

Ph.D. Dissertation

**Investigation the effect of activation and exfoliation on
carbon nanosheets properties**

By

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1 Introduction

2D carbon nanostructures – namely graphene and carbon nanosheets – are increasingly being researched as candidates for energy storage devices such as batteries or capacitors. The properties of carbon are a combination of the properties of glass and ceramic materials which are characterized by low density, high thermal and chemical resistance. Chemical and thermal treatments are the main steps of the preparation of carbon nanostructures. Among all the chemical activation agents, alkaline hydroxides such as potassium hydroxide (KOH) or sodium hydroxide (NaOH) are reported to be highly interesting from the performance point of view, allowing activated carbons to be prepared from many kinds of carbonaceous precursors. Chemical acids are used as intercalating agents to obtain exfoliated graphite by different processes. This activated carbon can be obtained from various agricultural wastes. Since no research has presented synthesis carbon by using two processes: activation and exfoliation. So this is an exciting novelty to the study. The preparation of nanostructured materials from wastes has drawn tremendous interest in recent years. Many researchers have demonstrated that carbon materials used as adsorbents or electronic materials can be synthesized from low-cost waste materials by using alkaline hydroxides. The structures of nettle and peanut shells consist of cellulose, hemicellulose and lignocellulose. These materials are the major contents of biowaste which can play the role of carbon precursors in producing highly ordered nanocarbons, and contribute to the porosity of biochar yield.

Energy storage and delivery are one of the most promising areas for the application of activated carbon. Supercapacitors, also called electric double-layer electrodes, are highly efficient in energy storage and delivery characteristics compared to batteries. They can deliver high rates of energy by using a mechanism of simple charge separation at the interface between the electrode and electrolyte. As far as it concerns, no previous studies have reported on using nettle stem or peanut shell as raw materials for producing carbon nanosheets by chemical activation and exfoliation processes. The activated carbon produced in this way can be used as electrode material for supercapacitors.

The goal of this research is to systematically study and investigate the effect of different alkaline hydroxides activators and acid exfoliators on the properties of carbon nanosheets, prepared from natural materials.

2 Literature overviews

Environmental awareness has given rise to the idea of utilizing natural waste and other everyday waste materials to be beneficial and cost-effective. The production of activated carbon (AC) from waste materials is a hot topic these days as sources of activated carbon are abundant and increasing. Activated carbon is widely used as a sorbent due to its low cost, exceptionally high porosity, customizable pore size and high absorbency. The activation process normally develops the pore structure of activated carbon. Natural materials are used as precursors for the carbon production. Activated carbon is made up of carbon as the main component, and other elements such as oxygen, hydrogen, nitrogen, sulfur and others. The type of activation method and carbon precursors have a significant effect on the final characteristics and the efficiency of the activated carbon obtained. Activated carbon has the advantages of superior physicochemical properties such as high surface area, physical and chemical stability. The substrate for activated carbon preparation is abundant, easy to prepare, inexpensive, and has low density.

2.1 The structure of carbon synthesized from natural materials

The plant is a natural material that is abundant and interesting for research. 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]. Hemicellulose can be used as a potential carbon material on account of its high carbon content, renewability, environmental sustainability, and special structure [2]. Lignin is an abundant biopolymer with high carbon content, high aromaticity, and it is an excellent precursor for the preparation of high-value carbon materials [3]. 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 fibre and high carbon content. Peanut (*Arachis hypogaea*) is a major

crop widely distributed throughout tropical and subtropical parts of Asia, Africa, Oceania, North and South America and Europe. Natural structures of peanut shell consisting of cellulose, hemicellulose and lignocellulose are the major contents of biowaste, which can play the role of carbon precursors in producing highly ordered nanocarbons [4-5].

2.2 Effect of organic components on carbon properties

Lignocellulosic waste materials are massively produced worldwide. Lignocellulose or lignocellulosic biomass is plant dry matter composed of carbohydrate polymers, namely cellulose and hemicellulose, and lignin [6]. Lignocellulosic materials are widely used as precursors and account for around 45% of the total raw materials used for the manufacture of activated carbon [7].

2.3 Effect of chemical activation and exfoliation on the surface properties

Two different methods are employed for the preparation of activated carbons with a wide variety of physicochemical properties. The so-called physical activation usually involves a two-step process: carbonization at 500-700°C followed by activation via the partial gasification of carbon at 800-1000 °C in a stream of steam, air, carbon dioxide, etc. On the other hand, chemical activation involves mixing the precursor with an activating reagent such as KOH, NaOH, ZnCl₂ etc. and subsequent pyrolysis in the absence of air. Depending on the activating agent, the temperature usually ranges between 500 and 900 °C. The resulting carbon is washed extensively to remove the chemical reagent [7]. Among all the chemical activation agents, alkaline hydroxides such as potassium hydroxide (KOH) or sodium hydroxide (NaOH) are reported to be interesting from the performance point of view, allowing activated carbons to be prepared from many kinds of carbonaceous precursors.

2.4 Effect of chemical and thermal treatment to the electrochemical properties

Supercapacitors are very interesting materials that are widely studied today, due to their excellent properties in power density, long cycle life and good efficiency for charging/discharging. Carbonaceous materials are very attractive to use as an electrode material for supercapacitors [8]. Carbon-based materials are the most extensively used supercapacitor electrodes due to the attractive physical and chemical properties. Furthermore, the development of supercapacitor needs accurate control over the electrical conductivity, surface area and pore size of the electrode materials. Carbonaceous materials show high electrical conductivity and large specific surface area ensuring low solution resistance and facile diffusion of the electrolyte. The specific surface area and the pore size of the activated carbon can be controlled by the various method of activation [9]. Crucially for energy storage applications are the high surface area values obtained by controlling the porosity of carbon.

2.5 Electrochemical performance of the carbon nanosheets electrode

Carbon materials have been studied and used as electrodes for supercapacitors due to their very attractive chemical and physical performance and low price. The difference in the surface properties of carbon materials can highly affect their electronic properties. The carbon materials can be classified as conductor or semiconductor depending on their orientation of the structure. Moreover, the electronic and electrochemical properties of the carbon nanomaterial can be improved by modifying the surface [9-10]. Performance parameters, such as operating voltage, internal resistance, capacitance, power density, energy density, the time constant and life cycle should be calculated based on currently established and accepted procedures. To calculate these parameters, some fundamental electrochemical measurements should be performed on the supercapacitor cells or electrochemical systems. Electrochemical characteristics distinguish ideal and practical supercapacitors. Cyclic Voltammetry (CV), galvanostatic charging/discharging (GCD), Electrochemical Impedance Spectroscopy (EIS) and other measurements are employed as electrochemical measurement techniques in evaluating the performance of supercapacitors.

Knowledge gap:

The application of activated carbon nanosheets prepared from nettle and peanut shell for supercapacitor material is new. However, there is only a small amount of research which systematically studied the effect of different exfoliating acids on the behaviour of carbon materials, while the effect of the state of alkaline hydroxide activation on the carbon nanostructures formation of nettle and peanut shell has not been investigated so far. Most research studies carbon preparation using a single activating agent for chemical activation. Therefore, it is worth to study the chemical

treatment of carbon using various chemicals activating and exfoliating agent to enhance its. Since no research have synthesized carbon using two processes: activation (KOH and NaOH) and exfoliation (HNO_3 , H_2SO_4 and H_3PO_4), therefore, it is worth to investigate.

2 Materials and methods

3.1 Organic composition of materials

The organic composition of the nettle stem and peanut shell was showed in Table 1. As nettle leaf has low organic (cellulose, hemicellulose and lignin) and carbon content. I chose to use the nettle stem to produce carbon in this dissertation.

Table 1 Organic composition of natural materials

Materials	DM ^a (g/kg)			Cellulose (wt.%)	Hemicellulose (wt.%)	Lignin (wt.%)
	ADF ^b	NDF ^c	ADL ^d			
Nettle stem	617 ± 31	770 ± 39	119 ± 6	49.8	15.3	11.9
Nettle leaf	183 ± 9	308 ± 15	22 ± 5	16.1	12.5	2.2
Peanut shell	699 ± 35	783 ± 39	272 ± 14	42.4	8.4	27.2

^aDM, Dry Matter, ^bADF, Acid Detergent Fibre, ^cNDF, Neutral Detergent Fibre and ^dADL, Acid Detergent Lignin

3.2 Synthesis of the carbon nanosheets

The synthesis of carbon nanostructured materials from nettle stem or peanut shell was carried out, as explained below (Fig. 1):

3.2.1 Sample preparation: The nettle stem (NS) and peanut shell (PS) were separately washed and dried at 80 °C for 24 hours, followed by cleaning with HCl [0.5M] for another 24 hours. This facilitates the removal of organic compounds and residual metallic oxides [11]. It was finally washed with distilled water and dried at 80 °C for 24 hours.

3.2.2 Pre-Carbonization: The samples was pre-carbonized (char) in a stainless-steel tubular furnace at 450 °C for 2 hours under argon environment.

3.2.3 Activation: The pre-carbonized sample was milled with a mortar for 1 hour before being adding to aqueous [1 mol L^{-1}] KOH or NaOH with a weight ratio of 1:1 [KOH or NaOH: Char sample (nettle stem or peanut shell)]. The mixture was stirred for an hour and dried at 80 °C for 24 hours. This method is referred to solute activation. KOH and NaOH were used in solid-state as well. In this case, KOH or NaOH pellet/powder with a weight ratio of 1:1 [KOH or NaOH: Char sample (nettle stem or peanut shell)] was milled with pre-carbonized samples in a mortar for 1 hour. This method is referred to solid activation.

3.2.4 Carbonization: The activated sample thus obtained was carbonized under Ar atmosphere in a tubular furnace for about 2 hours. The temperature was maintained at 800 °C for the process. Then these samples were exfoliated by different acids.

