Graduate School of Pure and Applied Sciences

Development of nitrogen containing porous carbons derived from microalgae

（微細藻類を由来とする含窒素多孔性炭素の開発）

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This thesis is composed of the following chapters.
Chapter 1 Introduction
Chapter 2 The preparation of nitrogen containing porous carbon from microalgae.
Chapter 3 The Preparation of mesoporous algal carbons via Mg-templated hydrothermal carbonization and pyrolysis
Chapter 4 Conclusion

Chapter 1 Introduction

In the chapter 1, I will discuss about biomass, microalgae carbon materials, biochars, porous carbons, applications of carbon materials, especially EDLC.
In the modern society, fossil fuels have a great contribution to the development of technology and life. They provide most of the energy for the global civilization. However, with the increasing in the utilizing of energy, the fossil resources are decreasing with a amazing speed, and energy crisis has already become an important issue that people must face in the world. For finding the alternative energy of the fossil fuels, the development and research were focused on the solar energy, wind energy, tidal energy, bioenergy and so on. With the development of the bioenergy, the biomass was stepping into the researchers' sight.(Fig 1)

Biomass was a renewable material which was from animals and plants, the using of biomass in the human society has continued for a long time, however, the utilization of biomass was limited to the making fire and fertilizer. With the development of the technology, the scope of use for biomass was expanded to some new areas, and at the same time, some new kinds of biomass attract the attention of the researchers.

In present studies, the main components of biomass were separated to five categories: starch, cellulose, hemicellulose, lignin and oils, which were existed in multiple products including fuels and high value chemical materials. Biomass conversion can reduce the produce of pollution for environment and improve the virtuous circle of nature. The research and methods on transform biomass into useful products have become the popular topic in recent years.

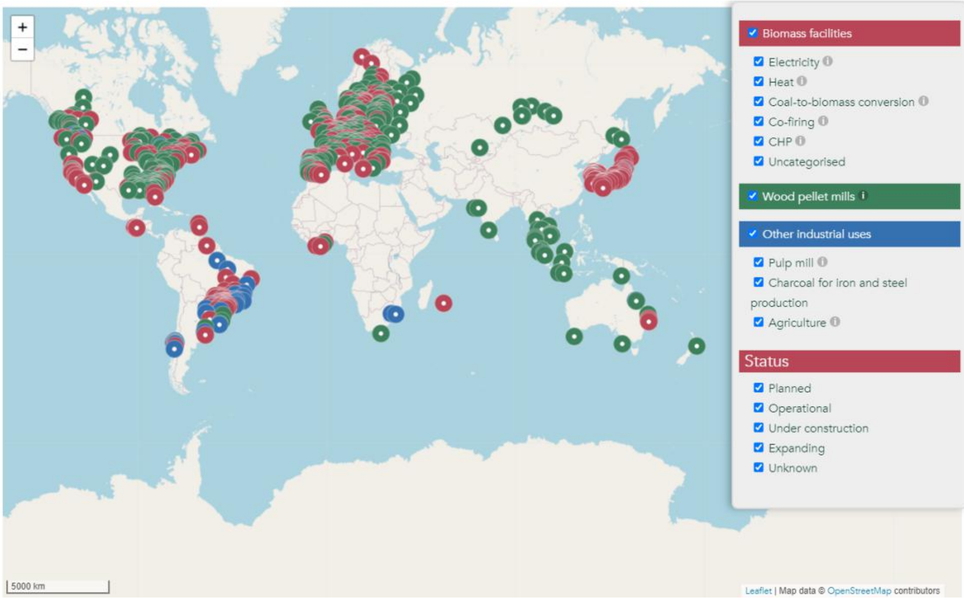

Fig 1. The biomass industry across the globe [1]

From now on, microalgae were as a key sustainable and clean resource, because the microscopic photosynthetic organisms are promising biomass sources, and their unicellular structure with high photosynthetic efficiency allow for a potentially higher yield of carbon sequestration per area than other crops. [2] The area of fresh water and marine water in the world was higher than the land area, so it provides a guarantee for the planting area of microalgae. Even in places, the harmful algal bloom has become the serious environment problem, development of the utilization of biomass in microalgae can provide the new method for dealing with the remains in harmful algal bloom.

