Synthesis and Characterization of Carbon Nanosheets from Stinging Nettle (Urtica Dioica)

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Abstract. Extensive research in nanotechnology has allowed us to improve and revolutionize technology and industry. Carbon nanostructures can be prepared by microwave plasma irradiation, pyrolysis in a tubular reactor, chemical vapour deposition, microwave plasma-enhanced chemical vapour deposition hydrothermal carbonization and mechanical exfoliation through probe sonication [8-15].

1. Introduction

Carbon is one of the most widely used materials in various industries, such as automotives, electronics, etc. [1-7]. It can be found in various forms such as graphene, carbon nanotubes (CNT), multi-walled carbon nanotubes (MWCNT), carbon nanofibre, carbon nanosheets (CNS), etc. Carbon nanosheets are a new kind of two-dimensional material. A nanosheet is a two-dimensional nanostructure with thickness ranging from 1 to 100 nm. Carbon nanostructured materials have become important due to their good physical and mechanical properties and high performance in composite materials. Extensive research in nanotechnology has allowed us to improve and revolutionize technology and industry. Carbon nanostructures can be prepared by microwave plasma irradiation, pyrolysis in a tubular reactor, chemical vapour deposition, microwave plasma-enhanced chemical vapour deposition hydrothermal carbonization and mechanical exfoliation through probe sonication [8-15].

The production of nanostructured materials from waste materials such as pineapple leaves, water hyacinth, peanut shell, corncob, rice husk and sunflower piths has appeared in recent years [16-21]. Carbon nanomaterials derived from natural waste materials reveal diversity and high performance.
Exfoliated graphite, an important industrial raw material for the production of flexible graphite sheets, is usually prepared by rapid heating of residue compounds of natural graphite flakes with acid, through formation of intercalation compounds [22]. In a previous study [23], carbon nanostructured material was produced from activated and exfoliated peanut shell. There are different methods for preparing carbon materials. Therefore, the search is on for cheap, abundant natural waste materials to protect the environment in the production of carbon materials [24-28].

This paper focuses on the effect of chemical activation with potassium hydroxide (solid and solute) and the sulphuric exfoliation on the formation of carbon nanosheets from stinging nettle (Urtica Dioica). This low-cost process (chemical activation/exfoliation and carbonization) is used to produce carbon nanostructured material from agro waste in simple steps, adding value to the products.

2. Materials and experiments

2.1 Materials
In the present work, nettle stem and nettle leaf were used as carbonaceous material precursors. Chemicals were used as follows: hydrochloric acid (HCl) as cleaner, potassium hydroxide (KOH) as activator and sulphuric acid (H\textsubscript{2}SO\textsubscript{4}) as exfoliator.

2.2 Experiments

2.2.1 Sample preparation and pre-carbonization process
The nettles (nettle stem and nettle leaf) were washed several times and dried at 80 °C for 24 hours, then treated by HCl 0.5 M for 24 hours to remove any metallic oxide or organic compounds. Finally, they were washed by distilled water and dried at 80 °C for 24 hours. The pre-carbonization process was carried out at 450 °C for 2 hours in a stainless-steel tube furnace under argon atmosphere.

2.2.2 Chemical activation and characterization process (a) Chemical activation by KOH (solid) method: The pre-carbonized samples (nettle stem and nettle leaf) were mixed with KOH (solid) at a weight ratio of 1:1 and milled for 1 hour by mortar. (b) Chemical activation by KOH (solute) method: First, the pre-carbonized samples were milled for 1 hour. Secondly, the pre-carbonized sample and KOH (solid) with a weight ratio of 1:1 were put into a beaker, filled with water and stirred into aqueous KOH (solute) for 1 hour then dried at 80 °C for 24 hours. For both methods, after being activated by KOH, samples were heat treated at 800 °C for 1 hour in a stainless-steel tube furnace under argon atmosphere. Then KOH was extracted from the mixture by ethyl acetate [29].

2.2.3 Exfoliation process Finally, to separate the layered structure of carbon, the carbonized samples were treated with 10% H\textsubscript{2}SO\textsubscript{4} solution, stirred for 1 hour and then washed with distilled water and dried at 80 °C for 24 hours. The schematic illustration of the preparation of carbon nanosheet from nettle is shown in Figure 1.

2.3 Characterization The microstructure and morphology of the samples were investigated by scanning electron microscopy (SEM, HITACHI S-4800 and ZEISS EVO-MA10), the chemical composition was analysed by energy-dispersive X-ray spectrometry (EDS, BRUKER AXS) and the crystal structure and the phase purity were examined using X-ray diffraction (XRD, BRUKER D8 ADVANCE CoK\textalpha X-ray source).
3. Results and discussion

The purpose of this work was to investigate the effect of chemical treatment (activation by using difference state of KOH and exfoliating with H$_2$SO$_4$ acid) and to study the microstructure of the carbon nanosheets produced from nettle stem or nettle leaf with a focus on the effect of chemical treatment by using different states of KOH activation and exfoliating process by H$_2$SO$_4$ acid.

