Modification of hydrothermal synthesis using microwave irradiation for ZnO/graphene nanocomposite

by Sugianto Fisika

Submission date: 12-Apr-2023 08:37AM (UTC+0700)
Submission ID: 2062090753
File name: 41._Modification_of_hydrothermal_synthesis_using_microwave.pdf (628.87K)
Word count: 2602
Character count: 13009

Modification of hydrothermal synthesis using microwave irradiation for ZnO/graphene nanocomposite

Modification of hydrothermal synthesis using microwave irradiation for ZnO/graphene nanocomposite

Sugianto*[1] and E F Rahayu[2]

[1]Department of Physics, Faculty of Mathematics and Natural Sciences, Universitas Negeri Semarang, Jl Raya Sekaran Gunungpati Semarang 50299, Indonesia.
[2]Department of Chemistry, Faculty of Mathematics and Natural Sciences, Universitas Negeri Semarang, Jl Raya Sekaran Gunungpati Semarang 50299, Indonesia.

*Corresponding author: sugianto@mail.unnes.ac.id

Abstract. Graphene has good physical properties such as electronic, optical and mechanical properties. The unique properties of graphene are interesting to study, especially in the field of electronic devices. Graphene was synthesised with chemical reduction using the Tour method. The oxidation process of graphite into graphene oxide (GO) occurs in a solution with the acidic atmosphere of H_2SO_4/H_3PO_4. ZnO/graphene nanocomposite was prepared by modification of hydrothermal synthesis using microwave irradiation. Characterisation of material structures includes SEM-EDX and FTIR. SEM micrograph shows that the morphology of the ZnO/graphene synthesis of oxidising acids H_2SO_4/H_3PO_4 9:1 ratio has better performance.

1. Introduction

Graphene is the allotrope of carbon that has a 2D layer with sp^2 hybridisation forming a hexagonal lattice [1]. Graphene has a lightweight material with good thermal conductivity and a large active surface area of up to 2675 m^2/gr supported by good mechanical and stability properties [2]. Other mechanical properties of graphene are Young's modulus of 0.1 TPa [3] and thickness of 0.335 with breaking strength of 40 N/m [4]. The good mechanical and thermal properties of graphene have the potential to be used as the materials for electrochemical resonators, chemical sensors and other electronic devices [5].

Numerous methods have been developed and conducted to produce graphene. Graphene can be synthesised by micromechanical exfoliation from graphite, such as exfoliation of graphite intercalation compounds, thermal chemical vapour deposition [6], and epitaxial growth [7]. The advantage of these methods is their high quality, while the disadvantage is impractical to use for commercial applications because of their low production and high cost. There is also an electrochemical method with the sulfuric acid solution as an electrolyte solution [8]. Another method used is chemical reactions such as the Brodie, Staudenmaier or Hummers method and its variations, namely Improved Hummers Method. An improved Hummers method was developed by Tour (Tour method) by eliminating $NaNO_3$, increasing the amount of $KMnO_4$ and performing the reaction in a 9:1 mixture of H_2SO_4/H_3PO_4 [9].

The graphene material that is applied as a supercapacitor is combined with metal oxides as a semiconductor to increase its conductivity [10-14]. In this study, ZnO metal oxide was selected as the active material. ZnO has a large binding energy (60 meV) and a wide bandgap (3.37 eV) [15]. ZnO also has an energy density of up to 650 Ah/g for the supercapacitor [16]. ZnO/graphene can be synthesised

using the solvothermal method [15], the hydrothermal method [17], and the microwave method [18]. The hydrothermal method has a high level of crystallinity without calcination. The hydrothermal synthesis was carried out by inserting a ZnO aggregate into the space between the graphene sheets, which can increase the specific capacity at good scanning speed and cycle duration [19]. Another advantage of this hydrothermal method is that the form of the powder obtained directly from the solution, the particle size and shape can be controlled based on the initial material. In this study, hydrothermal modification was carried out using microwave irradiation, and the synthesis of ZnO/graphene nanocomposite was also accomplished. The purpose of these modification methods is to optimise the reduction of ZnO in graphene surfaces.