Among the biomass, alga is one kind of widespread materials and gradually stepping into people's view because it is a promising source of carbon containing material and rich in nutrients (such as protein).. Algae are typically found in freshwater and marine systems. They are unicellular species and exist individually or in groups. Their sizes range from a few micrometers (μm) to a few hundred μm. Microalgae are different from other plants, and they do not have roots and leaves, only one cell, so they can provide higher photosynthesis efficiency than other plants. These micro-shape algae do not need grow up from soil and land. Microalge could also photosynthesize enough organic matter from part of mass is made up of lipids can be extracted and used as "crude oil" which attracts higher attention due to the high-purity hydrocarbon products.[3]

In the chapter 2 and chapter 3, I choose two kinds of microalgae with high content of nitrogen, *Chlorella* and *Spirulina* as the materials for the preparation of nitrogen containing carbons. In this study, the *Chlorella* and *Spirulina* were from NICHIE Co., Ltd., Japan. Protein, fat, and carbohydrates in the samples were 70 %, 8 %, and 8 % for the *Spirulina* sample and 59 %, 10 %, and 20 % for the *Chlorella* sample.(Fig.2)

Chlorella is a single-celled freshwater alga. The shape of the cells of *Chlorella* is spherical and diameter of cells is about 2-10μm (Fig 3). It is also a kind of high-quality green nutrient food. It contains lots of proteins and carbohydrate, low fat. Therefore, *Chlorella* is widely used as a source of healthy food.

Spirulina is a kind of unique algae, which is named for its regular spiral bending (Fig 3). It is growing in freshwater and seawater. It contains higher contents of proteins(nitrogen source) and lower fat than *Chlorella*.

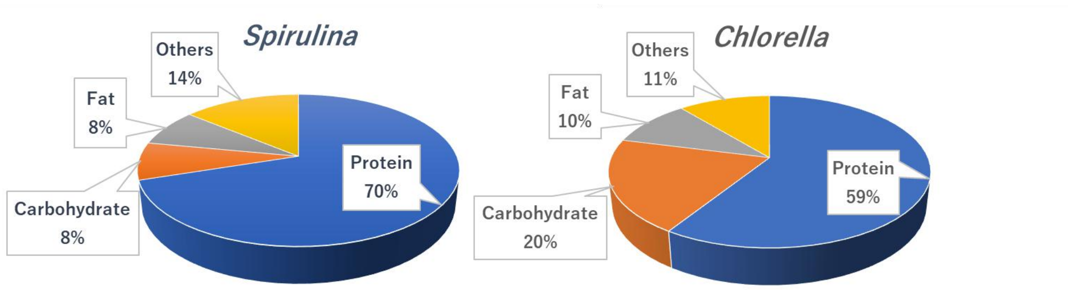

Fig. 2. Composition of *Spirulina* and *Chlorella* (wt %) (data provided by NICHIE Co., Ltd., Japan)

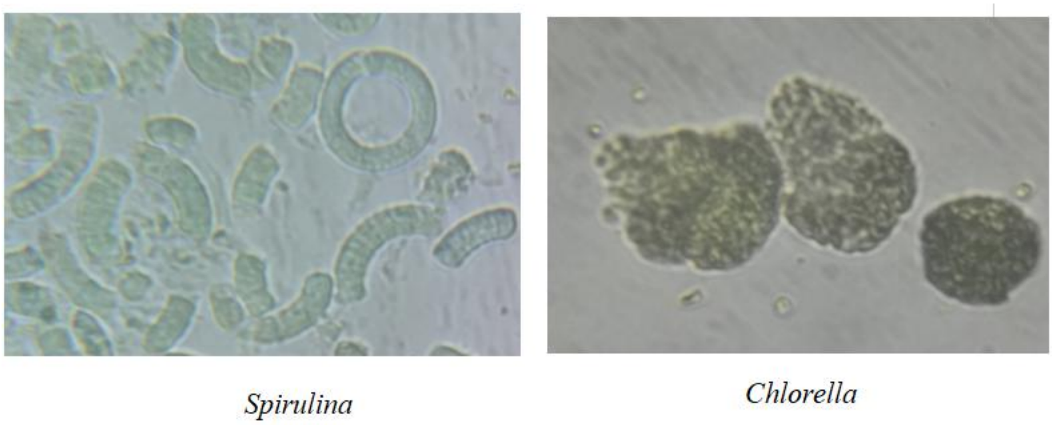

Fig. 3 The optical microscope picture of *Spirulina* and *Chlorella* (X 1000)