3.2.5 Exfoliation: The exfoliation process was carried out by three different acids; hence, three different samples were obtained. 2 mol L^{-1} of HNO_3 , H_2SO_4 , or H_3PO_4 was used as exfoliators. The samples were stirred for 1 hour and washed with distilled water several times until a neutral pH was obtained. The samples were then dried at 80 °C for 24 hours before subjecting them to characterization tests. For peanut shell, I changed the type of exfoliating acid with other diprotic and triprotic acids (ascorbic acid and boric acid, respectively) to study the relationship between the type of acids and the specific surface of the samples. Lignin is another sample in which I have done KOH activation and exfoliation by three types of acids (nitric acid, sulfuric acid, or phosphoric acid) to compare their effects with nettle stem and peanut shell.

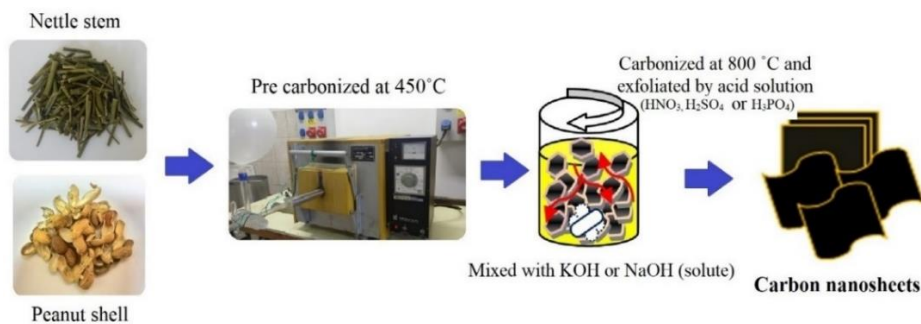


Figure 1 Schematic description of the carbon nanosheets preparation.

3.3 Physical and chemical characterization

The microstructure and the chemical composition of carbon nanosheets were characterized by using different characterization methods, these techniques including Scanning Electron Microscope (SEM), Transmission Electron Microscope (TEM), X-ray diffraction (XRD), Energy Dispersive Spectroscopy (EDS), CHNS analysis techniques, BET specific surface area (SSA), micropore volume and pore diameter.

3.4 Electrochemical characterization

For characterizing electrochemical properties, synthesized CNs sample, carbon black, and PTFE poly-tetrafluoroethylene were weighed in a mass ratio of 90:5:5 and mixed in the mortar. The mixture was pressed to form an electrode pellet (diameter = 10 mm). The electrode material was characterized by a three-electrode system of nettle stem carbon nanosheets (NSCNs) or peanut shell carbon nanosheets (PSCNs), Pt, and Ag/AgCl, where the latter two are used as the counter electrode and reference electrode respectively. 1 M sodium sulphate (Na₂SO₄) aqueous solution was used as an electrolyte. The electrochemical properties of the electrode material and cell were characterized by cyclic voltammetry (CV), galvanostatic charge-discharge (GCD), electrochemical impedance spectroscopy (EIS) and specific capacitance of a symmetric supercapacitor (C_s).

3 Results and discussions

4.1 The structure of carbon nanosheets synthesized from natural materials

4.1.1 Microstructure of raw material

4.1.1.1 Nettle stem: The microstructure of the dried nettle stem was examined by SEM. The cell wall in fibre is not a homogeneous layer. The cell walls of a plant can be considered as a composite consisting of cellulose fibrils embedded within a matrix of lignin and hemicellulosic polysaccharides [Smole, M. 2013]. It has a groove and hollow surface, composed of fibrous structure and has many hollow stinging hairs called trichomes on the surface (Fig. 2 a-b).

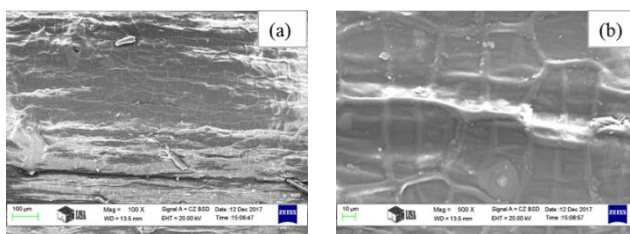


Figure 2 SEM micrographs of dried nettle stem at (a) 100X and (b) 500X.

4.1.1.2 Peanut shell: The SEM micrographs revealed the agglomerate of thin layered surface, interconnect hollow and micro-sized pores on the surface of the peanut shell (Fig. 3 a-b).

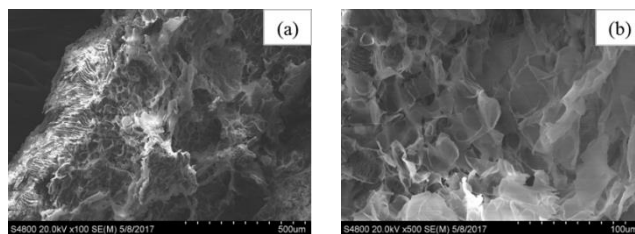


Figure 3 SEM micrographs of dried peanut shell at (a) 100X and (b) 500X.

4.1.2 Effect of KOH activation

The microstructure of nettle stem and peanut shell activated with KOH (solid) show lots of small angular and flake particles of carbon. Activation by KOH (solute) forms angulated sheets and nano-sheets in nettle stem. Peanut shell has thin-layered (nano-) structure with micro sized pores and fibrous structure.

4.1.3 Effect of NaOH activation

After activation by NaOH (solute), lots of angular and flake particles were found on the surface of the nettle stem. The SEM micrograph revealed the agglomerate of thin layered surface and interconnected hollow on the peanut shell's surface. The activated peanut shell shows multi-layered thin plates. It can be seen that both of the activated nettle stem and peanut shell have micropore structure and carbon fragmented structure dispersed in these samples.

Therefore, from the results of this experiment, I decided to use a hydroxide solution (carbonization time at 2 hours) to activate carbon before acid exfoliation to produce carbon nanosheets.

4.1.4 Effect of activation and exfoliation

4.1.4.2 Effect of activation and exfoliation to nettle stem

a) NSCNs activated by KOH and exfoliated by HNO₃, H₂SO₄ or H₃PO₄

The exfoliation process was carried out by using either nitric, sulfuric or phosphoric acid. Angular, thin sheets were found in NSCNs exfoliated by nitric acid showing thickness varying from 89 to 95 nm and having 70.70 wt.% carbon. The SEM micrograph of NSCNs exfoliated by sulfuric acid shows a smooth surface and clearly reveals the formation of separated carbon nanosheets with thickness from 42 to 71 nm. Chemical composition results show that carbon nanosheets mainly contain carbon (71.52 wt.%). Ultra-thin structures and overlapping carbon nanosheets were identified in the structure of NSCNs exfoliated by phosphoric acid. The thickness of the carbon nanosheet is ranging from 49 to 60 nm. Exfoliation with phosphoric acid yielded the highest carbon content (71.99 wt.%) among the exfoliated nettle specimens.

b) NSCNs activated by NaOH and exfoliated by HNO₃, H₂SO₄, or H₃PO₄.

The microstructure of NSCNs exfoliated by nitric acid shows the angular plates with thickness from 13 to 20 nm (76.5 wt.% carbon). The small particles and thin sheets with sharp edges having thickness from 55 to 60 nm (79.2 wt.% carbon) were found after exfoliating by sulfuric acid. Small thin sheets that are overlapped can be found in NSCNs exfoliated by phosphoric acid. The thickness of the carbon nanosheet is ranging from 9 to 15 nm (78.9 wt.% carbon). The carbon nanosheets' structure after activating with two alkaline hydroxide and exfoliating by three different acids is quite similar. By comparing the microstructures, it was found that carbon nanosheets are separated, and their surface is clean (*Claim 1, Fig. A*). The nanosheet structure was confirmed by TEM images (*Claim 1, Fig. C*).

4.1.4.3 Effect of activation and exfoliation to peanut shell

a) PSCNs activated by KOH and exfoliated by HNO₃, H₂SO₄, or H₃PO₄.

The SEM micrograph of PSCNs exfoliated by nitric acid shows small thin sheets and multilayer sheets with thickness varying from 31 to 92 nm and having 69.7 wt.% carbon. Thin nanosheets with thickness from 45 to 75 nm. were found in PSCNs exfoliated by sulfuric acid. Carbon nanosheets mainly contain carbon (72.2 wt.%). Micropore and thin layer carbon nanosheets were identified in the structure of PSCNs exfoliated by phosphoric acid. The thickness of the carbon nanosheet is ranging from 28 to 54 nm. Exfoliation with phosphoric acid yielded the highest carbon content (74.3 wt.%).

b) PSCNs activated by NaOH and exfoliated by H₂SO₄, H₃PO₄ or HNO₃

The agglomerated thin nanosheets and angular plates with thickness from 10 to 80 nm were found after exfoliating by nitric acid (77.2 wt.% carbon). The microstructure of PSCNs exfoliated by sulfuric acid shows small particles, hollows, and thin sheets with sharp edges with thickness from 10 to 50 nm (79.5 wt.% carbon). Small plates, angular and thin sheets can be found in PSCNs exfoliated by phosphoric acid. The thickness of carbon nanosheet is ranging from 10 to 60 nm (79.8 wt.% carbon) (*Claim 1, Fig. B*). The nanosheet structure was confirmed by TEM images (*Claim 1, Fig. C*).

4.1.5 Structure of carbon nanosheets

X-ray diffraction (XRD) was used to determine the structure of NSCNs and PSCNs. The results show a glassy carbon structure was developed in the exfoliated samples. The XRD patterns are quite similar. This suggests that the exfoliating acids do not have a significant effect on the crystal structure of carbon nanosheet. The alkaline hydroxide and acid solution does not dissolve the carbon material.

During the chemical activation with KOH, K intercalation can be considered as a relevant step which will have an important influence on the total reaction mechanism. The metal intercalation favours the process by separating the layers, that generates micropores or even new high energy sites for the redox reactions. The differences of efficiency found between KOH and NaOH for the activation of carbon of different crystallinity is explained by the fact that K intercalates better than Na [12].