2. Methods

The materials used were H_2SO_4, H_3PO_4, $KMnO_4$, graphite, HCl, H_2O_2 aquademin, $Zn(NO_3)_2$, and hydrazine hydrate having a purity of 99% purchased from Merc Ltd. The solution was prepared under the volume ratio of H_2SO_4:H_3PO_4 = 7:3 (#ZnO/G7:3 label) and the volume ratio of 9:1 (#ZnO/G9:1 label).

The graphene oxide (GO) synthesis was performed by entering the two solutions of H_2SO_4:H_3PO_4 into the Erlenmeyer and then stirred using a magnetic stirrer for 15 minutes. Next, 2 g of graphite and 5 g of $KMnO_4$ were slowly put into the solution and stirred for 2 hours. While stirring, 3 ml of H_2O_2 was then added into the solution for around 15 minutes. The 15 ml of HCl 5 % and aquademin were also added to the solution to stop the reaction. The synthesis result was centrifuged at 6000 rpm for 15 minutes. This result has a GO solution. The GO solution was heated in the oven at 110°C for 2 hours to obtain the GO powder.

The ZnO/graphene nanocomposite was prepared by modification of hydrothermal synthesis using microwave irradiation. The GO powder was diluted into 100 ml aquademin, and the solution was sonicated for 1 hour. While ultrasonication was applied, 20 mg $Zn(NO_3)_2$ and 10 µl hydrazine hydrate were slowly put in the solution. Afterwards, the solution was put into Teflon autoclave at 160°C for 2 hours. The ZnO/graphene suspension was centrifuged and dried in the oven at 110°C for 2 hours [19]. The ZnO/graphene powder was irradiated by microwave of 900 watt for 10 minutes to optimise the reduction of ZnO/graphene. In this study, ZnO nanoparticles were also synthesised by hydrothermal modification using microwave irradiation to be compared with ZnO/graphene nanocomposite.

The microstructure, morphology and elements of samples were characterised using scanning electron microscope–energy dispersive X-ray (SEM-EDX). The Fourier transform infrared (FTIR) spectra were recorded in the wave number range of 400-4000 cm^{-1}.

3. Results and Discussion

The first step in this research was done by synthesising graphene. Graphene was synthesised with chemical reduction using the Tour method. The Tour method is more eco-friendly than 'Hummers' method for graphite oxidation since the 'Hummers' method produces nitrogen dioxide (NO_2), which is hazardous for the environment. In the Tour method, only solvents H_2SO_4 and H_3PO_4 were mixed with $KMnO_4$, with $NaNO_3$ excluded from the process [20]. Graphite that reacts with the solvents first turns black, then green when $KMnO_4$ was added as a strong oxidant. Below is the reaction when graphene oxide (GO) synthesis occurs:

$$KMnO_4 + 3H_2SO_4 \rightarrow K^+ + MnO_3^+ + H_3O^+ + 3HSO_4^- \quad (1)$$

$$MnO_3^+ + MnO_4^- \rightarrow Mn_2O_7 \quad (2)$$

$$Mn_2O_7 + 3H_2SO_4 + C_{(graphite)} \rightarrow \begin{pmatrix} C-O-C \\ C-OH \\ COOH \end{pmatrix} + MnO_5 + H_2O + SO_4^{-2} \quad (3)$$

The existence of $KMnO_4$ contributed to the intercalation process of graphite. The active species which oxidises graphite was dimanganese heptaoxide (Mn_2O_7). When synthesis occurred, sulfuric acid and phosphoric acid increase the heat, creating exothermic conditions, resulting in graphite dissolution and forming GO [21]. We add H_2O_2 to prevent further oxidation and centrifugation aims to separate SO_4^{2-} from GO suspension. The advantages of this method are that the synthesis process becomes simpler and faster; the materials used are easy to attain, producing more GO. However, disadvantages include higher safety requirements because highly concentrated solutions are used; and after synthesis, the final compound must be rinsed to minimise graphene oxidation, which still might occur. The ZnO/graphene nanocomposite is made using hydrazine hydrate as a reducing agent to convert GO to graphene by microwave irradiation.

