# CARBONIZATION OF STINGING NETTLE (URTICA DIOICA) BY THERMAL AND CHEMICAL PROCESSING

**[1]KANOKON NUILEK, [2]ANDREA SIMON, [3]PETER BAUMLI**

[1,2]Department of Ceramics and Polymer Engineering, University of Miskolc, Miskolc, Hungary
[3]Department of Nanotechnology, University of Miskolc, Miskolc, Hungary
E-mail: [1]k.nuilek@gmail.com, [2]femandi@uni-miskolc.hu, [3]baumlipeter@gmail.com

**Abstract -** Carbon can be produced from natural materials by physical, chemical or physicochemical method. The stinging nettle is a natural waste material. Various nettle plants can be used in textile, food, medicine, agriculture and cosmetic products. However, there is no research studied production of carbon from stinging nettle by thermal and chemical processing. In this work stinging nettles were separated to nettle stem and nettle leaf, treated by hydrochloric acid and pre-carbonized at 450 ˚C, then stinging nettle was activated with potassium hydroxide and carbonized at 800 ˚C. The microstructure and chemical composition of nettle stem and nettle leaf were different in each process. The carbon nanostructure was found in nettle stem and nettle leaf after carbonization processing.

**Keywords -** Carbonization, Natural materials, Chemical activation

## I. INTRODUCTION

Plant is a natural material that is abundant and interesting to carry out research upon. The cell wall of the plant surrounds the cell membrane. It consists of several layers of cellulose, which are arranged in the primary and secondary walls. Cellulose is the most common organic compound in the world. [1]-[2]. Stinging nettle (Urtica dioica) is a wild plant that grows in Europe, Asia, northern Africa and western North America, usually found in the countryside. Nettle plant has a very strong fiber and high fixed carbon. The stinging nettles have many hollow stinging hairs called trichomes on the leaves and stems [3]. The applications of stinging nettle have been developed in textile products, medicine, cosmetics, food and bioenergy [4]-[7]. As cellulose has appreciable carbon content [8]-[12], it can be a suitable material for the preparation of activated carbon [13]-[14]. The carbon content in cellulose varies from 40% to 44%. However, this content may increase above 80% for carbonized samples and reach in the range of 95% for activated carbon [5], [15]

Production of activated carbon involves two steps: the carbonization of raw carbonaceous materials in an inert atmosphere and the activation of carbonized carbon. The purpose of activation is to enlarge diameters of fine pores and derive new pores after the carbonization step. Activation can be carried out by physical (hydro-thermal), chemical or physicochemical method [14], [16]-[17]. Potassium hydroxide (KOH) activation is a well-known method to generate the pore network in carbons [18]-[30].

Nobody used stinging nettle to produce carbonaceous material. This paper focuses on the effect of chemical and thermal processing to the microstructure and chemical composition of the nettle stem and nettle leaf.

## II. MATERIALS AND METHODS

### Materials

The biomass waste of nettle was used as carbonaceous material precursors. Nettle plants were collected in Miskolc, Hungary. Chemicals used are hydrochloric acid (HCl), potassium hydroxide (KOH) and ethyl acetate.

### Raw materials preparation

The nettles were separated to nettle stem and nettle leaf, washed several times and dried at 80˚C for 24 hours, then treated by HCl 0.5 M for 24 hours, finally washed by distilled water and dried at 80˚C for 24 hours.

### Pre-carbonization method

The pre-carbonization process was carried out at 450˚C for 2 hours in a stainless-steel tube furnace under argon atmosphere.

### Chemical activation by KOH (solid) method

The pre-carbonized nettle stem and nettle leaf (0.5 g) was mixed with KOH(solid) at a mass ratio of 1:1 and milled for 1 hour by mortar.

### Chemical activation by KOH (solute) method

The pre-carbonized nettle stem and nettle leaf (0.5 g.) was milled for 1 hour by mortar, then stirred into aqueous KOH (solute) with a weight ratio of pre-carbonized peanut shell : KOH = 1: 1 for 2 hours and dried at 80 ˚C for 24 hours.

### Carbonization method

The mixed nettles were heat treated at 800 ˚C for 2 hours in a stainless-steel tube furnace under argon atmosphere. After this process, carbon was extracted from KOH containing mixture with ethyl acetate [31].

