

PHYSICOCHEMICAL AND ELECTROCHEMICAL PROPERTIES OF PRISTINE
AND MODIFIED ORDERED MESOPOROUS CARBON SYNTHESIZED
USING SBA-15 AS TEMPLATE

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*Specially dedicated to my beloved parents, Razman Mohamed Puang and
Nafisah Md. Noor, husband, brothers, and wonderful friends.*

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ABSTRACT

Ordered mesoporous carbon based materials (OMC) are suitable for many applications because of their unique physicochemical properties. In this research, OMC materials with large surface areas up to $1226 \text{ m}^2 \text{ g}^{-1}$ were synthesized using the nanocasting method with SBA-15 silica as the hard template and sucrose as the carbon precursor. The mesoporous silica SBA-15 template was prepared by hydrothermal synthesis using tetraethyl orthosilicate (TEOS) and Pluronic P123 copolymer under acidic conditions which was later used to synthesize OMC. Based on small angle X-ray scattering (SAXS) data analysis, the (1 0 0) peak position of the OMC was exactly the same as for the template SBA-15 ($1.0^\circ 2\theta$), which is an indication of long-range structural ordering, implying a complete replication of the carbon from the SBA-15 silica template. Additionally, both the transmission electron microscopy (TEM) and field emission scanning electron microscopy (FESEM) images of SBA-15 and OMC were similar, showing well-ordered hexagonal pores and uniform pore sizes of less than 5 nm in diameter with rod-like particle morphology. Oxygen and nitrogen containing functional groups, respectively, were incorporated into the OMC surface in order to improve the electrochemical performance and hydrophilic properties. The oxygen functionalized OMC (OMC-O) was formed through oxidative treatment with 2M HNO_3 solution. X-ray photoelectron spectroscopy (XPS) measurements showed an increase in the amount surface oxygen (13.7%) in the form of carbonyl, carboxyl and quinone groups which were supported by the Fourier transform infrared (FT-IR) spectra. Modification of OMC with nitrogen containing functional group was performed by noncovalent functionalization method via adsorption of Basic Red 2 (BR2) dye, $\text{C}_{20}\text{H}_{19}\text{ClN}_4$, from aqueous solution to afford the nitrogen functionalized OMC (OMC-N). The highest adsorption capacity q of BR2 was obtained with solution concentration of 1000 mg L^{-1} at 60°C , pH of 10, OMC loading of 0.2 g L^{-1} and contact time of 180 min as determined by ultraviolet-visible (UV-Vis) spectroscopy. The experimental data showed excellent fit with Langmuir isotherm model ($R^2 = 0.989$) giving a maximum capacity q_{max} of 1000 mg g^{-1} . BR2 adsorption onto the OMC obeyed pseudo-second order kinetic model and the process is thermodynamically favourable, spontaneous, physical ($\Delta H_{\text{ads}} = 37.9 \text{ kJ mol}^{-1}$) and endothermic. Electrochemical behaviours of OMC, OMC-O and OMC-N were evaluated by cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS) and galvanostatic charge-discharge (GCD) using a three-electrode assembly in 1M KOH aqueous electrolyte. Both OMC-O and OMC-N demonstrated higher specific capacitance than OMC and good capacitance retention (> 50%) at the optimum scan rate (10 mV s^{-1}) and current density (0.5 A g^{-1}). However, BR2 functionalized OMC-O (OMC-ON) containing oxygen and nitrogen functionalities exhibited the highest capacitance (356.4 F g^{-1}) among the samples, but has the lowest capacitance retention (45%) upon increasing scan rate. The enhancement in specific capacitance of modified OMC was correlated to the pseudo-capacitance induced by redox reactions of oxygen and nitrogen functionalities in OMC prepared by oxidative modification and noncovalent functionalization method. The synergistic effects of the oxygen and nitrogen increase the hydrophilicity, while the presence of mesopores also promoted the formation of electrical double-layer, and consequently increased the specific capacitance of OMC in aqueous medium.

