



# GRAFTING-ON FUNCTIONALIZATION OF AZIDO-TERMINATED POLY ( $\epsilon$ -CAPROLACTONE) ONTO ULTRASONICATION-ASSISTED EXFOLIATED GRAPHENE

Nabihah Abdullah<sup>1</sup>, Aminul Hakim<sup>1</sup> and Masataka Kubo<sup>2</sup>

<sup>1</sup>Faculty of Chemical Engineering Technology, TATI University College, Kijal, Kemaman, Terengganu, Malaysia

<sup>2</sup>Division of Chemistry for Materials, Graduate School of Engineering, Mie University, Japan

E-Mail: [nabihah@tatiuc.edu.my](mailto:nabihah@tatiuc.edu.my)

## ABSTRACT

In this study, azido-terminated poly ( $\epsilon$ -caprolactone) ( $N_3$ -PCL) was used to attach the macromolecules poly ( $\epsilon$ -caprolactone) onto graphene sheets to give functionalized graphene (G-PCL) that can increase the solubility of graphene sheets. The key of the reaction is nitrene chemistry. Double bonds in graphene were being attacked by high reactivity nitrene radicals from azido groups to form covalent bonds of C-N. Most reported papers showed the grafting-on functionalization based on graphene oxide. On the contrary, we reported grafting-on functionalization using pristine graphene. The attachment of PCL macromolecules onto graphene sheets was determined using transmission electron microscope (TEM), thermal gravimetric analysis (TGA), Fourier transform infrared spectroscopy (FTIR) and solubility test using several solvents. TEM showed PCL coating onto graphene layers. PCL macromolecules content in the G-PCL was estimated about ~47%. Another relevant proof of the successful functionalization of G-PCL was using FTIR where the stretching vibration of azide group was completely vanished after the reaction due to the formation of C-N covalent bonds. The solubility of G-PCL was improved tremendously, especially in dichloromethane. Solubilization of graphene can open the door to various applications. G-PCL is expected to enhance the usage of nanomaterials in biomedical materials, biomedical engineering and materials for drug delivery system. The nanomaterials are likely to show a combination of beneficial properties.

**Keywords:** grafting-on, polycaprolactone, graphene, functionalization.

## INTRODUCTION

Graphene, the 2D form of carbon based material existing as a single layer of atoms. In 2004, Geim and co-workers at Manchester University successfully identified single layers of graphene arranged in a honeycomb lattice. Since in [1] reported its astounding electrical properties, interest in graphene increased dramatically. For the reason of its unique properties such as high surface area, strong mechanical strength, excellent thermal and electrical conductivities, graphene has stirred the interest of academic and industrial researchers in various fields [2-5].

Graphene-based nanomaterials have many promising applications in energy-related and environmental-related areas. For instance, in energy-related areas, modified graphene materials have been used in photovoltaic cells [6-7], lithium ion batteries [8-9], supercapacitors [10] and in fuel cells [11]. In the environmental remediation area, some graphene-based materials have been used for the degradation of toxic organic pollutants [12] and as sensor devices for pollutant analysis [13]. These studies have extended the research and application of graphene-based materials in multidisciplinary areas.

The inertness property of graphene due to  $\pi$ - $\pi$  interaction limits its great potential. Surface modification of graphene can enhance its solubilities and processabilities. Various efforts have been directed toward the functionalization of graphene using covalent and non-covalent modifications, and the covalent modification

plays an important role in improving the solubility of graphene [14]. Most of the covalent functionalization reported in the literature are based on graphene oxide (GO). There are functional groups on GO surface such as hydroxyl, carboxyl and epoxy groups. Functionalization of GO can be achieved utilizing these surface functionalities [15-18]. However, the existence of a few kinds of functional groups may cause trouble in its modification and characterization. Further, GO contains oxygen functional groups which disrupt the  $\pi$ -conjugation and thus lose the electrical conductivity.

Solvent-exfoliation of graphene followed by grafting of polymer chains onto the exfoliated graphene is a facile technique for obtaining soluble graphene. In [19] reported ultrasonication-assisted direct functionalization of graphene with polymers. They carried out ultrasonication of pristine graphene in a poly (vinyl alcohol) (PVA) aqueous solution. PVA macroradicals formed by sonochemical degradation of the PVA solution were successfully trapped by graphene to give soluble PVA-grafted graphene. However, the chemical structure of the resulted soluble graphene is ambiguous because it is not easy to control the generation of radicals onto the PVA chains during sonochemical treatment.

