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Graphene Oxide Assisted Biomass Carbonization

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By

Deepti Krishnan

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## ABSTRACT

### Graphene Oxide Assisted Biomass Carbonization

Deepti Krishnan

Increasing energy demand due to rapid growth in population and industrialization along with environmental crisis has led to the search for cheap, environmentally friendly, and nontoxic methods for generation of energy. However, most alternative energy sources such as photovoltaic, biofuels, hydraulic power, wind power, and geothermal energy, are characterized by high variability and discontinuity. The high unpredictability of the primary resource makes it difficult to forecast the energy production. In this context, electrochemical energy storage devices like supercapacitors holds great promises towards this goal. But high cost and poor electrode properties limits the use of these supercapacitors.

Biomass is a promising source for carbon materials in the field of energy storage, as it is cheap, environmentally friendly, renewable and abundantly available throughout the world. Hydrothermal carbonization (HTC) is a thermo-chemical process for the conversion of solid biomass matter to its more carbonaceous form at elevated temperature and pressure in the presence of water. But HTC of biomass typically produces non-porous insulating materials. Scientific interest in graphene oxide (GO) sheets, the product of chemical oxidation and exfoliation of graphite powder, has resurged in recent years because GO is considered a promising precursor for the bulk production of graphene-based sheets for a variety of applications. Adding catalytic amounts of GO to biomass can significantly alter the morphology of its HTC product, resulting in products with high conductivity and specific surface area, as well as exhibiting excellent

electrochemical performance when used as electrodes of supercapacitors. Control experiments with other carbon materials such as graphite, carbon nanotubes, carbon black, and reduced GO (r-GO) show that only GO has significant effect in promoting HTC conversion, likely due to its good water processability, amphiphilicity, and two-dimensional structure that may help to template the initially carbonized materials. Furthermore, by appropriately tuning the process parameters used for the reaction, such as moisture content and temperature, the carbon yield of the process could be significantly improved. Finally, by a microwave assisted approach, the carbonization time can be reduced from hours to few minutes and the resulting carbon products showed superior electrochemical performance compared to commonly used supercapacitor electrode materials like activated carbon.



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## TABLE OF CONTENTS

|                                                                                   |           |
|-----------------------------------------------------------------------------------|-----------|
| <b>ABSTRACT.....</b>                                                              | <b>3</b>  |
| <b>ACKNOWLEDGEMENTS .....</b>                                                     | <b>5</b>  |
| <b>LIST OF FIGURES .....</b>                                                      | <b>10</b> |
| <b>LIST OF TABLES .....</b>                                                       | <b>18</b> |
| <b>CHAPTER 1 .....</b>                                                            | <b>19</b> |
| <b>Introduction.....</b>                                                          | <b>19</b> |
| 1.1 Renewable Energy Storage .....                                                | 19        |
| 1.2 Supercapacitors .....                                                         | 21        |
| 1.2.1 Energy Storage Mechanism .....                                              | 21        |
| 1.2.2 Supercapacitor Performance Characteristics .....                            | 23        |
| 1.2.3 Supercapacitor Limitations .....                                            | 25        |
| 1.3 Lignocellulosic Biomass.....                                                  | 26        |
| 1.3.1 Biomass Composition .....                                                   | 27        |
| 1.4 Biomass Conversion Routes .....                                               | 31        |
| 1.4.1 Biochemical Pathways .....                                                  | 31        |
| 1.4.2 Thermochemical Pathways .....                                               | 32        |
| 1.5 Hydrothermal Carbonization .....                                              | 35        |
| <b>CHAPTER 2.....</b>                                                             | <b>40</b> |
| <b>Graphene Oxide Assisted Hydrothermal Carbonization of Carbon Hydrates.....</b> | <b>40</b> |

|                                                                                 |           |
|---------------------------------------------------------------------------------|-----------|
|                                                                                 | 8         |
| 2.1 Introduction.....                                                           | 40        |
| 2.1.1 Graphene Oxide .....                                                      | 41        |
| 2.3 Results and Discussion .....                                                | 47        |
| 2.4 Conclusion .....                                                            | 67        |
| 2.5 Experimental Conditions .....                                               | 67        |
| <b>CHAPTER 3.....</b>                                                           | <b>71</b> |
| <b>High Yield Hydrothermal Carbonization of Glucose.....</b>                    | <b>71</b> |
| 3.1 Introduction.....                                                           | 71        |
| 3.2 Results and Discussion .....                                                | 73        |
| 3.3 Conclusion .....                                                            | 82        |
| 3.4 Experimental Conditions .....                                               | 83        |
| <b>CHAPTER 4.....</b>                                                           | <b>84</b> |
| <b>Hydrothermal Reduction of Graphene Oxide in Bio-Oil.....</b>                 | <b>84</b> |
| 4.1 Introduction.....                                                           | 84        |
| 4.2 Results and Discussion .....                                                | 85        |
| 4.3 Conclusion .....                                                            | 91        |
| 4.4 Experimental Conditions .....                                               | 92        |
| <b>CHAPTER 5.....</b>                                                           | <b>93</b> |
| <b>Graphene Oxide Assisted Rapid Microwave Carbonization of Cellulose .....</b> | <b>93</b> |
| 5.1 An Introduction to Microwave Heating.....                                   | 93        |
| 5.1.1 Microwave Heating Mechanism .....                                         | 94        |
| 5.1.2 Microwave Heating of Solutions .....                                      | 98        |

|                                                                       |            |
|-----------------------------------------------------------------------|------------|
| 5.1.3 Microwave Heating of Carbon-Based Solids .....                  | 100        |
| 5.1.4 Advantages of Microwave Heating Over Conventional Heating ..... | 101        |
| 5.2 Microwave Heating of Lignocellulosic Biomass.....                 | 103        |
| 5.3 Microwave Assisted Heating of r-GO .....                          | 104        |
| 5.4 Results and Discussion .....                                      | 105        |
| 5.5 Conclusion .....                                                  | 118        |
| 5.6 Experimental Conditions .....                                     | 118        |
| <b>CHAPTER 6.....</b>                                                 | <b>121</b> |
| <b>Conclusion and Outlook.....</b>                                    | <b>121</b> |
| <b>REFERENCES.....</b>                                                | <b>125</b> |
| <b>VITA .....</b>                                                     | <b>140</b> |

## LIST OF FIGURES

**Figure 1.** Power density against energy density, also called a Ragone plot, for various energy storage and conversion devices – fuel cells, batteries, ultracapacitors and conventional capacitors. Batteries and fuel cells have higher energy density while conventional capacitors have higher power density. Supercapacitors act like a bridge between batteries and conventional capacitors and have values in between these two storage devices. Adapted from reference. 1. .... 20

**Figure 2.** Schematic of a conventional electrostatic capacitor. It contains two electrical conductors (plates) separated by a dielectric (non-conducting substance). When voltage is applied, one plate becomes positively charged while the other become negatively charged. But the opposite charges are not able to come close to each other due to the layer of dielectric between the two. This results in storage of electrostatic energy. The symbol of a capacitor is shown on the right. Adapted from reference. 13..... 22

**Figure 3.** Schematic of a supercapacitor. It has two electrodes, mechanically separated by a separator, which are ionically connected to each other via the electrolyte. The electrolyte is a mixture of positive and negative ions dissolved in a solvent such as water. When the electrodes are polarized by an applied voltage, ions in the electrolyte form electric double layers of opposite polarity to the electrode's polarity, resulting in energy storage. Reference. 14..... 23

**Figure 4.** Typical composition of lignocellulosic biomass of wood. It consists mainly of three organic compounds: cellulose, hemicellulose, and lignin. Cellulose is the main constituent and makes about 40-50% of biomass. This is followed by lignin (20-30%) and hemicellulose (10-20%). ..... 27

**Figure 5.** Schematic illustration of a cellulose polymer chain. It is a polysaccharide consisting of a linear chain of several hundred to many thousands of  $\beta$  linked D-glucose units. The glucose units in cellulose are combined in a way that results in the formation of very linear, flat molecules that can, in turn, form sheets that possess extensive networks of hydrogen bonds. The hydrogen bonds are both within individual sheets and between successive sheets. As a result of these bonds, sheets of cellulose are particularly strong—a property critical to the function of plant cell walls. Cellulose shows a variable degree of polymerization, with anywhere from 1,000 to 14,000 glucose residues comprising a single cellulose polymer. Reference. 27. .... 28

**Figure 6.** Schematic illustration of a xylan based hemicellulose polymer chain. The chemical structure of hemicellulose consists of long chains of a variety of pentoses, hexoses, and their corresponding uronic acids. The polysaccharides yielding pentoses on hydrolysis are called pentosans. Xylan is an example of a pentosan consisting of D-xylose units with  $1\beta \rightarrow 4$  linkages. Adapted from reference. 28. .... 29

**Figure 7.** Schematic illustration of a possible lignin structure. It is an amorphous, randomly cross-linked polyphenolic material formed from an enzyme-mediated dehydrogenative polymerization

of three phenylpropanoid monomers, conniferyl, sinapyl and para-coumaryl alcohols. Reference. 31..... 30

**Figure 8.** Biomass conversion routes can be divided into 2 types – biochemical and thermochemical processes. Biochemical processes mainly include anaerobic digestion and fermentation while thermochemical processes include pyrolysis, gasification, combustion, and hydrothermal carbonization. .... 32

**Figure 9.** Schematic illustrating the hydrothermal carbonization process. Biomass such as corn, wood, waste etc. is heated in a sealed autoclave in the presence of water, at temperatures varying from 160 – 280 °C and at pressure greater than 10 bar. It results in the formation of a brown colored coal like material called hydrochar. The hydrochars obtained, especially from carbohydrates usually have sphere like morphologies. .... 37

**Figure 10.** a) Scanning Electron Microscope (SEM) image of monodispersed hard carbon spheres. b) Transmission Electron Microscope (TEM) image of carbon spheres. Reference. 49..... 38

**Figure 11.** Layered structure of graphite showing the  $sp^2$  hybridized carbon atoms tightly bonded in hexagonal ring. The graphene sheets stack together to form graphite and are held together by weak Van der Waals forces at a distance of 0.34 nm from each other. Adapted from reference. 70. .... 41

**Figure 12.** Synthesis, structural model and microstructures of GO sheets. (a) GO is typically synthesized by reacting graphite powder with strongly oxidizing agents such as  $KMnO_4$  in concentrated  $H_2SO_4$ , followed by purification and exfoliation in water to yield a colloidal dispersion of single layers. (b) Structural model of graphene (left), GO (middle) and its reduction product r-GO. Graphene consists of a single atomic layer of  $sp^2$ -hybridized carbon atoms which are found stacked together in the form of graphite. Liquid-phase chemical oxidation of graphite powder results in GO which consists of a graphene sheet derivatized by epoxide and hydroxyl groups on the basal plane and carboxylic acid groups on the edges. The edge  $-COOH$  groups can ionize, resulting in an electrostatic repulsion between the sheets, allowing single-layers to form an aqueous colloidal dispersion. GO is insulating due to broken conjugation in the basal plane. After reduction, r-GO becomes conductive but is still a very defective structure compared to graphene. (c) Color coded high resolution TEM images showing the atomic structures of graphene (left), GO (middle) and r-GO (right). The green, purple and blue areas depict ordered, graphitic  $sp^2$  domains, disordered highly oxidized  $sp^3$  domains, and holes on the sheet, respectively..... 43

**Figure 13.** (a) At a concentration of 1 mg/ml, hydrothermal treatment of GO solution leads to a r-GO monolith (first vial on the left). Hydrothermal treatment of GO (1 mg/ml) and glucose mixture can also create monoliths with GO:glucose weight ratios up to 1:400 as shown in the photo. (b) The weight of the monoliths increased linearly with increasing glucose content. (c) Hydrothermal treatment of glucose in the presence of GO leads to higher carbonization rate (as indicated by the product yield) especially during the initial stage of the reaction. .... 48

**Figure 14.** TGA curves of the monoliths obtained after HTC of a GO and glucose mixture (1:400), compared with those of pure GO and glucose treated under similar conditions (180 °C for 16 hours), respectively. The concentration of GO was maintained at 0.02 mg/ml. TGA was carried out in N<sub>2</sub> atmosphere at a heating rate of 10 °C/min. The steady weight loss in the temperature regime of 200 to 600 °C corresponds to thermal decomposition of functional groups. .... 50

**Figure 15.** (a-e) SEM images of the HTC products of GO and glucose obtained with increase glucose content (1:0, 1:100, 1:300, 1:400, and 1:800) show that GO suppresses the formation of carbon spheres with GO/glucose ratio up to 1:800. (f) When even higher content of glucose (GO/glucose = 1:1000), the main product is carbon spheres, similar to those shown in Chapter 1. .... 52

**Figure 16.** FTIR spectra of carbon spheres and monoliths obtained from different ratios of GO and glucose (a) after HTC and (b) after microwave treatment for 1 minute. .... 54

**Figure 17.** Schematic formation model for carbon spheres obtained from glucose and cellulose. Cellulose first hydrolyses into glucose and fructose, which in turn undergo dehydration, polymerization and aromatization to form spherical hydrochars. These spheres have a hydrophobic core with a hydrophilic shell. Adapted from reference. 132..... 58

**Figure 18.** Schematic illustrating the formation model for monoliths obtained from HTC treatment of glucose in the presence of GO. .... 59

**Figure 19.** (a) SEM image of the carbon spheres obtained after HTC of glucose at 180 °C for 16 hours (b) SEM image of the platelets obtained after HTC of GO and glucose at a weight ratio of 1:300 at 180 °C for 16 hours. The overall GO concentration was 0.02 mg/ml. (c) AFM image of a GO sheet with line scan showing thickness of around 1 nm and (d) AFM image of the platelet obtained after HTC of GO and glucose. The line scan shows the thickness is increased to around 40 nm. .... 60

**Figure 20.** SEM images of (a) pure multiwalled CNTs and (b) the sample obtained after HTC of glucose with multiwalled CNTs (2 wt%), (c) pure activated carbon and (d) the sample obtained after HTC of glucose with activated carbon (2 wt%), (e) hydrazine reduced r-GO and (f) the sample obtained after HTC of glucose with hydrazine reduced r-GO (2 wt%), (g) HTC treated GO and (h) the sample obtained after HTC of glucose with HTC reduced GO (2 wt%). In all the cases, formation of carbon spheres was not suppressed..... 61

**Figure 21.** Galvanostatic charge/discharge curve of a supercapacitor prepared from microwave treated GO-glucose monolith with 1:400 weight ratio. Two-electrode symmetric coin cells were assembled with 5 M KOH of aqueous solution as the electrolyte. .... 64

**Figure 22.** GO assisted HTC of cellulose. Photos of (a) pure cellulose, (c) its HTC product and (e) product obtained from GO:cellulose mixture (weight ratio 1:100) after HTC treatment at 230 °C for 16 hours. (b), (d) and (f) are SEM images correspond to (a), (c) and (e), respectively. HTC treatment converts (b) sub-millimeter sized cellulose particles into (d) few-micron sized carbon



spheres. However, in the presence of GO, the HTC product shows thick sheet-like morphology.

..... 66

**Figure 23.** Products of hydrothermal carbonization, separated according to their state of aggregation – solids, liquids and gases. Solids comprise of the carbon product hydrochar, the liquids mainly contain sugars, organic acids and some inorganics formed during the process and gases include CO<sub>2</sub> generated during the process. The overall yield of hydrochar is ~10 %. Adapted from reference 61. .... 72

**Figure 24.** Schematic illustrating the hydrochar formation mechanism from glucose. It consists of mainly three steps – dehydration, polymerization and aromatization. After the dehydration step, an intermediary HMF product is formed, which in turn is converted to formic acid, levulinic acid and some carbon compounds. Adapted from reference. 136. .... 74

**Figure 25.** Schematic demonstrating the glucose dehydration pathway to HMF and its hydrolysis into levulinic acid and formic acid. .... 74

**Figure 26.** (a) Photos showing the products obtained after hydrothermal treatment of glucose:water at weight ratios from 0.01 to 10, compared with that of glucose powder heated under similar conditions in the absence of water. (b) The corresponding char obtained after washing and drying. Very little char was formed at low glucose:water weight ratios (i.e. high initial water content) of 0.01 and 0.05, as well for that obtained from glucose powders without any moisture. .... 75

**Figure 27.** Hydrochar yield as a function of glucose:water weight ratio. Yield increased with decreasing water content and reached a maximum at a glucose:water ratio of 2. Further increase in glucose:water ratio decreased the char yield, but in the absence of water the char yield dropped to less than 4 %. .... 76

**Figure 28.** FTIR spectra of glucose:water HTC treated carbons at weight ratios of 0.05, 2 and 10. Irrespective of water content, all the spectra showed similar IR peaks. The peaks at 1710 and 1620 cm<sup>-1</sup> correspond to C=O and C=C vibrations respectively and the peaks in the 1000–1300 cm<sup>-1</sup> range, include the C-OH stretching and OH bending vibrations. .... 78

**Figure 29.** (a-e) SEM images of the HTC products of glucose obtained with decreasing initial moisture content (0.05, 0.5, 1, 2, and 5) indicate that carbon spheres were formed in all these cases. But at weight ratios greater than 0.05, the spheres were interconnected in nature and larger in diameter. (f) Carbonization of glucose done in the absence of water shows the presence of random irregular particles similar to that of parent untreated glucose powders. .... 79

**Figure 30.** Hydrochar yield as a function of both glucose:water weight ratio and temperature. Yield increased as the temperature was raised from 160 °C to 200 °C. At 160 °C, char yield was less than 1%. At 180 °C and 200 °C, maximum yields of 40% and 50% were obtained at weight ratios of 2 and 5, respectively. .... 80

**Figure 31.** (a), (c) and (e) SEM images of the HTC products of glucose obtained at an initial glucose:water weight ratio of 2 at 160 °C, 180 °C and 200 °C, respectively. (b), (d) and (f) are the corresponding zoomed in images. In all the cases, carbon spheres were obtained but the size of the spheres increased with increasing temperature..... 81

**Figure 32.** SEM images of the platelets obtained after HTC of GO and glucose at 180 °C for 16 hours at GO:glucose weight ratios of (a) 1:50, (b) 1:100, (c) 1:200 and (d) 1:300, respectively. The overall GO concentration was 0.02 mg/ml. The products obtained were washed with methanol and DI water, re-dispersed in water and later deposited onto silicon substrates by using LB method (as mentioned in section 2.4. .... 86

**Figure 33.** SEM images of the products obtained after hydrothermal treatment of GO and glucose at 180 °C for 16 hours at a GO:glucose weight ratio of 1:100, without any washing or LB deposition. The product appears dirtier and there were lot of carbon spheres surround the r-GO:glucose carbon platelets. .... 87

**Figure 34.** SEM images at different magnifications of the r-GO:glucose carbon platelets obtained after hydrothermal treatment of GO in bio-oil (obtained from HTC of glucose) at 180 °C for 4 hours, at a GO:glucose weight ratio of 1:100. No carbon spheres can be seen in the images and the product was cleaner. The sheets showed better flexibility and conductivity..... 88

**Figure 35.** SEM images at different magnifications of the r-GO:glucose carbon platelets obtained after hydrothermal treatment of GO in bio-oil (obtained from HTC of glucose) at 180 °C for 4 hours, at GO:glucose weight ratios of (a), (b), (c) 1:200, (d), (e), (f) 1:400, (g), (h), (i) 1:800 and (j),(k),(l) 1:1000, respectively..... 90

**Figure 36.** Zoomed in SEM image of a r-GO:glucose carbon platelets obtained after hydrothermal treatment of GO in bio-oil (obtained from HTC of glucose) at 180 °C for 4 hours, at GO:glucose weight ratio of 1:400. Carbon spheres are preferentially getting deposited on the corner of the r-GO:glucose carbon sheets..... 91

**Figure 37.** The electromagnetic spectrum depicting the microwave regime with frequency between 0.3 – 300GHz and a corresponding wave length range of 1mm to 1m. .... 94

**Figure 38.** Schematic of an electromagnetic wave showing electric, magnetic field and direction of propagation. The magnetic and electric fields of an electromagnetic wave are perpendicular to each other and to the direction of the wave. .... 95

**Figure 39.** Frequency dependence of the real and imaginary parts of the dielectric constant in the presence of interfacial, dipolar, atomic and electronic polarization mechanisms.  $\epsilon'$  and  $\epsilon''$  denote the real and the imaginary part of the permittivity, respectively. Reference. 148..... 98

**Figure 40.** Schematic of an electric dipole. An electric dipole moment is defined as the measure of separation between positive and negative charges. It is equal to the magnitude of the charge (Q) multiplied by the distance (a) between them with the direction being towards the positive charge. .... 99

**Figure 41.** Schematic showing dipolar polarization and Maxwell-Wagner (or interfacial or space charge) polarization mechanisms. Dipolar polarization is found in molecules that contain permanent dipole moments. In the absence of electric field, the molecules are randomly oriented in the material and there is no net dipole moment. Under microwave frequencies, dipoles respond to the alternating electric field by rotating to align with the field; however, a phase difference exists between the orientation of the field and dipole. This phase difference cause energy to be released from the molecules, upon random collision with other molecules leading to dielectric heating. Maxwell-Wagner polarization involves accumulation of charges at interfaces within the material or between different materials. When an external electric field is applied, the more mobile charges are displaced and accumulate at barriers or at free surfaces, resulting in heating. .... 100

**Figure 42.** Schematic showing the difference between conventional and microwave heating process, Conventional heating usually involves the use of a furnace or oil bath, which heats the walls of the reactor by convection or conduction. The core of the sample takes much longer to achieve the target temperature, e.g. when heating a large sample of ceramic bricks. Acting as internal heat source, microwave absorption is able to heat the target compounds without heating the entire furnace or oil bath, which saves time and energy. .... 102

**Figure 43.** Schematic drawing illustrating GO enabled rapid microwave carbonization of cellulose. Microwave heating of cellulose powders is ineffective and results in incomplete degree of carbonization. In contrast, when GO is added as a microwave sensitizer, it helps to rapidly heat up the mixture and greatly accelerate the carbonization reaction, forming a char with much higher degree of carbonization. .... 106

**Figure 44.** (a) Temperature profiles of cellulose and GO:cellulose mixtures at different weight ratios of 1:400, 1:800 and 1:1000 during microwave heating. The upper limit of detected temperature was set to be 250 °C. All the GO:cellulose mixtures reached the temperature limit in about 60-90s, while cellulose powders were still below 200 °C even after heating for 900s; (b) Detailed Magnified temperature profiles of GO:cellulose mixtures corresponding to the region marked by the red dashed box in (a). .... 107

**Figure 45.** Temperature profiles of r-GO:cellulose mixtures during microwave treatment in a CEM microwave oven during the second heating cycle at 300 W. The maximum temperature was again maintained at 250 °C. GO:cellulose mixtures of weight ratios greater than 1:400 required 2 heating cycles to achieve sufficient carbonization. The temperature of the r-GO:cellulose mixture of initial weight ratio 1:800 and 1:1000 shot up much higher than 350 °C in just 10 and 25 s, respectively. .... 108

**Figure 46.** (a,b) Photos showing cellulose and GO:cellulose powders before and after microwave treatment, respectively. The cellulose powder gave a non-uniform brown and white char while GO:cellulose (weight ratio 1:1000) powder gave a uniform black powder after microwave treatment. .... 108

**Figure 47.** Comparison of TGA curves of GO:cellulose mixture at a weight ratio of 1:000 and cellulose powder indicates similar thermal decomposition characteristics of both the samples. The

final yield was ~13 mass % which is close to the yield of the microwaved GO:cellulose samples (~10 mass %). TGA was carried out in N<sub>2</sub> atmosphere at a heating rate of 10 °C/min till a temperature of 800 °C..... 109

**Figure 48.** FTIR spectra of all microwave treated samples clearly showing the drastic reduction in -OH band intensity around 3400 cm<sup>-1</sup> in GO:cellulose microwaved samples, compared to cellulose microwaved samples; (d) The magnified FTIR spectra of microwave reacted GO:cellulose mixtures corresponding to the dashed red circle in (c). The spectra in (c) were magnified ~110x to clearly see the IR peaks. Note: GO:cellulose microwaved samples of weight ratio greater than 1:400 were subject to two microwave heating cycles. The cellulose microwave treatment was done for 900 s. .... 110

**Figure 49.** XRD patterns of microwave treated cellulose and GO:cellulose mixtures at different weight ratios of 1:400, 1:800 and 1:1000 heated for 900 s, 60 s, 100 s and 115 s respectively. Increased degree of graphitization is observed for r-GO:cellulose microwaved carbons as indicated by the increased intensity of (002) and emergence of (100) graphite peaks at around 24.5° and 45°, respectively. .... 111

**Figure 50.** SEM images of microwave treated (a) cellulose and (b) GO:cellulose (weight ratio 1:1000) powders. While microwaved cellulose products have an irregularly shaped structure, the microwave treated GO:cellulose carbons have a more porous flaky structure..... 112

**Figure 51.** (a) SEM image of GO:cellulose microwaved sample (weight ratio 1:1000) after just 1 heating cycle shows a non-uniform not so porous structure; (b) FTIR spectra of GO:cellulose mixtures at a weight ratio of 1:1000, compared with the corresponding microwaved samples after first heating cycle and second heating cycle indicates significant reduction in -OH group intensity after each heating cycle..... 113

**Figure 52.** (a) The BET surface area calculated from N<sub>2</sub> gas adsorption and desorption isotherms. The specific surface areas of microwave treated GO:cellulose (weight ratio 1:1000) and cellulose carbons were 367 m<sup>2</sup> g<sup>-1</sup> and 18 m<sup>2</sup> g<sup>-1</sup> respectively. (b) The corresponding pore-size distribution calculated using the BJH method. It indicates the microwaved GO:cellulose carbon is mesoporous in nature while the microwaved cellulose powder is absent of any pores. .... 114

**Figure 53.** Electrochemical performance of carbon materials prepared from GO:cellulose mixture at a weight ratio of 1:1000. (a) Nyquist plot and the inset shows an enlarged scale; (b) CV curves measured at different scan rates; (c) Galvanostatic charge and discharge curves at different current densities; (d) Gravimetric based specific capacitance of the sample as a function of current density. .... 116

**Figure 54.** (a) SEM image of cellulose heated in a conventional furnace at a heating rate of 10 °C min<sup>-1</sup> to a temperature of 800 °C and maintained at that temperature for 1 hour in N<sub>2</sub> atmosphere shows a similar non-uniform irregular structure as shown in Fig 3a; (b) The corresponding FTIR spectrum, compared with GO:cellulose microwaved sample at a weight ratio of 1:1000 indicates a much higher degree of carbonization (reduction in-OH group intensity) of the microwaved

GO:cellulose sample compare to the conventionally heated cellulose sample. (c) Gravimetric based specific capacitance of the conventionally heated cellulose as a function of current density. .... 117

**Figure 55.** Schematic comparing the hydrothermal carbonization of glucose in the presence of various carbon sources such as GO, CNTs and activated carbon. Pure glucose powder results in the formation of carbon spheres after HTC process. Presence of GO, suppressed the sphere formation and resulted in thick sheets like structures. But, with other carbon sources i.e. CNTs and activated carbon, there was the presence of both carbon spheres as well the parent carbon source. .... 122

## LIST OF TABLES

|                                                                                                                                               |    |
|-----------------------------------------------------------------------------------------------------------------------------------------------|----|
| <b>Table 1.</b> Comparison of properties of capacitors, batteries and supercapacitors .....                                                   | 24 |
| <b>Table 2.</b> Operating conditions for the three pyrolysis methods based on the process heating rate - slow, fast and flash pyrolysis. .... | 34 |

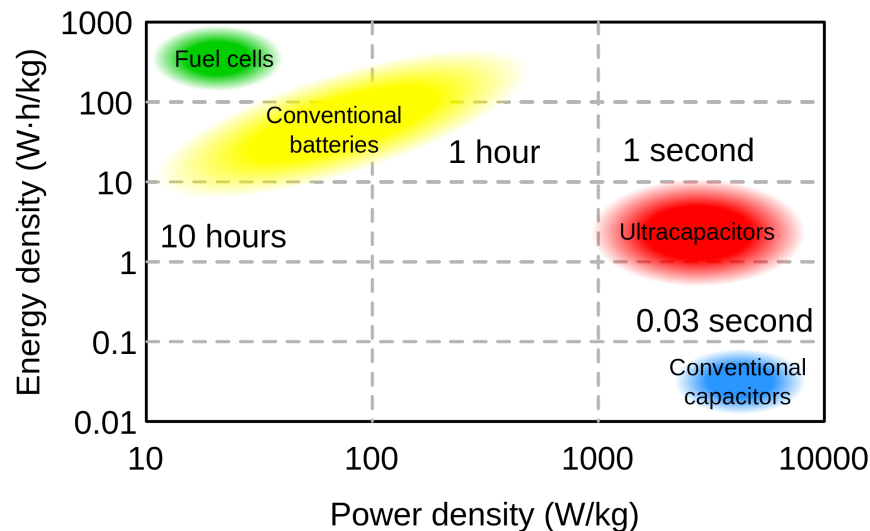
## **CHAPTER 1**

### **Introduction**

#### **1.1 Renewable Energy Storage**

Due to rapid growth in population and industrialization along with environmental crisis, energy has become a primary focus in the scientific and industrial communities. With increasing levels of environment pollution, mining cost and the depletion of fossil fuels, there is an urgent need for cheap, environmentally friendly, nontoxic and renewable energy sources, and energy storage techniques.<sup>1</sup> Though wind and solar power generation offers carbon dioxide (CO<sub>2</sub>) neutral electricity, they present some integration problems for energy system operators and planners due to the intermittent power output. A promising way of dealing with the intermittency from such renewable energy sources is the storage of energy. The method of storing energy in the electricity grid, especially by the means of electrochemical storage, has received a lot of attention over the past few years in the energy sector.

Currently, the three major commercialized electrochemical energy storage systems are capacitors, batteries and fuel cells. The Ragone chart shown in Figure 1 is a standard method to compare the performance of various electrochemical energy storage devices.<sup>2</sup> On such a chart the values of specific energy (in  $\text{W}\cdot\text{h}/\text{kg}$ ) are plotted versus the specific power (in  $\text{W}/\text{kg}$ ). The energy density indicates the amount of energy that can be stored in a given volume or weight of the material, while the power density describes the total energy per second which can be stored or delivered by the energy storage device.<sup>3</sup> Higher the power density, faster the loading and unloading of the amount of energy will be. The ideal energy storage device should be characterized by both high energy density and high power density. Batteries and fuel cells in general have high energy density, but poor power density i.e. poor dynamic response.<sup>4-6</sup> On the other hand, capacitors have low energy density, but high power density. They can be charged or discharged very quickly and generate high power, but can store very limited amount of energy per unit mass or volume.



**Figure 1.** Power density against energy density, also called a Ragone plot, for various energy storage and conversion devices – fuel cells, batteries, ultracapacitors and conventional capacitors. Batteries and fuel cells have higher energy density while conventional capacitors have higher power density. Supercapacitors act like a bridge between batteries and conventional capacitors and have values in between these two storage devices. Adapted from reference. 1.



## 1.2 Supercapacitors

Supercapacitors, also known as ultracapacitors or electrochemical double layer capacitors, have attracted great attention in recent years as an energy storage device due to their high power performance and long cycle life. They serve as the connecting link between a conventional capacitor and a battery. It combines the advantage of the capacitor as a fast supplier of electricity with that of the battery, as a notable energy reservoir.<sup>7, 8</sup> It indicates that supercapacitor can be charged or discharged rapidly and maintain a reasonable energy stored per unit mass. For this reason, it brings significant benefits in short time backup power and peak-power delivery applications, like electric vehicle acceleration, regenerative braking, and uninterruptible power supply.<sup>9-12</sup>

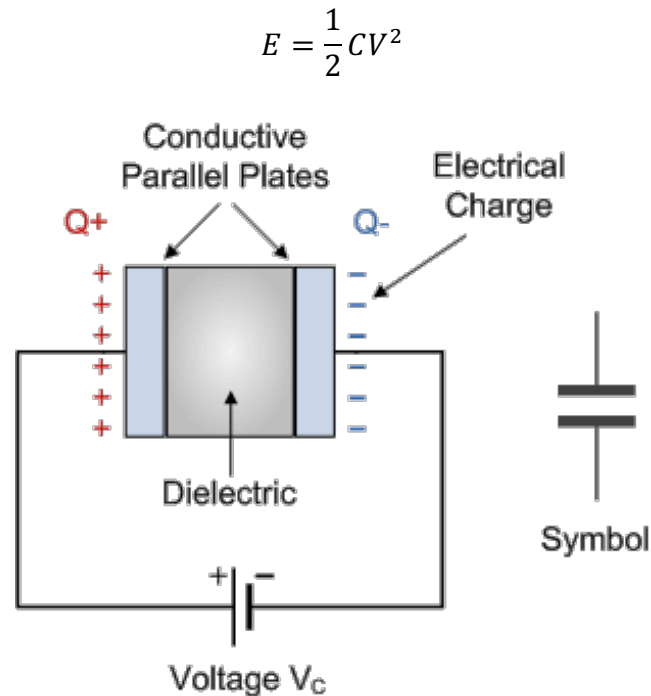
### 1.2.1 Energy Storage Mechanism

Traditional capacitors are made of two metal plates separated by a thin insulating layer, called a dielectric, as shown in Figure 2. When an external voltage is applied, charges accumulate on the surface of the two electrodes, which are isolated from each other by an insulating dielectric layer. The resulting electric field generated allows the device to store energy. Thus, the capacitor stores charge electrostatically in an electric field and the amount of charge is measured by its capacitance,  $C$ , which is a function of the area of the metal plates,  $A$ , and the spacing between them,  $d$ . So, the capacitance can be expressed as:

$$C = \varepsilon \frac{A}{d}$$

where  $\varepsilon$  represents the absolute permittivity of the dielectric material being used.

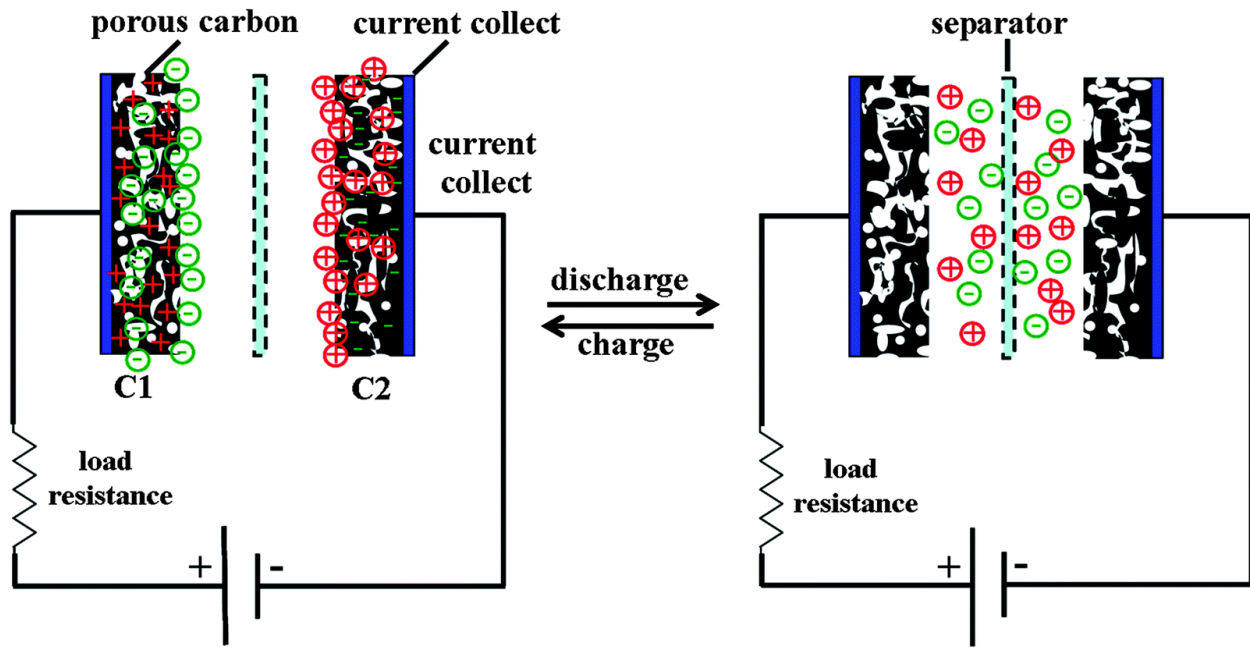
The corresponding energy stored in a capacitor is:



**Figure 2.** Schematic of a conventional electrostatic capacitor. It contains two electrical conductors (plates) separated by a dielectric (non-conducting substance). When voltage is applied, one plate becomes positively charged while the other become negatively charged. But the opposite charges are not able to come close to each other due to the layer of dielectric between the two. This results in storage of electrostatic energy. The symbol of a capacitor is shown on the right. Adapted from reference. 13.