ABSTRAK

Bahan berasaskan karbon mesoliat bertertib (OMC) sesuai digunakan untuk pelbagai aplikasi disebabkan oleh sifat fizikokimia yang unik. Dalam penyelidikan ini, bahan OMC dengan luas permukaan tinggi sehingga $1226 \text{ m}^2 \text{ g}^{-1}$ telah disintesis menggunakan kaedah penuangan nano dengan silika SBA-15 sebagai templat keras dan sukrosa sebagai sumber karbon. Templat silika mesoliat SBA-15 disediakan secara sintesis hidroterma menggunakan tetraetilortosilikat (TEOS) dan kopolimer Pluronic P123 dalam keadaan berasid yang kemudiannya digunakan untuk sintesis OMC. Berdasarkan data analisis sudut kecil penyerakan sinar-X (SAXS), kedudukan puncak (1 0 0) OMC adalah sama dengan templat SBA-15 ($1^\circ 20'$) yang menunjukkan ketertiban struktur jarak jauh, serta menandakan karbon direplikasi daripada templat silika SBA-15 secara lengkap. Tambahan pula, kedua-dua imej mikroskop pancaran elektron (TEM) dan mikroskop imbasan elektron pancaran medan (FESEM) untuk SBA-15 dan OMC adalah serupa, dengan menunjukkan susunan liang heksagon bertertib dan saiz liang seragam berdiameter kurang daripada 5 nm dengan morfologi zarah seakan-akan rod. Kumpulan berfungsi mengandungi oksigen dan nitrogen masing-masing, telah digabungkan dalam permukaan OMC bagi meningkatkan sifat elektrokimia dan sifat hidrofilik. OMC berfungsi oksigen (OMC-O) telah terbentuk melalui pengoksidaan dengan larutan HNO_3 2M. Pengukuran spektroskopi fotoelektron sinar-X (XPS) menunjukkan pertambahan jumlah oksigen permukaan (13.7%) dalam bentuk kumpulan karbonil, karboksil dan kuinon yang disokong oleh spektrum inframerah transformasi fourier (FT-IR). Pengubahsuaian OMC dengan kumpulan berfungsi mengandungi nitrogen telah dilakukan dengan kaedah pemfungsian bukan kovalen melalui penjerapan pewarna Basic Red 2 (BR2), $\text{C}_{20}\text{H}_{19}\text{ClN}_4$, dalam larutan akueus bagi menghasilkan OMC berfungsi nitrogen (OMC-N). Kapasiti penjerapan q tertinggi untuk BR2 telah dicapai menggunakan larutan yang mempunyai kepekatan 1000 mg L^{-1} pada 60°C , pH 10, muatan OMC berjumlah 0.2 g L^{-1} dan masa sentuhan selama 180 min, yang ditentukan oleh spektroskopi ultralembayung-nampak (UV-Vis). Data eksperimen mendapati kesesuaian dengan model isoterma Langmuir ($R^2 = 0.989$) adalah sangat baik di mana kapasiti maksimum q_{max} ialah 1000 mg g^{-1} . Penjerapan BR2 pada OMC mematuhi model kinetik tertib pseudo-kedua dan memuaskan daripada segi termodinamik, spontan, fizikal ($\Delta H_{\text{ads}} = 37.9 \text{ kJ mol}^{-1}$) dan endotermik. Kelakuan elektrokimia untuk OMC, OMC-O dan OMC-N telah dinilai menggunakan voltametri kitaran (CV), spektroskopi impedans elektrokimia (EIS) dan cas-nyahcas galvanostatik (GCD) menggunakan pemasangan tiga elektrod dalam elektrolit berakueus KOH 1M. Kedua-dua OMC-O dan OMC-N menunjukkan kapasitan spesifik lebih tinggi berbanding OMC dan penahanan kapasitan baik ($> 50\%$) pada kadar imbasan optimum (10 mV s^{-1}) dan ketumpatan arus (0.5 A g^{-1}). Walaubagaimanapun, BR2 berfungsi OMC-O (OMC-ON) yang mempunyai kumpulan berfungsi oksigen dan nitrogen mempamerkan kapasitan tertinggi (356.4 F g^{-1}) antara sampel, tetapi mempunyai penahanan kapasitan paling rendah (45%) dengan peningkatan kadar imbasan. Peningkatan kapasitan spesifik OMC terubahsuai adalah berhubungkait dengan pseudo-kapasitan yang teraruh oleh tindak balas redoks kefungsi oksigen dan nitrogen dalam OMC yang telah disediakan secara pengubahsuaian oksidaan dan kaedah pemfungsian bukan kovalen. Kesan sinergi oksigen dan nitrogen tersebut telah meningkatkan kehidrofilikan, manakala kehadiran mesoliat juga memacu pembentukan lapisan-ganda dua elektrik, seterusnya meningkatkan kapasitan spesifik OMC dalam medium berakueus.