We are interested in attaching of well-defined polymers onto the exfoliated graphene in order to make clear the structure of the polymer-grafted graphene. In this work will be reported functionalization of graphene via ultrasonication-assisted exfoliation of graphene followed by reaction with azido-terminated poly( $\epsilon$ -caprolactone)



(PCL) with a well-defined structure in order to solubilize graphene.

## METHODOLOGY

### Materials

Graphite nanoplatelets (GNPs) were purchased from XG Sciences USA which has nominal average size, 5  $\mu\text{m}$  and thickness, 5-10 nm.  $\epsilon$ -Caprolactone (CL) (Tokyo Kasei Kogyo, Japan) was distilled over  $\text{CaH}_2$  under reduced pressure. All other reagents were purchased from commercial sources and purified by conventional method.

### Preparation of $\text{N}_3$ -PCL

$\text{N}_3$ -PCL was prepared according to the reported procedure [20] by cationic ring-opening polymerization of CL in toluene using 5-azido-1-pentanol and diphenyl phosphate as a functional initiator and catalyst respectively. The degree of polymerization was designed to be around 25. These relatively short polymer chains should be sufficient to control the solubility of the attached graphene. Moreover, the low molecular weight simplifies characterization such as infrared (IR) spectra.

### Ultrasonication-assisted functionalization of graphene with $\text{N}_3$ -PCL

$\text{N}_3$ -PCL (300 mg) was added into the suspension of GNP (50 mg) in 50 mL N-Methylpyrrolidone (NMP) and the mixture was ultrasonicated (310 W, 300 min). The mixture was transferred into a round bottom flask. NMP is considered a combustible material in bulk, to decrease the risk of any reaction at high temperature; the mixture was stirred thoroughly for 15 minutes by bubbling with nitrogen. Then, the mixture was heated at  $160^\circ\text{C}$  for 24 hours under nitrogen atmosphere. When the reaction was finished, the mixture was cooled to room temperature before it was proceed to centrifugation. After centrifugation (1000 rpm, 30 minutes) to remove unreacted graphene and unexfoliated GNP, the supernatant was filtered by TEFLON filter (0.45  $\mu\text{m}$ ). The soluble mixture was precipitated in IPE and finally the obtained precipitation was thoroughly washed using benzene at least 3 times to remove the unlinked PCL and was named G-PCL.

### Characterization

The surface morphology of GNP and G-PCL was investigated using transmission electron microscope (TEM, Hitachi H-800) which operating at an accelerating voltage of 100kV. Fourier transform infrared (FTIR) spectra were recorded using a Jasco 4100 instrument which employing a KBr tablet that was made by the compression molding of KBr powder mixed with a small amount of sample. TGA was performed by heating samples at least more than 5mg for each condition at a heating rate of  $10^\circ\text{C}/\text{min}$  under nitrogen atmosphere.

## RESULTS AND DISCUSSION

### TEM

The morphological nanostructures of GNP and G-PCL were investigated by TEM. The image of G-PCL exhibited graphene sheets with some wrinkles with a dimension ranging from 500 nm to micrometers. As a comparison, Figure-1(a) is a starting material GNP. GNP shows darker contrast indicating of thicker layers of graphite. We can observe in Figure-1(b) that the surface of graphene is covered with a thin coating of PCL. This morphology is similar to the case of PVA functionalized graphene, where a relatively uniform polymer interface layer is created [19]. The G-PCL appears relatively shorter than those in the starting samples (GNP), probably due to the shortening effect associated with the prolonged sonication in the NMP.

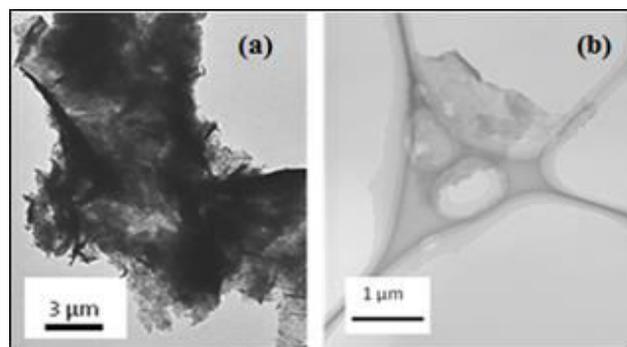


Figure-1. TEM images of (a) GNP (b) G-PCL.

