JMSAE
Journal of Materials Science and Applied Energy

Synthesis of graphene from food and agricultural wastes in ubon ratchathani province, thailand

Makabodee Ruaysap[a, *], Tontrakarn Pongphai[b], Kanya Sirilapphokhin[a],
Prin Sirilapphokhin[a], Udom Tipparach[c]

[a] Chemistry Program, Faculty of Scienced, Ubon Ratchathani Rajabhat University, Ubon Ratchathani, 34000 Thailand
[b] Department of Chemitry, Faculty of Science, Kasetsart university, Bangkok, 10700 Thailand
[c] Department of Physics, Faculty of Science, Ubon Ratchathani University, 34190 Thailand

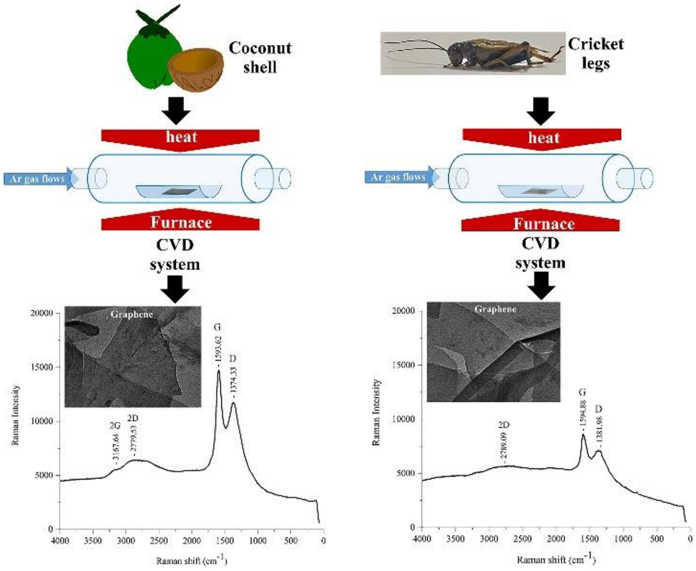
***Corresponding Author:** makabodee.r@ubru.ac.th

https://doi.org/10.55674/jmsae.v11i2.244465

Received: 20 May 2021 | **Revised:** 28 June 2021 | **Accepted:** 27 April 2022 | **Available online:** 1 May 2022

Abstract

This research aims to investigate the possibility of synthesis of graphene from food and agricultural waste materials by Chemical Vapor Deposition (CVD). The starting materials including coconut shells and cricket legs were used to synthesize graphene. The synthesized graphene specimens were characterized by Ultraviolet-visible spectroscopy (UV-Vis), Powder X-ray diffraction (XRD) technique, Dispersive Raman spectroscopy, SEM, and TEM. Both resultant graphene samples: coconut shells and cricket legs showed graphene characteristics with the maximum wavelength of UV spectrum of synthesized graphene in ethanol at ~244 nm comparable with a standard graphene. The graphene characteristics of coconut shells and cricket legs were also confirmed by XRD showing (002) peak at 2θ≈26°. The SEM images showed lamella structure and wrinkle texture, demonstrating the multilayered microstructure and crumpled sheets and folded sheets. The TEM images also confirmed the layered sheets restacking structure with the different numbers of sheets and expressed that the graphene is a semitransparent material. Data obtained from Raman spectroscopy indicated that the defect of structure band or D-band at 1,340 – 1,380 cm^{-1}, the graphite band or G-band at 1,500 – 1,600 cm^{-1} corresponding to sp^2 of carbon atom, the graphene band or 2D-band at 2,500 – 2,600 cm^{-1} showing that the structure of graphene is a multilayer with small sizes and the overtone band of graphite or 2G - band at 3,100 – 3,200 cm^{-1}. On the basis of the result, graphene was possibly synthesized from coconut shells and cricket legs.