In order to increase the amount of charge stored, one needs to minimize  $d$  and maximize  $A$  and that is what a supercapacitor does. It consists of two porous electrodes with a current collector on each electrode immersed in an electrolyte separated by a dielectric ion permeable porous separator (Figure 3). As voltage is applied to a supercapacitor, ions from the electrolyte diffuse into the pores of the electrode of opposite charge i.e. the positive electrode attracts negative ions in the electrolyte, while the potential on the negative electrode attracts positive ions. Charge accumulates at the interface between the electrodes and the electrolyte, forming two charged layers (known as electric double layers) with an extremely small separation distance in the order of 1 nm. Hence,

they are also known as electric double-layer capacitor. This charge accumulated at both electrode surfaces generates energy when discharging, which is when system returns to its original state.



**Figure 3.** Schematic of a supercapacitor. It has two electrodes, mechanically separated by a separator, which are ionically connected to each other via the electrolyte. The electrolyte is a mixture of positive and negative ions dissolved in a solvent such as water. When the electrodes are polarized by an applied voltage, ions in the electrolyte form electric double layers of opposite polarity to the electrode's polarity, resulting in energy storage. Reference. 14.

### 1.2.2 Supercapacitor Performance Characteristics

A comparison of the properties, performance and efficiency between capacitors, batteries and supercapacitors is given in Table 1. Having high energy and high discharge time makes supercapacitors superior to dielectric capacitors. Due to absence of chemical reactions, supercapacitors have longer cycle life compared to batteries.<sup>15-17</sup> Even though batteries have the highest energy density compared to dielectric capacitors and supercapacitors, they have the lowest power density and cycle life. Besides connecting the power gap between capacitors and batteries, supercapacitors also holds many other favorable properties that make them a promising candidate for the next generation energy storage device.<sup>18-21</sup> Some of these advantages are:

- fast charging/discharging capability
- unlimited cycle life, over > 100,000
- provides backup power
- very low impedance
- excellent reversibility
- environmentally friendly (no heavy metals or disposal issues as is common for conventional batteries)
- allows extreme working conditions (low/high temperature operations)

**Table 1.** Comparison of properties of capacitors, batteries and supercapacitors

| <b>Property</b>                         | <b>Capacitors</b> | <b>Batteries</b> | <b>Supercapacitors</b> |
|-----------------------------------------|-------------------|------------------|------------------------|
| <b>Lifetime (cycles)</b>                | >100k             | 150-1500         | >100k                  |
| <b>Charge/discharge time</b>            | 1 ps-1 ms         | 1-10 hours       | 1 ms-1 s               |
| <b>Energy density (Wh/kg)</b>           | 0.01-0.3          | 10-200           | 0.5-10                 |
| <b>Power density (W/kg)</b>             | >5000             | 100-3000         | 5000-10000             |
| <b>Operating Voltage (V)</b>            | 6-800             | 1.2-4.2          | 2.3-2.75               |
| <b>Operating temperature range (°C)</b> | -20 to 100        | -20 to 65        | -40 to 85              |
| <b>Cost per Wh</b>                      | 0.1 -1.0          | 1-2              | 10-20                  |

### 1.2.3 Supercapacitor Limitations

Despite of the technical advantages of the supercapacitors over other energy storage devices, they suffer from two critical obstacles that limits their applications – low energy density and high cost. The energy density of supercapacitors is  $\sim 0.5\text{-}10$  Wh/kg compared to  $10\text{-}200$  Wh/kg for batteries. At the same time the unit cost of batteries is only 1-2 dollars per watt hour, which is nearly one tenth of supercapacitors. Hence, to achieve a higher performance at a much reduced cost, researchers are exploring different routes to improve their capacitance, especially by developing low cost, high specific surface area and electronically conducting materials as supercapacitor electrodes.

Carbon based products are the preferred material for supercapacitor electrodes, due to their high surface area, high conductivity, electrochemical stability and open porosity.<sup>22-24</sup> A wide range of high surface area carbon materials have been tested including activated carbon, carbon nanotubes, carbon black, carbide-derived carbons, templated carbons, onion-like carbon, carbon nanofibers and graphene. Among these, activated carbons are the most widely used materials in the majority of supercapacitors currently available in the market, due to their lower cost, easy processing and manufacturing, high surface area and chemical stability.

Activated carbons are prepared by creating a three-dimensional porous network in the bulk of carbon materials through an activation process. This process consists of controlled oxidation of bulk carbon precursor using various activation techniques, such as oxidation in water vapor, KOH or CO<sub>2</sub>. Various carbon precursors have been used including carbonaceous materials derived from wood, coal, nutshells, etc. Depending on the activation process as well as the carbon precursor, activated carbons with surface areas of over  $2000\text{ m}^2/\text{g}$  can be achieved. The porous structures of

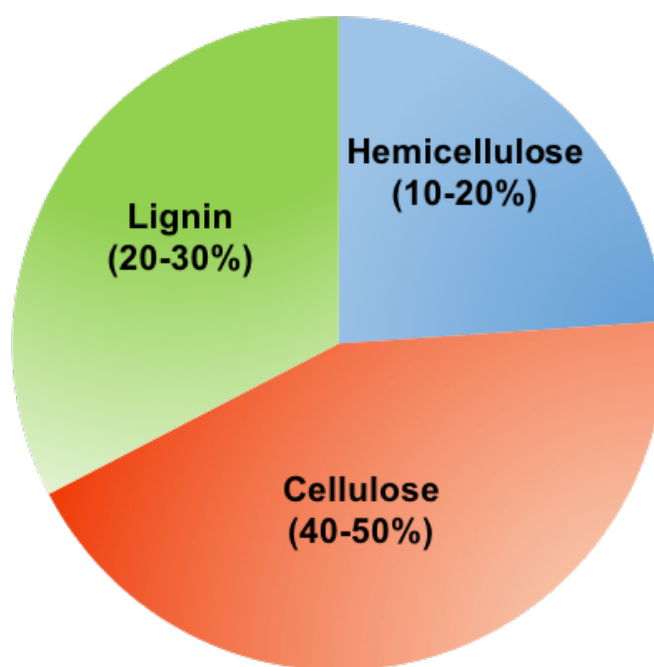
these activated carbons have a broad pore size distribution consisting of micropores ( $<2$  nm), mesopores (2–50 nm) and macropores ( $>50$  nm), which are responsible for the high specific surface area of activated carbons. However, the specific capacitance does not increase linearly with increasing specific surface area of the electrode. This is because not all micropores in the electrode are necessarily accessible to electrolyte ions, resulting in limited capacitance of only 60–120 F/g. In addition, the presence of oxygen-containing groups on the surface of activated carbons from the activation process can reduce its electrical conductivity and power performance. Although activated carbons are widely used in today's supercapacitors, their applications are still limited to only niche markets due to their limited energy density and rate capability. Hence, it is necessary to develop new low-cost carbon materials with controlled and interconnected pore structures, high electrical conductivity and high surface area that is easily accessible to the electrolyte so as to improve the energy and power performance of current supercapacitors.

### **1.3 Lignocellulosic Biomass**

Lignocellulosic biomass or biomass as it is commonly referred to is the biological or organic matter derived from living or recently living organisms. It is available in many forms and from various sources such as forestry products, agricultural crops, herbaceous and woody energy crops, municipal organic wastes as well as manure. It is abundant, widely available, and at the same time sustainable and environment friendly. A rough estimate of terrestrial biomass growth, when calculated as dry matter, amounts to  $118 * 10^9$  tons per year.<sup>25</sup> Hence, it is an ideal precursor for various applications, especially in the field of renewable energy storage.

### 1.3.1 Biomass Composition

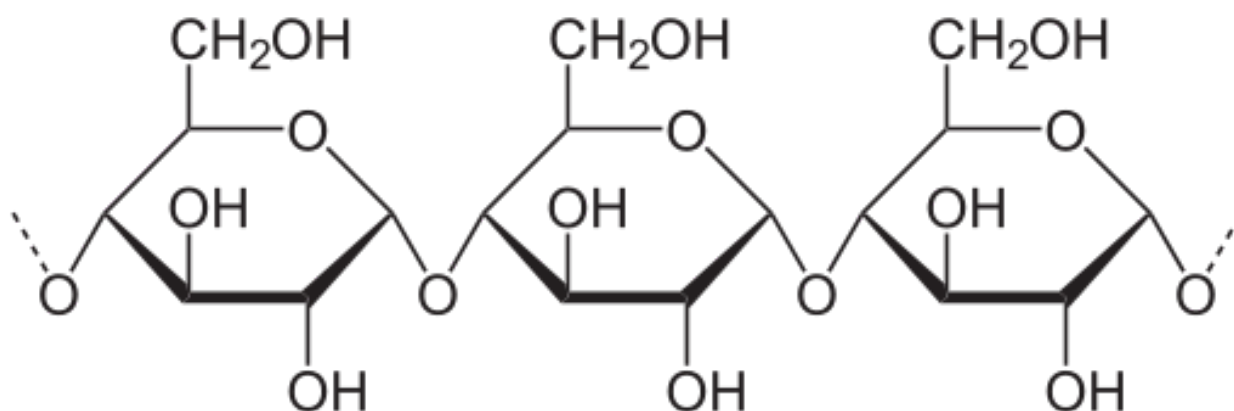
Biomass consists of mainly three polymers: cellulose, hemicellulose and lignin. These three components of biomass form three-dimensional polymeric composites to provide structure and rigidity to the plant. The composition of these constituents can vary from one plant species to another. Figure 4 shows the main constituents and their composition ranges of biomass of wood. Hardwoods for example have greater amounts of cellulose, whereas wheat straw and leaves have more hemicellulose. The ratios between various constituents within a single plant vary with stage of growth, age, and other conditions.



**Figure 4.** Typical composition of lignocellulosic biomass of wood. It consists mainly of three organic compounds: cellulose, hemicellulose, and lignin. Cellulose is the main constituent and makes about 40-50% of biomass. This is followed by lignin (20-30%) and hemicellulose (10-20%).

Cellulose is the most abundant renewable organic resource on Earth. The total annual amount of cellulose is several billion tons, revealing the huge economic value of it. The cellulose content of biomass varies between species in the range of 40-50 %. It is the main component of the plant cell

wall. Although some animals (such as tunicates) and some bacteria contain cellulose, the content of cellulose in these species is negligible when compared with plants. It is a linear homopolymer polymer chain composed of D-glucopyranose units linked together by  $\beta$ -(1,4)-glycosidic linkages (Figure 5). It mainly contains carbon (44.44 %), hydrogen (6.17 %), and oxygen (49.39 %) groups. The chemical formula of cellulose is  $(C_6H_{10}O_5)_n$ ;  $n$ , called the degree of polymerization (DP), represents the number of glucose groups, ranging from hundreds to thousands or even tens of thousands.<sup>26</sup>

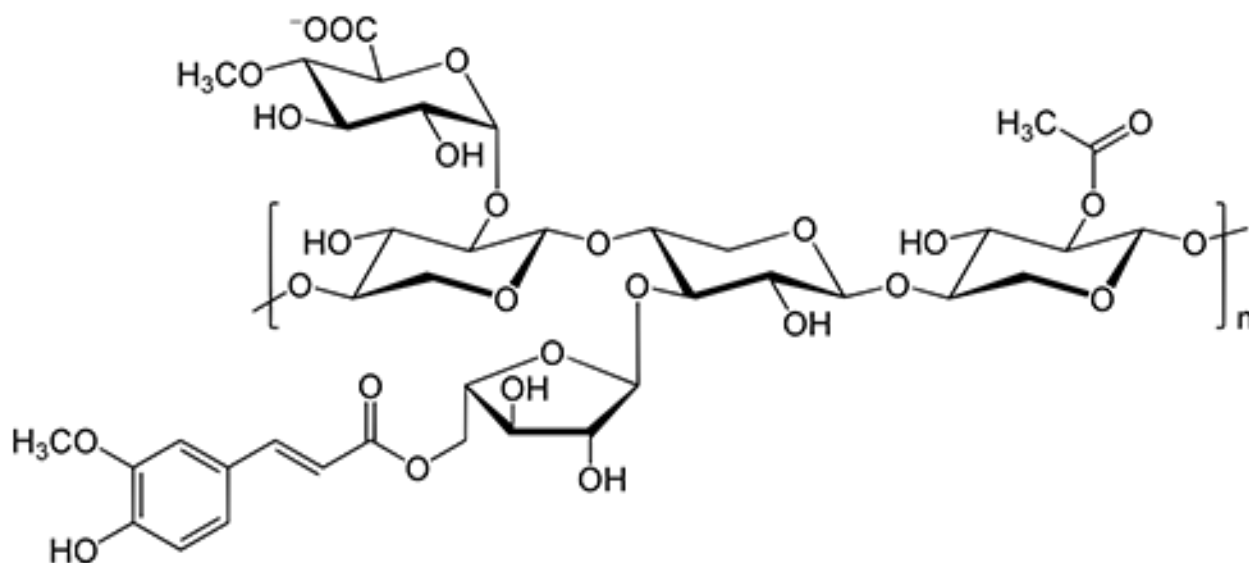


**Figure 5.** Schematic illustration of a cellulose polymer chain. It is a polysaccharide consisting of a linear chain of several hundred to many thousands of  $\beta$  linked D-glucose units. The glucose units in cellulose are combined in a way that results in the formation of very linear, flat molecules that can, in turn, form sheets that possess extensive networks of hydrogen bonds. The hydrogen bonds are both within individual sheets and between successive sheets. As a result of these bonds, sheets of cellulose are particularly strong—a property critical to the function of plant cell walls. Cellulose shows a variable degree of polymerization, with anywhere from 1,000 to 14,000 glucose residues comprising a single cellulose polymer. Reference. 27.

Hemicellulose, on the other hand, is a branched heteropolysaccharide with lower DP, only 150–200, and has different side groups on the chain molecule. It is made of various hexose and pentose monomers such as glucose, mannose, galactose, xylose and arabinose. The most common hemicelluloses are: xylan, glucuronoxylan, arabinoxylan, glucomannan and xyloglucan. Figure 6 depicts the chemical structure of xylan hemicellulose polymer chain. Compared to cellulose,

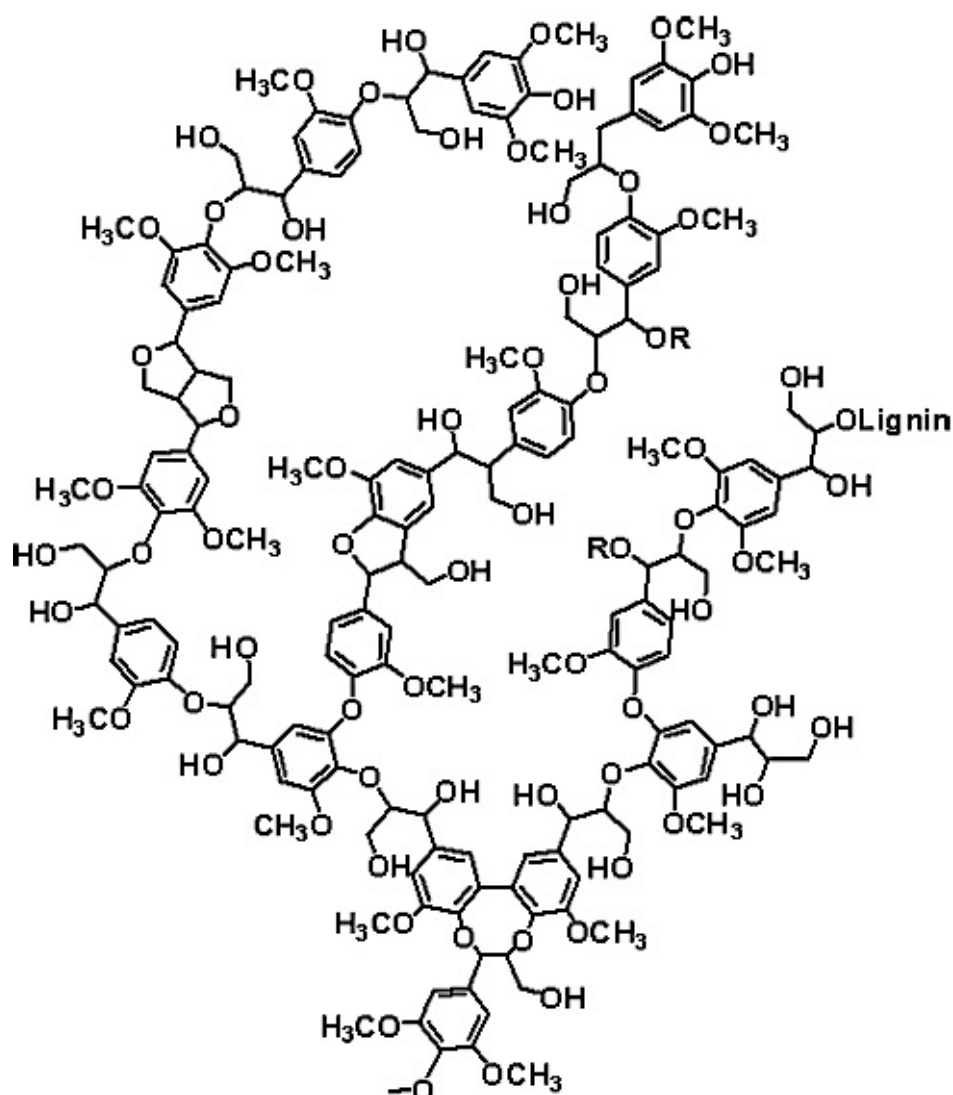


hemicellulose is amorphous in nature, making them soluble or partially soluble in water. They aid in strengthening the cell wall by interaction with cellulose and/or lignin. Hemicellulose can be found in plant stems, fruit and grain hulls. Even though it is not digestible, they can be fermented by yeasts and bacteria.



**Figure 6.** Schematic illustration of a xylan based hemicellulose polymer chain. The chemical structure of hemicellulose consists of long chains of a variety of pentoses, hexoses, and their corresponding uronic acids. The polysaccharides yielding pentoses on hydrolysis are called pentosans. Xylan is an example of a pentosan consisting of D-xylose units with 1 $\beta$ →4 linkages. Adapted from reference. 28.

Lignin is an organic polymer binding the cells, fibres and vessels, as in woods and straws. After cellulose, it is the most abundant renewable carbon source on Earth and makes up around 20-30% of biomass. Of the polymers found in plant cell walls, lignin is the only one that is not composed of sugar monomers. It is a complex, three-dimensional amorphous crosslinked polymer of aromatic functionality and is composed of three phenyl propane monomer units i.e. para-coumaryl alcohol, coniferyl alcohol, and sinapyl alcohol (Figure 7).<sup>29, 30</sup>



**Figure 7.** Schematic illustration of a possible lignin structure. It is an amorphous, randomly cross-linked polyphenolic material formed from an enzyme-mediated dehydrogenative polymerization of three phenylpropanoid monomers, conniferyl, sinapyl and para-coumaryl alcohols. Reference. 31.

Besides these three main components making plant biomass, a small portion of low molecular weight organic compounds (known as extractives) and inorganic mineral contents (known as ash) can also be found in biomass (less than 2%).

## **1.4 Biomass Conversion Routes**

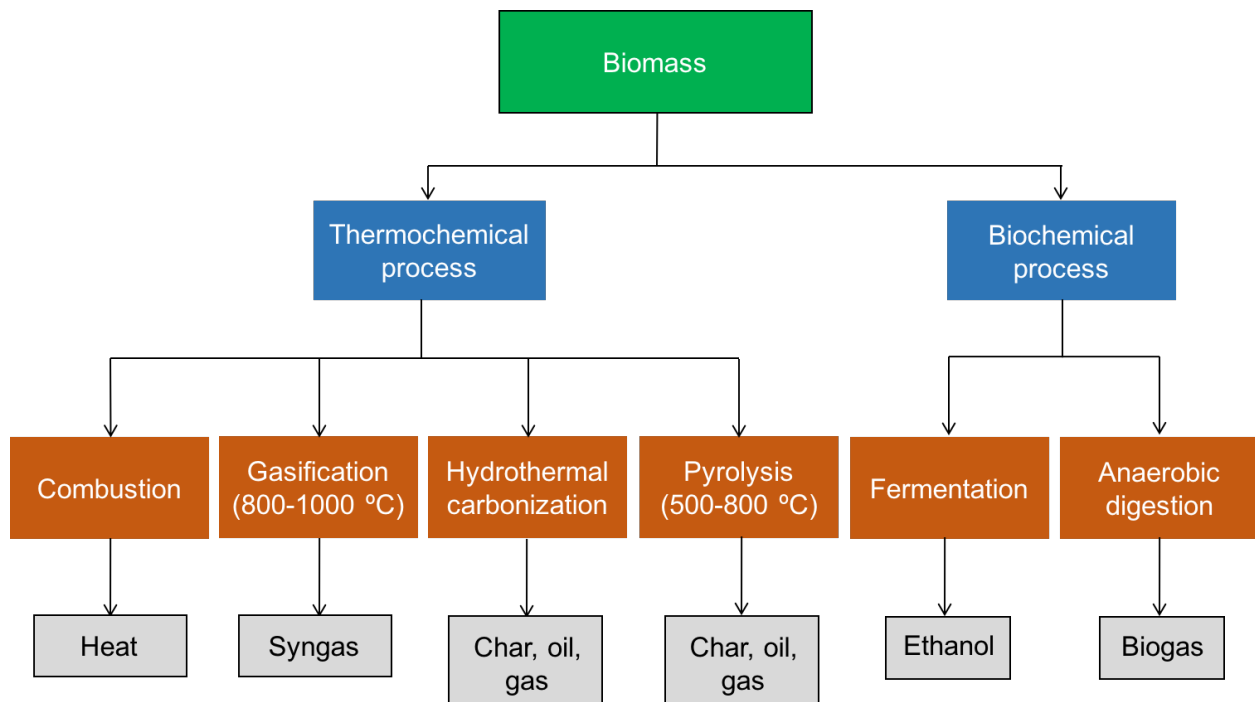
The low bulk density, high moisture content, poor grindability, and inferior heating value of biomass increases their cost of handling, transport, and storage. This challenge is further compounded by the expensive logistics of seasonal availability in the case of agricultural wastes or wide distribution in the case of forestry. In order to overcome these issues and to improve their material properties, they need to be converted into a more useful form. Figure 8 shows the main biomass conversion routes, along with their products. It can be divided into two types: biochemical processes (such as anaerobic digestion and fermentation) and thermochemical processes (i.e. pyrolysis, gasification, combustion, and hydrothermal carbonization).

### **1.4.1 Biochemical Pathways**

Biochemical processes take place at ambient to slightly higher temperature levels using a biological catalyst to bring out the desired chemical transformation. Ethanol from lignocellulosic biomass is produced mainly via biochemical routes. The biomass is first pretreated by different pretreatment methods for improving the accessibility of enzymes. After the pretreatment, biomass goes through the enzymatic hydrolysis for conversion of polysaccharides into monomer sugars such as glucose, xylose etc. Subsequently sugars are fermented to ethanol by the use of different microorganisms. Pretreated biomass can directly be converted to ethanol by using the process called simultaneous saccharification and fermentation. Therefore, pretreatment is a crucial step to overcome lignocellulose recalcitrance in the conversion of biomass to ethanol. It alters the physical and chemical properties of biomass and improves the enzyme access and effectiveness by:

- Altering or removing lignin and hemicelluloses,

- Changing the crystallinity of cellulose,
- Removing acetyl groups from hemicelluloses,
- Reducing the degree of polymerization in cellulose, and
- Increasing internal surface area and pore volume.



**Figure 8.** Biomass conversion routes can be divided into 2 types – biochemical and thermochemical processes. Biochemical processes mainly include anaerobic digestion and fermentation while thermochemical processes include pyrolysis, gasification, combustion, and hydrothermal carbonization.

#### 1.4.2 Thermochemical Pathways

Thermochemical processes depend on the relationship between heat and chemical action as a means of extracting and creating products and energy. When compared to common biological processes, they offer a number of advantages. Thermochemical processes generally take only hours, instead of the days or months common for biological treatments, allowing more compact reactor designs. Besides, some feedstocks are toxic and cannot be converted biochemically.

Furthermore, useful solid, gaseous and liquid end-products can be produced, that can be stored and handled more easily and used for various applications. Among the different thermochemical process, pyrolysis, gasification and combustion are dry biomass conversion routes i.e. in the absence of moisture, while hydrothermal carbonization is a wet synthesis. Though each of these methods has its own pros and cons, it improves the overall utilization of biomass.

*Pyrolysis:* Pyrolysis is the thermal degradation of biomass at elevated temperatures and in an inert atmosphere (absence of oxygen). The main operating parameters in pyrolysis are residence time, temperature, heating rate, feedstock, pressure, reactor configuration, etc.<sup>32, 33</sup> In addition, biomass properties such as chemical composition, ash content, particle size, moisture content, etc. also play an important role in a pyrolysis process. The products from biomass pyrolysis include a solid carbon product (biochar), a viscous liquid mixture (bio-oils) and some non-condensable gases. The products distribution strongly depends on the operating conditions. Low temperatures and long residence times favor the production of biochar while high temperatures and long residence times increase the gas yield. Moderate temperatures and short vapor residence times promote the bio-oil production. Generally, pyrolysis is divided into three categories based on the process heating rate: slow (0.1-1 °C/s), fast (10-200 °C/s), and flash pyrolysis (>1000 °C/s). Slow pyrolysis tends to produce more biochar than fast and flash pyrolysis, while the latter two aims at bio-oil production.<sup>34</sup> Table 2 compares the operating conditions for the 3 different pyrolysis processes, slow, fast and flash pyrolysis. Slow pyrolysis has a much longer residence time (300-500 s) compared to fast and flash pyrolysis.<sup>35</sup>

**Table 2.** Operating conditions for the three pyrolysis methods based on the process heating rate - slow, fast and flash pyrolysis.

| Parameters                 | Slow pyrolysis | Fast pyrolysis | Flash pyrolysis |
|----------------------------|----------------|----------------|-----------------|
| Heating rate (°C/s)        | 0.1-1          | 10-200         | >1000           |
| Pyrolysis temperature (°C) | 300-700        | 600-1000       | 800-1000        |
| Solid residence time (s)   | 300-500        | 0.5-10         | <0.5            |

*Gasification:* Gasification is the partial oxidation of biomass, resulting in production of product gas (consisting of hydrogen, carbon monoxide, methane, CO<sub>2</sub> (carbon dioxide), water (H<sub>2</sub>O) and other trace components). It offers a versatile, easier and clean ways to convert biomass into electricity, hydrogen, and other valuable products. But to achieve gasification, it is always necessary to pass through a pyrolysis process first. In other words, pyrolysis is the first step in biomass gasification. However, a gasification process is normally carried out at much higher temperatures than a pyrolysis process (>800 °C).<sup>36</sup> Gasification has a good potential for near-term commercial application due to the benefits over combustion including more flexibility in terms of energy applications, higher economical and thermodynamic efficiency at smaller scales, and potentially lower environmental impact when combined with gas cleaning and refining technologies.<sup>37</sup> Fisher-Tropsch synthesis can be used to convert the gaseous products into liquid fuels through the use of catalysts. Gasification requires feedstock that contains less than 10% moisture.

*Combustion*: It takes place when biomass is heated in the presence of oxygen in air to produce heat.<sup>38, 39</sup> The heat created by the burning of biomass is used in the operation of equipment such as boilers, furnaces, kilns, and engines. Along with heat, CO<sub>2</sub> and H<sub>2</sub>O are formed as byproducts of the exothermic reaction.

Though extensive research and development is happening in such dry biomass conversion technologies, they suffer from lot of limitations due to the properties and nature of the biomass types.<sup>40, 41</sup> To begin with as the moisture content in biomass is quite high (e.g. food waste), they need to undergo a long and highly energy intensive pre-drying step before conversion, which in turn increases the cost of the process.<sup>42-44</sup> Furthermore, as they are high temperature processes, it results in the production of innumerable tons of toxic gases such as CO<sub>2</sub>, which is continuously released into the atmosphere. Finally, the solid carbon product or biochar formed is quite low. All these factors combined restricts the use of such dry conversion technologies.

### **1.5 Hydrothermal Carbonization**

Hydrothermal carbonization (HTC) is a process similar to peat or coal formation. However, while the natural process of transformation of organic matter into peat or coal takes place on the time scale of some hundred (peat) to millions (black coal) of years, the time scale of the HTC process is that of day(s). In the process, sugars and carbohydrates are transformed into black soil, peat, brown coal or other carbonaceous materials.

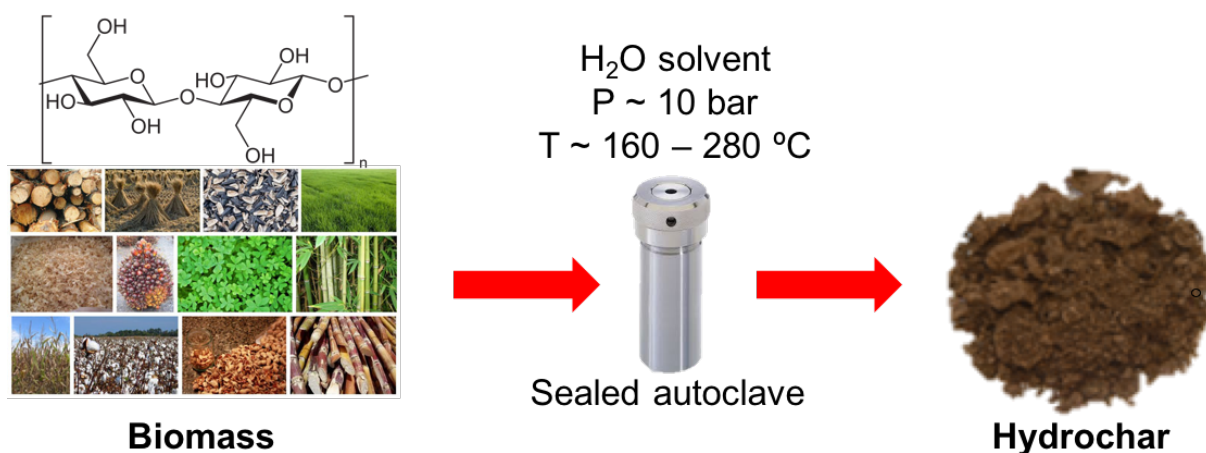
The method of producing bio-coal or biochar, from organic plant matters in an aqueous phase at moderate temperatures was first invented at the beginning of the 20<sup>th</sup> century by Bergius and Specht in 1913.<sup>45</sup> They described carbonization of biomass, specifically cellulose into bio-coal

within a few hours using a pressure chamber at moderate temperatures. Thus, the long lasting process known from nature was replaced in the laboratory with relatively higher temperature process, thereby accelerating the kinetics of the chemical reactions. The enormous discovery of Bergius was followed later on by other studies. For example, in 1932 Berl and Schmidt varied the biomass source and heated the different samples, at temperatures between 150 and 350 °C, in the presence of water. The latter authors summarized, *via* a series of papers the same year, the knowledge about the emergence of coal.<sup>46, 47</sup> Later, Schuhmacher, Huntjens and van Krevelen studied the effect of pH on the outcome of the HTC reaction and found serious dissimilarities in the decomposition schemes, as recognized by the C/H/O composition.<sup>48</sup> Starting from the new century, significant new interest in HTC has emerged followed by the synthesis of carbon products from simple carbohydrates. Since then a wide variety of HTC carbons and other hybrid materials have been synthesized and have been used for a wide variety of applications.<sup>25, 49-60</sup>

HTC is a thermochemical process in which the wet biomass is converted into a brown solid product, called hydrochar, in milder operational conditions, when compared to the other conversion technologies.<sup>61, 62</sup> It involves heating the biomass in the presence of water in a sealed autoclave at moderate temperatures and at pressures slightly higher than water saturation pressure, under an inert atmosphere (Figure. 9). The temperatures usually range from 180 °C to 250 °C, even though some authors have explored the behavior of the process up to 300 °C or even higher temperatures. The pressure is held as high so as to maintain water in the liquid phase (10 – 40 bar). Under these conditions, its dielectric constant decreases and its ionic product increases. Hence, water may act as an acid or base catalyst, as its  $\text{H}_3\text{O}^+$  and  $\text{OH}^-$  ion concentrations are most likely orders of magnitude higher than ambient water. As a result, water under subcritical conditions is a



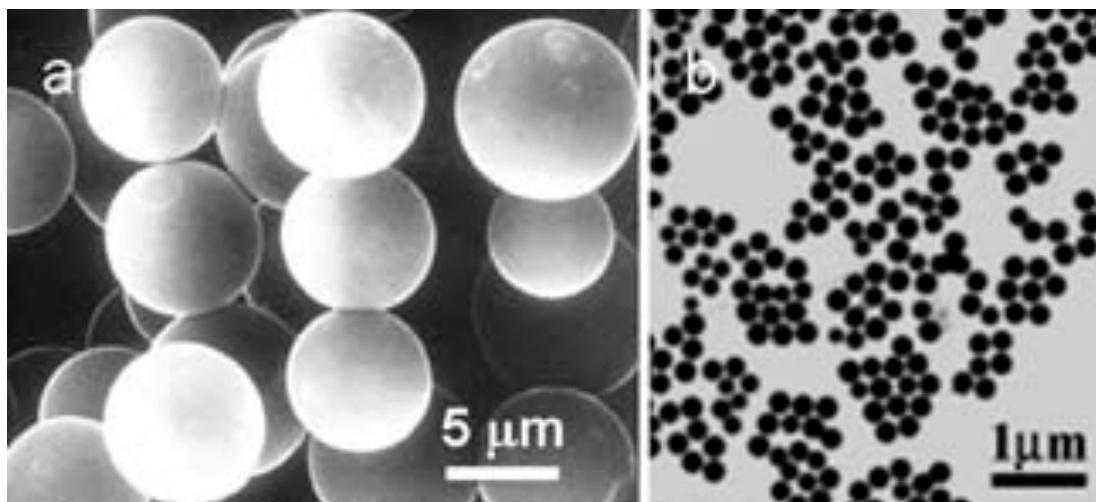
much better solvent, especially for hydrophobic organics. It can behave as a catalyst for reactions that normally requires the addition of an acid or base.<sup>63, 64</sup>



**Figure 9.** Schematic illustrating the hydrothermal carbonization process. Biomass such as corn, wood, waste etc. is heated in a sealed autoclave in the presence of water, at temperatures varying from 160 – 280 °C and at pressure greater than 10 bar. It results in the formation of a brown colored coal like material called hydrochar. The hydrochars obtained, especially from carbohydrates usually have sphere like morphologies.

