

Direct Synthesis of Graphene from a Recycled Battery Core by Solution Plasma Exfoliation and its Application for Removing Methylene Blue and Rhodamine B from Aqueous Solutions

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We present a novel method of the solution plasma exfoliated techniques for the production of graphene sheets from recycled battery core at room temperature. This is a fast, simple and efficient method to produce graphene sheets using electrode pairs with DC high voltage power sources which were immersed in a solution. The as-prepared samples were characterized by various techniques such as scanning electron microscopy (SEM), atomic force microscopy (AFM), Raman scattering, and optical emission spectroscopy (OES). The obtained results showed that graphene has an average diameter of 1.5 μm and a thickness of about 3 nm in respect of 7 to 10 layers. The prepared graphene was used as an effective adsorbent for the removal of methylene blue (MB) and Rhodamine B (RhB) from aqueous solutions. As a result, the adsorption efficiency of MB and RhB was determined to be 91% and 87 %, respectively. This is an attractive method to replace the previously reported graphene synthesis method.

Keywords: Graphene, Solution plasma, Plasma exfoliation, Ultrasonic-assisted plasma discharge.

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1. INTRODUCTION

Graphene is a single layer of carbon atoms arranged into two-dimensional hexagonal lattices (honeycomb lattices). Graphene was discovered by Andre Geim and Kostya Novoselov in 2004 [1, 2]. Graphene is a material with many special properties such as high thermal and electrical conductivity, very large hardness (hundreds of times higher than steel) and a large specific surface area. Therefore, this material has been strongly researched for many important application fields such as energy storage, solar cells, transparent electrodes, catalysts, sensors, composite polymer materials, and environmental treatment [3-12].

In recent years, considerable efforts have been made in developing various plasma device configurations for nanomaterial synthesis and liquid phase plasma processing for many potential applications [13-26]. High-quality, inexpensive materials are becoming more and more important to solve clean water environmental problems and energy production. Plasma in the liquid phase is divided into two types of configurations, such as, for example, the plasma generated by both electrodes immersed in the liquid [13-18, 25-30], and the plasma generated by only one electrode in the liquid and the other electrode above the liquid surface [19, 20, 31-34]. In configurations with two electrodes immersed in the liquid, the discharge is usually performed by pulsed or sinusoidal high-voltage sources with pulse widths from microseconds to nanoseconds. For plasma systems in the gas phase above the liquid surface, the plasma is generated by high-voltage

sources such as pulse, direct current (DC) and alternating current (AC) sources [19, 20, 33-36].

The gas-phase plasma configuration (liquid-interaction plasma) is suitable for nanomaterial synthesis because the reactions occur at the boundary between liquid and air. The in-liquid plasma method is simple without the use of catalyst materials and high synthesis efficiency compared to conventional techniques such as chemical vapor deposition (CVD) and the chemical reduction of graphene oxide [37-41]. The cost of synthesizing graphene materials is significantly reduced because this method consumes less energy in liquids and does not require vacuum equipment for operations at low pressure and high temperatures. However, the in-liquid plasma method also has difficulties due to the use of high-voltage pulse sources with high cost or the use of graphite rods that require high purity. Therefore, it is still necessary to continue the search for simpler, low-cost and more environmentally friendly techniques to prepare large-scale graphene for potential applications.

In this work, we focused on graphene synthesis by a new method – in-liquid plasma exfoliation at atmospheric pressure using a simple homemade high voltage DC source and a graphite rod from a recycled battery core.