3.1. Scanning Electron Microscope (SEM)

SEM analysis was used to check on the surface morphologies and composite structure of samples. Figure 1 shows the micrographs for ZnO nanoparticles and ZnO/graphene nanocomposite. Figure 1(a) shows micrograph of ZnO nanoparticles. ZnO synthesised by modification hydrothermal using microwave irradiation to produce ZnO nanoparticles has a nanorods-like structure. The micrograph of ZnO/graphene nanocomposite with oxidising acids H_2SO_4:H_3PO_4 of 7:3 (#ZnO/G7:3) is shown in Figure 1(b) and with oxidising acids H_2SO_4:H_3PO_4 of 9:1 (#ZnO/G9:1) is shown in Figure 1(c). The morphology of the #ZnO/G7:3 sample synthesis produces piles of flaked graphene, small random chunks of graphene, and the deposited of ZnO in the surfaces of graphene is too small. The SEM micrograph of #ZnO/G9:1 sample shows the graphene sheets' wrinkled structure is decorated with ZnO nanoparticles along with a few nanorods. During the synthesis process, the oxidation of graphite exceeded desired concentrations, and it caused the concentration of C to be reduced. The quantities of components in the ZnO/graphene nanocomposite samples can be seen in Table 1.

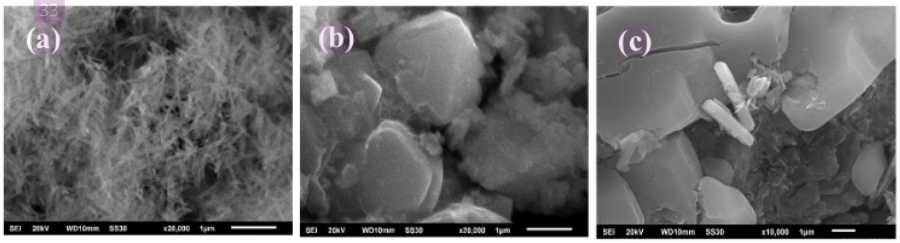

Figure 1. SEM micrograph of (a) ZnO nanoparticle, (b) #ZnO/G7:3, and (c) #ZnO/G9:1 sample

Table 1. The quantities of components in the ZnO/graphene nanocomposite samples

Atomic Number	Element	% Mass Concentration	
		#ZnO/G73 sample	#ZnO/G91 sample
6	C	47.84	39.24
8	O	17.08	3.75
7	N	30.70	42.59
30	Zn	4.38	14.42

Based on the data in the Table 1, it can be proven that the synthesis with a ratio of 9:1 (#ZnO/G9:1) has better results than the synthesis with a ratio of 7:3 (#ZnO/G7:3) which can be seen from the reduced concentration of oxygen. It is shows that the reduction of graphite oxide to graphene has a better performance. The ZnO quantity in graphene can be proven in the element quantity data from SEM-EDX

analysis. Based on Table 1, it can be seen the quantity of Zn element contained in the synthesis of #ZnO/G7;3 4.38%, so it can be seen the quantity of Zn element is smaller than #ZnO/G9:1 sample.

