This Doctoral thesis is on the synthesis and application of carbon-based materials. The emerging environmental and energy issues demand low cost and efficient ways to produce materials for application in energy storage, sensors and degradation of organic pollutants. The study demonstrates doping, a process which introduces material additives to improve the properties of the host material for the targeted applications.
Arūnas Meščeriakovas

SYNTHESIS, CHARACTERISTICS AND APPLICATION OF DOPED CARBON STRUCTURES

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Abstract

This Doctoral thesis is on the synthesis and application of carbon-based materials. The emerging environmental and energy issues demand low cost and efficient ways to produce materials with improved properties for application in energy storage, sensors and degradation of organic pollutants. The work elucidates the synthesis of doped carbon materials: gold nanoparticle/carbon nanoflower (AuNP/CNF) composite, Si@C, SiC@graphite, and Fe/graphene via induction annealing. This work provides insight into the material formation (e.g., crystal phase, size, shape, and agglomeration state) of silicon-doped carbon structures and their applicability in energy storage. Furthermore, iron-doped carbon structures were synthesized and characterized, and packed bed experiments were carried out to test their capability for tetracycline removal from aqueous media. Additionally, the CNF structures doped with AuNPs were tested for their stability in organic solvents and deposited as thin films using an aerosol filtration method.

This study explores the formation of carbon structures (amorphous carbon, graphene, and graphite) synthesized using barley straw-derived carbon mixed with silicon nanoparticles, via induction annealing. The formation of a new SiC phase from amorphous carbon and its re-nucleation to form graphene and graphite were studied in detail. It was observed that the characteristics and yield of the synthesized materials can be controlled by varying the temperature from 1000 °C for amorphous carbon to 2400 °C for graphitic carbon. Likewise, barley husk in combination with glucose was also found to be a viable material for the growth of graphene-like carbon.

The carbon doping studies resulted in the formation of an amorphous carbon-coated Si@C composite. The amorphous carbon was present atop the silicon particles as an approximately 5 nm-thick coating and as interstitial carbon between the silicon nanoparticles. The synthesized Si@C was tested as an anode material for Li-ion coin cells. Owing to the carbon coating, it demonstrated an improved cycling stability with an initial specific capacity of 1200 mAh g⁻¹ at 0.1 A g⁻¹. The iron doping studies resulted in the formation of approximately 1 µm-sized paramagnetic α-Fe and non-magnetic γ-Fe particles embedded in graphene sheets (Fe/graphene). The synthesized composite displayed an initial tetracycline adsorption of 442 mg g⁻¹, which further increased to 660 mg g⁻¹ owing to the self-regeneration capability of the composite.

The stabilities of the CNF suspensions were tested in a series of organic solvents. The dispersion of CNFs in poorly dispersing solvents, such as hexane and toluene, was improved by applying the Hansen solubility parameter theory. It was found that the addition of ethanol to hexane and toluene improved the short-term dispersion quality of CNFs. Furthermore, the gold doping of these dispersions resulted in gold nanoparticle surface-decorated carbon
nanoflowers (AuNP/CNFs). This composite material demonstrated light absorption at 530 nm, which was attributed to the surface plasmon resonance of the gold nanoparticles. Further, non-doped and gold-doped dispersions in ethanol/hexane were used to deposit thin films. The substrate surface area coverage (31–83 %) and deposited film thickness (43 nm-2.4 µm) were controlled by varying the spraying time.

Universal Decimal Classification: 539.23, 546.26, 546.28, 546.59, 620.3, 621.355

Library of Congress Subject Headings: Nanostructured materials; Nanoparticles; Carbon; Silicon; Graphene; Graphite; Gold; Thin films; Amorphous substances; Nanocomposites (Materials); Energy storage; Lithium ion batteries; Electrodes; Anodes; Water—Purification; Organic solvents; Adsorption; Biomass conversion

Yleinen suomalainen ontologia: nanomateriaalit; nanorakenteet; hiili; pii; grafiitti; grafeeni; kulta; ohutkalvot; amorfiset aineet; komposiitit; litiumioniakut; elektrodit; vedenpuhdistus; liuottimet; adsorptio; biomass
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I wish to express my gratitude to all the people involved in the presented work. The shared knowledge and practical experience contributed immensely in both the realization of this work and my personal scientific “baggage”.

I would also like to acknowledge the Fortum Foundation for the financial support, as well as University of Eastern Finland together with SIB Labs for providing the much-needed research facilities.

Kuopio, May 2021
Arūnas Meščeriakovas
<table>
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<th>Abbreviation</th>
<th>Description</th>
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<tr>
<td>AuNP</td>
<td>gold nanoparticle</td>
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<td>AuNP/CNF</td>
<td>gold doped carbon nanoflower</td>
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<td>CNF</td>
<td>carbon nanoflower</td>
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<td>EDS</td>
<td>energy dispersive X-ray spectroscopy</td>
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<td>Fe/graphene</td>
<td>iron and graphene composite</td>
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<td>HSP</td>
<td>Hansen solubility parameter</td>
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<td>SAED</td>
<td>selected area electron diffraction</td>
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<td>SEM</td>
<td>scanning electron microscopy</td>
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<td>Si@C</td>
<td>carbon-coated silicon</td>
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<td>SiC@graphene</td>
<td>graphite-coated silicon carbide</td>
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<td>transmission electron microscopy</td>
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<td>XRD</td>
<td>X-ray powder diffraction</td>
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List of original publications

This thesis consists of an introductory review followed by four research articles. In the introductory section, these are cited using the corresponding Roman numerals.


The original articles have been reproduced with permission of the copyright holders.
Review of original articles and author contributions

The publications presented in this dissertation are original research papers. The research was carried out in the period 2016–2020 at the Fine Particle and Aerosol Technology Laboratory at the University of Eastern Finland under the supervision of Associate Professor Anna Lähde and Professor Jorma Jokiniemi.

Article I describes a methodology for preparing CNF organic suspensions and the verification of their dispersion quality and stability. The CNFs were doped with AuNPs. This study also presents an aerosol filtration method for the deposition of the prepared organic suspensions and the subsequent transfer of CNF thin films onto transparent substrates. The author modified and optimized the system for film deposition. The author studied and optimized suspension parameters for the preparation of suspensions. The author performed all the characterizations and data analyses. The author was responsible for writing the manuscript. The principal aerosol deposition system was designed by T. Karhunen. The manuscript was prepared by the author in collaboration with T. Karhunen, J. Jokiniemi, and A. Lähde.

Article II describes the synthesis of Si@C and SiC@graphite composite structures and their application in lithium-ion coin cells. Barley straw-derived carbon was used as a precursor, together with SiNPs. Induction annealing in an argon atmosphere was used to induce phase and crystallinity changes. The study highlighted the influence of annealing temperature on the properties of produced materials. Electrochemical analysis revealed improved cycle retention owing to the applied carbon coating. The author optimized the synthesis parameters and performed the electron microscopy characterization and data analyses. The author was responsible for writing the manuscript. XRD measurements were carried out by the author with assistance from T. Karhunen, while Raman and TGA measurements were carried out with assistance from S.-M. Alatalo. The author performed the XRD, Raman, and TGA data analyses. The electrochemical testing and data analysis were performed by K. Murashko. The manuscript was prepared by the author in collaboration with K. Murashko, S-M. Alatalo, T. Karhunen, J.T.T. Leskinen, J. Jokiniemi, and A. Lähde.

Article III describes the synthesis and characterization of graphene-like carbon. Barley husk and sucrose were used as precursor materials, which were subjected to magnesiothermic reduction and induction annealing in argon, to yield graphene-like carbon. The author performed essential parts of the characterization of the materials using TEM/SEM/EDS imaging and interpretation of the data. The author contributed to the writing of the manuscript.
Article IV describes the synthesis of an Fe/graphene composite and its application in the removal of tetracycline from water. FeCl₃ and graphene were mixed and induction-annealed in an Ar atmosphere at 900 °C. The obtained Fe/graphene composite was used in column adsorption studies. This study investigated the influence of concentration, feed rate, and Fe/graphene loading ratio on the removal efficiency of tetracycline. Furthermore, this study provided insight into the possible reaction mechanism between Fe/graphene and tetracycline.

The author was responsible for material synthesis along with S-M. Alatalo and performed SEM/EDS imaging and interpretation of the data. The author contributed to the writing of the manuscript.
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1 Introduction

1.1 Background and motivation

In recent decades, the development and application of engineered nanomaterials has become a central focus in many fields of scientific research (Cao, 2004). The transition from micron scale to nanoscale yields a significant change in the physical and chemical properties of the materials (Das et al., 2009). In particular, carbon-based nanostructures have received considerable attention in recent decades. The first reported carbon nanostructure (1985) was fullerene ($C_{60}$) (Kroto et al., 1985). This nanostructure is composed of 60 carbon atoms arranged in hexagons and pentagons via sp² bonds to form a spherical structure (Dresselhaus, 1996; Georgakilas et al., 2015). This was followed by the discovery of carbon nanotube (CNT) materials (Iijima, 1991). The discovery of these materials, amongst others, demonstrated the uniqueness of carbon in its assumption of various nanostructures. Graphene, a unit layer of graphite, was experimentally identified in 1962 by Boehm et al. (Boehm et al., 1962) but it was only in 2004 that it was first isolated and characterized by Andre Geim and Konstantin Novoselov (Novoselov et al., 2004).

Graphene, due to its optical transparency (97–98 %), sheet resistance (~6 kΩ), and carrier mobility ($10^6$ cm² V⁻¹ s⁻¹), is suitable for application as a transparent conductive electrode (Gomez De Arco et al., 2010; Kim et al., 2014). Furthermore, owing to its high surface area (2630 m² g⁻¹), pristine graphene and its oxide derivative, which can be functionalized with nanomaterials, polymers, and surfactants, can be utilized as adsorbents in water desalination (Stoller et al., 2008). The mechanical strength (2.4 ± 0.4 TPa) and elongation (~20 %) of graphene are viewed as particularly useful properties in the preparation of composites with silicon for energy storage applications (Li et al., 2018). To put these values in perspective, we can say that graphene is the most conductive substance known to date, and while it weighs only a sixth of the weight of steel, its mechanical strength is 200 times greater (Wajid et al., 2012). These properties, coupled with its ability to be incorporated into various composites with inorganic structures, organic crystals, metal–organic frameworks, and biomaterials, enables its utilization in many other applications such as gas separation, chemical separation, sensors, supercapacitors, and photocatalysis (Huang et al., 2012; Coros et al., 2019). However, despite its remarkable material properties, more time is needed to develop economically viable graphene production methods that yield high-output, large-area, and defect-free graphene.

In this work, graphene, carbon nanoflowers (CNT) and the produced barley straw derived carbon underwent doping. A process which introduces material additives to improve the properties of the host material for the desired application. Additionally, storage or utilization of these materials may require processing to liquid medium in form of a dispersion. The preparation of such dispersions may be problematic due to material agglomeration and sedimentation, thus the Hansen solubility parameters were considered for the selection of dispersing solvents.
1.2 Objectives of the study

This study focuses on the development of novel carbon materials, their characterization, and their application in energy storage and water purification. The materials were synthesized by utilizing a readily scalable and energy-efficient induction annealing technology. The nanomaterials chosen as the anode materials in Li-ion cells were Si@C and SiC@graphite, and Fe/graphene was used for tetracycline adsorption from water.

The specific objectives of this study were:

- To investigate the interaction of a carbon nanoflower (CNF) nanomaterial with organic solvents to gain an understanding of the preparation of dispersions in low-boiling-point solvents for use in aerosol-based thin film deposition (I).
- To investigate the effect of annealing temperature on the characteristics of the silicon/carbon precursor to optimize the properties of materials for application in Li-ion cell anodes (II).
- The development of a biomass treatment method to fabricate nanomaterials with a graphene-like structure, from cheap and renewable biomass carbon sources (III).
- The development of a method to fabricate a recoverable Fe/graphene nanomaterial composite for application as an adsorbent in water systems (IV).
2 Scientific background

2.1 Carbon-based nanomaterials

2.1.1 Definition of nanomaterials

This thesis focuses primarily on nanomaterials; thus, it is critical to introduce the definitions of “nano” and “nanoscale.” The International System of Units (SI) uses “nano-” to indicate a factor of $10^{-9}$, and the International Organization for Standardization (ISO) uses the term nanoscale to indicate the length scale of materials with dimensions between 1 and 100 nm. When an object has several exterior dimensions, depending on how many dimensions fall between 1 and 100 nm, the nano-object may acquire a different description. Thus, the most commonly used definitions are: a) if only one exterior dimension is in the nanoscale—nanoplate, b) two exterior dimensions—nanofiber, and c) three exterior dimensions—nanoparticle (80004-1:2015, ISO/TS).

2.1.2 Carbon nanomaterials: graphite, graphene, and related structures

Carbon is a tetravalent non-metallic chemical element with four free electrons in the outer shell that can form bonds. Graphite is a crystalline form of carbon, in which $sp^2$ carbon atoms are arranged in a hexagonal network, forming sheets that are stacked on top of each other. A single sheet (or layer) made of these carbon hexagons is called graphene, as illustrated in Fig. 2.1 (a). Each carbon atom in graphene forms three horizontal covalent (sigma) bonds with three neighboring carbon atoms. This leaves the fourth electron in the outer shell to form a vertical (pi) bond, which weakly interacts with the graphene sheets above and below. As mentioned, a single layer of carbon arranged in a hexagonal pattern is termed graphene; however, when the number of vertically stacked layers is between 2 and 10, such a structure is called few-layer graphene, and when the layer count exceeds 10 layers, the structure is called graphite (Bianco et al., 2013; Wick et al., 2014).