Phosphoric acid affected the surface of carbon nanosheets more than sulfuric acid or nitric acid because it is a strong, polyprotic acid that is capable of donating more than one proton. Phosphoric acid is a triprotic acid having three dissociable protons that undergo stepwise dissociation. A triprotic acid reacts with the materials more intensely than diprotic sulfuric acid or monoprotic nitric acid. The reactions result higher micropore volume (more porous carbon surface), higher specific surface area and higher specific volume. The specific surface area of the samples after exfoliating by H₃PO₄ acid are higher than H₂SO₄ acid and HNO₃ acid because the bond length of H₃PO₄ is longer than those of H₂SO₄ and HNO₃. This leads to the breaking of van der Waals bonds more effectively and allowing more PO₄³⁻ anions move to be inserted into bilayer of carbon. Due to the much larger radius of ions, the interlayer distance of graphite is significantly larger and the surface area is higher [13]. Moreover, the microstructure of peanut shell contains higher amount of micropore than nettle stem. Consequently, the BET surface area of peanut shell is higher than that of nettle stem.

4.2 Effect of organic components on carbon properties

The nettle and peanut shell are mainly composed of cellulose, lignin and hemicellulose (nettle stem: 49.8, 11.9 and 15.3 wt.% /peanut shell: 42.4, 27.2 and 8.4 wt.%, respectively). The cell wall in the fibre is inhomogeneous, layered and mainly composed of cellulose, lignin and hemicellulose.

Table 2 Chemical composition of raw materials (CHNS analyser).

Dried materials	Elemental analysis by CHNS analyser (wt.%)				
	C	H	N	S	Others
Nettle stem	44.86	5.98	0.91	<0.01	48.25
Peanut shell	47.34	5.95	1.62	<0.01	45.09

The chemical composition analysis shows the presence of carbon lower than 50 wt.% for dried materials. Due to its higher cellulose and carbon content, nettle stem was used to prepare carbon nanostructure. Its higher carbon content can further be increased by activation and exfoliation processes (Table 2-3). *Find the results and more discussion in claim 2.*

Table 3 Chemical composition of carbon nanosheets prepared from nettle stem and peanut shell (CHNS analyser).

	Samples		Elemental analysis by CHNS analyser (wt.%)				
	Activation	Exfoliation	C	H	N	S	Others
Nettle stem	KOH	HNO ₃	70.70	1.09	0.89	<0.01	27.32
	NaOH	HNO ₃	76.48	0.88	1.15	<0.01	21.49
	KOH	H ₂ SO ₄	71.52	0.89	0.61	0.18	26.80
	NaOH	H ₂ SO ₄	79.21	0.64	0.61	0.13	19.41
	KOH	H ₃ PO ₄	71.99	0.70	0.72	<0.01	26.59
	NaOH	H ₃ PO ₄	78.90	0.91	1.00	0.03	19.16
Peanut shell	KOH	HNO ₃	69.74	0.67	0.91	<0.01	28.68
	NaOH	HNO ₃	77.16	0.78	1.13	<0.01	20.93
	KOH	H ₂ SO ₄	72.19	0.81	0.74	0.21	26.05
	NaOH	H ₂ SO ₄	79.45	0.81	0.75	0.08	18.91
	KOH	H ₃ PO ₄	74.31	0.49	0.76	<0.01	24.44
	NaOH	H ₃ PO ₄	79.75	0.94	0.99	<0.01	18.32

The difference in cellulose, lignin, and hemicellulose content affects carbon yields after activation and exfoliation processes. The activation and exfoliation of carbon have a greater impact on carbon yields than the organic composition. Plotting the specific surface area after heat treating against the weight percentage of lignin from different materials show a linear correlation (Fig. 4). The specific surface area of carbon after heat treating at high temperature (800 °C) is higher than at low temperature (450 °C). It was found that the highest weight percentage of lignin (from peanut shell) resulted the surface area increasing from 3 to 139 m² g⁻¹ compared to the thermal treatment at 450 °C. Material containing the mixture of cellulose, hemicellulose, and lignin can be a precursor to produce a three-dimensional porous structure (micropores, mesopores, and mesopores) when lignin has less than 50% [14].

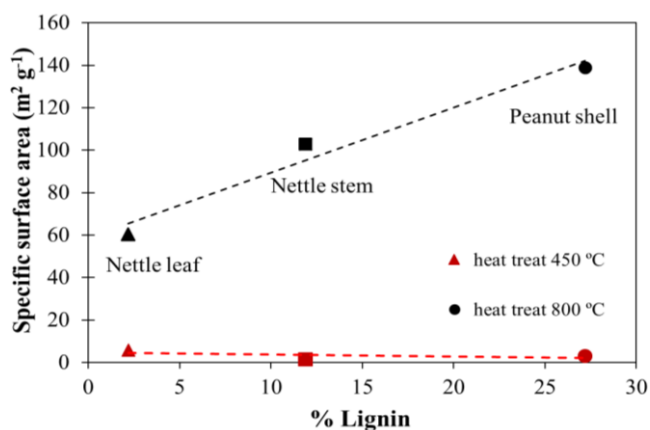


Figure 4 Relationship between specific surface area after heat treating (without chemical treatment) as a function of weight percent lignin from different materials.

At different raw materials, lignin to cellulose ratio has a linear relationship with the surface area of carbon after potassium hydroxide activating and phosphoric acid exfoliating (Fig. 5). The experimental results indicated that the appropriate ratio of lignin and cellulose (lignin/(cellulose+lignin) ratios: NL, NS and PS is 0.1, 0.2 and 0.4, respectively) induced the activated carbon to develop a microporous and mesoporous structure. After thermal and chemical treatment processes, the specific surface area of carbon is higher than 500 m² g⁻¹.

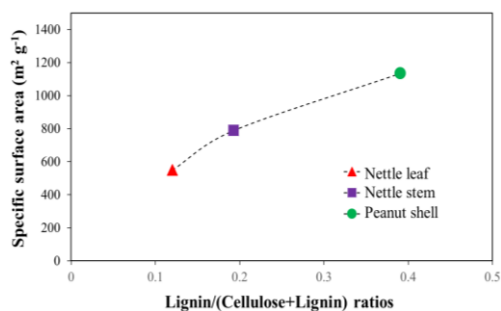


Figure 5 Specific surface area as function of lignin/cellulose ratios of KOH activated/ H_3PO_4 exfoliated samples.

4.3 Effect of chemical activation and exfoliation to the surface properties

During activation, KOH or NaOH can penetrate the pores of the carbonized material. Interlayered KOH or NaOH residue can react with the exfoliation acids (HNO_3 , H_2SO_4 , and H_3PO_4); thus, some chemical compounds, such as KNO_3 , K_2SO_4 , K_3PO_4 , $NaNO_3$, Na_2SO_4 , and Na_3PO_4 are possible to form. Based on their thermochemical properties, the formation of K_3PO_4 is the most likely as it has the most negative $\Delta_f G$. The molar volume of KNO_3 , K_2SO_4 , and K_3PO_4 is 47.94, 65.51, and $82.79 \text{ cm}^3 \text{ mol}^{-1}$. The molar volume of $NaNO_3$, Na_2SO_4 , and Na_3PO_4 is 37.61, 53.40, and $101.20 \text{ cm}^3 \text{ mol}^{-1}$, respectively (*Relationship between molar volume of compounds and BET of activated nettle stem and peanut shell see in claim 3.1.*). These compounds cause tension in the pores of the activated carbon. K_3PO_4 has a 26.4-72.7% higher molar volume than K_2SO_4 or KNO_3 , resulting in the carbon nanosheets with the highest specific surface area. But in the case of NaOH, it is different. The specific surface area of carbon nanosheet after NaOH activating and exfoliating is lower.

The isotherms from nitrogen adsorption presented porous structure (micropore/ IUPAC, Type I isotherm, Fig. 6-7) in the carbon materials, which can be changed by chemical activation and exfoliation. Without chemical activation or exfoliation, the dried samples (nettle stem and peanut shell) show the nonporous structure with a low specific surface area. The quantitative property of carbon nanosheets was confirmed by BET.

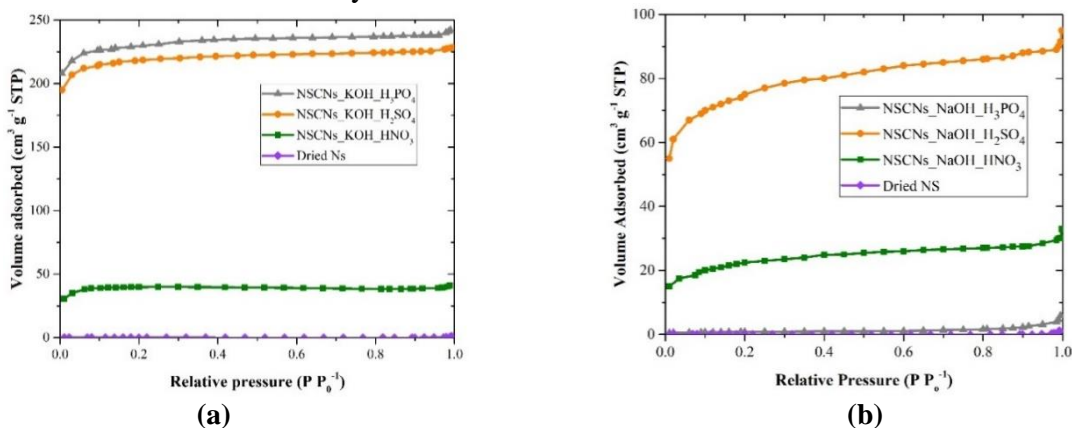


Figure 6 Nitrogen adsorption isotherms of nettle stem (a) KOH activation and (b) NaOH activation.