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LIST OF ABBREVIATIONS

A	-	Absorbance
AC	-	Activated carbon
BET	-	Brunauer–Emmet–Teller
BJH	-	Barrett–Joyner–Halenda
BR2	-	Basic Red 2
CHN	-	Carbon Hydrogen Nitrogen
CI	-	Colour index
CR	-	Capacitance retention
C _s	-	Specific capacitance
CV	-	Cyclic voltammetry
DSC	-	Differential scanning calorimetry
DTA	-	Differential thermogravimetry analysis
EDLC	-	Electric double-layer capacitor
EIS	-	Electrochemical impedance spectroscopy
FESEM	-	Field emission scanning electron microscopy
FSM-16	-	Folded Sheet Mesoporous-16
FT-IR	-	Fourier transform infrared spectroscopy
FWHM	-	Full width half maximum
GCD	-	Galvanostatic charge-discharge
H1	-	Hysteresis type 1
IUPAC	-	International Union of Pure and Applied Chemistry
MCM	-	Mobil Crystalline Material
MWCNT	-	Multiwalled carbon nanotube
NMP	-	<i>N</i> -methyl pyrrolidinone
OMC	-	Ordered mesoporous carbon
OMS	-	Ordered mesoporous silica
P	-	Pressure

P123	-	Pluronic P123
<i>p6mm</i>	-	Space group
PEO	-	Poly(ethylene oxide)
PPO	-	Poly(propylene oxide)
PVDF	-	Polyvinylidene fluoride
R	-	Resistance
RT	-	Room temperature
SAXS	-	Small angle X-ray scattering
SBA-15	-	Santa Barbara Amorphous-15
Si-OH	-	Silanol
Si-O-Si	-	Siloxane
T	-	Temperature
TEM	-	Transmission electron microscopy
TEOS	-	Tetraethyl orthosilicate
TG	-	Thermogravimetry
UV-Vis	-	Ultraviolet visible
XPS	-	X-ray photoelectron spectroscopy
XRD	-	X-ray diffraction

LIST OF SYMBLOS

%	-	Percent
°	-	Degree
°C	-	Celsius
Å	-	Angstrom
a.u	-	Arbitrary unit
a_0	-	Lattice parameter
C_e	-	Equilibrium concentration
cm	-	Centimeter
cm^{-1}	-	Wavenumber
C_0	-	Initial concentration
d	-	Interplanar distance
d_{BJH}	-	Pore diameter
eV	-	Electron volt
F	-	Farad
g	-	Gram
h	-	Hour
J	-	Joule
K	-	Kelvin
k	-	Rate constant
K_F	-	Freundlich constant
K_L	-	Langmuir constant
L	-	Liter
M	-	Molarity
m	-	Meter
m	-	Mass loss
mg	-	Milligram
mV	-	Millivolt

M_w	-	Molecular weight
n	-	Constant
nm	-	Nanometer
q	-	Scattering vector
q	-	Adsorbed capacity
q_e	-	Equilibrium adsorbed capacity
q_t	-	Adsorbed capacity at time t
R^2	-	Coefficient of determination
S_{BET}	-	BET specific surface area
t	-	Time
V	-	Volume
V	-	Volt
v/v	-	Volume over volume
V_{MESO}	-	Mesopore volume
V_{MICRO}	-	Micropore volume
V_{TOTAL}	-	Total pore volume
w	-	Wall thickness
θ	-	Scattering angle
λ	-	Wavelength
μ	-	Micron
μm	-	Micrometer
Ω	-	Ohm

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CHAPTER 1

INTRODUCTION

1.1 Research Background

Porous materials are classified into different kinds by their pore size. According to International Union of Pure and Applied Chemistry (IUPAC), microporous material have pore diameter of less than 2 nm and macroporous material have pore diameter of greater than 50 nm; the mesoporous category thus lies in the middle. Table 1.1 summarizes the categories of porous materials (Gregg and Sing, 1982).

Table 1.1: Classification of porous materials according to pore size.

Classification	Pore size
Microporous	< 2 nm
Mesoporous	2–50 nm
Macroporous	> 50 nm

Typical mesoporous materials include some kinds of silica (*e.g.*, HMS, SBA-15, and M41S family), alumina (*e.g.*, clay and zeolites), and carbon (*e.g.*, CMK-1, CMK-2, and CMK-3) that have similarly-sized fine mesopores. A mesoporous material can be disordered or ordered in a mesostructure. Research in this field has steadily grown concerning both of their structural properties and technological applications.

