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3-D GRAPHENE GROWTH BY CHEMICAL VAPOR DEPOSITION (CVD) FOR ENERGY APPLICATIONS

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Abstract:

The tremendous need for more efficient energy systems such as fuel cells, lithium ion batteries and supercapacitors production led to materials development of which 2D and 3D graphene are the most important in terms of better electrical conductivity, large area, easy of functionalization. The influence of few kinetic parameters on 3D graphene growth on Ni foam substrate catalyst is discussed in this study, among them being: the working temperature in the reaction chamber, time of reaction and ethylene gas flow used as carbon source during the chemical vapor deposition (CVD) process. In order to preserve the 3D-graphene shape during their transfer, the nickel matrix was removed without using poly(methyl methacrylate) (PMMA) as post growth stabilizer of the graphene foam. The samples were characterized by Raman spectroscopy, Scanning Electron Microscopy (SEM), Optical Microscopy (OM). The Brunauer-Emmett-Teller (BET) method was used to calculate the specific surface area, and the pore volume and pore radius were estimated by Barret-Joyner-Halenda method. The results have shown that a 1.6 mm thickness multilayer porous graphene that reproduces the Ni foam was obtained. The pore radius is about 1.9 nm, surface area 9.821 m^2/g, and the average graphene mass density is about 12 mg/cm^3. As compared with other methods, by CVD is possible to obtain in one step, large area (up to 100 cm^2 using the CVD installation presented in this paper) of graphene foam, with high porosity and plane surface that allow directly utilization for different applications.

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1. INTRODUCTION

Graphene, together with graphite, diamond, fullerenes, carbon nanotubes etc., is one of the allotrope forms of carbon and was discovered in 2004 by Professor Andre Geim and Professor Kostya Novoselov from the University of Manchester (Novoselov et al., 2004). Graphene is a single layer of carbon atoms arranged a two-dimensional (2D) benzene-ring hexagonal lattice (Geim and Novoselov, 2007; Geim, 2009). A graphene monolayer can be considered as the thinnest membrane reported so far, as its thickness is only one carbon atom with a theoretical thickness of 0.345 nm. It has extraordinary conductivity, flexibility, and transparency (Geim, 2009). Since then, graphene has been moving quickly from research laboratories to industrial applications. Beteween the large number of possible applications, it can be mentioned energy, transport, medicine, electronics, defence, desalination (Geim and Novoselov, 2007*). It has extraordinary conductivity, flexibility, and transparency (Geim, 2009).* In particular, graphene could improve the membranes ionic conductivity and enhance the catalysts electrocatalytic activity in fuel cells and electrolysers (Ion-Ebrasu et al., 2019; Marinoiu et al., 2017), increase the supercapacitors power (Liu et al., 2010) and enhance the lifetime of lithium ion batteries (Zhu et al., 2014). The high electrical conductivity and high optical transparency properties of graphene would be used for fabrication of the transparent electrodes employed in organic solar cells and light emitting diodes (OLEDs), touch screens, etc. (Bhattarai, 2012). 3D graphene foam is a porous open-cell foam made of single-layer sheets of graphene, with the microscopic characteristics of graphene (Banciu et al., 2017; Brownson et a., 2013). Graphene large area (cm^2) synthesis and reproducibility are one of the most critical conditions that have to be *fulfilled* in different type of devices fabrication. Nowadays, there are several methods used for graphene production, that include mechanical exfoliation (Novoselov et al., 2005), *graphene oxide chemical oxidation (Zhong et al, 2015),* catalyst-assisted synthesis in a chemical vapor deposition (CVD) process (Bhaviripudi et al. 2010; Fan et al., 2015).