3.2. Fourier Transform Infrared (FTIR)

The subsequent analysis is FTIR which function is to see the functional groups in a composite. The results of the #ZnO/G7:3 and #ZnO/G9:1 sample can be seen in Figure 2. Based on IR spectra, the peak of 3105.30 cm^{-1} stretching shows the OH functional group. Then at 1625.33 cm^{-1} there is a C = C wave vibration, and at 1047.12 cm^{-1} there is strong vibration of C-O. Based on these data, it can be said that the synthesis results have formed GO. The IR spectra of #ZnO/G9:1 sample observed that the peaks reveal the oxygen functional groups of GO at 3396.31, 1621.80 and 1056.65 cm^{-1} corresponding to C=O stretching, C-O stretching and C-O bending respectively. These oxygen functional groups are generated during the oxidation process of the graphite. In the case of ZnO/graphene composite, it could be observed that the oxygen functional groups were almost reduced, which is indicating the reduction of GO during hydrothermal process. The absorbance peak at 1621 and 415 cm^{-1} of graphene sheets and stretching vibration of Zn-O. These results indicate the formation of ZnO on the graphene matrix. These results are consistent with previous research conducted by Rahayu et al. [22] regarding the synthesis of graphene using the microwave irradiation method, showing the results that using 900 watts of microwave power for 10 minutes can synthesise a more uniform graphene layer.

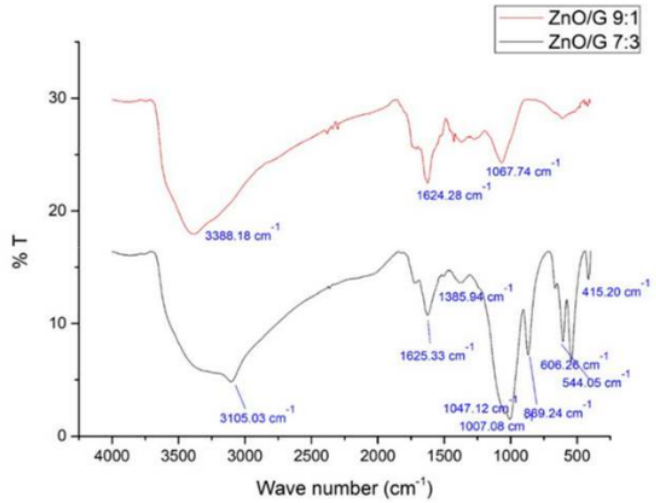

Figure 2. The FTIR spectra of ZnO/graphene with a ratio of H_2SO_4/ H_3PO_4 = 7:3 (#ZnO/Ga7:3) and 9:1 (#ZnO/G9:1).

4. Conclusions

The ZnO/graphene nanocomposite can be synthesis by the modification of hydrothermal using microwave irradiation. Based on this study's result, SEM micrograph shows that the morphology of the ZnO/graphene synthesis of oxidising acids H_2SO_4/H_3PO_4 9:1 ratio has better performance than the 7:3 ratio. It can be seen from the SEM image that the ZnO nanoparticle has more decorated in the graphene surface. The FTIR spectra, the synthesis results have formed GO with the peak of stretching the OH functional group, C = C wave vibration, and strong vibration of C-O.

Acknowledgement
The paper is supported by DIPA UNNES' Fundamental Research programme under grant agreement number: 132.23.4/UN37/PPK.3.1/2020.