Ordered mesoporous carbon (OMC) is a carbon material with well defined porosity, size ranges from 2 to 50 nm. OMC exhibits ordered pore structure, high surface area, large pore volume, chemical inertness, high mechanical stability and conductivity (Ryoo *et al.*, 2001; Hartmann *et al.*, 2005). OMC can be prepared by various techniques such as catalytic activation, physical and chemical activation, soft templating, and hard templating method. Among all, hard templating method allows control of structure, morphology, and pore dimension of the OMC (Lu and Schüth, 2006; Saini *et al.*, 2010). OMC has been used in wide area of applications such as adsorption, catalysis, energy storage, and electrochemistry due to distinct advantages over traditional porous materials such as zeolites, active carbon, and metal oxides.

Generally, hard templating method is a straightforward process in which a template with relevant nanoscale structure, is impregnated with carbon precursor, and the initial template is subsequently removed (Lu and Schüth, 2006; Saini *et al.*, 2010). This method is also known as nanocasting. The resulting carbon exhibits as mentioned criteria with variable three-dimensional structures such as cubic and hexagonal, depending on the structure of the template. In other words, the OMC prepared through this method is usually an inverse replica of the hard template. This method mainly used ordered mesoporous silica (OMS) as the hard template and sucrose, furfuryl alcohol, or phenol resin as the carbon precursor (Gierszal *et al.*, 2008).

Ordered mesoporous silica (OMS) is a material made up of Si–O–Si (siloxane) framework with uniform pore size and structure. OMS has also been used in diverse applications such as molecular sieving, adsorbent, sensor, stationary medium for biomolecules, and catalyst support (Fiorilli *et al.*, 2004; Busuioc *et al.*, 2006; de Oliveira *et al.*, 2011; Huang *et al.*, 2011). Santa Barbara Amorphous, SBA-15 is one of the famous OMS materials due to its large and well hexagonally arranged mesopore structure. SBA-15 also has thick silica walls therefore exhibits high hydrothermal and thermal stability (Newalkar *et al.*, 2000). SBA-15 is structured by a nonionic triblock copolymer (EO)₂₀(PO)₇₀(EO)₂₀ called Pluronic P123 and tetraethyl orthosilicate (TEOS) in acidic condition. The pore size and particle morphology of SBA-15 can be altered in a wide range by controlling the

synthesis conditions (*e.g.*, temperature, stirring rate, and Pluronic P123/TEOS ratio) and surfactants architecture (Zhao *et al.*, 1998b). In 2000, Jun and his friends have first reported an ordered mesoporous carbon material (CMK-3) using SBA-15 as hard template and sucrose as carbon source (Jun *et al.*, 2000). The resultant carbon exhibited similar structure characteristics to the SBA-15.

Introduction of heteroatoms other than carbon within a carbon matrix can be performed by chemical and physical modification methods. These modification methods alter the electronic structures of the carbon materials, enhancing its surface polarity, electrical conductivity, and electron-donor properties (Zhang *et al.*, 2013). A few modification methods have successfully enhanced the electrochemical properties of carbon material, as reported by Chen *et al.* (2013), Almeida *et al.* (2014), and Shi *et al.* (2015). The presence of electrochemical active functional groups such as oxygen and nitrogen provides additional pseudo-capacitance to the energy storage mechanism by means of redox process. These functional groups are able to improve the hydrophilicity of OMC based material in aqueous medium.

Dye is a coloured substance that has affinity to the substrate to which it is being applied. There are two types of dyes; basic and acidic dyes. A basic dye is cationic dye that dissolves in aqueous media and form positively charged chromophore. One of the commonly used basic dyes is Basic Red 2 (BR2), also known as Safranin. BR2 is a water soluble nitrogen containing compound and forms positively charged nitrogen cations when dissolves in water. Introduction of nitrogen containing functional groups generally creates basic properties, which can enhance the interactions between the carbon surface and acidic molecules. In addition, nitrogen functionalized carbon based material also has high affinity to water molecules thus improved its hydrophilic properties in aqueous media (Hou *et al.*, 2005). The influence of surface functional groups can be further confirmed by electrochemical performance tests in aqueous electrolyte.