About the carbon material, It is also considered as "old and new" material and widely applied throughout the world and history. In ancient time, the carbon was usually used as the heating tools, however, with the development of technology, more excellent characterizations such as heat and chemical resistance, electric conductivity, low thermal expansion, and light quantity were found from carbon materials. It is a sustainable element and has excellent functions due to its various structures, such as graphite structure, diamond structure and nanocarbon, which are used in the development of, conductive materials, energy storage and adsorption materials. Among those different structure of carbon, the amorphous carbon with micro- and meso- pore similar to activated carbon are the theme of this thesis due to the high surface area.

The porous carbon was widely studied on the energy storage, such as capacitor. For obtaining the capacitor with high capacitance , the surface area of materials was the most important (C=εS/d). According to some reports, the presence of nitrogen in carbon materials can enhance some functionalities such as capacitance with the pseudocapacitive effect and catalytic activity [3]. Electric double layer capacitor (EDLC) method was the common method to characterize the capacitance of materials, The electric double layer formed at the interface of solid (carbon with high surface area, electrode) and liquid (electrolyte) replaces the dielectric. The capacity is proportional to the surface area of electric double layer formed at the interface. Therefore, the electrode obtains a large capacity by using carbon with a large specific surface area. The basic structure of EDLC is that the positive and negative electrodes were filled with electrolyte. EDLC use the ions in the electrolyte to adsorb and detach from the electrode surface to charge and discharge.

In that case, for developing the application of microalgae on the high surface materials and capacitors, different reactions were carried out for conversion from organic materials into the carbon, and different characterizations were done for determining the properties of final materials.

Chapter 2 The preparation of nitrogen containing porous carbon from microalgae.

The biomass has been applied into developing various carbon-based materials, such as activated carbons, carbon blacks, coals, carbon fibers, and various carbon composites. However, until recently, algal biomass has not received much attention as a potential raw material for carbon production. Microalgae are a nitrogen-rich material due to the large content of protein (over approximately 60 wt%). It means that it is potential to make the nitrogen-containing carbon from microalgae.

The simplest and most typical method for preparing carbons from organic materials is heating the samples by 700–1000 °C under anaerobic conditions.However, *Spirulina* and *Chlorella* were carbonized at 900 °C under an Ar atmosphere, obtaining around 30 wt% carbon, with almost retained shapes but non-porous.Thus, hydrothermal carbonization of *Spirulina* and *Chlorella* were introduced to solve this problem of low yields. It is thought that the presence of aromatic aldehydes, such as hydroxymethylfurfural(HMF) and phthalaldehyde, should be effective in increasing the yields of production of hydrothermal carbons.[5] The high yield of solid production after hydrothermal reaction depends on the Schiff base (azomethine) from amino acid and aldehyde group to accelerate the insolubility and thermosetting properties of materials under hydrothermal (HT) conditions.

In this study, phthalaldehyde was added during the hydrothermal reaction. At the hydrothermal reaction of 220°C and 2.3 MPa, the hydrothermal algae carbon with the high-yield(over 50%,equation 1) and nitrogen-containing were obtained, and successive calcinated at 900 °C. The nitrogen-containing microporous carbons with surface areas of approximately 600 -700 m^2/g were synthesized successfully, It could also be demonstrated that these algal porous carbons exhibited high activity for electrochemical capacitors in aqueous acidic media.[6]

On the other hand, the algae residue from *Botryococcus braunii*, whose oil were excluded, were directly carbonized at 900 °C and almost no solid (gas) were obtained. Thus, the hydrothermal carbon of *Botryococcus braunii* with the addition of phthalaldehyde were prepared and successive calcinated at 900°C. the micropore carbons with 600 m^2/g were obtained.

$$\text{Yield of HT-alga (\%)} = \frac{\text{mass of insoluble solid products (g)}}{\text{total mass of microalga(g)and phthalaldehyde (g)}} \text{x} \, 100 \qquad (1)$$

