Advanced Carbon Materials for Environmental and Energy Applications

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EXAMINATION COMMITTEE APPROVALS FORM

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ABSTRACT

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Carbon based materials, including porous carbons and carbon layer composites, are finding increased usage in latest environmental and energy related research. Among porous carbon materials, hierarchical porous carbons with multi-modal porosity are proving out to be an effective solution for applications where the traditional activated carbons fail. Thus, there has been a lot of recent interest in developing low-cost, facile, easy to scale-up, synthesis techniques for producing such multi-modal porous carbons. This dissertation offers two novel synthesis techniques: (i) ice templating integrated with hard templating, and (ii) salt templating coupled with hard templating, for producing such hierarchically porous carbons. The techniques offer tight control and tunability of porosity (macro- meso- and microscale) in terms of both size and extent. The synthesized multi-modal porous carbons are shown to be an effective solution for three important environment related applications – (i) Carbon dioxide capture using amine supported hierarchical porous carbons, (ii) Reduction in irreversible fouling of membranes used for wastewater reuse through a deposition of a layer of hierarchical porous carbons on the membrane surface, (iii) Electrode materials for electrosorptive applications. Finally, because of their tunability, the synthesized multi-modal porous carbons serve as excellent model systems for understanding the effect of different types of porosity on the performance of porous carbons for these applications.
Also, recently, there has been a lot of interest in developing protective layer coatings for preventing photo-corrosion of semiconductor structures (in particular Cu$_2$O) used for photoelectrochemical water splitting. Most of the developed protective strategies to date involve the use of metals or co-catalyst in the protective layer. Thus there is a big need for developing low-cost, facile and easy to scale protective coating strategies. Based on the expertise gained in synthesizing porous carbon materials, and owing to our group’s interest in developing suitable photoelectrode materials, this dissertation also proposes a novel carbon-Cu$_2$O composite comprising of a carbon layer coated Cu$_2$O nanowire array structure as a high performance and stable photoelectrode material for photoelectrochemical water splitting.
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<tr>
<td>BET</td>
<td>Brumauer-Emmett-Teller</td>
</tr>
<tr>
<td>BJH</td>
<td>Barrett-Joyner-Halenda</td>
</tr>
<tr>
<td>CDI</td>
<td>Capacitive deionization</td>
</tr>
<tr>
<td>DBP</td>
<td>Disinfection by-products</td>
</tr>
<tr>
<td>DMA</td>
<td>Dynamic mechanical analysis</td>
</tr>
<tr>
<td>DRS</td>
<td>Diffuse Reflectence Spectra</td>
</tr>
<tr>
<td>EDLC</td>
<td>Electric Double-Layer Capacitance</td>
</tr>
<tr>
<td>EfOM</td>
<td>Effluent organic matter</td>
</tr>
<tr>
<td>EIS</td>
<td>Electrochemical Impedance Spectroscopy</td>
</tr>
<tr>
<td>GCD</td>
<td>Galvanostatic Charge Discharge</td>
</tr>
<tr>
<td>KAUST</td>
<td>King Abdulllah University of Science and Technology</td>
</tr>
<tr>
<td>KCU-C</td>
<td>KAUST Cornell University-Carbons</td>
</tr>
<tr>
<td>LC-OCD</td>
<td>Liquid Chromatography organic carbon detection</td>
</tr>
<tr>
<td>LPM</td>
<td>Low pressure membranes</td>
</tr>
<tr>
<td>LSV</td>
<td>Linear Sweep Voltametry</td>
</tr>
<tr>
<td>MFC</td>
<td>Microbial fuel cell</td>
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<tr>
<td>MPC</td>
<td>Mesoporous carbon</td>
</tr>
<tr>
<td>NOM</td>
<td>Natural organic matter</td>
</tr>
<tr>
<td>NWA</td>
<td>Nanowire Array</td>
</tr>
<tr>
<td>OMP</td>
<td>Organic micropollutant</td>
</tr>
<tr>
<td>PC</td>
<td>Porous Carbon</td>
</tr>
<tr>
<td>PEC</td>
<td>Photoelectrochemical</td>
</tr>
<tr>
<td>PAC</td>
<td>Powder activated carbon</td>
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<tr>
<td>Abbreviation</td>
<td>Full Form</td>
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<tr>
<td>--------------</td>
<td>----------------------------------------------</td>
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<tr>
<td>PCM</td>
<td>Porous carbon material</td>
</tr>
<tr>
<td>PEI</td>
<td>Polyethylenimine</td>
</tr>
<tr>
<td>PTFE</td>
<td>Polytetrafluoroethylene</td>
</tr>
<tr>
<td>$R_{ct}$</td>
<td>Charge transfer resistance</td>
</tr>
<tr>
<td>RHE</td>
<td>Reversible hydrogen electrode</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning electron microscopy</td>
</tr>
<tr>
<td>SPAC</td>
<td>Superground powder activated carbon</td>
</tr>
<tr>
<td>TEM</td>
<td>Transmission electron microscopy</td>
</tr>
<tr>
<td>TMP</td>
<td>Trans-membrane pressure</td>
</tr>
<tr>
<td>UV</td>
<td>Ultra-violet</td>
</tr>
<tr>
<td>WWTP</td>
<td>Wastewater treatment plant</td>
</tr>
<tr>
<td>XPS</td>
<td>X-ray Photoelectron Spectroscopy</td>
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CHAPTER 1. INTRODUCTION

1.1 Background

1.1.1 Porous Carbon Material - Definition

As the name suggests, a porous carbon material (PCM) is a carbon based material with pores. The carbon skeleton in a typical porous carbon is composed of an assembly of randomly distributed defective graphene layers or aromatic sheets, as shown below in Figure 1.1.1 The pores in a PCM are characterized based on their size: pores with size greater than 50 nm are termed as macropores, pores with size between 2-50 nm are termed as mesopores and pores with size less than 2 nm are termed as micropores. Based on the size of pores present in the carbon, the carbons can be termed as either macropore/mesopore/micropore dominated or a combination thereof.

1.1.2 Types of Porous Carbon Materials

A variety of porous carbon materials have been reported in literature ranging from activated carbons, templated carbons, carbon nanotubes, carbon nanofibers, carbon aerogels and combinations thereof. Among them, activated carbon is the most commonly used type of porous carbon material. Activated carbon is produced through either physical or chemical activation, wherein the physical or chemical agent reacts with the carbon precursor, thus generating porosity. Carbon dioxide and steam are the two most
commonly used physical activators. In case of chemical activation, the use of metal hydroxides (such as KOH, NaOH), metal chlorides (such as ZnCl₂, CaCl₂) and hygroscopic acids (such as phosphoric acid) has been proposed. The activation technique works very well for production of micropore dominated carbons. The biggest advantage of activated carbon over other kinds of porous carbon materials is that activated carbon can even be produced from waste biomass precursor, whereas most of the other porous carbons require special kind of high purity, synthetic, soluble or gaseous precursors. It is also important to note that among the various types of porous carbon materials, activated carbon is the most widely tested and commercially used porous carbon material, so much so that activated carbon is considered as the workhorse of the porous carbons.

Figure 1.1: Schematic representation of the structure of a typical porous carbon material (activated carbon)
The second kind of porous carbons comprise of templated carbons, which are produced through the process of templating, where a carbon matrix is grown around a suitable size template, and the subsequent removal of template upon carbonization generates the pores.\textsuperscript{10-13} In general, the preparation procedure of templated carbons is infiltration of a carbon precursor into the pores of the template, followed by a carbonization treatment and finally the removal of the template to leave behind a porous carbon structure.\textsuperscript{14} The schematic representation in Figure 1.2 shows the general concept of the templating technique and the porous carbons obtained from different templates.\textsuperscript{14} A variety of different sized templates (such as inorganic nanoparticles, decomposable polymers, nanoporous inorganic particles) have been explored for producing templated carbons.\textsuperscript{4,9,10} In general, the templating techniques require the use of a soluble carbon precursor and a suitable solvent for operation. Thus templating is an expensive technique as compared to activation. However, the templating technique is more suitable for the production of mesopore, macropore and combined mesopore-macropore dominated carbons as compared to activation.

Carbon nanotube, carbon nanofiber and carbon aerogel represent the remaining major types of porous carbon materials. Carbon nanotubes are generally mesoporous in nature and are electrically conductive. There are mainly two types of carbon nanotubes – single walled and multi-walled carbon nanotubes, as shown in Figure 1.3. On the other hand, carbon nanofibers are cylindrical nanostructures with grapheme layers arranged as stacked cones, cups or plates. Carbon nanofibers are generally produced through either
chemical vapor deposition or electrospinning. Porosity can be introduced in these nanometer diameter fibers through either chemical or physical activation.\textsuperscript{15}

Carbon Aerogels (CAs) represent another class of porous carbon materials that are generally produced using the sol-gel process. CAs generally consist of 3d interconnected carbon nanoparticles as can be seen in Figure 1.5(a). CAs are generally light weight, for example, the carbon aerogel shown in the Figure 1.5(b) has a density of 0.16 milligrams per cubic centimeter, about one-sixth the density of air.

Among the various existing porous carbon materials, this dissertation is aimed at exploring the synthesis and use of dual templated porous carbons. A vast body of literature already exists dealing with activated carbon and its use in environmental and energy applications. On the other hand, carbon nanotubes, carbon nanofibers and carbon aerogels do not have as high surface area as activated or templated carbons, thus limiting their use in applications requiring high surface areas, in addition to their high cost of production. Moreover, the application of templated carbons (which are generally mesopore dominated as compared to activated carbons which are generally micropore dominated) in environmental research is a relatively less explored field.
Figure 1.2: (a) Macroscopic representation showing the general concept of the templating technique; microscopic synthesis of (b) macroporous carbons using silica spheres as template, (c) mesoporous carbons using SBA-15 as template and (d) microporous carbons using zeolite Y as template. Reproduced ("Adapted") from\textsuperscript{14} with permission of The Royal Society of Chemistry.
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1.1.3 Use of carbon materials in environmental and energy applications

Carbon materials, in particular, porous carbons have been studied and used extensively for several environmental and energy applications such as water purification,\(^8\) CO\(_2\) capture,\(^9,10\) electrode materials for capacitive deionization, supercapacitors, batteries,\(^11,12\) electrode materials for microbial fuel cell for waste water treatment,\(^13,14\) and so on. It is important to note that these different applications require different pore sized carbons. For example, for organic micropollutant (OMP) removal from water, micropore dominated carbons are preferred. This is because sorbates sorb preferentially in pores having diameter similar to the size of the molecule.\(^15\) Since the predominantly encountered organic compounds in water are small molecular weight compounds close to sub-nanometer size range, they sorb preferentially in micropores and thus micropore dominated carbons are preferred for organic micropollutant removal. Also in the case of direct CO\(_2\) capture using porous carbons, the presence of micropores plays
a critical role as it provides high surface area and sites for the sorption of small CO₂ gas molecules. On the other hand, in the water industry, the use of porous carbons as a pre-treatment step before membrane filtration could benefit from the use of mesopore/macropore dominated carbons. This is because most of the identified foulants present in wastewater and/or surface water, have size ranging from 3-100nm. Thus, based on size exclusion phenomenon, only mesopores and macropores are accessible to such foulants. Even OMP removal in presence of natural organic matter is higher in case of mesoporous carbons. Also there are applications of carbon materials such as anode materials for microbial fuel cells which require the use of macropore dominated carbons. A suitable anode material for MFC should provide sites for growth of micrometer sized microbes and thus requires the presence of micrometer sized macropores.

