

Sains Malaysiana 46(7)(2017): 1039–1045  
<http://dx.doi.org/10.17576/jsm-2017-4607-05>

## Synthesis of Graphene Flakes over Recovered Copper Etched in Ammonium Persulfate Solution

(Sintesis Grafir Serpilh melalui Kuprum Pulih yang Dipunarkan  
dalam Larutan Ammonium Persulfat)

M.K. NIZAM, D. SEBASTIAN, M.I. KAIRI, M. KHAVARIAN & A.R. MOHAMED\*

### ABSTRACT

*The synthesis of high quality graphene via economic way is highly desirable for practical applications. In this study, graphene flake was successfully synthesized on Cu/MgO catalyst derived from recovered Cu via etching in ammonium persulfate solution. Recovered Cu acted as efficient active metal in Cu/MgO catalyst with good crystal structure and composition according to XRD and XRF results. FESEM, EDX, HRTEM, Raman spectroscopy and SAED analysis were carried out on the synthesized graphene. The formation of single, bilayer and few layer of graphene from Cu/MgO catalyst derived from recovered Cu was feasible.*

*Keywords: CVD; flake; graphene; MgO; recovered Cu*

### ABSTRAK

*Sintesis grafir berkualiti tinggi secara ekonomi adalah sangat diperlukan untuk aplikasi praktikal. Dalam kajian ini, grafir serpilh telah berjaya disintesis menggunakan pemangkin Cu/MgO yang diperoleh daripada Cu pulih melalui punaran dalam larutan ammonium persulfat. Cu pulih bertindak sebagai logam aktif yang cekap dalam pemangkin Cu/MgO dengan struktur kristal yang baik dan komposisi berdasarkan keputusan XRD dan XRF. FESEM, EDX, HRTEM, Raman spektroskopi dan analisis SAED telah dijalankan ke atas grafir yang disintesis. Pembentukan tunggal, dwilapisan dan beberapa lapisan grafir daripada pemangkin Cu/MgO yang diperoleh daripada Cu pulih telah dicapai.*

*Kata kunci: CVD; grafir; MgO; pemulihan Cu; serpilh*

### INTRODUCTION

Graphene is an atomically thin layer 2D carbon nanomaterial with  $sp^2$ -bonded carbon atoms arranged in hexagonal lattice structure. Graphene has been attractively studied due to its exceptional physical and electronic properties. Study of fundamental, synthesis methods and potential applications of graphene were actively conducted since its discovery in 2004 by Geim and Novoselov (2007). Several studies have been carried out to synthesis graphene with high structural order such as formation of graphene oxides from graphite (Chua & Pumera 2014) epitaxial growth of graphene from SiC (First et al. 2010) and graphene growth on metal substrate through catalytic chemical vapor deposition (CVD) (Li et al. 2009a). However, high cost to produce graphene is still a main factor that hinders the commercial production of graphene (Novoselov et al. 2012).

Chemical vapor deposition was a promising method for large scale production of graphene as well as the ability to produce high quality graphene. Transition metal such as Cu and Ni is used in CVD to catalyse the decomposition of carbon feedstock and act as substrate for graphene nucleation that leads to lateral growth of graphene layer. Carbon has limited solubility in Cu in

relativity to other transition metals such as Ni (Li et al. 2009b) chemical vapor deposition (CVD). This gives Cu an advantage of graphene formation without the precipitation of excess carbon that leads to formation of graphite (Sarno et al. 2013). The synthesized graphene needs to be isolated from catalyst and this can be carried out by etching process. Produced graphene can be transferred to desired substrate for further analysis and application after etching process. However, graphene flake synthesis by CVD is still not widely explored.

This study focuses on repurposing the etched copper to synthesize flake graphene using a similar method previously used in large area graphene synthesis. Graphene flake is useful in different applications while large area graphene is mostly synthesized for electronic application (Li et al. 2009b) chemical vapor deposition (CVD). For example, it can be used in solar cells (Zhang et al. 2011), composite (Yan et al. 2010), lubricant (Song & Li 2011), catalysis and energy applications (Wang et al. 2013; Yoo & Zhou 2011). This procedure is economically favourable, especially by not discarding the etched Cu as waste, but converting it into a value added material. This process allows the synthesis of large area graphene and graphene flake from a single copper catalyst.