The graphene family includes various other structures that comprise a single or few layers of graphene. They can be categorized according to their dimensionality: 0D—fullerenes (Fig. 2.1 (b)) and C-dots; 1D—carbon nanotubes (Fig. 2.1 (c)) and single-wall nanohorns; 2D—graphene (Fig. 2.1 (a)) and graphene nanoribbons. To an extent, these structures have similar properties (mechanical strength, chemical reactivity, electrical conductivity, and optical properties) because they are composed only of $sp^2$ carbon atoms arranged in a hexagonal network. However, significant differences can be observed due to variations in shape and size (Geim et al., 2007; Georgakilas et al., 2015).
Natural graphite is a mosaic combination of polytypes, where the dominant form is AB (accounting for ~80% of the total crystal) and the least common configuration is AA (<6%) (Haering, 1958; Hass et al., 2008). The graphene sheet stacking in these polytypes is shown in Fig 2.2. The figure displays the most common stacking configurations: AA (or hexagonal), AB (or Bernal), and ABC (or rhombohedral) (Hass et al., 2008). The AA-stacked graphite is composed of graphene sheets that are stacked in such a way that each carbon atom of a higher layer is directly above the ones in the lower layer. The AB configuration is achieved by rotating one of the layers in AA-stacked graphite by 60° along the z-axis. Such a configuration produces areas where only a fraction of the carbon atoms is aligned atop each other along the z-axis. The overlapping of the \( p_z \) electron orbitals creates weak bonds between the AB planes. In ABC graphite, the first two layers are oriented as in AB graphite; however, a third layer is positioned atop and translated by \((2a_G/3, b_G/2)\) in relation to the second layer. The spacing of these layers in graphite is approximately 0.341 nm and may vary slightly (<0.2%) depending on the configuration (Hass et al., 2008; Cai et al., 2012). Turbostratic graphite (from “turbo”—rotated, “strata”—layer) has no repeating stacking pattern along the z axis. That is, the layers are rotated in various angles relative to each other; therefore, there is no stacking order between the layers, and the interlayer distance is typically slightly larger than that for graphite (Pimenta et al., 2007; Wick et al., 2014).
2.2 Graphene synthesis and epitaxial growth

2.2.1 Graphene synthesis technologies

The first observed and characterized monolayer graphene sheet was produced in 2004 by the mechanical exfoliation (mechanical peeling) of graphite using adhesive tape (Novoselov et al., 2004). Since then, several different methods have been developed for the production of graphene-based structures. They can be divided into top-down and bottom-up methods. The former can be understood as a graphite 'stripping' methodology to obtain graphene, whereas the latter is focused on synthesizing graphene as the initial product. Mechanical methods can produce high-quality graphene sheets; however, their throughput and time consumption render them unsuitable for industrial production (Zhang et al., 2010). Chemical exfoliation is another top-down method, in which graphite or graphite oxide is exfoliated in the liquid phase (typically by ultrasound) to produce graphene or graphene oxide sheets (GO), which can then be chemically reduced to obtain reduced graphene oxide sheets (rGO). However, graphene prepared by this method contains structural defects and residual oxygen-containing groups in its structure, both of which have a retarding effect in applications where pristine graphene is required (Chen et al., 2017a). For example, the electrical conductivity of rGO is approximately two orders of magnitude lower than that of pure graphene (Wajid et al., 2012). On the other hand, these methods use cheap graphite, are large-scale, and can be paired with other chemical processes to enable chemical functionalization, in which case the aforementioned oxygen groups and defects can serve as "anchor points" (Cai et al., 2012; Chen et al., 2017a; Li et al., 2018).

Figure 2.2: a) AA graphite, b) AB graphite, c) ABC graphite, and d) turbostratic graphite
In bottom-up fabrication, the most widely studied methods are chemical vapor deposition (CVD) and epitaxial growth. CVD is a method that is typically carried out on single crystalline transition metals (Ni, Cu, Pt, Ir, Ru). The growth of graphene on all these metals is achieved in a similar fashion: a metal foil is placed into a hot wall reactor and exposed to a \( \text{H}_2/\text{CH}_4 \) gas mixture under ultra-high vacuum (UHV) or low-pressure conditions, wherein carbon nucleation and growth occur on the metal surface (Reina et al., 2009; Zhang et al., 2013). CVD is a promising method for the production of large-area graphene. However, it is yet to be cost-effective because of the need to remove the underlying metal substrate (Novoselov et al., 2012).

Another bottom-up method is epitaxial graphene growth involving the thermal decomposition of SiC in UHV or at standard pressure in an inert (Ar) atmosphere (Emtsev et al., 2009; Kruskopf et al., 2018). This method also produces high-quality graphene of hundreds of microns in size. However, the electronic properties vary depending on the location of graphene on the SiC substrate, for example, regions over steps display increased electrical resistance. Moreover, the decomposition of SiC is not self-limiting and can produce regions with varying numbers of layers, which also influences the electronic structure of the film (Emtsev et al., 2009; Kruskopf et al., 2015). This method yields graphene with a relatively low number of defects, which makes it suitable for electronic applications; however, it is not without drawbacks as it requires high annealing temperatures (>1000 °C), and SiC substrates are expensive. Furthermore, the size of graphene is limited by the dimensions of the SiC wafer (Emtsev et al., 2009; Novoselov et al., 2012).

2.2.2 Epitaxial growth, SiC faces, and step bunching

The growth of graphene and graphene-based structures can be achieved by means of silicon sublimation from silicon carbide (SiC) (Emtsev et al., 2009; Miettinen et al., 2014; Wang et al., 2016 a). SiC can appear in over 200 different crystalline structures (polytypes); however, only a few are stable, such as 3C, 4H, 6H, and 15R (Bechstedt et al., 1997). A SiC tetrahedron is considered the basic “building block” of all SiC crystals. The stoichiometry of Si/C in SiC is 50/50, irrespective of its polytype. The growth of a graphene layer on SiC can be observed at approximately 1280 °C in UHV and 1550 °C at atmospheric pressure (Ar environment) (Emtsev et al., 2009). An important feature of SiC, particularly with respect to epitaxial graphene growth, is the face at which the crystal is terminated along the c-axis. Epitaxial growth from Si-terminated (0001) and C-terminated (0001̅) faces proceeds differently (Emtsev et al., 2009; Sun et al., 2011; Rius et al., 2018). In the case of sublimation from SiC (0001), the initial carbon layer formed atop SiC is different from a typical graphene layer as it maintains a partial covalent bond with the surface of the SiC (Sadowski et al., 1998; Lui et al., 2011). This layer is called the buffer layer. Further sublimation breaks the covalent bonds between the buffer layer and SiC; at this point, the buffer layer becomes a layer of graphene. Subsequently, a new buffer layer is formed below the graphene layer, and the process is repeated (Ferrari, 2007). The sublimation process from SiC (0001̅) does not include the formation of a buffer layer. Furthermore, the relative spatial orientations of
the grown graphene layers in the case of SiC (0001) and SiC (000\̅1) are different. Sublimation from a Si-terminated face produces Bernal (AB) stacked graphene layers, whereas sublimation from a C-terminated face produces turbostratic layers (Hass et al., 2008; Bryan et al., 2011). Step bunching is another important phenomenon in epitaxial growth, wherein the SiC surface atoms migrate at high temperatures to form steps and terraces. This step bunching phenomenon occurs before the actual graphene growth, which is believed to suppress further step bunching (Bao et al., 2016). The height of the steps and the width of the terraces depend on the heating rate. Faster heating rates (270 °C min\(^{-1}\)) lead to small step formations (as small as half or one unit cell), whereas slower heating rates (40 °C min\(^{-1}\)) lead to large step formations with heights of up to 10 nm and over (Bao et al., 2016). The formation of high steps induces additional resistance and leads to the deterioration of the electronic properties of graphene (Kruskopf et al., 2016).

2.3 Suspensions of graphene and related materials

2.3.1 Preparation of graphene and related material suspensions

Graphene materials can be useful in thin-film form for solar cells, touch screens, sensors, displays, and defrosting windows (Gruner, 2006; Kiang Chua et al., 2013). The aforementioned attractive properties of graphene and graphene-based materials are mainly associated with their existence as individually separated entities (Li et al., 2008; Paredes et al., 2008; Ren et al., 2008). However, graphene tends to aggregate, which prevents it from demonstrating its excellent properties. Application of graphene-based materials in these products requires large-scale processing at a sufficient throughput while maintaining particle separation as much as possible. The method for avoiding this aggregation is liquid processing—the preparation of suspensions, which can then be utilized to produce thin films by means of spray coating and printing (Paredes et al., 2008; Carey et al., 2017).

An ideal, high-quality suspension is one in which the majority of dispersed material is in the form of individual particles, for example, single graphene sheets, single CNTs, fullerenes, etc. (Sun et al., 2008). However, in practice, small bundles and/or large agglomerates of dispersed materials are present in the suspensions. The formation of agglomerates is undesirable as it is often accompanied by sedimentation and a subsequent decrease in the material concentration in the bulk (upper) volume of the suspension. Thus, a good dispersing liquid medium should possess two key characteristics: (1) the ability to exfoliate the material into its primary particles and (2) stabilization for an extended duration (application dependent).

Graphene-based materials exhibit strong intermolecular interactions due to Van der Waals forces and π-bond interaction. Graphene is highly hydrophobic; thus, the material forms large agglomerates that are sedimented in hydrophilic liquid environments (Park et al., 2009; Zuaznabar-Gardona et al., 2019). Graphene can be dispersed in aqueous solutions by oxidizing it to graphene oxide (Paredes et al., 2008) by using surfactants (e.g., sodium cholate) or polymer stabilizers (e.g., polyvinylpyrrolidone (PVP)) (Lotya et al., 2010; Georgakilas
The dispersion of graphene-based materials in organic solvents is also a challenge. Dispersion is possible by the introduction of functional surface groups, which prevent agglomerate formation and improve the interaction of the graphene material with the surrounding liquid. However, such surface modifications are not preferred as they may change the bonding in the basal planes, which may lead to the deterioration of electronic properties (Park et al., 2009; Hernandez et al., 2010; Zuaznabar-Gardona et al., 2019). The removal of added surfactants and additives (both in water and organic solvents) would require additional chemicals post processing or high-temperature annealing/vacuum during deposition. Such conditions severely limit the applicability when dealing with deposition onto plastic and/or textile substrates (Carey et al., 2017). Relatively good dispersion is possible in pure organic solvents without additives, namely in N-methylpyrrolidone (NMP), dimethylformamide (DMF), dimethyl sulfoxide (DMSO), and cyclohexane. However, these are high-boiling-point solvents, which also require high-temperature treatment for their removal after deposition.

2.3.2 Hansen solubility parameters for graphene-based suspensions

The methodology to predict the solubility of polymers in organic solvents can be applied to predict the dispersion of carbon materials (graphene included) in organic solvents. In theory, the total cohesion energy of a material is divided into several parameters. The total cohesion energy can be understood as the energy/heat of vaporization that is required to break all the bonds present in the liquid phase. The Hansen solubility parameters (HSPs) outline three primary types of molecular interactions (cohesion energies) inside a liquid that make up the total cohesion energy (Hansen, 2007). First, the nonpolar or dispersion cohesion energies (or London dispersion) are forces that are present in every atom and are caused by uneven charge distributions. These are created in the form of temporary dipoles when the distribution of electrons is denser at a particular point in space around the nucleus for a split moment. The second type of interaction forces are polar interactions (polar cohesion energy), which are molecular interactions that are present in every molecule, with varying strength. These forces are created between permanent dipoles, which arise due to uneven charge distribution in the molecules. A typical permanent dipole occurs in a chemical bond between two nonmetals. The shared electrons in such a bond are “pulled” unevenly; that is, certain atoms will have a greater pull force owing to the size of the nucleus. Finally, hydrogen bonding cohesion energy is another type of molecular interaction that arises between molecules with hydrogen bonds. However, in the HSP theory, this bonding is typically used to represent all the remaining cohesion energies (excluding nonpolar and polar cohesion energies) present in the liquid (Hansen, 2007). The HSP theory has been used to predict the optimal solvents for several graphene-based material dispersions, including graphene, single-wall carbon nanotubes, multi-wall carbon nanotubes, fullerenes (C_{60}), and carbon nano-onions (Hansen et al., 2004; Detrich et al., 2008; Lotya et al., 2010; Zuaznabar-Gardona et al., 2019).
In the case of high-boiling-point solvents, the HSP theory can be used to select a suitable low-boiling-point solvent to dilute the high-boiling-point one. HSPs can also be used to prepare well-dispersing mixtures of solvents, which, individually, do not disperse graphene well. The solubility parameters (δ_d, δ_p, δ_H) for a mixture can be calculated as the fraction sum of the solubility parameters of both solvents.

\[
(\delta_{d_{mix}}, \delta_{p_{mix}}, \delta_{H_{mix}}) = \begin{cases} 
\delta_{d_{mix}} &= \varphi_{\text{solvent}1} \cdot \delta_{d_{\text{solvent}1}} + \varphi_{\text{solvent}2} \cdot \delta_{d_{\text{solvent}2}} \\
\delta_{p_{mix}} &= \varphi_{\text{solvent}1} \cdot \delta_{p_{\text{solvent}1}} + \varphi_{\text{solvent}2} \cdot \delta_{p_{\text{solvent}2}} \\
\delta_{H_{mix}} &= \varphi_{\text{solvent}1} \cdot \delta_{H_{\text{solvent}1}} + \varphi_{\text{solvent}2} \cdot \delta_{H_{\text{solvent}2}}
\end{cases}
\]  

(1)

Here, \( \varphi \) is the volume fraction of the solvent, and \( \delta_d, \delta_p, \) and \( \delta_H \) are the dispersive, polar, and hydrogen solubility parameters of a solvent, respectively. The affinity between the selected solvent and graphene-based materials can be expressed as the distance \( R_A \). This measure can be understood as the distance between two points in a three-dimensional coordinate system, where the axes represent the following values: \( x = \delta_d, y = \delta_p, z = \delta_H \). The strength of the affinity between the solvent and dispersed material decreases with increasing \( R_A \) value and can be calculated using equation 2:

\[
R_A = \sqrt{4(\delta_{d,G} - \delta_{d,S})^2 + (\delta_{p,G} - \delta_{p,S})^2 + (\delta_{H,G} - \delta_{H,S})^2}
\]  

(2)

where the subscripts G and S denote the graphene material and solvent, respectively.

