Rapid Synthesis of Graphene Nanosheets and Its Structural Properties Study for Direct Methanol Fuel Cell

Mohamad Fahrul Radzi Hanifah, Juhana Jaafar, Madzlan Aziz, Ahmad Fauzi Ismail

Advanced Membrane Technology Research Centre (AMTEC)
Faculty of Petroleum and Renewable Energy Engineering
Universiti Teknologi Malaysia, 81310 UTM Skudai
Johor, Malaysia
Department of Chemistry, Faculty of Science
Universiti Teknologi Malaysia, 81310 UTM Skudai
Johor, Malaysia
e-mail: agungsini@gmail.com, e-mail:aditchacha@yahoo.com,
e-mail:juhana@petroleum.utm.my

Abstract

Platinum is frequently used as the catalyst in direct methanol fuel cell (DMFC) due to high catalytic activity compared to other catalyst. However, the practical application using platinum is still limited due to high platinum cost. Graphene is the most precious carbon-based material used as the platinum support to reduce the platinum loading which is can reduce the cost. Herein, simple and rapid synthesis of graphene nanosheets (GNs) via chemical reduction of exfoliated graphene oxide nanosheets (GO) was carried out by using sodium oxalate ($Na_2C_2O_4$) as reducing agent. The comprehensive characterizations were conducted in term of structural and morphology analysis such as Raman spectrometer, high resolution transmission electron microscopy (HRTEM) and x-ray diffractometer (XRD). The number of layers of the GNs was determined by HRTEM which is almost revealed the formation of monolayer. The XRD analysis showed that the large interlayer distance of GO disappeared after reduction process due to the removal of oxygen functional groups to form GNs. Therefore, the reduction process using Na2C2O4 can lead to the efficient removal of the oxygen functional groups from the surface of GO to produce high quality of single layer GNs which is can be applied as the catalyst support in DMFC.

Keywords : *Graphene nanosheets, chemical reduction, structural, characterization*

1 INTRODUCTION

Direct methanol fuel cell (DMFC) is excellent power sources has been focused intensive interest for several decades due to their high efficiency of energy-conversion, low pollutant emission, availability of methanol fuel, easy handling and distribution (G. Wu et al. 2013). However, the practical applications are still limited due to the expensive platinum catalyst which is currently the most promising anode catalysts (K. Ji et al. 2012). Therefore, many efforts have been made to overcome this problem, while reducing the use of Pt-based catalysts. One of the best strategies is to use novel support of carbon-based materials to reduce the platinum loading. A Graphene nanosheet (GNs) is a carbon-based material of two-dimensional (2D) sheet consisting of sp2 hybridized carbon atom that arranged in a honeycomb lattice structure (H. J. Choi et al. 2012). Recently, it has received significant attention owing to its unique characteristics such as large surface area (K. Ji et al. 2012), strong mechanical (C. Lee et al. 2008), excellent electrical conductivity (R. F. Service 2009) and good thermal stability (A. A. Balandin 2008) making it as a promising candidate for the catalyst support in DMFC. The most typical method used to produce GNs in a large quantities with the low in cost is the chemical reduction of GO (Y. Jin et al. 2013).

Graphite powder can be used as the precursor to produce GNs through the formation of graphene oxide (GO) by oxidation reaction with concentrated acid using modified Hummers method and subsequently the chemical reduction process. Hydroxyl and epoxy groups are mostly decorated onto the basal plane of GO layers, while carboxyl and carbonyl groups are decorated at the edges (K. Satheesh and R. Jayavel 2013). Recently, the uses of green and environment-friendly reducing agents to synthesis GNs have been reported such as dipotassium hydrogen phosphate (X. Zhang et al. 2013), ascorbic acid (J. Zhang et al. 2009) and L-glutathione (T. A. Pham, J. S. Kim and Y. T. Jeong 2011). However, its feasibility still requires further evaluations due to some of its drawbacks such as high in cost, experimentally time consuming and limited applications (J. Gao et al. 2010). Sodium oxalate is cheap, effective and less hazardous in the reducing process as compared with other strong reducing agents such as hydrazine and its derivatives. Therefore, in this paper, we prepare GNs via chemical reduction of exfoliated GO by using sodium oxalate as the reducing agent, the morphology and structural properties of the prepared GNs was well investigated.