The microstructure of the dried nettle stem was examined (Figure 2a). The cell wall of a fibre is not a homogeneous layer and composed mainly from cellulose, lignin and hemicellulose [30]. The chemical composition investigated by EDS showed a high weight percentage of carbon (50.8 wt.%) and low weight percentage of other elements, as shown in Figure 2b. The bristly surface of a dried nettle leaf is shown in Figure 3(a). Nettle leaf contains veins covered by fine stinging hairs and a higher amount of silica, potassium and calcium (Figure 3b) than nettle stem.

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**Figure 1.** Schematic illustration of the preparation of carbon nanosheet

**Figure 2.** (a) SEM micrograph and (b) EDS spectrum of dried nettle stem

**Figure 3.** (a) SEM micrograph and (b) EDS spectrum of dried nettle leaf
Figure 4 represents the microstructure of nettles activated with potassium hydroxide. It is difficult to find the carbon nanosheet after this step, as agglomerates of small particles were found in both nettle stem and nettle leaf. Only a slight difference is observed between the KOH (solid) and KOH (solute) activator.

| KOH (solid) activated | Nettle stem | Nettle leaf |
|-----------------------|-------------|-------------|
| [Image 1]             | [Image 2]   | [Image 3]   |

| KOH (solute) activated | Nettle stem | Nettle leaf |
|-----------------------|-------------|-------------|
| [Image 4]             | [Image 5]   | [Image 6]   |

**Figure 4.** SEM micrographs of the samples after activating by potassium hydroxide

When comparing the microstructure of the stinging nettle before and after exfoliation (Figures 4-6), it can be concluded that the thickness of the layers decreases during the activation process, as melted potassium-hydroxide penetrates into the pores of the carbonized materials and rips apart the carbon layers. Thus, the exfoliator acid can intercalate between the carbon layers and break bonds between them [31]. The potassium hydroxide and the sulphuric acid can form compounds and move between the carbon layers to increase their distance. As a result, carbon layers are easily separated from each other and clear surfaces are found after acid exfoliation.

Carbon nanosheets found in nettle stem after activation by KOH (solid) and exfoliation with H$_2$SO$_4$ have thicknesses varying between 159-252 nm (Figure 5a). The SEM micrograph (Figure 5b) of the nettle stem activated with KOH aqueous solution and exfoliated by H$_2$SO$_4$ shows a smooth surface and clearly reveals the formation of carbon nanosheets with a thickness of 70 to 111 nm. Analysis shows that fully treated carbon nanosheets from nettle stem mainly contain carbon (88.83 wt.%) (Figure 7).
Figure 5. SEM micrographs of nettle stem activated with (a) KOH (solid) (b) KOH (solute) and heat treated at 800˚C for 1 h after exfoliation processing by H\textsubscript{2}SO\textsubscript{4}.

Figure 6. SEM micrographs of nettle leaf activated with (a) KOH (solid) (b) KOH (solute) and heat treated at 800˚C for 1 h after exfoliation processing by H\textsubscript{2}SO\textsubscript{4}.

Figure 7. Comparison of carbon yields of the samples.

| Sample Description | Nettle stem | Nettle leaf |
|--------------------|-------------|-------------|
| Dried sample      | 50.8        | 41.86       |
| Activated with KOH(solid) | 87.35       | 77.34       |
| Activated with KOH(solid) and exfoliated by sulfuric acid | 85.54       | 82.14       |
| Activated with KOH(solute) | 87.56       | 57.4        |
| Activated with KOH(solute) and exfoliated by sulfuric acid | 88.83       | 72.01       |
Carbon nanosheets can be also found in nettle leaf (Figure 6) but are not as sharply formed compared with nettle stem (see Figure 5). The SEM micrographs of the nettle leaf activated by KOH (solute) activation show a smooth surface and clearly reveal the formation of carbon nanosheets with 41-183 nm thickness, whereas the formation of carbon nanosheets in KOH (solid) activated samples reveal numerous multilayers and agglomerated small plates. The carbon yield of nettle leaf is less than that of nettle stem due to its original structure and chemical composition. The sulfuric exfoliation affects the weight percentage of carbon yields (Figure 7).

The microstructure of nanosheets activated with the KOH (solute) and exfoliated by H_2SO_4 shows clear formation of carbon nanosheet structures with flat surfaces. Activation with KOH (solute) also provides better dispersion of carbon nanosheets.

As for the carbon yield in nettle stem samples, an increase of 35-38 wt.% (68-75%) was achieved with a slight difference between the methods. Nettle leaf originally contains a lower amount of carbon (~42 wt.%) but the activation and exfoliation increase it by 30-40 wt.% (72-96%), meaning that with this method a significant enhancement is reached for both materials and a higher level of impurities can be removed.

4. Conclusion
Carbon nanosheets were successfully synthesized from stinging nettle. The SEM micrographs of the nettle stem with KOH (solid and solute) activation show a smooth surface and clearly reveal the formation of carbon nanosheets, whereas the formation of carbon nanosheets of nettle leaf also show carbon nanosheet formation but not as good as nettle stem.

The chemical (KOH and H_2SO_4) and thermal activation affects the formation of carbon and the separation of carbon layers to form nanosheets of graphite. This method is a simple and easy way for producing carbon nanosheets from natural materials and makes it possible to improve the purity of materials and to remove contaminants (metallic oxides and organic compounds) effectively.

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