In this paper there are presented the kinetic parameters namely, the working temperature in the reaction chamber, time of reaction and hydrocarbon (ethylene) flow rates used during the chemical vapor deposition (CVD) growth of 3D graphene on Ni foam substrate catalyst. *Although the graphene foam CVD growth was reported to be obtained in several papers (Banciu et al., Paronyan et. Al., 2016), the samples presented in this paper are specially adapted to our synthesis installation. Moreover, the structure and the electrochemical properties of the samples can be tailored according to the different applications such as batteries, fuels cells, supercapacitors. In order to preserve the 3D-graphene shape during their transfer, the nickel matrix was removed without using poly(methyl methacrylate) (PMMA) as post growth stabilizer of the graphene foam.* The samples were characterized *by* Raman spectroscopy, Scanning Electron Microscopy (SEM), Optical Microscopy (OM). The Brunauer-Emmett-Teller (BET) method was used to calculate the specific surface area, and the pore volume and pore radius were estimated by Barret-Joyner-Halenda method. *The samples obtained in the paper will be further functionalized and used for electrodes preparation and tested within different electrochemical systems such as batteries, fuel cells, electrolysers, supercapacitors, etc.)*

2. EXPERIMENTAL

2.1. Chemical Deposition (CVD) growth

3-D graphene foam *was* obtained by using in the EasyTube 3000ECT CVD Installation/CVD Equipment Corporation installation dedicated to graphene and carbon

nanotubes synthesis. *Basically, CVD graphene growth is one-stage method and takes place in a heated reaction chamber, by cracking the hydrocarbons (methane, ethylene, acetylene, etc.) in the presence of hydrogen and argon on the surface of different transition metal surface (Cu, Ni).* The advantage of this method comes from the fact that it is possible to produce graphene large area at once, without other mechanical and/or chemical surface treatment.

In the case of 3-D porous graphene, usually nickel foam is used as a template for its growth. A critical point is represented by the necessity of complete coverage of the entire nickel skeleton used as a matrix, uniform growth of graphene within the Ni pores, and metal total removal to obtain a self-standing porous graphene.

In order to obtain the graphene network, a commercial nickel foam from Alfa Aesar with a surface of 1.6 mm thickness and 70% porosity was used as a template, as received. *As carbon source 99.99% ethylene (C_2H_4) was employed.* The hydrocarbons are cracked under atmospheric pressure (*atm*), at 1000°C, and in the presence of hydrogen (99.999%) produced onsite by electrolysis, and argon (99.999%). H_2 plays the role of the metal substrate cleaning and hydrocarbons burning, and argon has the role of cleaning the residual oxygen in the reaction room, as well as protecting the metal surface from the oxidation reaction. Also, argon decreases the rate of deposition of the precursor (methane or ethylene) to a rate that will favour the 3-D graphene formation. 99.999% nitrogen is used for turbo pump controlling.

CVD process is shared in three stages: cleaning, growth, and cooling that are called "receipt", and is controlled by a dedicated software N0923RecipeEditor and N0923CVDWinPrc processing program. A receipt is formed by a succession of sequences that can run several associated segments in which are defined the working parameters (pressure, temperature, gas flows etc.). The detailed scheme of the process is presented in Figure 1.

Before introducing the samples into the processing chamber, nickel template is kept at 10^{-3} Torr pressure in the loadlock for pre-cleaning the substrates of any impurities. After introducing the samples, the processing chamber is evacuated up to 50 mTorr for about 17 minutes to clean the oven and check the tightness, followed by 6 minutes continuous argon introduction at atmospheric pressure and room temperature. The nickel catalysts is heated at 1000°C for 50 minutes, in an argon, and then hydrogen is introduced into the oven in order to clean and activate the metal template. Hydrogen, in combination with argon, is maintained for 30 minutes at 1000°C.

The graphene growth process is performed by introducing hydrocarbon (methane, ethylene) at a temperature of 1000°C. Also, the growth occurs in the presence of hydrogen, the partial pressure of hydrogen influencing the shape and size of the graphene growth domains.

After the synthesis process is finished, the oven is cooled at atmospheric pressure in three stages, each one for 5 minutes: the first stage is made up to 650°C in the argon and hydrogen atmosphere, followed by one up to 300°C and 200°C respectively in the argon atmosphere. Before removing, the sample is maintained in the loadlock for 60 minutes to cool to room temperature and then remove and store in a room with controlled atmosphere.