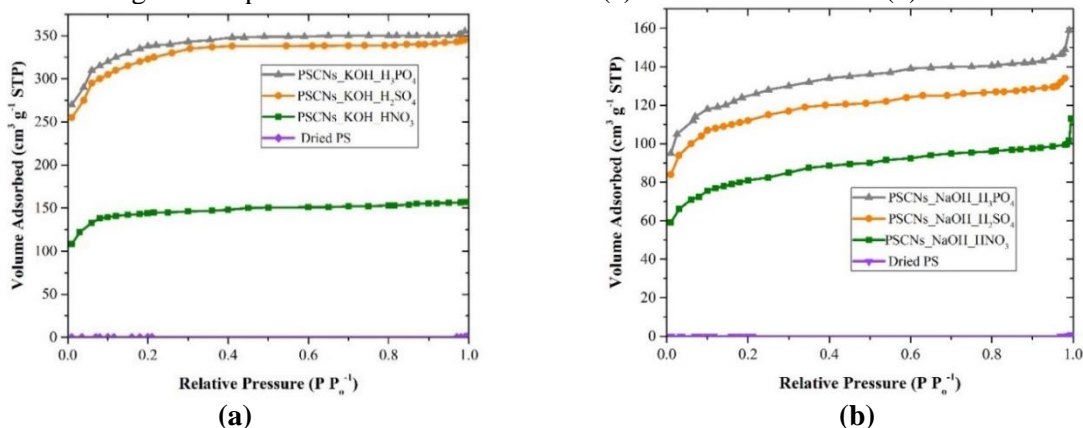


Figure 7 Nitrogen adsorption isotherms of peanut shell KOH activation and (b) NaOH activation.

The investigations assure the formation of carbon nanosheets with a higher specific surface area (which can describe the separation ability of carbon layer from this process) and small pore diameter and higher micropore volume. The specific surface area of CNs related with micropore volume (*Claim 3.2*), the highest specific surface area and micropore volume of NSCNs and PSCNs were found after activating with KOH and exfoliating by phosphoric acid.

When lignin was prepared under the same conditions as the nettle stem and peanut shell, it was found that the specific surface area of carbon obtained after exfoliation with phosphoric acid was the highest at $668 \text{ m}^2 \text{ g}^{-1}$, followed by sulfuric acid at $497 \text{ m}^2 \text{ g}^{-1}$ and nitric acid at $367 \text{ m}^2 \text{ g}^{-1}$, respectively (*Claim 3.2*). The result is the same as for the nettle and peanut shell. After that, I changed the type of exfoliating acid to other diprotic and triprotic acids (ascorbic acid and boric acid, respectively). The results in Fig. 8 show that the specific surface area of carbon (peanut shell) after exfoliating by boric acid is $825 \text{ m}^2 \text{ g}^{-1}$ and 14% higher than as for ascorbic acid. It means that triprotic acid (boric acid) resulted in a higher carbon specific surface area than that of diprotic acid (ascorbic acid).

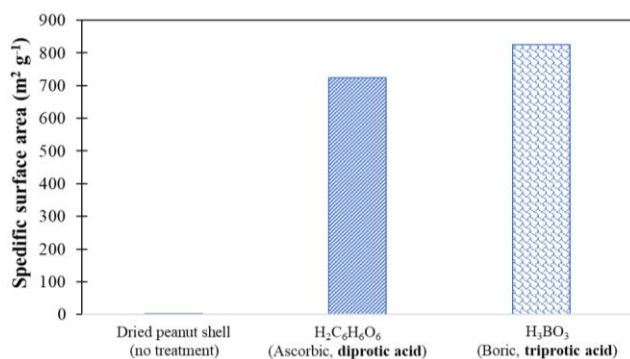


Figure 8 Specific surface area of peanut shell derived carbonas function of different acid exfoliators (using KOH activation).

4.4 Effect of chemical activation and exfoliation to the electrochemical properties

The electrochemical properties, including specific capacitance, energy density, and power density value of the electrodes are presented in Table 4. The specific capacitance of NSCNs and PSCNs is higher than char samples. PSCNs samples have higher specific capacitance than NSCNs due to their higher specific surface area and micropore volume. IUPAC classification of carbon nanosheet from nettle stem and peanut shell (Fig. 6-7) shows mostly micropore structure. Micropores contain bottlenecks that can drastically decrease ion mobility, thus reducing the electrode's power capability [15]. Surface area and porosity are important factors for higher capacitance. As for materials having low porosity, electrolyte and electrode are in minimal contact due to which less charge is stored on the electrode surface; hence low capacitance was observed [16].

The correlation in specific surface area and specific capacitance for some of the samples is too low. The reason could be the stacking of carbon black on the CNs surface (electrode material), which decreases the specific surface area and capacitance characteristics [17], or the agglomeration or re-stacking of CNs resulting reduced specific capacitance or specific surface area [15].

It can be seen that the specific surface area and specific capacitance of NSCNs activated by KOH, exfoliated by HNO_3 , H_2SO_4 , or H_3PO_4 increases with micropore volume. However, the existence of a too narrow pore size distribution makes the electrolyte's entry into the pores difficult. The non-accessible pores do not contribute to the total double-layer capacitance of the material [18]. High specific capacitance with the high specific surface area was found in samples activated by NaOH and exfoliated by H_2SO_4 , both for nettle stem and peanut shell. The highest specific capacitance (122.26 F g^{-1}) was found in PSCNs activated by NaOH and exfoliated by H_2SO_4 .

Table 4 Electrochemical properties obtained by cyclic voltammetry at scan rate 5 mV s⁻¹.

Samples		Specific surface area (m ² g ⁻¹)	Specific capacitance (F g ⁻¹)	Surface-capacitance (F m ⁻²)	Energy density (Wh kg ⁻¹)	Surface-energy density (Wh m ⁻²)	Power density (kW kg ⁻¹)	Surface-power density (kW m ⁻²)	
Activation	Exfoliation								
Nettle stem	Char NS*	1.6	0.15	0.094	0.01	6.3E-06	30.6	0.01913	
	KOH	HNO ₃	106	1.71	0.016	0.06	5.7E-07	26.7	0.00025
		H ₂ SO ₄	705	9.34	0.013	0.32	4.5E-07	20.9	0.00003
		H ₃ PO ₄	789	27.3	0.035	0.95	1.2E-06	24.8	0.00003
	NaOH	HNO ₃	72	0.61	0.008	0.02	2.8E-07	26.4	0.00037
		H ₂ SO ₄	220	7.86	0.036	0.27	1.2E-06	24.7	0.00011
H ₃ PO ₄		3	0.21	0.070	0.01	3.3E-06	37.9	0.01263	
Peanut shell	Char PS*	3	0.14	0.047	0.01	3.3E-06	80.6	0.02687	
	KOH	HNO ₃	468	115.57	0.247	4.01	8.6E-06	84.2	0.00018
		H ₂ SO ₄	1,104	44.27	0.040	1.54	1.4E-06	18.3	0.00002
		H ₃ PO ₄	1,135	1.73	0.002	0.06	5.3E-08	31.9	0.00003
	NaOH	HNO ₃	266	23.62	0.089	0.95	3.6E-06	24.4	0.00009
		H ₂ SO ₄	395	122.26	0.310	4.25	1.1E-05	27.1	0.00007
H ₃ PO ₄		420	15.57	0.037	0.81	1.9E-06	24.9	0.00006	

* Samples were heat treated at 450 °C (without activation and exfoliation)

The correlation between the composition (lignin/(cellulose+lignin) ratio) of the raw material and the surface capacitance of the carbon nanosheets prepared from the raw materials (*see in Claim 5, Fig. G*).

4.5 Electrochemical performance of the carbon nanosheets electrode

Cyclic voltammetry (CV) measurements at 5, 20, and 100 mV s⁻¹ in the potential range -0.2 to 0.8 V were used to calculate carbons' specific capacitance. CV curves show a quasi-rectangular shape at increased scan rates, indicating that the CNs can be used in energy storage applications [19]. The CV shape for exfoliated CNs is more rectangular, revealing a better charge propagation than char samples. The quasi-rectangle shapes are maintained even at a high scan rate of 100 mV s⁻¹, which is suitable for a typical, stable double-layer capacitor quick and efficient in charge transfer. They also have excellent capacitive behaviour [20].

The galvanostatic charge/discharge (GCD) curves of the samples at a current density of 0.05 A g⁻¹ in the voltage range of -0.2 to 0.8 V show typical triangular shapes. The GCD curves are imperfectly symmetrical; they are slightly distorted due to the pseudocapacitive behaviour [21], which is consistent with the CV graphs. The GCD curves show that PSCNs activated by NaOH and exfoliated by H₃PO₄ have the longest charge and discharge cycles (1,033 s), which implies the samples' best electrochemical performance. The longest charge and discharge cycles of NSCNs activated by KOH were found for H₃PO₄ exfoliator (27.3 s). For nettle stem activated by KOH, the increase of dissociable protons (polyprotic acid) affects the longer charge and discharge cycle time, resulting in the same effect as the specific surface area. The type of acid exfoliator affects the charge and discharge cycles. Cycle time for triprotic (H₃PO₄), diprotic (H₂SO₄), and monoprotic (HNO₃) exfoliators were 260, 112, and 17 s, respectively (*see in Claim 6.1-6.2*).

The electrochemical impedance spectroscopy (EIS) of NSCNs samples is presented with the Nyquist plots of each NSCNs electrode material in the frequency range between 0.1 Hz to 100 kHz. The straight-line slope is close to 45° in the middle-high frequency and is assumed to diffuse the electrolyte ions in the electrode pores. The steep linear curve in the low-frequency region of NSCNs is sharp, representing the diffusion-limited charge transfer characteristic close to ideal capacitance performance [22-25]. The equivalent series resistance (ESR) of NSCNs can be determined from the offsets on the x-axis in the high-frequency region. The ESRs of NSCNs exfoliated by H_3PO_4 , H_2SO_4 , HNO_3 , and char NS were approximately 14.6, 17.8, and 21.3 Ω , respectively, lower than that of char NS (107.0 Ω). The results confirmed NSCNs exfoliated by H_3PO_4 the best electrochemical performance. This observation agrees with the linear correlation between the peak current and square root of the scan rate (*see in Claim 6.3-6.4*).