A lot of above mentioned and other applications also benefit from the presence of a hierarchical porous structure or the presence of all the three kinds of pores. The presence of mesopores and macropores provide pathways for fast transport and the micropores provide sites for sorption. For example, for OMP removal from water, the presence of such meso and macro pores could ensure fast kinetics where as the presence of micropores would ensure high sorption capacity. Similarly, the use of porous carbons as electrode materials for capacitive deionization (CDI) also benefits from the presence of all three kinds of pores. For CDI, the micropores provide sites for ion sorption where as macro and mesopores provide pathways for fast ionic transport. Thus there is a lot of
interest and effort devoted to developing porous carbons with varying degrees of porosity, especially multi-modal or hierarchically porous carbons.\textsuperscript{4,10}

\textbf{1.1.4 Carbon layer coated nanostructures}\\

Recently, a lot of applications of carbon composite materials, in particular involving carbon based coating or layer on an inorganic nanostructured material, have also been reported for various environmental and energy applications.\textsuperscript{35-39} In particular, there is a lot of interest in developing permanent carbon layer coatings atop metal oxide nanostructures to either (i) enhance their electrical conductivity, or (ii) provide stability during operation, or (iii) provide unique chemical properties, or (iv) maintain nanostructure integrity.\textsuperscript{35-39} Similarly, recently, there has been a lot of interest in developing protective layer coatings for preventing photo-corrosion of semiconductor structures (in particular Cu\textsubscript{2}O) used for photoelectrochemical water splitting.\textsuperscript{40-44} Our group also previously reported an \textit{in situ} Cu\textsubscript{2}O protection strategy with CuO film as a protective layer.\textsuperscript{45} However, all of the above reported protective strategies involve the use of metals or co-catalyst in the protective layer. Thus there is an urgent need for developing low-cost, easy to scale, stable, metal/co-catalyst free, protective coating strategies for Cu\textsubscript{2}O based photoelectrodes.
1.2 Objective of the dissertation work

This dissertation has two major goals. The first is aimed at developing new synthesis techniques for producing porous carbons with tailor made porosity as required by the specific environmental application of interest. The applications chosen are currently explored fields of environmental research of global relevance, in line with KAUST’s research agenda. The goal is to make some useful contribution to the vast field of porous carbon synthesis and to the selected applications. The following applications have been selected, involving the use of:

a) Macropore-mesopore dominated carbons as support materials for amine based CO$_2$ capture, described in detail in chapter 2.

b) Macropore-mesopore dominated carbons for membrane fouling abatement of low pressure membranes used for pre-treatment of secondary wastewater effluent, described in detail in chapter 3.

c) Mesopore-micropore dominated carbons as electrode materials for capacitive deionization (CDI), described in detail in chapter 4.

The second objective of this dissertation work is related to our group’s interest in developing protective coating layer for photoelectrochemical electrode materials, in particular, exploring the effectiveness of a carbon layer protective coating for nanostructured cuprous oxide based photoelectrodes for water splitting, described in detail in chapter 5.
1.3 Organization of the dissertation

The dissertation is divided into four different chapters based on the respective research articles that have either been published or are currently under review/revision. Each chapter presents:

i) Literature review and objectives related to the particular application of interest

ii) Extensive literature review and objectives related to the material synthesis

iii) A novel synthesis technique for producing the material

iv) Material characterization results for the synthesized material

v) Application performance results for the synthesized material and compares it with either commercially available materials or previously reported best performing materials reported in literature.

In particular, chapter 2 describes a novel strategy - ice templating coupled with hard templating and physical activation, to synthesize hierarchical porous carbons (HPC) with porosity at all different length scales (macro- meso- and micro). The technique uses green chemistry, is sustainable and scalable, and even allows for the fabrication of monolithic structures with high surface area, pore volumes and pore size tunability at all three length scales. The HPCs are also shown to function well as amine impregnated supports for CO₂ capture.

In chapter 3, dual-templated hierarchical porous carbons (HPCs), produced from a coupled ice-hard templating approach (described in chapter 2), are shown to be a highly
effective solution to the commonly occurring problem of irreversible fouling of low-pressure membranes used for pre-treatment in wastewater reuse. Dual-templated HPCs, along with their respective counterparts - single-templated meso-porous carbon (MPCs) (without macropores) - are tested in terms of their fouling reduction capacity and ability to remove different effluent organic matter fractions present in wastewater and compared with a commercially available powdered activated carbon (PAC). Also, the effects of presence and extent of both macroporosity and mesoporosity in the porous carbon material on its fouling reduction ability is probed in detail.

In chapter 4, a low energy intensity, single-step, one-pot, combined hard-salt templating synthesis approach is proposed for synthesizing multi-modal porous (mesopore-micropore dominated) carbons. The superior flexibility of the proposed synthesis technique is also demonstrated by carrying out example synthesis involving (i) use of multiple salt templates resulting in the synthesis of metal nanoparticle embedded high surface area multi-modal carbons, (ii) use of multiple hard templates resulting in tri-modal carbons, (iii) low temperature (450 °C) carbonization afforded by the presence of Lewis acid salt (such as ZnCl₂), (iv) one step combined salt templating-hard templating-physical activation. The synthesized multi-modal carbons are used as electrode materials for capacitive deionization. The effect of electrode fabrication configuration on its electrosorption performance is also reported.

In chapter 5, a solution-based carbon precursor coating and subsequent carbonization strategy is proposed to form a thin protective carbon layer on unstable
semiconductor nanostructures as a solution to commonly occurring photo-corrosion problem of many semiconductors. A proof of concept is provided by using glucose as carbon precursor to form protective carbon coating onto cuprous oxide “Cu₂O” nanowire arrays which were synthesized from copper mesh. The carbon layer protected Cu₂O nanowire arrays exhibited remarkably improved photostability as well as considerably enhanced photocurrent density. The facile strategy presented in this chapter is a general approach that can address the stability issue of many non-stable photoelectrodes, and thus has the potential to make a meaningful contribution in the general field of energy conversion.
CHAPTER 2. A FACILE APPROACH FOR THE SYNTHESIS OF
MONOLITHIC HIERARCHICAL POROUS CARBONS - HIGH
PERFORMANCE MATERIALS FOR AMINE BASED CO$_2$ CAPTURE

(Paper published in Energy and Environmental Science)$^{46}$

2.1 Introduction

Recently, hierarchical porous carbons (HPCs) possessing well-defined macropores and interconnected meso- and micropores, have attracted much attention.$^{47-64}$ HPCs can combine in one system: improved mass transport facilitated by the macropores and high surface area and pore volume from micro-/mesopores.$^{29-32}$ Such hierarchically porous carbons provide better accessibility and active sites for several energy and environmental applications including electrode materials for batteries,$^{31,55}$ supercapacitors,$^{29,30,59,65,66}$ fuel cells,$^{67,68}$ and capacitive deionization,$^{33,69}$ as well as sorbents for CO$_2$ capture.$^{52}$

A large number of techniques have been explored for the synthesis of HPCs.$^{11,12}$ In general, most of the techniques for producing carbons combining macro- and mesoporosity are based on a dual templating strategy, where two templates with dimensions at different length scales are combined to generate the multimodal pores. These techniques either involve two hard templates$^{70,71}$ or a combination of hard and soft templates.$^{72,73}$ Removal of the templates, either through decomposition or etching leaves behind a porous scaffold. Other techniques involve template replication of hierarchical
inorganic materials,\textsuperscript{74,75} with hierarchical silica being the most commonly used template. The sol-gel method is another widely used technique for the production of hierarchical carbon, commonly termed as either carbon aerogels\textsuperscript{12,16} or carbon cryogels.\textsuperscript{76,77} Ice templating has been also explored for assembling micropore-mesopore dominated carbon materials, such as CNTs, into 3D interconnected hierarchical carbon materials.\textsuperscript{68,78}

A major challenge to date has been the development of HPCs, which can exhibit high surface areas, pore volumes and porosities at all three different length scales: macro-, meso-, and micro, in a simple material platform. Additional challenges with the synthesis techniques include the requirement to synthesize porous inorganic materials or special nanoparticles as hard templates, which involve multiple steps and are thus time consuming and costly. Furthermore, most of the soft templates used are based on surfactants and block-copolymers, which are rather expensive and non renewable.\textsuperscript{11} Moreover, the size of the mesopores can also be difficult to tune because of aggregation of the nanoparticles in the polymerizing carbon precursor matrix.\textsuperscript{79} In addition, techniques like sol-gel suffer from the critical drawback associated with the long synthesis period required for gelation, solvent exchange and supercritical drying in the case of aerogels.\textsuperscript{12}

Here we demonstrate a novel strategy to synthesize HPCs with high surface areas, large pore volumes (up to 2096 m\textsuperscript{2} g\textsuperscript{-1} and 11.4 cm\textsuperscript{3} g\textsuperscript{-1}, respectively), and more importantly, tunable micro/meso/macro porosities. Our approach is based on combining, ice templating alongside a hard template (colloidal silica), and physical activation for
generating interconnected macro-, meso-, and microporosity, respectively. We also demonstrate that the newly developed HPCs are promising candidates for amine supported sorbents for CO₂ capture. This new, simple, and inexpensive technique provides a suitable platform for producing state of the art HPCs for these applications and beyond. In addition, because of their easy tunability, the new HPCs provide excellent model systems to understand the effect of different types of porosity (e.g. macro, meso and micro) on their performance in a series of applications.

Ice templating \(^{80,81}\) has been used previously to synthesize macroporous \(^{82}\) and even hierarchical materials \(^{83,84}\) due to its simplicity and versatility. However this is the first time ice-templating has been used to synthesize HPCs with tunable porosity by combining it with hard templating and physical activation. Our approach offers several key additional advantages: 1) the range, size and extent of porosity can be easily controlled. For example, the distribution of the mesopores and the extent of mesoporosity can be simply tuned by either using silica of different size or varying the silica to carbon precursor weight ratio. The excellent control of the mesopore size distribution (vide infra) alleviates the need of using costly surfactants, \(^{79}\) fast stirring speeds and/or dilute carbon precursor concentrations. \(^{85}\) In addition, as has been shown in literature, \(^{86,87}\) the macropore size and structure can be controlled by controlling the dipping rate (of the colloidal silica-glucose mixture in liquid nitrogen), concentration of carbon precursor, concentration and size of colloidal particle and by other established techniques. Furthermore the activation reaction conditions can control the microporosity. 2) the synthesis is simple, reproducible, greener, and uses inexpensive and widely available starting materials (water/ice for
macropores, silica for mesopores, CO₂ for micropores), all of which make the process highly scalable.

2.2 Materials and Methods

2.2.1 Materials employed

Commercially available colloidal silica suspensions in water with different average size silica: 4 nm (15 wt%, Alfa Aesar) 8 nm (LUDOX SM-30, 30 wt%, Sigma Aldrich), 12 nm (LUDOX HS-30, 30 wt%) 20 nm (40 wt%, Alfa Aesar) were used as received. The carbon precursor was D-(+)-Glucose, ACS reagent grade, purchased from Sigma Aldrich.

2.2.2 Material Synthesis

In a typical synthesis, 10 g of a 15 wt% suspension of 4 nm colloidal silica and 1.5 g of glucose D is added to a 50 mL centrifuge tube and mixed well. Next the centrifuge tube (uncapped) is plunged into liquid nitrogen. Once the ice front (traveling radially from outside in) meets at the center of the suspension, the whole tube is submerged in the liquid nitrogen bath. The frozen sample is then subjected to freeze drying until the sample is completely dry. The freeze-dried glucose-silica composite is then pyrolyzed at 1000 °C at a ramp rate of 3 °C/min for a dwell time of 3 h under a nitrogen or argon environment, resulting in a carbon-silica composite. This carbon-silica composite is then placed in a 3M NaOH solution at 80 °C overnight under medium stirring to etch out the silica. The sample is finally washed with copious amounts of
deionized water and dried at 80 ºC for at least 12 hours before use. For convenience the
samples are denoted by KCU-C x-y, where KCU-C stands for KAUST Cornell
University-Carbons, x represents the average colloidal silica size (nm) and y represents
the ratio of silica to glucose (by weight) in the original suspension. To introduce
significant microporosity, CO₂ activation is used. Specifically for the CO₂ activation, the
sample (after silica etching) is heated first under an inert atmosphere up to a temperature
of 950 ºC, whereupon the inert gas is replaced by CO₂ at a flow rate of 50 cc/min. The
time for activation varies from 1 – 4 h. CO₂ activated samples are denoted by KCU-C x-
y-z, where z represents the time (h) for CO₂ activation.