The entire process and system can be visualized online through the GUI (Graphical User Interface).

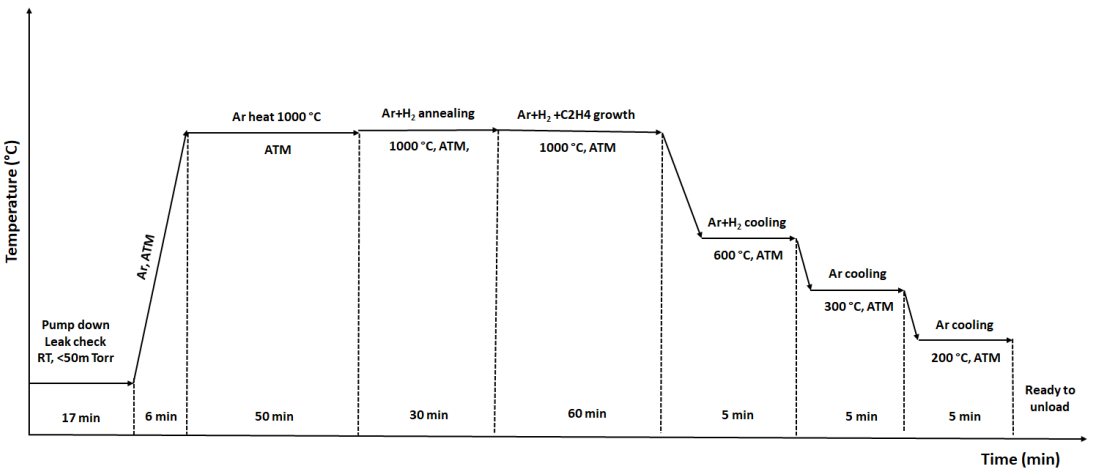

Figure 1. *The detailed scheme of graphene foam growing process*

In this paper there are presented the comparatively results between graphene growth at different ethylene gas flow (100, 200 and 300 sccm), at 1000°C and 1 ATM, during a 60 minutes synthesis process, and in presence of 0.3 slpm H_2 and 0.5 slpm Ar (Table 1).

Table 1. Principal graphene foam growing conditions during 60 minutes process, at 1000°C, 1 ATM and different ethylene gas flow

Sample	*Sample no.*	*Gas flow growing conditions*
Graphene/Ni foam	G1	300 sccm C_2H_4/0.3 slpm H_2 and 0.5 slpm Ar
Free-standing graphene foam	G2	100 sccm C_2H_4/0.3 slpm H_2 and 0.5 slpm Ar
Free-standing graphene foam	G3	200 sccm C_2H_4/0.3 slpm H_2 and 0.5 slpm Ar
Free-standing graphene foam	G4	300 sccm C_2H_4/0.3 slpm H_2 and 0.5 slpm Ar

2.2. Transfer and purification process

3-D graphene foam transfer and purification process was carried out using hydrochloric acid (36.5-38.0%) and demineralized water (18.2 MΩ cm) produced on-site. After graphene growth on the Ni foam, it is necessary to remove the metal, and this process was done in 3M HCl, boiling for about 20 hours at 90 °C on a hotplate acid resistant CP300, under the ventilated hoot. The process is repeated till the HCl solution is colourless (Figure 2). The samples were washed in demineralized water, and the procedure was repeated until complete elimination of acid. After each step, the washing solution's pH was tested. Celgard 2325 (PP/PE/PP) 25 mm foil from MTI was used as graphene support during the nickel foam removal in order to prevent samples sticking to the bottom of the glass dishes. The samples are dried for 24 hours at room temperature before testing and characterization. The results were free-stand graphene foam samples, with an average thickness of 1.6 mm and a mass density of about 12 mg/cm^3 corresponding to a 25 cm^2 area sample. In the Figure 2, the scheme of graphene foam synthesis, transfer and nickel foam removal is presented.