The diffusion coefficient in the case of the nettle stem carbon nanosheets (NSCNs), based on the relationship between peak current and the square root of the scan rate of cyclic voltammetry measurement, was identified (*see in Claim 6.5*).

The specific capacitance depends on the materials and condition of the electrolyte. The abundant availability of nettle stem and peanut shell are the advantages of these samples, so it certainly can be produced at a relatively low cost. This study has successfully demonstrated that nettle stem or peanut shell based carbon can be presented as raw material for a flexible carbon electrode in supercapacitor as an energy storage device. Specific capacitance, which is the intrinsic capacitance of electrode material, is a widely used property to characterize a material. A higher specific capacitance does not necessarily mean that the material will be a high performing supercapacitor electrode. Other factors substantially impact capacitance, such as electrical conductivity (both that of materials and electrode particles), which governs electron and ion transfer into the layer [18]. From the data compiled in Fig. 9, it can be seen that carbon from nettle stem and peanut shell in this work can be applied for an energy storage device. The carbons' energy density and power density in this work are in the range of supercapacitor materials at 0.01-4.25 $Wh\ kg^{-1}$ and 18.3-84.2 $W\ kg^{-1}$, respectively.

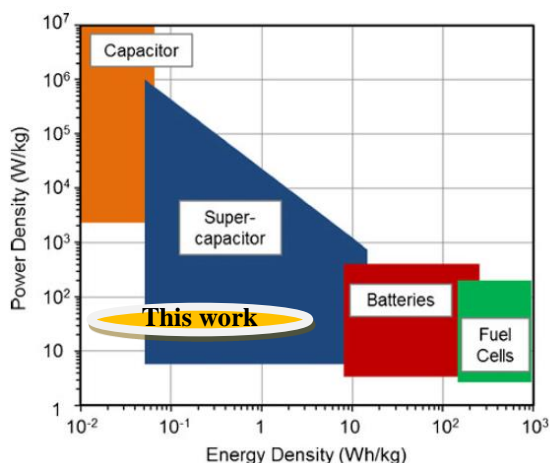


Figure 9 Energy density as a function of power density (Ragone plot) for different energy storage and conversion devices [26].

5 Conclusions

The goal of this research is to systematically study and investigate the effect of different alkaline hydroxides activators and acid exfoliators on the properties of carbon nanosheets, prepared from natural materials. In this work, the carbon nanosheets were studied for capacitor application by using as electrode material for an energy storage device.

- The carbon nanosheets synthesized from nettle stem or peanut shell using KOH or NaOH activation and exfoliation by H₂SO₄ or H₃PO₄ have high specific surface areas, especially peanut shell (activated by KOH and exfoliated by H₃PO₄) having 1,135 m² g⁻¹.

- The chemical activation and exfoliation affect the surface property of carbon nanosheets which can be described in terms of quantity of porous carbon. The micropore volume of carbon nanosheets activated by KOH is higher than that of activated by NaOH.

- Pore diameters in the exfoliated NSCNs and exfoliated PSCNs were found to be less than 2.5 nm which belongs to the micropore range (IUPAC, Type I isotherm).

- The process developed is simple and yields a high percentage (up to 70 %) of carbon particles in a nanostructured form.

- The CNs with an electrolyte 1M Na₂SO₄ is a material work as active part of the electrode for an energy storage device. Using this material as an electrode, the measured specific capacitances of NSCNs and PSCNs are higher than char samples (nettle stems and peanut shells without activation and exfoliation). Specific capacitance reached 27.3 F g⁻¹ at scan rate of 5 mV s⁻¹ for NSCNs activated by KOH and exfoliated by H₃PO₄. PSCNs activated by NaOH and exfoliated by H₂SO₄. had specific capacitance 122.26 F g⁻¹ at scan rate of 5 mV s⁻¹.

- Energy density (0.01-4.25 Wh kg⁻¹) and power density (18.3-84.2 W kg⁻¹) of carbons in this work is in the range of supercapacitor materials.

6 Claims/New scientific results

Carbon nanosheets were successfully synthesized from nettle stem or peanut shell with a 5-step method, which consists of the following process: sample preparation (cleaning), pre-carbonization, activation (KOH or NaOH aqueous solution), carbonization, and exfoliation (HNO₃, H₂SO₄, or H₃PO₄). The chemical and thermal activation affects the carbon formation, and the separation of carbon layers. The carbon nanosheets were studied for capacitor application by using as electrode material for supercapacitors.

Claim 1. The structure of carbon nanosheets synthesized from natural materials.

Carbon nanosheets were successfully synthesized from nettle stem (NSCNs) and peanut shell (PSCNs) (SEM, Fig. A-B and TEM Fig. C). I established that the layered nanosheet structure is highly porous and becomes thinner toward the edges of the material. In the TEM images, the bright and transparent regions are the ultrathin nanosheet. The less transparent areas reveal the overlapped or folding parts of carbon nanosheets, which further imply the ultrathin structure. These figures are representative for the samples. After the exfoliation process, the carbon nanosheets with the thickness lower than 100 nm were found and the successful exfoliation is confirmed by the increasing the specific surface area.

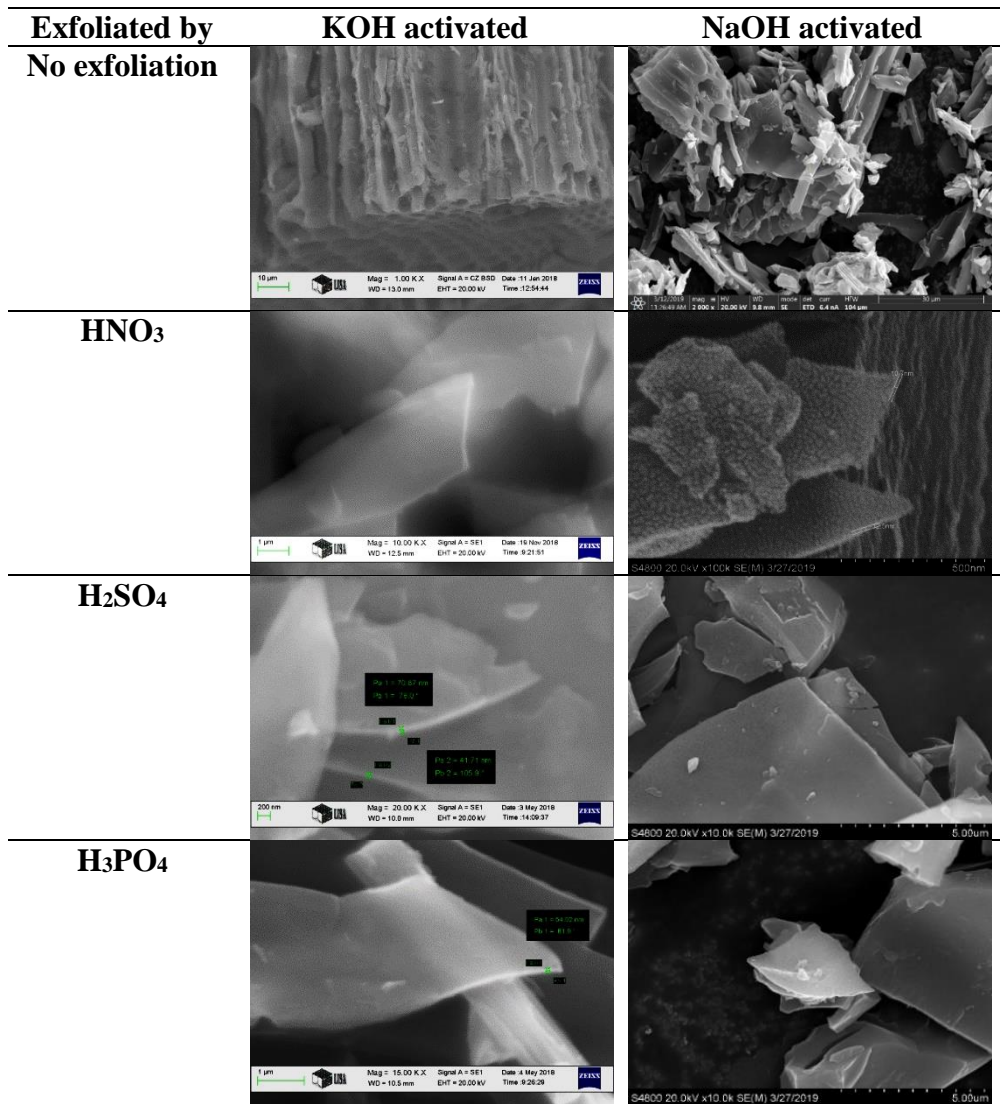


Figure A. SEM micrographs of activated and exfoliated nettle stem carbon nanosheets obtained by different agents.