2.2.3 Sorbent preparation for amine based CO₂ capture

Polyethylenimine (PEI) (average M₆ ~800, from Sigma Aldrich) was mixed with
absolute methanol to obtain a 20 wt% solution. The sorbents were prepared by adding a
fixed amount of this 20 wt% solution to 25 mg of KCU-C 4-3. The mixture was then
sonicated and kept under 70 mbar at 40 ºC for at least 12h. The CO₂ sorption
measurement was performed using a TA Instruments Q500 thermal graphic analyzer.
Sorption tests were performed with 1atm of dry CO₂. For the sorption tests, 5-10 mg of
the PEI-carbon composite was placed in a platinum pan, heated to 100 ºC @ 10 K/min
under N₂ (40 ml/min flow rate) and held at 100 ºC for 40 min to remove any moisture and
CO₂ sorbed from air. The sorbent was then cooled to 75 ºC @ 10 K/min and the gas was
switched over to CO₂ and held at 75 ºC for 45 min. The CO₂ capacity of the sorbents (in
mmol g⁻¹) was calculated based on the weight gain of the sorbent during the adsorption.
Tests were also conducted with 10% CO₂-90% N₂, under dry and moist (by passing the gas through a water bubbler maintained at room temperature) conditions.

2.2.4 Characterization Methods

**Scanning Electron Microscopy (SEM)**

The microstructure of the samples was investigated by a LEO 1550 FESEM operating between 2-20 keV. SEM sample preparation involved polishing the sample’s surface by a cryo-microtome (Leica EM FC7). The sample was placed in the microtome’s cryo-chamber, which was kept at a temperature below -80 °C to ensure sufficient stiffness. Then using a diamond knife Trimming tool (Diatome Cryotrim 45), progressively thinner slices of material were removed starting from a thickness of 5 microns until reaching a final polishing thickness of 30-50 nm. This approach allowed the sample to be examined at various depths.

**Transmission Electron Microscopy (TEM)**

TEM images were obtained using an FEI T12 Spirit TEM/STEM. The T12 is a 120 kV field emission TEM, equipped with a LaB₆ filament and an SIS Megaview II CCD camera. The sample was grounded and then added into a vial with ethanol. The sample was then sonicated and physically mixed by shaking the vial. After roughly 45 s, with the larger particles settling to the bottom of the vial, the top of the vial was pipetted out and placed on a carbon coated copper TEM grid.
Dynamic Mechanical Analysis (DMA)

Compression measurements were carried out using a TA Instruments DMA Q800 Dynamic Thermal Mechanical Analyzer. Cylindrical samples (all approximately 8 mm in diameter and 10 mm in length) were preloaded at 0.001 N. Stress-strain measurements were taken at a compression rate of 0.5 N/min until a maximum force of 18 N was reached. Measurements were taken at ambient temperature and pressure.

Mercury porosimetry

Monolithic samples were analyzed using mercury intrusion via a Micromeritics AutoPore IV (9500 Series) porosimeter. The cylindrical monolith samples were cut in half (axially) to fit into the penetrometer sample holder. Care was taken to analyze the data up to a pressure of 3617.27 psia, ensuring that pores with size below 50 nm were not analyzed. The apparent density was calculated by the AutoPore IV by measuring the volume of the sample at 0.60 psia and using the weight measured by the operator.

N$_2$ sorption

Nitrogen adsorption-desorption tests were carried out at 77K using a Micromeritics ASAP 2020 analyzer. Prior to gas adsorption measurement, the samples were degassed at 180 °C under vacuum for at least 12 hours. The specific surface area was calculated using the Brumauer-Emmett-Teller (BET) method. The pore volume was estimated from single point adsorption at a relative pressure of 0.994. The pore diameter was determined from the adsorption branch, according to the Barrett-Joyner-Halanda (BJH) method.
2.3 Results and Discussion

Figure 2.1 shows a graphical representation of the synthesis technique. The solidification of water, as a result of plunging the mixture into the liquid nitrogen, expels both the silica particles and glucose molecules away from the growing ice crystals. The ice is then simply removed by sublimation. Care must be taken during the freeze drying process to prevent the ice templated glucose-silica material from melting. The glucose-silica composite scaffold (shown in Figure A.1) is then carbonized, resulting in a macroporous carbon-silica structure. The network of interconnected macropores formed after sublimation (Figure A.1(a)) remains intact during pyrolysis and after silica etching (Figure A.1(b)). Figure 2.2 (a,c,d) shows the SEM images of the resultant HPC material after the silica etching using NaOH. The SEM images are consistent with an HPC scaffold whose macroporous walls are made up of an interconnected mesoporous carbon. This is further confirmed by TEM images (Figure 2.2 (e-f) and Figure A.2) that reveal an extensive network of mesopores. The mesopores seen in the TEM images are in good agreement with the N$_2$ adsorption data (vide infra).

The surface area and pore volume of the macropores measured by mercury porosimetry are 11 m$^2$ g$^{-1}$ and 9.1 cm$^3$ g$^{-1}$ respectively for the KCU-C 4-1 sample. Care was taken to vary the pressure applied under mercury porosimetry so that any pores under 50 nm were not analyzed and incorporated into the results. The macropore size distribution obtained via mercury porosimetry measurements (Figure 2.3) is in good agreement with those seen in SEM images in Figure 2.2. These results are consistent with
expectations from previous work\textsuperscript{82} that within the range of colloidal silica nanoparticles used, macroporosity is controlled mostly by the speed of ice formation (i.e. freezing speed).

\textbf{Figure 2.1:} Schematic showing the basic steps and the material thus produced after each step. The four steps shown clockwise from bottom left are: 1) (side view) Ice templating - ice front movement through the glucose and colloidal silica aqueous suspension forming ice crystals, 2) (top view) Freeze drying - the glucose-silica composite material with macropores after removal of ice, 3) (top view) Carbonization and silica etching - Macromesopore dominated carbon and finally, 4) (top view) Physical activation - Hierarchical carbon. Note: for simplification, the pores are not shown as interconnected. For convenience the samples are denoted by KCU-C \(x\)-\(y\)-\(z\), where \(x\) represents the average colloidal silica size (nm), \(y\) represents the mass ratio of silica to glucose and \(z\) represents the time (h) for CO\(_2\) activation.
Figure 2.2: (a-d) SEM images of HPC scaffolds. Images show: (a) the monolithic character of the HPCs, (b) the interconnected macroporous structure evident before etching of the colloidal silica and (c) a similar interconnected macroporous structure after etching. (d) Higher resolution SEM shows a roughened morphology consistent with mesopores. Representative TEM images of e) KCU-C 12-1 f) KCU-C 12-2 (scale bars for TEM images are 200 nm for the larger images and 20 nm for the inset images)
Figure 2.3: Pore size distribution via mercury porosimetry for the KCU-C 4-1 monolith sample. The pore size distribution shows macropores present mostly in the range from 3-12 microns. Some larger (above 15 μm) macropores are present, but to a relatively small degree. The analysis reveals the monoliths have a porosity of 83% and a bulk density of 0.09 g/mL (at 0.60 psia).

The total BET surface area and pore volume (excluding macropores) for a series of samples is summarized in Table 2.1. It is important to note that these pore volumes, calculated from N₂ sorption, for the KCU-C x-2 samples (from 3.0 - 4.1 cm³ g⁻¹) are among the highest values measured for mesoporous carbon materials.³⁸,³⁹ In contrast to macroporosity, the silica to glucose ratio and the size of silica affects the mesoporosity. For HPCs synthesized using silica to glucose ratio of 1, the surface area and pore volume decrease as the silica particle size increases. No such dependence is seen for the silica to glucose ratio of 2, where the surface area is generally the same regardless of silica size. For a given silica particle size, the surface area and the pore volume increase as the silica to glucose ratio increases from 1 to 2. The percent increase in surface area is much more pronounced for the 12 and 20 nm silica particles (the increase for all particle sizes are 1,
11, 36 and 53% for the 4, 8, 12 and 20 nm silica, respectively). The specific surface area and extent of microporosity can be further increased by CO$_2$ activation. Under CO$_2$ activation, the duration and flow rate of CO$_2$ are important factors in determining the increase in microporosity and surface area. CO$_2$ activation was performed on the KCU-C 4-1 sample, for different time holds at 950 °C, at a constant CO$_2$ flow rate of 50 cm$^3$ min$^{-1}$. 3-4 hours of activation time was found to be optimal. The thus synthesized KCU-C 4-1-4 sample had a BET surface area of 2096 m$^2$ g$^{-1}$ and pore volume of 3.0 cm$^3$ g$^{-1}$, comprising of increased microporous content and broadened mesoporosity (see Figure A.3).

Table 2.1: Textural characteristics of the synthesized carbons

<table>
<thead>
<tr>
<th>Sample name</th>
<th>BET surface area (m$^2$/g)</th>
<th>N$_2$ adsorption pore volume (cm$^3$/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>KCU-C 4-1-4</td>
<td>2096</td>
<td>3.0</td>
</tr>
<tr>
<td>KCU-C 4-1</td>
<td>1316</td>
<td>2.3</td>
</tr>
<tr>
<td>KCU-C 4-2</td>
<td>1327</td>
<td>4.1</td>
</tr>
<tr>
<td>KCU-C 8-1</td>
<td>1129</td>
<td>2.0</td>
</tr>
<tr>
<td>KCU-C 8-2</td>
<td>1265</td>
<td>3.6</td>
</tr>
<tr>
<td>KCU-C 12-1</td>
<td>893</td>
<td>1.9</td>
</tr>
<tr>
<td>KCU-C 12-2</td>
<td>1216</td>
<td>3.0</td>
</tr>
<tr>
<td>KCU-C 20-1</td>
<td>841</td>
<td>1.9</td>
</tr>
<tr>
<td>KCU-C 20-2</td>
<td>1289</td>
<td>3.7</td>
</tr>
</tbody>
</table>

A distinct advantage of our approach is the ability to easily control the pore sizes. For example, the size of the mesopores can be easily tuned by using different size silica particles. Figure 2.5 shows the pore size distribution calculated using the BJH model for a series of HPCs, synthesized using different size silica nanoparticles (4, 8, 12 and 20 nm).
In the past, special efforts were devoted to ensure that the pore size of the resulting carbons is the same as the size of the starting template.\textsuperscript{79,85} Such efforts typically focused on preventing aggregation of the hydrophilic silica nanoparticles within the pyrolyzing (and becoming increasingly hydrophobic) carbon precursor matrix. In our approach, the instantaneous locking of the silica nanoparticles within the glucose matrix and subsequent carbonization minimize such aggregation and phase separation. Note the high fidelity of the process in generating mesopores especially for the 1:1 ratio of silica to glucose; the size of the resulting mesopores corresponds well with the size of the silica nanoparticles used in the process (Figure 2.5). This fidelity holds true for the 20 nm silica particles even for SiO\textsubscript{2}/glucose ratio of 2. However at this higher silica/glucose ratio of 2, as the particle size decreases, aggregation of the particles during freezing leads to larger pore sizes and this is especially true for the 4 nm silica particles. Note that as the number of silica nanoparticles (relative to the glucose) increases, the amount of glucose present between the nanoparticles decreases, resulting in aggregation at higher ratios.
Figure 2.4: Nitrogen sorption isotherms for the KCU-C samples. The curves for KCU-C 8-y, KCU-C 12-y, KCU-C 20-y are offset vertically by 1500, 3000, 4500 cm$^3$/g respectively.
Figure 2.5: BJH pore size distributions for the KCU-C x-y samples. The BJH pore size distributions of the activated HPCs can be found in the appendix (Figure A.3).

Our approach also offers the possibility to easily make HPCs with bimodal mesoporosity distribution, by merely starting with two different sized silica nanoparticles. The bimodal nature of the mesoporosity can be clearly seen, in the pore size distribution shown in Figure 2.6, for the sample synthesized using 4 nm and 20 nm silica.