During HTC, the wet biomass is converted into a carbonaceous hydrochar, which is a solid phase enriched in its carbon content, similar to that of coal. HTC char obtained from nonstructural carbohydrates are generally agglomerations of micrometer-sized carbon spheres that result in a sponge-like network of particles (Figure 10); although, feedstock and process conditions control the exact nature of product morphology.<sup>53, 65-67</sup> Further, HTC particles exhibit different chemical properties in the inner core and on the outer shell of the sphere. These differences are related to the fact that fairly stable oxygen bonds are established in the core, and less stable oxygen bonds are found on the shell. As a result, the shells tend to be more hydrophilic while the cores are more hydrophobic. Apart from the hydrochar, other hydrothermal products obtained during HTC include

non-condensable gases (mostly CO<sub>2</sub>), aqueous phase products (residues, sugars and organic acids) and water.



**Figure 10.** a) Scanning Electron Microscope (SEM) image of monodispersed hard carbon spheres. b) Transmission Electron Microscope (TEM) image of carbon spheres. Reference. 49.

Compared to dry biomass carbonization technologies, HTC offers many advantages.

- It can convert wet feedstocks into carbonaceous solids (hydrochars) without the need for an energy-intensive pre drying step. This opens up the field of potential raw materials to a variety of nonconventional sources such as human waste, wet animal manures, municipal solid waste, sewage sludges, aquaculture and algal residues.
- It is a much lower temperature process compared to pyrolysis and gasification. This not only reduces the amount of toxic gases generated, such as CO<sub>2</sub> but also makes the method more cost efficient.
- The biochar yield obtained is higher than other biomass carbonization techniques.

Despite these advantages, the main issues with this process is that the as synthesized hydrochar products are insulating and also have extremely poor specific surface area. They need to undergo

extensive post treatment procedures which in turn increases the overall cost of the process. Besides, the post treatment methods include the introduction of a lot of toxic harmful chemicals such as potassium hydroxide and  $\text{CO}_2$ , that reduces the overall appeal of this biomass conversion method.

In this dissertation, I will be presenting new routes to improve the properties of biochar obtained from the biomass carbonization of simple carbohydrates. In particular, techniques to improve the hydrothermal treatment process of glucose and cellulose using catalytic amounts of graphene oxide (GO) will be discussed in Chapter 2. Chapter 3 will contain different ways to improve the overall hydrochar yield obtained from HTC of glucose, especially by varying the process conditions. Chapter 4 describes methods to separate or remove the carbon spheres from the graphene-glucose carbon products obtained after HTC (Chapter 2). Finally, in Chapter 5, a new fast and convenient method of biomass carbonization will be introduced, using microwave radiation with the help of GO.

## **CHAPTER 2**

### **Graphene Oxide Assisted Hydrothermal Carbonization of Carbon Hydrates**

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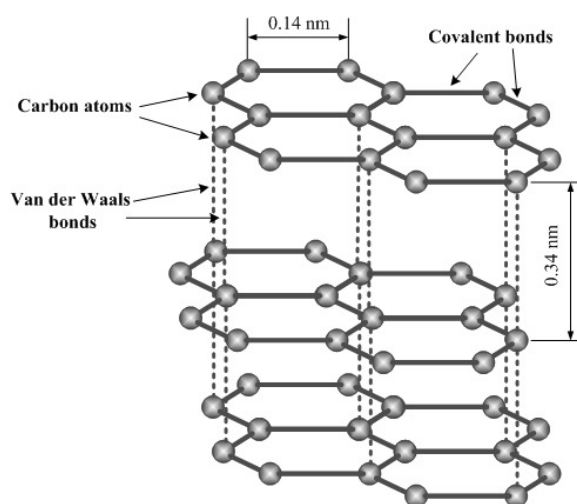
#### **2.1 Introduction**

Increasing energy demand due to rapid growth in population and industrialization along with environmental crisis has led to the search for cheap, environmentally friendly, and nontoxic materials for generation and storage of energy. Biomass is abundant and has been shown to be an efficient renewable resource for synthesizing functional carbonaceous materials. As mentioned in Chapter 1, HTC is one of the most promising techniques to convert biomass to functional

carbonaceous materials, and it involves hydrothermal heating the biomass at mild temperatures ( $\sim 200^\circ\text{C}$ ) under self-generated pressure in a closed container. Consequently, a variety of functional carbonaceous materials have been synthesized from biomass via the HTC process for potential applications in energy storage, water purification, hydrogen storage, and catalysis.

Since cellulose is one of the main components in lignocellulosic biomass, and glucose is the major structural unit and acid digestion product of biomass, they have often been used as model systems in HTC studies. HTC treatment of glucose or cellulose typically produces well dispersed, micron sized carbon spheres. However, these spheres are insulating and have very low surface area and porosity. Hence, they cannot be used as such for most applications, especially in the field of energy storage. They need to undergo extensive post treatment in the presence of toxic chemicals such as KOH, which in turn increases the cost of the process.

### 2.1.1 Graphene Oxide



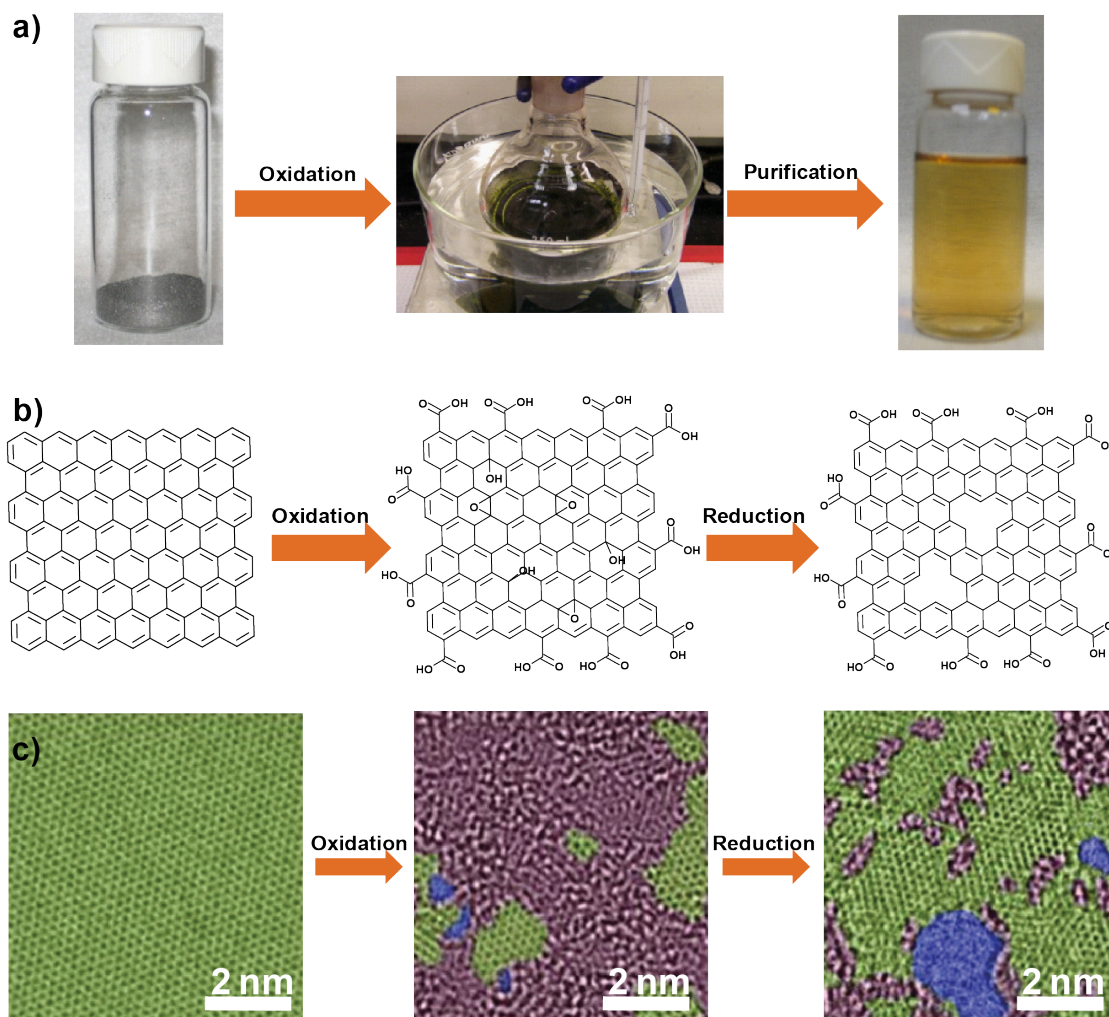
**Figure 11.** Layered structure of graphite showing the  $\text{sp}^2$  hybridized carbon atoms tightly bonded in hexagonal ring. The graphene sheets stack together to form graphite and are held together by weak Van der Waals forces at a distance of 0.34 nm from each other. Adapted from reference. 70.

Graphene is a two-dimensional (2D) crystal consisting of a single atomic layer of  $sp^2$ -hybridized carbon atoms arranged in a honeycomb crystal lattice. Graphite, on the other hand is a three-dimensional (3D) layered crystal lattice structure, formed by stacking parallel 2D graphene sheets, as is shown in Figure 11. The adjacent graphene sheets in graphite are held together by weak Van der Waals forces with the separation distance of 0.34 nm from each other. Graphene is the basic building block of all other graphitic forms of carbon such as nanotubes (CNTs) and fullerenes.<sup>71-</sup>

73

Various attempts have been made to synthesize graphene, but it was not until 2004 that groundbreaking research by Andre Geim and Konstantin Novoselov of the University of Manchester led to the isolation of a single sheet of graphene by mechanical exfoliation or the “scotch tape approach” on the top of a silicon wafer, and visualized successfully by optical microscopy and atomic force microscopy (AFM).<sup>74</sup> This led to their demonstration of graphene’s uniquely strong ambipolar effect and extraordinary electrical conductivity. Since then, the graphene field has aroused wide interest because of its unique 2D material structure and excellent mechanical, chemical and electrical properties.<sup>75-77</sup> For example, graphene was found to have a high optical transparency of 97.7%,<sup>78</sup> high charge carrier mobility of up to  $200,000 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ ,<sup>79</sup> high thermal conductivity of up to  $5,000 \text{ W m}^{-1} \text{ K}^{-1}$ ,<sup>80</sup> high nominal surface area of  $2,630 \text{ m}^2 \text{ g}^{-1}$ , and a high fracture strength of 125 GPa.<sup>81</sup> Therefore, many exciting applications ranging from electronics,<sup>82,</sup><sup>83</sup> polymer composites,<sup>84</sup> transparent conductors<sup>85</sup> and energy-storage materials<sup>20, 86</sup> have been envisioned and demonstrated for graphene. The novelty of the two-dimensional material and its great promise in applications led to the recognition of Geim and Novoselov with the 2010 Nobel

Prize in Physics for their “groundbreaking experiments regarding the two-dimensional material graphene”.<sup>87</sup>



**Figure 12.** Synthesis, structural model and microstructures of GO sheets. (a) GO is typically synthesized by reacting graphite powder with strongly oxidizing agents such as  $\text{KMnO}_4$  in concentrated  $\text{H}_2\text{SO}_4$ , followed by purification and exfoliation in water to yield a colloidal dispersion of single layers. (b) Structural model of graphene (left), GO (middle) and its reduction product r-GO. Graphene consists of a single atomic layer of  $\text{sp}^2$ -hybridized carbon atoms which are found stacked together in the form of graphite. Liquid-phase chemical oxidation of graphite powder results in GO which consists of a graphene sheet derivatized by epoxide and hydroxyl groups on the basal plane and carboxylic acid groups on the edges. The edge  $-\text{COOH}$  groups can ionize, resulting in an electrostatic repulsion between the sheets, allowing single-layers to form an aqueous colloidal dispersion. GO is insulating due to broken conjugation in the basal plane. After

reduction, r-GO becomes conductive but is still a very defective structure compared to graphene. (c) Color coded high resolution TEM images showing the atomic structures of graphene (left), GO (middle) and r-GO (right). The green, purple and blue areas depict ordered, graphitic  $sp^2$  domains, disordered highly oxidized  $sp^3$  domains, and holes on the sheet, respectively.

But despite its excellent properties, one major drawback limiting the large scale application of graphene is obtaining huge quantities of single-layer graphene material. Furthermore, graphene sheets usually tend to form aggregates in solvents and other matrices due to strong graphene-graphene intermolecular Van der Waals interactions and high specific surface area, consequently limiting dispersion and exfoliation. In order to overcome these processability issues, researchers have turned to the family of derivatized graphene sheets, in particular, graphite oxide sheets (GO). Graphite oxide sheets, now called graphene oxide (GO) is the product of chemical exfoliation of graphite that has been known for more than a century.<sup>88-90</sup> It is typically synthesized by reacting graphite powders (Figure 12a) with strong oxidizing agents such as  $KMnO_4$  in concentrated sulfuric acid.<sup>91, 92</sup> The oxidation of graphite breaks up the extended 2D -conjugation of the stacked graphene sheets into nanoscale graphitic  $sp^2$  domains surrounded by disordered, highly oxidized  $sp^3$  domains as well as defects of carbon vacancies (Figure 12b and 12c). The resulting GO sheets are derivatized by carboxylic acid at the edges, and phenol, hydroxyl and epoxide groups mainly at the basal plane.<sup>93, 94</sup> Therefore, the sheets can readily exfoliate to form a stable, light brown colored, single layer suspension in water.<sup>84, 95</sup> This severe functionalization of the conjugated network renders GO sheets insulating. However, conductivity may be partially restored conveniently by chemical, thermal, and photochemical treatments, producing chemically modified graphene sheets.<sup>96</sup> Therefore, interest in this century-old material has resurged after 2004's discovery on graphene.<sup>69, 74, 97-99</sup> The oxidization—exfoliation—reduction cycle effectively makes the insoluble graphite powders processable in water, enabling many ways of using the conducting



graphene or reduced GO (r-GO) products.<sup>100, 101</sup> Although the resulting graphene product or r-GO is more defective and thus less conductive than pristine graphene, it is sufficiently conductive for many applications such as electrodes for various energy devices.<sup>10, 20, 102-106</sup> Therefore, the ease of synthesizing GO and its solution processability have made it a very attractive precursor for large scale production of graphene in applications including transparent conductors, chemical sensors, biosensors, polymer composites, battery and ultracapacitors as described in a number of review articles.<sup>82, 107-116</sup>

Apart from making graphene, GO itself has many intriguing properties. Like graphene, GO sheets are characterized by two abruptly different length scales. The measured thickness is of typical molecular dimensions (ca. 1 nm), but the lateral dimensions are those of common colloidal particles, ranging from nanometers up to hundreds of micrometers.<sup>117, 118</sup> Therefore, GO sheets can be viewed as either molecules or particles, depending on which length scale is of greater interest. This molecule-particle duality makes GO an unconventional type of soft material of great fundamental scientific interest. An earlier structural model and recent high-resolution transmission electron microscopy study suggest that the basal plane of a GO sheet is composed of polyaromatic islands of unoxidized graphene nano-domains and heavily oxidized domains functionalized by hydroxyl and epoxide groups with hydrophilic carboxylic acid groups on the edges.<sup>119</sup> This makes GO effectively a 2D amphiphile with a hydrophilic periphery and largely hydrophobic center.<sup>120, 121</sup> Amphiphilic molecules contain both hydrophilic and hydrophobic regions, which are typically arranged in a linear, head-to-tail fashion. Such molecules are characterized by their ability to stabilize interfaces, or act as surfactants, for example, to form emulsions of oil and water or to act as a dispersing agent to solubilize incompatible solids in a liquid.<sup>122, 123</sup> Indeed, it has been shown

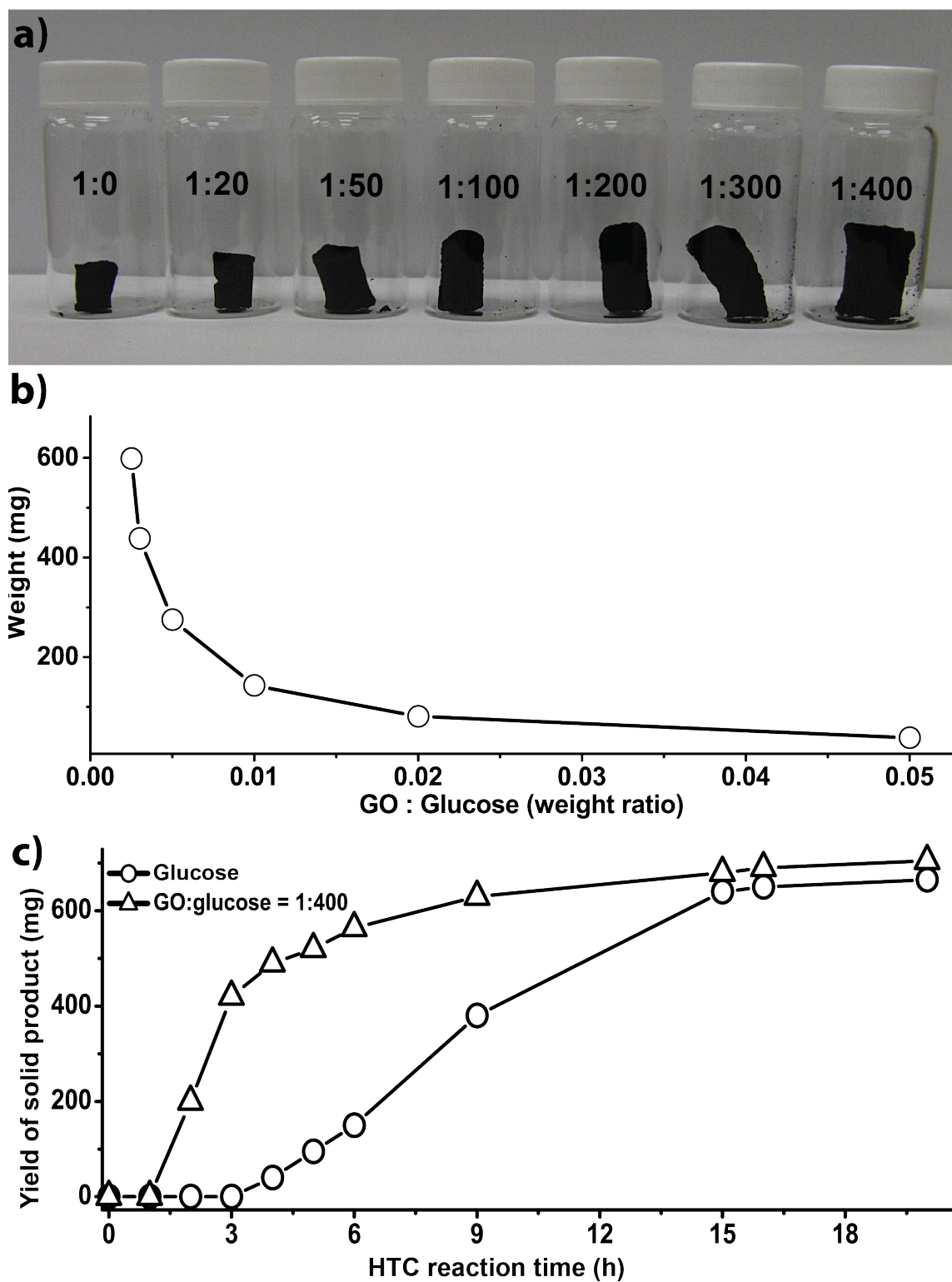
that GO sheets are surface active and can lower interfacial energies. They can accumulate at water surface during evaporation or by flotation, stabilize organic solvent in water and disperse hard-to-process materials such as graphite and carbon nanotubes in water, thus acting as a surfactant. An understanding of GO's amphiphilicity has led to improved knowledge of the structural—properties relationship of GO monolayer thin films, all-carbon composites for photovoltaics and energy storage, self-assembled GO windows for environmental scanning electronic microscopy (SEM), and GO/single walled carbon nanotubes based interfacial layers in solution processed polymer solar cells.<sup>123-127</sup> Furthermore, when interacting with other materials containing  $\pi$ -conjugated units, GO sheets are also capable of templating their assembly and even altering their molecular configurations.<sup>128</sup> Based on the above knowledge, I hypothesize that GO could act as a water dispersible agent, as well as a graphitic structural template to promote the carbonization of glucose and/or cellulose under hydrothermal conditions. It can easily interact with the biomass intermediate products and alter the carbonization route.

In this chapter, I report that GO can assist the HTC process of glucose and cellulose, leading to products with higher degree of carbonization and conductivity under the same reaction conditions. At low mass loading of GO, HTC of GO:glucose results in thick platelets having an average thickness of  $\sim 40$  nm. On the other hand, at higher mass loading level HTC of GO:glucose results in 3D monoliths which are conductive for a GO:glucose weight ratio as high as 1:800. Microwave irradiation provides an alternative cheap and fast technique for material processing to the conventional high temperature heating methods due to its high reaction rate, selectivity and increased yield of products. Microwave treatment of these HTC treated GO-glucose monoliths

helps to further enhance the conductivity of these samples due to the excellent microwave absorbent properties of r-GO.

### 2.3 Results and Discussion

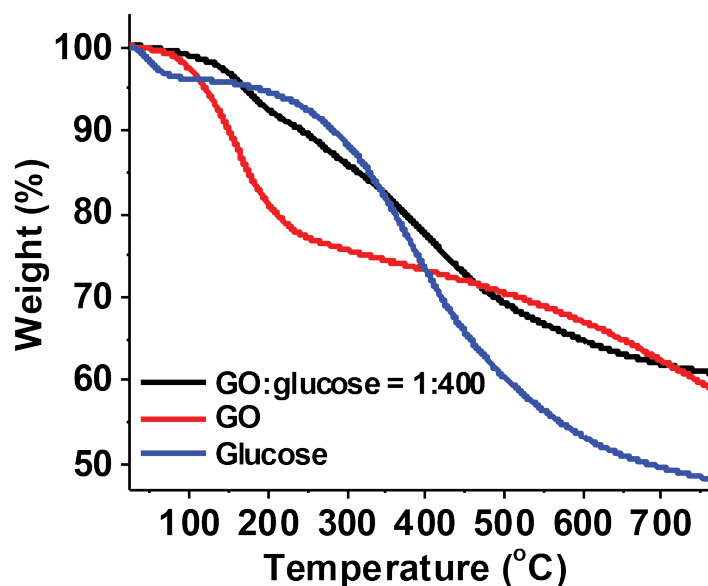
Glucose is the basic sugar building block of biomass, which has been extensively studied for synthesizing functional carbon spheres by HTC.<sup>129</sup> As mentioned in chapter 1, under hydrothermal conditions at relatively low temperatures ( $< 200\text{ }^{\circ}\text{C}$ ), glucose molecules underwent a series of dehydration and crosslinking reactions and eventually turned into carbonized spherical colloidal particles dispersed in water. The final yield of carbon spheres was about 10% by mass. Adding a small amount of GO to the reaction (GO concentration 1 mg/ml) did not affect the conversion yield, but completely altered the morphology of the HTC product. As reported earlier by Xu et al.,<sup>130</sup> HTC treatment of pure GO at a concentration of 1 mg/ml creates a 3D monolith of r-GO foam. HTC treatment of GO and glucose solution resulted in similar monolith-like products for a wide range of GO:glucose weight ratios up to 1:800. It is quite remarkable that such a small ratio of GO can influence the reaction product of large quantity of glucose. The sizes of the monoliths increased with increasing amount of glucose in the reaction mixture. Figure 13a shows a photo of the freeze-dried monoliths obtained by the HTC of 15 ml aqueous solution containing 15 mg GO with glucose amount varied from 0 mg to 6000 mg. The weight of the monoliths increased linearly with increasing amount of glucose in the starting reaction mixture, as shown in Figure 13b. The linear increase in the monolith weight indicates that glucose is being used efficiently in the monolith formation even at very high concentrations.



**Figure 13.** (a) At a concentration of 1 mg/ml, hydrothermal treatment of GO solution leads to a r-GO monolith (first vial on the left). Hydrothermal treatment of GO (1 mg/ml) and glucose mixture

can also create monoliths with GO:glucose weight ratios up to 1:400 as shown in the photo. (b) The weight of the monoliths increased linearly with increasing glucose content. (c) Hydrothermal treatment of glucose in the presence of GO leads to higher carbonization rate (as indicated by the product yield) especially during the initial stage of the reaction.

The effect of GO in the kinetics of HTC reaction is shown in Figure 13c using the HTC reaction of GO/glucose ratio of 1:400 as an example. To follow the reaction progress, two sets of parallel HTC reactions of glucose with and without the addition of GO were carried out with reaction time increased from 1, 2, 3, 4, 5, 6, 9, 12, 15, 16, and 21 hours. The solid products were collected by first quenching the autoclaves in cold water, followed by filtration. Figure 13c shows that hydrothermal treatment of glucose did not generate solid product within the first 3 hours. The amount of solid product increased nearly linearly afterward, and the reaction reached near completion at 15 hours. However, with GO sheets added, the reaction started after just 1 hour and proceeded much more rapidly. Nearly 60% of the final product was already produced within the first 3 hours. The reaction rate slowed down afterward, likely due to depletion of carbon precursors. Figure 13c clearly shows that the addition of GO sheets can significantly accelerate HTC carbonization reactions of glucose.

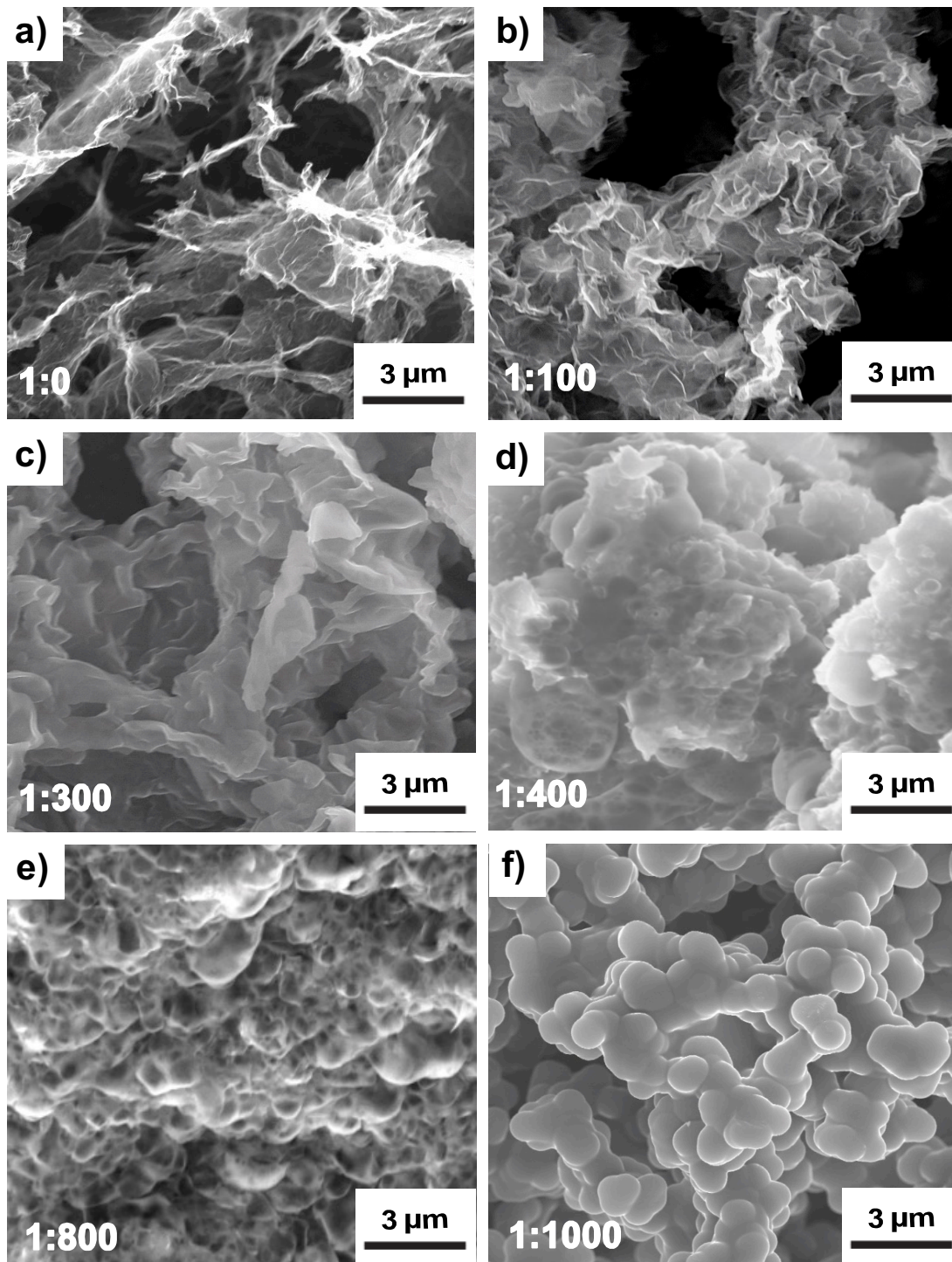


**Figure 14.** TGA curves of the monoliths obtained after HTC of a GO and glucose mixture (1:400), compared with those of pure GO and glucose treated under similar conditions (180 °C for 16 hours), respectively. The concentration of GO was maintained at 0.02 mg/ml. TGA was carried out in N<sub>2</sub> atmosphere at a heating rate of 10 °C/min. The steady weight loss in the temperature regime of 200 to 600 °C corresponds to thermal decomposition of functional groups.

The thermogravimetric analysis (TGA) curves of GO:glucose HTC product at a weight ratio of 1:400 is shown in Figure 14, and is compared with that of pure glucose and pure GO HTC products.

There is a significant difference in their thermal degradation characteristics. The thermal degradation of glucose derived carbon spheres undergoes two major weight loss stages. A first minor weight loss of around 5 wt% occurred at around 100 °C, which corresponds to the removal of moisture and volatile matter. Another major weight loss of nearly an additional 50 wt% occurred between 200-750 °C, which corresponds to the cracking of organic compounds. The monoliths obtained from GO:glucose exhibited much better thermal stability, showing only around 40% total weight loss when heated to 750 °C, which is comparable to the final weight loss of GO in the same temperature range. Under our HTC conditions, the yield of glucose carbonization is around 10 wt%. When GO is converted to r-GO after HTC treatment, the weight loss should be around 50%.

Assuming all GO sheets have turned into r-GO embedded in the platelets, the r-GO content should be around 1.7 wt%. Therefore, the over 10% difference in weight loss between the HTC products with and without GO cannot be attributed to a simple mixture of r-GO and HTC carbon. Figure 14 clearly shows that adding a small amount of GO (and its r-GO product) greatly improves the thermal stability of HTC product and even make it comparable to that of r-GO. The TGA results indicate that higher degree of carbonization and graphitization of glucose have been achieved by adding GO to the HTC reaction.



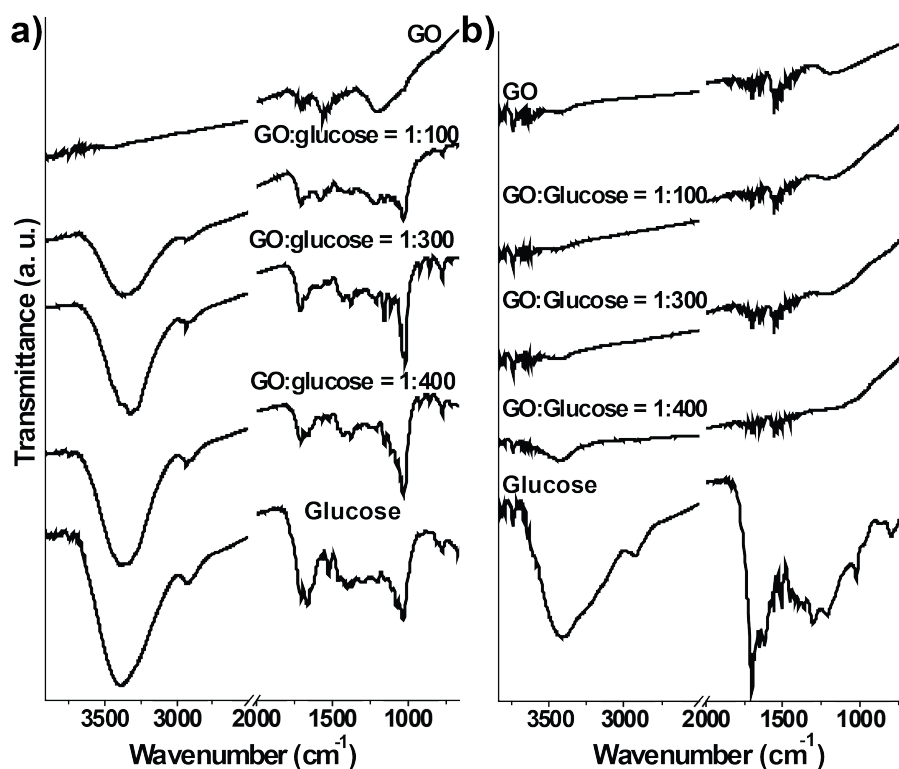
**Figure 15.** (a-e) SEM images of the HTC products of GO and glucose obtained with increase glucose content (1:0, 1:100, 1:300, 1:400, and 1:800) show that GO suppresses the formation of carbon spheres with GO/glucose ratio up to 1:800. (f) When even higher content of glucose (GO/glucose = 1:1000), the main product is carbon spheres, similar to those shown in Chapter 1.



The SEM images in Figure 15a-15f reveal the evolution of microstructures of the monolithic carbon products obtained with increasing amount of glucose in the precursor. As reported before, the monolith obtained from neat GO is made of interconnected graphene sheets forming a porous structure (Figure 15a). With increasing GO:glucose ratios up to 1:300, the resulting monoliths have similar open structure and are also made of sheet-like building blocks but with increasing thicknesses, suggesting that glucose carbonization product is uniformly coating the r-GO sheets. With GO:glucose ratio of 1:400, the resulting monolith is no longer porous and no platelet structure can be observed, as they may have been embedded in glucose derived carbon (Figure 15d). With further increase of glucose content to 1:800, the surface of the monolith starts to grow hemispherical buds, resembling the shape of the carbon spheres obtained without GO (Figure 15e). With GO:glucose ratio of 1:1000, the main HTC product is observed to be carbon spheres again, suggesting that the amount of GO is too little to alter the morphology of glucose HTC product (Figure 15f). However, the average diameter of the spheres had increased to micrometers and they were mostly interconnected, possibly due to the increased glucose concentration in the reaction vessel.