Easy noncovalent BR2 functionalization on the surface of OMC through adsorption makes such modification interesting. Adsorption is the binding of molecules or particles to a surface. The optimum adsorption conditions can be

accomplish by varying parameters such as solution pH, temperature, initial concentration, sample loading, and contact time. Equilibrium, kinetic, and thermodynamic studies are employed to describe the adsorption process. Heat of adsorption (ΔH_{ads}) value will determine the types of interaction between BR2 molecules and OMC host. BR2 was selected for the noncovalent functionalization in order to produce nitrogen containing OMC based material.

1.2 Statement of Problem

Hard templated OMC practices structure replication strategy. The replication procedure involves infiltration of the pores of the hard template with an appropriate carbon precursor, followed by inert atmosphere carbonization and template dissolution. Therefore, the hard template has to exhibit suitable and fine mesoporous system in order for the replication process to be successful; otherwise disordered microporous carbon is formed. It is important to produce a good quality hard template which will determine the structure of consequential OMC.

Previous reports have demonstrated that the application of this material is determined mainly by its structural properties as well as surface chemistry. Oxygen containing functional groups such as carboxylic acid, carbonyl, and hydroxyl are able to improve the carbon surface hydrophilic properties or wettability in aqueous media. These oxygenated functional groups can be introduced by chemical oxidative treatment with nitric acid (HNO_3), hydrogen peroxide (H_2O_2), sodium hypochlorite (NaOCl), or iron(III) nitrate ($\text{Fe}(\text{NO}_3)_3$), which consequently improved the electrochemical properties of the carbon materials.

Moreover, physical modification such as functionalization is necessary in order to alter the physicochemical properties of OMC. Functionalization is implied since this process can modify the electrical conductivity and surface chemistry of OMC. To further confirm this situation, electrochemical performance tests were conducted to determine charge storage capability and electrical response. The

functionalization process can be carried out by noncovalent method using nitrogen containing compound, BR2. The noncovalent functionalization of OMC was explained according to equilibrium, kinetic, and thermodynamic studies which were carried out at variable adsorption conditions.

Ordered mesoporous silica (OMS) materials are insulator. They are incapable of conducting any electrical flow resulting from electron transfer in between electrode and electrolyte during electrochemical performance tests. Herein, we consider the ability OMC so that variation of voltage throughout the performance tests can be detected. In addition, the oxidized OMC and BR2 functionalized OMC can be utilized as conductive electrode material by fabricating it onto a current collector which is directly connected to a power source in an electrochemical circuit.

1.3 Research Objectives

The objectives of this research are:

1. To synthesize ordered mesoporous silica hard template, SBA-15 and compare the efficiency of Pluronic P123 surfactant removal by calcination and Soxhlet extraction methods.
2. To synthesize ordered mesoporous carbon (OMC) with structural characteristics similar to SBA-15 hard template by replication strategy.
3. To modify physicochemical properties of the OMC by introduction of oxygen containing functional groups.
4. To modify physicochemical properties of the OMC by introduction of nitrogen containing functional groups through noncovalent functionalization method and study the equilibrium, kinetic, and thermodynamic behaviours of BR2 adsorption in aqueous solution.
5. To explore the electrochemical properties of the original OMC, oxidized OMC (OMC-O), BR2 functionalized OMC (OMC-N), and BR2 functionalized OMC-O (OMC-ON) materials in 1 M KOH electrolyte.

In this study, OMC was prepared by hard template method employing SBA-15 as the template, followed by surface oxidative modification with nitric acid (HNO₃) solution. All OMC and oxidized OMC samples were characterized with respect to their morphological and structural properties and their electrochemical performance was investigated. Then, the original OMC was functionalized with BR2 by noncovalent method to introduce nitrogen containing functional species. Investigation on the functionalization process was clarified based on equilibrium, kinetic, and thermodynamic studies. The main objectives of this study are to identify the fashion and differences in electrochemical performance of OMC, OMC-O, OMC-N, and OMC-ON materials and justify the achievement in accordance to the structural properties as well as surface chemistry.

1.4 Significance of Study

Ordered mesoporous carbon OMC has been selected in this study since it exhibits well-aligned mesopores, high surface area, chemical inertness, thermal stability, and electrical conductivity. Some modifications need to be carried out in order to improve the physicochemical properties of OMC materials. In this study, oxidation and noncovalent nitrogen functionalization methods are investigated. Besides, the large mesopores of OMC permit easier access of the electrochemical active nitrogen containing BR2 molecules to the active sites making the OMC excellent as host. Hence, the prepared OMC materials are employed for electrochemical performance investigation in 1 M KOH aqueous electrolyte. In addition, there is only few literatures on BR2 dye functionalized OMC as a material for electrochemical properties investigation. Due to this, the authors want to explore the contribution of oxidation and noncovalent functionalization methods to the electrochemical capacitive behaviours of OMC since this material has high potential to be commercialized.