## EXPERIMENTAL DETAILS

### CATALYST PREPARATION

Large area graphene synthesized on Cu foil (0.1 mm thickness, 99.7% purity from Merck, Germany) via methane CVD method in a tubular furnace reactor. The experimental work was carried in a CVD reactor at 950°C with 100 sccm H<sub>2</sub> and N<sub>2</sub> with 30 sccm CH<sub>4</sub> and reaction time which were set for 30 min. Then, the synthesized large area graphene was etched in 0.1 molar ammonium persulfate ((NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub>, Sigma-Aldrich) solution. The solution was drying at temperature of 60°C in an oven overnight. The prepared sample denoted as CU-S1. Then the sample was calcined at 800°C in a furnace for 1 h and denoted as CU-S2. For the preparation of Cu/MgO catalyst, 5 g of dried sample and 5 g of MgO (Brand) were dispersed in 10 mL ethanol and were stirred at 85°C to evaporate ethanol. The resulted viscous mixture was calcined at 900°C for 3 h.

### CATALYST CHARACTERIZATION TECHNIQUES

Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) from TA Instrument (SDT-Q600 Thermo Gravimetric Analyser) was used to determine thermal decomposition of CuSO<sub>4</sub> and (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>. The instrument was supplied with purified air with flow rate of 100 mL/min by increasing the temperature to 1000°C with the ramping rate of 10°C/min. Alumina ceramic crucible (90 µL alumina sample cups) were used as the sample pan. X-ray diffraction spectroscopy (XRD) was used to analyze the pattern of crystal structure of CuO. Diffraction pattern between the 2θ ranges of 20 to 90° was performed using

BRUKER D8 Advance with Cu Kα radiation operated at 40 kV and 40 mA. X'Pert High Score Plus software was used to analyse the diffraction pattern. Registered pattern from International Center for Diffraction Data (ICDD)-Powder Diffraction Files (PDF) databases were used as the comparison to the crystalline phases obtained. Furthermore, X-Ray Fluorescent (XRF) was utilized to conduct an elemental analysis to determine the final purity of the CuO. The XRF facility (Rigaku RIX3000) was used with Rh tube target and the sample was prepared as pressed powder pellet. The unit has a lower limit of detection of 100 ppm and the capability to detect elements from Beryllium to Uranium.

### GRAPHENE SYNTHESIS

Cu/MgO catalyst placed in a quartz boat inserted in the middle of a quartz tube (29 mm in diameter, 750 mm in length) in a horizontal tubular furnace. The furnace was heated to 950°C with a ramping rate of 15°C/min in atmospheric condition under constant N<sub>2</sub> and H<sub>2</sub> flow of 100 mL/min. When the temperature reached 950°C, methane was introduced to the reactor for 30 min. Then, the furnace was allowed to cool down in continues flow of N<sub>2</sub>. Next, the synthesized graphene flake was dissolved in nitric acid (HNO<sub>3</sub>) to remove the residual catalyst by filtering the mixture using a nylon membrane filter (0.2 µm pore size, Whatman). Then, the purified graphene flakes are recovered for further analysis.

### GRAPHENE CHARACTERIZATION TECHNIQUES

The quality of the produced graphene was examined using Raman spectrometer. Raman spectra were collected by using Renishaw InVia Raman Microscope equipped with