The degree of carbonization or de-functionalization of the HTC products were examined by Fourier transform infrared (FTIR) spectroscopy. Figure 16a compares the IR spectra of HTC products of GO, glucose, and their mixture. In the case of hydrochar obtained from HTC treatment of glucose, the bands at  $1710$  and  $1620\text{ cm}^{-1}$  (together with the band at  $1513\text{ cm}^{-1}$ ) can be attributed to C=O (carbonyl, quinone, ester, or carboxyl) and C=C vibrations respectively, whereas the bands in the  $1000\text{--}1450\text{ cm}^{-1}$  region correspond to C-O (hydroxyl, ester, or ether) stretching and -OH bending vibrations. The bands at  $875\text{--}750\text{ cm}^{-1}$  are assigned to aromatic C-H out-of-plane bending

vibrations, whereas the bands at approximately 2900 and 3000–3700  $\text{cm}^{-1}$  correspond to stretching vibrations of aliphatic C-H and OH (hydroxyl or carboxyl), respectively. The presence of  $\text{-C=O}$  and  $\text{-C=C}$  groups confirms the dehydration and aromatization of glucose during the HTC treatment. IR spectrum of the HTC treated GO:glucose monoliths looks very similar to that of the carbon spheres. However, the relative intensity of the peaks at around 3400  $\text{cm}^{-1}$  and 1030  $\text{cm}^{-1}$  decreased significantly. As the glucose concentration was increased, i.e. as the weight ratio was decreased from 1:100 to 1:400, there was a corresponding increase in the relative intensity of OH groups. Even though hydrothermal treatment of GO does produce even more graphitic r-GO (Figure 16a),<sup>131</sup> since only 0.3 wt% of GO was added to glucose, the decrease in the intensity of OH bands should be attributed to enhanced degree of carbonization of glucose.



**Figure 16.** FTIR spectra of carbon spheres and monoliths obtained from different ratios of GO and glucose (a) after HTC and (b) after microwave treatment for 1 minute.

Elemental analysis revealed that the C/O ratios of carbon spheres and hydrothermally treated GO are 1.8 and 4.5, respectively. GO assisted HTC products were found to have higher C/O ratios. For example, the monoliths obtained from GO:glucose with weight ratio of 1:100 and 1:400 have C/O ratio of 2.7 and 2.2, respectively. Since the weight percentages of r-GO in the final products are relatively insignificant, the increased C/O ratios should be attributed to higher degree of carbonization, which is consistent with the results from FTIR and TGA studies shown before.

While the use of GO seeds already improves the carbonization of glucose and leads to products with higher degree of carbonization, one can take advantage of the embedded r-GO sheets to further improve degree of carbonization through microwave treatment. The IR spectra of the samples after microwave irradiation using a 1250 W commercial microwave oven are seen in Figure 16b. Indeed, drastic reduction in the –OH band intensity around  $3400\text{ cm}^{-1}$  is observed for the GO seeded HTC samples. On the other hand, even after 5 minutes of microwave treatment, the carbonization degree of carbon spheres did not improve. This is further confirmed by elemental analysis. For example, the C/O ratio of HTC treated GO:glucose monoliths of weight ratio 1:400 increased from 2.2 to 12.5 after 1 minute microwave treatment, while that of the carbon spheres did not change after being microwaved for 5 minutes.

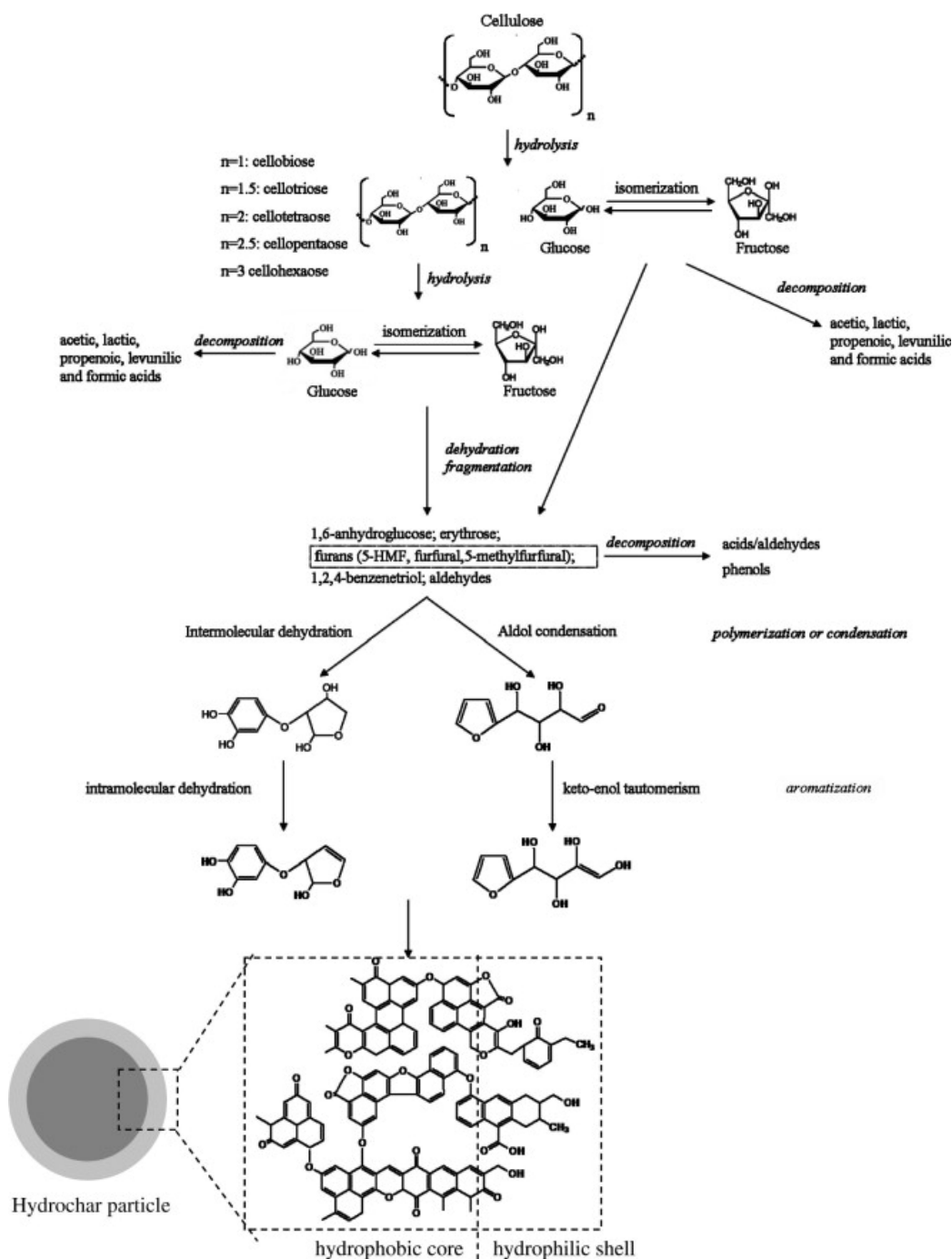
In order to clearly understand the increased carbonization of glucose in the presence of GO, it is necessary to comprehend the general hydrochar formation mechanism of pure glucose. The conversion of biomass into carbon materials by HTC is quite complex and follows several parallel pathways. Figure. 17 schematically illustrates the possible hydrochar formation mechanism from cellulose and glucose aqueous dispersions. Both these materials follow similar hydrochar formation routes. But in the case of hydrothermal treatment of cellulose, the first step involves its

hydrolysis at appropriate temperatures into its monomeric units i.e. glucose. At this stage, the hydronium ions generated by water autoionization catalyze the hydrolysis of cellulose giving rise to different oligomers (cellobiose, cellohexaose, cellopentaose, cellotetraose and cellotriose) and glucose, which subsequently isomerizes to form fructose. The decomposition of the monomers produces organic acids (acetic, lactic, propenoic, levulinic and formic acids), the hydronium ions formed from these acids being the catalysts of the degradation in subsequent reaction stages. The oligomers also hydrolyze into their monomers, which undergo dehydration and fragmentation reactions (i.e. ring opening and C=C bond breaking) leading to the formation of different soluble products, such as 1,6-anhydroglucose, erythrose, furfural-like compounds (i.e. 5-hydroxymethylfurfural, furfural, 5-methylfurfural), the hydroxymethylfurfural-related 1,2,4-benzenetriol, acids and aldehydes (acetaldehyde, acetonylacetone, glyceraldehyde, glycolaldehyde, pyruvaldehyde). The decomposition of the furfural-like compounds also generates acids/aldehydes and phenols. The subsequent reaction stages consist of polymerization or condensation reactions, which lead to the formation of soluble polymers. These reactions may be induced by intermolecular dehydration or aldol condensation. At the same time, the aromatization of polymers takes place. C=O groups appear due to the dehydration of water from the equatorial hydroxyl groups in the monomers. Alternatively, the C=C bonds may result from the keto-enol tautomerism of dehydrated species or from intramolecular dehydration. Aromatic polymer clusters may be produced by the condensation (by intermolecular dehydration) of the aromatized molecules generated in the decomposition/dehydration of the oligosaccharides or monosaccharides.

The growth of nucleated carbon particles may follow the LaMer model. When the concentration of aromatic clusters in the aqueous solution reaches the critical supersaturation point, a burst

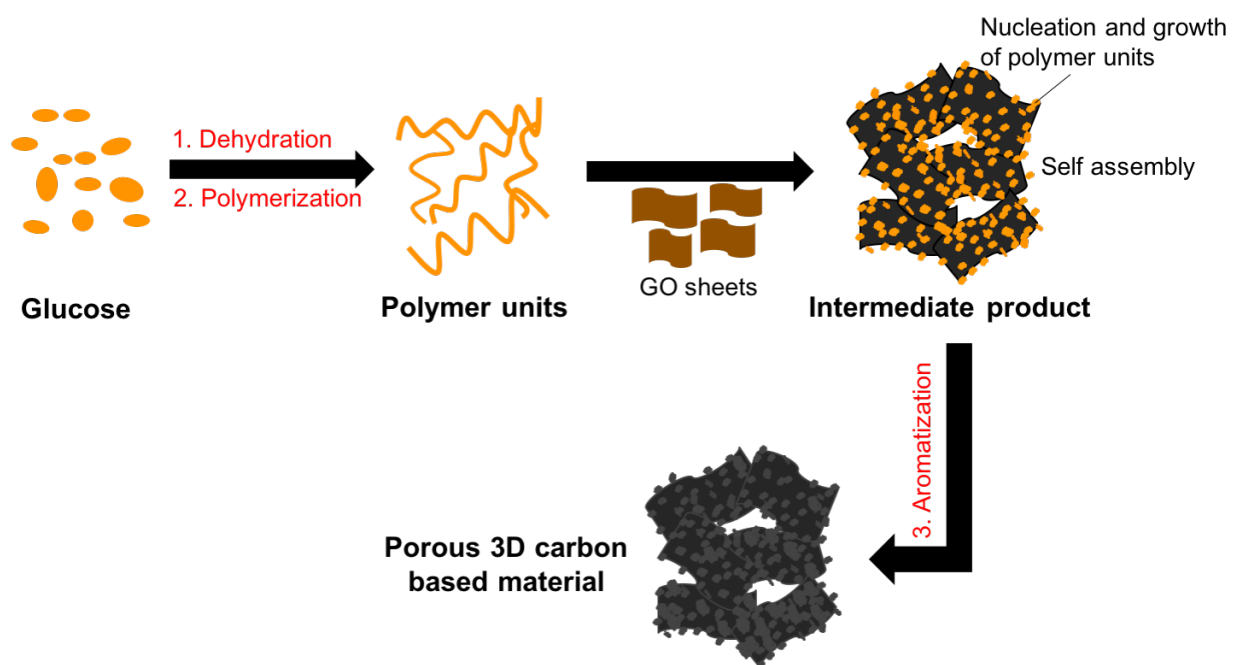
nucleation takes place. The nuclei so formed grow outwards by diffusion towards the surface of the chemical species present in the solution. These species are linked to the surface of the microspheres via the reactive oxygen functionalities (hydroxyl, carbonyl, carboxylic, etc.) present in both the outer surface of the particles and in the reactive species. As a result of this linkage, stable oxygen groups such as ether or quinone are formed. Under these circumstances, once the growth process stops, the outer surface of the hydrochar particles will contain a high concentration of reactive oxygen groups, whereas the oxygen in the core forms less reactive groups. Hence the hydrochar obtained has a highly hydrophobic core with hydrophilic functional groups on its surface.

Thus, the entire hydrochar formation from glucose can be divided into 3 steps: (a) dehydration/fragmentation, (b) polymerization and, (c) aromatization.



**Figure 17.** Schematic formation model for carbon spheres obtained from glucose and cellulose. Cellulose first hydrolyses into glucose and fructose, which in turn undergo dehydration, polymerization and aromatization to form spherical hydrochars. These spheres have a hydrophobic core with a hydrophilic shell. Adapted from reference. 132.

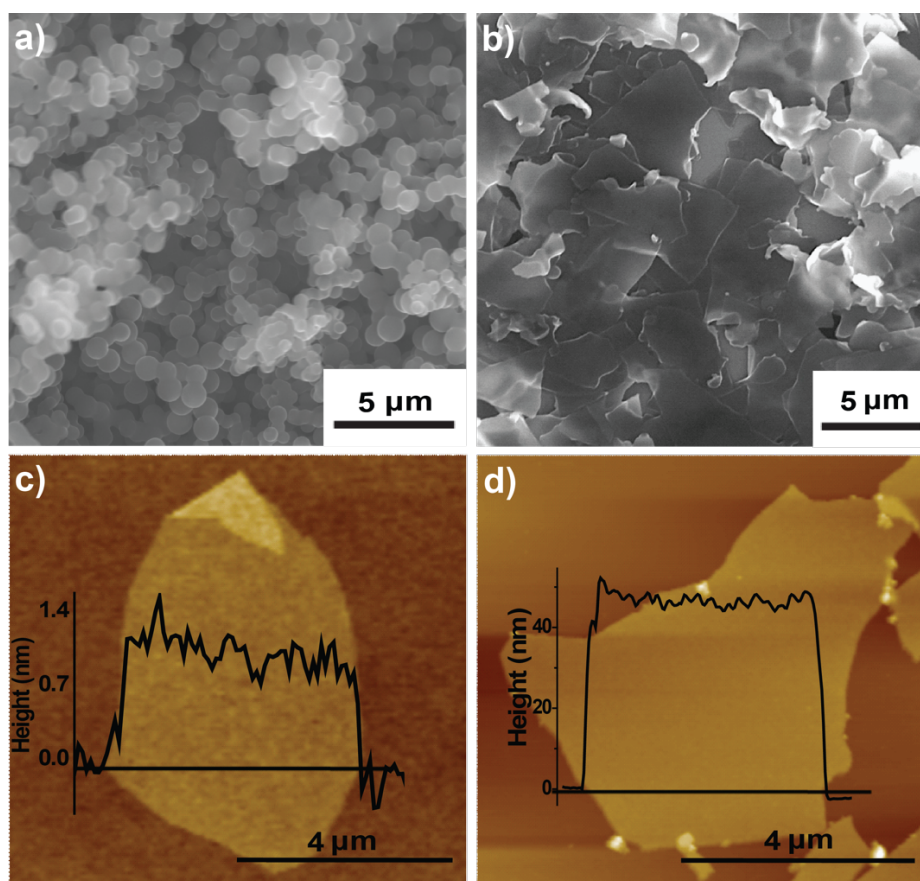
On the other hand, in the presence of GO, I believe carbonization of glucose follows a slightly different route, as shown in Figure 18. Glucose as usual undergoes dehydration and polymerization to form a cluster of polymeric units. At the same time, GO undergoes reduction to form r-GO. From here two processes can happen. r-GO sheets interact with one another and self assemble by Van der Waals interaction to form a 3D monolith. The glucose derived polymer units gets attached to the r-GO surface again by  $\pi$ - $\pi$  interaction and with the help of functional groups on its surface. The entire materials in turn aromatizes to form a highly porous 3D carbon based material.



**Figure 18.** Schematic illustrating the formation model for monoliths obtained from HTC treatment of glucose in the presence of GO.

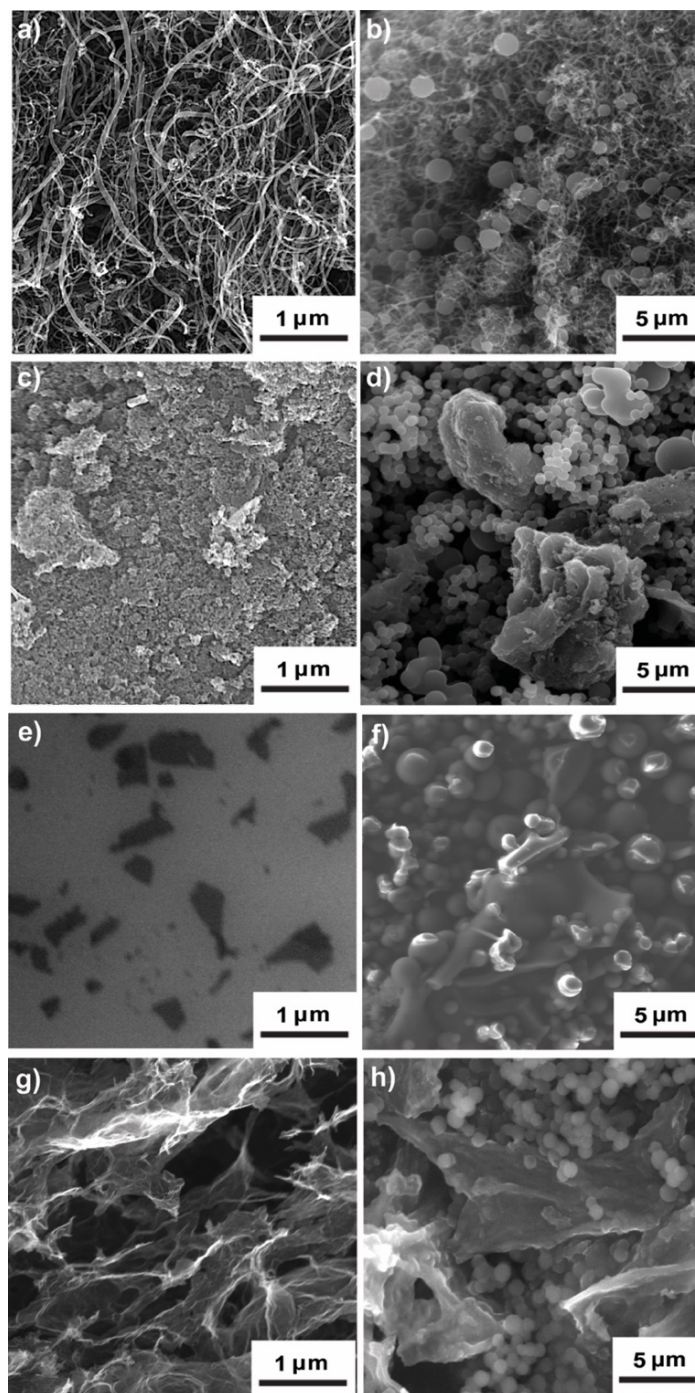
This is especially seen if I use a very dilute GO concentration for the HTC reaction. As mentioned before, hydrothermal carbonization of glucose results in carbon spheres. But, adding a small amount of GO to the reaction (final GO concentration 0.02 mg/ml, GO:glucose weight ratio of 1:300) resulted in thick platelets like structures. AFM studies (Figures 19c, 19d) shows that the

platelets obtained from HTC treatment of GO:glucose indeed resemble the appearance of GO sheets in terms of size and shape. The apparent thickness of GO sheets is around 1 nm (Figure 19c). However, the HTC platelets have an apparent thickness of around 40 nm (Figure 19d). Since no carbon spheres were observed, this implies that GO sheets can act as nucleation and growth sites for seeding the carbonization product of glucose.



**Figure 19.** (a) SEM image of the carbon spheres obtained after HTC of glucose at 180 °C for 16 hours (b) SEM image of the platelets obtained after HTC of GO and glucose at a weight ratio of 1:300 at 180 °C for 16 hours. The overall GO concentration was 0.02 mg/ml. (c) AFM image of a GO sheet with line scan showing thickness of around 1 nm and (d) AFM image of the platelet obtained after HTC of GO and glucose. The line scan shows the thickness is increased to around 40 nm.



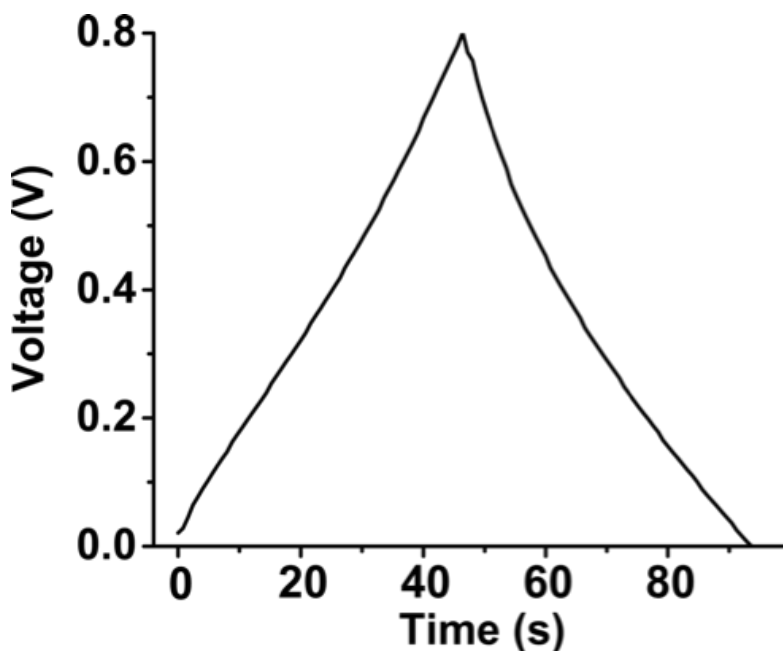


**Figure 20.** SEM images of (a) pure multiwalled CNTs and (b) the sample obtained after HTC of glucose with multiwalled CNTs (2 wt%), (c) pure activated carbon and (d) the sample obtained after HTC of glucose with activated carbon (2 wt%), (e) hydrazine reduced r-GO and (f) the sample obtained after HTC of glucose with hydrazine reduced r-GO (2 wt%), (g) HTC treated GO and (h) the sample obtained after HTC of glucose with HTC reduced GO (2 wt%). In all the cases, formation of carbon spheres was not suppressed.

Control experiments have been performed studying the glucose HTC products in the presence of other graphitic seeds such as graphite, carbon nanotubes, high surface area activated carbon, hydrazine reduced r-GO and HTC reduced r-GO. Figures 20a, 20c, 20e and 20g are SEM images showing the morphology of multiwalled carbon nanotubes (CNT), activated carbon, hydrazine reduced GO and HTC treated GO respectively. They were added into the glucose solution at a seed:glucose weight ratio of 1:50. Even at such high seed concentration, the main HTC product was carbon spheres. And no significant morphological change was observed for CNT (Figure 20b), activated carbon (Figure 20d), hydrazine reduced r-GO (Figure 20f) and HTC reduced r-GO (Figure 20h). Similar results were observed for graphite thin flakes. These results suggest that GO is unique or most effective in altering the morphology of HTC carbon. During glucose carbonization, the highly water soluble glucose is gradually converted to more aromatic and hydrophobic materials. Among the graphitic seed materials tested, GO is uniquely amphiphilic and can turn to more hydrophobic r-GO after HTC. Therefore, it should have favorable interaction with glucose, its reaction intermediates as well as the final carbon product throughout the HTC reaction, thus making it most effective to seed and template the formation of glucose carbonization product.

The conductivities of the monolith samples were measured after pressing them under high pressure into pellets of known dimensions and weight. Silver electrodes were deposited on both ends of the pellets. Current was measured by sweeping the voltage between  $\pm 0.5$  V. Pellets of carbon spheres and the HTC product from GO:glucose with weight ratio of 1:1000 did not show any current above the detection limit of the instrument (1 nA). However, all the other samples with GO:glucose ratio up to 1:800 were found to be conductive. 1:300 and 1:400 samples exhibit electrical conductivity

of around  $0.8 \text{ mScm}^2\text{g}^{-1}$ , which increased with increasing GO concentrations in the precursor solutions and reached  $95 \text{ mScm}^2\text{g}^{-1}$  for sample prepared with 1:20 GO:glucose weight ratio. Pure r-GO monolith exhibited a conductivity of  $200 \text{ mScm}^2\text{g}^{-1}$ . The sample prepared with 1:800 GO glucose ratio also showed a small conductivity value of  $3 \mu\text{Scm}^2\text{g}^{-1}$ . It is remarkable that a tiny fraction of GO in the starting reaction mixture has induced conductivity in large amounts of a material, which is otherwise an insulator. Although the embedded r-GO sheets also act as conducting channels, but to generate measurable conductivity at a macroscopic level the thick layer of glucose derived carbon should be able to support electron transport. In fact, casted thin films made of the platelets shown in Figure 19 were also found to be conductive. Since in such thin films, the r-GO sheets embedded in the platelets are largely parallelly aligned and not in direct contact with each other, it suggests that the glucose derived carbon coating the r-GO sheets must be conductive as well. Further, the conductivity of microwave treated GO seeded HTC products increased significantly after microwave treatment for just 1 minute. In contrast, 5 minutes of microwave treatment of carbon spheres did not make them conductive. For example, the normalized conductivity of the sample prepared with GO:glucose ratio of 1:400 increased from 0.8 to  $20 \text{ mScm}^2\text{g}^{-1}$  after 1 minute of microwave irradiation. r-GO sheets are strongly microwave absorbing,<sup>133, 134</sup> and thus can act as an *in-situ* heating element for rapidly annealing the surrounding HTC carbon materials. Apart from conductivity, the surface area of the glucose derived carbon improved significantly with the addition of GO. At a GO:glucose weight ratio of 1:400, the Brunauer–Emmett–Teller (BET) surface area of the monolith was around  $78 \text{ m}^2 \text{ g}^{-1}$ , which increased to  $205 \text{ m}^2 \text{ g}^{-1}$  after microwave treatment for 1 minute. But the surface area of carbon spheres remained at  $7 \text{ m}^2 \text{ g}^{-1}$ , even after microwaving for 5 minutes.

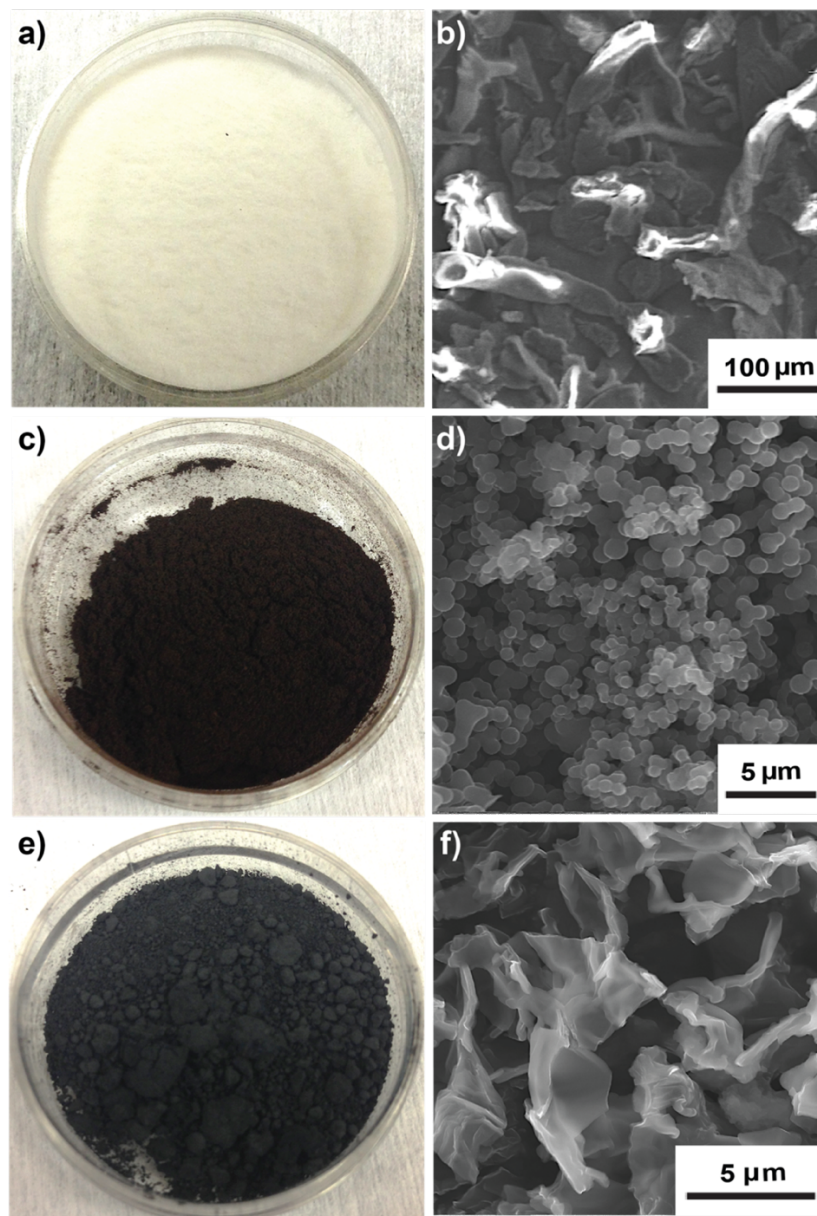


**Figure 21.** Galvanostatic charge/discharge curve of a supercapacitor prepared from microwave treated GO-glucose monolith with 1:400 weight ratio. Two-electrode symmetric coin cells were assembled with 5 M KOH of aqueous solution as the electrolyte.

Making biomass derived carbon materials conductive using catalytic amount of GO and further through r-GO assisted rapid microwave heating can lead to their more useful applications in electronics without significantly increasing material or processing cost. As a proof of concept, I have examined the performance of microwave treated monolith obtained from the GO:glucose precursor with weight ratio of 1:400 as ultracapacitor electrodes. Two-electrode symmetric coin cells were assembled with 5 M KOH of aqueous solution as the electrolyte. Figure 21 shows a typical cycle of charge/discharge curves of the resulting ultracapacitor device with a constant current density of 0.5 A/g. Symmetric and nearly linear charge/discharge curve was obtained, indicating excellent reversibility and high Coulombic efficiency. The specific capacitance value was calculated to be 143 F/g based on the weight of the active material on the electrode. The weight percentage of r-GO present in the final microwaved can be calculated by the following. In a control

experiment, 15 mg of GO was converted to a monolith of 4 mg after HTC and microwave treatments under the same conditions. While the final weight of the monolith prepared from 15 mg GO and 6 g glucose was found to be around 390 mg after microwaving. If we assume that GO inside the monolith undergoes the same extend of mass loss as neat GO after HTC and microwave treatments, the final product would contain around 1 % of r-GO. Note that the specific capacitance of neat r-GO monolith prepared by HTC treatment has been reported to be around 160 F/g. Therefore, the specific capacitance of 140 F/g should be largely contributed by the glucose derived carbon. It is also quite remarkable that adding such a small amount of GO in the starting reaction mixture and 1 minute of microwave treatment have transformed an otherwise insulating material into conductive carbon materials with specific capacitance value as good as many reported values for graphene itself.

Parallel experiments done with cellulose revealed that GO has similar effect in enhancing its HTC product. The starting white cellulose powders are made of irregularly shaped particles with sizes in the range of ten to hundreds of micrometers (Figure 22a, 22b). After HTC at 230 °C for 16 hours, dark brown powders of carbon spheres with diameter around 1 to 4  $\mu\text{m}$  were recovered from the resulting dispersion (Figure 22c and d). Adding 1 wt% of GO to cellulose changed the HTC product from a dispersion to a free-standing monolith. SEM examination of the freeze dried sample showed the presence of thick wrinkled platelets (Figure 22f) similar to those observed in GO:glucose HTC products. Elemental analysis shows that these samples have a C/O ratio of 4 while cellulose derived carbon spheres gave a C/O ratio of 3. The higher degree of carbonization is also evident by the black color of the GO:cellulose HTC product.



**Figure 22.** GO assisted HTC of cellulose. Photos of (a) pure cellulose, (c) its HTC product and (e) product obtained from GO:cellulose mixture (weight ratio 1:100) after HTC treatment at 230 °C for 16 hours. (b), (d) and (f) are SEM images correspond to (a), (c) and (e), respectively. HTC treatment converts (b) sub-millimeter sized cellulose particles into (d) few-micron sized carbon spheres. However, in the presence of GO, the HTC product shows thick sheet-like morphology.

## 2.4 Conclusion

The work here demonstrates that adding a small amount of GO can greatly improve the properties of biomass derived carbon without significantly increasing the cost of materials synthesis and processing. HTC of glucose and cellulose typically produces insulating micron-sized carbon spheres. However, HTC of GO and glucose resulted in thick platelets of glucose derived carbon coated r-GO sheets at low GO concentration. At high GO concentration, electrically conductive r-GO supported carbon monoliths were obtained. Adding 0.12 wt% of GO to glucose can already significantly alter the morphology, and improve the degree of carbonization and conductivity of its HTC carbon product. Control experiments with other carbon materials such as graphite, carbon nanotubes and carbon black show that only GO has significant effect in promoting HTC conversion, likely due to its good water processability, amphiphilicity and two-dimensional structure that may help to template the initially carbonized materials. Moreover, while glucose derived carbon spheres cannot be effectively heated by microwave, the embedded r-GO sheets can serve as *in-situ* microwave heating element for rapidly annealing the resulting composite to further increase the degree of carbonization and conductivity. 1 minute of microwave treatment in a commercial oven was able to enhance the conductivities of the HTC products by many orders of magnitude, making them readily useful for applications such as electrodes for ultracapacitors.

## 2.5 Experimental Conditions

**GO synthesis and purification:** All chemicals were purchased from Sigma-Aldrich and were used as received. GO was prepared using a modified Hummers' method and purified by two-step washing of HCl and acetone. Concentrated H<sub>2</sub>SO<sub>4</sub> (50 mL) was heated to 80 °C in a 250 mL round

bottom flask.  $\text{K}_2\text{S}_2\text{O}_8$  (10 g) and  $\text{P}_2\text{O}_5$  (10 g) were added to the acid and stirred until fully dissolved. Graphite powder (12 g, Bay Carbon Inc. SP-1 grade) was added to the solution and kept at 80 °C for 4.5 hours. The mixture was then cooled, diluted with deionized (DI) water, filtered using filter papers (Whatman, Grade No. 4), further rinsed with additional DI water (4 L) to remove residual reactants, and then dried in air. The pre-treated graphite powder was collected and transferred into a 2 L Erlenmeyer flask with concentrated  $\text{H}_2\text{SO}_4$  (460 mL) and chilled to 0 °C using an ice bath.  $\text{KMnO}_4$  (60 g) was slowly added to the mixture while stirring, taking caution to keep the temperature below 10 °C. The flask was then moved to a 35 °C water bath and left for 2 hours, and then transferred back into the ice bath. DI (1 L) water was slowly added to the flask while stirring, taking caution that the temperature did not rise above 55 °C. After dilution, 50 mL of a 30%  $\text{H}_2\text{O}_2$  solution was added to the mixture. This process induced violent bubble formation, so the solution needed to be added slowly to prevent overflowing. The color of the solution turned bright yellow. This mixture was filtered using filter paper (Whatman, Grade No. 4), and rinsed with 3.4%  $\text{HCl}$  solution (5 L) to remove residual salts. The resulting wet solid was collected and centrifuged at slow speed (around 1 000 rpm). The supernatant was removed, and remaining solid was re-dispersed in acetone. The mixture was filtered again using a PTFE membrane (Millipore) and rinsed with additional acetone (approximately 4 L) to remove residual acid. The final solid GO cake was dried in air, which could then be easily detached from the membrane, and stored in ambient condition for future use.

**Synthesis of GO:glucose and GO-cellulose HTC monoliths:** For GO-glucose monoliths, 15 ml aqueous dispersion of GO was mixed with different amount of glucose and annealed inside a Teflon-lined autoclave at 180 °C for 16 hours. The concentration of GO was maintained at 1



mg/ml. The weight ratio of GO and glucose was adjusted from 1:0 to over 1:800. HTC of GO-cellulose was performed at a higher temperature of 230 °C. The resulting HTC monoliths were washed few times with both water and methanol solution and later freeze-dried for 6 hours. Microwave treatment was done by irradiating the freeze-dried monoliths in a commercial kitchen microwave oven of 1250 W for 1 minute. For glucose HTC products with other carbon sources such as CNTs, activated carbon and r-GO, similar HTC experiments were done at a carbon:glucose ratio of 1:50.