2.4 Biomass-derived carbon/silicon in lithium-ion batteries

2.4.1 Current anode materials and Si as an alternative

Lithium-ion batteries (LIBs) are secondary batteries with high energy density and long cycle life and are a lightweight option for energy storage (Liu et al., 2016). Currently, LIBs are the dominant energy storage option for portable electronics, electric vehicles, and wind and solar generators (Dunn et al., 2015; Wang et al., 2015 b; Saez-De-Ibarra et al., 2016; Xu et al., 2020; Zhao et al., 2020). Presently, the anode material in most commercial LIBs is graphite, an electrochemically stable material that displays an energy density of approximately 372 mAh g⁻¹ (Shen et al., 2017). However, flake graphite is listed as a critical mineral owing to the ever-increasing production of electronics (COM/2020/474, 2020). Moreover, the increased demand for batteries with higher capacity and energy density necessitates new management strategies, such as the use of alternative sustainable sources of graphite (biomass) and/or application of different materials and material composites for anodes (Moradi et al., 2016; Natarajan et al., 2020).
Silicon is a potential candidate for replacing graphite as an anode material. Silicon has a theoretical specific capacity of 4200 mAh g⁻¹ and is abundant in natural reserves (Kwon et al., 2020). However, bare silicon cannot be used on its own owing to several drawbacks, specifically, (1) the low conductivity of Si and (2) volumetric expansion of up to 300% during charge/discharge cycles. Additionally, this expansion leads to the subsequent pulverization of silicon, isolation and loss of interparticle charge transfer, and consumption of electrolyte for the formation of a solid–electrolyte interphase on newly formed Si surfaces (Xu et al., 2010; Tang et al., 2015; Wu et al., 2016).

### 2.4.2 Biomass and its treatment for application in LIBs

To overcome the shortcomings of pure silicon as an anode material, composite Si/C structures and carbon-coated silicon (Si@C) are being actively studied as viable solutions. Carbon can act as both a conducting matrix and a physical barrier to mitigate the Si volume expansion (Zhou et al., 2016). The most commonly reported Si/C composite architectures are core@shell (Si@C), core@void@shell (Si@void@carbon), and silicon embedded in a three-dimensional carbon matrix (Lisowska-Oleksiak et al., 2014; Niu et al., 2017; Shen et al., 2017; Xie et al., 2017; Jiao et al., 2018). Carbon in such structures can be present in several forms: amorphous, fully graphitized (graphite, graphene), or partially graphitized (amorphous + graphitic regions) (Kwon et al., 2020). The synthesis of these composite structures may include materials that are expensive and may require complex multi-step processing and synthesis and may not be environmentally friendly. A solution to this problem is the utilization of biomass/biowaste as a source of carbon (and silicon).

The use of biomass-derived carbon can potentially provide more sustainable LIBs and could be a partial solution to decreasing the price of graphite and carbon-based materials. Biomass-derived carbon-materials can act as substitutes for traditional graphite and also form composites with silicon (Shen et al., 2017). Currently, emerging studies in the energy storage sector are centered on the utilization of industrial, marine, and agricultural biowastes (or just biomass) and crops as precursors for application in LIBs. Materials such as barley straw, duckweed, reed flowers, flour, walnut shells, dandelions, jute, corn starch, lignin, and aquatic biomass, have been reported as carbon sources in anode preparation (Deng et al., 2016). Likewise, Si can also be extracted from biomass sources, such as bagasse husk, wheat husk, rice husk, and rice straw, and can be used in the preparation of anode materials (Zhu et al., 2011; Pode, 2016; Terzioğlu et al., 2019).

Most biomass consists of three main components: lignin, cellulose, and hemicellulose, and to a lesser extent, inorganic compounds. Before application as a feedstock in material synthesis, the biomass undergoes a reduction in size by means of grinding or chipping, followed by washing with water or diluted acid (HCl, H₂SO₄, HF, HNO₃) for demineralization (Pingali et al., 2010; Asadieraghi et al., 2014). These methods can be paired with thermo-chemical treatments (removal of unnecessary compounds by pyrolysis) before the biomass is used as a feedstock for material synthesis (Long et al., 2017).

During pyrolysis, different temperature ranges target specific compounds in the biomass. Typically, temperatures greater than 100 °C are for the removal of moisture, 220–315 °C
for hemicellulose degradation, and 315–400 °C for cellulose degradation; lignin degradation occurs across a wide temperature range. Pyrolysis also removes several different organics and all volatile compounds, leaving behind solid carbon as the residual material. For the application of biomass-derived carbon in electrochemical processes, its electrical conductivity and electrochemical behavior are of great importance. These properties are directly linked to the purity and crystalline structure of carbon, or more specifically, the sp² bonded carbons. The transformation of amorphous feedstock to crystalline carbon is energy demanding. High thermal treatment temperatures are required, and they vary greatly (1000–3000 °C) depending on the precursor material, synthesis conditions, and the desired degree of carbonization (ratio of amorphous to graphitized carbon) (Inagaki et al., 2014). Additionally, high levels of graphitization are often associated with a low specific surface area and poor pore structure; therefore, a compromise must be made to balance these properties for the best electrochemical performance (Wang et al., 2017).
3 Experimental methods

3.1 Materials and synthesis methods

3.1.1 Materials and pretreatment

A summary of the materials and methods used is shown in Table 1. In paper I, gold nanoparticles (AuNPs) were used as received from Blacktrace Holdings Ltd., UK. The synthesis and characteristics of the CNFs used have been described previously (Miettinen et al., 2014). Briefly, the CNF synthesis was a two-step process consisting of: (1) chemical vapor synthesis (CVS) using hexamethyldisilane (Sigma Aldrich) at 1400 °C, and (2) induction annealing of the CVS-produced preceramic SiC at 2600 °C in argon at atmospheric pressure. The produced CNFs were sphere-like multilayered (4–15 layers) carbon nanoparticles that resembled spread flower buds.

In paper II, the silicon nanoparticles (SiNPs) were used as received from Nanopow AS, Norway. Barley straw was obtained from Finnish farmers after grain harvest. The barley straw was mechanically ground through a 0.5 µm sieve. The obtained powder was stirred in 37 wt % HCl for 3 h at room temperature (approx. 20–21 °C). The mixture then underwent a series of purification steps: Buchner filtration and rotary evaporation, before being wet-mixed with SiNPs.

In paper III, the barley husk (BH) used was obtained from Altia Oyj, Finland, from the side stream of a process. The carbon source, D(+) - sucrose, was obtained from VWR (Finland). Initially, nanostructured silica (nSiO2) was obtained by leaching and washing the BH. The obtained nSiO2 was mixed with sucrose and annealed at 160 °C for 5 h in the presence of 2.7 vol % H2SO4. The sucrose was dehydrated to elemental carbon (reaction 1), after which the residual water and H2SO4 were removed by annealing in a N2 atmosphere at 700 °C for 2 h. The resultant nSiO2/C was converted into nSiC/C through magnesiothermic reduction in a N2 atmosphere.

\[
C_nH_{2n}O_n + H_2SO_4 \rightarrow nC + H_2SO_4 + nH_2O
\]

(1)

In paper IV, the FeCl3 (purity 97 %) used was obtained from Sigma Aldrich, and the few-layered graphene was obtained from Angstron Materials Inc., USA. The precursor for the synthesis of Fe/graphene was prepared by the absorption of FeCl3 by graphene via wet mixing.
<table>
<thead>
<tr>
<th>Product</th>
<th>Methods</th>
<th>Precursors</th>
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<th>Ref.</th>
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<tbody>
<tr>
<td>CNF/AuNP</td>
<td>CVS, Induction annealing,</td>
<td>CNF, AuNP</td>
<td>SEM, TEM, TGA, Raman, UV–vis</td>
<td>Paper I</td>
</tr>
<tr>
<td>Si@C, SiC@graphite</td>
<td>Acid leaching, Induction annealing</td>
<td>SINP, barley straw</td>
<td>SEM, TEM, TGA, Raman, XRD, Electrochemical</td>
<td>Paper II</td>
</tr>
<tr>
<td>Graphene-like carbon</td>
<td>Acid leaching, Magnesiothermic reduction, Induction annealing</td>
<td>Barley husk, glucose</td>
<td>SEM, TEM, TGA, Raman, XRD, N₂ sorption</td>
<td>Paper III</td>
</tr>
<tr>
<td>Fe/graphene</td>
<td>Wet mixing, Induction annealing</td>
<td>FeCl₃, graphene</td>
<td>SEM, TEM, TGA, Raman, XRD, XPS, Zeta Potential, N₂ sorption, Magnetization, MS</td>
<td>Paper IV</td>
</tr>
</tbody>
</table>
The CNFs used for thin film deposition and suspension testing in paper I, Si@C and SiC@graphite from barley straw-derived carbon in paper II, graphene-like carbon from barley husk-derived silicon in paper III, and Fe/graphene in paper IV were all synthesized via induction annealing. The materials were annealed at atmospheric pressure in argon (AGA 5.0) using an induction furnace. Fig. 3.1 depicts the induction oven set-up. Prior to annealing, the furnace was flushed with nitrogen (N$_2$, industrial quality) for 10 min to remove air from the system. After flushing, argon was fed through the bottom of the furnace at 1.5 lpm to maintain an inert atmosphere throughout the annealing process. The exhaust gases were diluted using a 30 lpm N$_2$ line and collected in a bag filter. The powder precursor sample was poured into a graphite crucible that was enclosed by graphite insulation felt. Both the crucible and insulation felt had an opening at the top to allow the escape of volatile compounds and to enable the pyrometer laser to measure the internal temperature. The samples in paper II were annealed at 1000, 1400, 1800, 2000, 2200, and 2400 °C. The heating ramp used was approximately 35 °C min$^{-1}$ with a 10 min hold at the target temperature. In paper III, the sample was annealed at 2400 °C and held for 20 min before cooling. In paper IV, the FeCl$_3$/graphene precursor was annealed at 900 °C and held for 45 min.

The induction annealing system is unique in that the transferable heat can be up to 1500 times that in heat conduction methods (Rudolf et al., 2000). Induction annealing is widely used in the metalworks industry (preheating, surface hardening, welding, melting) and home appliances (induction cookers). The heating principle of the induction annealing system is based on the coupling of a conductive workpiece (crucible) with the magnetic field produced by the coil (Lucia et al., 2014). The three main components of the induction annealing system are the induction coil, an alternating current source, and the work piece. Depending on the workpiece material, which can be conductive and ferromagnetic or non-ferromagnetic, energy losses in the form of heat can occur through Joule heating and magnetic hysteresis. Joule heating is the primary phenomenon in both materials, whereas magnetic hysteresis occurs only in ferromagnetic materials.

The basic operation of induction annealing is as follows. An alternating current source is connected to the coil. The flow of current through the coil generates a magnetic field. The direction of the magnetic field lines can be determined by the "right-hand" rule, where the thumb is pointing in the direction of the current flow, while the rest of the fingers indicate the direction of the generated magnetic field. The strength of the generated magnetic field is directly related to the frequency and amount of current passing through the coil. For efficient induction annealing, determining the adequate frequency is a key aspect. The selection of the frequency depends on several factors, including material properties (magnetic permeability and resistivity), work piece geometry (size and shape), and consideration of the “skin effect” (Zinn et al., 1988). Magnetic hysteresis is a phenomenon induced by the changing magnetic field created by the alternating current. This phenomenon can be understood as the rotation of the molecular dipoles of the workpiece material, while the energy required for the rotation is dissipated in the form of heat. The rate at which these rotations (in tandem heating) occur depends directly on the frequency of the alternating current. Furthermore,
Joule heating can be understood as the dissipation of heat from a resistor when a flowing current is present. In induction annealing, the flowing currents or "eddy currents" in the workpiece are induced by the changing magnetic field (or magnetic flux) generated by the induction coil. In turn, the induced eddy currents flow in the workpiece (and its internal resistances), thereby dissipating heat. This dissipated heat heats the nonconductive sample inside the workpiece by means of heat conduction (Zinn et al., 1988).

Figure 3.1: Schematic of the induction oven set-up used to anneal materials in papers II, III, and IV. (Published in paper III.)
3.1.3 Aerosol spray deposition set-up and film transfer

The aerosol filtration deposition system used in paper I is displayed in Fig. 3.2. The system consisted of a constant output atomizer (model 3076, TSI Inc., USA), which was used to atomize the organic CNF suspensions. Air (3.5 lpm) was used as the atomizing and carrier gas with a corresponding precursor uptake rate of 0.5 ml s$^{-1}$. The generated droplets (mean $\phi$ 300 nm, manufacturer data) underwent drying in the air stream and were collected downstream on PTFE (Zefluor, 1 $\mu$m, $\phi$ 47 mm) filter membranes. A Magnehelic pressure gauge was used to observe the pressure drop across the filter. Manual pressure release was carried out to maintain the decrease in pressure at a constant $-15$ Pa. The precursor used was a 50/50 v/v % mixture of hexane/ethanol with a 0.2 mg ml$^{-1}$ concentration of CNFs. The suspensions were sprayed for 4, 7, 14, and 21 min, and the transferred films were named G-4, G-7, G-14, and G-21, respectively. For substrate coverage calculations, the scanning electron microscopy (SEM) images were converted into binary images, and the average covered surface was calculated from the black/total pixel ratio.