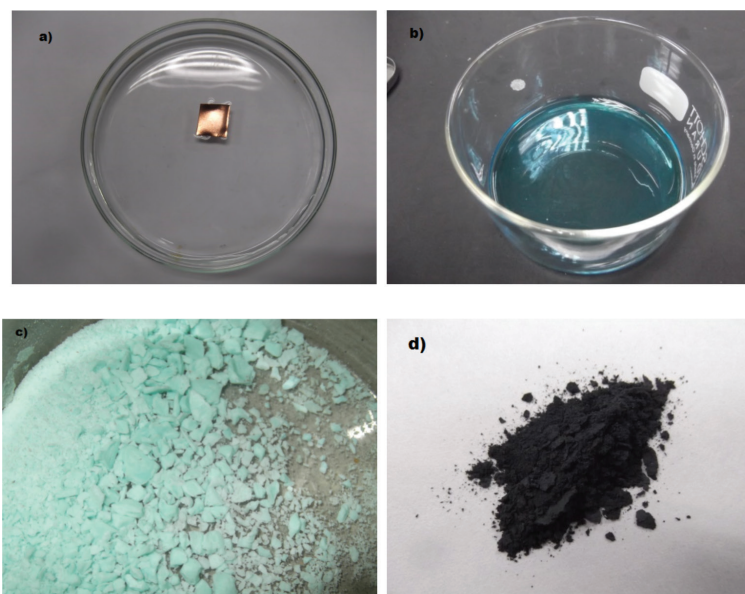


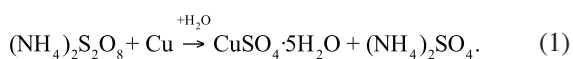
FIGURE 1. (a) Floating Cu with graphene on ammonium persulfate solution, (b) Cu completely etched and light blue solution obtained indicating the Cu presence in the ammonium, (c) the solution after drying at 60°C (CU-S1 sample) and (d) the sample after thermal treatment at 800°C in a furnace for 1 h (CU-S2 sample)

633 nm HeNe laser (20 mW) excitation, 10% laser power and 50X objective lenses. Surface analysis of graphene flake was conducted by ultra high resolution field emission scanning electron microscope (UHR-FESEM) (model FEI Nova NanoSEM 450) equipped with energy dispersive x-ray spectrometer (EDS) for elementary analyses. High resolution transmission electron microscope (HRTEM) was used to obtain images of graphene flakes by depositing the graphene on a holey carbon grid. This analysis was conducted using FEI TECNAI G2 S-TWIN F20 TEM operated at 200 kV. Selected area diffraction (SAED) analysis was performed on selected graphene areas to further investigate the crystallographic of synthesized graphene.

## RESULTS AND DISCUSSION

### RECOVERY OF COPPER FROM ETCHING SOLUTION

In the etching process, the residual Cu in large area graphene was oxidized by ammonium persulfate. Figure 1(a) shows the floating synthesized large area graphene on ammonium persulfate solution and Figure 1(b) illustrates the obtained light blue solution which is indicated the presence of Cu in the ammonium persulfate solution. The obtained solution is containing copper (II) sulphate ( $\text{CuSO}_4$ ) and ammonium sulphate  $(\text{NH}_4)_2\text{SO}_4$  as shown by (1). Figure 1(c) shows the solution after drying process (CU-S1 sample). Ammonium sulphate was removed from the CU-S1 sample using thermal treatment at 800°C (dehydration and desulfurization) as shown in Figure 1(d).



TGA/DTA used to analyse the decomposition temperature of ammonium persulfate and the CU-S1 sample as shown in Figure 2(a) and 2(b), respectively. As shown in Figure 2(b), the decomposition of ammonium persulfate took place at the temperature of 179°C and 447°C with 6% and 94% of total weight loss. Figure 2(a) shows the different trend of thermal decomposition for CU-S1 sample. An initial weight loss from ambient temperature to 200°C was attributed to the removal of absorbed water. A second weight loss observed at temperatures in between 200°C and 440°C was attributed to the removal of unreacted ammonium sulfate. At temperatures higher than 450°C, it is expected that only  $\text{CuSO}_4$  remains and at temperature of 800°C, it is found that about 98% of  $\text{SO}_4$  is removed. The final residual after thermal decomposition was due to the un-decomposed compound (CuO) with about 19% of the total weight.

XRF was used to conduct an elemental analysis of the resulted sample to determine the final purity of the Cu. XRF was employed to determine the final composition of CU-S1 sample after thermal decomposition at 450°C and 800°C as shown in Figure 2(c). At thermal decomposition of 450°C, the residual of the CU-S1 sample contained about 55.5 wt. % and 43.56 wt. % of CuO and  $\text{SO}_3$ , respectively. At thermal decomposition of 800°C, the

CU-S1 sample included 97.51 wt. % of CuO with only 1.28 wt. % of  $\text{SO}_3$ . It is in agreement with Siriwardane et al. (1999) result. The XRF analysis results indicated the formation of CuO with small impurities.