Another advantage of this approach is the flexibility it offers to produce carbon scaffolds either in powder form or as monoliths of desired shape and size, just by altering the mold used (see Figure 2.7). SEM imaging and adsorption measurements confirm that the monoliths possess surface area, specific pore volume and pore size distribution...
similar to the powder samples. The apparent density of the cylindrical monoliths was found to be approximately 0.09 g cm\(^{-3}\), by measuring the bulk samples’ weight and apparent volume, and was confirmed via Hg porosimetry. The modulus of the monoliths evaluated using compression testing was \(\sim 1\) MPa, consistent with other porous carbon materials.\(^{90}\) Figure 2.8 below shows a typical compressive stress/strain plot. In general, the stress/strain curves exhibit a behavior typical of porous cellular solids. At small strains the material behaves elastically and the slope of the curve equals the compressive modulus of the porous material. At higher strains the material collapses in brittle failure until it reaches to a maximum compact state, where the stress starts to increase sharply.
Figure 2.6: (a) N\textsubscript{2} sorption isotherm and (b) BJH pore size distribution for a KCU-C synthesized using both 4 and 20 nm sized colloidal silica (as specified by the manufacturer). The sample was prepared using equal parts (by weight) of each colloidal silica and adding glucose to the suspension until the glucose to the combined silica weight ratio was 1:1. The sample has a BET surface area of 1025 m\textsuperscript{2}/g and a mesopore volume of 2.4 cm\textsuperscript{3}/g. (c) TEM image of the bimodal HPC sample with a bimodal pore size distribution consistent with the peaks seen in b (8 and 20 nm). Inset image is a higher resolution TEM image.
Figure 2.7: Photographic images of: (a) the brass mold employed to fabricate monolithic cylindrical samples with (b) a KCU-C 4-1 monolith shown in the mold before carbonization. The finished cylindrical monoliths (c, d) were approximately 8 mm in diameter and 10 mm in length after being pyrolyzed. The monoliths (e) are shown as they were measured under nitrogen sorption.

Figure 2.8: Stress strain curve representative of KCU-C 4-1 cylindrical monoliths. The modulus was obtained by measuring the slope of the curve before the collapse of the material under brittle failure.
Lately there has been much interest in developing multi-modal (macropore and mesopore dominated) support materials (metal oxides) for amine based CO$_2$ capture. However, the synthesis of most of such porous metal oxide based sorbents involve the use of costly non renewable chemicals such as surfactants or pore expanders, which limits their use for large scale CO$_2$ capture. Our HPCs with their inherent high pore volumes and specifically, the samples with large pore sizes appear to be excellent alternative candidates for amine based CO$_2$ capture. Thus, a KCU-C 4-3 sample, with ultralarge mesopores of ~50 nm, was synthesized (Figure 2.9), impregnated with polyethyleneimine (PEI), achieving a PEI loading of 73 wt% and its CO$_2$ capture capacity was briefly evaluated. As shown in Figure 2.10, a sharp weight gain was observed after the sorbent was exposed to CO$_2$ in the first 5 min and 97% of the adsorption (4.1 mmol g$^{-1}$) was obtained after 10 min. A capacity of up to 4.2 mmol g$^{-1}$ was achieved after 45 min.

Figure 2.9: (a) N$_2$ sorption isotherm and (b) BJH pore size distribution for KCU-C 4-3 synthesized using 4nm colloidal silica and silica/glucose ratio of 3. The sample has a BET surface area of 760 m$^2$/g and a mesopore volume of 3.6 cm$^3$/g. KCU-C 4-3 sample was impregnated with amine and used for CO$_2$ capture.
Figure 2.10: CO$_2$ sorption capacity of PEI-KCU-C 4-3 (73 wt% PEI) composite.

which is among the highest reported value for amine-impregnated carbon-based sorbents.$^{94}$ More importantly, for dilute CO$_2$ (10% CO$_2$-90% N$_2$ gas mixture), the sorption capacity measured under dry and moist conditions was the same, unlike physisorption of moist dilute CO$_2$ in microporous carbons, which is severely effected by the presence of moisture.$^{20}$

### 2.4 Conclusion

In summary, this chapter described a novel approach to synthesize HPCs, which combine macro-, meso- and microporosity in a simple material platform. The approach integrates ice templating with hard templating and physical activation to produce HPCs with interconnected porous structure, large surface area, and pore volume. The technique offers tight control and tunability of porosity (macro- meso- and microscale) in terms of both size and extent. It also offers the ability to make HPC monoliths of desired shape
and size. The hierarchical carbons show excellent performance as sorbents for amine based CO$_2$ capture.
CHAPTER 3. IRREVERSIBLE MEMBRANE FOULING ABATEMENT
THROUGH PRE-DEPOSITED LAYER OF HIERARCHICAL POROUS
CARBONS

(Manuscript submitted to Water Research)\textsuperscript{95}

3.1 Introduction

In the past few years, considerable effort has been devoted to understanding and
addressing the problem of fouling of low-pressure membranes (LPMs) used for pre-
treatment in drinking water treatment and wastewater reuse.\textsuperscript{96-101} Natural organic matter
(NOM),\textsuperscript{27,102,103} in the case of surface water and effluent organic matter (EfOM),\textsuperscript{103-105} in
the case of waste water, are considered to be the major foulants of LPMs. Among the
various components comprising the natural organic matter, small organic colloids,
ranging from about 3-20 nm in diameter, have been demonstrated to be the important
membrane foulants in the case of surface waters.\textsuperscript{27} On the other hand, in the case of
EfOM, organic colloids, polysaccharides, and proteins with sizes in the range of 10 to
100 nm were shown to be the major foulants.\textsuperscript{104} Among the various colloidal organic
matter components, biopolymers have been characterized as the major, irreversible, LPM
membrane foulant based on liquid chromatography with on-line organic carbon detection
(LC-OCD).\textsuperscript{106-112}

Many pre-treatment methods such as coagulation,\textsuperscript{113-115} biological filtration,\textsuperscript{116,117}
ion exchange,\textsuperscript{115,118} adsorption using porous carbon material (PCM)\textsuperscript{119-121} or metal oxide
particles,\textsuperscript{122-124} and oxidation with ozone,\textsuperscript{125} as well as modifying membrane
surface,\textsuperscript{126,127} and combinations thereof,\textsuperscript{115,128} have been investigated for reducing organic fouling of membranes. Among these, adsorption using PCM is of great interest because PCM, in addition to removing the foulant organic matter fraction, can also remove precursors for the formation of disinfection by-products (DBPs) as well as synthetic organic compounds.\textsuperscript{121} Some studies have indicated that the addition of PCM can increase membrane flux and enhance organic removal but other studies have suggested otherwise.\textsuperscript{121,129-131} Most of the studies involving the successful use of PCM in removing NOM, and thus mitigating membrane fouling, involve use of sub-micron powder activated carbon (PAC) particles.\textsuperscript{120,132-134} Pre-deposited, crushed PAC particles with a mean size \textasciitilde1 \textmu m were reported to give excellent fouling reduction as compared to non-crushed PAC particles which gave a similar trans-membrane pressure (TMP) profile as the membrane alone.\textsuperscript{134}

On the other hand, hardly any studies have been reported on the use of templated carbons for addressing the membrane fouling issue. Moreover, the effect of PCM’s porosity on EfOM removal and its corresponding effect on reducing membrane fouling has not been explored. Since it has been previously established that the organic matter fraction that causes fouling of LPMs has size larger than 3nm,\textsuperscript{27,104} mesopore dominated (2-50 nm) or mesopore-macropore dominated (>2 nm) hierarchical carbons should thus be the obvious material of choice for removing such organic matter components instead of the micropore dominated PCMs. However, to the best of our knowledge, no study has ever been reported on the use of any templated or hierarchically porous carbon for preventing fouling of LPMs. Only studies involving powder activated carbons, which
pre-dominantly consist of small micropores ($< 2$ nm) that dramatically limit their capability for the removal of large-sized molecules,$^{135-137}$ have been reported so far and that too with conflicting findings.$^{121,129-131}$ Although lack of mesoporosity has been reported as one of the reasons for the poor performance of PCMs in reducing membrane fouling,$^{131}$ no systematic study probing the effects of the presence and extent of mesoporosity in PCMs on their ability to prevent membrane fouling has been reported yet. Only one non-carbonized polymeric mesoporous adsorbent (polysulfone colloids with pore size $\sim 25$ nm) has been reported for reducing membrane fouling.$^{138,139}$ Similarly, the effect of the presence or absence of macroporosity in PCMs on membrane fouling abatement, has not been investigated at all.

Over the past few years, a large number of dual templating strategies have been reported for the synthesis of hierarchical (mesopore-macropore dominated) carbons.$^{11,12,46,70-72,75,140-144}$ Such techniques involve the use of soft templates (such as surfactant, block co-polymers) and/or hard templates (such as colloidal silica, colloidal polymers), where two templates with dimensions at two different length scales are used together to generate macropores and mesopores. Recently, our group developed a combination of ice and hard templating for producing such hierarchical porous carbons (HPCs),$^{46}$ as described in chapter 2. The technique involves freeze casting of an aqueous solution of colloidal silica and glucose. The removal of ice template upon freeze drying generates macropores and the removal of hard template (colloidal silica) through NaOH etching generates mesopores.
In this study, first of all, a successful application of the synthesized dual templated hierarchical porous carbons (HPCs) is reported for reducing fouling of LPMs. Secondly, to explore the effects of different types of porosities in PCMs - mesoporosity and macroporosity - on irreversible fouling abatement, a set of four different carbons with varying types and levels of pore size distributions were synthesized. Two HPCs, having similar size macropores, but different size mesopore peaks, were synthesized to explore the effect of mesoporosity. Also, two more carbons having similar mesoporosity as the first two, but without macroporosity (synthesized using hard templating alone, without ice-templating) were also synthesized to test the favorable or unfavorable effect of presence of macropores. It is important to note that the differences in fouling mitigation performance of synthesized carbons can be safely assigned to differences in their respective porosities, as all the carbons were synthesized using the same precursor, same template and same synthesis protocol and thus have similar surface chemistry. A commercial PAC, Norit SA-Super, previously shown to be the best performing carbon for biopolymer removal,\textsuperscript{119} was also tested for comparison purposes.

Recently, pre-deposition of adsorbent particles on a membrane surface\textsuperscript{145} or microgranular adsorption\textsuperscript{122,132,134} has been proposed as a novel technology for combating membrane fouling. The adsorbent layer sorbs the foulants and thus prevents them from reaching the membrane surface. Since the sorbent layer works on the principle of sorption, once the saturation capacity of the sorbent layer is reached, the intention is to replace the saturated sorbent layer with a fresh one, ideally during the backwashing step. Thus, in such systems, only pre-deposition of the sorbent layer is performed, rather than
permanent coating on the membrane surface. However, performance comparisons between systems involving pre-deposited adsorbent particles with the traditional way of using adsorbents, i.e., through mixing with the feed, has not been explored in detail, other than for small size organic micropollutants. In this study, we also compared the performance of PCMs in controlling membrane fouling in two different ways – (a) pre-deposited on top of the membrane surface, (b) stir mixed with the feed. For carbons with macroporosity, pre-deposition was found to be much more effective than stir-mixing. Whereas, for carbons without macroporosity, pre-deposition was found to be similar or only slightly better than stir-mixing. This is in addition to the low energy cost (no need for stirring) and low spatial footprint (as no special contactors are required for adsorbent-foulant contact) of pre-deposited systems. Based on the highly superior performance of such pre-deposited HPC layer, a HPC-0.45 μm membrane hybrid (where the 0.45 μm membrane simply acts as a support) is proposed as a high performance, high permeability and ultra-low-pressure membrane for wastewater reuse application.

3.2 Materials and Methods

3.2.1 Materials

Feed Water

The feed water for this study was the secondary wastewater effluent collected from a wastewater treatment plant (WWTP) in Jeddah, Saudi Arabia, collected on two different dates. Raw feed water was pre-filtered with a 0.45 μm membrane (HVLP04700
- Millipore) to remove particulate matter. All filters were initially soaked in MilliQ water for conditioning. The pre-filtered feed water was subsequently stored at 4 °C to avoid degradation. The average quality of pre-filtered feed water is presented in Table 3.1. All the tests were performed with feed-a, other than tests reported in Figure 3.8, which were carried out with feed-b, as no more feed-a remained.