The filter membranes collected with the CNF filter cakes were dried overnight at room temperature. Before transfer, the target substrate (transparent polyethylene terephthalate, PET) polymer slides were rubbed with isopropanol. The filter membranes were then placed face down onto the PET slides and manually rolled over using a polytetrafluoroethylene roller. The filter membranes were then peeled off, leaving behind a CNF film on the PET slide.

Figure 3.2: Schematic of the aerosol spray deposition set-up used to deposit CNF material from organic suspensions (Published in paper I)
3.1.4 Adsorption column set-up

Tetracycline studies were conducted in a fixed-bed column with an inner diameter of 6.6 mm and a height of 100 mm. The adsorption studies were conducted at a temperature of 23 °C and a pH of 5, which were selected based on a literature review (Basu et al., 2019; Batra et al., 2019; Dong et al., 2019; Qu et al., 2019; Zhang et al., 2019). The column was operated in the down-flow mode, and the tetracycline solution was transported to the top of the column by a peristaltic pump. The adsorption tests were conducted at two different tetracycline concentrations (25 mg L⁻¹, 50 mg L⁻¹) and flow rates (1.2 mL min⁻¹, 2.5 mL min⁻¹) and two different quantities of the Fe/graphene adsorbent (25 mg, 50 mg). The effluent tetracycline solution was sampled at certain time intervals and analyzed by mass spectrometry.
3.2 Analysis methods

3.2.1 Electron microscopy

The morphological and compositional information of the fabricated materials was obtained via electron microscopy. The scanning electron microscope (Zeiss Sigma HD VP) was equipped with in-lens, secondary electron (SE2), back-scattering electron (BSE), and energy dispersive X-ray spectroscopy (EDS) detectors. In paper I, SEM was used to obtain information on the substrate coverage area, CNF film thickness, and distribution of AuNPs in the films. In paper II, SEM was used to observe Si@C and the particle size, shape, terrace formation, and graphite growth of SiC@graphite. In paper III, SEM was used to obtain the particle size, shape, and composition of graphene-like carbon. In paper IV, SEM was used to observe the shape, composition, and distribution of Fe in the graphene matrix.

Transmission electron microscopy (TEM, JEOL JEM-2100F) was used in paper I to observe the structure of CNF and the distribution of AuNPs on the CNF particles. In paper II, TEM was used to observe the sizes and shapes of Si@carbon and SiC@graphite, and the core size, graphite layer thickness, layer count, and interplanar distance in the layers of SiC@graphite. In papers III and IV, TEM was used to observe the size, shape, and layering of the graphene-like carbon and Fe/graphene structures.

3.2.2 X-ray powder diffraction

X-ray powder diffraction (XRD) was carried out with zero background sample holders and was used to identify the crystalline phases in the fabricated Si/C (papers II and III) and Fe/graphene (paper IV) materials. XRD analysis was performed using a Bruker AXS D8 Advance with a Cu Kα source operating at 40 kV and 40 mA. Topas 3 software was used for the fitting of the diffractogram and phase identification.

3.2.3 Raman spectroscopy

Raman spectroscopy was carried out to investigate the degree of disorder in the carbon materials. In paper I, the analysis was performed using Bruker Senterra II and in papers II and III, it was performed using Thermofisher DXR2xi; both devices were equipped with a λ = 523 nm laser. The analyses were carried out on dry powder samples deposited on microscope slides. The obtained peaks were identified by comparing the peak positions with those reported in literature.

3.2.4 UV–vis spectroscopy

In paper I, ultraviolet (UV, 100–400 nm) and visible (vis, 400–750 nm) spectroscopy was performed to measure both the light absorbance of carbon/gold suspensions and the transmittance of thin films prepared from these suspensions. A Perkin Elmer Lambda 25 spectrophotometer equipped with quartz cuvettes of 10 mm path length was used for absorbance
measurements of suspensions, and a solid sample holder was used for thin-film transmittance measurements.

3.2.5 Thermogravimetric analysis

Thermogravimetric analysis (TGA) was conducted in papers I, III, and IV to identify the mass change of compounds by utilizing the difference in thermal stability under air atmosphere. A TA Instruments Q50 thermogravimetric analyzer was used to carry out the TGA analyses. The samples were prepared by loading an aliquot of the sample powder onto a platinum TGA pan.

3.2.6 Mass spectrometry

In paper IV, mass spectrometric analysis was carried out to identify the tetracycline decomposition products in the adsorption studies. The analysis was carried out using a 12 T solar-iXTM XR hybrid Qh-Fourier transform ion cyclotron resonance (FT-ICR) mass spectrometer (Bruker Daltonics, Bremen, Germany) coupled with an electrospray ionization source (ApolloTM-II) in positive ion mode at a flow rate of 2 μL/min. Acetonitrile was used to dilute the tetracycline solution. Nitrogen was used as both the nebulizing (80 °C, 1 bar) and drying gas (4 lpm). The accumulation time and time of flight were 0.8 s and 0.5 ms, respectively.

3.2.7 X-ray photoelectron spectroscopy

In paper IV, the composition of elements and their chemical states on the Fe/graphene material surface was analyzed with a VG Multilab 2000 instrument using Al Kα radiation. The acquired spectra were fitted using the XPSPEAK41 software. The peaks were identified by comparison with the binding energies reported in literature.

3.2.8 Zeta potential

In paper IV, the surface charge of Fe/graphene in aqueous solution was analyzed using a Zetasizer Nano ZS (Malvern Instruments Ltd). The analysis was performed at pH values of 1 to 10 and adjusted using 0.1 M HCl and 0.1 M NaOH.

3.2.9 Surface area measurements

In paper IV, the active adsorption surface area of the Fe/graphene composite performing tetracycline adsorption was measured with liquid N₂ temperature (−196 °C) using a Quantachrome Autosorb gas sorption analyzer. Prior to measurement, the sample was treated in vacuum at 125 °C for 2 h. Isotherms were obtained from 80 measurement points. The pore size distribution and total pore volume were calculated using the Barrett–Joyner–Halenda (BJH) theory, and the specific surface areas were calculated using the Brunauer–Emmett–Teller (BET) theory.
3.2.10 Electrochemical analysis

In paper II, the electrochemical performance of the materials was tested to assess the effect of carbon coatings on silicon nanoparticles. Arbin LBT 21084a (Arbin Instruments, USA) was used as the battery testing equipment. The measurements were done against a metallic lithium reference electrode. Cyclic voltammetry (CV) and galvanostatic charge–discharge curves were measured in the voltage range of 0.01–1.5 V at a scanning rate of 0.1 mVs⁻¹. Rate capabilities were also measured. All electrochemical tests were performed after the creation of a solid electrolyte interphase, to decrease the effect of all side reactions on the test results.

4 Results and discussion

4.1 Formation of graphene and graphene-like structures

The CNF nanoparticles used in paper I and the carbon structures produced in papers II and III followed the same formation process based on Si sublimation from SiC. This phase separation process of SiC is illustrated by the thermodynamic equilibrium calculation presented in Fig. 4.1. The figure shows the phase separation of SiC in the temperature range of 1600–3000 °C. The equilibrium data were obtained from the Fact53 and Ftmisc LMLQ (liquid light metal alloy) databases. The thermodynamic data were in agreement with the decomposition scheme of SiC, as reported by Lilov (Lilov, 1993). In argon, at atmospheric pressure, the conversion of SiC to solid carbon is initiated at approximately 1550 °C. At this temperature, the process is at the atomic scale, and thus the yield is hardly visible in Fig. 4.1. At 2660 °C, the solid carbon yield was at its maximum. A further increase in the temperature resulted in the formation of gaseous products (SiC2, Si2C, and Cx) and decreased the formation of solid carbon structures.

Figure 4.1: Phase separation of crystalline SiC in the temperature range of 1600–3000 °C. (Published in paper III.)
In paper II, graphene-based structures were synthesized using a mixture of SiNPs and barley straw-derived carbon. The analytical data obtained to experimentally verify the growth process (morphology and phase transitions) from precursor to crystalline graphene-based materials are shown in Fig. 4.2. The initial annealing (1000 °C) of the precursor resulted in amorphous carbon, as verified by TGA (Fig. 4.2 (c)). The TGA curves displayed a combustion onset temperature of approximately 350 °C, which is typical for amorphous carbon (Sun et al., 2016).

An increased annealing temperature (1800 °C) promoted the formation of SiC and a small amount of graphite, which is in agreement with the presented thermodynamic calculations. The existence of SiC-3C and graphite-3R was confirmed by XRD analysis. The TGA curves displayed a mass loss of 0.9 wt % with a characteristic combustion onset temperature of approximately 600 °C for graphitic carbon. (Sun et al., 2016). The formation of graphitic carbon was a result of silicon sublimation from the SiC lattice as Si sublimation in an argon atmosphere starts at approximately 1550 °C (Emtsev et al., 2009; Wang et al., 2016 a). Silicon sublimation typically proceeds from the surface faces of SiC crystals, leaving behind carbon-rich areas. This carbon typically nucleates to form a continuous graphene layer. Such growth is often referred to as epitaxial graphene growth (Greek, epi—above, taxis—an ordered manner) (Emtsev et al., 2009). After the first surface layer of graphene is formed, Si continues to sublimate from the next Si-C bilayer below the just formed graphene layer, and this process proceeds throughout the volume of the SiC precursor.

![Figure 4.2: a) X-ray diffractograms, b) Raman spectra, and c) TGA curves of Si/C precursor annealed at 1000, 1400, 1800, 2000, 2200, and 2400 °C. (Published in paper II.)](image-url)
Figure 4.3: a) SEM image of graphite produced from annealing the Si/C composite at 2400 °C, b) TEM image showcasing graphite comprising 36 graphene layers, c) graphite (2400 °C) area selected for SAED analysis, d) SAED pattern obtained from (c). (Published in paper II.)

As proposed by the thermodynamic calculations, annealing at higher temperatures (2000, 2200, and 2400 °C) resulted in the same sublimation processes; however, the product yield was higher. This increased yield of graphite was verified by the TGA results (Fig. 4.2 (c)). The amount of graphitic material formed increased with the annealing temperature (1800–2400 °C) and ranged from 0.9 wt % to 24.1 wt %. Fig. 4.3 (a, b) displays the grown graphite flakes with observable diameters of up to 5 µm and thicknesses of up to 12.8 nm (approximately 36 graphene layers).

According to the XRD results (Fig. 4.2 (a)), two graphite polytypes were identified in the sample: graphite-2H and graphite-3R. However, the Raman results (Fig. 4.2 (b)) displayed a single Lorentzian 2D peak at 2700 cm\(^{-1}\), which is not typical for graphite because it should display a double Lorentzian peak (Ferrari, 2007). A single Lorentzian peak is typically characteristic of <5 layered graphene or turbostratic graphite. A single 2D Raman peak for turbostratic graphite originates from electronic decoupling between the layers (caused by rotational faults between layers) and gives rise to electronic properties similar to those of single-
layer graphene (Pimenta et al., 2007; Warner et al., 2009; Version, 2016). They can be differentiated by measuring the full width at half maximum (FWHM) of the 2D peak, which is typically wider for turbostratic graphite. The measured FWHM of the sample treated at 2400 °C was 42 cm⁻¹ and was in agreement with previously reported values (Ferrari et al., 2006; Pimenta et al., 2007; Malard et al., 2009). The presence of turbostratic graphite was further verified by selected area electron diffraction (SAED). Fig. 4.3 (c, d) displays the SAED pattern in which one sheet of graphene produces a single hexagonal dot pattern, with multiple patterns originating from the same center point representing multiple graphene sheets. The hexagonal patterns were rotated with respect to each other, and the angle between them represents the rotational angle between the graphene sheets. In this particular instance, a total of 11 patterns (layers) were observed, and the measured angles were 0°, 0.4°, 1.1°, 20.4°, 28.7°, 29.6°, 32.3°, 34.8°, 51°, 58°, and 58.6°.

In paper III, the silicon used was derived from barley husk, while glucose was used as an additional carbon source. The nSiC/C precursor was composed of (1) well-defined particles of observable size in the range 100–600 nm and (2) spherical particles forming larger porous structures. As revealed by EDS, the precursor particles were composed of silicon and carbon, which corresponded to SiC, whereas the porous structures contained mostly amorphous carbon. The SiC was confirmed by XRD to be present in two polytypes, namely SiC-2H and SiC-3C (Fig. 4.5 (a)). During induction annealing in Ar at 2400 °C, the precursor material underwent the same epitaxial growth process as described in paper II. The graphene-like carbon obtained is shown in Fig. 4.4 (a) and is primarily composed of spherical particles ranging from 50 to 500 nm in diameter. The particles were hollow, as identified by TEM (Fig. 4.4 (b)), and showed a multilayered shell structure. Fig. 4.5 (a, b, c) shows the XRD, Raman spectroscopy, and TGA results, respectively, of the precursor and product materials. The diffractogram revealed the presence of graphitized carbon structures, as evidenced by the diffraction peak at approximately 26°, arising from the scattering of 00l plane atoms (Iwashita, 2016). Induction annealing of the precursor led to its complete conversion to graphene-like carbon, as indicated by the complete mass loss in TGA at 900 °C (Fig. 4.5 (c)). Raman spectroscopy was used to verify the presence of graphene domains and defects. The Raman spectrum displayed typical peak values for graphene: a single Lorentzian 2D peak at 2700 cm⁻¹ with a FWHM of 24.4 cm⁻¹ and a G peak at 1581 cm⁻¹. The presence of a low-intensity D peak at 1349 cm⁻¹, which arises from local defects such as flake edges or in-plane defects, indicates that the produced material had only minor defects (Lui et al., 2011).
Figure 4.4: a) SEM image of graphene-like carbon synthesized from nSiC/C at 2400 °C, b) TEM image of graphene-like carbon synthesized from nSiC/C at 2400 °C. (Published in paper III.)