Keywords : Graphene; Chemical vapor deposition; Food or agricultural waste

Introduction

Reducing food and agricultural wastes will not only help to earn more income but also to save the world from environmental problems [1]. Food and agricultural wastes significantly created from thrown away food and garbage each day by human activities are serious causes of the global warming crisis [2, 3]. Greenhouse gases (e.g. carbon dioxide, methane and water vapor), especially methane produced by continuously increased food waste each year are the cause of global warming that are contributed by continuously increased food and agricultural wastes [2, 4] each year. The recycle of food and agricultural wastes is one of the reduction methods of many greenhouse gases [5]. Here, an approach of recycle of food and agricultural wastes as starting materials of graphene synthesis will be another interesting choice of saving the world from the global warming effect. The possibility of using the different starting materials instead of the highly pure graphite not only helps to reduce the global warming but also offers the alternatively suitable choices in the future when there is lack of graphite sources left around the world. These alternative starting materials will possibly help to lower the cost of expensive graphene synthesis since the highly pure graphite is very expensive due to its refining process [6 – 8]. Almost a decade, many researchers have studied on synthesis of graphene from various graphite-like resources such as natural, industrial carbonaceous and agricultural wastes. The significant reason behind using alternative graphitic starting materials [6,8] is to reduce the expenditure of synthesis as mentioned above. Not only switching from expensive high pure graphite to cheaper or free of charge to lower the cost of graphene production but also simplifying the complexity of growing graphene will remarkably help to reduce production costs. Based on the literature articles, we found that there are two principal courses of action to fabricate graphene from cheaper alternative graphitic materials: with and without purification of raw materials. The first procedure with purification of raw materials includes 3 steps. Step 1 is the preparation of carbonaceous substances from food, semi-industrial and industrial wastes by burning the wastes at high temperature at approximately 400-500 °C. Step 2 is the graphitization of carbonaceous substances with a potential sewage and industrial waste remover which is Iron (III) chloride hexahydrate ($FeCl_3 \cdot 6H_2O$) under the pH = 2 of hydrochloric acid (HCl). After the treatment, the treated carbonaceous substances are left for a week to remove some water at room temperature, and then the treated carbonaceous substances will be dried at 100 °C for 5 h to collect the black solid substances which will be ground to black powder that it is a graphitic material. Step 3 is the Hummer's method which will be applied to change graphitic material to graphene oxide and then finally get reduced graphene oxide or graphene [8]. The second approach without purification process of raw materials consists of only one step by burning waste samples such as food or insects at very high temperature at 1,050 °C by using Chemical Vapor Deposition technique (CVD technique) directly to form graphene on Cu-foils used as a mold under the H_2/Ar ambient [6, 7].

Even though graphene consists of a simple structure of the two dimensional array of tightly bonded of sp^2 hybridized carbon atoms creating a monolayer honey comb shape [9, 10], it has eminently incredible physical and chemical properties including the strongest and thinnest material [11] but fordable, compared to diamond [12 – 14] with transparent properties [15], low electrical resistance [16], high thermal conductivity [9, 17], and high electronic mobility [14, 18]. There are very great in a number of applications and technology of it, especially in electronic filed consisting of electronic devices [19], supercapacitors [13, 20 – 22], batteries [20, 23], composite materials [24], nanocomposites [25], solar cells [13, 26], sensors [13, 27, 28], photocatalysis [29], energy storages [30] and transistors [31] etc.

CVD technique was selected to grow our graphene based on our principles of simple or no sample's preparation and production and no rigorous chemical treatment. CVD is a vapor coating on a metal such as copper, nickel, iron, cobalt or platinum [6] to form the product [32].

The main object of this work is to provide an alternative method and information of other possible options of starting material precursors for graphene production to reduce the amount of food and agricultural wastes.

Materials and Methods

Materials

The samples: two coconut shells and cricket legs (fresh markets in Ubon Ratchathani province, Thailand), 99.80 % purity of copper foil (Cu foil) (SP Med Science Limited company), ethanol (AR grade, BDH), acetic acid (AR grade, J.T Beaker), standard graphene powder (#900713, Sigma Aldrich), filter paper No. 1 (Whatman), and VTF2 Vecstar high temperature tube furnace served as a chemical vapor deposition (CVD) instrument.

Sample Preparation

Two coconut shell and cricket leg wastes were first washed to remove some dirt without weighing out the amount of waste samples. Both starting materials were dehydrated in a vacuum oven at 65 °C for 10 h to eliminate some moisture before weighing out 1 g of each sample waste to be used as the feed material in the next step. The process of sample preparation for graphene synthesis from coconut shell and cricket leg wastes is illustrated in Fig. 1.

Synthesis of Graphene

A copper foil (Cu foil) with purity or 99.80 % was cut acid for 10 min and then rinsed with ethanol. 1 g of each prepared coconut shells and cricket legs was put on the cleaned 2 × 2 cm^2 Cu foil and the sample material on the Cu foil was put in a clean quartz boat and this set of sample material was then sled in the middle of CVD furnace and calcined at 1,050 °C for 15 min [6], with Ar flow into 2 × 2 cm^2 and then was washed with 10 % v/v of acetic at ~ 500 cm^3 min^{-1}. The sample was left in the CVD system to cool down naturally. The cool and black annealed sample on the Cu foil was washed with ethanol and filtered to get the graphene product solution. All the previous processes of the graphene synthesis were repeated several times, depending on the starting materials used, to collect more graphene

Fig. 1 The process of sample preparation for graphene synthesis from coconut shell and cricket leg wastes.

solution. To get the graphene powder, the ethanol solvent was drained out and the left wet graphene powder and scooped out of the container to be dried in the oven at ~ 79 °C for ~ 5 – 8 h and finally put the room temperature product in the vacuum desiccator.

Samples Characterizations

Graphene characteristics were studied by Ultraviolet-visible spectroscopy (UV-Vis) (Brand: Shimadzu Corporation, Model: UV-2401PC) to identify the graphene absorption, powder X-ray diffraction (XRD) (Brand: Philips, Model: XPert) to examine the crystal structure of the samples and Dispersion. The data were collected from 10 to 80 degrees with 0.02° steps and the scan speed of 0.5 second per step using CuKα line (1.54 Å). Raman spectroscopy with 532 nm laser as excitation sources, Power laser: 20 mW, spectral range: 4500 – 70 cm^{-1} and Detector: TE-cooled CCD (Brand: Bruker Optics, Model: Senterra) to study chemical and structural information, Scanning Electron Microscope (SEM), acceleration voltage of 15 kV (Brand: JEOL, Model: primus 7600+) to study surface morphology and Transmission Electron Microscope (TEM), acceleration voltage of 80 kV (Brand: TECNAI, Model: 10/21) to study microstructure of the products.