The N-containing carbons with high surface area from algae which are rich in protein has been obtained Adding terephthalaldehyde during the hydrothermal reaction for algae can increase the yields of hydrothermal algae materials. After the hydrothermal reaction, HT-pht-algae materials have the higher yields (around 50%) than HT-algae. After pyrolyzing of those HT-pht-algae, the CHT-pht-algae with high surface (686 and 766 m^2/g) were obtained. From the SEM of HT-algae, HT-pht-algae, and CHT-pht-algae. During the hydrothermal reaction, the algae were decomposed into soluble components and change to a lamellar surface (Fig. 4 (a, b)). When terephthalaldehyde was added to the hydrothermal reaction, sphere of HT-pht-Spirulina and flake-agglomerates of HT-pht-Chlorella were observed on their surfaces (Fig. 4 (c, d)). After carbonization, smaller-sized CHT-pht-algae were observed in both cases (Fig. 4 (e, f)).

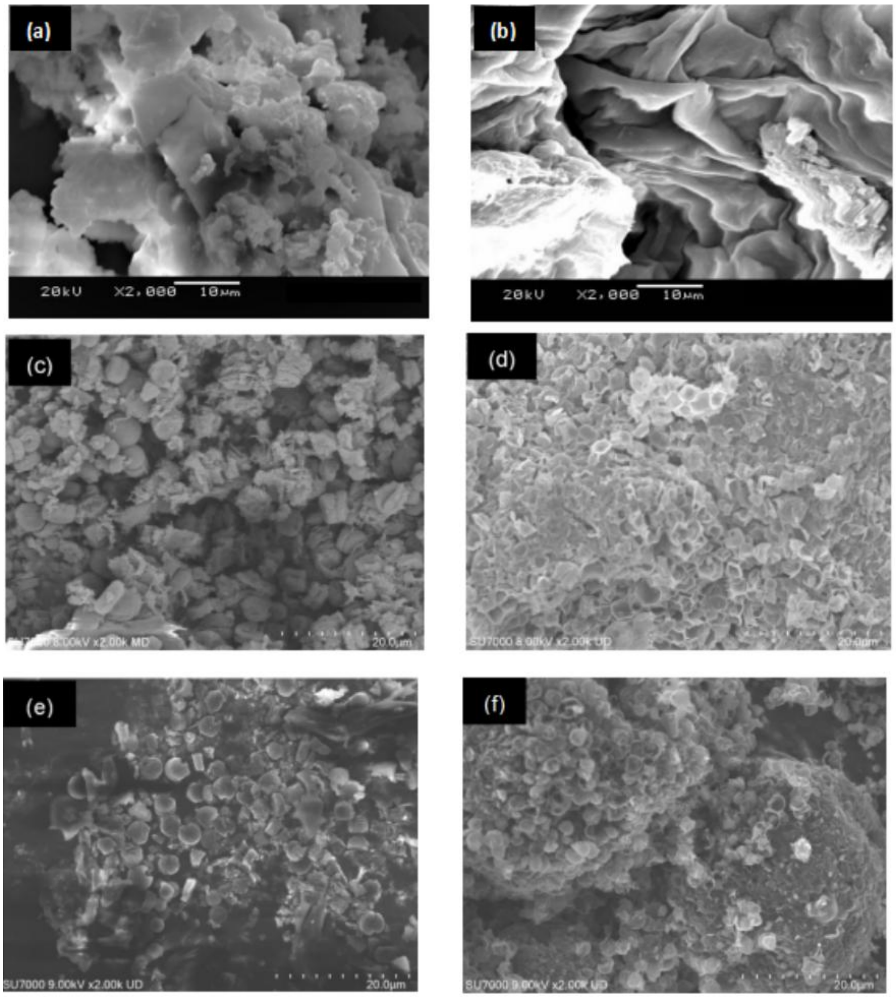

Fig.4.SEM pictures of HT-*Spirulina* (a), HT-*Chlorella* (b), HT-pht-*Spirulina* (c), HT-pht-*Chlorella* (d), CHT-pht-*Spirulina* (e), and CHT-pht-*Chlorella* (f).