2. MATERIALS AND METHODS

Fig. 1a shows an experimental setup diagram of a solution plasma processing. The system consists of two electrodes placed in parallel and immersed in the electrolyte solution. The first electrode is a graphite rod removed from AA size alkaline battery (Panasonic,

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Malaysia) 50 mm long and 5 mm diameter (Fig. 1b). The second electrode is a pure platinum rod (99.9 %) with a diameter of 2 mm and one end bent as shown in Fig. 1a. The two electrodes are held together by two quartz tubes. The electrolyte is composed of 0.238 mM KOH and 0.111 mM $(\text{NH}_4)_2\text{SO}_4$ in 500 ml distilled water. The graphite electrode is connected to the anode and the platinum electrode is connected to the cathode of a high-voltage DC source (applied voltage is 2.95 kV and current is 272 mA). The plasma is generated between the positive and negative electrode tips at a distance of 0.5 mm. After that, the obtained solution is filtered and cleaned by using the PVDF membrane (pore size of 200 nm) to remove impurities and organic matter from the battery core. Finally, the obtained samples were dried at 60 °C in a vacuum for 12 h.

The samples were characterized by Raman spectroscopy using 532 nm wavelength at room temperature (XploRA, Horiba Jobin-Yvon), atomic force microscopy (AFM, PARK XN100) and field emission scanning electron microscopy (FESEM, Hitachi S4800). The optical emission spectroscopy (OES) of the plasma is obtained by using a fiber optical spectrometer (AvaSpec-ULS2048, Avantes) with a wavelength range of 200-1100 nm and a resolution of 0.5 nm. The absorption spectral characteristics of methylene blue (MB) and Rhodamine B (RhB) solutions were measured by UV-Vis spectrophotometer (Jasco-V770).

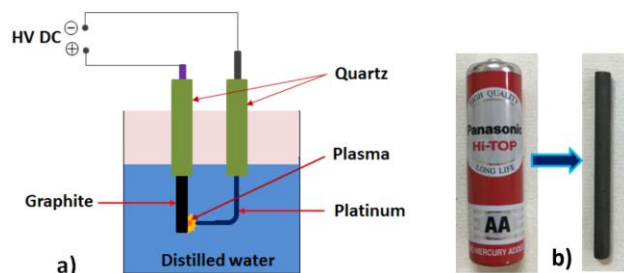


Fig. 1 – (a) Experimental setup for the solution plasma processing, (b) raw graphite from the battery core

3. RESULTS AND DISCUSSION

Fig. 2 shows the morphology of graphene prepared from the recycled battery core using the solution plasma exfoliation technique. Fig. 2a shows a typical FESEM image of graphene at high magnification. As can be seen, graphene exists in the form of nanosheets. To further investigate the morphology of the prepared graphene, AFM measurement was conducted. The obtained result is shown in Fig. 2b. As seen, the thickness of nanosheets is below 3 nm in respect of 7 to 10 layers, the average diameter is about 1.5 μm with high cleanliness.

Fig. 3 shows the Raman spectrum of the initial graphite rod and prepared graphene. As can be seen, all spectra reveal the most prominent features of graphite materials, including D (1330 cm^{-1}), G ($\sim 1579\text{ cm}^{-1}$) and 2D ($\sim 2687\text{ cm}^{-1}$) bands. The intensity of the D band (defective signature) of graphite is low, implying the high graphitic quality of the used graphite rod. The intensity ratio of D band to G band (I_D/I_G) is quite different between graphite and prepared graphene. The I_D/I_G ratios were determined to be 0.05 and 0.95 corresponding to graphite and graphene, respectively. The increase in

I_D/I_G indicated that further defects were induced in the graphite structure of graphene during the plasma exfoliation process. This is attributed to the presence of the oxygen atoms on the surface of graphene nanosheets. Besides, it is interesting to note that the 2D band of graphene is slightly shifted to lower wavenumbers compared to the initial graphite rod. This demonstrated that the exfoliation of the graphite structure happened thus resulting in the formation of graphene sheets.