**Synthesis of GO:glucose HTC films:** A 15 ml aqueous dispersion of GO, at a concentration of 0.02 mg/ml, was mixed with glucose at a weight ratio of 1:300 and annealed inside a autoclave at 180 °C for 16 hours. The resulting solution was washed few times by both methanol solution and DI water and the precipitate was collected with the help of filtration. It was re-dispersed in DI water at a concentration of 0.5 mg/ml and later transferred onto silicon substrates with the help of Langmuir Blodgett (LB) assembly. For LB, the trough (Nima Technology, model 116) was carefully cleaned with acetone and then filled with DI water. The HTC treated GO-glucose solution was slowly spread onto the water surface dropwise using a glass syringe with speed of 100  $\mu\text{l}/\text{min}$  up to a total of 8-12 ml. The monolayer was then stabilized for about 20 min before isothermal compression. Surface pressure was monitored using a tensiometer attached to a Wilhelmy plate. The film was compressed by barriers at a speed of 20  $\text{cm}^2/\text{min}$ . The dimensions of the trough are 10 cm  $\times$  25 cm. Typical initial and final surface areas were around 240 and 40  $\text{cm}^2$ , respectively. The HTC treated GO-glucose sheets were transferred to substrates at various points during the compression by vertically dipping the substrate into the trough and slowly pulling it up (2 mm/min).

**Characterization:** SEM images were taken on a FEI Nova 600 SEM. TGA of the samples was carried out in a Mettler Toledo TGA/SDTA851 under N<sub>2</sub> atmosphere with a heating rate of 5°C/min. FTIR were acquired in transmission mode on a Nicolet Nexus 870 FTIR spectrophotometer. Elemental analysis was performed by Atlantic Microlab, Inc., Norcross, GA, using combustion (carbon, hydrogen)- and pyrolysis (oxygen)-based analysis. The specific surface area was calculated from N<sub>2</sub> adsorption–desorption isotherms measured using a Micromeritics 3Flex surface characterization analyzer using the BET equation. For conductivity measurements, samples were densified under high pressure (41 MPa) and then cut into rectangular pellets of known dimensions and weight. Silver electrodes were deposited on either end of the pellet. A Keithley 2601A source meter was used to measure the currents between two electrodes by sweeping the voltage between  $\pm 0.5$  V. For electrochemical characterization, microwave treated 1:400 GO:glucose monoliths were grinded and mixed with polytetrafluoroethylene (PTFE) solution (5 % in isopropanol) in a weight ratio of 1:60 (PTFE:monolith) and then drop casted on stainless steel current collectors ( $\sim 3$  mg of sample per electrode was maintained). The capacitor electrodes made as such were characterized by constant current charge/discharge with two symmetric electrodes in CR2016-type coin cell using an Autolab electrochemical interface instrument (PGSTAT 302N). Waterman, grade no. 4 filter paper was used as the separator with 5 M KOH solution as the electrolyte.

## CHAPTER 3

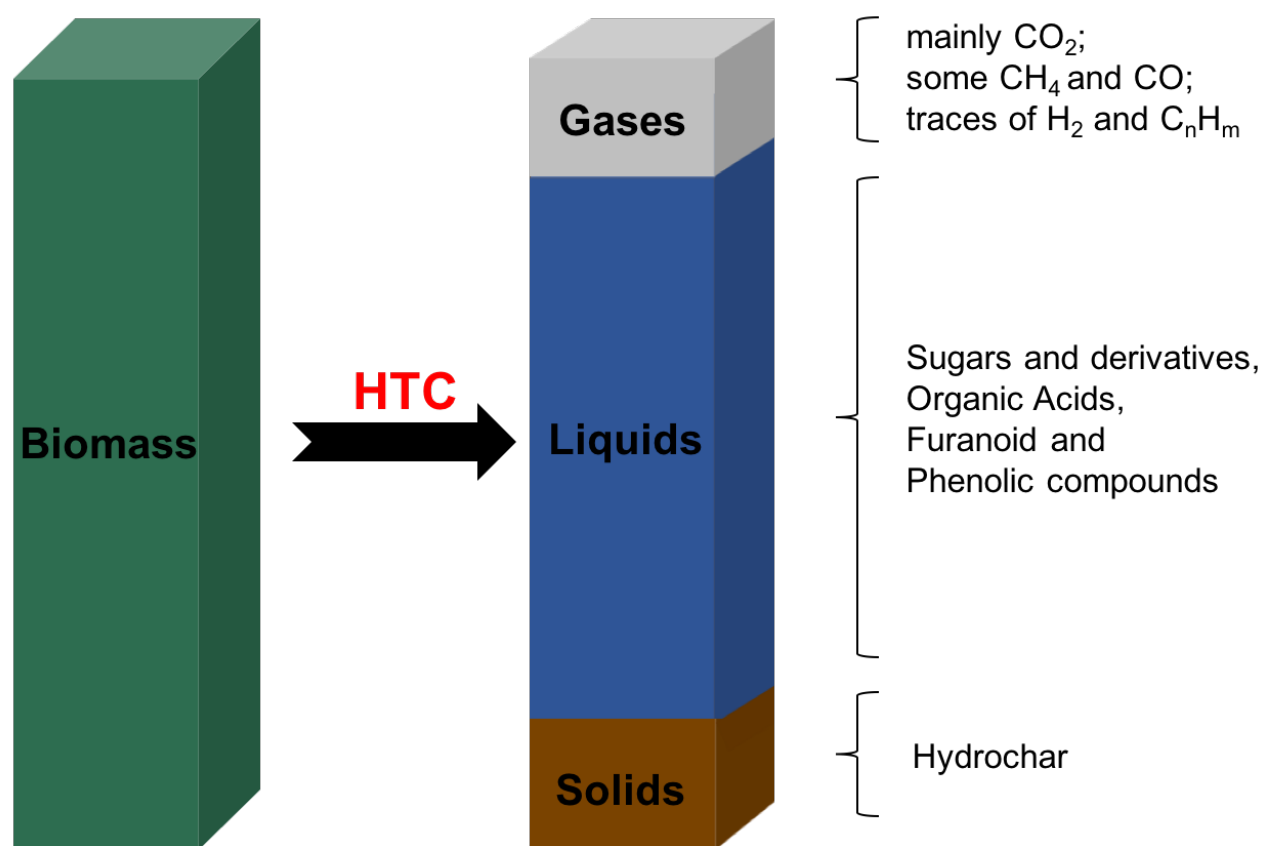
### High Yield Hydrothermal Carbonization of Glucose

Material in this chapter is reproduced in part from reference 135, “High Yield Hydrothermal Carbonization of Glucose” by Ying Tao, Deepti Krishnan and Jiaying Huang; In Preparation (2016).

#### 3.1 Introduction

The hydrothermal reaction of glucose in an autoclave at temperatures above 160 °C generates a solid carbon-based residue called hydrochar. The hydrochar material is made up of spherical particles that have diameters ranging from 0.4–6.0  $\mu\text{m}$ . During such HTC treatment, glucose undergoes a series of reactions, including hydrolysis, dehydration, decarboxylation, aromatization and condensation, which generates gas, liquid and solid products. The solid refers to the brown coal-like product obtained at the bottom of the autoclave, i.e. hydrochar. The liquid part, or the bio-oil, consists primarily of sugars, acetic acid, organic acids, alcohols, ketones, aldehydes, furans, phenols, guaiacols, syringols, and other oxygenates dissolved in the liquid phase. It has a

high load of organics along with some inorganics, many of which represent potentially valuable chemicals. The gas formed during hydrothermal treatment mainly consists of  $\text{CO}_2$ . Minor fractions of  $\text{CO}$ ,  $\text{CH}_4$  and  $\text{H}_2$  as well as traces of  $\text{C}_n\text{H}_m$  have been reported widely, too. Figure 23 shows the quantitative distribution of these three products obtained during HTC treatment of glucose.<sup>61</sup>



**Figure 23.** Products of hydrothermal carbonization, separated according to their state of aggregation – solids, liquids and gases. Solids comprise of the carbon product hydrochar, the liquids mainly contain sugars, organic acids and some inorganics formed during the process and gases include  $\text{CO}_2$  generated during the process. The overall yield of hydrochar is  $\sim 10\%$ . Adapted from reference 61.

More than 80 % of the original glucose goes into the liquid phase, with the remaining 20 % or so distributed equally between the solid and gaseous phases (Figure 23). So, the overall yield of these carbon spheres or hydrochars obtained from HTC of glucose is just  $\sim 10\%$ . But, for successful

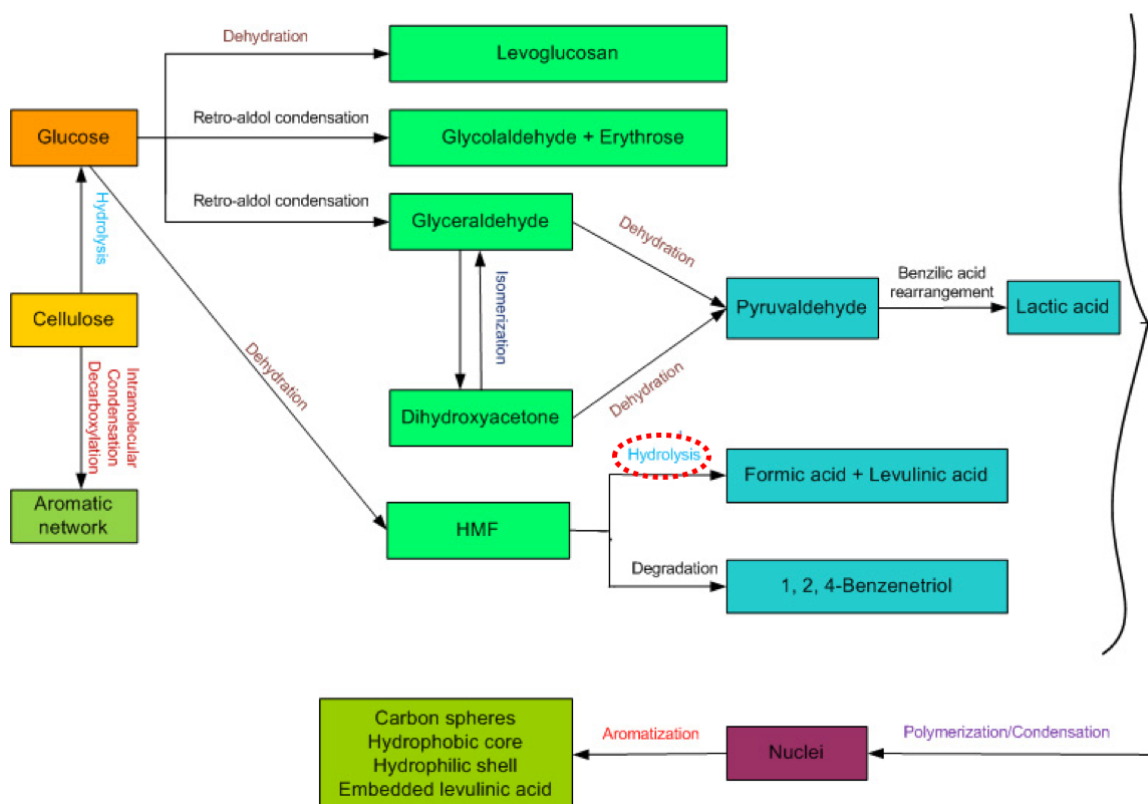
industrial-scale applications of these char materials, it is essential to improve the current hydrothermal treatment process to obtain higher carbon yield. Though the liquid phase contains large amount of dissolved carbon, it cannot be recovered by filtration and other separation techniques. In chapter 2, we saw that the addition of catalytic amounts of GO to glucose and subsequent hydrothermal treatment of the mixture can significantly enhance the rate of char formation. But this process did not seem to improve the overall yield of hydrochar, which still remained at 10 %. In this chapter, I shall talk about how we can improve the char yield during HTC of glucose by tuning various process parameters and conditions, such as water content and temperature of the process.

### **3.2 Results and Discussion**

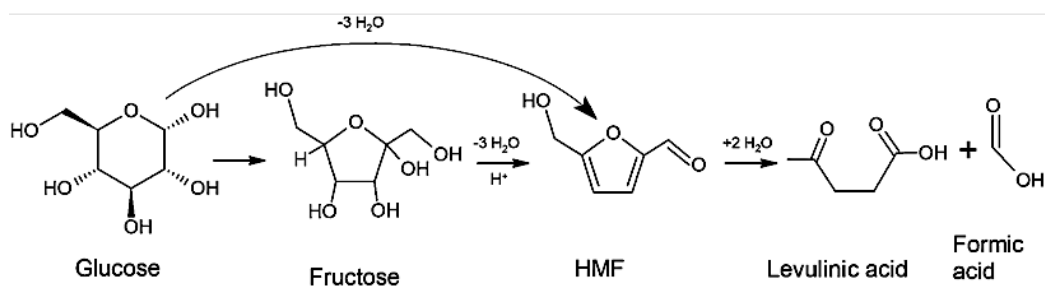
As mentioned before (chapter 2), during hydrothermal treatment glucose molecules decompose to form intermediary products, which in turn polymerize to form a cluster of polymeric units. When the solution reaches a critical supersaturation, a short single burst of nucleation resulted. The as-formed nuclei then grow uniformly and isotropically by diffusion of solutes towards the particle surfaces, until a final carbon sphere size is attained.

The first major step involves the acid catalyzed dehydration of glucose into hydroxymethyl furfural (HMF) (Figure 24). With increasing residence time, the HMF successively decomposes into levulinic acid and formic acid on one hand and into polymeric carbonaceous material on the other. Figure 25 illustrates the detailed chemical pathway for the conversion of glucose to HMF and in turn to levulinic acid and formic acid. The major hydrochar weight loss happens in this hydrolysis step, wherein HMF forms levulinic acid and formic acid. The activation energy for the conversion of HMF into 1, 2, 4-benzenetriol is ~142 KJ/mol while rehydration of HMF into levulinic acid is

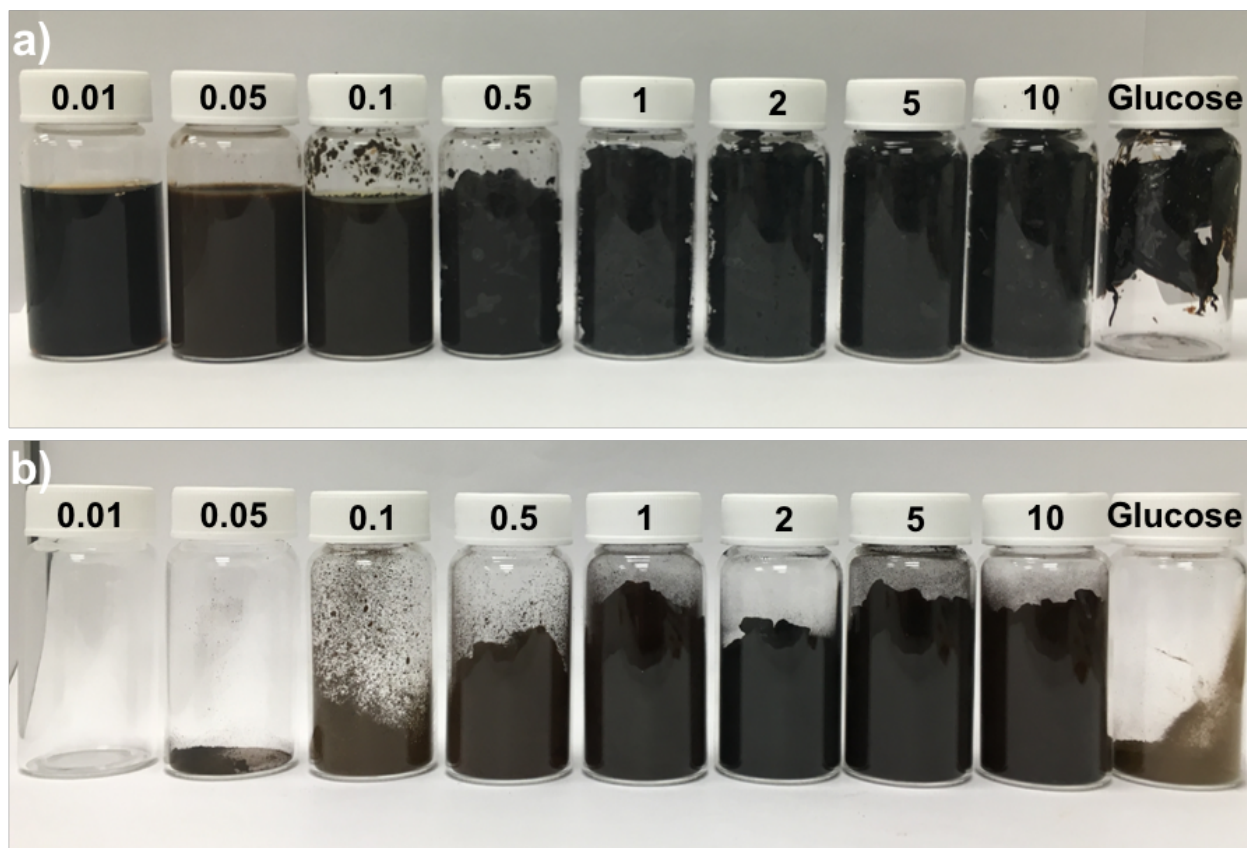
just 95 KJ/mol. Hence there is an enhanced selectivity for the latter. But, by controlling the amount of water added to the process, we can restrict this hydrolysis reaction and decompose even more HMF into carbonaceous polymers, thus increasing the hydrochar yield.



**Figure 24.** Schematic illustrating the hydrochar formation mechanism from glucose. It consists of mainly three steps – dehydration, polymerization and aromatization. After the dehydration step, an intermediary HMF product is formed, which in turn is converted to formic acid, levulinic acid and some carbon compounds. Adapted from reference. 136.



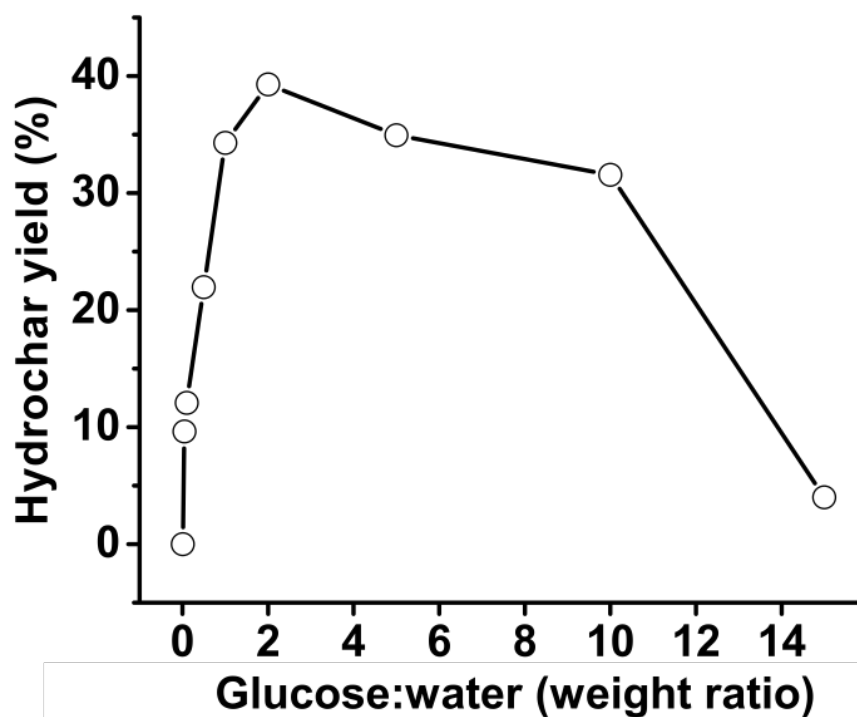
**Figure 25.** Schematic demonstrating the glucose dehydration pathway to HMF and its hydrolysis into levulinic acid and formic acid.



**Figure 26.** (a) Photos showing the products obtained after hydrothermal treatment of glucose:water at weight ratios from 0.01 to 10, compared with that of glucose powder heated under similar conditions in the absence of water. (b) The corresponding char obtained after washing and drying. Very little char was formed at low glucose:water weight ratios (i.e. high initial water content) of 0.01 and 0.05, as well for that obtained from glucose powders without any moisture.

Glucose was mixed with water at various weight ratios from 0.01 to 10 and hydrothermally treated in a closed container at 180 °C. Figure 26a shows the photo of the complete products obtained after the HTC processes and Figures 26b indicates the corresponding char after washing and drying. At a high initial water content i.e. glucose:water weight ratio of 0.01, no hydrochar was obtained. As the water content was decreased, the amount of hydrochar formed increased. But for similar reactions in the absence of water, the char yield again decreased. Additionally, with increasing glucose:water weight ratios the hydrochar appears more black in color, indicating higher degree

of carbonization. Thus, by limiting the amount of water added during HTC of glucose, the hydrochar yield as well as the carbonization degree of the resulting products improved.



**Figure 27.** Hydrochar yield as a function of glucose:water weight ratio. Yield increased with decreasing water content and reached a maximum at a glucose:water ratio of 2. Further increase in glucose:water ratio decreased the char yield, but in the absence of water the char yield dropped to less than 4 %.

The yield of the char formed as a function of glucose:water weight ratio is plotted in Figure 27.

The percentage yield is calculated as

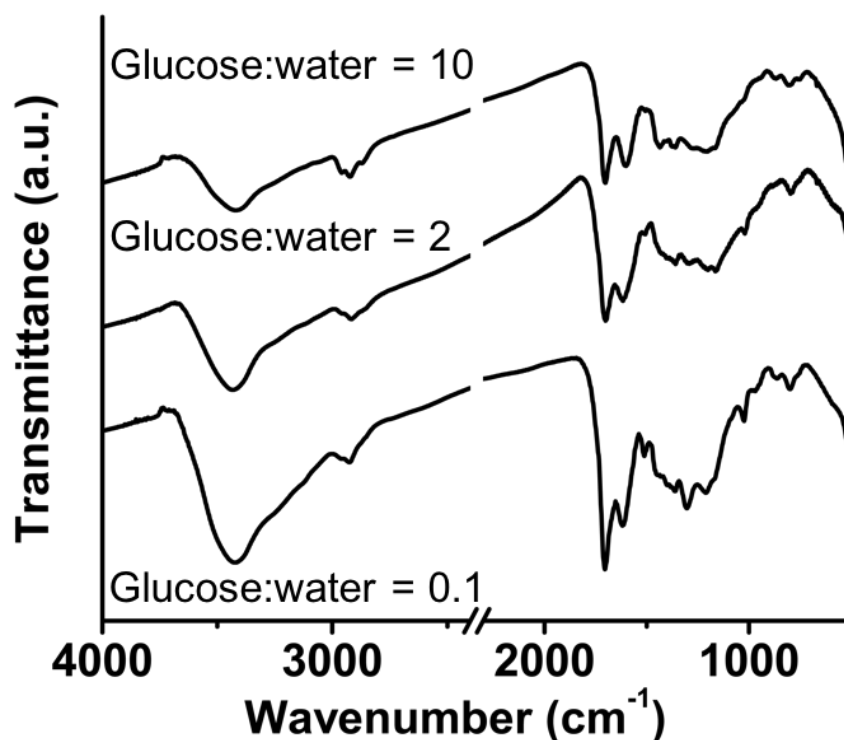
$$\text{Yield (\%)} = \frac{\text{Weight of final char formed}}{\text{Weight of initial glucose added}} * 100$$

At a GO:glucose weight ratio of 0.01, the hydrochar yield was close to zero. With further decrease in the moisture content, the yield increased significantly. A maximum yield of ~40% was obtained at a glucose:water ratio of 2. This huge increase in the hydrochar yield is most likely due to the reduced selectivity of HMF towards levulinic acid and formic acid, in the absence of excess



amounts of water. However, when glucose:water weight ratio was increased to greater than 2, the char yield dropped slightly. For example, when a highly concentrated glucose aqueous dispersion was used for HTC at glucose:water weight ratios of 5 and 10, the char yield was 35% and 32%, respectively. This could be because of the decrease in the amount of  $H^+$  ions provided by water under subcritical conditions, that is needed for acid-catalyzed ( $H^+$ ) dehydration of glucose or fructose to HMF (Figure 24 and 25). On the other hand, when similar reaction was done without water, the char yield was only ~4%. Thus, the presence of water during the HTC reaction of glucose is required for hydrochar formation, though in limited quantities. By restricting the amount of water added, the char yield increased remarkably from 10% to 40%.

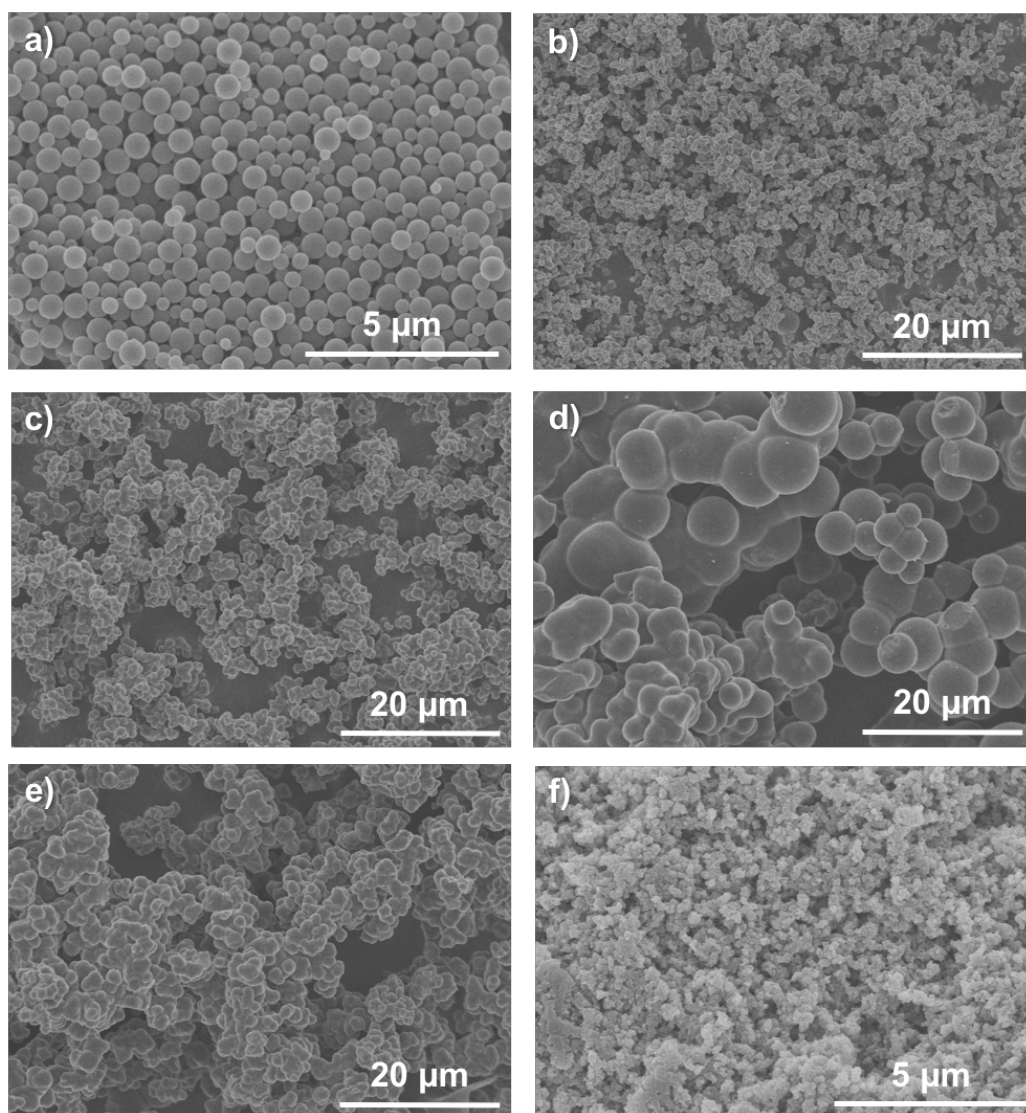
The FTIR spectra (Figure 28) of the dried hydrochars was used to identify the functional groups present after hydrothermal treatment. HTC-treated glucose samples at glucose:water ratios of 0.05, 2 and 10 showed similar IR peaks. In all three hydrochar products, the bands at 1710 and 1620  $cm^{-1}$  were attributed to C=O and C=C vibrations, respectively, supporting the concept of aromatization of glucose during hydrothermal treatment (Chapter 2). The bands in the 1000–1300  $cm^{-1}$  range, which include the C-OH stretching and OH bending vibrations, imply the existence of large numbers of residual hydroxyl groups. This shows that changing the water content during hydrothermal treatment did not significantly affect the distribution of functional groups in the carbon spheres.



**Figure 28.** FTIR spectra of glucose:water HTC treated carbons at weight ratios of 0.05, 2 and 10. Irrespective of water content, all the spectra showed similar IR peaks. The peaks at 1710 and 1620  $\text{cm}^{-1}$  correspond to C=O and C=C vibrations respectively and the peaks in the 1000–1300  $\text{cm}^{-1}$  range, include the C-OH stretching and OH bending vibrations.

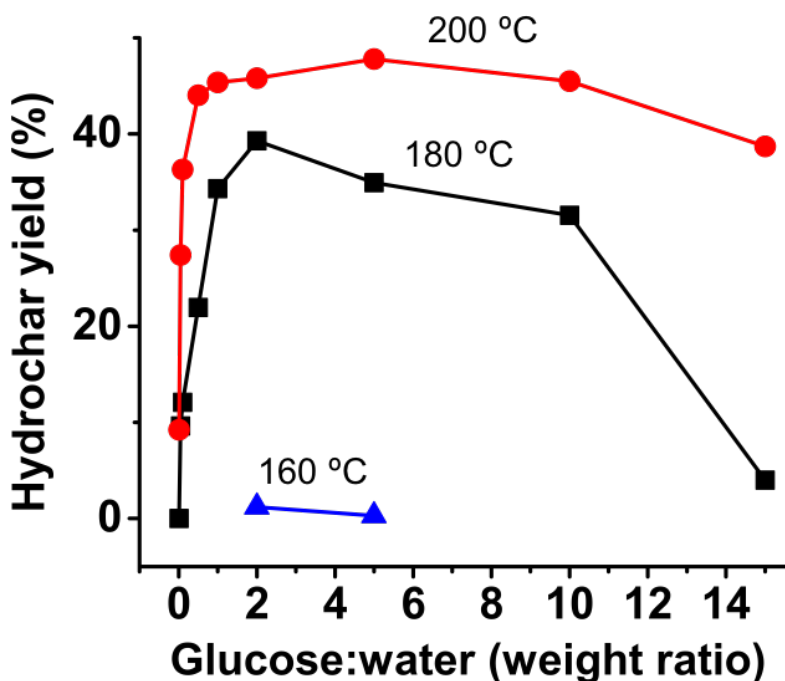
Figure 29a-29f shows the SEM images of the hydrochars at glucose:water weight ratios from 0.05 to 5, compared with char obtained from glucose carbonization in the absence of water. At a weight ratio of 0.05, independent monodisperse spheres were obtained having an average diameter of around 500 nm. As the initial moisture content was decreased, the spheres became larger in diameter. At a weight ratio of 0.5, the average diameter was around 1  $\mu\text{m}$ . The size of the carbon spheres further increased and yielded a maximum diameter ranging from  $\sim 5\text{--}7\ \mu\text{m}$  at a glucose:water ratio of 2. But, further increase in glucose:water ratios decreased the size of spheres, probably due to the depletion of HMF required for char formation. Apart from this, increasing the initial water content made the spheres more interconnected in nature. This could be due to the

increased cross linking reactions happening when the nuclei are at close proximity to each other. On the other hand, when carbonization of glucose was done in the absence of water, no carbon spheres were obtained. Instead irregular random particles were formed, similar to that of pure glucose powders.



**Figure 29.** (a-e) SEM images of the HTC products of glucose obtained with decreasing initial moisture content (0.05, 0.5, 1, 2, and 5) indicate that carbon spheres were formed in all these cases. But at weight ratios greater than 0.05, the spheres were interconnected in nature and larger in

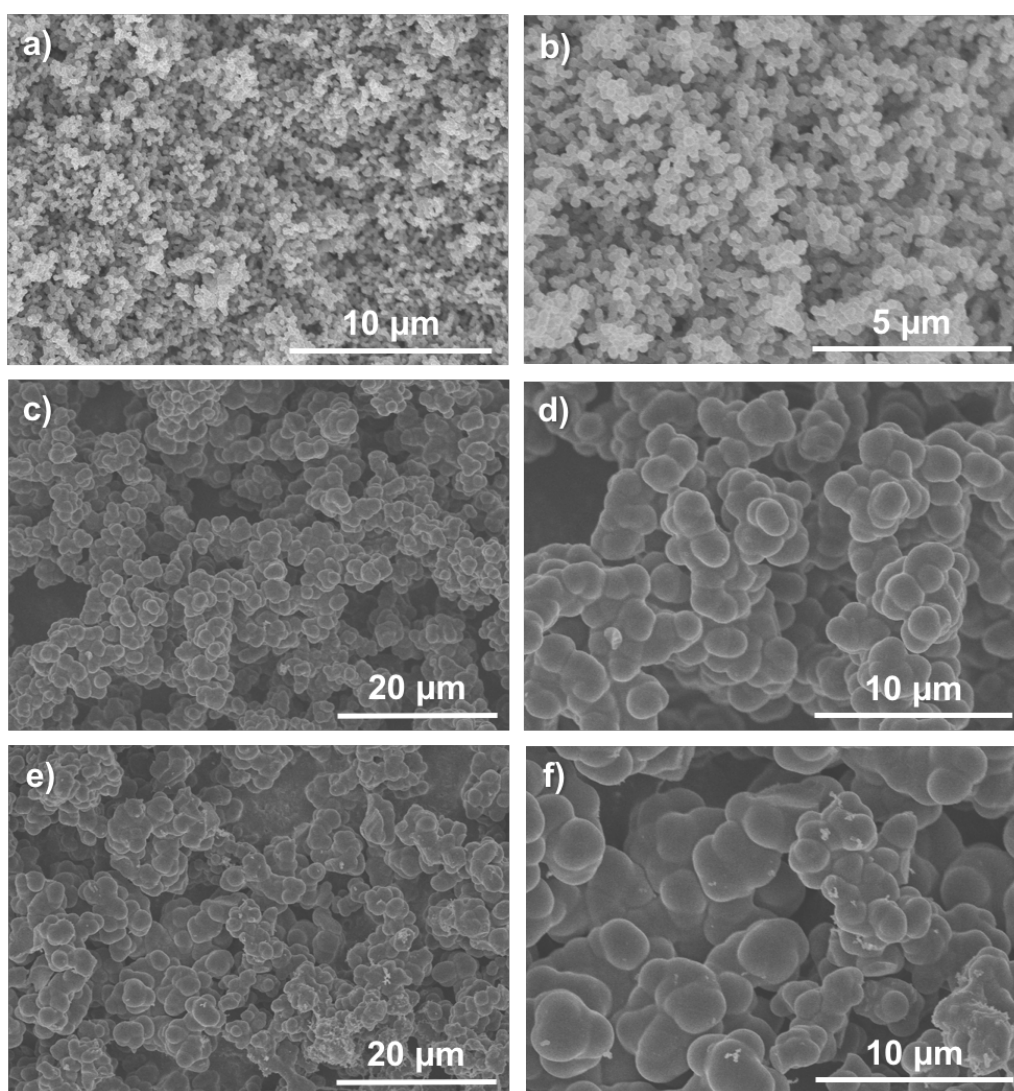
diameter. (f) Carbonization of glucose done in the absence of water shows the presence of random irregular particles similar to that of parent untreated glucose powders.