The microstructure and morphology of the samples were investigated by scanning electron microscopy (SEM, HITACHI S-4800, ZEISS EVO-MA10), the

chemical composition was analysed by energy-dispersive X-ray spectrometry (EDS).

## III. RESULTS AND DISCUSSION

The SEM micrographs of raw materials before treating with HCl solution are shown in Fig.1-2. The treated samples are shown in Fig.3-6. The nettle stem, nettle leaf and peanut shell were treated by HCl solution for removing metallic oxide or organic [32] and then pre-carbonized at 450 ˚C. These synthesized samples were studied by SEM and EDS.




**Fig. 1 Dried materials (a) Nettle stem (b) Nettle leaf**

The microstructure of the dried nettle stem was examined by SEM (Fig.2 (a)). The cell wall in a fiber is not a homogeneous layer. It has grooved and hollowed surface, composed of fibrous structure and has many hollowed stinging hairs (trichomes) on the surface. The main chemical elements of the sample are carbon, oxygen, zinc as shown in Table 2.

The bristly surface of dried nettle leaf is shown in Fig. 2 (b). Nettle leaf contains veins covered by fine stinging hairs (each hair contains a fine tube, stiffened by calcium carbonate at its base and by silica at its tip) [33]. The rough fiber with surface irregularities is shown in Fig.2(b). The main chemical elements of the sample are carbon and oxygen. The nettle leaf has lots of stinging hairs on the surface; therefore, it has higher silica content (Table 2) than nettle stem.

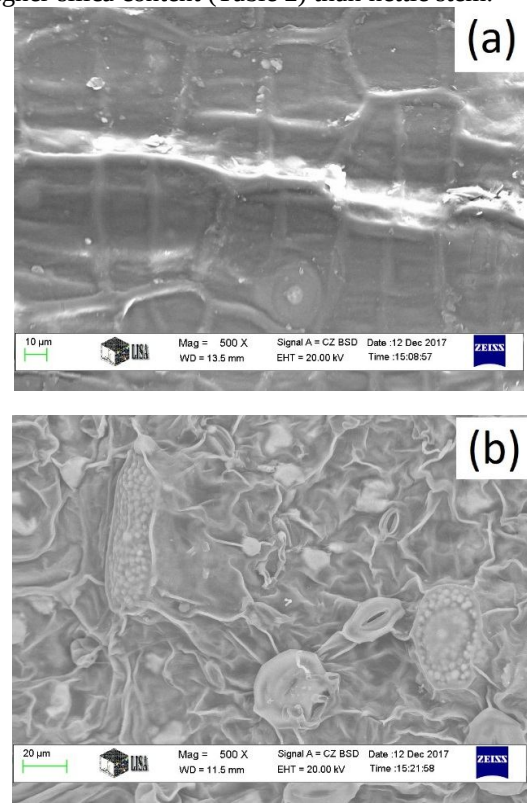



**Fig. 2 SEM micrograph of (a) Dried nettle stem and (b) Dried nettle leaf**

The microstructure of the nettle samples, after treating by HCl solution, is shown in Fig.3. The grooved surface was clear and found to be hollowed and having fibrous structure (Fig.3 (a)). The microstructure of nettle stem after treating by HCl shows clean surface and it has not changed compared to the dried nettle stem. The chemical elements of the nettle stem such as carbon, oxygen and small amounts of other elements are shown in Table 2. Some elements such as zinc are removed during this process.

The microstructure of nettle leaf treated by HCl solution is shown in Fig. 3(b). Nettle leaf still has bristly surface and lots of large and small stinging hairs, with high amount of calcium and silica [33]. Zinc is removed by chemical treatment. The chemical analysis (Table 2) of the sample shows mainly carbon and oxygen. Thermal activation affects the microstructure, weight (Table 1) and chemical composition (Table 2) of the samples stronger than chemical activation.

| Samples | % yield | |
|---|---|---|
| | Treated by HCl | Pre-carbonized at 450 ˚C for 2h |
| Nettle stem | 70.4 | 31.0 |
| Nettle leaf | 62.8 | 36.7 |