Figure 4.5: a) X-ray diffractograms of nSiC/C precursor and graphene-like carbon, b) Raman spectrum of graphene-like carbon, c) TGA curves of commercial SiC, precursor (nSiC/C), and graphene-like carbon after annealing. (Published in paper III.)
4.2 Doped carbon structures

4.2.1 Silicon/carbon structures and transition to SiC

In paper II, carbon-coated silicon (Si@C) structures were synthesized from a Si/C composite by induction annealing at 1000 °C. The XRD pattern (inscription over the 1000 °C diffractogram in Fig. 4.2 (a)) shows the presence of trace amounts of SiC at this temperature. However, SiC formation was considerably slow at this temperature, which enabled the formation of a carbon shell instead of forming carbides. As seen in Fig 4.6 (a), the amorphous carbon was situated interstitially between the SiNPs and as layers of approximately 5 nm thickness on top of the SiNPs. The amorphous nature of the carbon was verified by the XRD pattern (Fig. 4.2 (a)), which displayed no crystalline carbon, as all the peaks were ascribed to silicon. This was supplemented by TGA measurements (Fig. 4.2 (c)), which showed a low combustion onset temperature (~350 °C), which is typical for amorphous carbon (Sun et al., 2016).

Annealing of the Si/C composite at 1400 °C resulted in a phase transition, and the amorphous carbon reacted with silicon to form SiC-3C (Fig. 4.6 (b)). The complete reaction of silicon was confirmed by XRD, and the diffractogram contained peaks belonging only to SiC-3C (Fig. 4.2 (a)). The TGA analysis revealed no loss of mass (carbon combustion), which proved that the carbon had completely reacted with the silicon to form SiC-3C. Annealing at 1800, 2000, and 2200 °C promoted the formation of larger and more deformed particles (Fig. 4.6 (c, d, e)), as a result of SiC particle sintering. This produced irregularly shaped hard agglomerates, which were observed via SEM as having sizes of up to 100 µm. Annealing at these temperatures also resulted in larger SiC crystallites compared to those at 1400 °C. This was evident from the XRD results, which showed narrower and sharper SiC-3C peaks at these temperatures. However, at 2400 °C, the particle size of SiC decreased significantly to sizes below 100 nm, owing to intense Si sublimation (Fig. 4.6 (f)). In addition, while SiC-3C was still the dominant polytype at all temperatures, the XRD data of the samples treated at 2200 and 2400 °C revealed the presence of new SiC polytypes, namely SiC-6H and SiC-15R. These polytypes became more prominent at higher temperatures, and their formation is explained by the partial transition of the metastable polytype SiC-3C (Yoo et al., 1991). Owing to the graphene growth process mentioned in Section 4.1, the SiC particles synthesized at temperatures from 1800 to 2400 °C possessed layers of graphene atop the surface. Particularly at 2400 °C, sublimation was most intense, resulting in the creation of thick graphite layers. This subsequently led to a significant shrinkage of the core SiC particles (Fig. 4.6 (f)).
Figure 4.6: Synthesized products from annealing the Si/C precursor: a) carbon-coated silicon (Si@C) produced at 1000 °C, b) SiC particles produced at 1400 °C, c) agglomerated SiC particles produced at 1800 °C, d) agglomerated SiC particles produced at 2000 °C, e) agglomerated SiC particles produced at 2200 °C, d) graphite-coated SiC (SiC@graphite) produced at 2400 °C (Published in paper II)
4.2.2 Iron-doped carbon structures

The characteristics of the Fe/graphene material produced in paper IV are shown in Fig. 4.7. As observed in the SEM images and the EDS map (Fig. 4.7 (a, b)), the bulk volume of the material was composed of few-layer graphene sheets with embedded cubic Fe particles. The TGA analysis (Fig. 4.7 (c)) revealed a mass drop between 640 and 700 °C, which can be attributed to the combustion of graphitic carbon (Kamali et al., 2015). This carbon combustion accounted for 85 wt % of the total mass, while the remaining 15 wt % was attributed to Fe. The carbon and iron phases were identified by XRD, as shown in Fig. 4.7 (d). Carbon was confirmed to be partially graphitized, as evidenced by the broad peak at 25.5° (Goodwin et al., 1997; Howe et al., 2003). Two iron phases were identified from the peak positions in the diffractogram, namely, α-Fe and γ-Fe (Hoch et al., 2008). The quality of graphene in the Fe/graphene composite was analyzed by Raman spectroscopy, and the spectra are shown in Fig. 4.7 (e). The peak at 1380 cm\(^{-1}\) is called the D peak and is associated with edge or in-plane defects. The peak at 1590 cm\(^{-1}\) is called the G peak and is associated with sp\(^2\) bond stretching in chains and rings (Ferrari et al., 2001). The remaining 2D peak at 2673 cm\(^{-1}\) is typically associated with the presence of graphitic features (Ferrari et al., 2013).

The surface area of the Fe/graphene was 306 m\(^2\) g\(^{-1}\), and the average pore size was determined to be approximately 4 nm. These results differed from those of the initial pristine graphene with a surface area of 575 m\(^2\) g\(^{-1}\) and a pore size distribution between 5 and 300 nm (Fig. 4.7 (f)). The change in pore size was attributed to the absorption of FeCl\(_3\) onto graphene, filtration, and atmospheric drying (95 °C). All of these may have caused the densification of graphene and the loss of interparticle voids.

The surface functional groups present on graphene were determined via x-ray photoelectron spectroscopy (XPS). The deconvolution results indicated the presence of four chemical states: 284.78 eV (C=C; 30 % area), 285.03 eV (C-C; 34.9 % area), 286.57 eV (C-OH/C-O-C; 9.7 % area), 289.2 eV (C=O/O-C-C; 25.4 % area). The deconvolution of the O(1s) spectra revealed only one chemical state at 532.52 eV (C=O/O-C-C, 100 % area) which was expected, as the graphene precursor had an oxygen content of up to 2.5 wt % (Da Silva et al., 2014). In addition, the paramagnetic properties of the Fe/graphene composite were confirmed by the introduction of an permanent magnet, which attracted part of the Fe/graphene composite particles. Paramagnetic properties of iron structures are likely formed by annealing above 727 °C and are mostly due to α-Fe, since γ-Fe is nonmagnetic (Ruskov et al., 2006; Leonov et al., 2011; Boi et al., 2014).
4.2.3 Gold-doped carbon structures

The doping of CNFs with AuNPs was performed by the ultrasonication of CNFs and 1-dodecanethiol-stabilized AuNPs in an EtOH/hexane (50/50 v/v %) mixture. The introduction of gold nanoparticles (AuNPs) into CNFs is known to (1) improve charge transfer by physically bridging CNF particles, and (2) enable photocurrent generation (light harvesting) by plasmon resonance effect (Kiang Chua et al., 2013; Notarianni et al., 2014). The surface
plasmon effect was verified by UV–vis analysis. The AuNP/CNF suspension in EtOH/hexane showed a peak at 530 nm, which is a characteristic attributed to surface plasmon resonance arising due to the oscillation of electrons in the conduction band (Goncalves et al., 2009; Pruneanu et al., 2013). Fig. 4.8 (a, b) shows the SEM images of a fragment of the deposited AuNP/CNF film and a TEM image of the AuNP/CNF suspension that was drop cast onto a TEM grid, respectively. In both cases, the AuNPs appeared as small spherical particles on top of the CNF structure’s surface. Fig. 4.8 (c) shows the BSE image of the AuNP/CNF film. The contrast difference originates from the difference in atomic mass of the elements, and the gray areas in the image represent carbon, whereas the light dots represent AuNPs. The AuNPs were embedded in the volume of the CNF film mostly as single particles or agglomerates of 2–5 particles. However, larger (180 nm) gold agglomerates were also observed. The occurrence of agglomerated structures was attributed to the loss of bonded 1-dodecanethiol ligands from the AuNP surface, which acts as a steric barrier to prevent attraction between the AuNPs (Moon et al., 2010). Cleavage of the gold–dodecanethiol bond (Au–S) could be a result of ultrasonication to prepare the suspension. Sonication induces acoustic cavitation in the suspension, resulting in the formation and subsequent collapse of bubbles. Cavitation generates brief microsecond spikes in pressure and temperature, producing enough energy to cleave some of the covalent Au-S bonds and desorb the ligand from the AuNP surface (Jin et al., 2007).

Figure 4.8: a) SEM image, b) TEM image, and c) backscattered electron image of AuNP/CNF material, d) EDS spectra obtained from the region shown in (c). (Published in paper I.)
4.3 Carbon nanoflower suspensions and thin films

4.3.1 Suspension stability studies

First, the extinction coefficient ($\alpha$) was obtained to estimate the mass of CNFs in the suspension after centrifugation. The extinction coefficient is an intrinsic material property that describes the interaction of materials (absorption) with light. The CNF particles were first dispersed in NMP. Fig. 4.9 (a) shows a series of absorption spectra obtained from the dispersion of CNFs in NMP. The absorption values were obtained from a featureless region ($\lambda = 660$ nm), and the extinction coefficient was calculated using the Lambert–Beer law. The coefficient was found to be 3098 mL mg$^{-1}$ m$^{-1}$ and was comparable to that of graphene exfoliated in NMP (3620 mL mg$^{-1}$ m$^{-1}$), which indicates that CNFs have optical properties similar to those of graphene sheets (Khan et al., 2010).

CNF suspensions were prepared in different organic solvents, as shown in Table 2. The table lists the HSPs of the solvents used, calculated $R_A$ values, and the estimated suspended CNF (wt %) after centrifugation. Initially, UV–vis measurements ($A_0$) were carried out for the prepared suspensions to rank the solvents from best to worst according to the measured absorbance values. The best solvent for dispersing CNFs was NMP with an absorption value of 0.62, and the worst solvent was hexane (0.01). The solvents were ranked, based on their performance, as follows: NMP (0.62), DMF (0.59), butanol (0.50), EtOH (0.42), toluene (0.20), and hexane (0.01). The measured absorbance values were plotted against the calculated $R_A$ values to verify the validity of the HSP theory for estimating suitable solvents for the preparation of CNF dispersions. A linear trend was observed in the data (Fig. 4.8 (b)), indicating that the selection of well-dispersing solvents by means of $R_A$ calculations is viable. However, toluene and hexane were outliers, and their performance did not follow the prediction. This can be attributed to the low/absent values of $\delta_p$ and $\delta_H$ compared to the other solvents. These findings indicate that solvent polarity and electron-donating groups are necessary in CNF suspensions (Hernandez et al., 2010; Tessonnier et al., 2012). Later, the same suspensions were centrifuged to sediment weakly suspended SiC crystals and graphene/CNF aggregates. The supernatants were sonicated, and their absorbances were measured once more via UV–vis spectroscopy. The solvent absorbance values followed the order of the previous series in terms of the measured intensity: NMP (0.52), DMF (0.39), butanol (0.19), EtOH (0.05), toluene (0.006), and hexane (0.001).

Toluene and hexane demonstrated the poorest performance as dispersing solvents. However, they are of interest in the deposition process owing to their low boiling points. Thus, hexane and toluene were mixed with ethanol to tune their solubility parameters, namely $\delta_p$ and $\delta_H$, and thus, improve the CNF suspensions. Ethanol was chosen because of its relatively high values of $\delta_p$ (8.8) and $\delta_H$ (19.4) compared to those of hexane ($\delta_p = 0$, $\delta_H = 0$) and toluene ($\delta_p = 1.4$, $\delta_H = 2$). The new solubility parameter of the mixture is equal to the sum of the corresponding solubility parameters multiplied by their respective volume fractions in the mixture (Eq. 1). The fraction of ethanol added was chosen by interpolation to achieve the smallest $R_A$ value using Eq. 2. The volume ratios of EtOH/hexane and EtOH/toluene were 40/60 v/v % and 50/50 v/v %, respectively. The $\delta_d$ values of the new mixtures differed only
by 3–5% from those of pure hexane and toluene. Such a change is considered to have a negligible effect on the suspension properties; most effects occur due to the increase in \( \delta_p \) and \( \delta_H \). The absorption values \((A_0 \text{ and } A_1)\) of the EtOH/hexane and EtOH/toluene mixtures are plotted in Fig. 4.9 (b). The addition of EtOH showed improvement in dispersion over pure solvents for EtOH/hexane \((A_0, \quad 0.205 \rightarrow 0.553)\) and EtOH/toluene \((A_0, \quad 0.014 \rightarrow 0.62)\), as reflected by the increased absorbance values. However, the post-centrifugation absorbance \((A_1)\) measurements showed a significant decrease compared to \(A_0\) and reflected poor suspension stability. To represent the absorbance measurements in a more quantitative form, the previously calculated extinction coefficient was used to calculate the mass percent \((\Delta m\%)\) of the suspended CNF remaining after centrifugation, as shown in Table 2. For both pure solvents (hexane and toluene) and their mixtures (EtOH/hexane, EtOH/toluene), \(\Delta m\) was less than 1%. This suggests that the mechanism (or its magnitude) for the initial CNF dispersion is not identical to that involved in long-term CNF suspensions.

Figure 4.9: a) Absorbance spectra of a CNF dilution series suspended in NMP (calibration curve of CNF in NMP measured at \( \lambda = 660 \text{ nm} \)), b) Pre-centrifugation (\(A_0\)) and post-centrifugation (\(A_1\)) absorbance values of CNF suspended in various solvents plotted against \(R_A\). (Published in paper I.)

Table 2: Solvent HSPs, calculated \(R_A\), and remaining CNF mass (\(\Delta m\)) post centrifugation. (Published in paper I.)