XRD used to measure the crystalline structure of copper oxide in CU-S2 sample and Cu foil as shown in Figure 3(a) and 3(b). Figure 3(a) shows the polycrystalline structural of Cu foil used in large area graphene at three major peaks of 43.342° (111), 50.479° (002) and 74.174° (022). The obtained peaks are aligned with the reference PDF number (calculated powder diffraction data) of 01-089-5898. By using Scherrer's equation with dimensionless shape factor, K equal to 0.9 and X-ray wavelength for Cu-K $\alpha$  radiation,  $\lambda$  equal to 1.541 Å, and data obtained from respective XRD pattern for

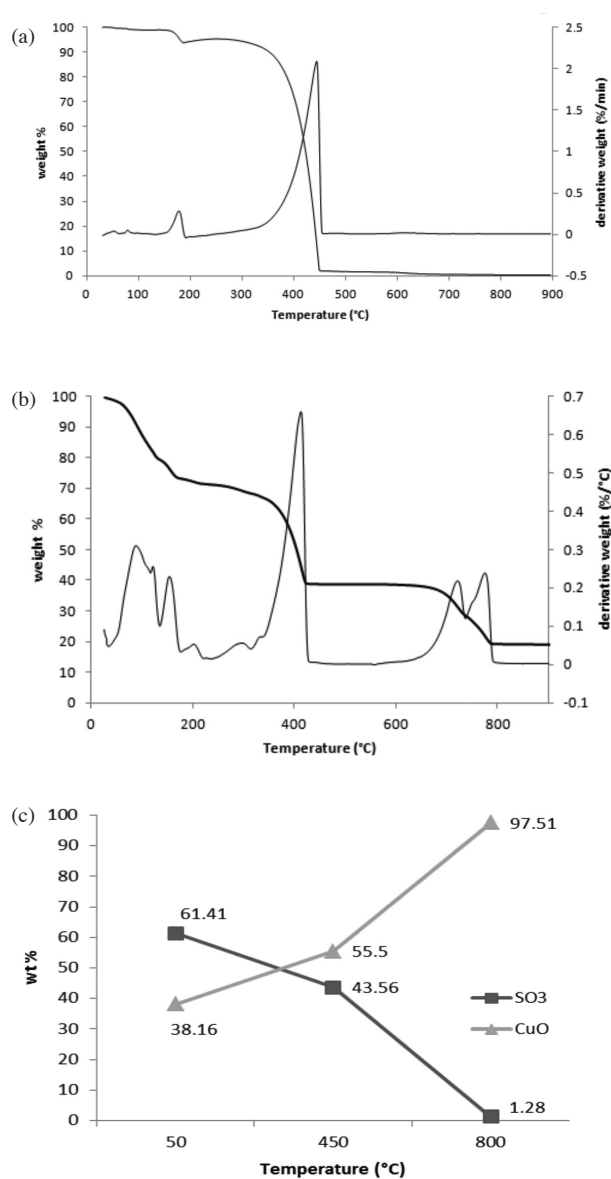


FIGURE 2. (a) TGA/DTA result of ammonium persulfate solution, (b) TGA/DTA result of CU-S1 sample, (c) XRF elemental analysis of CU-S1 sample at different thermal degradation of 450°C and 800°C