**Table 1 Yield of the samples**

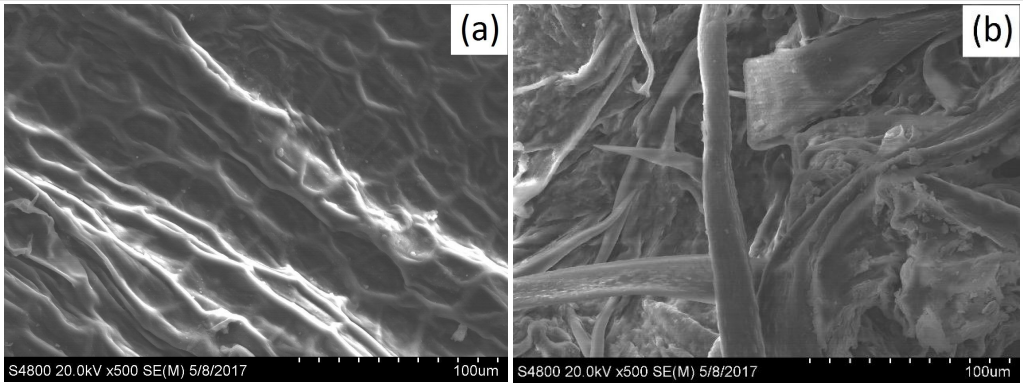



**Fig. 3 SEM micrograph of (a) nettle stem and (b) nettle leaf after treating with hydrochloric acid solution**

| Samples | Chemical compositions (wt. %) | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | C | O | Zn | Cl | Si | K | Ca | Mg | P | Al |
| Dried nettle stem | 61.64 | 35.66 | 1.45 | 0.67 | 0.14 | 0.22 | 0.22 | - | - | - |
| Treated by HCl | 51.67 | 41.70 | - | 0.37 | 0.01 | 5.2 | 0.94 | 0.11 | - | - |
| Pre-carbonized at 450˚C 2h | 90.35 | 6.77 | - | - | 0.78 | 1.78 | - | - | - | 0.32 |
| Treated by KOH(solid) and carbonized at 800 ˚C 2h | 88.00 | 8.83 | - | - | - | 3.17 | - | - | - | - |
| Treated by KOH(solute) and carbonized at 800 ˚C 2h | 93.84 | 4.78 | - | - | - | 1.38 | - | - | - | - |
| Dried nettle leaf | 64.51 | 33.95 | 0.64 | - | 0.80 | - | 0.10 | - | - | - |
| Treated by HCl | 46.98 | 40.15 | - | 0.17 | 1.41 | 4.43 | 5.00 | - | 1.86 | - |
| Pre-carbonized at 450˚C 2h | 74.36 | 12.65 | - | - | 9.98 | - | 0.75 | 0.42 | 1.84 | - |
| Treated by KOH(solid) and carbonized at 800 ˚C 2h | 66.16 | 14.35 | - | 0.16 | 12.99 | 5.24 | 1.10 | - | - | - |
| Treated by KOH(solute) and carbonized at 800 ˚C 2h | 74.02 | 7.79 | - | - | 6.77 | 8.01 | 3.41 | - | - | - |

**Table 2 Chemical composition of samples**

The microstructure of nettle stem heat treated at 450 ˚C is shown in Fig. 4. Thin layered structure, several hollowed microtubes and abundant pore network were found on the surface of the heat-treated samples. After this process, higher weight percent of carbon was measured as shown in Table 2.

The microstructure of nettle leaf heat treated at 450 ˚C shows roughly divided surface having trichomes and thin layers on it (Fig. 4(b)). The latter reveals circular structure. Carbon and silica ratio is higher than it was after the previous step.