Results and Discussion

Graphene characteristics of samples were confirmed by UV spectrum of standard graphene (Sigma Aldrich, 2018) in ethanol with λ_{max} at ~ 242 – 244 nm. Fig. 2 shows that UV spectra of graphene synthesized from both coconut shells (Fig. 2(a)) and cricket legs (Fig. 2(b)) in ethanol exhibit λ_{max} at 244 nm with sharp/flat feature [33, 34]. The absorbance of the synthesized graphene shows a very sharp peak with low intensity of approximately 0.40 because the concentration of graphene of the synthesized graphene is very low relatively to the intensity of absorbance of the standard graphene. The shape of absorbance of the standard graphene is broad with high intensity of 2.50 since the concentration of the standard graphene used to determine the characteristic of graphene was high. The high amount of graphene molecules causes the induction between molecules of graphene. Therefore, the spectrum is the peak of the absorption of induced molecules not free molecules that results in a broad band. The high amount of graphene also causes accompanying both vibrational energy and rotation energy levels of the electronic transition of absorbing molecules. This phenomenon leads to the broad band as well. To confirm the graphene characteristic, adding the standard graphene into the synthesized graphene to observe the feature and the intensity of the peak was applied. The result shows that the spectra of the mixture of the standard graphene and the synthesized graphene from coconut shells or cricket legs are also broad bands which are similar to the spectrum of the standard graphene. However, the intensities of the spectra of the mixtures are lower than the intensity of the standard graphene. This is because the amount of the standard graphene added into the synthesized graphene was reduced so the total amount of the mixture of the standard

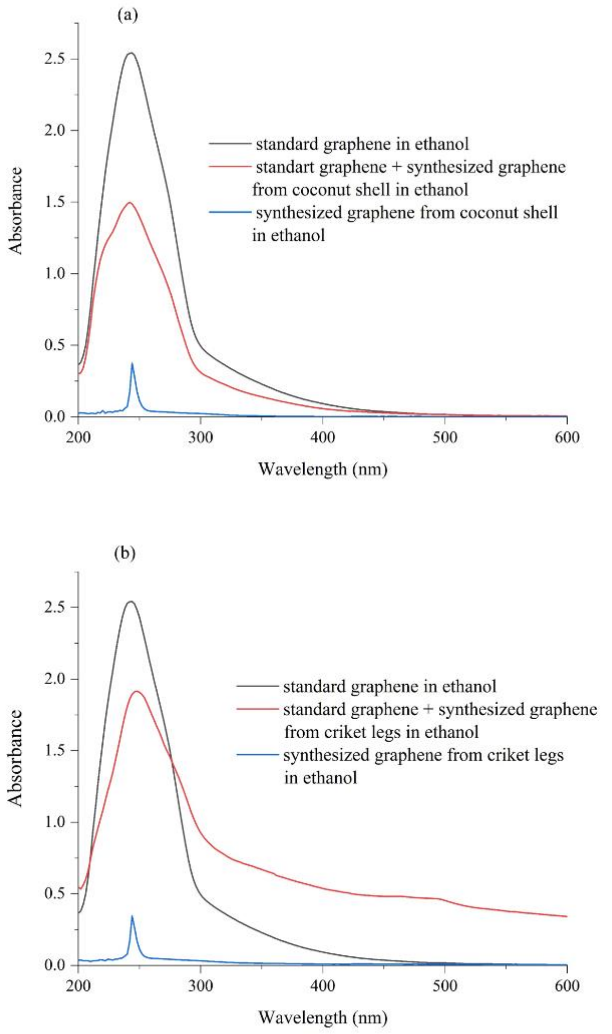


Fig. 2 UV-vis spectra of standard graphene and synthesized graphene products in ethanol (a) standard graphene, standard graphene + synthesized graphene from coconut shells and synthesized graphene from coconut shells (b) standard graphene, standard graphene + synthesized graphene from cricket legs and synthesized graphene from cricket legs.

graphene and the synthesized graphene was lower than the amount of the standard graphene alone.

Powder X-ray diffraction (XRD) technique indicated graphene characteristics of synthesized coconut shells and cricket legs of (002) plane at 2**θ** ≈ 26° (Fig. 3) corresponding to disorder packing of multiple graphene sheets [35]. This position of spectra demonstrates the (002) plane of graphite with interlayer spacing of ~ 0.34 nm. [36 – 39]. The XRD patterns of synthesized graphene from both coconut shells and cricket legs are analogous to those of the graphene produced by Fatima Tuz Johra and coworkers [37]. Their graphene was made by the enhanced Hummer's method with graphite as a feed material and the graphene fabricated by Xiangrong Liu et al. [35]. They applied hydrothermal exfoliation method to construct graphene by using graphite as a starting material. The only difference of the XRD patterns of the synthesized graphene from the sample wastes is the shape of the spectra. The XRD pattern of the synthesized graphene from coconut shells (Fig. 3(a)) is obviously broader than that of synthesized graphene from cricket legs (Fig. 3(b)). The broadening spectrum demonstrates disorder of graphite layers caused by expansion of empty rooms between graphite layers. It means the synthesized graphene from cricket legs (Fig. 3(b)) is less disorder of graphite stack after expansion than the synthesized graphene from coconut shells.