### Table 3.1: Feed water quality for pre-filtered secondary wastewater effluent from Jeddah WWTP

<table>
<thead>
<tr>
<th></th>
<th>DOC (mg/L)</th>
<th>Biopolymers (mg/L)</th>
<th>Humic Substances (mg/L)</th>
<th>Building Blocks (mg/L)</th>
<th>UV@254nm (cm⁻¹)</th>
<th>SUVA (L/mg/m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Feed-a</td>
<td>6.25±0.58</td>
<td>0.22±0.02</td>
<td>2.48±0.2</td>
<td>1.51±0.12</td>
<td>0.15±0.003</td>
<td>2.4±0.15</td>
</tr>
<tr>
<td>Feed-b</td>
<td>6.12±0.12</td>
<td>0.15±0.01</td>
<td>2.45±0.08</td>
<td>1.32±0.02</td>
<td>0.14±0.001</td>
<td>2.29±0.12</td>
</tr>
</tbody>
</table>

### Membranes

A ceramic microfiltration membrane (Anodisc 0.2 μm, 25 mm, Whatman, alumina based) was chosen as an example of a low-pressure microfiltration membrane. The tests with 0.45 μm membrane were done with a PVDF hydrophilic membrane (HVL02500 - Millipore).

### Carbon Materials

Five different types of porous carbon materials were employed in this study, one commercially purchased powder activated carbon, Norit SA Super, and four synthesized porous carbons – two hard templated mesoporous carbons and two dual templated
hierarchical carbons. The dual-templated carbons were synthesized as per our recently developed ice and hard templating coupled approach, with a slight variation. Briefly, 40 g of a 15 wt% suspension of 4 nm colloidal silica and 3 g of glucose D is added to a 50 mL centrifuge tube and mixed well. Next the centrifuge tube is plunged and held fixed in liquid nitrogen. The frozen sample is then subjected to freeze drying until the sample is completely dry. The freeze-dried glucose-silica composite is then carbonized at 1000 ºC at a ramp rate of 3 ºC/min for a dwell time of 2 hours under nitrogen environment, resulting in a carbon-silica composite. The silica in the carbon-silica composite is then etched using a 3M NaOH in an autoclave placed in an oven at 95 ºC overnight. The sample is finally washed with copious amounts of deionized water and dried at 130 ºC for at least 12 hours before use. For convenience the samples are denoted by HPC-\(x\), where HPC stands for Hierarchical-Porous Carbon and, \(x\) represents the average colloidal silica size (nm) in the original suspension. A higher weight ratio (silica/glucose) of 2 was chosen so as to obtain large pore size carbons resulting from the aggregation of silica nanoparticles. Two different size silica nanoparticles (4 nm and 12 nm) were chosen to obtain carbons with different size mesopores. Two mesoporous carbons produced through hard templating alone were also synthesized through direct vacuum drying of the silica-glucose suspension. The vacuum dried glucose-silica mixture was then subjected to similar carbonization and etching procedure. The carbons thus produced are denoted by MPC-\(x\), where MPC stands for Meso-Porous Carbon and, \(x\) represents the average colloidal silica size (nm) in the original suspension. All the carbon materials were sieved and only particles with size greater than 20 \(\mu\)m, characteristic of non-crushed powdered carbon materials, were used.
3.2.2 Methods

Material characterization

Surface area and pore size measurement

Nitrogen adsorption-desorption tests were carried out at 77K using a Micromeritics TriStar II 3020 analyzer. Prior to gas adsorption measurement, the samples were degassed at 180 °C under N₂ for at least 12 hours. The specific surface area was calculated using the Brumauer-Emmett-Teller (BET) method. The pore volume was estimated from single point adsorption at a relative pressure of 0.994. The pore diameter was determined from the adsorption branch, according to the Barrett-Joyner-Halanda (BJH) method.

Scanning Electron Microscopy (SEM)

The microstructure of the samples was investigated by a LEO 1550 FESEM operating between 2-20 keV.

Mercury porosimetry

Powder PCM samples were analyzed using mercury intrusion via a Micromeritics AutoPore IV (9500 Series) porosimeter. The powder samples were placed in the penetrometer sample holder and measurements were taken for intrusion pressures between 1.5 psi to 60000 psi.
Transmission Electron Microscopy (TEM)

TEM images were obtained using an FEI T12 Spirit TEM/STEM. The T12 is a 120 kV field emission TEM, equipped with a LaB$_6$ filament and an SIS Megaview II CCD camera. The sample was ground and then added into a vial with ethanol. The sample was then sonicated and physically mixed by shaking the vial. After roughly 45 s, with the larger particles settling to the bottom of the vial, the top of the vial was pipetted out and placed on a carbon coated copper TEM grid.

Water sample analysis

The feed water and the permeate samples were analyzed by ultraviolet absorbance at 254nm wavelength (UV$_{254}$), using a DR 5000$^{TM}$ UV-Vis Spectrophotometer (HACH). Liquid chromatography–organic carbon detector (LC-OCD), Model 8 (DOC-Labor, Germany), was used for analyzing the EfOM composition of feed and permeate water samples.

Experimental set-up for filtration tests

Bench scale experiments were performed under constant-pressure dead-end filtration mode using an Amicon cell with the experimental set-up shown in Figure A.4. Nitrogen gas was utilized to pressurize feed water from the pressure vessel to the membrane cell. The weight of the collected permeate was measured using an automatic balance at an interval of one minute. A constant pressure of 0.3 bar and 0.05 bar was maintained for filtration tests involving the 0.2 μm ceramic membrane and the 0.45 μm polymeric membrane respectively. A low constant pressure of 0.05 bar was chosen for
the 0.45 μm membrane tests, so as to match the starting flux values (~1500 L/m²/h) for the ceramic membrane filtration tests that were conducted at constant pressure of 0.3 bar. The results presented are an average of two measurements. The feed water was brought to room temperature before carrying out the filtration tests. New clean membranes were used for each test.

**Carbon pre-deposition**

A required dose of porous carbon material (PCM) was measured on a balance and gently mixed with pure MilliQ water to form a PCM solution. The PCM solution was then filtered through the membrane placed in the amicon cell to form a PCM layer on the membrane surface.

**Adsorption batch tests**

For batch mode kinetics test, pre-filtered feed water mixed with PCM was filled into glass media bottles such that the PCM concentration was 30 mg/L. Bottles were shaken on a horizontal shaker for different amounts of time (15 min, 30 min, 60 min, 90 min, 180 min and, 24 hours) under ambient conditions (20-25°C). The kinetic tests were performed for all of the five carbons. For sorption isotherm tests, different volumes of wastewater were used corresponding to six different PCM concentrations of 200, 120, 60, 30, 20 and 15 mg/L. The sorption isotherm tests were performed with the top two best performing synthesized carbons and the commercial carbon. The results presented are an average of two measurements, except for the kinetics test. Afterwards, the PCM was removed by filtration through a 0.45 μm filter. UV₂₅⁴ and LC-OCD measurements were
performed to measure the residual liquid phase concentrations of organic matter.

3.3 Results and Discussion

3.3.1 PCM Characterization

The textural and physical characteristics of the various PCMs are presented in Table 3.2. The first key textural differences between the commercial and the synthesized PCMs is in their size and extent of mesoporosity. As can be seen from Figure 3.1(b), both the synthesized HPCs and MPCs have much higher contribution to the pore volume coming from the mesopores (i.e. pore size greater than 2 nm). Both HPC-4 and MPC-4, have a pore size maximum in the range around ~34 nm, also confirmed by TEM in Figure 3.1(f) for HPC-4 material. Moreover, the synthesized PCMs have very high pore volumes, shown in Table 3.2 (based on N$_2$ sorption), as compared to the commercial carbon (5-6 fold higher). This could translate to the synthesized PCMs being able to accommodate larger amounts of EfOM components, and thus higher sorption capacities for EfOM components, and in turn reduced membrane fouling for the PCM-Membrane hybrids. It is also important to note that both HPC-x and MPC-x have very similar mesoporosity distribution, as confirmed in Table 3.2 and Figure 3.1(a, b), as they are made from same silica nanoparticles. The only major difference between the synthesized HPCs and MPCs is the presence of macroporosity in case of HPCs. As can be seen in Figure 3.1(e), the HPCs have a very high fraction of 1-2 um macropores produced from ice templating, confirmed by the SEM images in Figure 3.1(c, d) as well. The effect of the presence of this macroporosity in HPCs and determination of optimum mesopore size
in PCMs for membrane fouling abatement, i.e. removal of biopolymers considered to be the major membrane foulant\textsuperscript{104,110}, are some of key questions explored in this study.

**Table 3.2: Surface characteristic of PCMs**

<table>
<thead>
<tr>
<th>PCM</th>
<th>Total Surface Area (m(^2)/g)</th>
<th>Total Pore Volume (cm(^3)/g)</th>
<th>Pore Size Maximum (nm)</th>
<th>Hg Pore Volume (cm(^3)/g) (50nm to 5(\mu)m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SA Super</td>
<td>903±42</td>
<td>0.80±0.06</td>
<td>2.3</td>
<td>0.83</td>
</tr>
<tr>
<td>MPC-12</td>
<td>1206±40</td>
<td>3.52±0.10</td>
<td>15.0</td>
<td>2.34</td>
</tr>
<tr>
<td>MPC-4</td>
<td>1277±81</td>
<td>4.52±0.29</td>
<td>32.5</td>
<td>4.45</td>
</tr>
<tr>
<td>HPC-12</td>
<td>1364±37</td>
<td>3.61±0.08</td>
<td>14.3</td>
<td>6.67</td>
</tr>
<tr>
<td>HPC-4</td>
<td>1173±91</td>
<td>4.32±0.22</td>
<td>36.0</td>
<td>7.40</td>
</tr>
</tbody>
</table>
Figure 3.1: (a) N$_2$ sorption isotherm and (b) pore size distribution based on N$_2$ sorption for the various PCMs, inset shows magnified representation for SA Super; (c, d) SEM image for HPC-12 showing the macropores; (e) pore size distribution curves for the various PCMs based on Hg porosimetry; (f) TEM image for HPC-4 showing the mesopores.
3.3.2 PCM-Membrane Hybrid Filtration

First of all, constant-pressure tests were conducted with MilliQ water to determine the amount of permeability loss as a result of pre-depositing a carbon layer on the membrane surface. As shown in Table 3.3, very low permeability loss was observed as a result of carbon layer pre-deposition for the various PCM-Membrane hybrid cases, as expected with the large particle size carbons used in this study, unlike super-ground activated carbon.

Table 3.3: Permeability loss as a result of pre-depositing a carbon layer on the membrane surface

<table>
<thead>
<tr>
<th>PCM layer (Pre-deposited on Ceramic Membrane)</th>
<th>SA Super</th>
<th>MPC-12</th>
<th>MPC-4</th>
<th>HPC-12</th>
<th>HPC-4</th>
<th>Ceramic Membrane Alone</th>
</tr>
</thead>
<tbody>
<tr>
<td>Permeability Loss (%) (Measured using MilliQ Water)</td>
<td>1.29</td>
<td>3.56</td>
<td>8.27</td>
<td>1.25</td>
<td>5.06</td>
<td>0</td>
</tr>
<tr>
<td>Starting Flux Values (L/m²/h) (For pre-filtered feed passed through PCM-Ceramic Membrane Hybrid @ 0.3 bar)</td>
<td>1564±15</td>
<td>1565±77</td>
<td>1621±27</td>
<td>1685±47</td>
<td>1602±54</td>
<td>1568±69</td>
</tr>
</tbody>
</table>