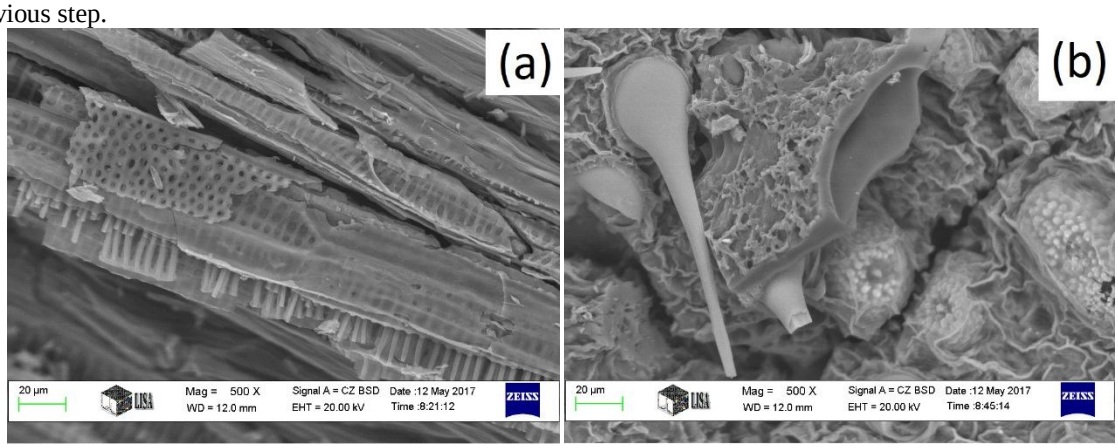



**Fig. 4 SEM micrographs of the pre-carbonized samples at 450 ˚C 2h of (a) nettle stem (b) nettle leaf**

After activating by KOH(solid) and heat treated at 800 ˚C for 2 hours, nettle stem has thin-layered (nano-) structure with microsized pores, as shown in Fig.5(a)-(b). Activation by KOH (solute) forms angulared sheets in nettle stem (Fig.5(c)-(d). The sheet thickness ranges between 60-681.4 nm and 1.135 µm - 940.4 nm after activating by KOH (solid) and KOH (solute), respectively. The fracture of grooved surface is shown in (Fig. 5(a),(c)). KOH activation generated many mesopores on the fiber wall and micropores on the mesopores wall but did not destroy porous fibrous skeleton [34].

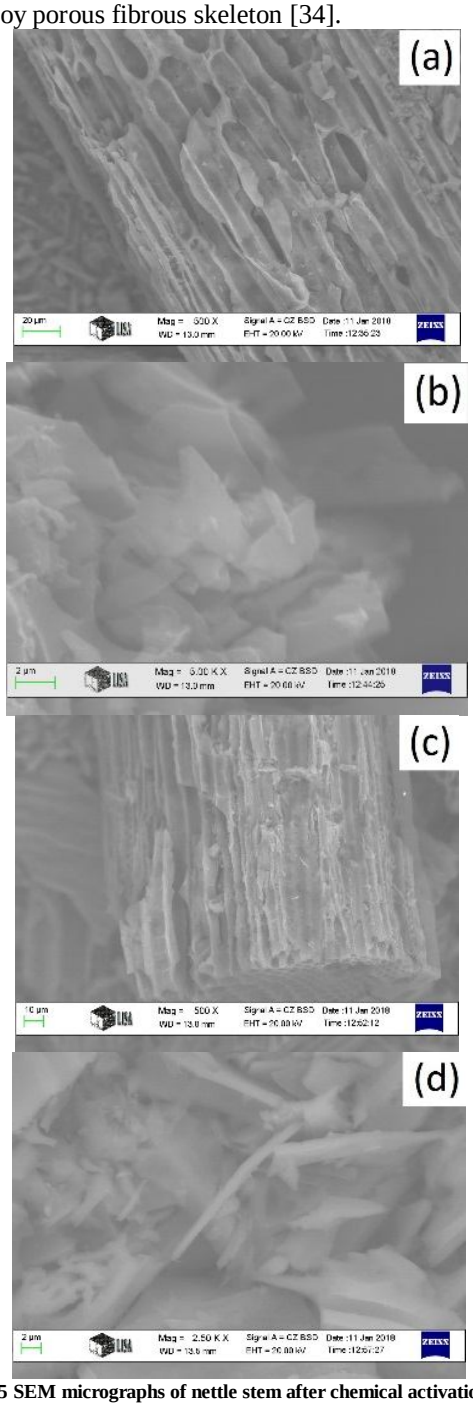



**Fig. 5 SEM micrographs of nettle stem after chemical activation by KOH (solid) and carbonization (a) original structure remained (b) carbon nanostructure formed, after chemical activation by KOH (solute) and carbonization (c) original structure remain (d) the formation of carbon nanostructure**