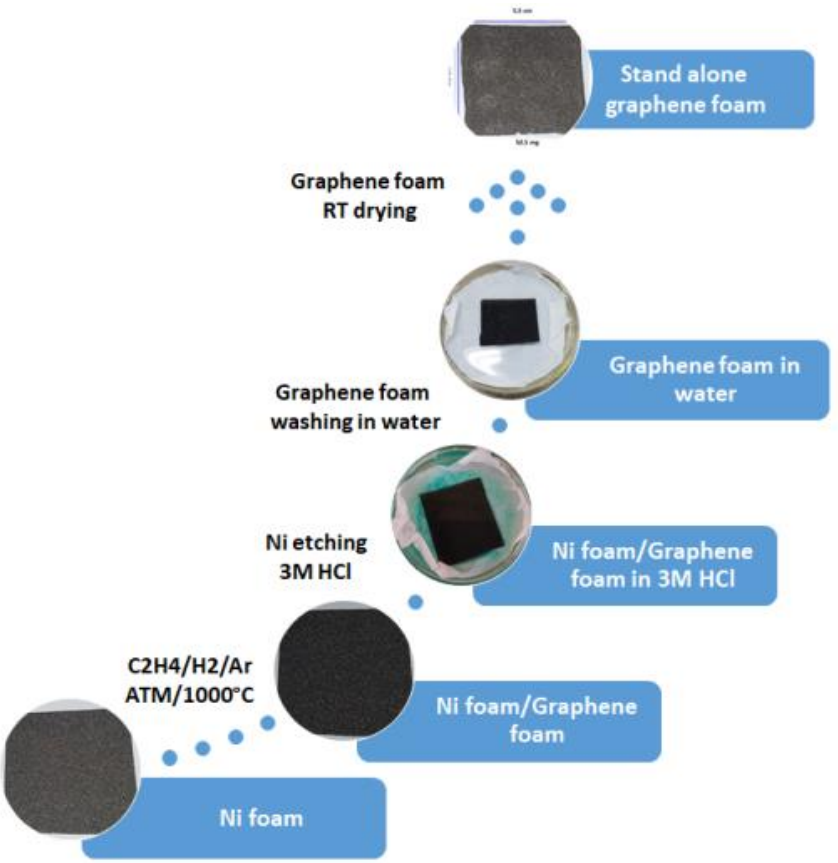

Figure 2. Scheme of graphene foam synthesis and transfer

2.3. Characterization

The morphology of the nickel foam template and graphene surface was studied using a scanning electron microscope (Sigma VP FEG Carl Zeiss SEM) and an optical microscope (AxioImager A2m de la Zeiss-OM). The defects and number of graphene layers were investigated by a AFM-Raman Witec alpha-300 RAS+ system. The spectral range used was between 1000 and 3000 cm^{-1}, the excitation source being an Argon-ion laser with a wavelength of 532 nm and 5s integration time. The nitrogen adsorption-desorption isotherms were carried out at 77 K using Autosorb IQ Quantachrome. The Brunauer-Emmett-Teller (BET) method was used to calculate the specific surface area. The pore volume and pore radius were estimated by Barret-Joyner-Halenda method. The sample was degassed at 388 K for 10 h before the adsorption measurements.

3. RESULTS AND DISCUSSION

In Figure 3 (a-e) there are presented the SEM micrographs of graphene foam at different ethylene flows (c-e) in comparison with nickel foam coated with graphene layers (b) and Ni foam substrate (a). SEM images show a complete cover of the nickel foam, even at a growing flow of 100 sccm C_2H_4. These results are also confirmed by the optical analysis (Figure 4). Graphene sample G3 was characterized by BET and the results are presented in Table 2.