1.5 Scope of Study

The overall study including preparation, characterization, and testing for the prepared samples was divided into six sub sections and simplified in Figure 1.1.

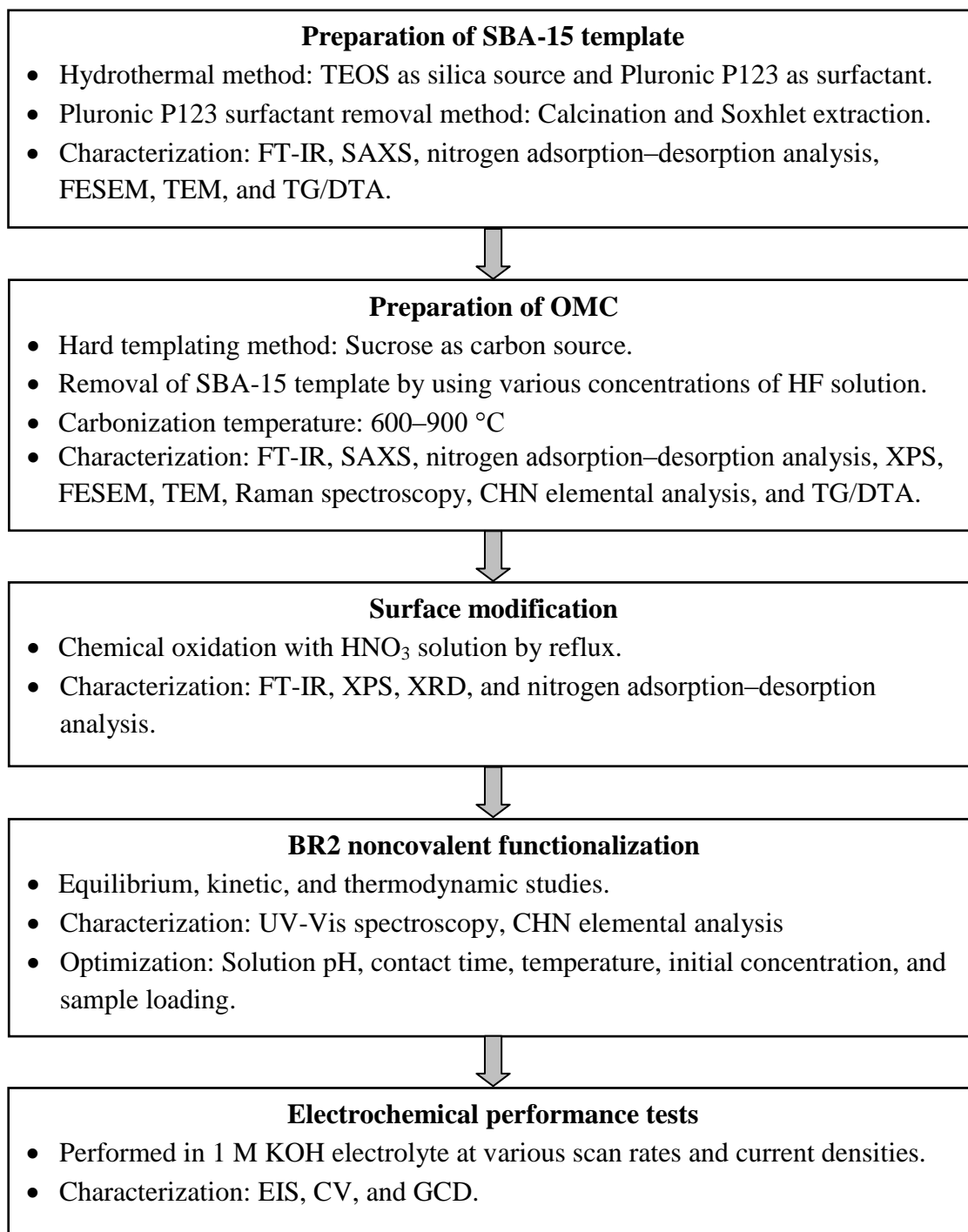


Figure 1.1: Scope division of the study.

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