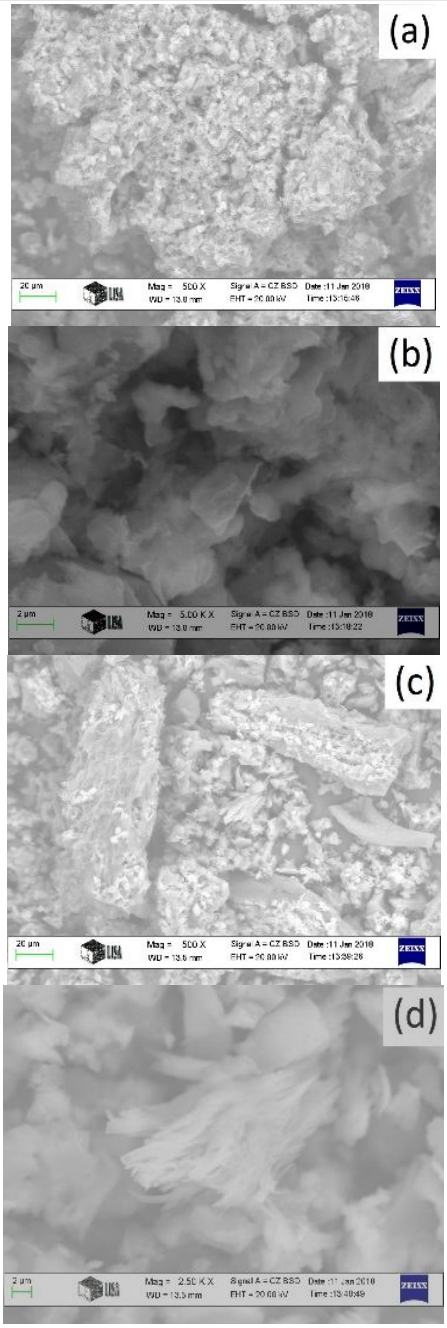



**Fig. 6 SEM micrographs of nettle leaf after chemical activation by KOH (solid) and carbonization (a) original structure remained (b) carbon nanostructure formed, after chemical activation by KOH (solute) and carbonization (c) original structure remained (d) carbon nanostructure formed**

The microstructure of nettle leaf carbon, as shown in Fig.6(a)-(d), has multiple layers. Agglomerated small plates were found after activating by KOH (solid) (Fig. 6 (b)). Fibrous structure was found after activating by KOH (solute), in Fig.6 (d). Both nettle stem and nettle leaf have higher carbon content after this processing step (Table 2).

## CONCLUSION

The chemical and thermal activation affects the chemical composition and the microstructure of the

stinging nettle. Carbon nanostructure was formed in layered structure from nettle stem and nettle leaf. Carbon sheets tended to form agglomerates more after activation with KOH (solid) than with KOH(solute). Stinging nettle is a natural material newly used to produce carbon.

## ACKNOWLEDGEMENTS

The authors thank Dr. Maria Sveda, Dr. Anna Sycheva and Dr. Daniel Koncz-Horvath for examining and characterizing (SEM and EDS) samples in this research work.

## REFERENCES

[1] M. Sfiligoj, S. Hribernik, K. Stana, and T. Kree, “Plant Fibres for Textile and Technical Applications,” Advances in Agrophysical Research, 2013.

[2] "Plant Structure & Function", Sci.waikato.ac.nz, 2018. [Online].Available:http://sci.waikato.ac.nz/farm/content/plantstructure.html. [Accessed: 08- Mar- 2018].

[3] "Urtica dioica", En.wikipedia.org, 2018. [Online]. Available: https://en.wikipedia.org/wiki/Urtica_dioica#cite_note-uc-1. [Accessed: 8- Mar- 2018].

[4] I. Agus Suryawan, N. Suardana, I. Suprapta Winaya, I. Budiarsa Suyasa and T. Tirta Nindhia, "Study of stinging nettle (urtica dioica l.) Fibers reinforced green composite materials : a review", IOP Conference Series: Materials Science and Engineering, vol. 201, p. 012001, 2017.

[5] N. Di Virgilio, E. Papazoglou, Z. Jankauskiene, S. Di Lonardo, M. Praczyk and K. Wielgusz, "The potential of stinging nettle (Urtica dioica L.) as a crop with multiple uses", Industrial Crops and Products, vol. 68, pp. 42-49, 2015.