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Mixture</th>
<th>Hansen Solubility Parameters</th>
<th>(R_A)</th>
<th>(\Delta m)%</th>
</tr>
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<tbody>
<tr>
<td></td>
<td></td>
<td>(\delta_{\text{MPS}}^{\text{1/2}})</td>
<td>(\delta_{\text{HMPs}}^{\text{1/2}})</td>
<td></td>
</tr>
<tr>
<td>NMP</td>
<td>-</td>
<td>18.0</td>
<td>12.3</td>
<td>7.2</td>
</tr>
<tr>
<td>DMF</td>
<td>-</td>
<td>17.4</td>
<td>13.7</td>
<td>11.3</td>
</tr>
<tr>
<td>Butanol</td>
<td>-</td>
<td>16.0</td>
<td>5.7</td>
<td>15.8</td>
</tr>
<tr>
<td>Ethanol</td>
<td>-</td>
<td>15.8</td>
<td>8.8</td>
<td>19.4</td>
</tr>
<tr>
<td>Toluene</td>
<td>-</td>
<td>18.0</td>
<td>1.4</td>
<td>2.0</td>
</tr>
<tr>
<td>EtOH/Tol</td>
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<td>17.1</td>
<td>4.4</td>
<td>9.0</td>
</tr>
<tr>
<td>EtOH/Hex</td>
<td>50/50</td>
<td>15.4</td>
<td>4.4</td>
<td>9.7</td>
</tr>
<tr>
<td>Hexane</td>
<td>-</td>
<td>14.9</td>
<td>0.0</td>
<td>0.0</td>
</tr>
</tbody>
</table>
4.3.2 Thin film characteristics

Table 3 presents the properties of the thin films prepared from the EtOH/hexane CNF suspensions. The table shows the thicknesses of the thin films measured via SEM and the surface area (%) of the substrate covered by the CNF thin film. Furthermore, the table contains the transmittance data obtained from UV–vis measurements. Suspensions of CNF (0.2 mg mL\(^{-1}\)) in EtOH/hexane (50/50 v/v %) were used to deposit thin films, which were then transferred onto transparent PTFE substrates. The influence of the deposition time on the film thickness and surface area coverage was studied systematically. A top view of the transferred films is shown in Fig. 4.10. The CNF films appear to be islands of agglomerated CNF particles, as indicated by the appearance of spherical CNFs (inset Fig. 4.10 (c)). Increased magnification of the films revealed graphene sheets and SiC crystals embedded in the CNF matrix (insets Fig. 4.10 (a, b)). The increase in spray time resulted in more interconnected and denser islands on the substrate. It was discovered via SEM that prolonging the spraying time from 4 to 21 min increased the surface coverage from 31 to 83 %. The side view of the transferred CNF films is shown in Fig. 4.10 (e, f, g, h). The G-4 film (Fig. 4.10 (e)) displayed the most uniform surface morphology; however, a random increase in thickness was observed at the terminating edges of the CNF island. The thinnest observable regions were approximately 43 nm thick, which corresponds to a mono/bi-layer of CNFs, whereas the thickest regions were 1.2 µm thick. Upon increasing the spray time, the overall thickness and variation in the surface morphology increased. The observed minimum and maximum thicknesses for samples G-7, G-14, and G-21 were (66 nm; 2.1 µm), (120 nm; 1.3 µm), and (130 nm; 2.5 µm), respectively. Regions of varying thickness on the same film can be attributed to the tearing path inside the film during the transfer process. During the transfer process, tearing occurred between the CNF particles. Owing to the varying size distribution of the CNF particles, the packing efficiency varies with the volume of the film. This variation gives rise to regions where film tearing is more favorable owing to smaller CNF interparticle contact areas.

The UV–vis transmittance data presented in Table 3 correlate well with the SEM thickness measurements, that is, thinner films displayed higher transmittance and vice versa. The average transmittance (%) calculated from multiple measurements across the diameter of each film ranged from 63 to 27 % for the thinnest (G-4) and thickest (G-21) films, respectively. It is worth noting that the variation in transmittance values was influenced not only by the varying film thickness but also by the surface coverage. The UV–vis equipment had no optical viewing system for the user to guide the measurement beam. Thus, the area for transmittance measurements may include both thinner and thicker regions, as well as regions where the substrate may not be completely covered by the CNF film.
Table 3: Substrate surface coverage, thickness, and transmittance results of the transferred CNF films. (Published in paper I.)

<table>
<thead>
<tr>
<th>Sample</th>
<th>AuNP conc. [mg/mL]</th>
<th>Thickness [min;max [nm]]</th>
<th>Coverage [%]</th>
<th>Transmittance [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>G-4</td>
<td></td>
<td>43; 1200</td>
<td>31.2 ± 5.9</td>
<td>63.9 ± 0.7</td>
</tr>
<tr>
<td>G-7</td>
<td></td>
<td>66; 2100</td>
<td>41.7 ± 6.1</td>
<td>48.7 ± 2.7</td>
</tr>
<tr>
<td>G-11</td>
<td></td>
<td>120; 1300</td>
<td>65.2 ± 6.1</td>
<td>54.5 ± 1.8</td>
</tr>
<tr>
<td>G-21</td>
<td></td>
<td>2440</td>
<td>83.3 ± 13.9</td>
<td>27.1 ± 2.1</td>
</tr>
<tr>
<td>AuNP/CNF - 0.25</td>
<td>0.05</td>
<td>-</td>
<td>57.2 ± 4</td>
<td>80.8 ± 1.9</td>
</tr>
<tr>
<td>AuNP/CNF - 0.5</td>
<td>0.1</td>
<td>-</td>
<td>36.2 ± 7.4</td>
<td>77.4 ± 5.4</td>
</tr>
</tbody>
</table>

Figure 4.10: SEM images of transferred CNF films: a) sample G-4 (inset of embedded SiC crystal), b) sample G-7 (inset of protruding graphene sheets), c) sample G-11 (inset of CNF particles composing the film at a higher magnification), d) sample G-21, e) side view of G-4, f) side view of G-7, g) side view of G-11, h) side view of G-21. (Published in paper I.)
4.4 Application of Si@carbon and SiC@graphite in Li-ion batteries

In paper II, the fabricated Si@C and SiC@graphite were electrochemically tested as anode materials in Li-ion coin cells. Fig. 4.11 shows the electrochemical testing results of the pure silicon and Si@C anode materials. The high-temperature annealing (1000 °C) of silicon and barley straw-derived carbon created interstitial carbon sites as well as ~5 nm thick carbon coats on the silicon particles. This resulted in an improved cycling stability over the bare silicon anode. Fig. 4.11 (a) displays the rate capability curves for a pure silicon electrode. After 10 cycles, the specific capacity of the pure Si electrode dropped significantly from 2100 to 700 mAh g\(^{-1}\). The initial capacity was not restored after the current density was set back from 1.0 to 0.1 A g\(^{-1}\); this was attributed to the Si pulverization phenomenon during cycling (Hass et al., 2008). For the carbon-coated silicon electrode (Fig. 4.11 (d)), the rate capability testing did not display such a capacity drop and was attributed to the protective carbon layer. Furthermore, the improved capacity retention was comparable to that of other biomass-based Si/C composites reported in literature (Liu et al., 2009, 2012; Hwa et al., 2012; Shao et al., 2013).

The electrochemical results of the SiC@graphite material are shown in Fig. 4.12. However, the composite material did not perform well. The CV curves of the SiC@graphite electrode (Fig. 4.12 (b)) did not display peaks that are typically visible for the SiC material. We believe that the graphite shell on the SiC cores was too thick and prevented Li ions from intercalating into the SiC. This finding proves the importance of controlling the thickness of the graphite layer to allow SiC participation in electrochemical reactions. However, even though SiC was inactive in the electrochemical reactions, the biomass-grown graphite displayed a capacity of 78 mAh g\(^{-1}\). At 24 wt % (according to TGA), the biomass-derived graphite displayed a capacity value that corresponded to an electrode containing 21 wt % of commercial graphite.
Figure 4.11: Bare Si electrode: a) charge–discharge curves, b) CV curves, c) rate capability curves; Si@C electrode: d) charge–discharge curves, e) CV curves, f) rate capability curves. (Published in paper II.)

Figure 4.12: SiC@graphite electrode: a) charge–discharge curves, b) CV curves, c) rate capability curves. (Published in paper II.)
4.5 Application of Fe/graphene in tetracycline adsorption

The iron-embedded graphene sheet composite (Fe/graphene) produced in Paper IV was applied in tetracycline adsorption studies. The parameters for the tetracycline adsorption experiments are listed in Table 4. Increasing the Fe/graphene adsorbent mass in the adsorption column from 25 to 50 mg resulted in an improved total removal efficiency from 65.0 to 76.4 % (Experiment 2). This result was attributed to the greater availability of adsorption sites due to the increase in adsorbent material (Honeyman et al., 1988). Additionally, the column width dimension was fixed; thus, introducing more Fe/graphene into the column increased its occupied column volume in the vertical direction. This provided a longer contact time and, consequently, a greater diffusion depth between Fe/graphene and tetracycline, which contributed to the improved removal efficiency. Similar findings were reported by Golie et al., in which an increase in column height led to an improvement in the adsorption of NO₃ from water utilizing a chitosan/alumina composite (Golie et al., 2016).

The influence of the increased influent flow rate (Q) was studied under a constant influent tetracycline concentration (C₀) and constant Fe/graphene adsorbent amount (Mₐ) in the column. A higher flow rate improved the sorption kinetics, which decreased the breakthrough time from 140 to 90 min and reduced the operation time from 530 to 210 min. However, the high flow rate had a negative impact on the removal efficiency, which decreased from 65.0 to 55.2 %. This decrease is attributed to the reduced contact time between the pollutant and Fe/graphene adsorbent in the column. Therefore, the full capacity of the adsorbent was not utilized. In addition to the flow rate, the adsorption performance was also influenced by the influent concentration. Experiments 1 and 4 in Table 4 depict two experiments with constant adsorbent amount and influent flow rate but varied influent tetracycline concentrations (25 mg L⁻¹ and 50 mg L⁻¹). The increase in the concentration did not influence the removal efficiency. However, the breakthrough point was lowered and the total operation time decreased. In addition, with increasing influent concentration, the adsorption capacity and total adsorbed quantity decreased from 422 to 363 mg g⁻¹ and from 10.5 to 9.0 mg, respectively. The total volume of the treated influent also decreased from 636 to 288 mL, while the non-adsorbed tetracycline concentration at equilibrium increased from 8.93 to 17.67 mg L⁻¹.
Table 4: Experimental table of tetracycline adsorption: $c_0$ – initial TC concentration, $M_a$ – Fe/graphene adsorbent amount, $Q$ – flow rate, $t_b$ – breakthrough time, $t_{total}$ – total operation time, $q_{total}$ – total adsorbed quantities, $q_{bed}$ – maximum adsorption capacities, $m_{total}$ – adsorbate amount delivered to column, $Y\%$ - total removal efficiency, $V_{eff}$ – total treated volumes, $C_{eq}$ – unadsorbed adsorbate concentration

<table>
<thead>
<tr>
<th></th>
<th>$C_0$ (mg/L)</th>
<th>$M_a$ (mg)</th>
<th>$Q$ (mL/min)</th>
<th>$t_b$ (min)</th>
<th>$t_{total}$ (min)</th>
<th>$q_{total}$ (mg)</th>
<th>$q_{bed}$ (mg/g)</th>
<th>$m_{total}$ (mg)</th>
<th>$Y%$</th>
<th>$V_{eff}$ (mL)</th>
<th>$C_{eq}$ (mg/L)</th>
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<td>25</td>
<td>1.20</td>
<td>140</td>
<td>530</td>
<td>10.56</td>
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<td>16.24</td>
<td>65.02</td>
<td>636</td>
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</tr>
<tr>
<td>Experiment 2</td>
<td>25</td>
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<td>1.20</td>
<td>400</td>
<td>620</td>
<td>14.26</td>
<td>285.20</td>
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<td>76.46</td>
<td>744</td>
<td>5.90</td>
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<tr>
<td>Experiment 3</td>
<td>25</td>
<td>25</td>
<td>2.50</td>
<td>90</td>
<td>210</td>
<td>7.33</td>
<td>293.20</td>
<td>13.28</td>
<td>55.20</td>
<td>525</td>
<td>11.33</td>
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<tr>
<td>Experiment 4</td>
<td>50</td>
<td>25</td>
<td>1.20</td>
<td>100</td>
<td>240</td>
<td>9.09</td>
<td>363.60</td>
<td>14.18</td>
<td>64.10</td>
<td>288</td>
<td>17.67</td>
</tr>
</tbody>
</table>