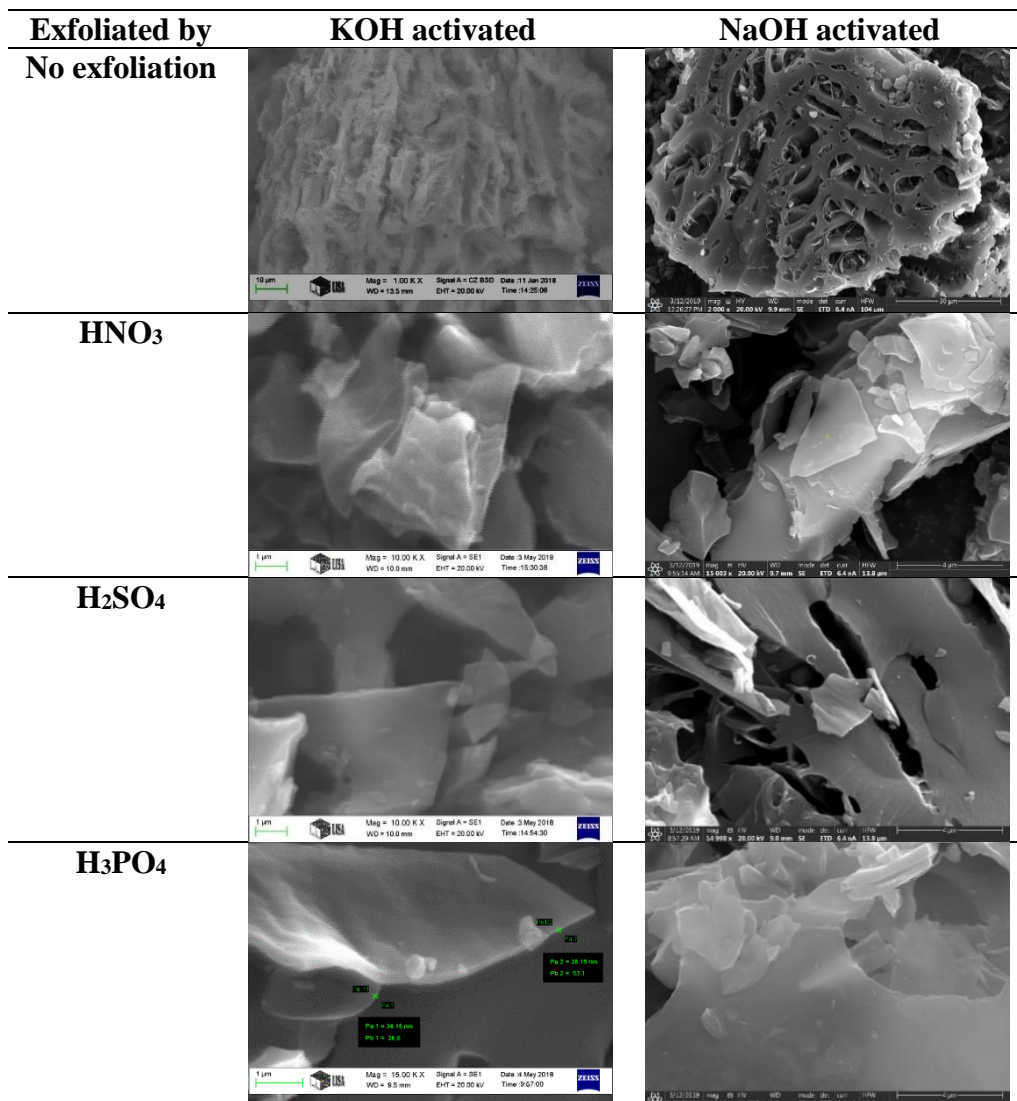


Figure B. SEM micrographs of activated and exfoliated peanut shell carbon nanosheets obtained by different agents.

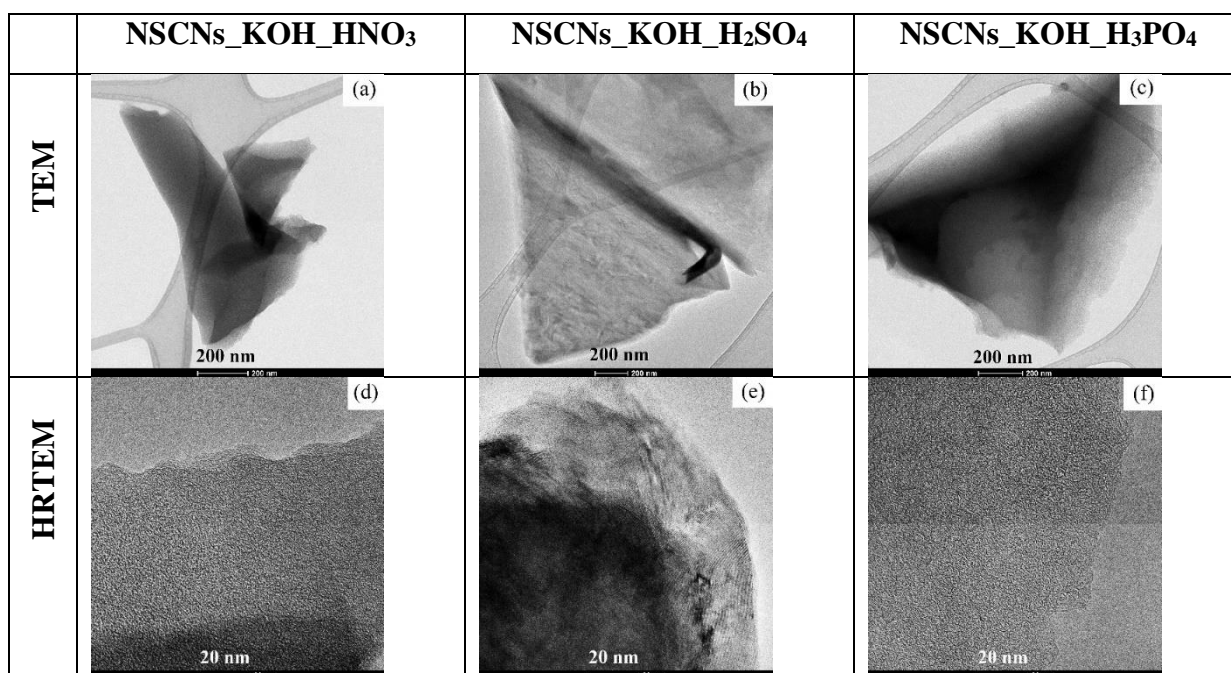


Figure C. TEM (a-c) and HRTEM (d-f) micrographs of the nettle stem carbon nanosheets activated by KOH and exfoliated by (a, d) HNO₃, (b, e) H₂SO₄, or (c, f) H₃PO₄.

Claim 2. Effect of organic components on carbon properties.

I established that the natural structure of the material affected the increase of carbon content and the specific surface area of carbon materials after thermal and chemical treatment processes.

2.1 Carbon content: I established that microstructure and carbon content depends on the natural structure of materials. Dried nettle stem and peanut shell have 11.9 and 27.2 wt.% lignin, and 44.86 and 47.34 wt.% carbon content, respectively (as a high wt.% of lignin has a high carbon content). After exfoliation, the carbon was found in the range of 70-80 wt.% (CHNS analyser). In the case of KOH activation, nettle stem carbon nanosheets and peanut shell carbon nanosheets have up to 57-60 % and 47-57 % higher carbon yield than dried samples. For NaOH activation, nettle stem carbon nanosheets and peanut shell carbon nanosheets have up to 70-77 % and 63-68 % higher carbon yield than dried samples.

Dried nettle stem has higher cellulose and hemicellulose content than peanut shell (by 17.5 % and 82.1 %, respectively) and has higher carbon content after exfoliation. The carbon content of nettle stem carbon nanosheets and peanut shell carbon nanosheets is up to > 70 wt.% and reaches the range of 80 wt.% for NaOH activation. The difference in cellulose, lignin, and hemicellulose content affects carbon yields after activation and exfoliation processes. The activation and exfoliation of carbon have a greater impact on carbon yields than the organic composition.

2.2 Specific surface area: I established that at different raw materials, lignin to cellulose ratio has a linear relationship with the surface area of carbon after potassium hydroxide activation and phosphoric acid exfoliation. The BET surface area gradually increased with the cellulose content. The experimental results indicated that the appropriate ratio of lignin and cellulose (lignin/(cellulose+lignin) ratios: nettle leaf, nettle stem and peanut shell is 0.1, 0.2 and 0.4, respectively) induced the activated carbon to develop a microporous and mesoporous structure. After thermal and chemical treatment processes, the specific surface area of carbon is higher than 500 m² g⁻¹.

Claim 3. Effect of chemical activation and exfoliation to the surface properties.

I established that the chemical activation and exfoliation affect the surface property of carbon nanosheets, which can be described in terms of the quantity of porous carbon. Due to the fact that potassium ions (K⁺) are 40% larger than sodium ions (Na⁺), the specific surface area and micropore volume of carbon nanosheets activated by KOH are higher than those of activated by NaOH.

3.1 During activation, KOH or NaOH can penetrate the pores of the carbonized material. Interlayered KOH or NaOH residue can react with the exfoliation acids (HNO₃, H₂SO₄, and H₃PO₄). Thus some chemical compounds, such as KNO₃, K₂SO₄, K₃PO₄, NaNO₃, Na₂SO₄, and Na₃PO₄ may form. The relationship between the molar volume of these compounds and BET results of the samples is shown in Fig. D (this valid for the investigated system, till the molar volume is 83 cm³ mol⁻¹). These compounds cause tension in the pores of the activated carbon. As K₃PO₄ has 26.4 and 72.7% higher molar volume than K₂SO₄ and KNO₃, respectively, it resulted in the highest specific surface area, and micropore volume in KOH activated carbon nanosheets both for nettle stem and peanut shell.

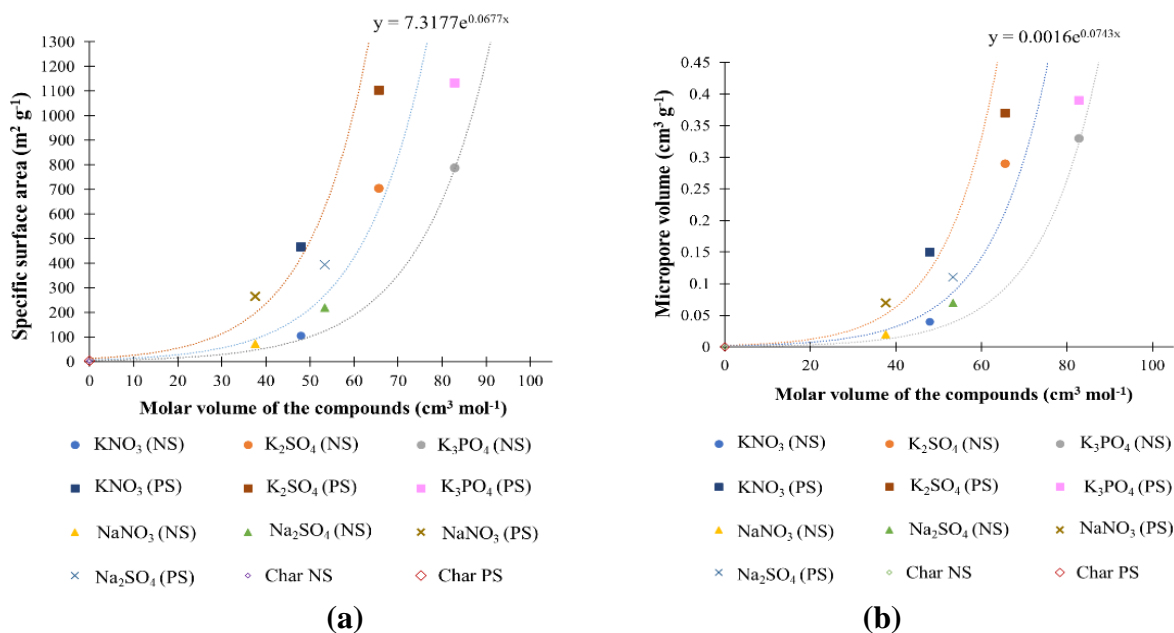


Figure D Relationship between molar volume of the compounds (formation) and (a) specific surface area, (b) micropore volume of nettle stem derived carbon and peanut shell derived carbon.

