded on printed GO electrode, printed r GO 300 ^{o}C electrode and r GO 600 ^{o}C electrode.

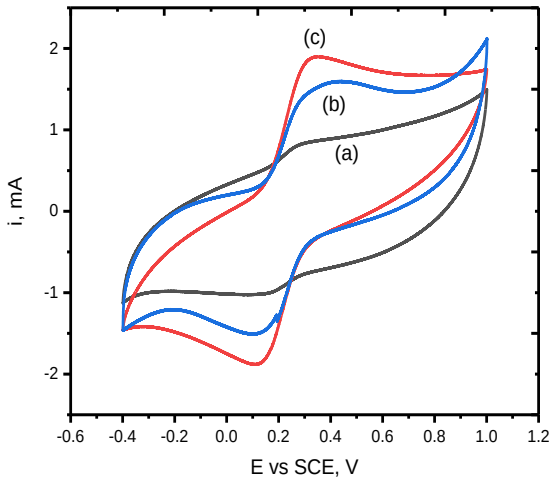


Figure 4. *Cyclic voltammogram recorded in 5 mmol.L^{-1} $K_3[Fe(CN)_6]/K_4[Fe(CN)6]$ system at 50 mV.s^{-1} of thin films: (a) GO, (b) rGO 300 ^{o}C, (c) rGO 600 ^{o}C.*

As show in the figure 4, we can be seen that in the case of pure GO thin film, a pair of redox peak observed quite weak (curve a), the current intensity at the anode (I_{pa}) reached the value of 0.81 mA, indicating that GO was a poor electrically material. The peak redox of r GO thin flim annealed at 300 ^{o}C increased highly, approximately two times compare with pure GO, from 0.81 mA to 1.56 mA. Moreover, the CV (curve b) represented well-defined redox couples at 0.12 V and 0.36 V, indicating the reduction of GO had taken place, that meaning r GO 300 ^{o}C becomes good conducted material. In

addition, the value of current intensity peak oxidation and peak reduction continuously increased with raising temperature heating until 600 ^{o}C (curve c), the value of I_{pa} reached of 1.9 mA, respectively. This result shows that the peak current in voltammogram of r GO 300 ^{o}C (curve b) observed lower than r GO 600 ^{o}C (curve C), that is because probably of lower reduced GO content in the thin film. These consequences can explain that when GO is further reduced, the conductivity also increases significally as the electrochemical activity of material raise noticeably.

From the recorded CV curves, the peak-to-peak separation (ΔE_p) of cathodic and anodic signals of model redox system could be also calculated. The lowest value ΔE_p (0.20 V) obtained in the case of rGO 600 ^{o}C, which could be related to the faster electron transfer kinetics on this electrode. The ΔE_p value determined clearly higher, 0.24 And 0.26 V, for the rGO 300 ^{o}C and GO.