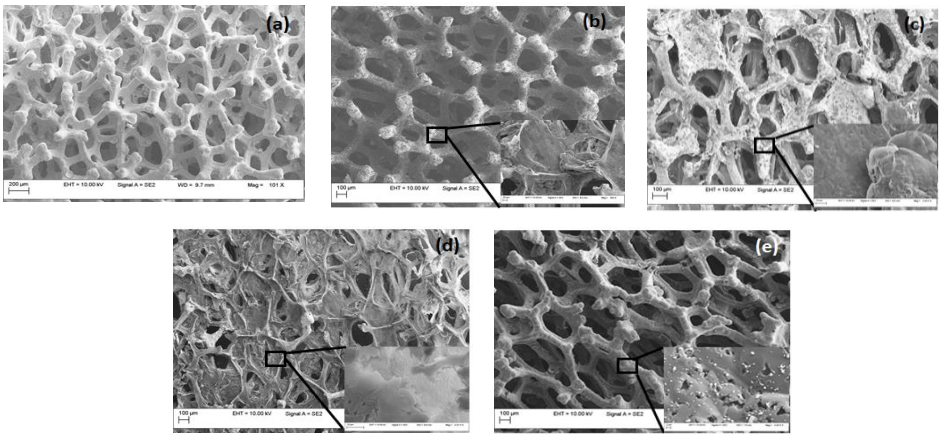

Figure 3. SEM micrographs of Ni foam and G1-G4 samples

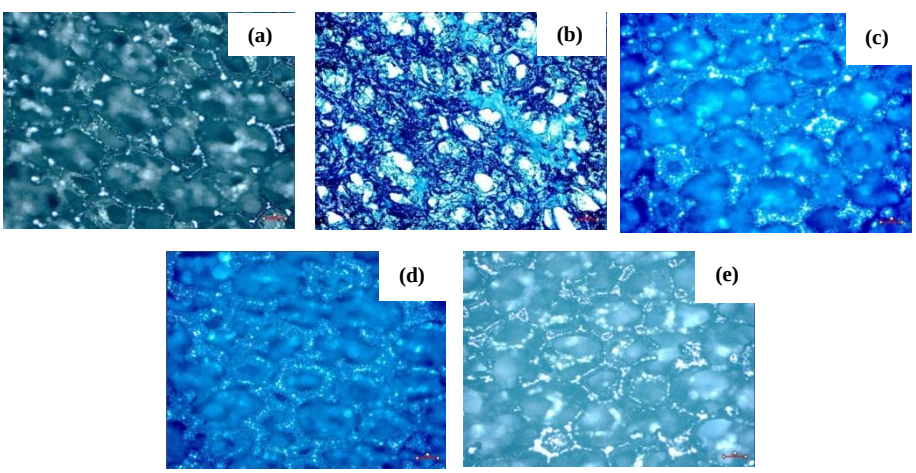

Figure 4. Optical images of Ni foam and G1-G4 samples

Table 2. Pore size distribution desorption by BET

Surface area (m^2/g)	*Pore volume (cm^3/g)*	*Pore radius (nm)*
9.821	0.032	1.9

In Figure 5 there are shown the overlaid Raman spectra of G2-G4 samples. All three spectra present the G band around 1587 cm^{-1}, known as the "graphite band", is a result of in-plane (intralayer) vibrations of the sp2-hybridized carbon atoms, and 2D band (2709 cm^{-1}) corresponding to the dispersion of the laser excitation energy. Moreover, G3 and G4 presents the D band situated at about 1357 cm^{-1} corresponding to the defects present in the samples. Analysing the I_{2D}/I_G ratio, it can be estimated the number of graphene layers. For one-layer $I_{2D}/I_G>2$, for bi-layer $1<I_{2D}/I_G<2$, and for multi-layer $I_{2D}/I_G<1$ (Malard et al., 2009). In Table 3 there are shown the I_{2D}/I_G values calculated from the Raman spectra associated with the G2, G3 and G4. The G band intensity increases with the number of layers, in the same time with the decreasing of the intensity of 2D peak. From Table 3 it can be noticed a decrease of I_{2D}/I_G ratio from 0.343 to 0.266 associated to the increase of graphene layers with the ethylene flow growth. *Moreover, from the I_G/I_{2D} it was estimated the number of layers of 2.9 to 3.43 that increase with ethylene flow rate. These results are in agreement with the calculated values of 68-78 cm^{-1} corresponding to*

the 2D full width at half maximum (FWHM), and confirm few layers graphene formation during CVD growing process within Ni foam template.