Filtration tests, with pre-filtered feed, were carried out for the uncoated ceramic membrane and PCM layer coated ceramic membrane to measure the fouling reduction capability of the various PCMs. Such integrated PCM-Membrane hybrid systems eliminate the need for any separate contactor which is one of their major advantages. The results for these constant pressure filtration tests are plotted below in Figure 3.2. Figure 3.2(a) shows the normalized flux (normalized with respect to the starting flux value for each test) as a function of filtered volume. The decrease in flux with increased...
filtered volume is characteristic of membrane fouling. And Figure 3.2(b) represents the amount of filtered volume (permeate) collected as a function of time. There are two important things to note from Figure 3.2(a, b). First, the flux drop in the case of PCM-coated membranes is lower as compared to the membrane alone case for all the PCMs. Even for the lowest performing PCM (i.e., SA Super) case, the filtration happens in less than half the time as compared to the bare membrane case, signifying lower fouling for the SA Super-membrane hybrid. Such fouling reduction would in turn imply reduced frequencies of chemical cleaning. Also it is important to note that backwashing the membranes with MilliQ water (after the filtration test) did not result in any improvement in permeability (Figure 3.3), suggesting that only irreversible fouling is happening in this system. This is in line with the previously reported findings that EfOM, and in particular biopolymers (shown later to be the major foulant for this particular membrane system also) mainly cause irreversible membrane fouling. Second, among the various PCMs, HPC-4 and HPC-12 gave the highest fouling reduction, taking only 12% of the time needed for the bare membrane case (8-fold time reduction) to filter the same amount of feed and ~4 fold reduction as compared to the time taken in case of commercial carbon SA Super pre-deposited membrane. Also, a substantial reduction in membrane fouling is seen for the case of HPC-4 (and even HPC-12) as compared to the other synthesized PCMs (i.e. MPC-4 and MPC-12). This can be attributed to the presence of macropores in the case of HPC-4 and HPC-12, produced through ice templating. This is because both HPCs and MPCs, other than having differences in their macroporous structure, have very similar chemical and physical characteristics as they are made using the same carbonization temperature, same precursor and similar silica nanoparticle template. Thus,
HPCs and MPCs differ only in terms of the presence of macropores in the case of HPCs, as confirmed by the pore size distribution measured using Hg porosimetry presented in Figure 3.1(e). The reason for the favorable effect of the presence of macropores in PCMs towards their membrane fouling reduction capacity is explored in later sections. Among the two MPCs, MPC-4 and MPC-12, MPC-4 performs only slightly better in terms of lower flux drop. This could imply that bigger size mesopores, as in the case of MPC-4 (~33 nm) as compared to MPC-12 (~15 nm), have a favorable effect towards membrane fouling reduction, which is supported by findings reported in the later sections as well. All of the above findings are further confirmed by the higher biopolymer removal % for the HPC-Membrane hybrids as reported in Figure 3.2(c). There are three important things to observe in Figure 3.2(c). First, the ceramic membrane alone gives a fairly decent biopolymer removal, which is also probably the reason for the fast decline in its flux. Since the ceramic membrane does not remove any other EfOM component, its fouling (flux decline) can be safely attributed to be caused by biopolymers alone. That is why, in this study, biopolymers are referred to as the only foulants with respect to the particular membrane used. Second, among the PCM-Ceramic membrane hybrids, HPC-4 and HPC-12, not only help in reducing membrane fouling of the supporting membrane, but also provide much higher total % biopolymers removal as compared to the ceramic membrane alone. This could be useful in further reducing fouling of high-pressure membranes that might be installed downstream in the wastewater treatment line (such as nanofiltration or reverse osmosis membranes). Third, the PCM-membrane hybrids provide fairly good removal of other EfOM fractions (humics and building blocks) as well, as compared to zero removal for these fractions by the ceramic membrane alone. This is another
important advantage of pre-depositing the membrane with a PCM layer. The removal of these humics and building blocks is important from the point of view of their ability to act as potential precursors to the formation of DBPs as well as their ability to foul high-pressure membranes that might be installed downstream in the treatment train. The ceramic membrane by itself does not provide any removal for such small-size EfOM fraction molecules, as they pass through the membrane pores. And thus they are referred to as non-foulants with regards to the membrane used in this particular study. Whereas, in the case of the PCM-Membrane hybrid, the PCM layer sorbs such EfOM fractions. It is also important to observe that for the case of HPC-4 and HPC-12, in spite of providing decent removals for non-foulant EfOM fractions, they still maintain good selectivity towards the removal of the foulant EfOM fraction, i.e., the biopolymers. It is important to note that comparing biopolymer removal for different PCMs for the PCM-Membrane hybrid case is not ideal, as explained in the next section 3.3.
Figure 3.2: a) Normalized flux as a function of filtered volume and b) Filtered permeate volume as a function of filtration time - for pre-filtered feed passed through PCM-Ceramic Membrane hybrid for different PCMs; (c) Removal (%) of biopolymers, humics and building blocks calculated using LC-OCD measurements; removal (%) based on UV measured at 254 nm; on pre-filtered feed and filtered volume collected at the end of the filtration cycle for the various PCM-Ceramic Membrane hybrid filtration tests.
**Figure 3.3:** Ratio of MilliQ Water flux through the ceramic membrane after backwashing ($J_1$) and before backwashing ($J_0$), measured at 0.3 bar, for various PCM-Ceramic membrane hybrids. The membrane hybrids had been used to filter pre-filtered feed, as described in section 3.2 in the main article, before being backwashed. The backwashing was carried out by flushing with MilliQ Water for 1 min at a pressure of 1.2 bar.

**3.3.3 Batch Sorption Tests**

Batch sorption tests (kinetics and sorption isotherm tests) were also carried out for the following main reason. For the different PCM-Membrane hybrid cases, because of the different extents of fouling of the supporting membrane, the feed and the carbon layer are in contact for different amounts of time for the different PCM cases. Moreover, the membrane itself contributes to biopolymer removal. Thus, to truly compare the effectiveness of different PCMs in sorbing biopolymers (and thus to compare their ability to reduce the fouling propensity of feed), batch sorption tests with different PCM dosages and controlled time intervals were performed for the various carbons. Thus batch sorption tests could provide a suitable basis to rank different PCMs as far as their use in reducing membrane fouling is concerned.
The percentage removals for each EfOM fraction as a function of time for the various PCMs tested in this study are given below in Figure 3.4. These % removals were calculated based on the concentration of different EfOM fractions measured using LC-OCD before and after the sorption test.119 There are three important things to note from the kinetics test results. First, for shorter contact times (i.e. 15 min and 30 min), SA Super and MPC-12 have the lowest biopolymer removal. Among all the selected carbons, MPC-12 and SA Super have the lowest meso and macroporosity as well. Thus to ensure fast biopolymer removal, it can be said that the presence of macropores and/or large size mesopores is essential. Secondly, at longer contact times, HPC-x’s provide higher biopolymer removals as compared to respective MPC-x’s. This could suggest two possibilities: (i) the macropores in HPCs themselves act as sorption sites for larger size biopolymers that cannot enter the mesopores, (ii) the macropores in HPCs provide higher accessibility to the mesopores present within the carbon walls. Thirdly, the % removal for smaller size EfOM fraction such as humics and building blocks is similar for the various synthesized carbons. However, the % removals for the synthesized PCMs is higher than the commercial carbon SA Super, especially for shorter contact times, because of faster diffusion of these molecules within the large size mesopores and macropores of MPCs and HPCs. These small sized EfOM components can easily enter and quickly diffuse into the large number of mesopores available in both the MPCs and HPCs, which explains their similar removals.
Figure 3.4: Removal (%) of (a) biopolymers, (b) humics and (c) building blocks calculated using LC-OCD measurements; (d) removal (%) based on UV measured at 254 nm; on pre-filtered feed contacted with different PCMs for different amounts of time.
Figure 3.5: Amount of different EfOM components - (a) biopolymers, (b) humics, (c) building blocks, - (d) dissolved organic carbon, adsorbed on different PCMs, calculated using LC-OCD measurements on pre-filtered feed contacted with PCMs for different amounts of time.

The percentage removal for each EfOM fraction as a function of increasing PCM concentration for three PCMs (two best performing synthesized PCMs and SA Super) are given below in Figure 3.6. The % removal of various fractions increases as the PCM concentration increases. In order to achieve substantial removal (say 90%) of the foulant biopolymer fraction, a PCM concentration of ~ 200 mg/L is required for the commercial carbon SA Super. Whereas, for the HPCs, a concentration of only 60 mg/L is required (almost one-third of the amount of SA Super), indicating their superior performance. For
the lowest tested PCM dosage, i.e., 15 mg/L, there are two important things to note from the sorption results. First, the % removal of biopolymers (foulant fraction) is the highest for the synthesized HPC-4, almost four to five times higher than the commercial carbon SA Super, and slightly higher than HPC-12. Thus, the presence of macropores and large size mesopores definitely play a favorable role towards HPC-4’s high biopolymer sorption capacity as compared to other PCMs. Second, the % removal of the non-foulant fractions, i.e., humics and building blocks, in case of synthesized carbons HPCs is lower than their % removal of the foulant fraction, i.e., biopolymers. Thus HPCs have higher selectivity towards the foulant fraction removal. On the other hand, the commercial carbon SA Super, gave higher removal for the non-foulant fraction as compared to the foulant fraction. This can be easily explained by the fact that porous carbons provide higher removal for species having size similar to the size of their pores. 26 This indicates that such commercial carbons are not suitable candidates for addressing the problem of membrane fouling because of their poor selectivity towards the foulant fraction. For a PCM dose of 30 mg/L, used for the PCM-Membrane hybrid tests, N2 sorption isotherm tests were carried out after the sorption test as well, to see how the micro and mesoporosity change as a result of EfOM sorption. The results are presented in Figure A.5 and Table A.2 in the appendix, which shows that the commercial PAC, SA Super, undergoes the maximum loss in porosity, despite its lowest sorption capacity. This is because SA Super has very low meso and macroporosity, which gets filled up or blocked by the various big size EfOM components. Also the sorption isotherm plots for the different EfOM components adsorbed on the various carbons are given in Figure 3.7.
Figure 3.6: Removal (%) of (a) biopolymers, (b) humics, and (c) building blocks calculated using LC-OCD measurements; (d) removal (%) based on UV measured at 254 nm; on pre-filtered feed contacted with different PCMs for different PCM dosage amounts.

Now it is important to note that the % biopolymer removal for the HPCs at a contact time of 30 min (Figure 3(a)) is much lower than the % biopolymer removal for the HPC-Ceramic membrane hybrid (Figure 2(c)), where the HPC-Ceramic membrane hybrid also had a total filtration time of ~ 25min (Figure 2(b)). This could be either due to the fact that: (i) batch sorption tests were conducted at ambient pressure where as an excess pressure of 0.3 bar was used for the HPC-Ceramic membrane hybrid tests; (ii)
Figure 3.7: Sorption isotherm of different EfOM components - (a) biopolymers, (b) humics, (c) building blocks, - (d) dissolved organic carbon, adsorbed on different PCMs, calculated using LC-OCD measurements, on pre-filtered feed contacted with different PCMs for different PCM dosage amounts.

with the carbon layer approach, the adsorbent is continually in contact with the fresh feed solution, where as in the batch sorption testing mode, the adsorbent maintains contact with a bulk solution at a lower concentration than the feed;\textsuperscript{145} (iii) the ceramic membrane itself could also be contributing to some biopolymer removal in the case of the HPC-Ceramic membrane hybrid. To overcome these dissimilar comparison conditions associated with the batch mode testing, and to truly compare pre-deposited carbon layer performance with the stirring mode (well mixed) configuration, as well as to quantify the
relative contribution of carbon layer alone in removing foulants, a new test was strategically designed, as described in the next section.

3.3.4 Performance comparison between pre-deposited sorbent layer versus traditional sorbent-feed mixing approach

To assess the effectiveness of the pre-deposition approach as compared to the traditional way of using adsorbents, i.e., through mixing with the feed, two sets of tests were done: (1) PCM layer pre-deposited on a 0.45 µm membrane, (2) PCM stirred within the amicon cell volume, where the 0.45 µm membrane prevents any PCM from flowing out with the permeate. This test assures a much fairer comparison between the stirring and non-stirring approach as compared to comparing results from batch sorption tests and PCM-Ceramic membrane hybrid tests because of the following three reasons. First, a 0.45 µm membrane was chosen as the supporting membrane because it did not provide any EfOM removal (data not shown), as the feed had prior been filtered by passing through a 0.45 µm membrane only. Thus, all the biopolymer removal in the case of PCM-0.45 µm membrane hybrid case happens because of sorption within the PCM material only. Thus, it provides a suitable way to compare the pre-deposition and stir-mixing approach, as well as to compare different PCMs. Secondly, the same pressure of 0.05 bar is applied for both the stirring and non-stirring (pre-deposition) case. Thirdly, for both the stirring and non-stirring (pre-deposition) case, the carbons were in contact with the same concentration feed. Fourthly, the total filtration time for both the configurations was also similar, thus there is no separate need to control the contact time, unlike in the
case of batch sorption. SA Super, because of its inferior performance, was not included in this particular test. The % removal of different EfOM components, based on LC-OCD, for the different synthesized PCMs for the pre-deposition and stir-mixing approach is given below in Figure 3.8(a). There are three important things to note in Figure 3.8(a).