2 RESEARCH METHODOLOGY

2.1 Chemicals

Purified graphite powder was obtained from Superior Graphite Co. and all the other chemicals were analytical grade and used as received without further purification.

2.2 Preparation of graphene nanosheets

The GO was synthesized through the oxidation of the purified graphite powder via modified Hummers method. Three grams of $NaNO_3$ was dissolved in 140 mL of concentrated H_2SO_4 in an ice bath. Then, 15 g of $KMnO_4$ and 3 g of graphite powder were gradually added into the mixture. The temperature was kept below $20°C$ under vigorous stirring using a mechanical stir bar for 2 hours. The temperature of the mixture was then increased and maintained at $35°C$. The mixture was continuously stirred for another 12 hours until it turned into a brown paste. After that, 250 mL of deionized water was added into the mixture

and stirred for 30 minutes. Next, 20 mL of 35% H2O2 and 800 mL of deionized water were added into the mixture. The stir was continued until the mixture color changed from brown into brilliant yellow. The mixture was filtered and washed using 1 M HCl and deionized water until the pH of the filtrate became neutral. Lastly, the mixture was dried in oven at $80°C$. In typical synthesis of GNs, 200 mg of solid GO was dispersed in 200 mL of deionized water under ultra-sonication for 3 hours by using a high power ultrasonic pole at $0°C$ until it turned into a dark-brown GO aqueous colloid. In typical reduction process from GO to RGO, 100 mL of GO colloid was mixed with 40 mL of sodium oxalate solution in a 250 mL conical flask under vigorous stirring. The final solution was kept at $\pm 95°C$ for a period 2 hours. Then, the products were centrifuged for 20 minutes at 3000 - 4000 rpm and washed using deionized water repeatedly. Finally, the products were dried at $80°C$ in oven.

2.3   Characterization

The X-ray diffraction (XRD) patterns were taken on a high resolution x-ray diffractometer (Bruker D8 Advance) using $Cu-K\alpha(\lambda = 1.54\square)$ radiation with 2θ range between $5°$ and $40°$. The morphology of the synthesized GO and GNs were characterized by transmission electron microscopy (TEM, FEI/Philips CM12) and high-resolution transmission electron microscopy (HRTEM, FEI TECNAI G2) at acceleration voltage of 120 and 200 kV, respectively. Raman spectra were recorded from 800 to 3000 cm-1 on a Renishaw 1000 confocal Raman microprobe (Renishaw instruments) using 514 nm argon ion laser.

3   RESULTS AND DISCUSSION

3.1   Morphology analysis

TEM images of the GO and GNs are shown in Fig. 1a and b, respectively. GO consists of aggregation of corroded sheets while for GNs, there is wrinkle with a decrease in thickness. The clear idea of the number of the layers could be given by the folder edges of the GNs (P. Liu et al. 2013). The HRTEM images that capture the border of GNs are shown in Fig.1c. It showed that the produced GNs has the single layer as indicated by the arrow. Therefore, we can conclude that the nanoscale structure of GNs was likely to be monolayer.

3.2   XRD analysis

XRD was used to identify the interlayer changes of GO and GNs. The XRD patterns of the GO and GNs are shown in Fig. 2a. A typical broad diffraction peak near $12.0°$ which corresponded to the (002) basal plane with d-spacing $\sim 7.37A$ was observed for the GO. This is due to the existence of oxygenated functional group on the GO and also the intercalation of water molecules (Y. Jin et al. 2013). For the XRD pattern of the GNs, the intensity of the peak at $12.0°$ was totally disappeared after reduction process. The disappearance was accompanied by a little shift of the broad band to a higher 2θ angles at $24.6.0°$ (inset of XRD pattern of GNs). The band corresponded to (002) plane with d-spacing $\sim 3.61A$ This suggests that the produced GNs have better order in two-dimensional (2D) structures with the removal of oxygenated functional groups from the surface of GO.