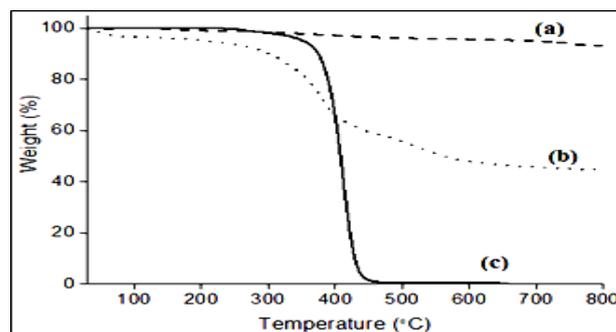


Figure-2. Thermograms of (a) GNP (b) G-PCL and (c)  $\text{N}_3$ -PCL.

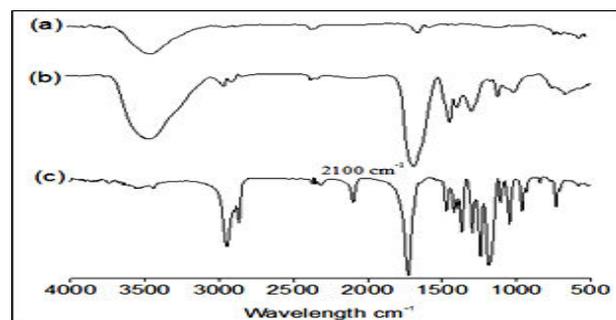


Figure-3. IR spectra in KBr pallet (a) GNP (b) G-PCL (c)  $\text{N}_3$ -PCL.



## TGA

TGA was utilized to investigate the thermal stability of carbonerous materials and the amount of PCL grafted on graphene surface. It is an extension method that is capable of determining the amount of organic groups in the functionalized graphene [21]. We can hardly identify the percentage degradation of GNP in Figure-2 due to the stability of GNP towards increasing of temperature. The disordered or amorphous carbon tended to be oxidized at around 500°C due to the lower activation energies for oxidation. However, a well graphitized structure started to oxidize at higher temperature around 800°C [22]. The overall weight loss of GNP is about 8% at 800 °C (Figure-2(a)), which showing its good thermal stability. Degradation temperature of N<sub>3</sub>-PCL started at 270 °C and finally reached the equilibrium at a temperature of 550 °C, which indicating that all N<sub>3</sub>-PCL has burned out (Figure-2(c)). In the case of G-PCL, the weight loss observed from 250 °C to finally reach equilibrium at 700°C (Figure-2(b)). The weight loss corresponds to the decomposition of organic segment attached on the graphene.

By comparing with the weight loss of GNP, G-PCL and N<sub>3</sub>-PCL, the PCL macromolecules content in G-PCL was evaluated to be ~47%. In order to confirm that the result was due to the covalent bonding of PCL macromolecules onto the graphene surface, the mixture of GNP, N<sub>3</sub>-PCL and NMP was prepared without being heated at 160°C in N<sub>2</sub> atmosphere. Thermally generated nitrene radicals from azido groups possess high reactivity and can attack the double bonds in carbon nanomaterials such as graphene. As a result, the filtrate color was clear due to no soluble graphene presented in the mixture.

## IR

Figure-3 shows the FTIR spectra for the G-PCL, GNP and N<sub>3</sub>-PCL. The significant bands that appear in the FT-IR spectra indicating the presence of functional groups on the surface of GNP as shown in Figure-3(a): at 1620 cm<sup>-1</sup> (carboxyl group) and 3455 cm<sup>-1</sup> (hydroxyl group). These functional groups are produced on the surface of GNP. This increases the surface polarity and further alters the surface charges. Based on the IR spectrum of N<sub>3</sub>-PCL (Figure-3(c)) shows the adsorption peak at 2100 cm<sup>-1</sup>, which is the characteristic of azide group. This is supporting the successful synthesis of N<sub>3</sub>-PCL. The peaks at 2949 cm<sup>-1</sup>, 2865 cm<sup>-1</sup> and 1740 cm<sup>-1</sup>, characteristics of asymmetric and symmetric stretching of CH<sub>2</sub> and carbonyl stretching of PCL.