[6] İ. Gülçin, Ö. Küfrevioğlu, M. Oktay and M. Büyükokuroğlu, "Antioxidant, antimicrobial, antiulcer and analgesic activities of nettle (Urtica dioica L.)", Journal of Ethnopharmacology, vol. 90, no. 2-3, pp. 205-215, 2004.

[7] Y. Loetscher, M. Kreuzer and R. Messikommer, "Utility of nettle (Urtica dioica) in layer diets as a natural yellow colorant for egg yolk", Animal Feed Science and Technology, vol. 186, no. 3-4, pp. 158-168, 2013.

[8] S. Dridi-Dhaouadi, N. Douissa-Lazreg and M. M'Henni, "Removal of lead and Yellow 44 acid dye in single and binary component systems by rawPosidonia oceanicaand the cellulose extracted from the raw biomass", Environmental Technology, vol. 32, no. 3, pp. 325-340, 2011.

[9] V. Kocherbitov, S. Ulvenlund, M. Kober, K. Jarring and T. Arnebrant, "Hydration of Microcrystalline Cellulose and Milled Cellulose Studied by Sorption Calorimetry", The Journal of Physical Chemistry B, vol. 112, no. 12, pp. 3728-3734, 2008.

[10] V. Lapina and G. Akhremkova, "Correlations between the adsorption and structural properties of SV-1 phytoadsorbent and its main components", Russian Journal of Physical Chemistry, vol. 80, no. 7, pp. 1164-1166, 2006.

[11] K. Wu, B. Gao, J. Su, X. Peng, X. Zhang, J. Fu, S. Peng and P. Chu, "Large and porous carbon sheets derived from water hyacinth for high-performance supercapacitors", RSC Advances, vol. 6, no. 36, pp. 29996-30003, 2016.

[12] L. Bacci, S. Baronti, S. Predieri and N. di Virgilio, "Fiber yield and quality of fiber nettle (Urtica dioica L.) cultivated in Italy", Industrial Crops and Products, vol. 29, no. 2-3, pp. 480-484, 2009.

[13] P. Sugumaran, V. P. Susan, P. Ravichandran and S. Seshadri, “Production and characterization of activated carbon from banana empty fruit bunch and Delonix regia fruit pod”, Journal of Sustainable Energy and Environment, vol.3, no.3, pp. 125-132, 2012.

[14] M. Yahya, Z. Al-Qodah and C. Ngah, "Agricultural bio-waste materials as potential sustainable precursors used for activated carbon production: A review", Renewable and Sustainable Energy Reviews, vol. 46, pp. 218-235, 2015.

[15] Suhas, V. Gupta, P. Carrott, R. Singh, M. Chaudhary and S. Kushwaha, "Cellulose: A review as natural, modified and activated carbon adsorbent", Bioresource Technology, vol. 216, pp. 1066-1076, 2016.

[16] H. R. Hafizi-Atabak, H. Ghanbari-Tuedeshki, A. Shafaroudi, M. Akbari, J. Safaei-Ghomi and M. Shariaty-Niassar, “&, Production of Activated Carbon from Cellulose Wastes”, Journal of Chemical Petroleum Engineering, vol. 47, pp. 13-25, 2013.

[17] A. Jain, R. Balasubramanian, and M. Srinivasan, “Hydrothermal conversion of biomass waste to activated carbon with high porosity: A review,” Chemical Engineering Journal, vol. 283, pp. 789–805, 2016.

[18] R. Kumar, R. K. Singh, and D. P. Singh, “Natural and waste hydrocarbon precursors for the synthesis of carbon based nanomaterials: Graphene and CNTs,” Renewable and Sustainable Energy Reviews, vol. 58, pp. 976–1006, 2016.

[19] H. M. Yang, D. H. Zhang, Y. Chen, M. J. Ran, and J. C. Gu, “Study on the application of KOH to produce activated carbon to realize the utilization of distiller’s grains,” IOP Conference Series: Earth and Environmental Science, vol. 69, p. 012051, 2017.