3.3 Raman spectra analysis

Raman spectrometer is used to determine the structural and electronic properties of prepared GNs and GO. Fig. 2b showed the Raman spectra of the GO and GNs. The D and G bands in the spectra of the GO and GNs are corresponded to the breathing mode of point photons of A1g symmetry and the first order scattering of the E2g phonons of sp2 hybrid carbon atoms respectively (P. Song et al. 2012). D and G bands are related to the defects of sp2 carbon lattice of GNs and disordered conformations (X. Zhang et al. 2014). The G band of the GO was located at 1600 cm-1 while for GNs, it shifted to $1598 cm-1$ which is closer to the pristine graphite after the reduction. It indicates that the GO has been successfully reduced. The D band of the GNs shifted to 1351 cm-1 from the original GO location which was at 1352 cm-1 indicating the presences of defect and disorder of the in-plane sp2 domains in the sample. Measurement of relative disorder present in a graphitic structure can be detected through a ratio between D and G bands intensities (ID/IG). The intensity ratio of the D and G bands (I_D/I_G) increased from 0.96 (GO) to 1.02 (GNs). This is due to the formation of some new sp2 carbon lattice structures during the reduction process (X. Zhang et al. 2014). In addition, the Raman spectrum of GNs exhibited a broadened 2D band at around 2719 cm-1 as evidence that the analyzed region presence of almost single layer of GNs.
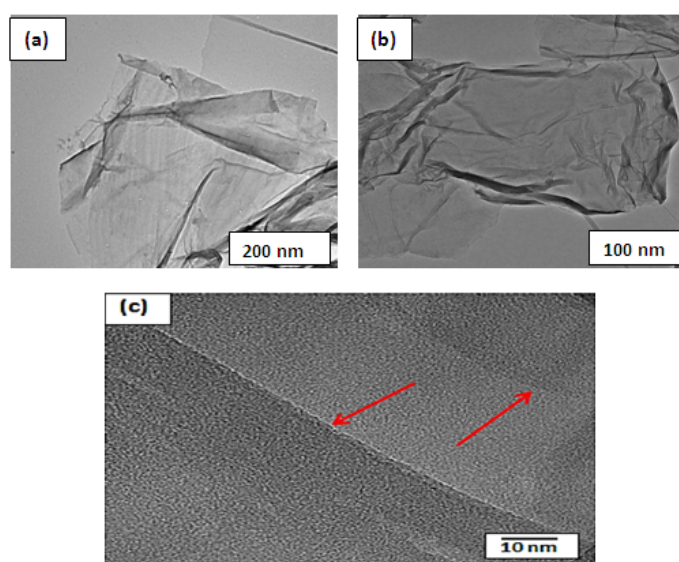

Figure 1: TEM image of (a) GO and (b) GNs, (c) HRTEM image of GNs layer

4 CONCLUSION

A rapid synthesis of GNs using sodium oxalate as the reducing agent has been reported. The morphology analysis of the produced GNs by the HRTEM almost revealed the formation of single layer. The XRD analysis showed that the peak of the large interlayer distance almost disappeared after reduction process due to the removal of the oxygen containing functional group. Based on the Raman spectra, the ID/IG ratio increased after the reduction
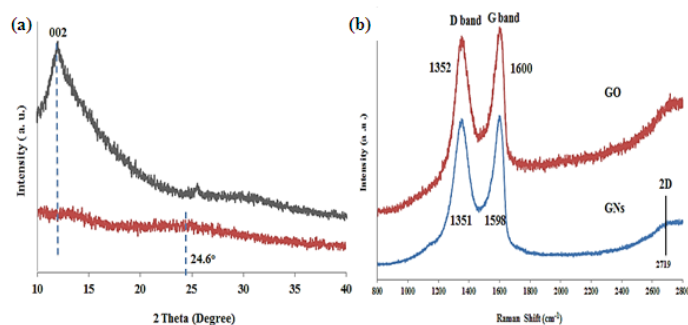
Figure 2: XRD pattern of GO and GNs (b) Raman spectra of GO and GNs

process indicating a higher degree of disorder that results in a more defective state of GO. This produced single layer of GNs could be valuable for the practical application in direct methanol fuel cell.