**Figure 30.** Hydrochar yield as a function of both glucose:water weight ratio and temperature. Yield increased as the temperature was raised from 160 °C to 200 °C. At 160 °C, char yield was less than 1%. At 180 °C and 200 °C, maximum yields of 40% and 50% were obtained at weight ratios of 2 and 5, respectively.

Another way to improve the char yield is by increasing the temperature used for the hydrothermal process. Raising the temperature will increase the rate of chemical reaction, as per the Arrhenius equation, as the increase in the number of high energy collisions at higher temperature can easily overcome the activation energy barrier. In the case of HTC of glucose, it will help to speed up the different reactions involved in the hydrochar formation, especially the conversion of glucose into HMF. Increasing the temperature also accelerates the rate of nucleation by lowering the Gibbs free energy. It will allow more polymer units formed during the HTC process to nucleate and be converted to carbon spheres, thus increasing the char yield. Figure 30 show the yield of hydrochar

obtained during HTC at different temperatures as the initial glucose:water weight ratio was varied. At a low temperature of 160 °C, very little char was formed due to the poor reaction rate. When the temperature was increased to 180 °C, yield increased significantly and gave a maximum of 40% at a glucose:water weight ratio of 2. Further increase in temperature to 200 °C, raised the char yield to 50% at a glucose:water ratio of 5. However, too high a temperature boosted gasification reactions, resulting in lower hydrochar yield.



**Figure 31.** (a), (c) and (e) SEM images of the HTC products of glucose obtained at an initial glucose:water weight ratio of 2 at 160 °C, 180 °C and 200 °C, respectively. (b), (d) and (f) are the

corresponding zoomed in images. In all the cases, carbon spheres were obtained but the size of the spheres increased with increasing temperature.

Figure 31 shows the SEM images of the carbon spheres obtained after hydrothermal treatment of glucose, for a glucose:water weight ratio of 2. As the temperature was raised from 160 °C to 200 °C, the average diameter of the spheres increased from less than 1  $\mu\text{m}$  to  $\sim 7\text{-}10\ \mu\text{m}$ . Also, the carbon spheres obtained became more polydisperse and interconnected in nature.

### 3.3 Conclusion

Because of its low cost, abundance, rapid regeneration, easy access and environmental friendship, biomass has the qualifications as a promising starting material for the synthesis of a variety of functional materials. HTC is a convenient way to convert biomass such as glucose at rather moderate conditions into carbonaceous nanostructures. However, the overall yield of the carbon spheres formed during the HTC of glucose is just 10%. This limits its large-scale applications, especially in the field of renewable energy storage. The work here shows that by carefully controlling the amount of water added during the hydrothermal process, the yield can be improved. When weight ratio of glucose:water was raised from 0.05 to 2, the hydrochar yield increased significantly from 10% to 40% . The char yield can be further improved by increasing the temperature used for the HTC process. At 200 °C, the hydrochar yield was around 45 and 50% for glucose:water ratios of 2 and 5, respectively. However, further increasing the temperature leads to gasification reactions which again reduces the char yield. Though the work here demonstrates the HTC process of pure glucose powders, it can be easily extended to the GO-glucose HTC process (chapter 2), by appropriately varying the GO:glucose:water ratio.

### 3.4 Experimental Conditions

**Synthesis of glucose:water hydrochars**: All chemicals were of analytical grade and used without further purification. Glucose was mixed with different amount of water and annealed inside a 20 ml Teflon-lined autoclave at 180 °C for 16 hours. The concentration of glucose was maintained at 1 g. The weight ratio of glucose and water was adjusted from 0.01 to over 10. The resulting HTC chars were washed few times with both water and methanol solution and centrifuged at 10000 rpm for 20 minutes. The precipitate was later dried in an oven overnight.

**Characterization**: SEM images were taken on a FEI Nova 600 SEM. FTIR spectra were acquired in transmission mode on a Nicolet Nexus 870 FTIR spectrophotometer.

## CHAPTER 4

### Hydrothermal Reduction of Graphene Oxide in Bio-Oil

#### 4.1 Introduction

Graphene, single-layer graphite with unusual electronic, thermal, and mechanical properties has attracted tremendous attentions for their potential applications in various fields. Current methods for preparation of graphene include chemical vapor deposition, micromechanical exfoliation of graphite, silicon carbide pyrolysis, GO reduction etc. Among them, the reduction in GO is the most promising route for the bulk production of graphene sheets due to its simplicity, reliability, and relatively low cost. However, the reduction process leads to the aggregation of r-GO sheets due to the strong  $\pi$ - $\pi$  interaction.<sup>137-141</sup> As a result, the as-prepared r-GO sheets generally have poor dispersion in water, which greatly limits their applications in many areas.

Up to now, considerable efforts have been devoted to improve the water dispersibility of r-GO, especially by further developing the GO reduction process using thermal, microwave, photo, and chemical methods. Among them, chemical reduction is a much more cost friendly and easier



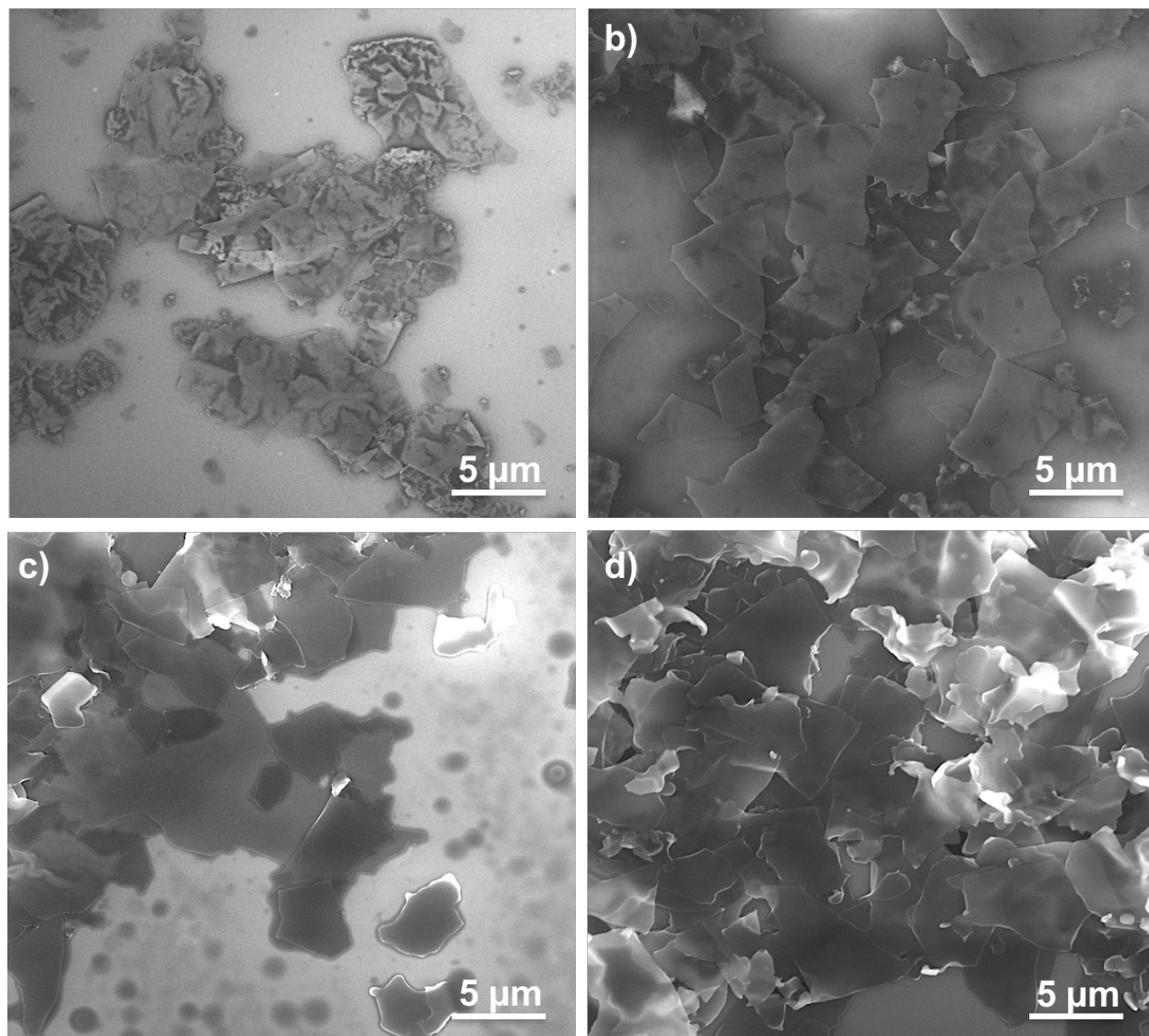
option for the bulk production of water dispersible r-GO. In Chapter 2, we have seen that addition of dilute amounts of GO to glucose and hydrothermally treating the mixture in a simple one-pot synthesis, resulted in the formation of thick sheet like structures, with an average thickness of ~40 nm (GO:glucose weight ratio = 1:300). However, the as obtained r-GO based glucose polymer sheets have lots of carbon spheres present around them. Hence, it is necessary to improve the hydrothermal synthesis route to remove these spheres from the final product, especially for their large scale applications.

In this chapter, I report a new route to synthesize carbon sphere free r-GO:glucose sheets by using the residual solution obtained from HTC of glucose as the solvent for the process. The resulting product did not have any spheres in them, at the same time was conductive and water dispersible.

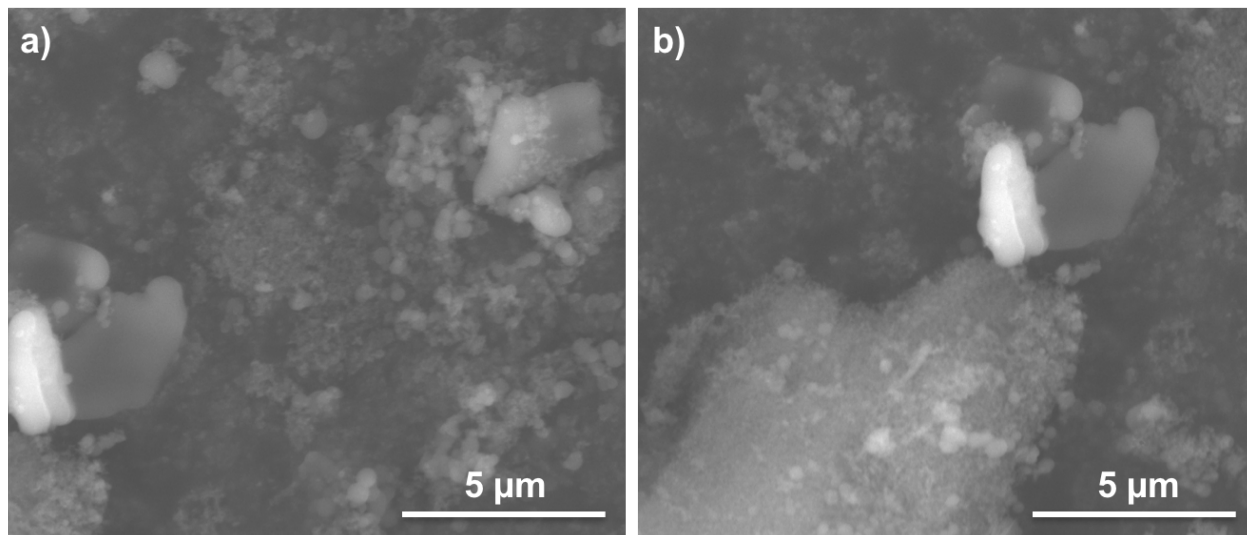
## 4.2 Results and Discussion

Hydrothermal treatment of glucose results in the formation of carbon spheres. Adding a small amount of GO to the reaction (final GO concentration 0.02 mg/ml), produces thick platelets like structures. During the HTC process, GO gets reduced to r-GO in this high-temperature hydrothermal system. Meanwhile, the glucose undergoes dehydration and carbonization to form polymeric units which could chemically bond to carbon atoms of the r-GO sheets to form C–O–C bond on the surface. This results in the formation of r-GO:glucose carbon platelets with hydrophilic functional groups enriched glucose polymer growth in situ on the r-GO surface. The average thickness of the sheets varies from 20 nm to 40 nm, as GO:glucose weight ratio was increased from 1:50 to 1:300. Figure 32(a)-(f) shows the corresponding SEM images of the r-GO:glucose carbon platelets obtained. In all these cases, the sheets were filtered under vacuum, washed with methanol and DI water multiple times and dispersed in water after an intensive

sonication step. The product was later deposited onto silicon substrates with the help of LB method, as described in Chapter 2. For a GO:glucose weight ratio of 1:50, the sheets were irregular and non-uniform and have a maximum thickness of  $\sim 20$  nm. With further increase in glucose content, the sheets became more even in nature.



**Figure 32.** SEM images of the platelets obtained after HTC of GO and glucose at 180 °C for 16 hours at GO:glucose weight ratios of (a) 1:50, (b) 1:100, (c) 1:200 and (d) 1:300, respectively. The overall GO concentration was 0.02 mg/ml. The products obtained were washed with methanol and DI water, re-dispersed in water and later deposited onto silicon substrates by using LB method (as mentioned in section 2.4).

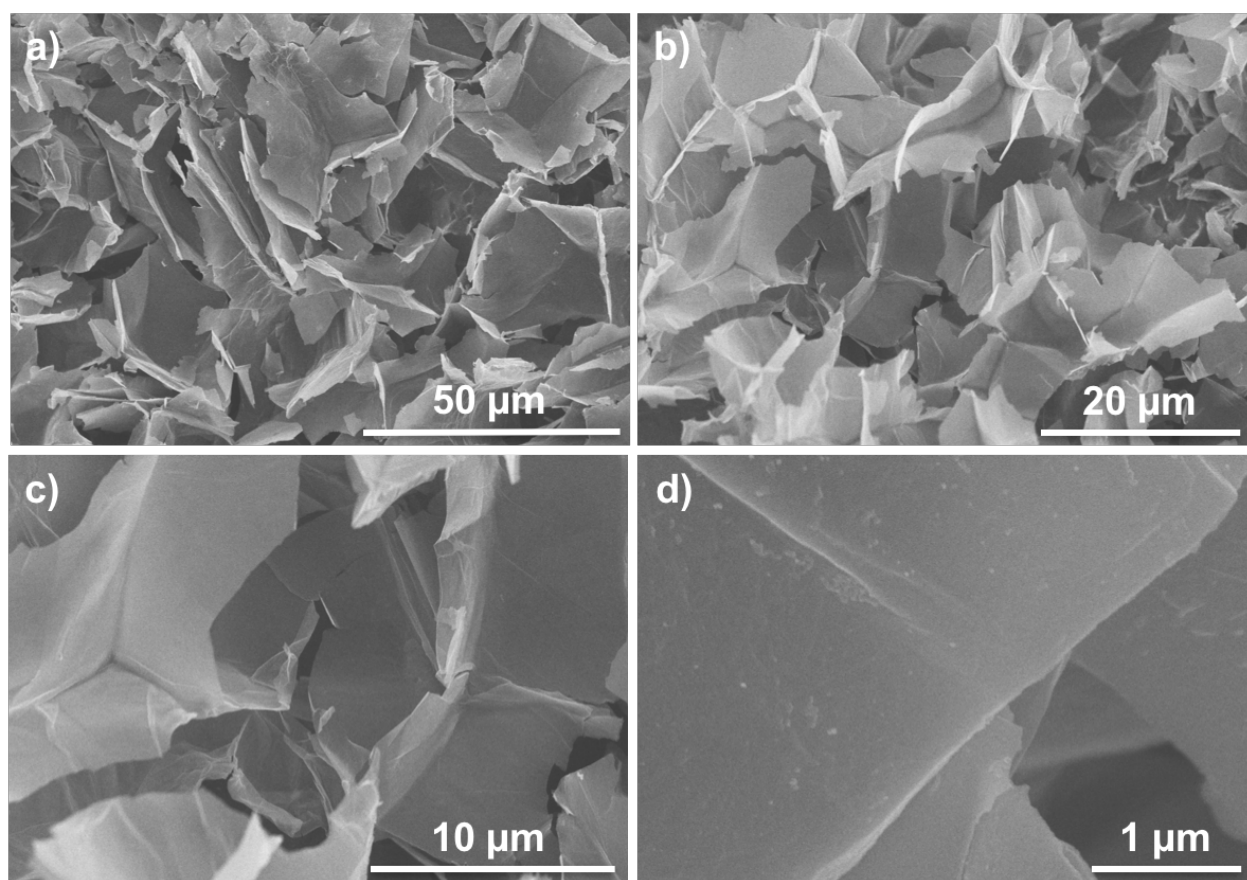


**Figure 33.** SEM images of the products obtained after hydrothermal treatment of GO and glucose at 180 °C for 16 hours at a GO:glucose weight ratio of 1:100, without any washing or LB deposition. The product appears dirtier and there were lot of carbon spheres surround the r-GO:glucose carbon platelets.

For comparison, the SEM images of the HTC product without any washing or LB deposition is shown in Figure 33. For a GO:glucose weight ratio of 1:100, a large no of carbon spheres decorates the r-GO:glucose carbon sheets. This not only lowers the conductivity of the product but makes the material less water dispersible. As a result, it is essential to remove these spheres from the final product before they can be further utilized. During HTC process, though most of the glucose carbonized intermediate products gets attached to the r-GO surface, the excess polymer units has a tendency to nucleate and form carbon spheres instead. Thus, increasing the GO:glucose weight ratio is one way to restrict the carbon spheres formation, by providing more r-GO surface for the excess glucose polymer carbon to get attached to. But this in turn leads to non-uniform uneven sheets, as seen in Figure 32a.

The LB deposition step described in chapter 2 was mainly used to separate the carbon spheres from the platelets. The hydrophilic functional groups on the sheet surface, along with the

hydrophobic core makes the platelets amphiphilic in nature, similar to that of GO. Hence, during deposition on water surface, the sheets tends to float on the surface unlike carbon spheres. But despite the extensive purification followed by deposition technique, the platelets still appeared dirty (Figure 32). Though it could to an extent remove the carbon spheres found in the product as well as further clean it up, for bulk production of such r-GO based sheets, this not a very viable method. Hence, it is necessary to explore more cost effective and user friendly ways to remove or prevent the carbon sphere formation.



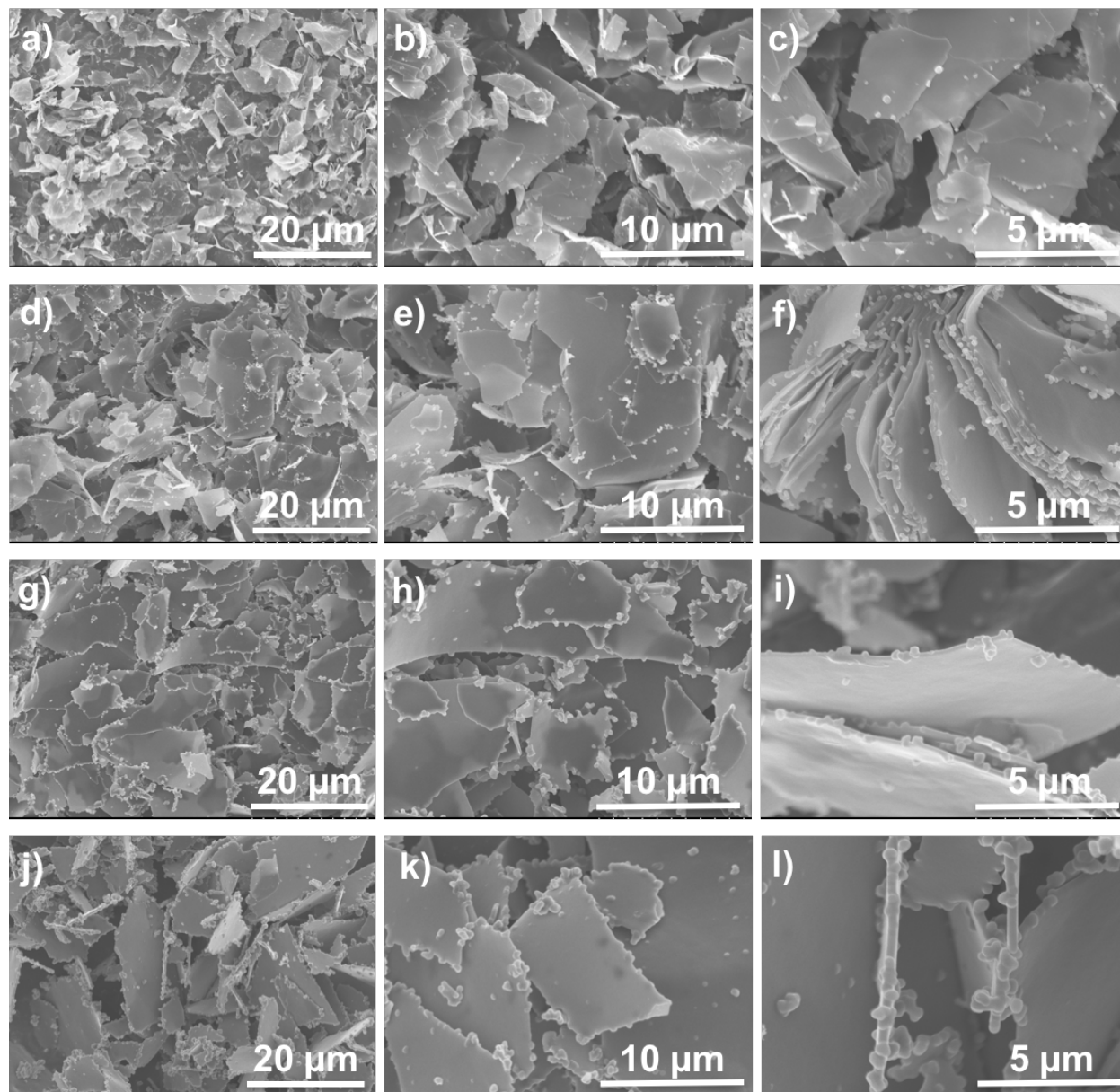
**Figure 34.** SEM images at different magnifications of the r-GO:glucose carbon platelets obtained after hydrothermal treatment of GO in bio-oil (obtained from HTC of glucose) at 180 °C for 4 hours, at a GO:glucose weight ratio of 1:100. No carbon spheres can be seen in the images and the product was cleaner. The sheets showed better flexibility and conductivity.

One way to prevent the carbon sphere from forming is to use the residual oil obtained from hydrothermal treatment of glucose as the biomass source for the GO reduction process. We know from Chapter 3 that along with the hydrochar, there is the formation of liquid and gaseous products as well. The aqueous phase products include sugars, organic acids and dissolved carbon products. The dissolved organic carbon mainly contains intermediate glucose carbonization products which can interact with the r-GO sheets during the additional hydrothermal treatment, and deposit on it without forming spheres.

Figure 34 shows the SEM images of the sheets obtained after hydrothermal reduction of GO in bio-oil. The product appears much cleaner. The zoomed in images in Figure 34c and Figure 34d indicates the complete removal of carbon spheres. Thus, by using HTC bio-oil as the solvent for the hydrothermal treatment of GO, the product was further purified. Besides, the dissolved carbon in the bio-oil which is usually thrown away as waste, can be better utilized. The as obtained sheets were more flexible and exhibited higher conductivity. They also possess better water dispersibility, owing to the large amount of hydrophilic groups (hydroxyl, carboxyl, and C–O functional groups) within the in situ generated glucose carbon on r-GO surfaces.

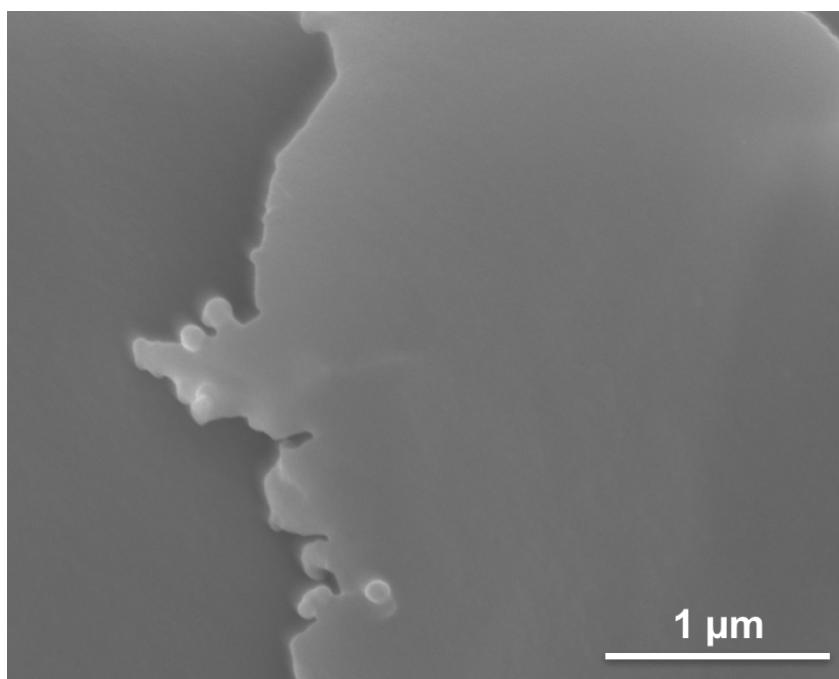
Further increase in glucose concentration from 1:200 to 1:1000, also resulted in thick platelets like structures. The sheets were found to be conductive, including the one obtained at a low initial GO:glucose weight ratio of 1:1000. The SEM images of the sheets at GO:glucose weight ratios of 1:200, 1:400, 1:800 and 1:1000, are shown in Figure 35a, 35d, 35g and 35j, respectively. With increasing glucose concentration, the thickness of the sheets increased. Though some amount of carbon spheres were formed during the process, due to the addition of excess quantities of glucose,

it is much lower compared to the previous case when HTC of glucose and GO was done simultaneously.



**Figure 35.** SEM images at different magnifications of the r-GO:glucose carbon platelets obtained after hydrothermal treatment of GO in bio-oil (obtained from HTC of glucose) at 180 °C for 4 hours, at GO:glucose weight ratios of (a), (b), (c) 1:200, (d), (e), (f) 1:400, (g), (h), (i) 1:800 and (j), (k), (l) 1:1000, respectively.

Moreover, the carbon spheres preferentially deposit on the edges of the sheets. This can be easily seen in the magnified image of a thick platelet obtained after HTC of GO:glucose at an initial weight ratio of 1:400 (Figure 36). It could be due to the increased number of  $\pi$  electrons accumulating at the edges of the r-GO:glucose carbon sheets, which attracts the carbon spheres by Van der Waals interaction.



**Figure 36.** Zoomed in SEM image of a r-GO:glucose carbon platelets obtained after hydrothermal treatment of GO in bio-oil (obtained from HTC of glucose) at 180 °C for 4 hours, at GO:glucose weight ratio of 1:400. Carbon spheres are preferentially getting deposited on the corner of the r-GO:glucose carbon sheets.

### 4.3 Conclusion

Hydrothermal treatment of glucose in the presence of GO results in the formation of thick platelets containing r-GO sheets decorated with glucose carbon. However, along with these sheets, a large amount of carbon spheres was also formed, making them insulating. In this chapter, I have demonstrated a method to remove the spheres from the sheets by hydrothermally reducing GO in

the residual bio-oil obtained from the HTC treatment of glucose. For a GO:glucose weight ratio of 1:100, the resulting HTC products did not show the presence of any carbon spheres. At higher glucose content, small amount of carbon spheres was seen. However, all the HTC products were conductive and highly dispersible in water even at a low GO:glucose weight ratio of 1:1000.

#### **4.4 Experimental Conditions**

**Materials and methods:** All chemicals were of analytical grade and used without further purification. GO powder was synthesized from graphite by a modified Hummers method, as reported in section 2.4. An aqueous solution of glucose was annealed inside a 20 ml Teflon-lined autoclave at 180 °C for 16 hours. The supernatant obtained was mixed with GO by ultrasonication and again hydrothermally treated at 180 °C for 4 hours. The weight ratio of GO and initial glucose content was varied from 1:100 to over 1:1000. The resulting HTC platelets was filtered under vacuum, washed with ethanol and distilled water repeatedly, and then dried by freeze-drying for 4 hours. SEM images were taken on a FEI Nova 600 SEM.



## CHAPTER 5

### Graphene Oxide Assisted Rapid Microwave Carbonization of Cellulose

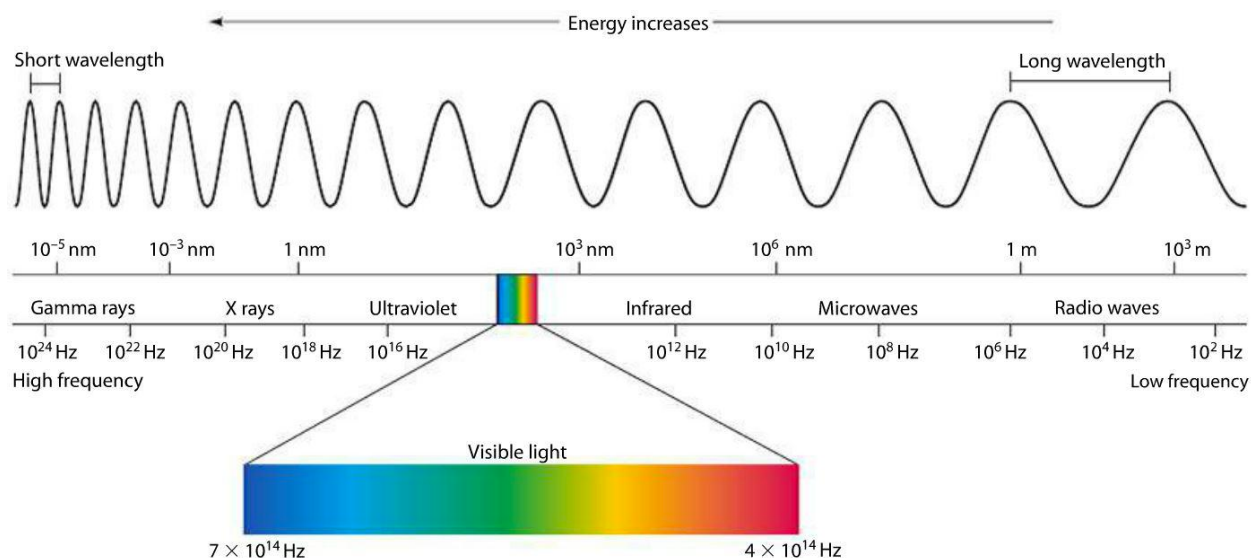
Material in this chapter is reproduced in part from reference <sup>142</sup>. “Graphene Oxide Assisted Rapid Microwave Carbonization of Cellulose” by Deepti Krishnan, Ying Tao, Hee Dong Jang and Jiaying Huang; In Preparation (2016).

#### 5.1 An Introduction to Microwave Heating

Microwaves are a form of electromagnetic radiation with wavelengths ranging from one meter to one millimeter; with frequencies between 300 MHz (100 cm) and 300 GHz (0.1 cm), as shown in Figure 37.<sup>143</sup> They lie in the region of the electromagnetic spectrum between millimeter wave and radio wave i.e. between I.R and radio wave. They are mainly used for telecommunication and radar equipment, but are also employed in the heating of materials. All frequencies used in the microwave regime are strictly regulated and controlled, with designated frequencies for ‘Industrial, Scientific and Medical’ (ISM) applications. Of these, there are four frequencies that are allowed by the government for commercial microwave use: 915 MHz, 2450 MHz, 5800 MHz, and 22,125

MHz. The wavelength at which industrial and domestic microwave apparatus operate is commonly standardized to 2.45 GHz.<sup>144</sup>

The difference between microwave energy and other forms of radiation, for example X-ray or  $\gamma$ -ray, is that microwave energy is non-ionizing - it does not carry enough energy per quantum to ionize atoms or molecules, that is, to completely remove an electron from an atom or molecule, and therefore it provides only thermal activation. For example, a microwave frequency of 2.45 GHz is equivalent to 0.00001 eV, which is far below the energy corresponding to even a weak bond energy such as the hydrogen bonding of 0.21 eV.

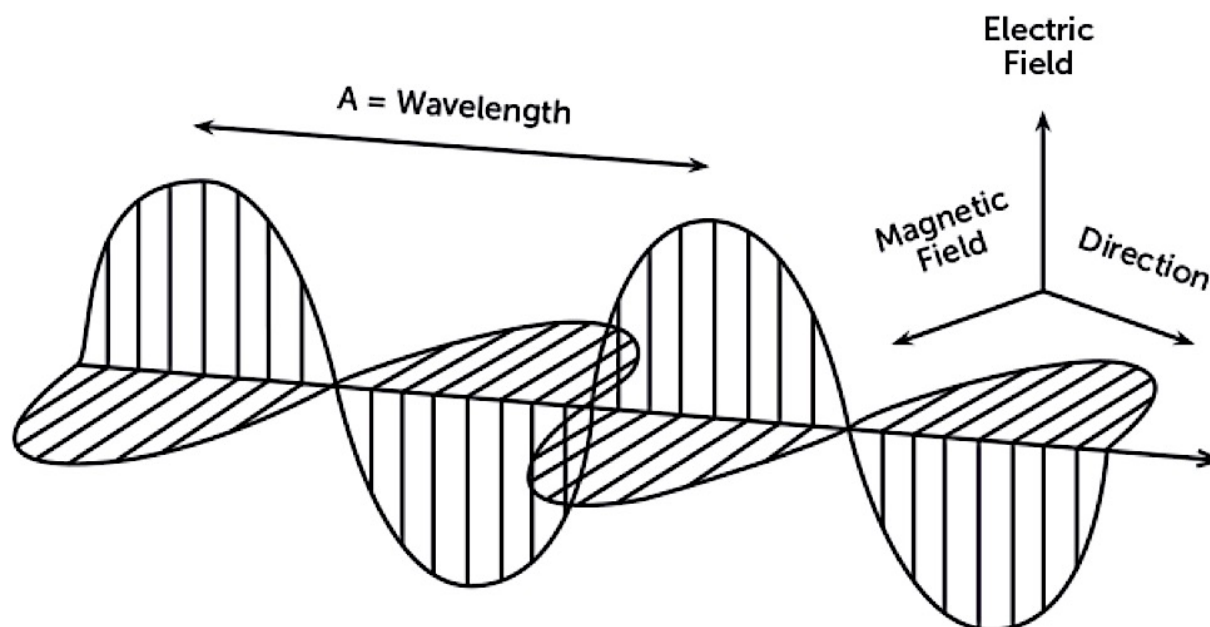


**Figure 37.** The electromagnetic spectrum depicting the microwave regime with frequency between 0.3 – 300GHz and a corresponding wave length range of 1mm to 1m.

### 5.1.1 Microwave Heating Mechanism

The mechanism of microwave heating varies according to the interaction between the microwaves and target materials. There are two components of a microwave: an electric field and a magnetic field, oscillating in phase and in planes perpendicular to the direction of wave propagation (Figure

38).<sup>145</sup> The electric field plays the major role of transferring energy to heat a substance. It will interact with the charged particle of the reaction material, causing microwave assisted heating. The phenomena of producing heat by electromagnetic irradiation is either by collision or by conduction, some times by both. Because it is a wave, at any given point in time, the electric field is constantly oscillating and changing its polarity from positive to negative with each cycle of the wave. This cause rapid orientation and reorientation of molecule, resulting in heating by collision. If the charge particles of material are free to travel through the material, a current will induce which will travel in phase with the field. If charge particles are bound within regions of the material, the electric field component will cause them to move until opposing forces balance the electric force.