Influence of scan rate

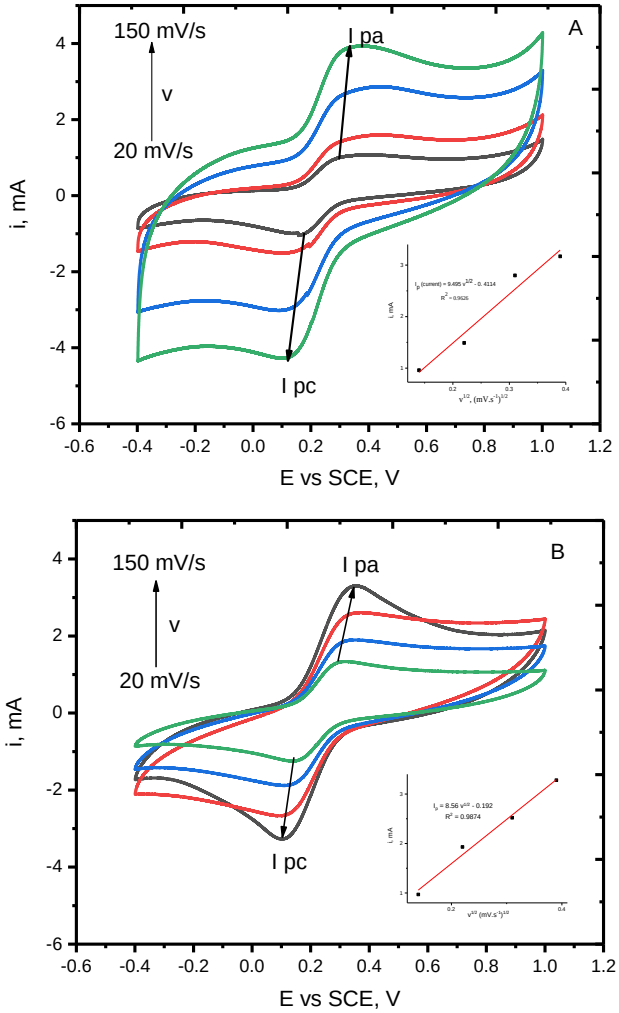


Figure 5. *Cylic voltammograms recorded in 5 mmol.L^{-1} $K_3[Fe(CN)_6]/K_4[Fe(CN)_6]$ system at different scan rates of 20, 50, 100, 150 mV.s^{-1} on thin film r GO 300 ^{o}C (figure 5A) and r GO 600 ^{o}C (figure 5B).*

In order to illustrate that the reduction GO of printed thin film could improve the surface area and conductivity of this electrode, electroactive surface area (A) of thin film electrode before and after reducing was determined by CV in 5.0 mmol.L^{-1} redox solution $[K_3Fe(CN)_6]/K_4[Fe(CN)_6]$ at different sweep rates (υ) according to the RAndles – Sevcik equation. Both anodic and cathodic peaks increase when scan rates increases from 20 to 150 mV.s^1. As show in figure 5 A and figure 5 B, both the peak current (I_p) of reduced electrode were proportional to the square root of scan rate. Therefore, with the constant parameters of D, C and n, we could successfully obtain an approximate value of *A* according to the Randles-Sevcik equation. The electrode surface area of 0.31 cm^2, 2.37 cm^2 and 2.56 cm^2 for GO thin film, r GO 300 ^oC thin film and r GO 600 ^oC thin flim were acquired, respectively. From the resulted CV in figure 5 A, 5B, the relation between redox peak current and square root of scan rate can be calculated, the linear of r GO 300 ^oC was: $i_{pa} = 9.495\ \upsilon^{1/2} - 0.4114$; $R^2 = 0{,}9626$; the linear of r GO 600 ^oC was: $i_{pa} = 8.56\ \upsilon^{1/2} - 0.192$; $R^2 = 0{,}9874$. The observed linear relationship between i_{pa} and $\upsilon^{1/2}$ indicates a reversible redox reaction on the electrode surface. The electroactive surface area of r GO thin films increased significantly compare with GO thin film, which provide an effective evidence for the superior conductivity of thin film as expected.

4. CONCLUSIONS

In this work, GO ink was synthesis via chemical oxidation using the modified Tour's method. Thin film electrodes were fabricated easily and conveniently by direct writing on a 3D printer. GO has been reduced at high temperature in Ar gases at 300 ^oC and 600 ^oC, in order to reach the best electrochemical properties of the thin film electrode. The cyclic voltammetric performances exhibited the linear relationship between anodic and cathodic signals of redox solution. Additionally, the linner of peak current and square root of scans rate indicated well a reversible redox reaction on the electrode surface. The electroactive surface area of rGO thin films increased significantly compare to GO thin film from 0.31 to 2.56 cm^2, approximately higher than 8 times, which describes an expected result for the superior conductivity of thin film electrode.

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TÓM TẮT

TỔNG HỢP ĐIỆN CỰC MÀNG MỎNG GRAPHEN BẰNG KỸ THUẬT IN 3D VÀ XÁC ĐỊNH TÍNH CHẤT ĐIỆN HÓA

Điện cực màng mỏng graphen có nhiều ứng dụng quan trọng, nhưng việc tổng hợp gặp khó khăn do khả năng khó phân tán của graphen. Bài báo này trình bày kết quả nghiên cứu tổng hợp điện cực màng mỏng graphen từ mực in graphen oxit bằng kỹ thuật in 3D. Graphen oxit được tổng hợp bằng phương pháp hóa học. Các đặc trưng của điện cực màng mỏng graphen oxit và điện cực màng mỏng graphen oxit khử được xác định bởi ảnh kính hiển vi điện tử quét phân giải cao (FESEM) và phổ tán sắc năng lượng tia X (EDX). Diện tích hoạt động điện hóa của điện cực được xác định bằng kỹ thuật quét thế vòng đa chu kỳ. Số liệu tính toán cho thấy, diện tích hoạt động điện hóa của điện cực màng mỏng graphen oxit khử cao hơn rất nhiều so với điện cực màng mỏng graphen oxit, lần lượt là 2,56 cm^2 và 0,31 cm^2tương ứng, điều này thể hiện tính dẫn điện vượt trội của điện cực màng mỏng.

Từ khóa: Mực in 3D; Điện cực; Graphen; Màng mỏng.

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