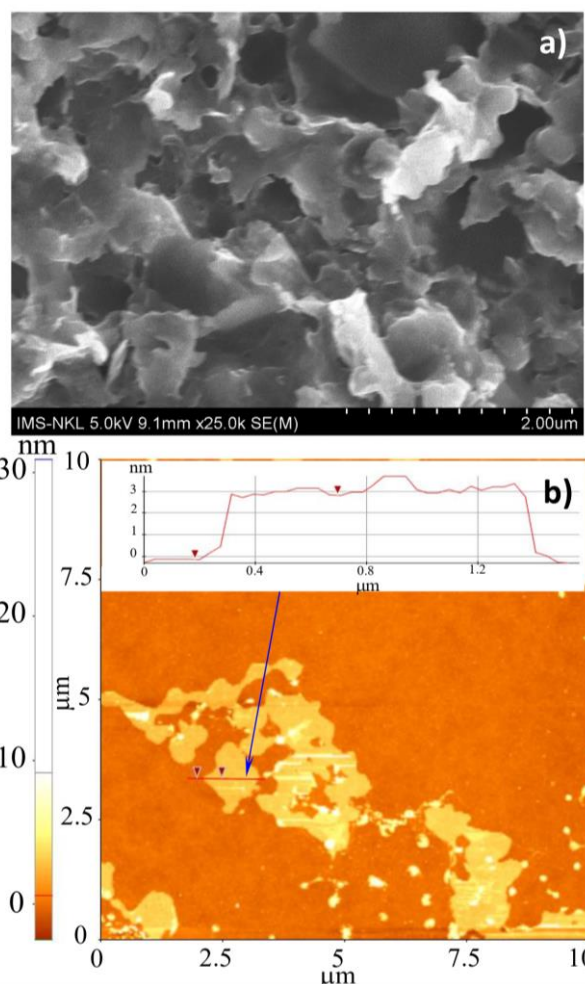


Fig. 2 – (a) FESEM and (b) AFM images of graphene synthesized by solution plasma processing

Fig. 4 shows the optical emission spectrum of the plasma during graphene synthesis. Plasma optical emission spectra (OES) are collected in the range of 200-900 nm. The results showed that OES contain H, O, C and OH atoms. This suggests that the bubbles that form and surround during the synthesis process are composed mostly of water vapor, small amounts of hydrogen and oxygen. A further observation of the color of the plasma shows that the plasma has a bright purple color and some bubbles during graphene synthesis. This result is similar to that reported by Hoonseung Lee et al. [42].

To demonstrate the potential applications, we used the prepared graphene as an adsorbent to remove methylene blue (MB) and Rhodamine B (RhB) from aqueous solutions. The initial solution has a concentration of 20 mg/l, 25 ml with characteristic colors are blue and pink. After 2 h adding of about 25 mg graphene,

the colors of the solutions changed to light blue and light pink, indicating that graphene can remove MB and RhB effectively. Fig. 5 shows the UV-Vis absorption spectrum of MB and RhB solutions with and without graphene. The results show that the adsorption efficiency of MB and RhB is 91 % and 87 %, respectively. Therefore, our fabricated graphene has great adsorption potential to treat organic pigments in water.

4. CONCLUSIONS

We have successfully prepared graphene nanosheets from the recycled battery core at room temperature by

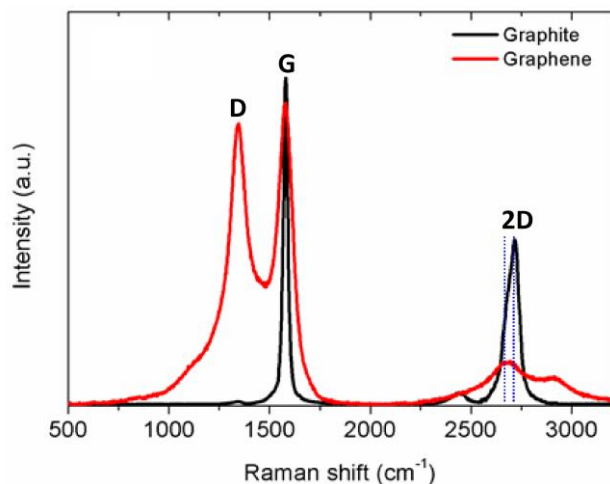


Fig. 3 – Raman spectra of graphene prepared by solution plasma exfoliation and raw graphite from battery core