[20] A. Robau-Sánchez, F. C.-D. L. Rosa, J. Aguilar-Pliego, and A. Aguilar-Elguézabal, “On the reaction mechanism of the chemical activation of Quercus Agrifolia char by alkaline hydroxides,” Journal of Porous Materials, vol. 13, no. 2, pp. 123–132, 2006.

[21] J. Guo, J. Zhang, F. Jiang, S. Zhao, Q. Su, and G. Du, “Microporous carbon nanosheets derived from corncobs for lithium–sulfur batteries,” Electrochimica Acta, vol. 176, pp. 853–860, 2015.

[22] G. Nagaraju, S. M. Cha, and J. S. Yu, “Ultrathin nickel hydroxide nanosheet arrays grafted biomass-derived honeycomb-like porous carbon with improved electrochemical performance as a supercapacitive material,” Scientific Reports, vol. 7, p. 45201, 2017.

[23] G. Lin, R. Ma, Y. Zhou, Q. Liu, X. Dong, and J. Wang, “KOH activation of biomass-derived nitrogen-doped carbons for supercapacitor and electrocatalytic oxygen reduction,” Electrochimica Acta, vol. 261, pp. 49–57, 2018.

[24] Y. S. Yun, M. H. Park, S. J. Hong, M. E. Lee, Y. W. Park, and H.-J. Jin, “Hierarchically Porous Carbon Nanosheets from Waste Coffee Grounds for Supercapacitors,” ACS Applied Materials & Interfaces, vol. 7, no. 6, pp. 3684–3690, Mar. 2015.

[25] J. Sodtipinta, T. Amornsakchai, and P. Pakawatpanurut, “Nanoporous carbon derived from agro-waste pineapple leaves for supercapacitor electrode,” Advances in Natural Sciences: Nanoscience and Nanotechnology, vol. 8, no. 3, p. 035017, 2017.

[26] T. Purkait, G. Singh, M. Singh, D. Kumar and R. Dey, "Large area few-layer graphene with scalable preparation from waste biomass for high-performance supercapacitor", Scientific Reports, vol. 7, no. 1, 2017.

[27] H. Liu, X. Wu, H. Geng and X. Teng, "Effects of several nano-carbon materials on the microstructure and properties of copper", Materials Research Express, vol. 4, no. 2, p. 025801, 2017.

[28] J. Liu, U. Khan, J. Coleman, B. Fernandez, P. Rodriguez, S. Naher and D. Brabazon, "Graphene oxide and graphene nanosheet reinforced aluminium matrix composites: Powder synthesis and prepared composite characteristics", Materials & Design, vol. 94, pp. 87-94, 2016.

[29] J. Romanos, M. Beckner, T. Rash, L. Firlej, B. Kuchta, P. Yu, G. Suppes, C. Wexler and P. Pfeifer, "Nanospace engineering of KOH activated carbon", Nanotechnology, vol. 23, no. 1, p. 015401, 2011.

[30] A. Romero-Anaya, M. Ouzzine, M. Lillo-Ródenas and A. Linares-Solano, "Spherical carbons: Synthesis, characterization and activation processes", Carbon, vol. 68, pp. 296-307, 2014.

[31] T. Gábor, F. Kármán, J. Sytchev, E. Kálmán and G. Kaptay, "The separation of carbon nanotubes from chlorides", Carbon, vol. 47, no. 4, pp. 1195-1198, 2009.

[32] K. Wu, B. Gao, J. Su, X. Peng, X. Zhang, J. Fu, S. Peng and P. Chu, "Large and porous carbon sheets derived from water

hyacinth for high-performance supercapacitors", RSC Advances, vol. 6, no. 36, pp. 29996-30003, 2016.

[33] "Clip D30_11_579, from Dissolve", Dissolve, 2018. [Online]. Available: http://dissolve.com/video/ Animated -scanning -electron-micrograph-SEM-leaf-rights-managed-stock-video-footage/002-D30-11-579. [Accessed: 4- Jan- 2018].

[34] Z. Qiu, Y. Wang, X. Bi, T. Zhou, J. Zhou, J. Zhao, Z. Miao, W. Yi, P. Fu and S. Zhuo, "Biochar-based carbons with hierarchical micro-meso-macro porosity for high rate and long cycle life supercapacitors", Journal of Power Sources, vol. 376, pp. 82-90, 2018.

★★★