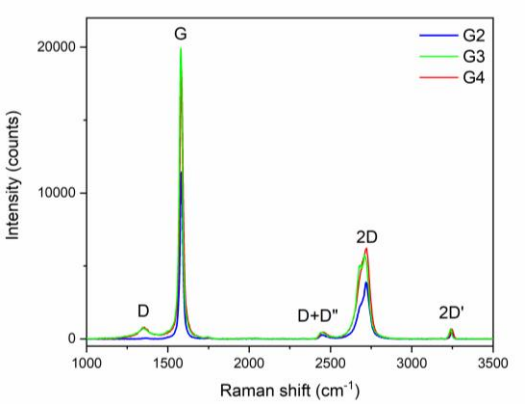

Figure 5. Overlaid Raman spectra of G2, G3 and Ge samples

Table 3. The intensity ratio between the I_{2D}/I_G band

Sample	I_{2D}/I_G	I_G/I_{2D}	FWHM of 2D band (cm^{-1})
G2	0.343	2.9	68
G4	0.300	3	77
G5	0.266	3.43	78

4. CONCLUSIONS

25 cm^2 macroporous graphene layers were obtained by chemical vapor deposition method on the nickel skeleton. The growing was carried out using various ethylene gas flow, at atmospheric pressure and 1000 °C. *The transfer process was optimized without using PMMA stabilizer.* From SEM and optical microscopy images it was shown a complete coverage of the metal foam, and formation of dense graphene interpenetrating network with pore radius about 1.9 nm, pore volume of 0.032 cm^3/g, surface area 9.821 m^2/g, and an average graphene mass density of about 12 mg/cm^3. *Furthermore, Raman spectroscopy spectra proved an increase of graphene number of layers, up to 3.43, with ethylene gas flow.* The presence of low intensity D band proves synthesis by CVD of low defect free-standing graphene foam. This procedure can be applied to obtain large area (100 cm^2) of porous graphene with controlled porosity and lack of intense mechanical and/or chemical treatments. Further experiments will be carried out for graphene foam doping and functionalization, testing, and utilization *for electrodes fabrication* for different electrochemical energy systems (fuel cells, batteries, supercapacitors etc.) development.

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Author Contributions: D. Ion-Ebrasu designed the experiments, synthesized the 3-D graphene samples, and wrote the manuscript with support of R.D. Andrei who contributed to the graphene transfer process. S. Enache did the Raman measurements, A. Enache contributed to the samples'

preparation, and A. Soare carried out the SEM characterization. E. Carcadea checked the manuscript and M. Varlam supervised the experiments.

Conflict of Interest Statement: The authors declare that there is no conflict of interest.

REFERENCES

Banciu, C., Lungulescu, M., Bara, A., Leonat, L., Teisanu, A. (2017). 3D graphene network investigation by Raman spectroscopy. *Optoelectronics and advanced materials – Rapid communications, 11*(5-6), 368-372.

Bhattarai, L.N. (2012). Graphene: A Peculiar Allotrope Of Carbon. *Himalayan Physics*, *3*(3), 87-88. https://doi.org/10.3126/hj.v3i0.7314.

Bhaviripudi, S., Jia, X., Dresselhaus, M.S., Kong, J. (2010). Role of Kinetic Factors in Chemical Vapor Deposition Synthesis of Uniform Large Area Graphene Using Copper Catalyst, *Nano Lett., 10*(10), 4128-4133. https://doi.org/10.1021/nl102355e.

O'Brien, M., Nichols, B. (2010) CVD Synthesis and Characterization of Graphene Thin Films, *Army Research Laboratory*: Adelphi, MD 20783-1197. ARL-TR-5047; U.S. http://www.dtic.mil/cgi-bin/GetTRDoc?AD=ADA513793.