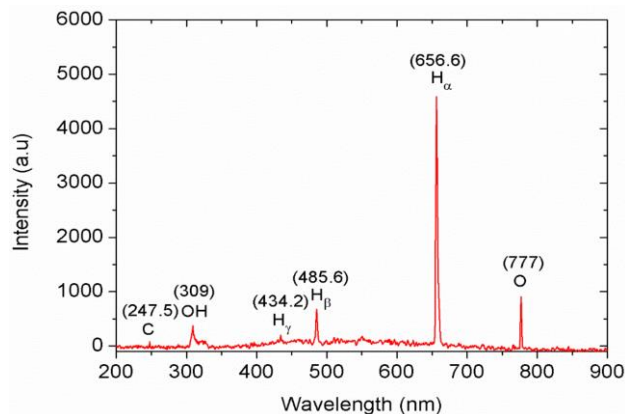


Fig. 4 – OES of the plasma generated during the synthesis of graphene from the recycled battery core

REFERENCES

1. G. Andre, K.S. Novoselov, *Nat. Mater.* **6** No 3, 183 (2007).
2. G. Andre, K.S. Novoselov, *Science* **306**, 666 (2004).
3. V. Georgakilas, J.N. Tiwari, K.C. Kemp, J.A. Perman, A.B. Bourlino, K.S. Kim, R. Zboril, *Chem. Rev.* **116**, 5464 (2016).
4. M. Balasubramaniam, S. Balakumar, *Mater. Lett.* **182**, 63 (2016).
5. L. Li, P. Gao, S. Gai, F. He, Y. Chen, M. Zhang, P. Yang, *Electrochimica Acta* **190**, 566 (2016).
6. S. Bae, H. Kim, Y. Lee, X. Xu, J.S. Park, Y. Zheng, J. Balakrishnan, T. Lei, H.R. Kim, Y.I. Song, Y.J. Kim, K.S. Kim, B. Ozyilmaz, J.H. Ahn, B.H. Hong, S. Iijima, *Nat. Nanotechnol.* **5**, 574 (2010).
7. M. Hu, Z. Yao, X. Wang, *Ind. Eng. Chem. Res.* **56**, 3477 (2017).
8. Z. Arefinia, A. Asgari, *Mater. Sci. Semi. Proc.* **35**, 181 (2015).
9. A. Naga, A. Mitra, S.C. Mukhopadhyay, *Sens. Actuat. A* **270**, 177 (2018).
10. Y. Du, D. Li, L. Liu, G. Gai, *Polymers* **10**, 114, (2018).
11. Liu X, Ma R, Wang X, Y.M. Yongping, Li Zhuang, S. Zhang, R. Jehan, J. Chen, X. Wang, *Environ. Pollut.* **252 Pt A**, 62 (2019).
12. I. Alia, A. A. Basheer, X.Y. Mbiandad, A. Burakove, E. Galunine, I. Burakovae, E. Mkrtychyan, A. Tkacheve, V. Grachevf, *Environ. Int.* **127**, 160 (2019).