The V-t curve from EDLC method (Fig 5) can reflect the relationship between current density and charge/discharge time of carbon materials. It shows that the at current density of 0.2 A/g, 0.4 A/g, 0.6 A/g, 0.8 A/g and 1.0 A/g, CHT-*Spirulina* have the capacitance of 269 F/g, 225 F/g, 192 F/g, 184 F/g, 170 F/g and CHT-*Chlorella* have the capacitance of 248 F/g, 238 F/g, 227 F/g, 219 F/g, 209 F/g, respectively. With the increasing of current density, the capacitance of CHT-carbon decreased. The result of EDLC suggests that the nitrogen-contained carbon show the better electrochemical performance than the simple activated carbon. And the nitrogen-contained and nanosphere structure endow the excellent potential application in supercapacitor. Those results indicate that the method using in this experiment provide a good path for preparing hydrothermal algae materials, and those carbon materials have the potential to be applied as the electrochemical carbon materials.

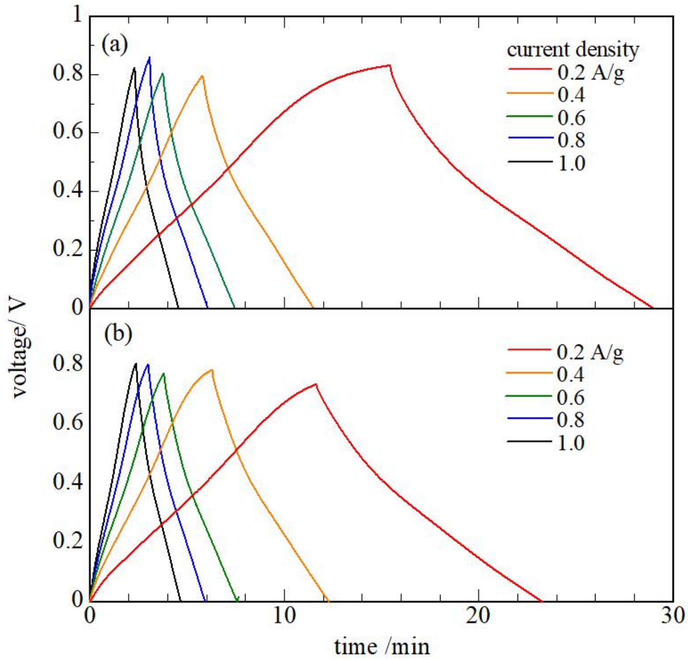

Fig. 5 V-t curves of CHT-pht-*Spirulina* (a) and CHT-pht-*Chlorella* (b).

Chapter 3 Preparation of mesoporous algal carbons via Mg-templated hydrothermal carbonization and pyrolysis

In the chapter 2, nitrogen-containing microporous algal carbons, which have specific surface area of 600-700 m^2/g in good yields via the hydrothermal reaction using the terephthalaldehyde additive and successive calcination. The content of the micropore was around 0.44 ml/g, and around 80 vol% of pores were micropore (Table 1), although the carbon materials with most micropore show good electrical property through characterization of EDLC, the carbon with major mesopore was also expected in this study. In chapter 3, I prepared the carbon with higher amount of mesopore (2 nm-50nm), preparation of algal carbons with mesoporosity in addition to the microporosity is attempted to develop high-performance electrochemical active biocarbon, *i.e.*, two kinds of microalgae, *Spirulina* and *Chlorella,* were hydrothermally reacted at 220°C in the presence of terephtalaldehyde with a Mg porogen, since hydrothermal reaction of Mg salts can afford MgO particles with several tens in nm size [7] that might be worked as a porogen template. The template was removed from the biocarbon by washing with acid before or after the successive calcination at 900°C.In this chapter, according to the time for make the Mg-template, it will be separated into 3 kinds of section.

1. Mg-template was prepared during the hydrothermal reaction and clean the Mg-template during the process of pyrolysis.

2. Mg-template was prepared during the hydrothermal reaction and keep the template until the finishing of the pyrolysis.

3. Mg-template was prepared only during the process of pyrolysis and be not existed during the process of hydrothermal reaction.

1 would be explained on 3.2 section and 2 and 3 would be explained on 3.3 section.