The Raman spectrum of synthesized graphene from coconut shells (Fig. 4(a)) exhibits the three distinctive peaks of the defect structure band or D-band at 1,340 – 1380 cm^{-1}, the graphite band or G - band at 1,500 – 1,600 cm^{-1} corresponding to sp^2 of carbon atom. The graphene band or 2D - band at 2,500 – 2,600 cm^{-1} showing that the structure of graphene is multilayers with small size. The Raman spectrum of the synthesized graphene from cricket legs Fig. 4(b) also shows the main three peaks of D – band, G-band and 2D – band, but also the overtone band of graphite or 2G - band at 3,100 – 3,200 cm^{-1}. [6 – 8, 23, 25, 33, 35, 37 – 41]. Both Raman spectra of the synthesized graphene from coconut shells and cricket legs are analogous to those of graphene created by Fatima Tuz Johra et al. [37] and Liurong Shi et al. [40]. Liurong Shi and team operated CVD technique to grow graphene on sodium chloride (NaCl) crystals by using the mixture of argon, ethylene and hydrogen gases as a primary material.

The surface morphology of both synthesized graphene from coconut shells (Fig. 5(a)) and synthesized graphene from cricket legs (Fig. 5(b)) is explained by the SEM images that reveals lamella structure and many wrinkle texture, demonstrating crumpled sheets and folded sheets, and the multilayered microstructure which is supported with a strong evidence of the TEM images (Fig. 6) of both synthesized graphene from coconut shells (Fig. 6(a)) and synthesized graphene from cricket legs (Fig. 6(b)). The TEM images also confirm the layered sheets restacking structure with different numbers of sheets and express that the graphene is a semitransparent material [14, 23, 29, 30, 39, 42 – 44]. The SEM image of the synthesized from coconut shells is comparable to that of graphene nanosheets (GNs) on platinum substrates. The GNs were produced from the mixture of hydrogen and acetylene gases with the ratio of 2:1 by electron cyclotron resonance plasma CVD technique [46] and are also in agreement to that of graphene cultivated from artificial graphite (such as petroleum coke and coal tar pitch) which was thermally expanded the space between graphite layers with high temperature [47]. Whereas the SEM image of the synthesized graphene from cricket legs is similar to the GNs fabricated the same starting gases which were the mixture of hydrogen and acetylene gases with the ratio of 2:1 but the growing was operated on copper substrates [46].

Both TEM images of the synthesized graphene of the two waste materials are comparable to those of graphene produced from graphite powder by the modified Hummer's method and hydrothermal reduction [38] and graphene cultivated from artificial graphite (such as petroleum coke and coal tar pitch) which was thermally expanded the space between graphite layers with high temperature [47]. The difference of the synthesized graphene from coconut shells and cricket legs and both previous work is the number of layers of graphene sheets. The synthesized graphene has more layers than the previously prepared graphene.

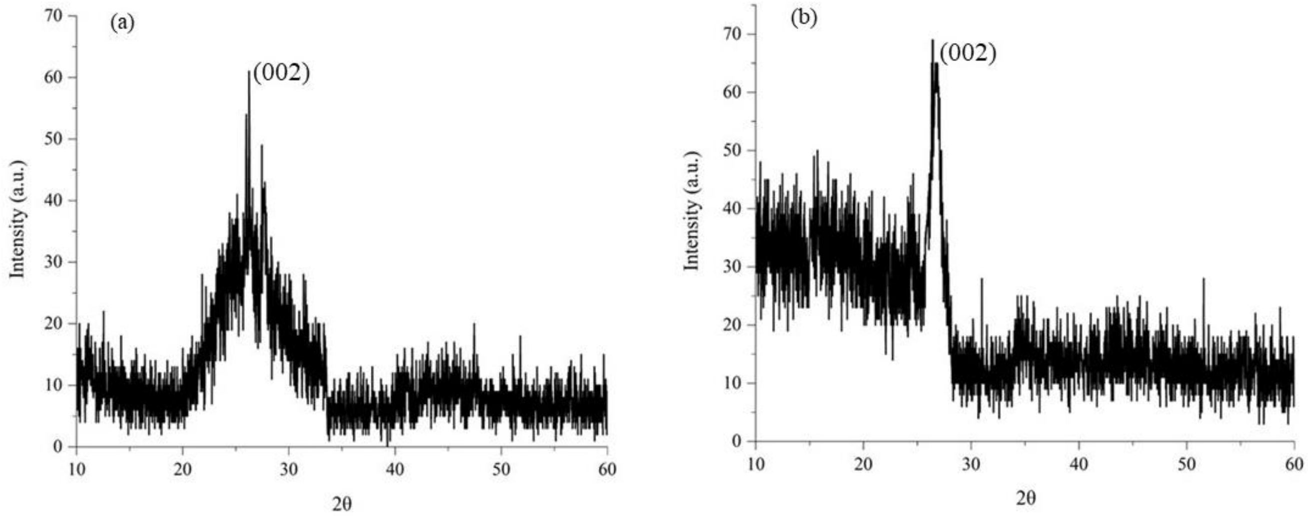


Fig. 3 XRD patterns of (a) synthesized graphene from coconut shells and (b) synthesized graphene from cricket legs.