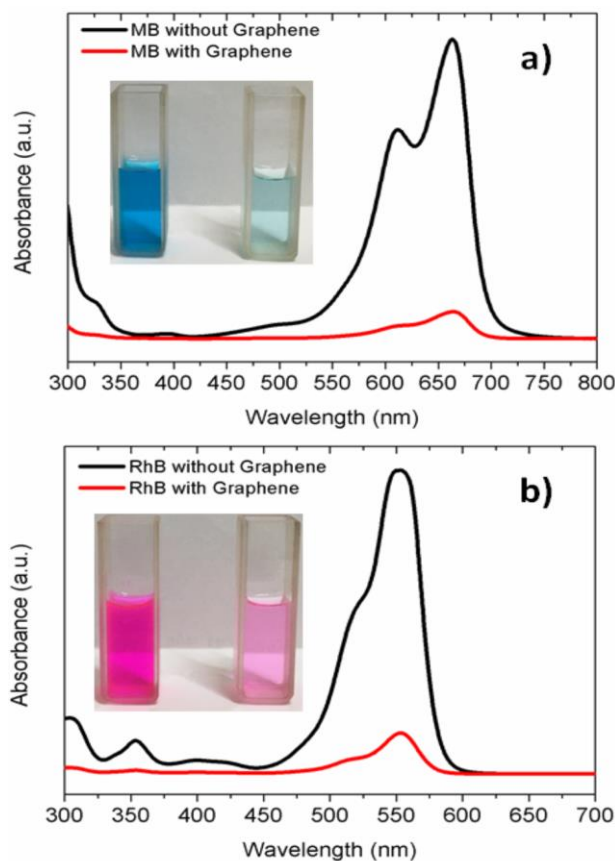


Fig. 5 – UV-Vis spectra of MB (a) and RhB (b) solutions corresponding to the presence (red) and absence (black) of graphene

using solution plasma exfoliated technique. This technique exhibits a fast, simple and efficient method to produce graphene sheets using electrode pairs with DC high voltage power sources which were immersed in a solution. The prepared graphene has an average thickness of 3 nm and a length of 1.5 μm . We used these graphene samples as effective adsorbents for the removal of methylene blue and Rhodamine B from aqueous solutions. The obtained results indicated that the adsorption efficiency of MB and RhB was determined to be 91 % and 87 %, respectively, as using the prepared graphene.