The successful grafting of PCL macromolecules onto graphene could be proved by the IR spectra. The IR spectrum of non-functionalized graphite (GNP) does not possess any characteristic due to PCL moiety (Figure-3(a)). But after the reaction with N<sub>3</sub>-PCL, characteristic absorption peaks due to PCL moiety were clearly observed in Figure-3(b). The IR spectrum of N<sub>3</sub>-PCL and the stretching vibration of azide group were completely vanished on G-PCL, which could be ascribed to its reaction with graphene and successfully attached on

graphene. The azide group was disappeared due to the tiazole ring opening. This suggested the presence of PCL macromolecules in the functionalized graphene.

## Solubility

The G-PCL dissolved in few solvents to investigate the solubility. A small amount (ca. 5 mg) of G-PCL was added to 3 mL of solvents (dichloromethane, methanol, ethyl acetate and benzene). G-PCL was completely soluble in dichloromethane to give dark brown homogeneous clear solution. Judging from the coloring of the liquid phase, the following is the solubility order of G-PCL: dichloromethane >> methanol > ethyl acetate > benzene as shown in Figure-4.

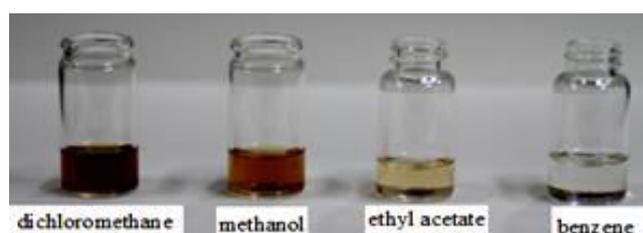


Figure-4. Photographs of G-PCL in various solvents.

## CONCLUSIONS

We have developed a technique for functionalization of graphene with PCL using starting material GNP. Based on the results, we can conclude that the PCL was covalently attached onto the graphene surface to form the G-PCL. Graphene can be dissolved in a wide variety of organic solvent through covalent functionalization with PCL, which can widen its practical applications.

## ACKNOWLEDGEMENTS

This work is funded by Ministry of Higher Education, Malaysia under FRGS/1/2015/TK02/TATI/03/2.

## REFERENCES

- [1] K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, Y. Zhang, S. A. Dubonos, I. V. Grigorieva and A. A. Firsov. 2004. Electric field effect in atomically thin carbon films. *Science*. 306(5696):666-669.
- [2] A. K. Geim and K. S. Novoselov. 2007. The rise of graphene. *Nature Materials*. 6(3):183-191.
- [3] S. Sahoo and S. K. Sahoo. 2009. Graphene: A fascinating material. *Indian Journal of Science and Technology*. 2(12):74-78.
- [4] A. Fazli, R. Moosaei, M. Sharif and S.J. Ashtiani. 2015. Developments of graphene-based polymer composites processing based on novel methods for innovative applications in newborn technologies.