3.2 I observed that the triprotic acid (H_3PO_4) reacts more intensely with the materials than diprotic (H_2SO_4) or monoprotic (HNO_3). The reactions result in higher micropore volume with 0.33 and $0.39\text{ m}^3\text{ g}^{-1}$ for nettle stem and peanut shell, respectively (more porous carbon surface) and a higher specific surface with 789, 1,135 and $668\text{ m}^2\text{ g}^{-1}$ for nettle stem, peanut shell, and lignin, respectively (Fig. E-F).

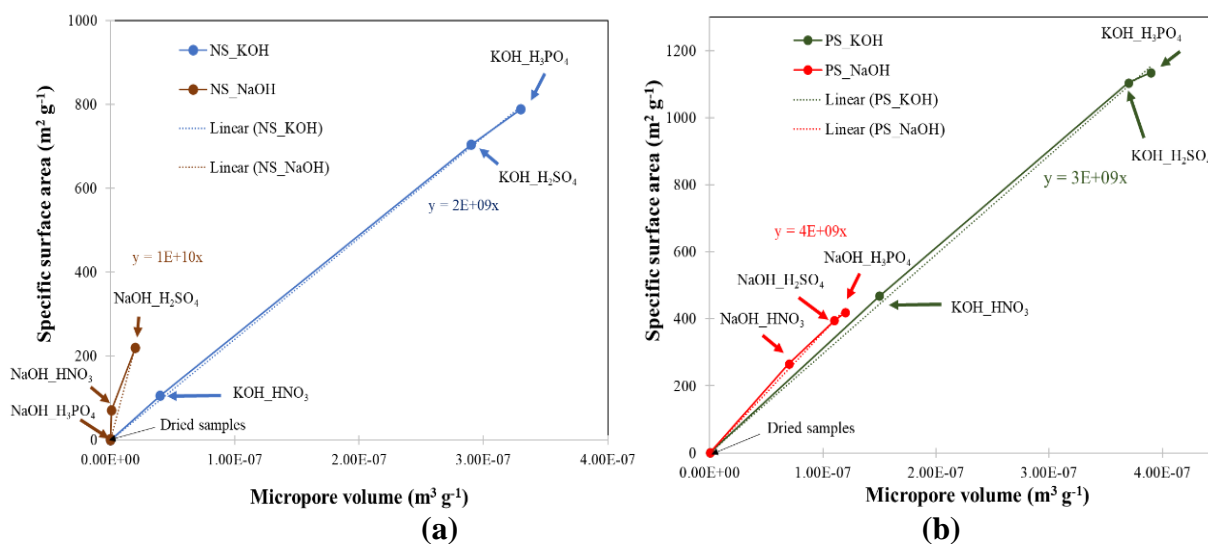


Figure E Specific surface area of samples as function of micropore volume of (a) nettle stem and (b) peanut shell.

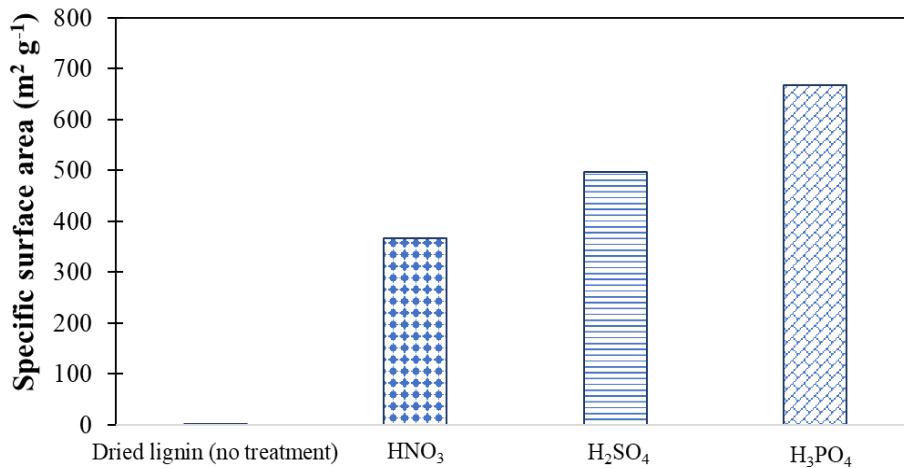


Figure F Specific surface area of lignin derived carbons as function of different acid exfoliators (using KOH activation).

Claim 4. Effect of chemical activation and exfoliation to the electrochemical properties.

I established that the energy density (0.01-4.25 Wh kg⁻¹) and power density (18.3-84.2 W kg⁻¹) of carbons in this work is in the range of supercapacitor materials.

The specific capacitance of activated and exfoliated nettle stem carbon nanosheets (KOH activation and H₃PO₄ exfoliation) and peanut shell carbon nanosheets (NaOH activation and H₂SO₄ exfoliation) is 27.3 F g⁻¹ and 122 F g⁻¹, respectively, and which are higher than the specific capacitance of pre-carbonized nettle stem (0.15 F g⁻¹) and peanut shell (0.14 F g⁻¹) samples. It means peanut shell carbon nanosheets samples have higher specific capacitance (122 F g⁻¹) than nettle stem carbon nanosheets due to their higher specific surface area (1,135 m² g⁻¹) and micropore volume (0.39 cm³ g⁻¹).

Claim 5. Relationship between organic components and electrochemical properties

Based on the literature and my experimental results, I found a correlation between the composition (lignin/(cellulose+lignin) ratio) of the raw material and the surface capacitance of the carbon nanosheets prepared from the raw materials (Fig. G). The correlation can be described with the following equation:

$$C_A = 0.33\phi \quad (6.1)$$

, where C_A is the surface capacitance (F m⁻²), ϕ is the lignin/(cellulose+lignin) ratio.

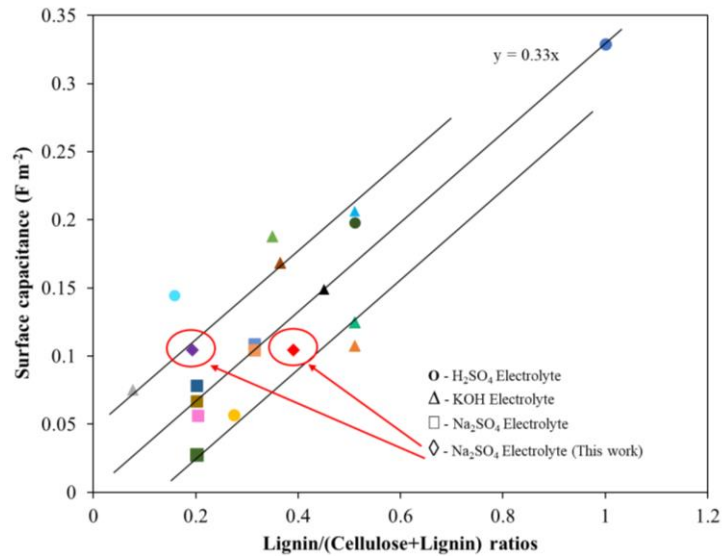


Figure G Surface-capacitance as function of lignin/(cellulose+lignin) ratios of carbon from difference natural samples (with difference electrolytes).

●	Lignin [27]	▲	Coconut shell [28, 30]	■	Bamboo Shoot (1) [38-39]
●	Coconut kernel [28-29]	▲	Cherry stone (2) [31]	■	Bamboo Shoot (2) [38-39]
●	Pistachio shell [28, 30]	▲	Cherry stone (3) [31]	■	Durian husk [40-41]
●	Cherry stone (1) [31-32]	▲	Cherry stone (4) [31]	◆	Nettle stem (This work)
▲	Coffee shell [28, 33]	■	Banana fiber (1) [36-37]	◆	Peanut shell (Thiswork)
▲	Corn grains [28, 34]	■	Banana fiber (2) [36-37]		
▲	Rice husk [28, 35]	■	Banana fiber (3) [36-37]		

Claim 6. Electrochemical performance of the carbon nanosheets electrode.

Carbon materials have been studied and used as electrodes for supercapacitors due to their very attractive chemical and physical performance and low price. The difference in the surface properties of carbon materials affect their electronic properties. Moreover, the electronic and electrochemical properties of the carbon nanomaterial can be improved by modifying the surface.

6.1 I established that for nettle stem activated by KOH, the increase of dissociable protons (polyprotic acid) results in longer charge and discharge cycle time, resulting in the same effect as the specific surface area. The type of acid exfoliator affects the charge and discharge cycles. Cycle time for triprotic (H_3PO_4), diprotic (H_2SO_4), and monoprotic (HNO_3) exfoliators were 260, 112, and 17 s, respectively (Fig. H).