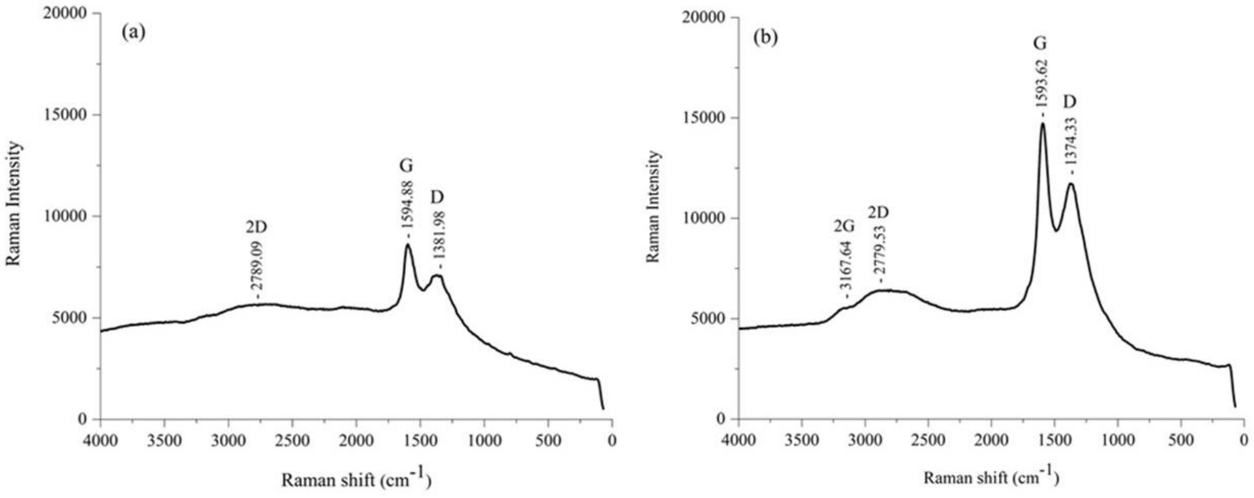


Fig. 4 Raman spectra of (a) synthesized graphene from coconut shells and (b) synthesized graphene from cricket legs.

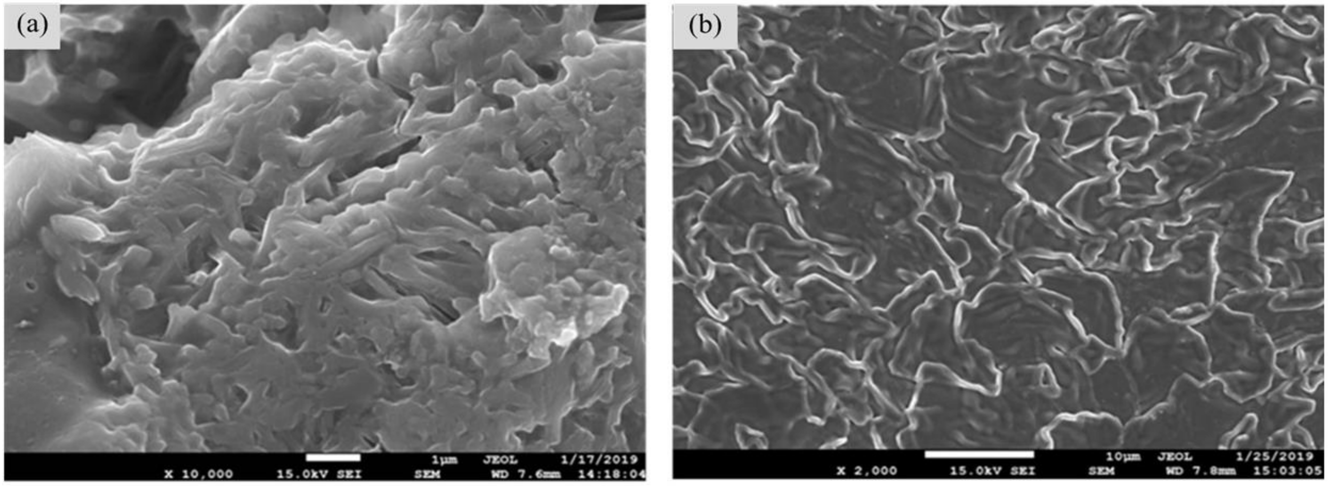


Fig. 5 SEM images of (a) synthesized graphene from coconut shells and (b) synthesized graphene from cricket legs.