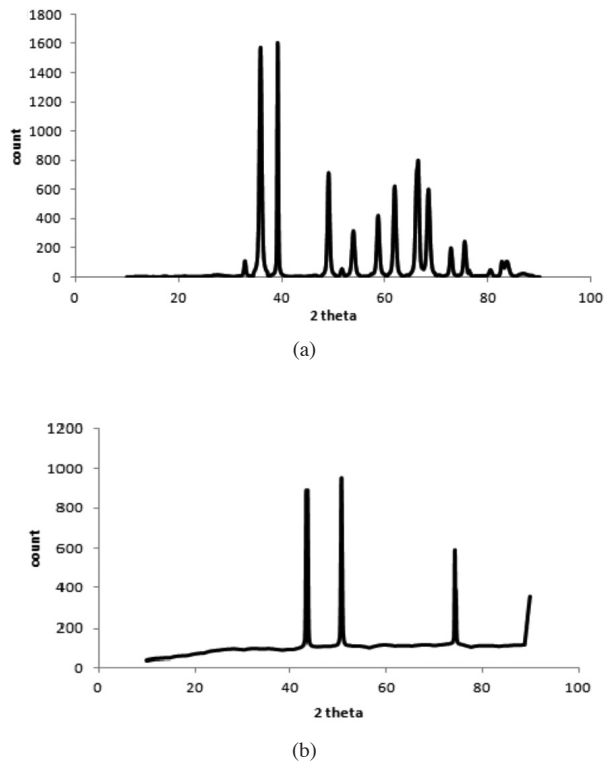


FIGURE 3. XRD pattern of (a) CU-S2 sample and (b) Cu foil

line broadening at the full width half maximum (FWHM) intensity,  $\beta$  and Bragg angle ( $\theta$ ). From the reference and the records obtained, the calculated crystallite size for Cu foil is 44.8 nm. XRD pattern of CU-S2 sample in Figure 3(b) shows two significant peaks at  $2\theta$  ( $^\circ$ ) of which is dominated by (111) plane at  $35.5^\circ$  and  $38.7^\circ$  and (002) plane at  $35.4^\circ$ . Monoclinic structure (PDF no: 01-089-5898) is also observed in CU-S2 sample. By using Scherrer's equation, the calculated average crystallite size for CuO is 22.9 nm which is in agreement with the crystal size of CuO by Farrouji et al. (2015).

#### GRAPHENE FLAKES SYNTHESIS AND ANALYSIS

FESEM with EDX, Raman spectroscopy and HRTEM with SAED was utilized to determine the quality of the graphene flakes were synthesized on Cu-MgO catalyst. The morphology of the grown graphene was investigated using FESEM as shown in Figure 4. Figure 4 shows a crumpled feature on the agglomerated catalyst surface which is due to the thin structure of graphene sheets. This crumpled form is a typical morphology of graphene flakes (El Rouby 2015; Fan et al. 2015).

Figure 5 shows the results of EDX to evaluate the elemental analysis of graphene flakes after acid treatment. Figure 5(b) shows the selected area which the EDX performed on. The result shows the high purity of

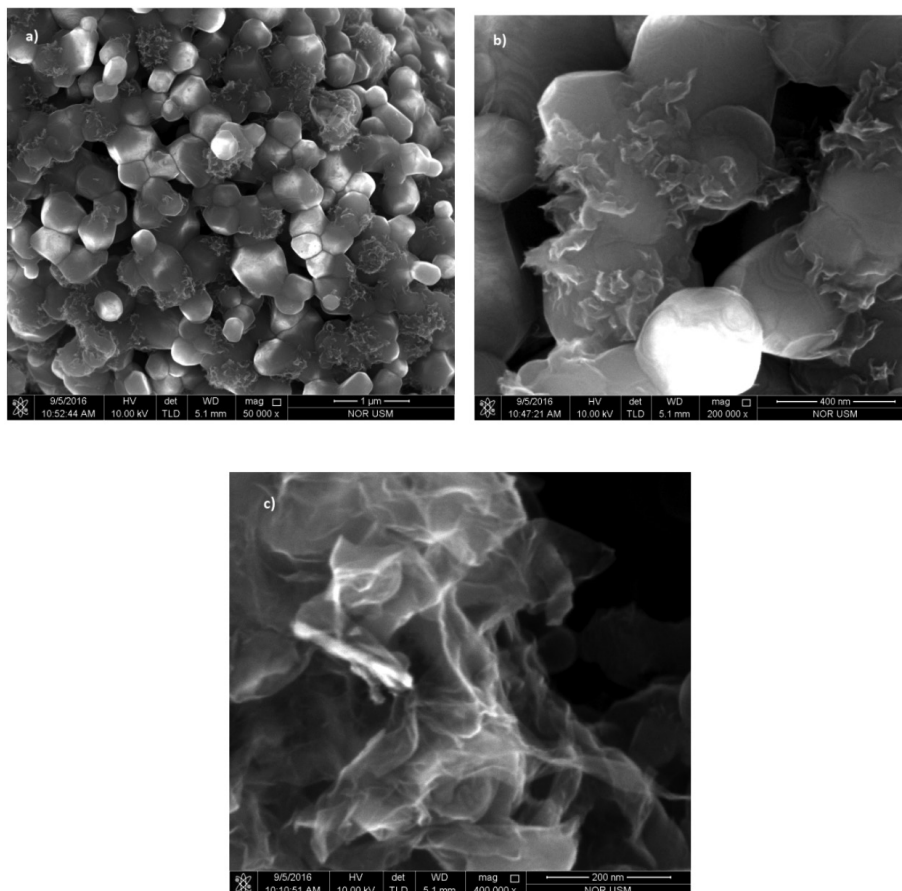


FIGURE 4. FESEM images of (a) and (b) synthesized graphene before purification and (c) after purification