First, the % biopolymer removal is higher in the pre-deposition mode as compared to the stir-mixing mode. The difference is more dominant for HPCs as compared to MPCs. This could be explained on the basis that macropores in case of HPCs could also be involved in sorption of large size biopolymer molecules (greater than the size of carbon mesopores). During fast stirring conditions, it is hypothesized that the presence of shear force can disturb the adhesion of biopolymer molecules onto the macropore walls on the carbon surface, which probably causes lower biopolymer sorption. It is fairly well known that shear fluid flow affects adhesive strength and even causes sloughing of biofilm from a surface,\textsuperscript{147,148} where the microorganisms are generally attached onto a surface mainly through proteins (such as biopolymers).\textsuperscript{149} Moreover, application of fluid shear force, through tangential or cross flow flushing, to remove foulants from membrane surface is also fairly common practice.\textsuperscript{150} Thus, lack of fluid shear force as in the case of pre-deposited systems is thus thought of to result in enhanced biopolymer sorption on the macropores present on the HPC surface. Secondly, the removal of smaller size EfOM components such as humics and building blocks is quite similar for both stirring and pre-deposition configurations. Since sorption of such small sized humics and building blocks takes place within the mesopores, which are equally accessible in both stirring and non-stirring conditions and where the presence or absence of shear force does not affect the sorption within the mesopores, thus their removal remains unaffected. Thirdly, the
biopolymer removal is higher for dual-templated HPC-x as compared to the their respective single-templated counterpart MPC-x. As the only difference between HPCs and MPCs is the presence of macroporosity in the case of HPCs, produced from ice templating, it signifies that macroporosity in PCM plays a key role in the removal of large size biopolymer molecules considered to be the major membrane foulant.

The permeate collected after the PCM-0.45 μm membrane hybrid tests was then passed through the ceramic membrane to measure its fouling potential, by measuring the flux drop for the ceramic microfiltration membrane. The findings regarding superior performance of (i) pre-deposition over stirring and (ii) HPCs over MPCs, from LC-OCD measurements, are reconfirmed by flux drop measurements in Figure 3.8(b, c). The EfOM concentration in the permeate, collected from the ceramic membrane, is also characterized by LC-OCD. Thus, by comparing % removals in Figure 3.8 (a) and Figure 3.8 (d), the relative contributions of a PCM pre-deposited layer and the ceramic membrane in a PCM-ceramic membrane hybrid can be easily estimated. The data show that for HPC-ceramic membrane hybrids, the bulk of the biopolymer removal happens within the HPC pre-coated layer. This explains the reason for the low flux drop for the HPC-Ceramic membrane hybrid.

Another important thing to notice from the HPC-0.45 μm membrane hybrid tests is that the superior performance of the HPC-0.45 μm membrane hybrids qualifies them as highly efficient ultra-low-pressure, microfiltration membrane systems. As compared to the traditional microfiltration ceramic membrane, which gave ~30% biopolymer removal
(Error! Reference source not found. (c)), the HPC-4-0.45 μm membrane hybrid, gave ~80% biopolymer removal (Figure 3.8(a)), within 20% of the time taken by the uncoated ceramic membrane, at a much lower applied pressure (0.05 bar as compared to 0.3 bar for the ceramic membrane), for same starting flux values. Not only that, such HPC-0.45 μm membrane hybrids also sorb other EfOM components such as humics and building blocks as compared to zero removal by the ceramic membrane alone, where these components could potentially cause fouling of high-pressure membrane systems that might be installed downstream in the WWTP. Thus, such hierarchical porous carbon-large pore size membrane hybrids, where the carbon layer provides the EfOM fraction removal and the high permeability large pore size membrane merely acts as a support, could very well become the LPM system of the future (especially for the case of microfiltration membranes). It is important to note that the use of large pore size membranes is only possible with these non-crushed, hierarchical porous carbons. Crushed PCMs such as SPAC (superground powdered activated carbon) cannot be used with large pore sized membranes as the crushed PCMs can themselves pass through the membrane or block the membrane pores.
Figure 3.8: a) Removal (%) of biopolymers, humics, and building blocks calculated using LC-OCD measurements and removal (%) based on UV measured at 254 nm, on pre-filtered feed and filtered volume collected at the end of the filtration cycle for the various synthesized PCM-0.45 μm membrane hybrid tests. (b) Normalized flux drop as a function of filtered volume and c) Filtered permeate volume as a function of filtration time - for permeate from PCM-0.45 μm membrane hybrid tests passed through the ceramic membrane. (d) Removal (%) of biopolymers, humics, building blocks calculated
using LC-OCD measurements and removal (%) based on UV measured at 254 nm, on
pre-filtered feed and filtered volume collected at the end of the filtration cycle for
permeate from PCM-0.45 µm membrane hybrids passed through ceramic membrane.

3.4 Conclusions

1. Templated carbons, especially dual-templated hierarchical porous carbons, were
   found to give exceptional irreversible fouling abatement for low pressure membranes
   as compared to activated carbon.

2. Carbons with large size mesopores and higher mesoporosity content gave higher
   biopolymer removal and fouling control.

3. Comparison between dual-templated hierarchical porous carbons and single-
   templated mesoporous carbons revealed that macropores in PCMs also play a very
   favorable role towards biopolymer removal.

4. For HPCs, pre-deposition of sorbents gave better biopolymer removal and thus better
   fouling control as compared to traditional sorbent-feed mixing approach, mainly
   ascribed to the lack of fluid shear force resulting in enhanced sorption of biopolymers
   on the carbon surface within the macropore walls.

5. A novel ultra-low pressure membrane - dual-templated hierarchical porous carbon
   pre-deposited on a large pore size (0.45 µm) membrane support – completely
   outperformed the microfiltration ceramic membrane in terms of fast, energy efficient
   and high EfOM removal capacity.
CHAPTER 4. COMBINED SALT TEMPLATING-HARD TEMPLATING APPROACH FOR THE SYNTHESIS OF MULTI-MODAL POROUS CARBONS - PROBING THE EFFECT OF ELECTRODE ENGINEERING ON ELECTROSORPTIVE PERFORMANCE

(Manuscript under preparation)

4.1 Introduction

Capacitive deionization is an attractive separation technology for separating ionic species from aqueous solution.\textsuperscript{151,152} The technology involves adsorption of charged ions by oppositely charged electrodes on application of an external electric field. The saturated electrodes can be easily recovered by turning off the external electric field and thus releasing back the sorbed ions. A large number of materials, including carbon aerogels,\textsuperscript{16,153,154} activated carbon,\textsuperscript{21} mesoporous carbons,\textsuperscript{69,155-157} hierarchical carbons,\textsuperscript{33,34,158} graphene,\textsuperscript{159} carbon nanotube,\textsuperscript{160} carbon nanofiber,\textsuperscript{158} and combinations thereof\textsuperscript{161-165} have been investigated as electrode materials for the CDI process. Among them multi-modal porous carbons or hierarchical porous carbons (HPCs) hold great potential because of their multimodal porosity. The advantage of HPCs for this application is that the presence of mesopores and macropores can provide pathways for fast ionic transport and the micropores can provide sites for ion sorption.

As a result of the high performance of such mutli-modal porous carbons as CDI electrode materials and even in other related fields such as batteries, water purification, CO\textsubscript{2} capture, sensors, lately, a lot of research effort has also been devoted towards
developing efficient synthesis techniques for producing such hierarchically porous carbon materials. The most commonly used methods for producing such multi-modal porous (mesopore-micropore dominated) carbons usually involve two steps: (1) synthesis of a single or dual templated mesopore/macropore dominated carbon material (through either hard or soft templating), (2) introduction of microporosity through a second step of activation (either physical or chemical activation). Although, such techniques ensure a tight control on porosity at different levels, but it can make the synthesis technique cumbersome and highly energy intensive. In order to produce such multi-modal porous carbons for commercial purposes, a simple, one step approach for their synthesis is highly necessary and urgently needed. Recently, salt templating, involving carbonization of a carbon precursor around molten salt at elevated temperature, has emerged as a highly simple and sustainable technique for producing functional porous carbons. However, it mainly results in the generation of micropore and some small mesopore containing carbons, with pores generated from washing of the salt nano-clusters.

Herein, we propose a single-step approach, based on a combination of salt templating and hard templating, for producing high surface area multi-modal porous carbon materials. The approach involves mixing an inorganic salt (ZnCl$_2$) with a carbon precursor (glucose) and an inorganic hard template (colloidal silica) solution, followed by vacuum assisted drying and carbonization. The salt (ZnCl$_2$) initially melts during carbonization with the glucose precursor forming a carbon matrix around the molten ZnCl$_2$ nano-pools, which eventually boil off during carbonization at elevated temperature.
(1000 °C), generating micropores and small mesopores. On the other hand, the removal of colloidal silica from the porous carbon-silica composite through etching with NaOH generates the mesopores. Different size mesopores, macropores and even tri-modal porous carbons can be generated by using colloidal silica of different sizes and combinations there-of. By using a mixture of two salts, this work also demonstrates that the proposed technique can be used for the synthesis of a metal nanoparticle embedded, high surface area multi-modal porous carbon. In addition, a single step, low energy intensity, combined salt templating-hard templating-physical activation approach for the production of very high surface area (~ 2500 m²/g) multi-modal porous carbons is also demonstrated.

EDLC (electric double layer capacitor) is a related application based on the similar concept of electrosorption of ions from an aqueous solution, just like CDI. The basic difference between EDLC and CDI is that while EDLC uses the electrosorption of ions from aqueous solution as a means to store energy, CDI is only concerned with removal of ions from aqueous solution as a result of electrosorption for producing desalinated water. For EDLC, among the various factors governing the electrosorption performance, the electrode processing conditions have been recently shown to have a significant effect. For example, forced electrolyte infiltration was found to overcome, to some extent, the capacitance retention problem (at high current densities) associated primarily with microporous carbons. Similarly, the application of pressure during electrode fabrication, forcing the electrolyte into the pores, was also found to play a favorable role in enhancing the capacitive performance and lowering the ohmic loses,
with the effect of applied pressure being different for different size electrolyte ions.\textsuperscript{182,183} However, on the other hand, Ruoff et al. reported that electrode compression led to an enhanced equivalent series resistance and low EDLC performance (on gravimetric basis), ascribing it to the loss of a fraction of mesopores in their electrode material.\textsuperscript{189} In another study, application of pressure during electrode preparation was found to have no effect on the capacitance, while resulting in reduced ohmic drop.\textsuperscript{184} Thus, currently there is not much consensus in reported literature on the effect of pressure applied during electrode fabrication on its electrosorption performance.

Thus, in this study, we explored the potential of using the synthesized salt-hard templated carbons as electrode materials for electrosorption, as well as investigated the effect of electrode fabrication pressure on its electrosorption performance. The electrosorption performance was measured as a function of increasing pressure applied during electrode manufacturing. For such testing, the electrodes were pressed in three different configurations: (i) in the presence of electrolyte, (ii) in the presence of MQ water, (iii) pressing under dry conditions, and the differences in their performances were measured.

4.2 Experimental

4.2.1 Material Synthesis

In a typical synthesis, 10 g of a 30 wt% suspension of 22 nm colloidal silica and 3 g of glucose D are mixed in a plastic centrifuge tube. Then 6 g of ZnCl\textsubscript{2} salt dissolved in
6 mL of MilliQ Water is added to the solution and shaken well. The sample is then subjected to vacuum drying at room temperature at 0.014 mbar until the sample is completely dry. The glucose-silica-ZnCl\textsubscript{2} composite is then pyrolyzed at 1000 °C at a ramp rate of 3 °C min\textsuperscript{-1} for a dwell time of 2 h under nitrogen environment, resulting in a carbon-silica composite. During the course of pyrolysis, ZnCl\textsubscript{2} acts as an in-situ nano-template and finally boils off as vapor, leaving behind secondary micropore and small size mesopores. Thus, finally a carbon-silica composite is obtained, which is then stirred in a 3M NaOH solution at room temperature for 4 hours and finally kept at 95 °C for 24 hours in an autoclave to etch out the silica. The sample is finally washed with copious amount of deionized water and dried at 130 °C for at least 12 hours before use. For convenience the samples are denoted by PC \textit{x-y-z}, where PC stands for porous carbon, \textit{x} represents the average colloidal silica size (nm) and \textit{y} (=0 or 1) represents the mass ratio of silica to glucose in the original suspension, and \textit{z} (= 0 or 2) represents the mass ratio of ZnCl\textsubscript{2} to glucose. Five different carbon materials were synthesized and tested in this study (i) PC produced by salt templating alone: PC 0-0-2 (having only secondary micropores and small size mesopores-confirmed later), (ii) PCs produced by hard templating alone: PC 4-1-0, PC 22-1-0 (having only big size mesopores-confirmed later), (iii) PCs produced by single-step, combined salt templating-hard templating: PC 4-1-2, PC 22-1-2 (having multi-modal porosity, with both secondary micropores as well as big size mesopores-confirmed later).