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13. H. Lee, M.A. Bratescu, T. Ueno, N. Saito, *Royal Soc. Chem. Adv.* **4**, 51758 (2014).
14. T. Morishita, T. Ueno, G. Panomsuwan, J. Hieda, A. Yoshida, M.A. Bratescu, N. Saito, *Sci. Rep.* **6**, 36880 (2016).
15. S. Kim, R. Sergiienko, E. Shibata, Y. Hayasaka, T. Nakamura, *Mater. Trans.* **51**, 1455 (2010).
16. J. Kang, O.L. Li, N. Saito, *Carbon* **60**, 292 (2013).
17. O.L. Li, H. Hayashi, T. Ishizaki, N. Saito, *RSC Adv.* **6**, 51864 (2016).
18. D. Kim, O.L. Li, N. Saito, *Phys. Chem. Chem. Phys.* **17**, 407 (2015).
19. M. Matsushima, M. Noda, T. Yoshida, H. Kato, G. Kalita, T. Kizuki, H. Uchida, M. Umeno, K. Wakita, *J. Appl. Phys.* **113**, 114304 (2013).
20. D. Kozak, E. Shibata, A. Iizuka, T. Nakamura, *Carbon* **70**, 87, (2014).
21. P. Pohl, *Nanomaterials* **9**, 278 (2019).
22. N.K. Kaushik, N. Kaushik, Ng. Nhat Linh, Bh. Ghimire, An. Pengkit, J. Sornsakdanuphap, Su-Jae Lee, Eun Ha Choi, *Nanomaterials (Basel)* **9** No 1, 98 (2019).
23. C.B. Ke, T.L. Lu, J.L. Chen, *Nanomaterials* **8**, 372 (2018).
24. R.R. Borude, H. Sugiura, K. Ishikawa, T. Sutsumi, H. Kondo, M. Hori, *J. Phys. D: Appl. Phys.* **52** 175301 (2019).
25. A. Ando, K. Ishikawa, K. Takeda, T. Ohta, M. Ito, M. Hiramatsu, H. Kondo, M. Sekine, M. Hori, *Chem. Nano Mat.* **6**, 604 (2020).
26. A. Ando, K. Ishikawa, H. Kondo, T. Tsutsumi, K. Takeda, T. Ohta, M. Ito, M. Hiramatsu, M. Sekine, M. Hori, *Jpn. J. Appl. Phys.* **57**, 026201 (2018).
27. J.E. Foster, *Phys. Plasmas* **24**, 055501 (2017).
28. S.N. Gucker, J.E. Foster, M.C. Garcia, *Plasma Sources Sci. Technol.* **24**, 055005 (2015).
29. T. Miyahara, M. Oizumi, T. Nakatani, T. Sato, *AIP Adv.* **4**, 047115 (2014).
30. O.L. Li, J. Kang, K. Urashima, N. Saito, *Int. J. Plasma Environ. Sci. Technol.* **7**, 31 (2013).
31. G.R. Stratton, C.L. Bellona, F. Dai, T.M. Holsen, S.M. Thagard, *Chem. Eng. J.* **273**, 543 (2015).
32. M. Tokushige, A. Matsuura, T. Nishikiori, Y. Ito, *J. Electrochem. Soc.* **158**, E21 (2011).
33. M. Ito, M. Hayakawa, S. Takashima, E. Asami, T. Aoki, M. Oka, H. Asano, M. Kitahara, S. Nakata, K. Yamaguchi, Y. Murase, *Jpn. J. Appl. Phys.* **51**, 116201 (2012).
34. M. Tokushige, T. Nishikiori, Y. Ito, *Rus. J. Electrochem.* **46**, 619 (2010).
35. T. Hagino, H. Kondo, K. Ishikawa, H. Kano, M. Sekine and M. Hori, *Appl. Phys. Express* **5**, 035101 (2012).
36. P. Bruggeman, E. Ríbežl, J. Degroote, J. Vierendeels, C. Leys, *Adv. Mater.* **10**, 1964 (2008).
37. A. Reina, X. Jia, J. Ho, D. Nezich, H. Son, V. Bulovic, M.S. Dresselhaus, J. Kong, *Nano Lett.* **9**, 30 (2009).
38. H. Tan, D. Wang, Y. Guo, *Coatings* **8**, 40 (2018).
39. F. Qing, Y. Hou, R. Stehle, X. Lim *APL Mater.* **7**, 020903 (2019).
40. M.E. Schmidt, C. Xu, M. Cooke, H. Mizuta, H.M.H. Chong, *Mater. Res. Express* **1**, 025031 (2014).
41. X. Wang, H. You, F. Lin, M. Li, L. Wan, S. Li, Q. Li, Y. Xu, R. Tian, Z. Yu, D. Xiang, J. Cheng, *Chem. Vap. Deposition* **15**, 53 (2009).
42. H. Lee, M.A. Bratescu, T. Ueno, N. Saito, *RSC Adv.* **4**, 51758 (2014).

Прямий синтез графену з переробленого сердечника акумулятора методом ексфолюації плазми низької густини та його застосування для видалення метиленового синього та родаміну В з водних розчинів

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Ми представляємо новий метод ексфолюації плазми низької густини для отримання графенових шарів із переробленого сердечника акумулятора при кімнатній температурі. Це швидкий, простий та ефективний метод виробництва графенових шарів з використанням електродних пар з джерелами постійного струму високої напруги, занурених у розчин. Підготовлені зразки характеризувались різними методами, такими як скануюча електронна мікроскопія (SEM), атомно-силова мікроскопія (AFM), комбінаційне розсіювання та оптична випромінювальна спектроскопія (OES). Отримані результати показали, що графен має середній діаметр 1,5 мкм і товщину близько 3 нм у випадку 7-10 шарів. Виготовлений графен використовували як ефективний адсорбент для видалення метиленового синього (MB) та родаміну В (RhB) з водних розчинів. Як результат, ефективність адсорбції MB та RhB була визначена відповідно 91 % та 87 %. Це привабливий метод для заміни методу синтезу графена, про який повідомлялося раніше.

Ключові слова: Графен, Плазма низької густини, Ексфолюація плазми, Ультразвуковий плазмовий розряд.