**Self-regeneration**

<table>
<thead>
<tr>
<th></th>
<th>$C_0$ (mg/L)</th>
<th>$M_a$ (mg)</th>
<th>$Q$ (mL/min)</th>
<th>$t_b$ (min)</th>
<th>$t_{total}$ (min)</th>
<th>$q_{total}$ (mg)</th>
<th>$q_{bed}$ (mg/g)</th>
<th>$m_{total}$ (mg)</th>
<th>$Y%$</th>
<th>$V_{eff}$ (mL)</th>
<th>$C_{eq}$ (mg/L)</th>
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<td>140</td>
<td>530</td>
<td>10.56</td>
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<td>25</td>
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<td>260</td>
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<td>7.96</td>
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<tr>
<td>Cycle 3</td>
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<td>120</td>
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<td>25</td>
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<td>–</td>
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<td>660.51</td>
<td>27.88</td>
<td>–</td>
<td>1092</td>
<td>–</td>
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</tbody>
</table>
Tetracycline-saturated Fe/graphene was tested for self-regeneration using a series of adsorption cycles. After each adsorption cycle, the peristaltic pump was shut down and the material was left to stay packed in the column overnight until a new cycle was started. The three adsorption cycles lasted 530, 260, and 30 min, resulting in adsorption capacities of 422.4, 159.6, and 62.4 mg g\textsuperscript{-1}, respectively. The ability of the material to self-regenerate during sequential cycles increased the total adsorption capacity and enabled the treatment of larger volumes of the solution. It is known that the chelating behavior of iron and tetracycline family compounds promotes their degradation (Wang et al., 2016 b). Fe\textsuperscript{0} has been shown to have a strong reducing power, whereas Fe\textsuperscript{III} has been reported to cause oxidative degradation (Chen et al., 2011; Wang et al., 2015 a). Additionally, certain activated mesoporous carbons, with surface areas around 1500–2000 m\textsuperscript{2} g\textsuperscript{-1} and functional oxygen groups, have been reported to be capable of removing tetracycline (Chen et al., 2017 b). It has been suggested that carbon materials and tetracycline interact through π–π electron coupling, and surface oxygen groups have been reported to improve adsorption efficiency (Ji et al., 2009; Yu et al., 2014). One reason for the increased adsorption capacity of Fe/graphene in the regeneration studies could be the formation of sites for adsorption due to the oxidation of metallic Fe\textsuperscript{0} by slightly acidic water (Cao et al., 2018). Indeed, Raman analysis of post-adsorption Fe/graphene displayed two new peaks at 219 cm\textsuperscript{-1} and 283 cm\textsuperscript{-1}, which originated from Fe\textsubscript{2}O\textsubscript{3} (Vereda, 2016). The degradation of tetracycline was expected to produce products. Thus, to fully understand the mechanism, the degradation products of tetracycline were analyzed from the effluent using mass spectrometry. The reference tetracycline sample analysis spectrum displayed a protonated molecule at m/z 455 and a sodium adduct at m/z 467. While the treated effluent samples displayed only a minor signal of tetracycline, which is consistent with the adsorption, it did not show any dissociation products. The absence of degradation products in the mass spectra could be due to the attachment of the products to the graphene matrix through a variety of interactions—π–π electron donor interactions, Van der Waals forces, or through cation exchange when oxygen groups are present (Ji et al., 2009; Yu et al., 2014).
5 Conclusions

A substantial amount of work has been dedicated to nanomaterial advancements, particularly for carbon-related materials. The fascination with these materials is justified by their unique properties and the possibility that these materials can be tailored for numerous applications. However, application-specific research as well as improvements in the development of large-scale, defect-free, and greener synthesis methods is needed.

In this work, the synthesis and characteristics (composition, crystallinity, phase, agglomeration, shape, and size) of Si@C, SiC@graphite, Fe/graphene, and graphene-like carbon were studied. In addition, application studies were carried out, specifically, electrochemical testing of Si@C, SiC@graphite as anode materials for Li-ion batteries, and Fe/graphene as a tetracycline adsorbent in water purification studies. CNF nanomaterial dispersion studies were also conducted to investigate the influence of the Hansen solubility parameter on the CNF dispersion quality and stability in organic solvents.

First, it was demonstrated that the initial dispersion quality of CNF nanoparticles suspended in organic solvents can be estimated using Hansen solubility parameters. The application of Hansen solubility parameters enabled the creation of a well-dispersed mixture from two low-boiling-point, poorly dispersing solvents. This was achieved by mixing ethanol with hexane and toluene. Their volume ratios were chosen in accordance with their dispersive, polar, and hydrogen solubility parameter affinities with CNFs. The prepared suspensions were used to deposit thin films of CNFs. The CNF film thickness and substrate area coverage increased proportionally with the deposition time.

Second, the study demonstrated that cheap and green carbon feedstock (barley husk/straw) can be utilized to produce graphene-like carbon and carbon coatings for Si. The product yield of induction annealing was 100% graphene-like carbon material with minor structural defects, as indicated by TGA and Raman analysis. Furthermore, the induction annealing temperature had a profound effect on the characteristics of the Si/C composite precursor. This finding enables the selection of appropriate temperatures to control the phase and carbon structure originating from the Si/C precursor. At a low temperature of 1000 °C, the carbon maintained its amorphous form and acted as a coating to silicon nanoparticles (Si@C). However, an increased annealing temperature of greater than 1400 °C resulted in the formation of SiC and SiC@graphite, and the subsequent sublimation of silicon. The sublimation process caused the formation of graphite and its continued growth at high temperatures. In comparison to the bare Si anode, the synthesized Si@C showed improved capacity retention after increasing the current from 0.1 to 1 A g⁻¹. Furthermore, it was found that the synthesized SiC core (SiC@graphite) did not participate in the electrochemical reactions. However, the synthesized biomass-derived graphite displayed electric capacities similar to those of commercial graphite.

Finally, a Fe/graphene composite was synthesized in which α-Fe and γ-Fe particles were embedded in graphene sheets. The composite material showed the ability to adsorb tetracycline from water, self-regenerate, and further improve the tetracycline removal efficiency.
The removal efficiency was dependent on the composite loading ratio, liquid flow rate, and initial pollutant concentration.

Further research is required to optimize the synthesized nanomaterials to achieve the best performance in their respective applications. More in-depth studies are required to gain the ability to control the three-dimensional structure and thickness of carbon coatings for silicon composites. Furthermore, an in-depth TEM study of the graphene growth process would be of high interest to the author, especially at the initial growth temperature. Additionally, the self-regeneration mechanism in Fe/graphene is not yet fully understood and requires further study.
References


COM/2020/474, 2020: Communication from the commission to the european parliament, the council, the european economic and social committee and the committee of the regions critical raw materials resilience: Charting a Path towards greater Security and Sustainability COM/2020/.


with Corn Starch Biowaste as Anode Materials for Li-Ion Batteries. *Nano Letters.*, 20, 625–635.


Ren, M. M.; Zhou, Z.; Gao, X. P.; Peng, W. X.; Wei, J. P., 2008: Core-shell Li3V2(PO4)3@C composites as cathode materials for lithium-ion batteries. *Journal of Physical Chemistry C.*, 112, 5689–5693.


Sadowski, H.; Helbig, R., 1998: Sublimation studies of SiC by using a quadrupole mass...


Version, D., 2016: Spintronics and thermoelectrics in exfoliated and epitaxial graphene van den Berg, Jan Jasper Publication date :, 10–12.


Wu, H.; Du, N.; Shi, X.; Yang, D., 2016: Rational design of three-dimensional macroporous silicon as high performance Li-ion battery anodes with long cycle life. *Journal of Power Sources.*, 331, 76–81.

Xie, J.; Tong, L.; Su, L.; Xu, Y.; Wang, L.; Wang, Y., 2017: Core-shell yolk-shell Si@C@Void@C nanohybrids as advanced lithium ion battery anodes with good electronic conductivity and corrosion resistance. *Journal of Power Sources.*, 342, 529–536.

Xu, R.; Zhang, K.; Wei, R.; Yuan, M.; Zhang, Y.; Liang, F.; Yao, Y., 2020: High-capacity flour-based nano-Si/C composite anode materials for lithium-ion batteries, 1–11.

Xu, Y.; Yin, G.; Ma, Y.; Zuo, P.; Cheng, X., 2010: Nanosized core/shell silicon@carbon anode material for lithium ion batteries with polyvinylidene fluoride as carbon source. *Journal of Materials Chemistry.*, 20, 3216–3220.


Zhao, W.; Wen, J.; Zhao, Y.; Wang, Z.; Shi, Y.; Zhao, Y., 2020: Hierarchically porous carbon derived from biomass reed flowers as highly stable li-ion battery anode. *Nanomaterials.*, 10, 1–11.


Synthesis of graphene-like carbon from agricultural side stream with magnesiothermic reduction coupled with atmospheric pressure induction annealing

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Keywords: agricultural side stream, biomass, graphitization, induction annealing, atmospheric pressure, magnesiothermic reduction, pyrolysis

Abstract

Generally, large-scale production of graphene is currently not commercially viable due to expensive raw materials, complexity and the high-energy consumption of the processes currently used in the production. The use of biomass precursors and energy efficient procedures for carbonization have been proposed to reduce the cost of the graphene materials. However, low-cost graphene production has not been accomplished yet. Herein, we present a sustainable procedure and renewable starting materials to synthesize carbon nanostructures with graphene-like features. First, a SiC/C composite was synthesized from phytoliths and sucrose through magnesiothermic reduction. The phytoliths were obtained from barley husk that is an abundant side stream of agricultural industry. Second, graphene-like structures were achieved by the graphitization of SiC/C composite with high temperature induction annealing at 2400 °C under atmospheric pressure. The formation of graphene-like carbon was initiated by vaporization of silicon from the pre-ceramic SiC/C. Complete transformation of SiC/C to hollow, spherical graphene-like carbon structures and sheets were verified with thermogravimetry, x-ray diffraction, energy dispersive spectroscopy, electron microscopy and Raman spectroscopy. Also, the theoretical thermodynamic consideration of the phase separation of silicon carbide and the role of free carbon in the process has been discussed.

1. Introduction

Graphene is a single atom layer thick sheet of carbon that was first found in 2004 [1, 2]. The unique electrical, thermal and optical properties of graphene combined with its mechanical integrity have attracted attention since its discovery [3]. Variable techniques have been reported to produce graphene but the most common techniques to produce graphene sheets, platelets and flakes still rely on methods such as exfoliation of graphite, epitaxial growth on SiC substrate and chemical vapor deposition (CVD). High-quality graphene is produced mainly with the energy intensive CVD method [4].

From the industrial production point of view these techniques suffer from high cost, low purity, heterogeneous features and limited upscaling [5, 6]. For this reason more sustainable and cost-efficient methods and starting materials are needed for the production of high purity graphene [7]. Utilization of biomass would reduce starting material cost but production of graphene from it is challenging particularly, when thermal treatment techniques are used. Thermally treated biomass typically results in partially ordered amorphous carbon/graphene stack composites, and carbon structures composing of randomly organized small crystalline domains. In addition, biomasses contain inherently heteroatoms (H/N/O/S) bound to carbon and other elements (K, Na, Mg, Fe etc), which can be problematic in the synthesis [8–10]. Therefore, approaches such as the use of catalysts or the pre-treatment of the biomass are required to obtain ordered graphitic or graphene-like
Nanostructured silicon carbide (nSiC) can be produced through several synthetic routes such as CVD, sol-gel process, thermal or laser ablation from organic compounds but also derived from biomass [17, 18]. However, current techniques often require expensive precursors, and toxic reactants that result in highly agglomerated husk using magnesiothermic reduction coupled with atmospheric pressure induction annealing. First, the gel process, thermal or laser ablation from organic compounds but also derived from biomass nanostructured SiC with high purity, uniform size and morphology, while, strong agglomeration of the SiC particles can be prevented [17, 19–21]. Furthermore, MTR can be considered a sustainable approach to synthesize nSiC due to its low energy consumption, short reaction time and low temperature compared to the carbothermal reduction process known as the Acheson process [18, 22].

Herein, we report an alternative method for production of graphene-like carbon nanostructures from barley husk using magnesiothermic reduction coupled with atmospheric pressure induction annealing. First, the biomass based nanostructured silica (nSiO2, phytoliths) was extracted from barley husk. Phytoliths are amorphous silica materials with porous structure that are produced by specific plants like barley, rice and sugarcane. Second, nSiO2 and a small amount of carbohydrate in the form of sucrose was converted into silicon carbide/carbon composite (nSiC/C) using magnesiothermic reduction. Third, graphene-like structures were formed via nSiC/C dissociation at 2400 °C under atmospheric pressure using induction annealing. As the result, the formation of carbon materials through the complete removal of Si was accomplished and the product was a mixture of partially folded graphene-like and multi-layered carbon structures. For comparison, only partial removal of Si was observed with a crystalline, commercial SiC treated in similar conditions.

2. Materials and methods

2.1. Materials

Barley husk was obtained from Alitia Oyj (Koskenkorva, Finland) as a side stream of their process. The chemicals used in the study were: 37% HCl (Merck), NaOH pellets (purity 99.5% Fisher Scientific), D(+)-Sucrose (AnalaR Normapur VWR Chemical), 95%–97% H2SO4 (J.T. Baker) and Mg powder <0.1 mm particles size (purity ≥ 97.0% Merck). Silicon carbide (SiC, 200–450 mesh particle size, Sigma Aldrich) was used as a crystalline SiC reference in the studies.

2.2. Extraction of silica from barley husk

Nanostructured silica (nSiO2) was produced from barley husk (BH). The BH was leached with 10% HCl at 100 °C for 2 h to remove inorganic impurities and hemicellulose. The HCl was removed by vacuum filtration and the solid material, nSiO2, was washed with deionized water to remove chlorides after leaching. The washed nSiO2 was dried at 100 °C and calcined in air at 550 °C.