References

[1] Terrones M, Botello-Méndez A R, Campos-Delgado J, López-Urías F, Vega-Cantú Y I, Rodríguez Macías F J and Terrones H 2010 *Nano Today* **5** 351
[2] Wang X, Zhi L J and Mullen K 2008 *Nano Lett.* **8** 323
[3] Phiri J, Johansson L S, Gane P and Maloney T 2018 *Compos. B: Eng.* **147** 104
[4] Kumar P, Singh A K, Hussain S, Hui K N, Hui K S, Eom J and Singh J 2013 *Rev. Adv. Sci. Eng.* **2** 1
[5] Wu Y H, Yu T and Shen Z X 2010 *J. Appl. Phys.* **108** 071301
[6] Dao T D and Jeong H M 2015 *Mater. Res. Bull.* **70** 651
[7] Emtsev K V, Bostwick A, Horn K, Jobst J and Kellog G L 2009 *Nat. Mater* **8** 203
[8] Poh H L, Ńaněk F, Amborsi A, Zhao G, Sofer Z and Pumera M 2012 *Nanoscale* **4** 3515
[9] Marcano D C, Kosynkin D V, Berlin J M, Sinitskii A, Sun Z, Slesarev A, Alemany L B, Lu W and Tour J M 2010 *ACS Nano* **4** 4806
[10] Zhu J, and He J 2012 *ACS Appl. Mater. Interfaces* **4** 1770
[11] Huang J Q, Huang J, Chong W G, Cui J, Yao S, Huang B and Kim J K 2019 *J. Energy Chem.* **35** 204
[12] Guan C, Wang Y, Hu Y, Liu J, Ho K H, Zhao W, Fa Z, Shen Z, Zhang H and Wang J 2015 *J. Mater.* **3** 23283
[13] Li S, Jiang H, Yang K, Zhang Z, Li S, Luo N and Wei R 2018 *J. Alloys Compd.* **746** 670
[14] Liu Y Z, Li Y F, Yang Y G, Wen Y F, and Wang M Z 2013 *Scr. Mater.* **68** 301
[15] Ezeigwe E R, Tan M T, Khiew P S and Siong C W 2015 *Ceram. Int.* **41** 715
[16] Alver Ü, Tanrıverdi A and Akgül Ö 2016 *Synth. Met.* **211** 30
[17] Rajeswari V, Jayavel R and Dhanemozhi A C 2017 *Materials Today: Proceedings* **4** 645
[18] Ramadoss A and Kim S J 2013 *Mater. Chem. Phys.* **140** 405
[19] Li Z, Zhou Z, Yun G, Shi K, Lv X and Yang B 2013 *Nanoscale Res. Lett.* **8** 1
[20] Emiru T F and Ayele D W 2017 *Egypt. J. Basic Appl. Sci.* **4** 74
[21] Cao N and Zhang Y 2015 *J. of Nanomaterials* **2015** 1
[22] Rahayu E F, Bunnari and Hardyansyah A 2020 *J. Molekul* **15** 57

Modification of hydrothermal synthesis using microwave irradiation for ZnO/graphene nanocomposite

ORIGINALITY REPORT

18%	13%	15%	5%
SIMILARITY INDEX	INTERNET SOURCES	PUBLICATIONS	STUDENT PAPERS

PRIMARY SOURCES

1	manu56.magtech.com.cn Internet Source	1%
2	W D Toledo, A B Couto, D A L Almeida, N G Ferreira. " Facile synthesis of TiO /rGO neatly electrodeposited on carbon fiber applied as ternary electrode for supercapacitor ", Materials Research Express, 2019 Publication	1%
3	Li, Songzhan, Jian Wen, Tian Chen, Liangbin Xiong, Jianbo Wang, and Guojia Fang. "In situ synthesis of 3D CoS nanoflake/Ni(OH)2 nanosheet nanocomposite structure as a candidate supercapacitor electrode", Nanotechnology, 2016. Publication	1%
4	Fang Wang, Lv Li, Da Lei, Yongpeng Li, He Yang, Weili Zhu, Fengxiang Zhang. "Quaternized polymer binder for lithium–sulfur batteries: The effect of cation structure	1%

	on battery performance", Journal of Energy Chemistry, 2020 Publication	
5	scholars.ncu.edu.tw Internet Source	1 %
6	pubs.acs.org Internet Source	1 %
7	scholar.google.co.in Internet Source	1 %
8	softmag.nimte.ac.cn Internet Source	1 %
9	www.chemmethod.com Internet Source	1 %
10	www.openaccessrepository.it Internet Source	1 %
11	Submitted to Bharati Vidyapeeth Deemed University College Of Engineering Student Paper	1 %
12	repositorio.unb.br Internet Source	1 %
13	Submitted to Chulalongkorn University Student Paper	1 %
14	Dinh Trinh Tran, Noi Van Nguyen. "rGO/persulfate metal-free catalytic system for the degradation of tetracycline: effect of	1 %