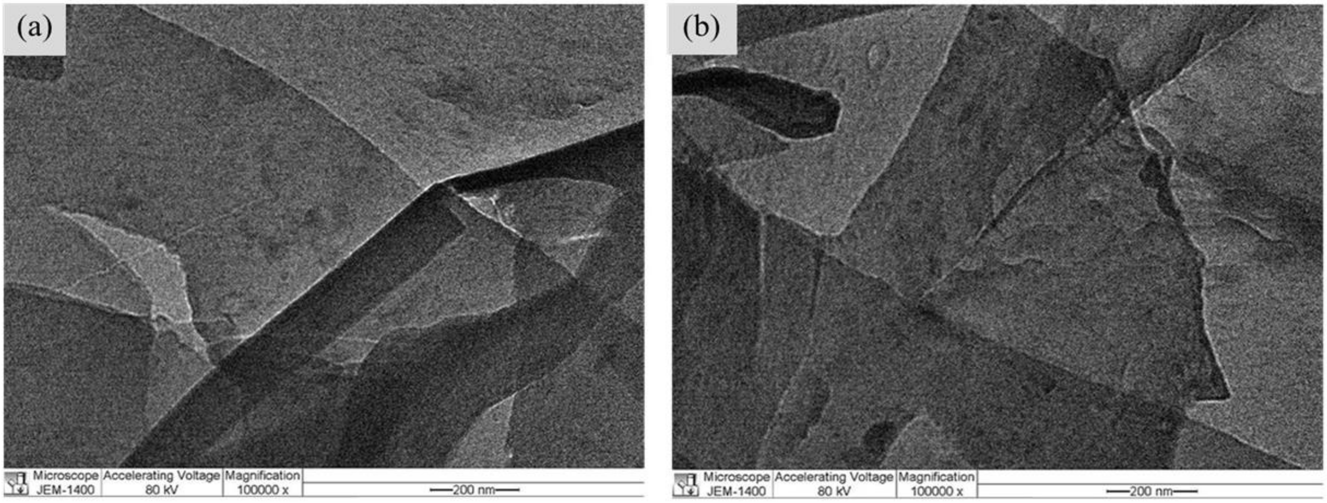


Fig. 6 TEM images of (a) synthesized graphene from coconut shells and (b) synthesized graphene from cricket legs.

Conclusion

We have offered an alternative option of the reuse of food and agricultural wastes as starting materials for growing graphene via chemical vapor deposition method under the condition of annealing at 1,050 °C and Ar flow. The sources were used without carbon purification, successfully providing multiple-layer sheets of graphene with semitransparent property. The organic components of the sources may be a cause of different defects in the synthesized graphene. Further enhancement in the quality may be achieved by pre- carbon purification to remove other components that probably affects the quality of synthesized graphene. The most crucial benefit of this preparation approach is that the method is simple and environmentally friendly process.

Acknowledgement

Financial support from National Research Council of Thailand (NRCT) grant No. 3947. This work was supported by Ubon Ratchathani Rajabhat University, Thailand and Thin Film Fabrication Laboratory at Physics Department, Ubon Ratchathani University, Thailand.

References

[1] B. Wang, F. Dong, M. Chen, J. Zhu, J. Tan, X. Fu, Y. Wang, S. Chen, Advance in recycling and utilization of agricultural wastes in China: based on

environmental risk, crucial pathways, influencing factors, policy mechanism. The tenth international conference on waste management and technology (ICWMT), Procedia Environ. Sci. 31 (2016) 12 – 17.

[2] K. Abeliotis, K. Lasaridi, V. Costarelli, The implications of food waste generation on climate change: The case of Greece, Sustain. Prod. Consum. 3 (2015) 8 – 14.

[3] F. Girotto, L. Alibardi, R. Cossu, Food waste generation and industrial uses: A review, J. Waste Manag. 45 (2015) 32 – 41.

[4] G. Kibria, Food Waste Impacts on Climate Change & Water Resources. https://www.researchgate.net/profile/Golam_Kibria7/publication/316547640_Food_Waste_Impacts_on_Climate_Change_Water_Resources/links/5903e1c2aca272116d2fc686/Food-Waste-Impacts-on-Climate-Change-Water-Resources.pdf, 29 April 2017.

[5] H.M. El-Mashhad, W.K.P. Loon, G. Zeeman, G.P.A. Bot, G. Lettinga, Reuse potential of agricultural wastes in semi-arid regions: Egypt as a case study, Rev. Environ. Sci. Biotechnol. 2 (2003) 53 – 66.

[6] G. Ruan, Zh. Sun, Z. Peng, J.M. Tour, Growth of Graphene from Food, Insects, and Waste, ACS Nano. 5(9) (2011) 7601 – 7607.

[7] E. Ruiz-Hitzky, M. Darder, F.M. Fernandes, E. Zatile, F.J. Palmares, P. Aranda, Supported Graphene from Natural Resources: Easy Preparation and Applications, Adv. Mater. 23(44) (2011) 1 – 6.