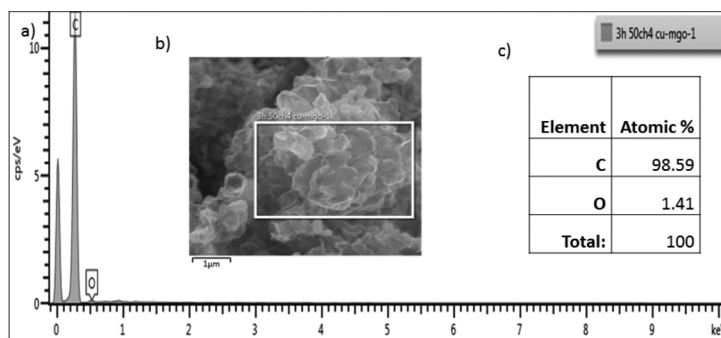


FIGURE 5. EDX for synthesized graphene after purification (a) the elemental graph, (b) selected area and (c) elemental analysis (atomic %)

C (98.59%) with extremely low oxygen element in the sample. This could be due to minor effect of oxidation brought by  $\text{HNO}_3$  particularly at the unfilled carbon bonds at the edges of the graphene (Hu et al. 2003; Tchoul et al. 2007). The oxygen may come from the surrounding ambient gas as result of reaction with unfilled carbon bonds at the edges of the graphene (Wolf 2014). The result showed no trace of Cu or MgO from the used catalyst which it confirms the effective removal of the catalyst by mild nitric acid treatment. The EDX data shows the effectiveness of catalyst removal using nitric acid treatment as there was no presence of Cu or Mg detected.

HRTEM is utilized to evaluate the structure and the number of graphene layers as shown in Figure 6(a) and 6(b). It can be observed there are two and three layers of graphene. As the graphene tendency to restack, SAED was also performed to show layer formation in the graphene sample. As shown in Figure 6(c) and 6(d), SAED proved the formation of single layer and bilayer graphene.

Raman spectroscopy used to determine the structure of graphene layers of the synthesized graphene flake as shown in Figure 6. Raman spectra for graphene flakes show the presence of clear peak of 2D, G and D bands. Raman peak ratios between 2D and G peak suggested the formation of