**Figure 38.** Schematic of an electromagnetic wave showing electric, magnetic field and direction of propagation. The magnetic and electric fields of an electromagnetic wave are perpendicular to each other and to the direction of the wave.

When a dielectric material is exposed to an external electric field, the electric charges cause dielectric polarization, which arises from the displacement of charges from their average

equilibrium position. This polarization can be categorized as follows: 1) electronic polarization ( $a_e$ ) by displacement of electrons from the nuclei, 2) atomic polarization ( $a_a$ ) by displacement of atomic nuclei, 3) dipolar polarization ( $a_d$ ) by reorientation of molecules which have permanent dipoles, and 4) interfacial polarization ( $a_i$ ) by accumulation of relatively mobile charges at grain/phase boundaries or surfaces. The total polarization ( $a_t$ ) of the material arising from the displacement of charges may be expressed as the sum of a number of components

$$a_t = a_e + a_a + a_d + a_i$$

As the electric field component of the microwave changes direction and magnitude continuously with time, the polarization they induce is also changed with time. In general, polarization has a phase lag with the electric field oscillation because a material's polarization does not respond instantaneously to an applied field. Therefore, permittivity ( $\epsilon$ ), which describes the electric field flux generated by polarization, is usually expressed as a complex vector form ( $\epsilon' + i\epsilon''$ ) to show the magnitude and the phase of polarization at the same time. The real part of  $\epsilon$ ,  $\epsilon'$ , represents the ability of a material to be polarized by an external electric field. It determines how much of the incident energy is reflected and how much is absorbed. At very high and very low frequencies, and with static fields,  $\epsilon'$  will equal the total dielectric constant of the material. The dielectric loss factor ( $\epsilon''$ ) measures the dissipation of electric energy in form of heat within the material. A further quantity, the loss angle  $\delta$ , is also commonly used in the literature, and is more usually given in the form of its tangent.<sup>146, 147</sup> It is related to the complex dielectric constant by;

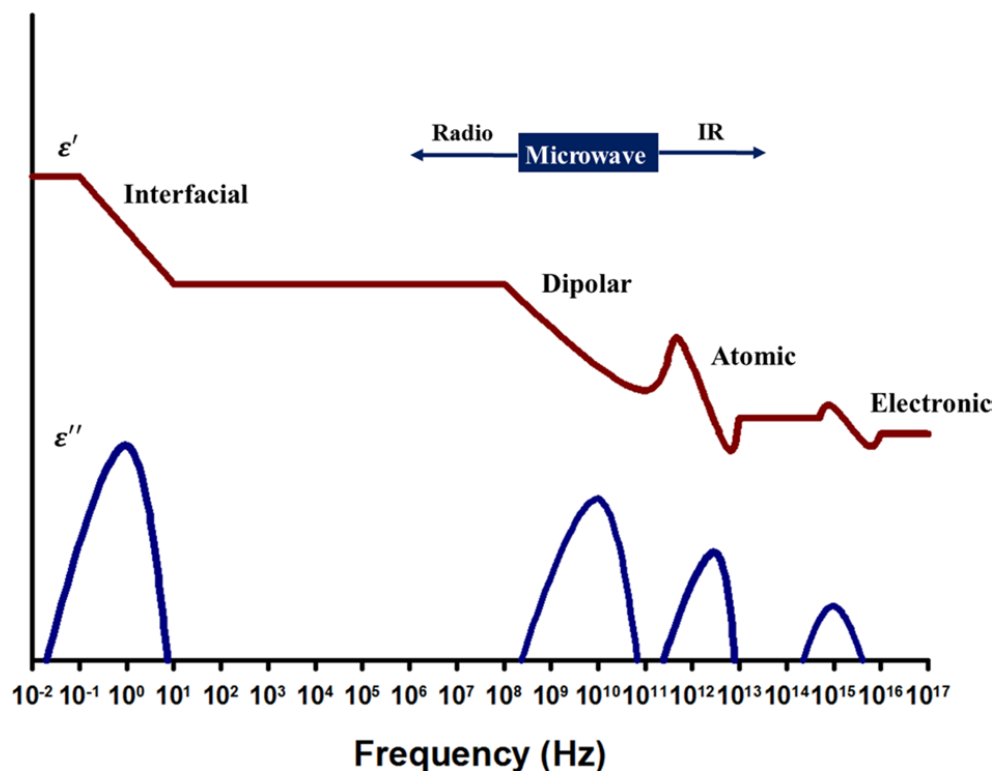
$$\tan(\delta) = \epsilon'' / \epsilon'$$

The angle  $\delta$  is the phase difference between the electric field and the polarization of the material. For optimum microwave energy coupling, a moderate value of  $\epsilon'$  should be combined with high values of  $\epsilon''$  (and so high values of  $\tan\delta$ ), to convert microwave energy into thermal energy. Thus, while some materials do not possess a sufficiently high loss factor to allow dielectric heating (transparent to microwaves), other materials, e.g. some inorganic oxides and most carbon materials, are excellent microwave absorbers. On the other hand, electrical conductor materials reflect microwaves.

When the frequency of an electric field oscillation is increased over a certain point, some polarization stops contributing to the total polarization because there is an increasing phase lag between the electric field oscillation and reorientation of the polarization. In this case, the real part of the permittivity decreases while the imaginary part of the permittivity increases, which means the dissipation of energy in the form of heat increases. The frequency dependence of dielectric permittivity is shown in Fig. 39. Electronic polarization and atomic polarization don't contribute to microwave absorption because they start to have phase lag at a frequency higher than the microwave frequency. Generally, interfacial polarization occurs far below the microwave frequency, but the peak frequency of dielectric loss factor of interfacial polarization can vary considerably according to the conductivity and dielectric properties of the material. Thus, interfacial polarization as well as dipolar polarization are considered to be the polarizations involved in microwave heating.

Magnetic polarization may also contribute to the heating effect observed in materials where magnetic properties exist, and a similar expression for the complex permeability of such materials

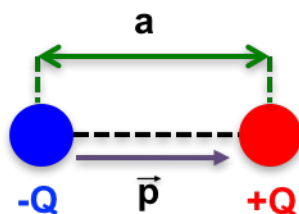
may be formulated. Although such cases are relatively uncommon, a familiar example of its importance is in the microwave heating of  $\text{Fe}_3\text{O}_4$ .



**Figure 39.** Frequency dependence of the real and imaginary parts of the dielectric constant in the presence of interfacial, dipolar, atomic and electronic polarization mechanisms.  $\epsilon'$  and  $\epsilon''$  denote the real and the imaginary part of the permittivity, respectively. Reference. 148.

### 5.1.2 Microwave Heating of Solutions

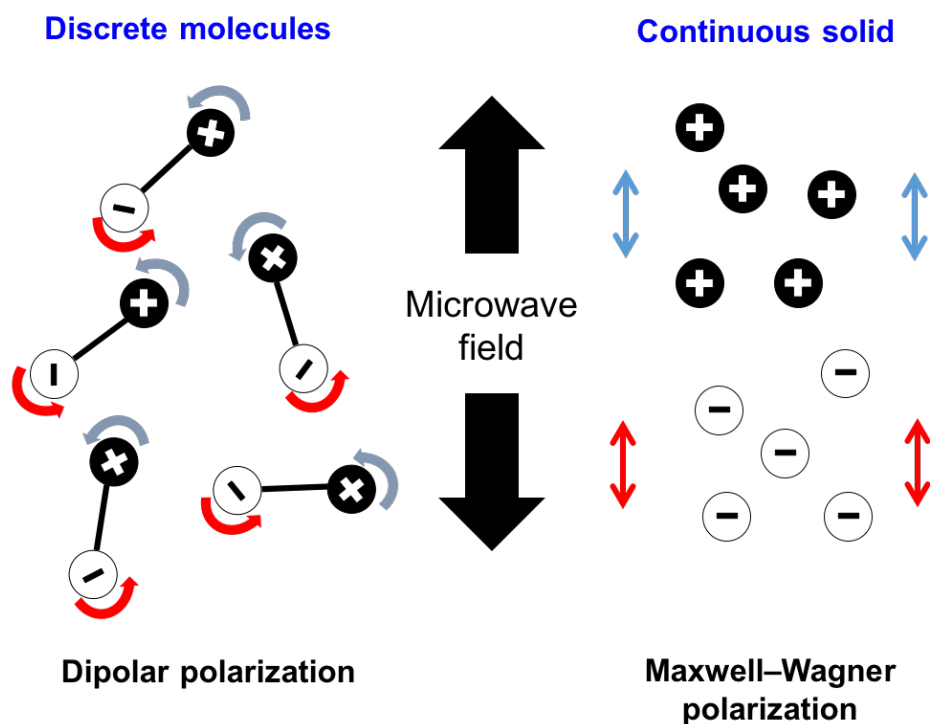
The dipolar polarization mechanism requires materials to have a positive and negative charge which is separated over a distance (see Figure 40). When placed in an electric field they will become polarized through the formation and rotation of dielectric dipoles or magnetic dipoles, if present. The dipole moment is described as a vector from the negative to positive charge on the molecule.<sup>149</sup>



**Figure 40.** Schematic of an electric dipole. An electric dipole moment is defined as the measure of separation between positive and negative charges. It is equal to the magnitude of the charge ( $Q$ ) multiplied by the distance ( $a$ ) between them with the direction being towards the positive charge.

Most solvents such as water, dimethylformamide, tetrahydrofuran and ethanol have permanent dipoles. Upon application of an electric field, the dipoles rotate, attempting to align with the passing electric field. When at extremely low frequencies, molecules are able to align themselves precisely with the field, with little energy being gained in the process. At high frequencies the molecules are unable to follow the oscillating electric field and do not rotate, hence little or no transfer of energy occurs. However, at intermediary frequencies, dipoles are able to rotate following the electric field but the frequency is sufficient that full rotation cannot be achieved; as such a phase difference arises, known as relaxation time. When this occurs, energy is lost through molecular friction/collisions and is dissipated as heat throughout the material (Figure 41).<sup>150, 151</sup>

The ionic conduction mechanism is the second mechanism of microwave heating in solutions.<sup>152</sup> It is less commonly seen than the dipolar polarization and it is applicable to heating of solutions containing ions. The mechanism involves the long range transportation of charges or ions in the solution, when a charge carrier is exposed to an electric field, inducing a current. Both these methods have some limitations, as follows: 1) most of the microwave energy used for the heating of polar solvents is dissipated, and 2) there is no macroscopic difference in the distribution of temperature within the reactor, while the absorption of microwave energy may be selective.



**Figure 41.** Schematic showing dipolar polarization and Maxwell-Wagner (or interfacial or space charge) polarization mechanisms. Dipolar polarization is found in molecules that contain permanent dipole moments. In the absence of electric field, the molecules are randomly oriented in the material and there is no net dipole moment. Under microwave frequencies, dipoles respond to the alternating electric field by rotating to align with the field; however, a phase difference exists between the orientation of the field and dipole. This phase difference cause energy to be released from the molecules, upon random collision with other molecules leading to dielectric heating. Maxwell-Wagner polarization involves accumulation of charges at interfaces within the material or between different materials. When an external electric field is applied, the more mobile charges are displaced and accumulate at barriers or at free surfaces, resulting in heating.

### 5.1.3 Microwave Heating of Carbon-Based Solids

In the case of dielectric carbon-based solids which have few or no freely rotating dipoles, microwave heating can't be explained as above. Instead, the interaction between microwaves and electrons is important. It is mainly explained by interfacial polarization or so called Maxwell-Wagner-Sillars polarization. For solid materials with charged particles which are free to move in a delimited region of the material, such as  $\pi$  electrons in carbon materials, a current traveling in phase with the electromagnetic field is induced. As the electrons cannot couple to the changes of



phase of the electric field, energy is dissipated in the form of heat. In these cases, Joule heating plays an important role in the heating of carbon-based solids by microwave. Compared to solution heating, microwave heating of carbon based solids is much more efficient and selective because the microwave energy is solely absorbed by the target material.

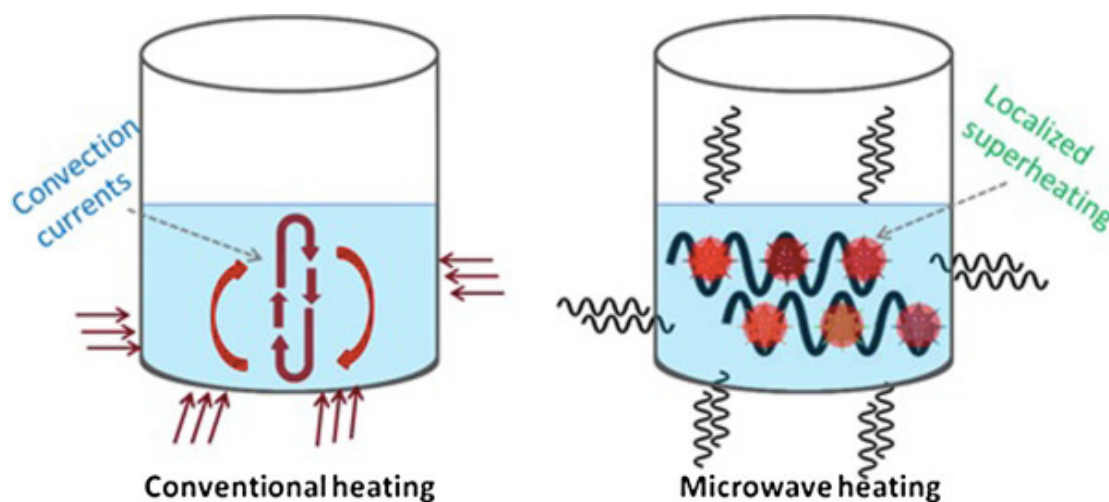
#### **5.1.4 Advantages of Microwave Heating Over Conventional Heating**

Microwave-assisted heating is different from conventional (conductive) heating, based on the dielectric character of microwaves that provides non-contact heating. In the case of microwave heating, direct interaction between the reacting agents and the microwaves occur leading to faster and more uniform rise in temperature as well as an instantaneous localized superheating. Hence, higher reaction rates can be achieved. The increased reaction rates can be explained by the Arrhenius equation that can be attributed to the higher temperature attainable in the microwave reactor:

$$k = Ae^{-\frac{E_a}{RT}}$$

Also, the energy transfers generated by microwave irradiation occurs very rapidly ~every nanosecond. The almost constant energy input is achieved at a rate greater than the molecular relaxation rate, which is on the order to  $10^{-5}$  seconds. As the energy is added at a much faster rate than molecular relaxation, a constant state of disequilibria will be present in the system. This disequilibria situation will also help to overcome the activation energy barrier ( $E_a$ ) and drive the reaction to completion.

In conventional heating on the other hand, heating initiates from the surface of the reaction vessel and the energy is then transferred to bulk of the mixture and finally to the reacting species. Due to the large number of materials to be penetrated, the reaction kinetics is very slow making it a very inefficient process of heat transfer. Further, in open reaction vessels, the highest temperature that can be attained is limited by the boiling point of the solvent. Figure 42 shows the comparison of microwave heating and conventional heating.



**Figure 42.** Schematic showing the difference between conventional and microwave heating process, Conventional heating usually involves the use of a furnace or oil bath, which heats the walls of the reactor by convection or conduction. The core of the sample takes much longer to achieve the target temperature, e.g. when heating a large sample of ceramic bricks. Acting as internal heat source, microwave absorption is able to heat the target compounds without heating the entire furnace or oil bath, which saves time and energy.

Thus, the microwave heating of a dielectric material, which occurs through the conversion of electromagnetic energy into heat within the irradiated material, offers a number of advantages over conventional heating such as: (i) non-contact heating; (ii) energy transfer instead of heat transfer; (iii) rapid heating; (iv) selective material heating; (v) volumetric heating; (vi) quick start-up and stopping; (vii) heating from the interior of the material body; (viii) environmental friendly process;

(ix) perform reactions under solvent free conditions and, (x) higher level of safety and automation.<sup>153, 154</sup>

Due to these advantages, microwaves are used in various technological and scientific fields in order to heat different kinds of materials. Most of the industrial applications of microwave heating are based on heating substances that contain polar molecules, for example: food processing, sterilization and pasteurization, different drying processes, rubber vulcanization, polymerization or curing of resins and polymers by elimination of polar solvents, etc. In addition, solid materials with a high dielectric loss factor, i.e., microwave absorbers, can be subjected to different processes based on microwave heating. Among these materials, carbons are, in general, very good microwave absorbers, so they can be easily produced or transformed by microwave heating. Moreover, carbon materials can be used as microwave receptors to indirectly heat materials which are transparent to microwaves. For example, carbon materials have been used as microwave receptors in soil remediation processes, the pyrolysis of organic wastes, catalytic heterogeneous reactions, etc.

## **5.2 Microwave Heating of Lignocellulosic Biomass**

A number of studies have been performed to investigate the microwave heating and pyrolysis of lignocellulosic materials such as cellulose, wood, coffee hulls, rice straw, wheat straw, corn stover etc.<sup>155-165</sup> Though these studies include the microwave pyrolysis of the structural components of cellulose, hemicellulose, and lignin, they do not study them in their pure form.

The first study of significance was undertaken by Allan et al. in 1980 in which the microwave pyrolysis of pure cellulose was investigated.<sup>166</sup> He found that water content has a significant effect

on the heating profile of the cellulose material wherein, vacuum dried cellulose resulted in lower heating rates, especially at temperatures below 100 °C. In the presence of water, significantly increased heating rate was observed below 100 °C; conducive with significant microwave absorption due to the strongly absorbing moisture. Nevertheless, pyrolysis was achieved in those circumstances with the formation of char, tar and condensate. Tar was found to contain high levels of levoglucosan, but low levels of other products. This is conducive with the decomposition and dehydration of cellulose and glucose, respectively. Recently, Fan et. al. studied the effect of parameters affecting a microwave pyrolysis and microwave hydrolysis process of microcrystalline cellulose, providing a fundamental insight into the processes of cellulose degradation.<sup>167</sup> He studied the influence of microwave power, microwave duration, sample density, sample pre-heating and maximum pyrolysis temperature on the microwave heating of cellulose aqueous dispersion. All these studies indicate that pure cellulose is a bad microwave absorber. Only in the presence of water, sufficient carbonization was attained. Although microwave treatment in the presence of water is a viable option in the processing of biomass, limitations arise when rapid large-scale sustainable production of biochars is attempted, especially in the field of energy storage due to the low specific surface area and ultralow conductivity or even insulating feature of the char obtained. Hence, further development of the current microwave technique of biomass carbonization is urgently needed, to improve the efficiency and quality of the products.

### **5.3 Microwave Assisted Heating of r-GO**

GO, the chemical exfoliation product of graphite, has been used extensively in recent years as a precursor for bulk production of r-GO. It has been reported that the residual defects and functional groups remaining in r-GO after reduction are beneficial for absorbing electromagnetic waves.

Together with delocalized  $\pi$  electrons from  $sp^2$ -hybridized carbon networks, this absorption characteristic of r-GO makes it a very promising and effective microwave absorbing materials.<sup>168-</sup>

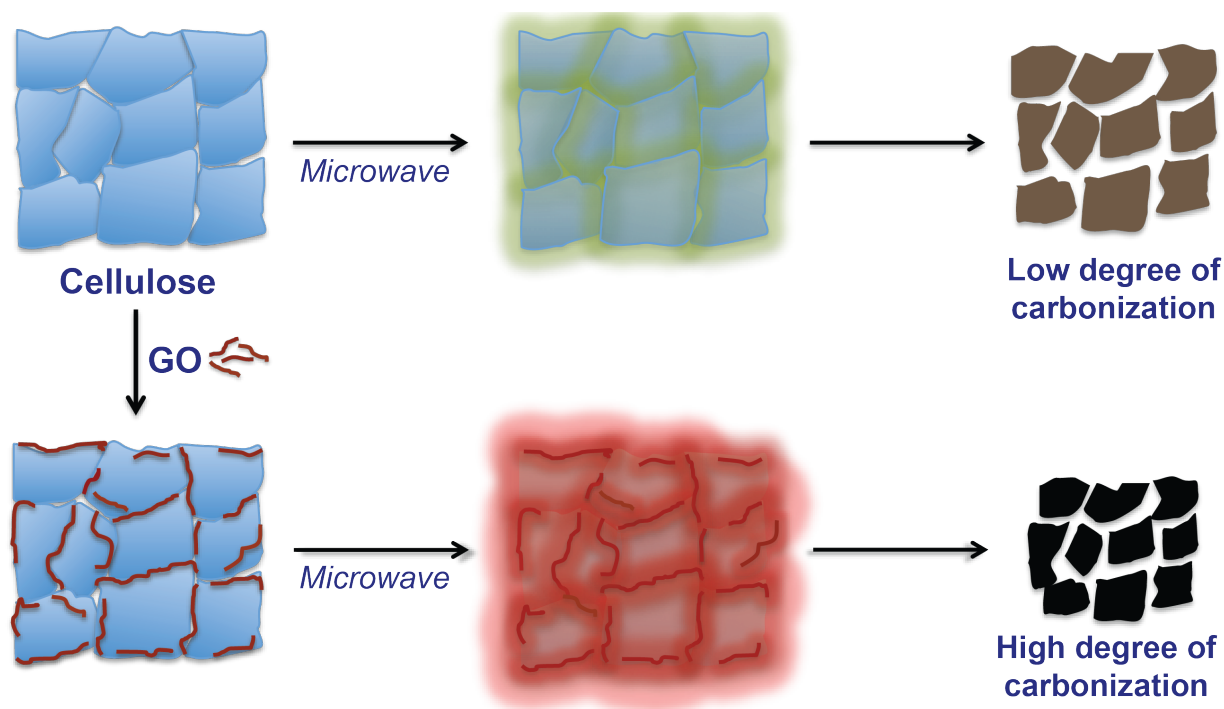
<sup>171</sup> Indeed, compared to traditional microwave absorption materials, r-GO has been receiving increasing attention as a microwave absorbent, due to its desirable physical and chemical properties such as high specific surface area, thermal conductivity, mechanical properties and electron mobility.

In our previous work, I have shown that GO can promote the hydrothermal carbonization (HTC) of carbon hydrates and template the structure of HTC produces. Highly conductive carbon materials could be obtained after further rapid microwave treating these samples. Here, I report a one-step method wherein cellulose is directly microwaved in the presence of GO to produce biomass-derived carbon materials with high degree of carbonization, conductivity and surface area in just a few minutes at a GO:cellulose weight ratio as low as 1:1000. The chemical and structural characteristics of the microwaved carbonized products as well as their electrochemical performance as supercapacitor electrodes are also investigated.

## 5.4 Results and Discussion

Cellulose, the main constituent of lignocellulosic feedstock, was used as the biomass source. The schematic in Figure 43 illustrates the microwave-assisted carbonization reaction of cellulose in the presence of catalytic amounts of GO. Pure cellulose is a bad microwave absorber. In the presence of microwave, very little increase in temperature was observed and the final carbon or char obtained showed low degree of carbonization. Compared to the case of pure cellulose, the

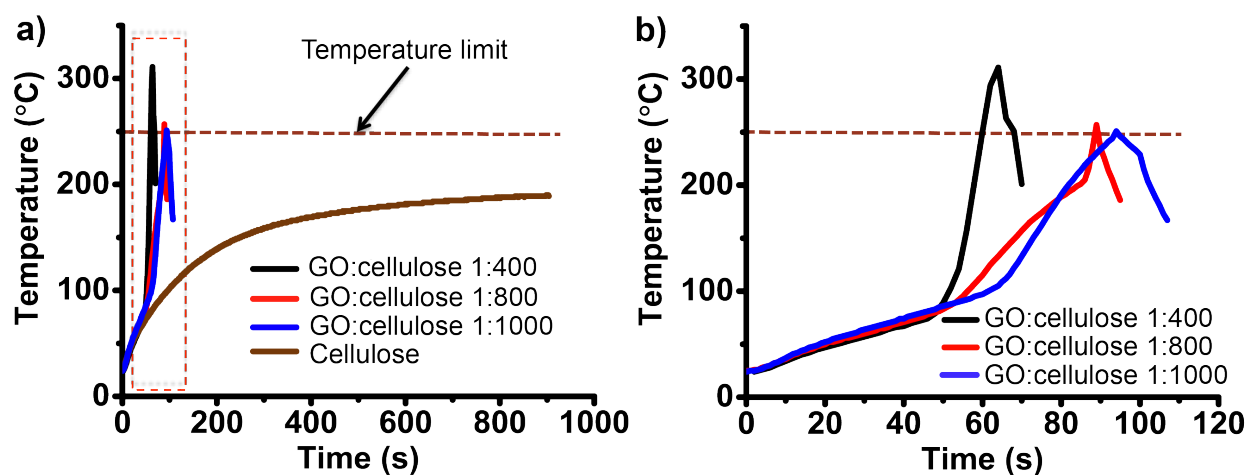
temperature of GO:cellulose mixtures increased drastically during microwave treatment and the products showed a higher carbonization degree.



**Figure 43.** Schematic drawing illustrating GO enabled rapid microwave carbonization of cellulose. Microwave heating of cellulose powders is ineffective and results in incomplete degree of carbonization. In contrast, when GO is added as a microwave sensitizer, it helps to rapidly heat up the mixture and greatly accelerate the carbonization reaction, forming a char with much higher degree of carbonization.

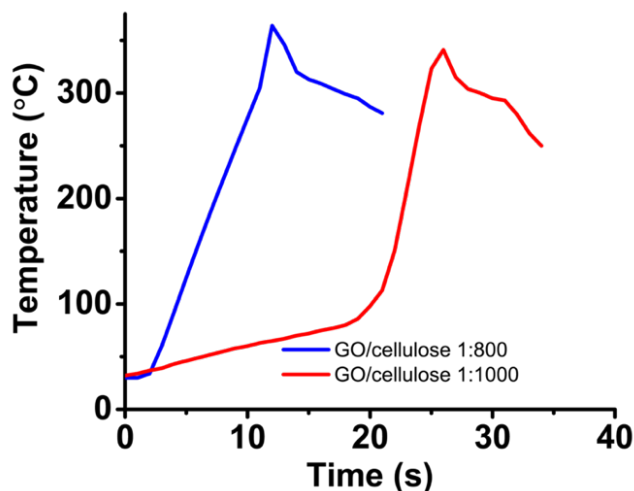
Figure 44 shows the corresponding heating profiles for cellulose and GO:cellulose mixtures of weight ratios ranging from 1:400 to 1:1000. All the samples followed the same heating rate the first 50 s. In contrast to cellulose powders, whose rate of heating decreased drastically and plateaued at less than 200 °C even after 900 s, all GO:cellulose mixtures reached the limiting temperature within 100 s (Figure 44a). These results demonstrate that the addition of GO sheets could initiate the thermal pyrolysis of surrounding cellulose in a short time and thus enable a much faster heating rate. This could be attributed to the excellent microwave absorption capacity of r-

GO, obtained from the reduction of GO in 50 s, which could act as heat source to further accelerate the thermal pyrolysis of cellulose.

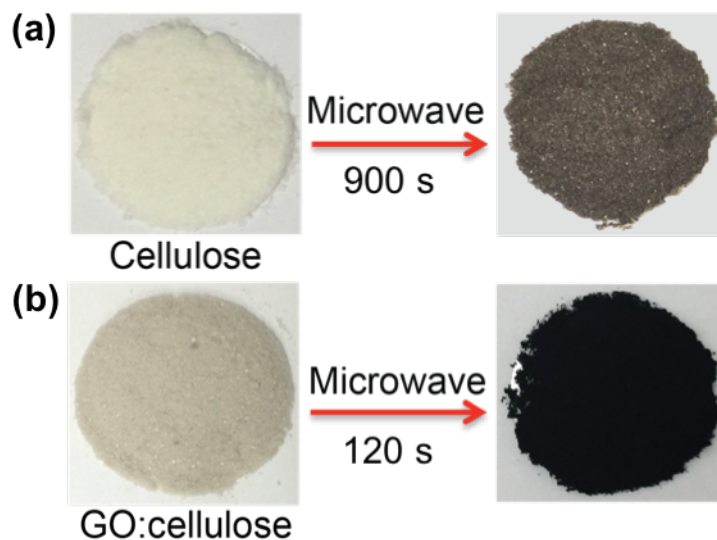


**Figure 44.** (a) Temperature profiles of cellulose and GO:cellulose mixtures at different weight ratios of 1:400, 1:800 and 1:1000 during microwave heating. The upper limit of detected temperature was set to be 250 °C. All the GO:cellulose mixtures reached the temperature limit in about 60-90s, while cellulose powders were still below 200 °C even after heating for 900s; (b) Detailed Magnified temperature profiles of GO:cellulose mixtures corresponding to the region marked by the red dashed box in (a).

Two microwave heating cycles are needed for GO:cellulose mixtures at weight ratios smaller than 1:400, to achieve sufficient carbonization. Figure 45 gives the heating profiles of GO:cellulose mixtures at weight ratios of 1:800 and 1:1000 during the second heating cycle, in which more rapid heating is observed and they reached temperatures greater than 350 °C within 12 and 25 s, respectively. The complete carbonization of cellulose was achieved after two microwave heating cycles.



**Figure 45.** Temperature profiles of r-GO:cellulose mixtures during microwave treatment in a CEM microwave oven during the second heating cycle at 300 W. The maximum temperature was again maintained at 250 °C. GO:cellulose mixtures of weight ratios greater than 1:400 required 2 heating cycles to achieve sufficient carbonization. The temperature of the r-GO:cellulose mixture of initial weight ratio 1:800 and 1:1000 shot up much higher than 350 °C in just 10 and 25 s, respectively.



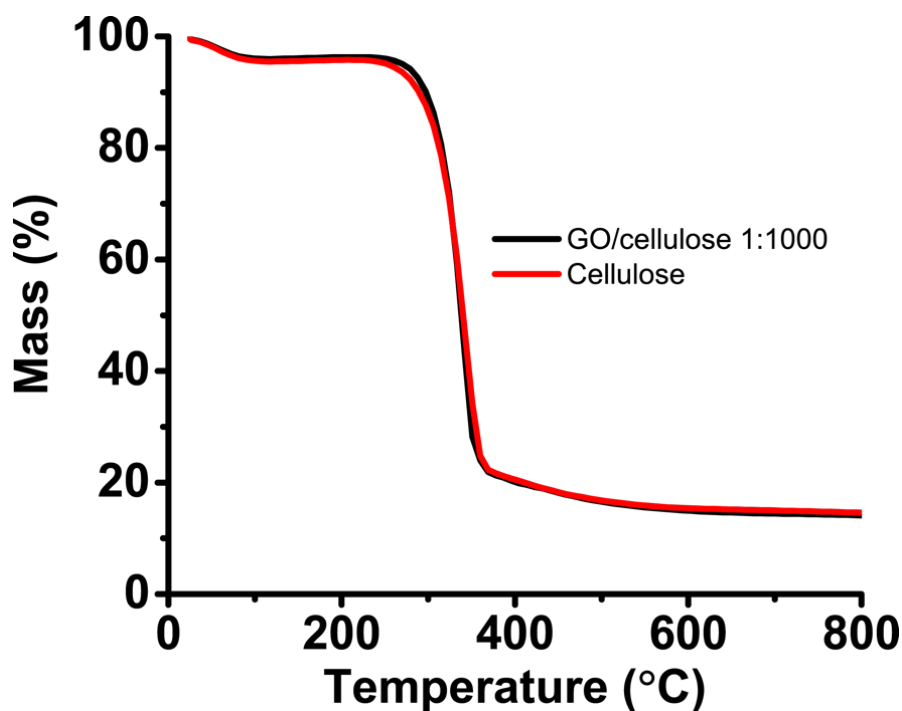
**Figure 46.** (a,b) Photos showing cellulose and GO:cellulose powders before and after microwave treatment, respectively. The cellulose powder gave a non-uniform brown and white char while GO:cellulose (weight ratio 1:1000) powder gave a uniform black powder after microwave treatment.

The photos of cellulose and GO:cellulose powders before and after microwave treatment are presented in Figures 46a and b, respectively. A non-uniform, brown and white powder was



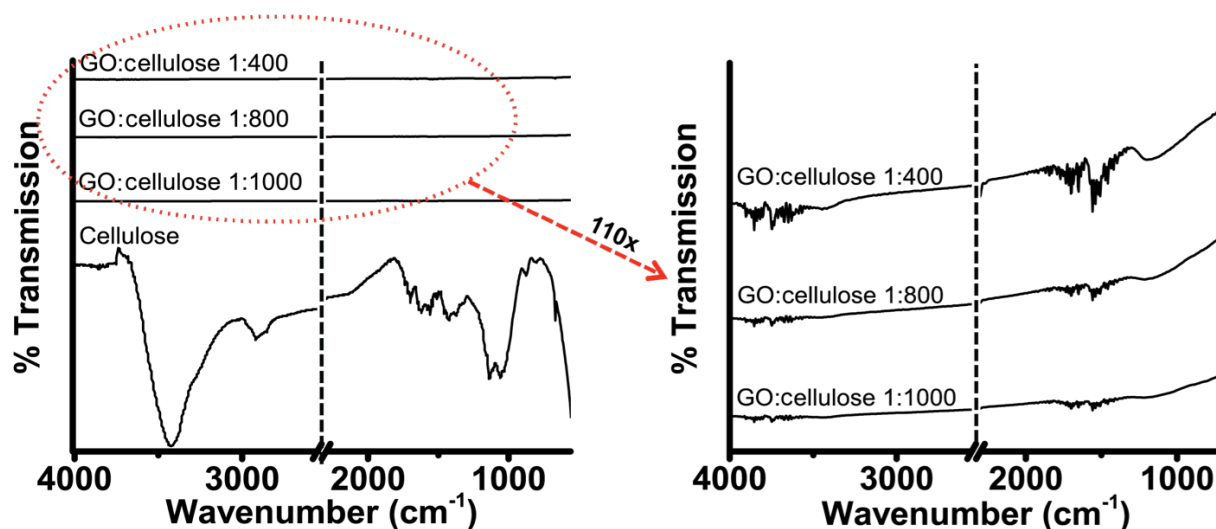
obtained from the white cellulose powders after microwave treatment for 900 s, indicating incomplete carbonization of cellulose. On the other hand, a uniform black powder was obtained only after microwave treatment for 60-120 s for GO:cellulose mixtures.

The overall yield of the microwaved GO:cellulose carbon is ~10%. Figure 47 shows the TGA curves of pure cellulose and GO:cellulose mixture at a weight ratio of 1:1000, under N<sub>2</sub> atmosphere. Both samples followed almost the same thermal degradation characteristics and gave a final yield of less than 14%, which is comparable to the yield of carbon obtained by the microwave heating of GO:cellulose.



**Figure 47.** Comparison of TGA curves of GO:cellulose mixture at a weight ratio of 1:000 and cellulose powder indicates similar thermal decomposition characteristics of both the samples. The final yield was ~13 mass % which is close to the yield of the microwaved GO:cellulose samples (~10 mass %). TGA was carried out in N<sub>2</sub> atmosphere at a heating rate of 10 °C/min till a temperature of 800 °C.