[8] O. Akhavan, K. Bijanzad, A. Mirsepah, Synthesis of graphene from natural and industrial carbonaceous wastes. RSC. Adv. Chem. Adv. 4 (2014) 20441 – 20448.

[9] A.K. Geim, K. Novoselov, The Rise of Graphene. Nat. Mater. 6(3) (2007) 183 – 91.

[10] C.N.R. Rao, U. Maitra, H.S.S. Tamakrishna Matte, Graphene: Synthesis, Properties, and Phenomena. First Edition. Wiley-VCH Verlag GmbH & Co. KGaA, 2013, pp. 47.

[11] A. Shekhawat, R.O. Ritchie, Toughness and Strength of nanocrystalline graphene. Nat. Commun. 7 (2016) 10546.

[12] Z.H. Ni, H.M. Wang, J. Kasim, H.M. Fan, T. Yu, Y.H. Wu, Y.P. Feng, Z.X. Shen, Graphene Thickness Determination using reflection and Contrast Spectroscopy, Nano Lett. 7(9) (2007) 2758 – 2763.

[13] E.P. Randviir, A.C.D. Brownson, E.C. Banks, A decade of grapheme research: production, applications and outlook, Mater. Today. 17(9) (2014) 426 – 432.

[14] C. Soldano, A. Mahmood, E. Dujardin, Production, Properties and Potential of graphene. Carbon. 48 (2010) 2127 – 2150.

[15] R.R. Nair, P. Blake, A.N. Grigorenko, K.S. Novoselov, T.J. Booth, T. Stauber, N.M.R. Peres, A.K. Geim, Fine Structure Constant Defines Visual Transparency of Graphene, Science. 320 (2008) 1308.

[16] K.C. Sasaki, J. Jiang, R. Saito, S. Onari, Y. Tanaka, Theory of Superconductivity of Carbon Nanotubes and Graphene, J. Phys. Soc. Jpn. 76(30) (2007) 0337021 – 0337024.

[17] K.M.F. Shahil, A.A. Balandin, Thermal properties of grapheme and multilayer grapheme: Applications in thermal interface materials, Solid State Commun. 152 (2012) 1331 – 1340.

[18] K.I. Bolotin, K.J. Sikes, Z. Jiang, M. Klima, G. Fudenberg, J. Hone, P. Kim, H.L. Stormer, Ultrahigh electron mobility in suspended graphene, Solid state Commun. 146 (2008) 351 – 355.

[19] J. Wu, M. Agrawal, H.A. Becerril, L.Z. Bao, Y. Chen, Organic Light-Emitting Diodes on Solution-Processed Graphene Transparent Electrodes, ACS Nano. 4(1) (2010) 43 – 48.

[20] Z. Li, Z. Zhou, G. Yun, K. Shi, X. Lv, B. Yang, High-performance solid-state supercapacitors based on graphene-ZnO hybrid nanocomposites, Nanoscale Res. Lett. 8 (2013) 473.

[21] J. Hou, Y. Shao, M.W. Ellis, R.B. Moore, B. Yi, Graphene-based electrochemical energy conversion and storage: fuel cells, supercapacitors and lithium ion batteries, Phys. Chem. Chem. Phys. 13 (2011) 15384 – 15402.

[22] M. Khawaja, Synthesis and Fabrication of Graphene/Conducting Polymer/Metal Oxide Nanocomposite Materials for Supercapacitor

Applications, University of South Florida, South Florida, 2015.

[23] D. Wang, S.H. Vijapur, G.G. Botte, Coal Char Derived Few-Layer Graphene, nodes For Lithium Ion Batteries, Photonics. 1 (2014) 251 – 259.

[24] S. Stankovich, D.A. Dikin, G.H.B. Dommett, K.M. Kholhaas, E.J. Zimney, E.A. Stach, R.D. Piner, S.T. Nguyen, R.S. Ruoff, Graphene-based composite materials, Nature. 442(7100) (2006) 282 – 286.

[25] S. Gurunathan, J.W. Han, J.H. Park, E. Kim, Y.-J. Choi, D-N. Kwon, J-H. Kim, Reduced Graphene oxide-silver nanoparticle nanocomposite: a potential anticancer nanotherapy, Int. J. Nanomed. 110 (2016) 6257 – 6276.

[26] J. Roy-Mayhew, I.A. Aksay, Graphene Materials and Their Use in Dye-Sensitized Solar Cells. ACS Chem. Rev. 114 (2014) 6323 – 6348.

[27] W. Li, X. Geng, Y. Guo, J. Rong, Y. Gong, L. Wut, X. Zhang, P. Li, J. Xu, G. Cheng, M. Sun, L. Liu, Reduced Graphene Oxide Electrically Contacted Graphene Sensor for Highly Sensitive Nitric Oxide Detection, ACS Nano. 5(9) (2011) 6955 – 6961.

[28] E. Hwang, H.M. Hwang, Y. Shin, Y. Yoon, H. Lee, J. Yang, S. Bak, H. Lee, Chemically modulated graphene quantum dot for tuning the photoluminescence as novel sensory probe, Sci. Rep. 6(39448) (2016) 1 – 10.