reaction parameters", Materials Research Express, 2020
Publication

15	Ji-Li Tian, Hua-Yu Zhang. "Preparation and characterization of reduced graphene oxide using ascorbic acid and sodium citrate as binary reductant", Fullerenes, Nanotubes and Carbon Nanostructures, 2016 Publication	1 %
16	Joo, Kisu, Sahng-Kyoon Jerng, Yong Seung Kim, Bumho Kim, Seunghyun Moon, Daeyoung Moon, Gun-Do Lee, Yoon-Kyu Song, Seung-Hyun Chun, and Euijoon Yoon. "Reduction of graphene damages during the fabrication of InGaN/GaN light emitting diodes with graphene electrodes", Nanotechnology, 2012. Publication	1 %
17	"Metal and Metal Oxides for Energy and Electronics", Springer Science and Business Media LLC, 2021 Publication	<1 %
18	cftrpathway.com Internet Source	<1 %
19	www.ludiserv.com Internet Source	<1 %

20	Xiao, Junwu, Yangyang Xu, and Shihe Yang. "High-Performance Supercapacitors Based on Novel Graphene Composites", Graphene-based Energy Devices, 2015. Publication	<1 %
21	bradscholars.brad.ac.uk Internet Source	<1 %
22	Rui Gao, Hanyue Zhu, Shan Gao, Lihong Liu, Yingming Xu, Xianfa Zhang, Xiaoli Cheng, Lihua Huo. "Synthesis of ZnO@poly-o-methoxyaniline nanosheet composite for enhanced NH3-sensing performance at room temperature", Microchimica Acta, 2020 Publication	<1 %
23	Topics in Current Chemistry, 2014. Publication	<1 %
24	jurnal.ugm.ac.id Internet Source	<1 %
25	www.semanticscholar.org Internet Source	<1 %
26	Ajit Sharma, Gansukh Erdenedelger, Han Mo Jeong, Byeong-Kyu Lee. "Controlled oxygen functional groups on reduced graphene using rate of temperature for advanced sorption process", Journal of Environmental Chemical Engineering, 2020 Publication	<1 %

27	Jenel Vatamanu, Xiaojuan Ni, Feng Liu, Dmitry Bedrov. "Tailoring graphene-based electrodes from semiconducting to metallic to increase the energy density in supercapacitors", Nanotechnology, 2015 Publication	<1 %
28	Submitted to Queen Mary and Westfield College Student Paper	<1 %
29	Sharma, Maya, Giridhar Madras, and Suryasarathi Bose. "Critical insights into the effect of shear on in situ reduction of graphene oxide in PVDF: assessing by rheo-dielectric measurements", Materials Research Express, 2016. Publication	<1 %
30	eprints.eudl.eu Internet Source	<1 %
31	Meiyong Liao, Yasuo Koide. "Carbon-Based Materials: Growth, Properties, MEMS/NEMS Technologies, and MEM/NEM Switches", Critical Reviews in Solid State and Materials Sciences, 2011 Publication	<1 %
32	Prathik Roy, Arun Prakash Periasamy, Chi-Te Liang, Huan-Tsung Chang. "Synthesis of Graphene-ZnO-Au Nanocomposites for	<1 %

Efficient Photocatalytic Reduction of Nitrobenzene", Environmental Science & Technology, 2013
Publication

33	downloads.hindawi.com Internet Source	<1 %
34	moam.info Internet Source	<1 %
35	vdoc.pub Internet Source	<1 %
36	www.degruyter.com Internet Source	<1 %

Exclude quotes	On	Exclude matches	< 5 words
Exclude bibliography	Off		

Modification of hydrothermal synthesis using microwave irradiation for ZnO/graphene nanocomposite

GRADEMARK REPORT

FINAL GRADE

/0

GENERAL COMMENTS

Instructor

PAGE 1

PAGE 2

PAGE 3

PAGE 4

PAGE 5

PAGE 6