2.3. Synthesis of nanostructured silicon carbide with high carbon content

Nanostructured silicon carbide/carbon composite (nSiC/C) was synthesized from the purified nSiO2 and sucrose. First 28.6 g of sucrose was dissolved in 20.2 ml of 2.7 v-% H2SO4. Then nSiO2 was added to this reaction solution in a mass ratio 1.2 sucrose/nSiO2. This mixture was heated up to 160 °C for 5 h to enhance dehydration of sucrose to elemental carbon CnH2nOx + H2SO4 → nC + H2SO4 + nH2O. To remove residual H2O and decompose H2SO4, further treatment under N2 atmosphere at 700 °C for 2 h was performed. Finally, magnesiothermic reduction was conducted in a custom-made reactor under N2 atmosphere to obtain nSiC/C composite. Magnesium powder was mixed with the nSiO2/C composite in mass ratio 2:1 and placed into the reactor. The temperature was increased to 1000 °C and kept at this temperature for 30 min prior to the reduction. Reduction was initiated with a resistively-heated tungsten wire. The reaction propagated as high temperature reaction through the sample, in which maximum temperature within the powder reached 1000 °C. Synthesized nSiC/C was washed with 37% HCl at 70 °C for 1 h and 1 M NaOH at room temperature for 16 h to remove by-products, and dried at 65 °C for 2h.
2.4. Graphitization of nanostructured silicon carbide/carbon composite by atmospheric pressure induction annealing

Conversion to graphene-like nanostructured carbon was achieved through induction annealing of the nSiC/C composite under atmospheric pressure in argon atmosphere. The induction furnace had 50 kW heating power. The induction annealing is an efficient high temperature treatment due to the high heat transfer capacity of induction \[23\]. The temperature of the sample was monitored with a Kleiber 730-LO pyrometer at temperatures between 350 °C and 2600 °C. The previously prepared nSiC/C powder \( (m = 0.5 \text{ g}) \) was placed inside a graphite crucible, which was enclosed except for a small pyrometer view hole. The crucible was placed inside the induction oven between heating coils that generate an alternating magnetic field and heats up the crucible. The sample was heated up to 2400 °C under atmospheric pressure in Ar atmosphere and kept at this temperature for 20 min. Schematic illustration of the induction furnace is presented in the figure 1. More detailed explanation of induction annealing set up has been described elsewhere \[16\].

2.5. Characterization

Thermogravimetry analysis was performed with TA instruments TGA Q50. The measurements were performed under air, first at 80 °C for 30 min and followed by a heating ramp at 20 °C min \(^{-1}\) from 80 °C to 900 °C. The N\(_2\) adsorption/desorption measurements were performed with Micromeritics Tristar II 3020 at 77 K. Before the N\(_2\) sorption measurements the samples were degassed at 120 °C under vacuum for 1 h. The specific surface area was determined using the multipoint BET (Brunauer–Emmett–Teller) method.

X-ray powder diffraction examination was carried out with the Bragg-Brentano geometry utilizing the Bruker D8 Discover diffractometer equipped with Cu-tube, \( \lambda = 1.54 \text{ Å} \). Generator was set to 40 kV and 40 mA.
and the K,,-radiation was removed with a 0.02 mm Ni-filter. The measurement was performed in the 2θ range 20°-90° with the step size of 0.038° and the step time of 1.2 s.

The structure of the particles was analyzed with scanning electron microscopy (SEM, Zeiss Sigma HDVP) and transmission electron microscopy (TEM, JEM-2100F JEOL Ltd). SEM imaging was conducted using 5 kV EHT, Inlens detector and WD 5 mm. Powder samples for SEM were placed on the aluminium stub and analyzed without coating. The size of the particles was estimated by measuring single particle sizes with ImageJ software. HSBD detector was used in the EDS studies. The TEM samples were prepared by pipetting a droplet of ethanol suspension to a holey carbon TEM grid. 200 kV acceleration voltage was used for the imaging.

Raman spectroscopy (Thermo DXR2xi Raman) was conducted at wavelength \( \lambda = 532 \text{ nm} \), 100 x objective and 50 μm confocal pinhole aperture. Laser power of 2.5 mV and exposure time of 0.02 s were used in the analysis.

Thermodynamic equilibrium calculations were carried out with the Equilib-module of the FactSage 6.2 software in order to estimate the decomposition temperature of SiC, and its further reactions during the induction heating experiments. Thermodynamic data of the condensed and gas-phase species were taken from the Fact53 and Pitzer-LMLQ (liquid light metal alloy) databases. The calculation was carried out at pressure of 1 bar and temperature range of 300 °C–3000 °C. During induction annealing the substance (SiC) is surrounded by argon gas. Therefore, the global equilibrium was calculated at SiC mixing ratio of 0.1 in argon gas. In addition, a local equilibrium without the presence of Argon gas was calculated.

### 3. Results and discussion

#### 3.1. Production and properties of nanostructured silicon carbide/carbon composite

Synthesis of nSiC/C was carried out in two phases: (1) Extraction of nanostructured SiO₂ (nSiO₂) from agricultural side stream barley husk and (2) Production of nSiC/C composite through magnesiothermic reduction from nSiO₂ and sucrose. Barley husk is naturally rich in SiO₂ accumulated in phytoliths, which makes it an attractive source of SiO₂ [24]. However, prior to calcination barley husk must be acid-treated to remove metallic impurities, mainly Na and K to ensure high purity of the final product. These metallic impurities can form ternary oxides with SiO₂, e.g. Na₂Si₆O₁₉ or Na₂Si₃O₅ and consequently decrease the melting point of the ash during the heat treatment of the biomass. Presence of ternary oxides enable carbon in the biomass to dissolve and remain in such ternary oxides decreasing the purity of the final nSiO₂ product [25]. The extracted nSiO₂ was mixed with sucrose and treated under magnesiothermic reduction resulting in the formation of a nSiC/C composite. The mixture contained sucrose above the stochiometric amount needed for the formation of SiC in order to increase the amount of free carbon in the composite. This additional carbon improved the formation of graphitic structures in the induction annealing during the graphitization.

Figure 2 shows the thermogravimetric analysis, nitrogen adsorption-desorption isotherm and XRD diffractogram of the nSiC/C composite. Based on the analysis the total amount of free carbon in nSiC/C composite before induction annealing was 21 wt% (figure 2(A)). The nitrogen adsorption-desorption isotherm of nSiC/C resembled the type II isotherm with the H3 type hysteresis loop, which indicates mesoporous structures with BET surface area of 234 ± 2 m² g⁻¹ (figure 2(B)).

XRD analysis showed that nSiC/C composed of two different polytypes, namely SiC-3C and SiC-2H (figure 2(C)) [26–28]. The average crystallite size calculated from 2θ peaks 60.0° and 71.8° was 16.7 nm. In addition, a single diffraction peak of graphitic carbon was observed at 25.9°. The absence of the other diffraction peaks of graphitic carbon was due to the low crystallinity of the carbon in nSiC/C as can be expected based on the reaction temperature used in the magnesiothermic reduction (1000 °C).

Figure 3A and 3 show the SEM images of the nSiC/C composite. The nSiC/C appeared to be composed of sharp-edged crystals with the size varying between 100 nm and 600 nm, and spherically shaped primary particles forming larger porous structures. The elemental mapping conducted with energy dispersive x-ray spectroscopy (EDS) coupled with SEM indicated that the sharp-edged crystals composed of SiC and the porous structures were amorphous free carbon (figure 4(A)). The Mg peak in the EDS spectrum is due to a Mg residue from the magnesiothermic reduction and the Al peak is due to the SEM specimen stub. The oxygen peak may indicate the presence of unreacted SiO₂, MgO or silicon oxycarbide [29]. Also, some oxygen may be contributed by oxygen surface functional groups on free carbon.

#### 3.2. Properties of graphitized carbon nanostructures formed by induction annealing at atmospheric pressure

Conversion of nSiC/C to graphene-like carbon was obtained with induction annealing at 2400 °C under Ar atmosphere and atmospheric pressure. XRD analysis showed formation of the highly graphitized carbon structures presented in figure 2(C). The diffraction peak at 83.5° particularly indicates the presence of the
multilayered carbon sheets as also seen in the TEM images (figures 3(C), (D)) [28]. As expected, the specific surface area of nSiC/C was reduced during the induction annealing as $S_{\text{BET}}$ surface area of graphene-like carbon was only 19.0 ± 3 m² g⁻¹. According to the nitrogen sorption-desorption isotherm (figure 2(D)) resembles the type III sorption isotherm referring to the non-porous or macroporous material. The nSiC/C went through a complete morphological change as can be observed from the SEM images (figures 3(A) - (E)). The nSiC/C transformed mainly to hollow spherically shaped carbon structures with particle sizes varying from 50 to 500 nm in size. In addition to the spherical structures, sheet structures were observed as well as presented in figure 3(C). The atomic plane distance, based on the estimation from TEM images, between the multilayered carbon structures was 0.32 nm. This value is slightly lower than the atomic plane distance of crystalline graphite, which is 0.3354 nm [30]. Based on the Raman analysis shown in figure 3(F), there may be graphene domains present in the sample matrix in addition to the graphitic structures. Peak set up in Raman spectra correlated well with the values for graphene, i.e. dominant single Lorentzian 2D peak band at 2700.1 cm⁻¹ with 24.4 cm⁻¹ full width half maximum (FWHM) and G band at 1581.3 cm⁻¹. Minor D peak at 1349.8 cm⁻¹ indicates minor defects in the material structure [31]. According to the thermogravimetric analysis complete conversion of nSiC/C composite to high carbon content material was achieved (figure 2(A)), which corresponds well to the results obtained from XRD and SEM-EDS analysis (figures 2(C) and 4(B)). This is significant improvement compared to the commercial SiC (Sigma-Aldrich) which resulted in only 25 wt% carbon conversion under similar thermal conditions (figure 2(A)). High conversion of nSiC/C to carbon achieved in this study is in a good agreement with our previous studies conducted with pre-ceramic, nanocrystalline SiC/C produced from organometallic compounds using the same induction annealing approach [16, 32].

3.3. Phase separation of silicon carbide and the role of free carbon
Figure 5 shows the thermodynamic equilibrium of bulk SiC under Ar atmosphere between 1600 °C and 3000 °C, based on the thermodynamic data of the condensed and gas-phase species provided in the Fact53 and Ftmisc-LMLQ (liquid light metal alloy) databases. According to the thermodynamic data, the decomposition of SiC

![Figure 2](image-url)
initiates above 2000 °C, which is in accordance with the SiC dissociation scheme presented by Lilov et al (1993), proceeding through the following reactions.

\[
\text{SiC}(s) \leftrightarrow \text{Si}(g) + C(s) \quad (1)
\]
\[
\text{2SiC}(s) \leftrightarrow \text{SiC}_2(g) + \text{Si}(l, g) \quad (2)
\]

However, the rate of sublimation is typically very slow at these temperatures and complete removal of Si from SiC would take very long time unless low pressures are used. Therefore, sublimation of silicon and subsequent graphitization of SiC has been typically carried out in ultrahigh vacuum conditions (UHV 10^{-8} to 10^{-9} Torr) around 1470 K [33, 34].

According to equilibrium, the maximum solid carbon conversion (26%) with the used SiC mixing ratio is achieved at 2660 °C, while further increase in temperature declines the carbon conversion and gaseous compounds, such as SiC_2(g), Si_2C, Si(g) and C_x(g), become predominant (figure 5). The calculated maximum carbon conversion is in a very good agreement with the experimentally determined carbon conversion of commercial SiC at 2400 °C in which 25 wt% of material was graphitized (figure 2(A)). Furthermore, the local equilibrium without the presence of Ar-atmosphere indicates that the decomposition of SiC may also lead to a formation C-Si liquid alloy [35]. Induction annealing of nSiC/C at same reaction temperature resulted complete conversion to graphene-like structures. This may indicate lower onset temperature compared to temperature predicted with thermodynamic equilibrium calculations and behavior of commercial SiC. Enhanced reaction kinetics is most likely related to the pre-ceramic, nanocrystalline features of the precursor nSiC, which lower the Si and C phase separation temperature [16]. Si begins to evaporate from the powder due its higher vapor
pressure compared to the C leading to the formation of graphene and graphitic structures \([2]\). It has been suggested that the Si evaporates in a layer by layer fashion but the exact chemical composition of the Si atoms leaving the surface is not fully understood. In addition, the amount of free carbon seems to be an important factor affecting the growth of the graphene layers observed in the study. When the amount of free carbon was increased in pre-ceramic nSiC/C mixture produced in this study, the onset temperature for the phase separation decreased. This is most likely due to Si/C interactions, enabling the formation of the graphene-like structures already at temperatures between 1900 °C and 2600 °C \([16]\). The effect of free carbon is in agreement with the simulations carried out by Wang et al (2007) \([34]\). Based on the simulations the SiC surface is rapidly covered with carbon through cap nucleation of carbon once the top Si atom layer has been removed.

4. Summary

In summary, the study shows that graphene-like carbon nanostructures can be achieved from biomass-based precursors through energy efficient bottom-up synthesis procedures, magnesiothermic reduction and induction annealing. The nSiC/C composite, used as the precursor in the synthesis of graphene-like carbon nanomaterial, was obtained from sucrose and nSiO\(_2\). The nSiO\(_2\) was extracted from an agricultural side stream, namely barley husk. The precursor nSiC/C composed of nSiC and 21 wt% of free carbon. Crystalline and low defect graphene-like carbon, composing of nano-sized individual spherical particles 50–500 nm in size and sheet structures, was obtained through magnesiothermic reduction coupled with induction annealing. Reaction mechanism leading to the formation of graphene-like carbon was initiated by the evaporation of Si. We observed

![Figure 4. Energy dispersive x-ray spectroscopy analysis including backscattering images (top), elemental mappings (middle) and elemental spectrums (bottom) of the (A) nSiC/C composite and (B) graphene-like carbon.](image-url)
significant improvement in the reaction kinetics of nSiC/C compared to commercial SiC. Lowering of the phase separation temperature is related to the nanocrystalline structure of biogenic SiC and the large amount of free carbon in the nSiC/C precursor composite.

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References


Figure 5. Thermodynamic equilibrium calculation of the phase separation of well crystalline SiC to silicon and carbon.


[33] Sutter P 2009 How silicon leaves the scene Nat. Mater. 8 171–2


[35] Ansara M, Dinsdale I and Rand A T 1998 Definition of thermochemical and thermophysical properties to provide a database for the development of new light alloys COST 2
This Doctoral thesis is on the synthesis and application of carbon-based materials. The emerging environmental and energy issues demand low cost and efficient ways to produce materials for application in energy storage, sensors and degradation of organic pollutants. The study demonstrates doping, a process which introduces material additives to improve the properties of the host material for the targeted applications.