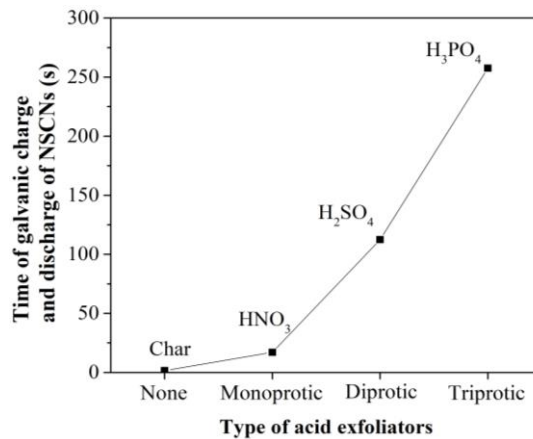


Figure H The time of galvanic charge and discharge of nettle stem derived carbons as a function of different types of acid exfoliators (at a current density of 0.05 A g^{-1}).

6.2 The galvanostatic charge and discharge curves (Fig. I) show that nettle stem carbon nanosheets activated by KOH and exfoliated by H₃PO₄ have the longest charge and discharge cycles (260 s), which implies the samples' best electrochemical performance. The longest charge and discharge cycles were found from peanut shell carbon nanosheets activated by NaOH and exfoliated H₂SO₄ exfoliator (1,033 s).

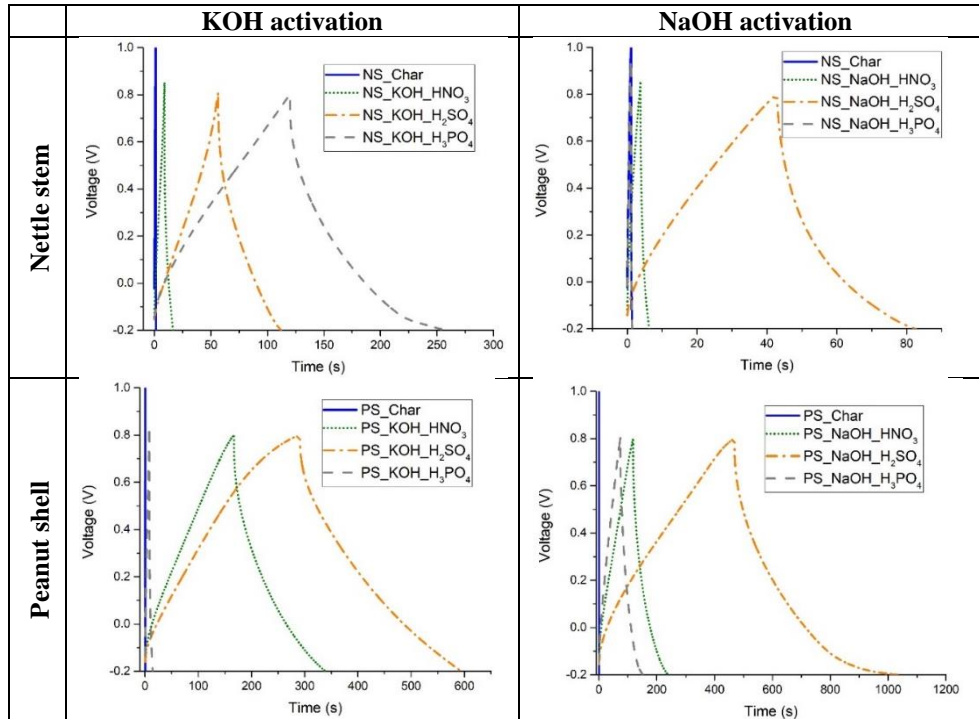


Figure I Galvanostatic charge and discharge of samples at a current density of 0.05 A g⁻¹.

6.3 I identified the electrochemical impedance spectroscopy (EIS, Fig. J) of the carbon nanosheets samples presented with the steep linear curve in the low-frequency region of carbon nanosheets is sharp, representing diffusion-limited charge transfer characteristic close to ideal capacitance performance.

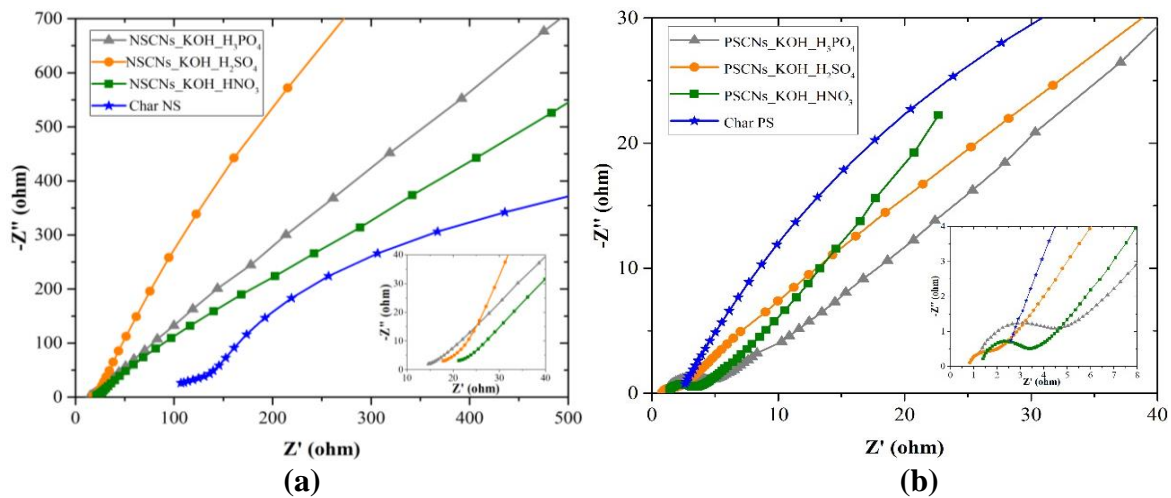


Figure J Nyquist plots of (a) nettle stem and (b) peanut shell derived carbons at an alternating current amplitude of 5 mV.

6.4 I identified the correlation between the peak current and square root of the scan rate of cyclic voltammetry measurement of nettle stem carbon nanosheets. This observation agrees with the linear correlation between the peak current and square root of the scan rate in Fig. K.

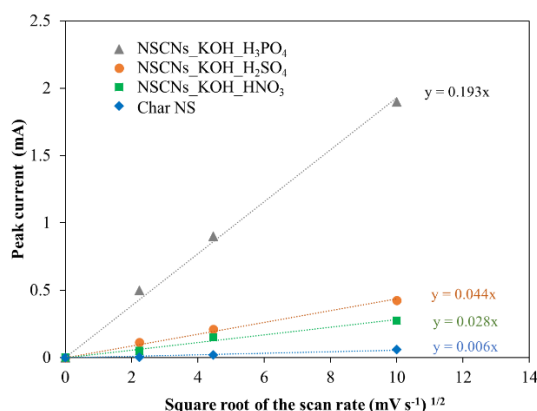


Figure K Relationship between peak current and the square root of the scan rate of cyclic voltammetry measurement of nettle stem derived carbons (potential range -0.2 to 0.8 V).

6.5 I identified the diffusion coefficient in the case of nettle stem carbon nanosheets, based on the relationship between peak current and the square root of the scan rate of cyclic voltammetry measurement. The diffusion coefficients were calculated based on the Randles-Sevcik equation (6.2):

$$I_p = (2.69 \times 10^5) n^{3/2} A D^{1/2} C v^{1/2} \quad (6.2)$$

Where I_p is peak current (A), n is number of electrons involved in the reaction, A is electrode area (cm^2), D is diffusion coefficient ($\text{cm}^2 \text{s}^{-1}$), C is the concentration of the electroactive species (mol cm^{-3}) and v is scan rate (V s^{-1}), respectively. The diffusion coefficient depends on the slope of $I_p \propto v^{1/2}$ (Fig. K). The higher diffusion coefficient indicates a better electrode reaction activity due to the faster ionic transportation. The diffusion coefficients obtained by the Randles-Sevcik equation are listed in table A.

Table A The diffusion coefficients of samples (at scan rate 100 mV s^{-1}).

Samples/Electrode	I_p (10^{-5} A)	n	A (cm^2)	C (mol cm^{-3})	$I_p/v^{1/2}$ (As V^{-1})	D ($10^{-8} \text{ cm}^2 \text{s}^{-1}$)
Char NS	6.1	1	0.79	0.001	0.006	1.37
NSCNs_KOH_HNO ₃	27.5	1	0.79	0.001	0.028	6.17
NSCNs_KOH_H ₂ SO ₄	42.5	1	0.79	0.001	0.044	9.53
NSCNs_KOH_H ₃ PO ₄	190	1	0.79	0.001	0.193	42.6

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9 Publications related to this thesis work

Journal papers

- J1. Nuilek, K., Wongwiriyan, W., Sattayarut, V., Simon, A., Koncz-Horvath, D., Ferenczi, T., Kristaly, F. & Baumli, P. (2020). Comparison of acid exfoliators in carbon nanosheets synthesis from stinging Nettle (*Urtica dioica*) for electrochemical applications. *Scientific Reports*, 10(1), 1-12 (D1).
- J2. Nuilek, K., Simon, A., Kurovics, E., Ibrahim, J. F. M., Varanasi, D., & Baumli, P. (2020). Effect of activation and exfoliation on the formation of carbon nanosheets derived from natural materials. In *Journal of Physics: Conference Series* (Vol. 1527, No. 1, p. 012036). IOP Publishing (Q3).
- J3. Nuilek, K., Simon, A., & Baumli, P. (2019, October). Synthesis and Characterization of Carbon Nanosheets from Stinging Nettle (*Urtica Dioica*). In *IOP Conference Series: Materials Science and Engineering* (Vol. 613, No. 1, p. 012017). IOP Publishing.
- J4. Nuilek, K., Simon, A., & Baumli, P. (2018). Carbonization of stinging nettle (*Urtica dioica*) by thermal and chemical processing. *International Journal of Advances in Science, Engineering and Technology (IJASEAT)*, 6 (2) (Spl. Iss-2 Jun, 2018), 6-10.
- J5. Nuilek, K., Simon, A., & Baumli, P. (2018). Influence of KOH on the carbon nanostructure of peanut shell. *Resolution and Discovery*, 3(2), 29-32.