[29] D.D. Nguyen, N.H. Tai, Y.L. Chueh, S.Y. Chen, Y.J. Chen, W.S. Kuo, T.W. Chou, C.S. Hsu, L.J. Chen, Synthesis of ethanol-soluble few-layer graphene sheets for flexible and transparent conducting composite films, Nanotechnology. 22 (2011) 1– 8.

[30] H. Choi, S. Jung, J. Seo, D.W. Chang, L. Dai, J. Baek, Graphene for energy conversion and storage in fuel cells and supercapacitors, Nano Energy. 1 (2012) 534 – 551.

[31] F. Schwierz, Graphene transistors, Nat. Nanotechnol. 5 (2010) 487 – 496.

[32] A. Reina, X. Jia, J. Ho, D. Nezich, H. Son, V. Bulovic, M.S. Dresselhans, J. Kong, Large area, few-layer graphene films on arbitrary substrates by chemical vapor deposition, Nano Lett. 9(1) (2009) 30 – 35.

[33] X. Zhang, A.C. Coleman, N. Kasonis, W.R. Browne, B.J. Van Wees, B.L. Feringa, Dispersion of graphene in ethanol using a simple solvent exchange method, Chem. Commun. 46 (2010) 7539 – 7541.

[34] C.H. Manoratne, S.R.D. Rosa, I.R.M. Kottegoda, XRD-HTA, UV Visible, FTIR and SEM Interpretation of Reduced Graphene Oxide Synthesized from High Purity Vein Graphite, Mater. Sci. Res. India. 14(1) (2017) 19 – 30.

[35] X. Liu, M. Zheng, K. Xiao, Y. Xiao, Ch. He, H. Dong, Simple, green and high-yield production of single- or few-layer graphene by hydrothermal exfoliation of graphite, Nanoscale RSC. 6(9) 4598 – 45603.

[36] F.T. Thema, M.J. Moloto, E.D. Dikio, N.N. Nyangiwe, L. Kotsedi, M. Maaza, M. Khenfoch, Synthesis and Characterization of Graphene Thin Films by Chemical Reduction of Exfoliated and Intercalated Graphite Oxide, J. Chem. 2013(2013) 1 – 6.

[37] F.T. Johra, J. Lee, W. Jung, Facile and safe graphene preparation on solution based platform, J. Ind. Eng. Chem. 20 (2014) 2883 – 2887.

[38] D. Pan, J. Zhang, Z. Li, M. Wu, Hydrothermal Route for Cutting Graphene Sheets into Blue-Luminescent Graphene Quantum Dots, Adv. Mater. 22 (2010) 734 –738.

[39] K. Krishnamoothy, M. Veerapandian, G. Kim, S.J. Kim, A One Step Hydrothermal Approach for the Improved Synthesis of Graphene Nanosheets, Curr. Nanosci. 8 (2012) 934 – 938.

[40] J. Peng, W. Gao, B.K. Gupta, Z. Liu, T.R. Romero-Aburto, L. Ge, L. Song, L.B. Alemay, X. Zhan, G. Gao, S.A. Vithayathil, B.A. Kaippartettu, A.A. Marti, T. Hayashi, J.-J. Zhu, P.M. Ajayan, Graphene quantum dots derived from carbon fibers, Nano Lett. 12 (2012) 844 – 849.

[41] L. Shi, K. Chen, R. Du, A. Bachmatiuk, M.H. Rummeli, M.K. Priydarshi, Y. Zhang, A. Manivannan, M. Liu, Direct Synthesis of Few-layer Graphene on NaCl Crystals, Small. 11(47) (2015) 6302 – 6308.

[42] L.M. Malard, M.A. Pimenta, G. Dresselhaus, M.S. Dresselhaus, Raman spectroscopy in graphene, Phys. Rep. 473 (2009) 51 – 87.

[43] C. Zhu, S. Yang, G. Wang, R. Mo, P. He, J. Sun, Z. Di, Z. Kang, N. Yuan, J. Ding, G. Ding, X. Xie, A

new mild, clean and high-efficient method for preparation of graphene quantum dots without by-product, J. Mater. Chem. B. 3 (2015) 6871 – 6876.

[44] Z. Xu, C. Gao, Graphene fiber a new trend in carbon fibers, Mater. Today. 18(9) (2015) 480 – 492.

[45] A.B. Bourllinos, V. Georgakilas, R. Zboril, T.A. Steriotis, A.K. Stubos, Liquid-Phase Exfoliation of Graphite towards Solubilized Graphenes, Small. 16 (2009) 1840 – 1845.

[46] R. Thomas, G. Mohan Rao, Synthesis of 3-dimensional porous graphene nanosheets using electron cyclotron resonance plasma enhanced chemical vapor deposition, RSC Adv. 5(2015) 84927 – 84935.

[47] X. Peng, Y. Li, G. Zhang, F. Zhang, Z. Pan, Functionalization of Graphene with Nitrile Groups by Cycloaddition of Tetracyanoethylene Oxide, J. Nanomatter. 2013(2013) 1 – 5.