Brownson, D.A.C., Figueiredo-Filho, L.C.S., Ji, X., Gómez-Mingot, M., Iniesta, J., Fatibello-Filho, O., Kampourisa, D.K., Banks, C.E. (2013). Freestanding three-dimensional graphene foam gives rise to beneficial electrochemical signatures within non-aqueous media. *Journal of Materials Chemistry A, 1*(19), 5962-5972, doi.org/10.1039/C3TA10727B.

Ion-Ebrasu, D., Pollet, B.G., Spinu-Zaulet, A., Soare, A., Carcadea, E., Varlam, M., Caprarescu, S. (2019). Graphene Modified Fluorinated Cation-Exchange Membranes for Proton Exchange Membrane Water Electrolysis. *International Journal of Hydrogen Energy, 44*(21), 10190-10196, doi.org/10.1016/j.ijhydene.2019.02.148.

Fan, X., Chen, X., Dai, L. (2015). 3D graphene based materials for energy storage, *Current Opinion in Colloid & Interface Science 20*(5) 429–438. http://dx.doi.org/10.1016/j.cocis.2015.11.005

Paronyan, T.M, Thapa, A.K., Sherehiy, K., Jasinski, J.B., Jangam, J.S.D. (2016). Incommensurate Graphene Foam as a High Capacity Lithium Intercalation Anode, *Sci Rep 7*, 39944. https://doi.org/10.1038/srep39944

Geim, A.K. (2009). Graphene: status and prospects. *Science, 324*(5934), 1530-1534. DOI: 10.1126/ science.1158877.

Geim, A. K., Novoselov, K. S. (2007). The rise of graphene. *Nature Materials, 6*, 183-191, doi.org/10.1038/nmat1849.

Zhong, Yu Lin, et al. (2015). Scalable production of graphene via wet chemistry: progress and challenges, *Materials Today* 18(2): 73-78, doi: 10.1016/j.mattod.2014.08.019

Liu, C., Yu, Z., Neff, D., Zhamu, A., Jang, B.Z. (2010). Graphene-Based Supercapacitor with an Ultrahigh Energy Density, *Nano Lett., 10*(12), 4863-4868, doi.org/10.1021/nl102661q.

Malard, L. M., Pimenta, M. A., Dresselhaus, G., Dresselhaus, M. S. (2009). Raman spectroscopy in graphene, *Physics Reports, 473*(5-6), 51-87, doi.org/10.1016/j.physrep.2009.02.003.

Marinoiu, A., Raceanu, M., Carcadea, E., Varlam, M., Balan, D., Ion-Ebrasu, D., Stefanescu, I., Enachescu, M. (2017). Iodine-doped graphene for enhanced electrocatalytic oxygen reduction reaction in proton exchange membrane fuel cell applications, *Journal of Electrochemical Energy Conversion and Stor*age, *14*(3), 79-97, doi.org/10.1115/1.4036684.

Novoselov, K.S., Geim, A.K., Morozov, S.V., Jiang, D., Zhang, Y., Dubonos, S.V., Grigorieva, I.V., Firsov, A.A. (2004). Electric field effect in atomically thin carbon films, *Science, 306*(5696), 666-669, DOI: 10.1126/science.1102896.

Novoselov, K.S., Jiang, D., Schedin, F., Booth, T.J., Khotkevich, V.V., Morozov, S.V., Geim, A.K. (2005). Two-dimensional atomic crystals, *Proceeding of the National Academy of Science of the United State of America (PNAS), 102*(30), 10451-10453, doi.org/10.1073/pnas.0502848102.

Zhu, J., Duan, R., Zhang, S., Jiang, N., Zhang, Y., Zhu, J. (2014). The application of graphene in lithium ion battery electrode materials. *SpringerPlus, 3*, 585, doi.org/10.1186/2193-1801-3-585.

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