- Indian Journal of Science and Technology. 8(S9): 38-44.
- [5] J. Wu, M. Agrawal, H. A. Becerril, Z. Bao, Z. Liu, Y. Chen and P. Peumans. 2009. Organic light-emitting diodes on solution-processed graphene transparent electrodes. *ACS Nano*. 4(1): 43-48.
- [6] C. N. Rao, A. K. Sood, R. Voggu and K. S. Subrahmanyam. 2010. Some novel attributes of graphene. *The Journal of Physical Chemistry Letters*. 1(2):572-580.
- [7] Z. Chen, M. Zhou, Y. Cao, X. Ai, H. Yang and J. Liu. 2012. In situ generation of few-layer graphene coatings on SnO<sub>2</sub>-SiC core-shell nanoparticles for high-performance lithium-ion storage. *Advanced Energy Materials*. 2(1): 95-102.
- [8] F. Kokai, R. Sorin, H. Chigusa, K. Hanai, A. Koshio, M. Ishihara, Y. Koga, M. Hasegawa, N. Imanishi and Y. Takeda. 2012. Ultrasonication fabrication of high quality multilayer graphene flakes and their characterization as anodes for lithium ion batteries. *Diamond and Related Materials*. 29: 63-68.
- [9] D. W. Wang, F. Li, J. Zhao, W. Ren, Z. G. Chen, J. Tan, Z. S. Wu, I. Gentle, G. Q. Lu and H. M. Cheng. 2009. Fabrication of graphene/polyaniline composite paper via in situ anodic electropolymerization for high-performance flexible electrode. *ACS Nano*. 3(7): 1745-1752.
- [10] R. Kou, Y. Shao, D. Wang, M. H. Engelhard, J. H. Kwak, J. Wang, V. V. Viswanathan, C. Wang, Y. Lin, Y. Wang and I. A. Aksay. 2009. Enhanced activity and stability of Pt catalysts on functionalized graphene sheets for electrocatalytic oxygen reduction. *Electrochemistry Communications*. 11(5): 954-957.
- [11] D. Zhao, G. Sheng, C. Chen and X. Wang. 2012. Enhanced photocatalytic degradation of methylene blue under visible irradiation on graphene@TiO<sub>2</sub> dyade structure. *Applied Catalysis B: Environmental*. 111: 303-308.
- [12] F. Schedin, A. K. Geim, S. V. Morozov, E. W. Hill, P. Blake, M. I. Katsnelson and K. S. Novoselov. 2007. Detection of individual gas molecules adsorbed on graphene. *Nature Materials*. 6(9):652-655.
- [13] X. Xu, W. Lv, J. Huang, J. Li, R. Tang, J. Yan, Q. Yang, J. Qin and Z. Li. 2012. Functionalization of graphene by tetraphenylethylene using nitrene chemistry. *RSC Advances*. 2(18): 7042-7047.
- [14] S. Stankovich, D. Piner, S. T. Nguyen and R. S. Ruoff. 2006. Synthesis and exfoliation of isocyanate-treated graphene oxide nanoplatelets. *Carbon*. 44(15): 3342-3347.
- [15] S. Niyogi, E. Bekyarova, M. E. Itkis, J. L. McWilliams, M. A. Hamon and R. C. Haddon. 2006. Solution properties of graphite and graphene. *Journal of the American Chemical Society*. 128(24): 7720-7721.
- [16] H. Yang, C. Shan, F. Li, D. Han, Q. Zhang and L. Niu. 2009. Covalent functionalization of polydisperse chemically-converted graphene sheets with amine-terminated ionic liquid. *Chemical Communications*. 26: 3880-3882.
- [17] Y. Xu, Z. Liu, X. Zhang, Y. Wang, J. Tian, Y. Huang, Y. Ma, X. Zhang and Y. Chen. 2009. A graphene hybrid material covalently functionalized with porphyrin: Synthesis and optical limiting property. *Advanced Materials*. 21(12): 1275-1279.
- [18] B. Shen, W. Zhai, D. Lu, J. Wang and W. Zheng. 2012. Ultrasonication-assisted direct functionalization of graphene with macromolecules. *RSC Advances*. 2(11): 4713-4719.
- [19] K. Makiguchi, T. Satoh and T. Kakuchi. 2011. Diphenyl phosphate as an efficient cationic organocatalyst for controlled/living ring-opening polymerization of  $\delta$ -valerolactone and  $\epsilon$ -caprolactone. *Macromolecules*. 44(7): 1999-2005.
- [20] C. Gao, H. He, L. Zhou, X. Zheng and Y. Zhang. 2008. Scalable functional group engineering of carbon nanotubes by improved one-step nitrene chemistry. *Chemistry of Materials*. 21(2): 360-370.
- [21] C. C. Teng, C. C. Ma, C. H. Lu, S. Y. Yang, S. H. Lee, M. C. Hsiao, M. Y. Yen, K. C. Chiou and T. M. Lee. 2011. Thermal conductivity and structure of non-covalent functionalized graphene/epoxy composites. *Carbon*. 49(15): 5107-5116.
- [22] S. K. Yadav, H. J. Yoo and J. W. Cho. 2013. Click coupled graphene for fabrication of high-performance polymer nanocomposites. *Journal of Polymer Science Part B: Polymer Physics*. 51(1):39-47.