The water suspensions of microalgae, *Spirulina* /*Chlorella,* and phthalaldehyde were hydrothermally reacted at 220 °C for 14 h with magnesium compound in an autoclave; different Mg-compound bring the different yields of hydrothermal carbons according to their pH. At the alkaline conditions, the higher yields of algal hydrothermal carbons could be contained, meanwhile, the acid conditions would decrease the yields of hydrothermal carbons; via carbonization from room temperature to 900 °C under an argon and acid washing after cooling down, the algal carbons with large amount of mesopore and specific surface area of approximately 600 m^2/g were prepared.

Table 1 summarized results of the yields of HT of *Chlorella* after washing with acid, carbonization yields of the acid-washed HT, and their surface analysis data. The addition of $MgCl_2$ caused decreasing the HT yield and becoming pH in acidic region, while addition of $Mg(OAc)_2$ and $Mg(OH)_2$ resulted in increasing the HT yields under the condition of weak alkaline. The N_2 adsorption/desorption isotherms (Fig. 5) showed that the addition of $Mg(OAc)_2$ was effective to add mesoporosity on the algal carbons in addition to microporosity in comparison with the result without the Mg additive. On the other hand. The addition of $Mg(OH)_2$ and $Mg(OH)_2$ /MgO decreased microporosity but increased mesoporosity on the carbons.

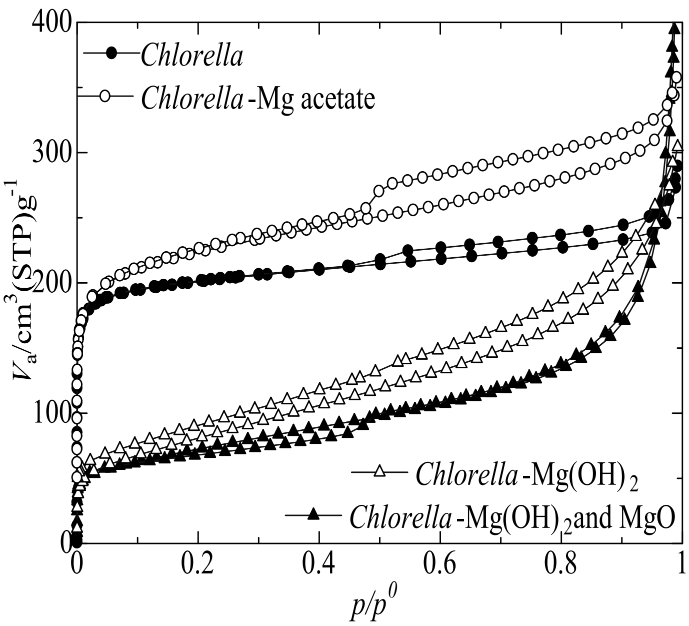

Fig. 5. The N_2 adsorption isotherms of *Chlorella* carbons

Table.1The yields and surface analysis data of *Chlorella* carbons

algae	Mg additive	HT Yield	carbonization Yield	S_{BET}	S_{total}	V_{micro}	w_{micro}	V_{total}	V_{meso}	V_{meso}/ V_{total}
	(1 wt %)	wt%	wt%	m^2/g	m^2/g	mL/g	nm	mL/g	mL/g	%
Chlorella	/	61	33	766	920	0.28	0.66	0.44	0.29	37
	$MgCl_2$	5	/	/	/	/	/	/	/	/
	$Mg(OAc)_2$	84	32	1587	1601	0.51	0.91	1.22	0.7	57
	$Mg(OH)_2$	82	33	273	257	0.02	3.54	0.45	0.45	98
	$Mg(OH)_2$/MgO	84	30	257	258	0.04	0.92	0.68	0.64	94

In this chapter, the different kinds of Mg-template algal carbon were prepared, three kinds of method were selected for the preparation of the algal carbon. Among them, the method 1 that Mg-template was prepared during the hydrothermal reaction and clean the Mg-template during the process of pyrolysis show the better results when $Mg(OAc)_2$ was used as the resource of Mg-templates and got the carbon with good electric properties. The method 2 show a better result when $MgO/Mg(OH)_2$ as the resource of Mg-templates. And The method 3 need more improvement. The carbon with the S_{BET} of 1500 m^2/g and 60 vol% mesoporosity has been prepared, and the carbon with over 98 vol% mesoporosity also has been prepared.

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