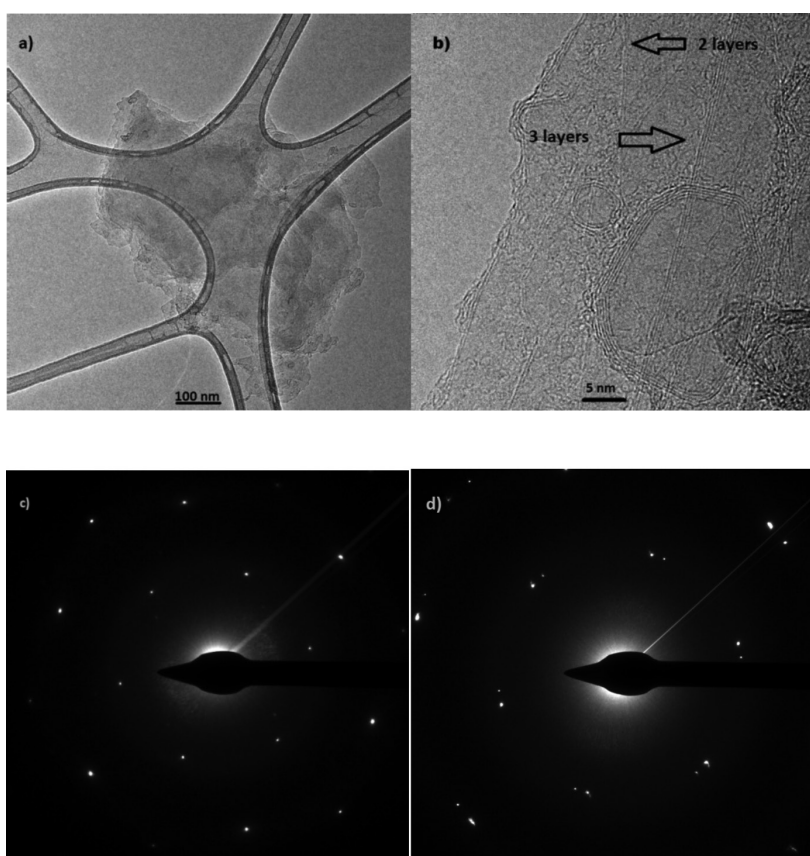


FIGURE 6. (a) and (b) HRTEM images of synthesized graphene after purification (c) SAED of synthesized graphene after purification with single layer and (d) and bilayer

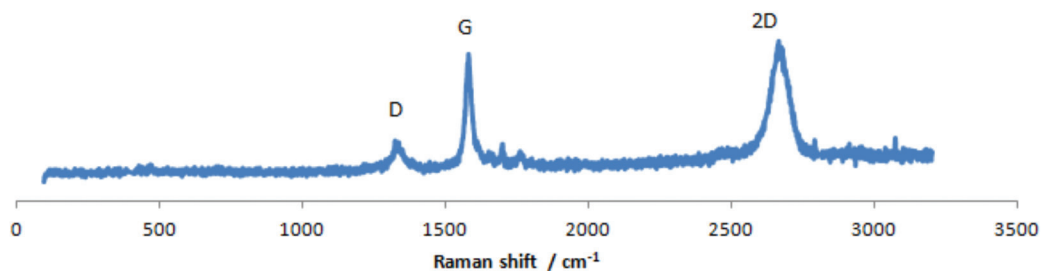


FIGURE 7. Raman spectra for graphene sheets produced

multilayer graphene. Raman spectra for graphene flakes produced at 1 h show the presence of clear peak of D, G and 2D in both samples that confirms graphitic signature of the sample (Figure 7). 1% MgO shows D peak at 1334  $\text{cm}^{-1}$ , G peak at 1583  $\text{cm}^{-1}$  and 2D peak at 2667  $\text{cm}^{-1}$ . FWHM for 2D peak and G peak is 76 and 25, respectively. The  $I_{2D}/I_G$  ratio is 1.03,  $I_G/I_{2D}=0.96$ , that indicates the presence of double layer graphene (Sun et al. 2010).

#### CONCLUSION

It has been demonstrated that MgO-supported recovered Cu from large area graphene etching in ammonium persulfate solution is effective for graphene flake formation via CVD method. The characteristics of the copper sulphate after etching process are investigated using TGA and XRF. Decomposition of copper sulphate into copper oxide take place at temperature above of about 800°C, about 98% purity of copper oxide obtained. The recovered Cu in the Cu/MgO catalyst shows the sufficient catalytic activity for single and few layers graphene formation. Conversion of recovered etched Cu of graphene waste into the efficient catalyst for graphene flake formation provides an alternative way for a cost effective high structural graphene production.

#### ACKNOWLEDGEMENTS

The authors gratefully acknowledge the financial support provided by Fundamental Research Grant Scheme (FRGS) (203/PJKIMIA/6071278).