5   ACKNOWLEDGEMENT

References

A. A. Balandin, S. Ghosh, W. Bao, I. Calizo, D. Teweldebrhan, F. Miao, and C. N. Lau (2008). Superior Thermal Conductivity of Single-Layer Graphene, *nano letters 8*, 902-907.

C. Lee, X. Wei, J. W. Kysar, J. Hone (2008). Measurement of the Elastic Properties and Intrinsic Strength of Monolayer Graphene, *Science 321* (5887): 385-388.

G. Wu, H. Huang, X. Chen, Z. Cai, Y. Jiang, X. Chen (2013). Facile synthesis of clean Pt nanoparticles supported on reducedgraphene oxide composites: Their growth mechanism and tuning oftheir methanol electro-catalytic oxidation property, *Electrochimica Acta 111*, 779 783.

H. J. Choi, S. M. Jung, J. M. Seo, D. W. Chang, L. Dai, J. B. Baek (2012). Graphene for energy conversion and storage in fuel cells and supercapacitors, *Nano Energy 1*, 534551.

J. Gao, F. Liu, Y. Liu, N. Ma, Z. Wang, and X. Zhang (2010). Environment-Friendly Method to Produce Graphene That Employs Vitamin C and Amino Acid, *Chem. Mater. 22*, 22132218.

J. Zhang, H. Yang, G. Shen, P. Cheng, J. Zhang and S. Guo (2010). Reduction of graphene oxide via L-ascorbic acid, *Chem. Commun. 46*, 11121114.

K. Ji, G. Chang, M. Oyama, X. Shang, X. Liu, Y. He (2012). Efficient and clean synthesis of graphene supported platinum nanoclusters and its application in direct methanol fuel cell, *Electrochimica Acta 85*, 84 89.

K. Satheesh, R. Jayavel, (2013). Synthesis and electrochemical properties of reduced graphene oxide via chemical reduction using thiourea as a reducing agent, *materials letters 113*, 5-8.

P. Liu, Y. Huang, L. Wang (2013). Synthesis of reduced graphene oxide using indole as a reducing agent and preparation of reduced graphene oxide-Ag nanocomposites, *Synthetic metals 167*, 25-30.

P. Song, X. Zhang, M. Sun, X. Cui and Y. Lin (2012). Synthesis of graphene nanosheets via oxalic acid-induced chemical reduction of exfoliated graphite oxide, *RSC Advances 2*, 11681173.

R. F. Service, (2009). *Carbon Sheets an Atom Thick Give Rise to Graphene Dreams*, 324 (5929): 875-877.

T. A. Pham, J. S. Kim and Y. T. Jeong (2011). One-step reduction of graphene oxide with L-glutathione, *J. Colloids Surf. A: Physicochem. Eng. Aspects 384*, 543-548.

X. Zhang , K. Li, , H. Li, J. Lu, Q. Fu, Y. Chu (2014). Graphene nanosheets synthesis via chemical reduction of graphene oxide using sodium acetate trihydrate solution, *Synthetic metals 193*, 132-138.

X. Zhang, K. Li, H. Li, J. Lu (2013). Dipotassium hydrogen phosphate as reducing agent for the efficient reduction of graphene oxide nanosheets, *Journal of Colloid and Interface Science 409*, 1-7.

Y. Jin, S. Huang, M. Zhang, M. Jia , D. Hu (2013). A green and efficient method to produce graphene for electrochemical capacitors from graphene oxide using sodium carbonate as a reducing agent, *Applied Surface Science 268*, 541 546.