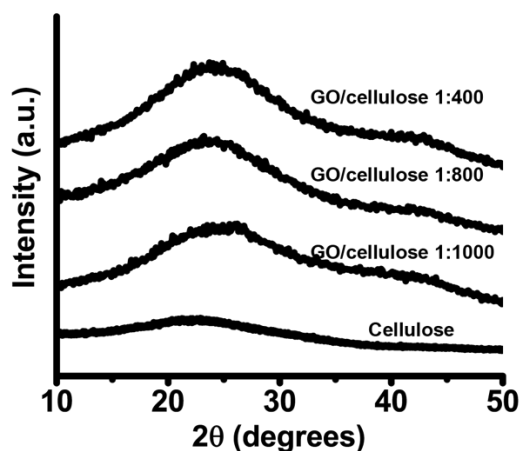
The carbonization degree of the final products obtained from microwave treatment was analyzed by FTIR spectroscopy. Figure 48 compares the IR spectra of the microwaved products obtained from GO:cellulose mixtures with that of cellulose powders. Note that products from GO:cellulose mixtures at weight ratios of 1:800 and 1:1000 were exposed to two microwave heating cycles. The peaks centered at around 3400 and 1030  $\text{cm}^{-1}$  correspond to the stretching and bending vibrations of residual OH groups, respectively. The FTIR spectrum of microwave-heated cellulose powders (900 s) was found to be similar to that of cellulose powders, indicating incomplete carbonization of the materials. In contrast, all GO-containing samples showed a significant decrease in the intensity of the -OH groups after microwave treatment. Figure 48 shows the magnified FTIR spectra of the GO:cellulose carbons, in which the peaks of the functional groups for the microwaved GO:cellulose mixtures are almost invisible. This demonstrates that the presence of GO during the microwave heating of cellulose could significantly improve the carbonization degree of cellulose.



**Figure 48.** FTIR spectra of all microwave treated samples clearly showing the drastic reduction in -OH band intensity around 3400  $\text{cm}^{-1}$  in GO:cellulose microwaved samples, compared to cellulose

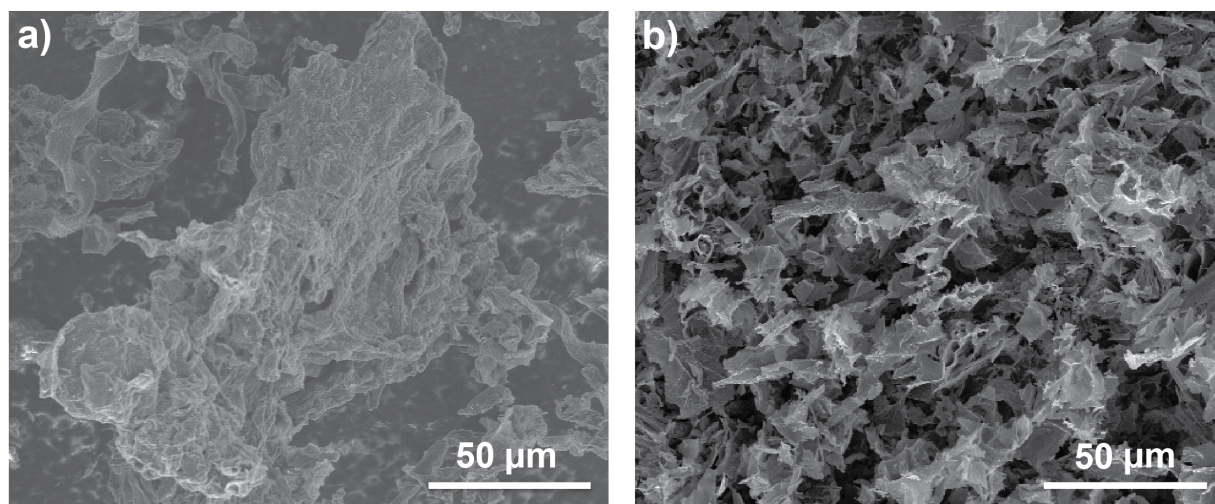
microwaved samples; (d) The magnified FTIR spectra of microwave reacted GO:cellulose mixtures corresponding to the dashed red circle in (c). The spectra in (c) were magnified  $\sim 110\times$  to clearly see the IR peaks. Note: GO:cellulose microwaved samples of weight ratio greater than 1:400 were subject to two microwave heating cycles. The cellulose microwave treatment was done for 900 s.

This is further confirmed by elemental analysis. Microwave treatment of pure cellulose only slightly increased its C/O ratio from 2.7 to 3.1. On the other hand, the C/O ratios of microwave-treated GO:cellulose samples increased to 26.5, 27.8 and 28.3 for weight ratios of 1:400, 1:800 and 1:1000, respectively. During microwave treatment, the weight loss for GO and cellulose is around 50% and 90%, respectively. Hence, for the GO:cellulose-microwaved carbon produced from the precursor at a weight ratio of 1:1000, the overall r-GO content should be around 0.5 wt.%. As the amount of r-GO present in the final product is quite negligible, the increase in C/O ratios is mainly due to the increase in carbonization degree of cellulose. Thus ultrafast, highly efficient microwave carbonization of cellulose can be achieved by adding catalytic amounts of finely dispersed GO sheets to cellulose.



**Figure 49.** XRD patterns of microwave treated cellulose and GO:cellulose mixtures at different weight ratios of 1:400, 1:800 and 1:1000 heated for 900 s, 60 s, 100 s and 115 s respectively. Increased degree of graphitization is observed for r-GO:cellulose microwaved carbons as indicated by the increased intensity of (002) and emergence of (100) graphite peaks at around  $24.5^\circ$  and  $45^\circ$ , respectively.

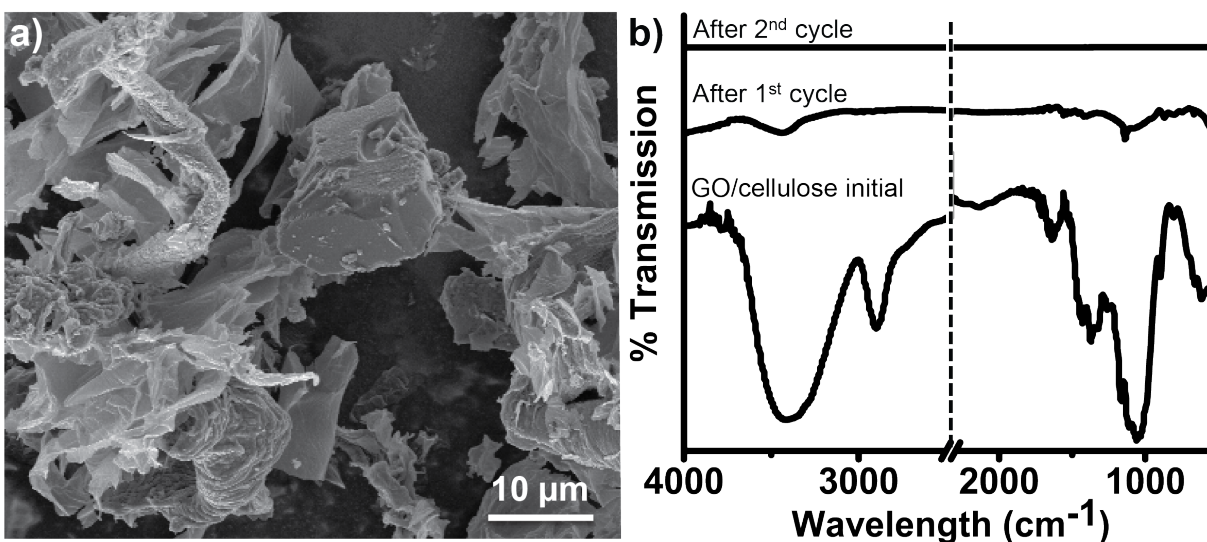
The X-ray diffraction (XRD) patterns of GO:cellulose and cellulose after microwave treatment are shown in Figure 49. Microwave-heated carbons from GO:cellulose mixtures exhibited a pronounced, broad peak centered at around  $24.5^\circ$ , which corresponds to graphite (002). The intensity of the (002) peak increased with GO content, indicating the increased graphitization of cellulose after microwave treatment. The above results suggest that ultrafast, highly efficient microwave carbonization of cellulose can be achieved by adding catalytic amounts of finely dispersed GO sheets to cellulose.



**Figure 50.** SEM images of microwave treated (a) cellulose and (b) GO:cellulose (weight ratio 1:1000) powders. While microwaved cellulose products have an irregularly shaped structure, the microwave treated GO:cellulose carbons have a more porous flaky structure.

The microstructure of materials before and after microwave treatment was observed by SEM. Raw cellulose has an irregularly shaped, fiber-like structure with lengths of tens to hundreds of micrometers, as shown in chapter 2. Cellulose gave a similar non-uniform and non-porous structure, even after microwave heating for 900 s (Figure 50a). But when GO was added, the microstructure of the final product was altered enormously. Take the case of GO:cellulose mixture at a weight ratio of 1:1000 as an example. The resulting product after microwave heating for 115

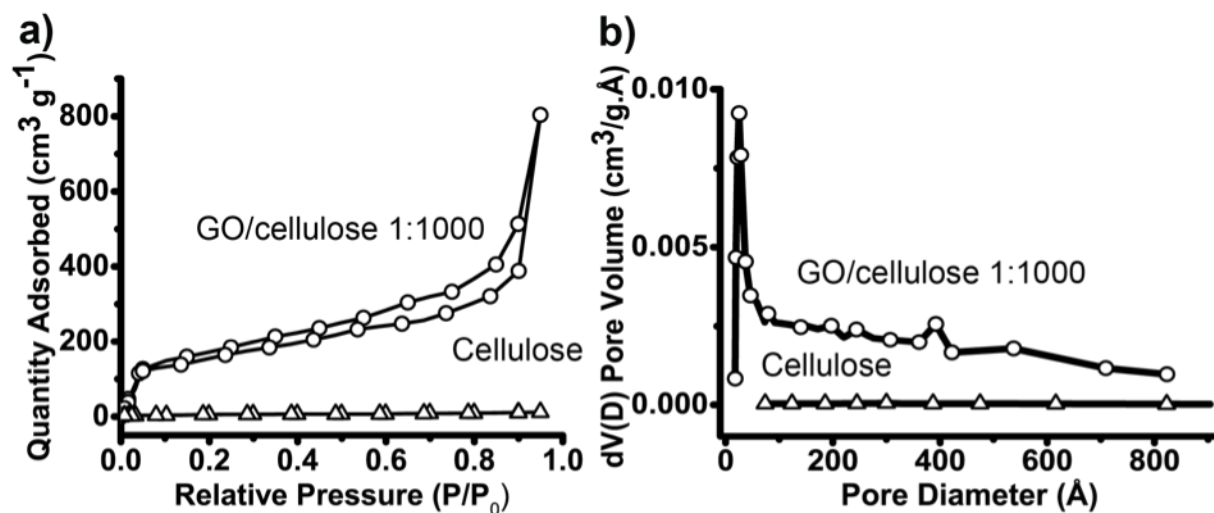
s has a porous, two-dimensional sheet-like structure, as shown in Figure 50b. Note that GO:cellulose sample (1:1000 weight ratio) were subject to 2 microwave cycles.



**Figure 51.** (a) SEM image of GO:cellulose microwaved sample (weight ratio 1:1000) after just 1 heating cycle shows a non-uniform not so porous structure; (b) FTIR spectra of GO:cellulose mixtures at a weight ratio of 1:1000, compared with the corresponding microwaved samples after first heating cycle and second heating cycle indicates significant reduction in  $-OH$  group intensity after each heating cycle.

Figure 51 shows the morphology of microwave treated GO:cellulose sample at a weight ratio of 1:1000 after just one heating cycle. It indicates a non-uniform irregular structure with certain areas looking more porous and flaky. Hence, it is necessary to do an additional microwave heating step to achieve the highly porous structure shown in Figure 50b. This is also seen in the FTIR spectra wherein after just 1 heating cycle, the amount of  $-OH$  groups present is significantly higher than after the 2<sup>nd</sup> heating cycle. So, complete carbonization of GO:cellulose (weight ratio 1:1000) can be only achieved after two heating cycles. Further microwave heating the samples did not seem to improve their carbonization degree.

To reveal the overall porous structure of microwave-treated cellulose and GO:cellulose at a weight ratio of 1:1000, N<sub>2</sub> adsorption/desorption measurements were conducted. Microwave treated GO:cellulose carbon exhibits typical characteristics of Type IV isotherms with Type H3 hysteresis loop, as seen in Figure 52a.<sup>172</sup> This is normally associated with slit-shaped pores in sheet-like materials. The presence of a narrow hysteresis loop in a wide pressure range suggests that the pores are open and non-uniform, with a broad pore size distribution. On the other hand, the microwave treated cellulose carbon is a non-porous material. The BET surface area of microwaved GO:cellulose carbons is about 367 m<sup>2</sup> g<sup>-1</sup>, while that of the cellulose carbon is only 18 m<sup>2</sup> g<sup>-1</sup>. The Barrett-Joyner-Halenda (BJH) pore size distribution of the samples is shown in Figure 52b. The GO:cellulose samples showed remarkably higher micropore volumes of 0.49 cm<sup>3</sup> g<sup>-1</sup>, with an average pore diameter of 134.9 Å. This indicates that the GO coatings on cellulose may act as templates to form porous carbon sheets during microwave treatment.

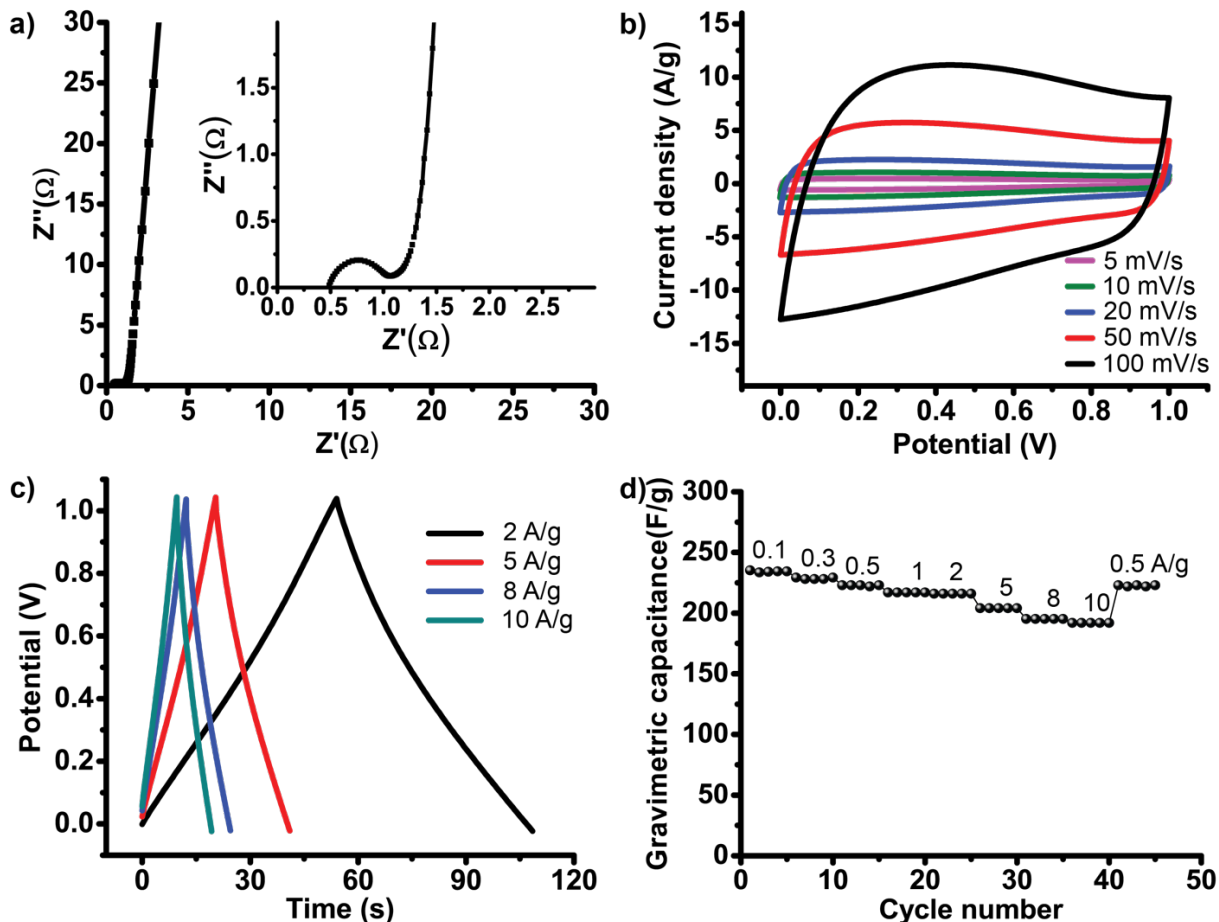


**Figure 52.** (a) The BET surface area calculated from N<sub>2</sub> gas adsorption and desorption isotherms. The specific surface areas of microwave treated GO:cellulose (weight ratio 1:1000) and cellulose carbons were 367 m<sup>2</sup> g<sup>-1</sup> and 18 m<sup>2</sup> g<sup>-1</sup> respectively. (b) The corresponding pore-size distribution calculated using the BJH method. It indicates the microwaved GO:cellulose carbon is mesoporous in nature while the microwaved cellulose powder is absent of any pores.

The conductivities of the samples were measured after pressing them into pellets of known dimensions and weight under high pressure. Microwave-treated GO gave a specific conductivity normalized with respect to density of  $\sim 9.1 \text{ S cm}^2 \text{ g}^{-1}$ . When GO was added to cellulose and microwaved at a weight ratio of 1:400, the normalized specific conductivity was  $\sim 1.1 \text{ S cm}^2 \text{ g}^{-1}$ . With further decrease in GO:cellulose weight ratio to 1:800 and 1:1000, the specific conductivity dropped slightly to  $0.68 \text{ S cm}^2 \text{ g}^{-1}$  and  $0.44 \text{ S cm}^2 \text{ g}^{-1}$  respectively. On the other hand, pellets of microwaved product of cellulose powders did not show any current above the detection limit of the instrument (1 nA). Hence, by adding less than 0.3 wt.% of GO to cellulose and microwave heating, a significant increase in conductivity of the cellulose carbonaceous product can be obtained.

The electrochemical performance of the final carbon materials was further evaluated using two-electrode symmetric supercapacitor cells with 6 M KOH solution as the electrolyte. The conductive, high surface area carbon sheets prepared from GO:cellulose mixture at a weight ratio of 1:1000 was taken as an example to demonstrate their potential use as electrode materials. The Nyquist plot exhibits a very small equivalent series resistance, revealing its high conductivity, low internal resistance as well as fast ion diffusion process associated with the abundant porous structure (Figure 53a). The cyclic voltammetry (CV) curves at different scan rates are presented in Figure 53b, and no obvious distortion is observed as the scan rate increased from 10 to  $100 \text{ mV s}^{-1}$ , which is an indicator of ideal capacitive behavior.



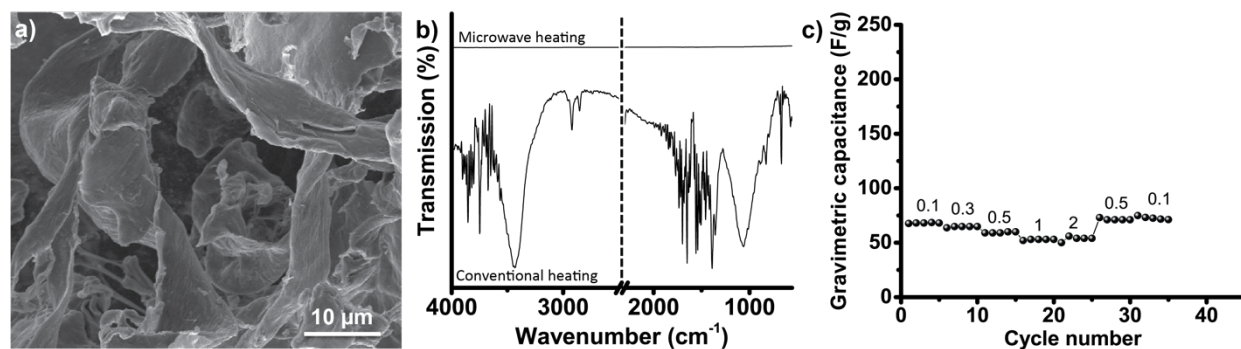


**Figure 53.** Electrochemical performance of carbon materials prepared from GO:cellulose mixture at a weight ratio of 1:1000. (a) Nyquist plot and the inset shows an enlarged scale; (b) CV curves measured at different scan rates; (c) Galvanostatic charge and discharge curves at different current densities; (d) Gravimetric based specific capacitance of the sample as a function of current density.

To further investigate the capacitive performance, the galvanostatic charge-discharge measurements were performed at different current densities. As shown in Figure 53c, the charge-discharge curves display similar symmetrical triangle shape, confirming the good capacitive response, which is consistent with CV results. The specific capacitances were calculated based on the slopes of galvanostatic charge/discharge curves. The final carbon materials delivered a high specific capacitance of  $234 \text{ F g}^{-1}$  at a current density of  $0.1 \text{ A g}^{-1}$ . The specific capacitances were calculated based on the galvanostatic charge/discharge curves. The final carbon materials



delivered a high specific capacitance of  $234 \text{ F g}^{-1}$  at a current density of  $0.1 \text{ A g}^{-1}$ , which is close to that of the microwave-exfoliated graphite oxide. When the current density was increased to  $10 \text{ A g}^{-1}$ , the specific capacitance was still able to retain  $192 \text{ F g}^{-1}$  with a capacitance retention of 82%, indicating an excellent rate performance (Figure 53d). The superior rate capability of the obtained materials could be attributed to its unique sheet structure as well as high conductivity and surface area, which is crucial for fast ion transport and electron transfer.



**Figure 54.** (a) SEM image of cellulose heated in a conventional furnace at a heating rate of  $10 \text{ }^{\circ}\text{C min}^{-1}$  to a temperature of  $800 \text{ }^{\circ}\text{C}$  and maintained at that temperature for 1 hour in  $\text{N}_2$  atmosphere shows a similar non-uniform irregular structure as shown in Fig 3a; (b) The corresponding FTIR spectrum, compared with GO:cellulose microwaved sample at a weight ratio of 1:1000 indicates a much higher degree of carbonization (reduction in-OH group intensity) of the microwaved GO:cellulose sample compare to the conventionally heated cellulose sample. (c) Gravimetric based specific capacitance of the conventionally heated cellulose as a function of current density.

However, cellulose treated by conventional heating at  $800 \text{ }^{\circ}\text{C}$  under  $\text{N}_2$  atmosphere, showed a very low specific capacitance of only  $70 \text{ F/g}$  (Figure 54c). This maybe due to its fibrous shaped structures (Figure 54a) and low carbonization degree, as confirmed by the FTIR spectrum in Figure 54b. Thus, highly conductive carbonaceous products prepared by microwave treating of cellulose with a tiny fraction of GO for just a few minutes exhibit excellent electrochemical performance, which make it possible to fabricate low cost energy storage devices.

## 5.5 Conclusion

Biomass is a promising source for carbon materials in the field of energy storage, as it is cheap, environmentally friendly, renewable and abundantly available throughout the world. In this chapter, I have presented an effective procedure for rapidly carbonizing cellulose, an abundant source of biomass, by introducing catalytic amounts of GO sheets in the microwave irradiation process. Microwave treatment is a promising method to convert biomass into its carbonaceous form. But microwave treatment of biomass such as cellulose, typically takes a long time and produces only insulating carbon material. Due to the excellent microwave absorbing properties of r-GO, a fast and efficient annealing of cellulose to its carbonaceous form was triggered and successfully completed in a few minutes. The final microwave treated GO-cellulose carbon showed superior properties and higher carbonization degree up to a weight ratio of 1:1000. The as-prepared materials possess porous structure with high conductivity and high specific surface area, exhibiting an excellent electrochemical performance when used as electrode materials of supercapacitors. Compared to conventional pyrolytic carbon prepared from cellulose, the rapid microwaved carbon presented here shows superior electrochemical performance, when tested as electrodes for supercapacitors. The work I reported here suggests a rapid microwave thermal method to produce low cost, carbon-rich materials with high conductivity from biomass.

## 5.6 Experimental Conditions

**Microwave treatment of cellulose and GO-cellulose:** All chemicals were of analytical grade and used without further purification. Graphite oxide was prepared by a modified Hummers' method and purified by a two-step washing of HCl and acetone, as reported earlier. An aqueous dispersion

of GO was mixed with cellulose at various weight ratios and then dried in an oven at 60 °C overnight. The microwave heating of cellulose and GO:cellulose mixtures were performed in a laboratory CEM Discover SP (CEM) microwave oven under N<sub>2</sub> atmosphere. As the reaction is highly exothermic and the CEM microwave oven has a maximum temperature limit of 300 °C, experiments were performed in a cyclic mode with a power input of 250 W and the programmed maximum temperature limit set to 250 °C. 100 mg cellulose or GO:cellulose powders at specific weight ratios were heated in a microwave safe vial under nitrogen atmosphere until it reached the programmed set temperature limit, and then later cooled to room temperature. The resulting powder was washed with acetone, DI water and ethanol multiple times to remove any impurities. For GO:cellulose samples of weight ratios smaller than 1:400, two microwave cycles were required. The samples were microwave heated twice to the programmed limit of 250 °C, followed by an acetone, DI water and ethanol washing cycle.

**Characterization:** SEM images were taken on a FEI Nova 600 SEM. TGA of the samples was carried out in a Mettler Toledo TGA/SDTA851 under N<sub>2</sub> atmosphere with a heating rate of 5°C/min. FTIR were acquired in transmission mode on a Nicolet Nexus 870 FTIR spectrophotometer. XRD patterns were obtained using an INEL CPS120 powder diffractometer with Cu K $\alpha$  radiation. Elemental analysis was performed by Atlantic Microlab, Inc., Norcross, GA, using combustion (carbon, hydrogen)- and pyrolysis (oxygen)-based analysis. The specific surface area was calculated from N<sub>2</sub> adsorption–desorption isotherms measured using a Micromeritics 3Flex surface characterization analyzer using the BET equation. The pore-size distributions were obtained from the desorption branches using the BJH method. For conductivity measurements, samples were densified under high pressure (41 MPa) and then cut into rectangular

pellets of known dimensions and weight. Silver paste was then deposited on either end of the pellets. A Keithley 2601A source meter was used to measure the currents between two electrodes by sweeping the voltage between  $\pm 0.5$  V. For electrochemical characterization, microwave-treated 1:1000 precursor weight ratio GO:cellulose was grinded and mixed with polytetrafluoroethylene (PTFE) solution in a weight ratio of 1:9 (PTFE/carbon), and then drop-casted on nickel foam current collectors ( $\sim 3$ -4 mg sample per electrode was maintained). The capacitor electrodes made as such were used to assemble symmetric supercapacitor in a CR2032-type coin cell. The porous nonwoven cloth was used as the separator, with 6 M KOH solution as the electrolyte. The measurements were performed on an Autolab electrochemical instrument (PGSTAT 302N).

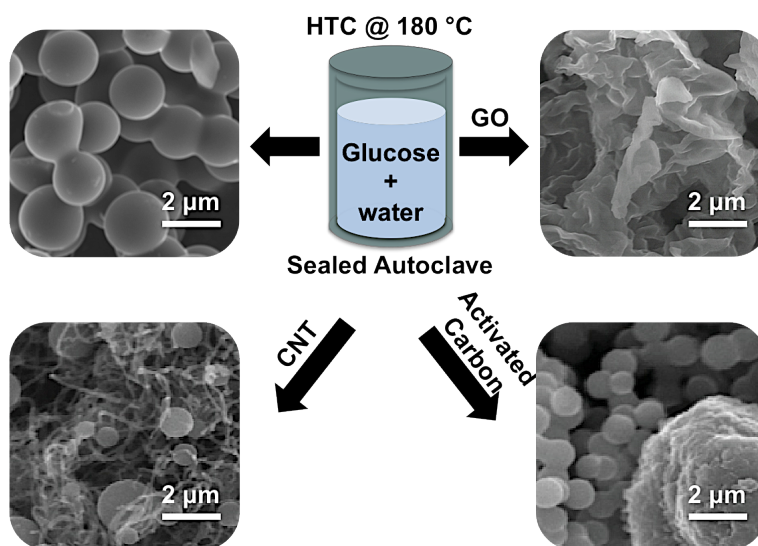
## **CHAPTER 6**

### **Conclusion and Outlook**

Energy plays a major role in today's modern society, it drives our lives and heats our homes. Due to high industrial growth and the extensive use of electrical equipment and gadgets around the modern home, the day-to-day need for electricity is increasing at an alarming rate worldwide. As a result, the availability of energy has never been so important. The United States currently depends on heavily on coal, oil, and natural gas for its energy production. Fossil fuels are non-renewable, i.e., they draw on finite resources which will eventually diminish, become too expensive or too environmentally damaging to retrieve. In contrast, the many types of renewable energy resources-such as wind and solar energy are constantly replenished and will never run out. A major shortcoming of the two is the uneven energy supply which can change significantly over the course of a day. A viable option to overcome this problem is to store energy into an intermediate form and release it on demand rather than just producing a constant amount which might not be needed.

This can be done with the help of energy storage systems like supercapacitors. The work carried out in this thesis was aimed at the development of valuable carbon materials from cheap, sustainable and environmentally friendly biomass precursors. The as prepared carbon materials have been evaluated for their electrochemical performance as electrodes for supercapacitors.

Hydrothermal carbonization offers a simple yet green approach towards the synthesis of functional carbonaceous materials from biomass. However, the HTC carbons obtained from glucose and cellulose shows very poor surface area and was found to be insulating. In order to extent the surface area and introduce conductivity to the material, GO was introduced in the reaction. The resulting carbon was highly porous and conductive, and when microwave treated showed electrochemical performance almost as good as that of pure graphene itself. Control experiments with other carbon sources indicate that only GO is able to change the carbonization route and improve the material properties, mainly due to its amphiphilic nature (Figure 55).



**Figure 55.** Schematic comparing the hydrothermal carbonization of glucose in the presence of various carbon sources such as GO, CNTs and activated carbon. Pure glucose powder results in the formation of carbon spheres after HTC process. Presence of GO, suppressed the sphere formation and resulted in thick sheets like structures. But, with other carbon sources i.e. CNTs and activated carbon, there was the presence of both carbon spheres as well the parent carbon source.

However, the main challenge in this area is the low yield of the hydrochar obtained from HTC of glucose. This can be improved by limiting the moisture content of the reaction and slightly increasing the process temperature. As a result, the overall carbon yield increased almost five times. But the work here was done with respect to pure glucose powders. In order to get hydrochar products that are conductive and at a high yield without extensive post treatments, further experiments need to be done in the presence of GO, by carefully monitoring the GO:glucose:water weight ratio.

Furthermore, by taking into account the excellent microwave heating capability of r-GO, biomass was converted to its more carbonaceous form in the presence of catalytic amounts of GO, under microwave treatment. This method provides an extremely fast, energy efficient and user friendly route to convert biomass into porous, high surface area conductive carbon materials. The carbon product showed electrochemical performance comparable to present day advanced materials, such as graphene and CNTs.

In summary, this dissertation systematically unveils simple and effective strategies to achieve high performance carbon-based supercapacitors with high power density and high energy density by exploiting principles from hydrothermal carbonization and microwave assisted heating. The char produced can be used as an alternative to activated carbon for electrodes, which can be used in hybrid electric automobile batteries or home energy storage in solar panels.

However, there are few directions that need to be further explored. For example, throughout this study mainly pure carbohydrates i.e. glucose and cellulose have been employed as precursors for the synthesis of such highly functional carbon materials. Whilst still comparatively inexpensive

and sustainable, the production of such high performance materials will be even more valuable if entirely based on (waste) biomass. Besides, the process conditions need to be appropriately optimized to take into account the complex nature of biomass waste. Along with the char, a large amount of other side products is formed during the carbonization process. Detailed studies need to be done on these aqueous and gaseous products obtained from biomass carbonization, and if possible valuable products need to be recovered. Finally, for successful industrial application of these materials, the scalability of the processes should be extensively investigated, including process optimization and integration.



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## VITA

### Deepti Krishnan

Place of birth: Kochi, Kerala, India

### Education

2016      Doctor of Philosophy in Materials Science and Engineering

**Northwestern University**, Evanston, IL

2010      Bachelor of Technology in Chemical Engineering

**National Institute of Technology, Surathkal**, Karnataka, India

Graduated with High Honors

### Professional Experience

2011 – 2016    Research Assistant

**Northwestern University**, Evanston, IL

Department of Materials Science and Engineering

Advisor: Professor Jiaying Huang

2010 – 2011    Research Assistant

**Indian Institute of Technology Madras**, Chennai, India

Department of Chemistry

Advisor: Professor T. Pradeep



2009      Research Intern  
  
    **Rice University**, Houston, Texas  
  
    Department of Materials Science and NanoEngineering  
  
    Advisors: Professor Pulickel Ajayan

2008      Research Assistant  
  
    **Indian Institute of Technology Madras**, Chennai, India  
  
    Department of Chemistry  
  
    Advisor: Professor T. Pradeep

### **Publications**

1. Deepti Krishnan, Ying Tao, Hee Dong Jang and Jiaying Huang “Graphene Oxide Sensitized Carbonization of Biomass with Rapid Microwave Heating”, In preparation, **2016**.
2. Ying Tao, Deepti Krishnan and Jiaying Huang “Graphene Oxide Sensitized Carbonization of Biomass with Rapid Microwave Heating”, In preparation, **2016**.
3. Deepti Krishnan, Kalyan Raidongia, Jiaojing Shao and Jiaying Huang “Graphene Oxide Assisted Hydrothermal Carbonization of Carbon Hydrates”, ACS Nano, **2013**, 8, 449.

4. Shihabudheen M. Maliyekkal, Deepti Krishnan, T. S. Sreeprasad, Summayya Kouser, Abhishek Kumar Mishra, Umesh V. Waghmare and T. Pradeep “Graphene: A Reusable Substrate for Unprecedented Adsorption of Pesticides”, *Small*, **2013**, 9, 273
5. Deepti Krishnan, Franklin Kim, Jiayan Luo, Rodolfo Cruz-Silva, Laura J Cote, Hee Dong Jang and Jiaying Huang "Energetic Graphene Oxide: Challenges and Opportunities", *Nano Today*, **2012**, 7, 137.
6. T. S. Sreeprasad, Shihabudheen M. Maliyekkal, Deepti Krishnan, Kamalesh Chaudhari, Paulrajpillai Lourdu Xavier and T. Pradeep, “Transparent, Luminescent, Antibacterial and Patternable Film Forming Composites of Graphene Oxide/Reduced Graphene Oxide”, *ACS Applied Materials & Interfaces*, **2012**, 3, 2643.
7. Deepti Krishnan and T. Pradeep “Precursor-controlled Synthesis of Hierarchical ZnO Nanostructures Using Oligoaniline-coated Au Nanoparticle Seeds”, *J. Cryst. Growth*, **2009**, 311, 3889

### Awards

|           |                                                                                        |
|-----------|----------------------------------------------------------------------------------------|
| 2015-2016 | Terminal Year Fellowship, Northwestern University                                      |
| 2014      | Dow Sustainability Innovation Student Challenge Award                                  |
| 2013-2016 | Ryan Fellowship, Northwestern University                                               |
| 2011      | Graduate Research Fellowship, Materials Science & Engineering, Northwestern University |

- 2010-2011      Research Internship Award, Indian Institute of Technology
- 2008            Summer Research Fellowship, Indian Academy of Sciences
- 2008            Best Poster Award, Department of Chemical Engineering, National Institute of Technology