#### REFERENCES

- Chua, C.K. & Pumera, M. 2014. Chemical reduction of graphene oxide: A synthetic chemistry viewpoint. *Chemical Society Reviews* 43(1): 291-312.
- El Rouby, W.M.A. 2015. Crumpled graphene: Preparation and applications. *RSC Adv.* 5(82): 66767-66796.
- Fan, T., Zeng, W., Niu, Q., Tong, S., Cai, K., Liu, Y., Huang, W., Yong, M. & Epstein, A.J. 2015. Fabrication of high-quality graphene oxide nanoscrolls and application in supercapacitor. *Nanoscale Research Letters* 10: 192.
- Farrouji, A., Eddine, A., Bouzit, S., Boualy, B., Mehdi, A., Firdoussi, L. & Ali, M. 2015. Degradation of methylene blue using synthesized nanostructured CuO with high specific surface area through catalytic oxidation. *International Research Journal of Pure and Applied Chemistry* 8(4): 190-197.
- First, P.N., De Heer, W.A., Seyller, T., Berger, C., Stroschio, J.A. & Moon, J.S. 2010. Epitaxial graphenes on silicon carbide. *MRS Bulletin* 35(April): 296-305.
- Geim, A.K. & Novoselov, K.S. 2007. The rise of graphene. *Nature Materials* 6(3): 183-191.
- Hu, H., Zhao, B., Itkis, M.E. & Haddon, R.C. 2003. Nitric acid purification of single-walled carbon nanotubes. *The Journal of Physical Chemistry B* 107(50): 13838-13842. doi: 10.1021/jp035719i.
- Li, X., Cai, W., An, J., Kim, S., Nah, J., Yang, D., Piner, R., Velamakanni, A., Jung, I., Tutuc, E., Banerjee, S.K., Colombo, L. & Ruoff, R.S. 2009a. Large-area synthesis of high-quality and uniform graphene films on copper foils. *Science* 324(5932): 1312-1314. doi:10.1126/science.1171245.
- Li, X., Cai, W., Colombo, L. & Ruoff, R.S. 2009b. Evolution of graphene growth on Ni and Cu by carbon isotope labeling. *Nano Letters* 9(12): 4268-4272.
- Novoselov, K.S., Fal'ko, V.I., Colombo, L., Gellert, P.R., Schwab, M.G., Kim, K. & Fal-ko, V.I. 2012. A roadmap for graphene. *Nature* 490(7419): 192-200.
- Sarno, M., Cirillo, C., Piscitelli, R. & Ciambelli, P. 2013. A study of the key parameters, including the crucial role of H<sub>2</sub> for uniform graphene growth on Ni foil. *Journal of Molecular Catalysis A: Chemical* 366(January): 303-314.
- Siriwardane, R.V., Poston Jr., J.A., Fisher, E.P., Shen, M-S. & Miltz, A.L. 1999. Decomposition of the sulfates of copper, iron (II), iron (III), nickel, and zinc: XPS, SEM, DRIFTS, XRD, and TGA study. *Applied Surface Science* 152(3): 219-236.
- Song, H-J. & Li, N. 2011. Frictional behavior of oxide graphene nanosheets as water-base lubricant additive. *Applied Physics A* 105(4): 827-832.
- Sun, Z., Yan, Z., Yao, J., Beitler, E., Zhu, Y. & Tour, J.M. 2010. Growth of graphene from solid carbon sources. *Nature* 468(7323): 549-552.
- Tchoul, M.N., Ford, W.T., Lolli, G., Resasco, D.E. & Arepalli, S. 2007. Effect of mild nitric acid oxidation on dispersability, size, and structure of single-walled carbon nanotubes. *Chemistry of Materials* 19(23): 5765-5772. doi: 10.1021/cm071758l.
- Wang, L., Ara, M., Wadumesthrige, K., Salley, S. & Simon Ng, K.Y. 2013. Graphene nanosheet supported bifunctional catalyst for high cycle life Li-air batteries. *Journal of Power Sources* 234: 8-15.
- Wolf, E.L. 2014. Chapert 2. Practical productions of graphene, supply and cost. In *Applications of Graphene*, SpringerBrief in Materials. New York: Springer. pp. 19-38.

- Yan, J., Wei, T., Shao, B., Fan, Z., Qian, W., Zhang, M. & Wei, F. 2010. Preparation of a graphene nanosheet/polyaniline composite with high specific capacitance. *Carbon* 48(2): 487-493.
- Yoo, E. & Zhou, H. 2011. Li-air rechargeable battery based on metal-free graphene nanosheet catalysts. *ACS Nano* 5(4): 3020-3026.
- Zhang, D.W., Li, X.D., Li, H.B., Chen, S., Sun, Z., Yin, X.J. & Huang, S.M. 2011. Graphene-based counter electrode for dye-sensitized solar cells. *Carbon* 49(15): 5382-5388.

School of Chemical Engineering, Engineering Campus  
Universiti Sains Malaysia, Seri Ampangan  
14300 Nibong Tebal  
Seberang Perai Selatan, Pulau Pinang  
Malaysia

\*Corresponding author; email: chrahman@usm.my

Received: 21 December 2016

Accepted: 1 March 2017