For carbon materials produced through the combined salt templating-hard templating-physical activation procedure, the synthesis procedure is exactly the same
except for the carbonization step. During the hold at 1000 °C, the inert nitrogen gas is replaced with CO₂. For the low energy intensity synthesis, the glucose-silica-salt mixture is carbonized at 450 °C at a ramp rate of 3 °C min⁻¹ for a dwell time of 2 h under nitrogen environment. The resulting carbon-silica-salt composite is then treated with 1M HCl at 85 °C for 4 hours to remove the ZnCl₂ salt, followed by washing with copious amounts of MilliQ water. The silica nanoparticle is then etched out using the same procedure as described above. For multi salt mixture synthesis, first a solution of glucose-colloidal silica-ZnCl₂ is obtained as described above. Then 1 g of cobalt nitrate hexahydrate solution (dissolved in 2 mL MilliQ water) was added to the glucose-colloidal silica-ZnCl₂ solution, mixed well and subjected to vacuum drying. The dried glucose-silica-ZnCl₂-Co(NO₃)₂ composite was then carbonized at 1000 °C at a ramp rate of 3 °C min⁻¹ for a dwell time of 2 h under nitrogen environment. The obtained carbon-silica-cobalt composite is then subjected to NaOH etching to remove the silica template, leaving behind a cobalt nanoparticle embedded multi-modal porous carbon. The cobalt nanoparticle can further be etched out by using 1M HCl solution at 85 °C for 24 hours.

4.2.2 Electrode preparation and electrochemical characterization

The electrodes were made for PC 22-1-2 synthesized using vacuum assisted drying. For electrode preparation, the PC was first grounded using a mortar and pestle. Then 92.5 wt% of PC and 7.5 wt% polytetrafluoroethylene (PTFE) (60 wt% PTFE obtained from Sigma Aldrich) were mixed in ethanol to form a slurry. The PC-PTFE-Ethanol slurry was sonicated for ~30 minutes and then dried by placing in an oven at 80 °C for an hour to obtain a dough like paste. The paste was then rolled into a film and then
pressed onto a stainless steel mesh (Alfa Aesar) at a pressure of 1 bar, using a hydraulic press. The electrochemical performance, galvanostatic charge-discharge (GCD) measurements, were carried out using a two electrode configuration at different current densities \((I/2m, \text{ where } m \text{ is the mass of a single electrode})\), with 0.25M NaCl as the electrolyte in the potential range between 0-1V. The effect of pressure on electrosorption performance was measured by successively pressing the electrode at increasing pressure values for three different cases – (i) in the presence 0.25M NaCl soaked cotton, (ii) in the presence of MilliQ water soaked cotton, (iii) in the presence of dry cotton. The electrochemical impedance spectroscopy measurement was performed at 0 V using a sinusoidal signal of 10 mV over the frequency range from 100 kHz to 100 mHz. The specific capacitance \((C_s)\) and the energy efficiency \((\xi_{\text{charge}})\) for the charging cycle are calculated using the following formula:

\[
C_s = 2 \left( \frac{I}{m} \right) \left( \frac{dt}{dV} \right) 
\]

\[
\xi_{\text{charge}} = \frac{E_s}{E_{as} + E_s} = \frac{1/2 t_c \left( V - \Delta V_{ohmic} \right)}{\left( t_c \Delta V_{ohmic} + 1/2 t_c \left( V - \Delta V_{ohmic} \right) \right)}
\]

where

- \(C_s\) is the specific capacitance of the material
- \(m\) is the mass of a single electrode
- \(I\) is the current
- \(V\) is the maximum applied potential (1 Volt)
- \(dV/dt\) is the rate of potential decline during the discharge (excluding IR drop)
- \(\xi_{\text{charge}}\) is the energy efficiency of the charge cycle
$E_s$ represents energy stored during charging, as shown in Figure 4.1

$E_{ns}$ represents energy not stored during charging, as shown in Figure 4.1

$\Delta V_{ohm,c}$ is the ohmic drop during charging

$t_c$ represents time taken for charging the electrode from 0 volt to 1 volt

---

**Figure 4.1**: Energy components in a typical charge-discharge cycle. Reproduced (“in part”) from 191 with permission of the PCCP Owner Societies. Please note the terms $t_c$ and $t_d$ in the figure have been mistakenly swapped.

The capacitive frequency response was calculated from the EIS data using the following formula:

$$C = \frac{1}{j\omega Z} = \frac{1}{j\omega(\text{Re}(Z) + j\text{Im}(Z))}$$

$$|C| = \left[\left(\text{Re}(C)\right)^2 + \left(\text{Im}(C)\right)^2\right]^{\frac{1}{2}}$$

$$\omega = 2\pi f$$

**4.2.3 Material Characterization**

Surface area and pore size measurement
Nitrogen adsorption-desorption tests were carried out at 77K using a Micromeritics TriStar II 3020 analyzer. Prior to gas adsorption measurement, the samples were degassed at 180 °C under N₂ for at least 12 hours. The specific surface area was calculated using the Brumauer-Emmett-Teller (BET) method. The pore volume was estimated from single point adsorption at a relative pressure of 0.994. The pore diameter was determined from the adsorption branch, according to the Barrett-Joyner-Halanda (BJH) method.

**Scanning Electron Microscopy (SEM)**

The electrodes were characterized by scanning electron microscopy using a FEI, Quanta 600. The electrodes were pressed in the presence of electrolyte at various pressures, followed by rinsing in MilliQ water for at least 30 min to rinse out the electrolyte, followed by vacuum drying, before performing SEM.

**Transmission Electron Microscopy (TEM)**

TEM images were obtained using an FEI T12 Spirit TEM/STEM. The T12 is a 120 kV field emission TEM, equipped with a LaB₆ filament and an SIS Megaview II CCD camera. The sample was ground and then added into a vial with ethanol. The sample was then sonicated and physically mixed by shaking the vial. After roughly 45 s, with the larger particles settling to the bottom of the vial, the top of the vial was pipetted out and placed on a carbon coated copper TEM grid.
4.3 Results and Discussion

4.3.1 Physical Characterization of synthesized porous carbon materials

The textural and physical characteristics of the various PCs are presented in the Table 4.1 and Figure 4.2(a, b). There are four important things to note from the porosity data. First, the PC 0-0-2 sample (produced through salt templating alone), has high surface area arising from the presence of secondary micropore and mesopores of size around ~2 nm. (ii) Second, the samples PC 4-1-0 and PC 22-1-0 (produced through hard templating alone), have large pore volumes arising from the presence of large size mesopores ~7 nm and ~26 nm generated through their respective silica template. Third, the sample PC 4-1-2 and PC 22-1-2 (produce through single step coupled hard templating-salt templating) have both high surface areas and very high pore volumes. The high surface area comes from the presence of secondary micropores and mesopores around 2 nm generated through the carbon matrix formed around the salt (ZnCl₂) nanoclusters. The mesopores and macropores (~22 nm and ~64 nm for PC 4-1-2 and PC 22-1-2 respectively) are produced through the removal of silica nanoparticle clusters. The silica nanoparticle clusters are formed as a result of the addition of ZnCl₂ solution (a Lewis acid) to the glucose-silica solution, thus resulting in a controlled aggregation of the colloidal silica, due to pH modification. Now since the carbonization proceeds under solvent free conditions, no phase segregation appears to take place. That is probably why the mesopores/macropores generated from silica etching still retain a relatively sharp peak in their respective pore size distributions. This solution free carbonization strategy, prevents uncontrolled phase segregation of hydrophilic silica nanoparticle solution within
the carbonizing (or increasingly becoming hydrophobic carbon precursor matrix) and thus alleviates the need for using costly surfactants, fast stirring speeds and/or dilute carbon precursor concentrations. In order to confirm this finding, another set of carbonization experiments were performed, where the glucose-colloidal silica-salt solution was directly subjected to carbonization without removing the solvent through the vacuum drying step. As can be seen in Figure 4.2(c, d), the carbons produced through drying using heat have a very broad pore size distribution indicative of uncontrolled phase segregation, unlike the relatively sharp peak obtained for carbons produced from vacuum drying of glucose-collidal silica-salt solution. Fourthly, the multi-modal porosity of carbons produced through coupled hard-salt templating, could translate to their ability to provide both high energy density (because of their surface area) and high retention capability (because of the presence of big mesopores (~22 nm in case of PC 4-1-2) or macropores (~64 nm in case of PC 22-1-2), which could act as both electrolyte reservoirs and highways for efficient electrolyte transport.

Another important alternative feature of this proposed synthesis technique is that even higher surface area multi-modal carbons can be produced by through single-step, low energy intensity combined salt templating-hard templating-physical activation approach. The only difference in the synthesis procedure in this case is that during the hold at 1000 °C, the inert nitrogen gas is replaced with CO₂. The CO₂ activation is known to proceed through reaction between CO₂ and carbon matrix, thus leaving behind pores within the carbon matrix in the process. The porosity (produced in-situ due to the boiling off of ZnCl₂ nanoclusters) can provide easy in-diffusion of CO₂ to active sites and out-
diffusion of reaction products. The presence of ZnCl$_2$ also ensures a higher degree of carbonization of the glucose-silica composite. On the other hand, direct single-step combined hard templating-physical activation, under same thermal conditions and CO$_2$ flow rates, resulted in almost zero yield. This could be attributed to the lower degree of carbonization of silica-glucose composite, which leads to higher gasification rate upon reaction with CO$_2$. For the combined hard templating-salt templating-physical activation, the degree of physical activation can be easily controlled by varying the CO$_2$ flow rate. At high CO$_2$ flow rate (such as 25 ml/min tested in this study), the carbon matrix between adjacent silica nanoparticles also seems to react with CO$_2$, resulting in merger and enlargement of mesopores, as can be seen in Figure 4.3(b).

Another advantage of the combined salt templating-hard templating approach is that the carbonization can be achieved at a much lower temperature. The ZnCl$_2$ salt, apart from acting as an in-situ template around which carbon matrix is formed, also acts as a dehydrating agent ensuring effective carbonization of glucose even at a low temperature, such as 450 °C. In the absence of ZnCl$_2$ salt, i.e., for the case of hard-templating alone, incomplete carbonization happens at such low temperature and the whole carbon matrix collapses upon etching of the silica template. This lack of porosity in low temperature carbonization of silica-glucose composites is highly evident from N$_2$ porosimetry, as shown in Figure 4.4(a, b). Whereas, very high degree of porosity is obtained for the combined salt-hard templated samples, in spite of the lower carbonization temperature. Such multi-modal low temperature (and thus highly energy efficient) carbonized samples could be highly useful candidates for water purification applications or as polymer
impregnated supports for CO$_2$ capture. Since the carbonization is carried out at low temperature, such samples have low electrical conductivity as compared to their respective high temperature (1000 °C) carbonization counterparts, and are thus not so useful for electrochemical applications.

Another advantage of this new synthesis technique is the possibility of using a combination of different metallic salts, where one salt acts as a template to produce porous carbon, while the other acts as a precursor for the formation of metallic nanoparticles embedded both within the pores as well as walls of the carbon matrix. One example of such synthesis is shown here where a combination of ZnCl$_2$ and a sample metal nitrate (Cobalt nitrate hexahydrate) is used. The nitrogen sorption isotherm and the corresponding pore size distribution for the Cobalt nanoparticle embedded high surface area multi-modal carbon is given in Figure 4.5 (a, b). As reported in Figure 4.5, in spite of having a high metal nanoparticle content (~27%, calculated using sample weights before and after HCl etching), the carbon has a very high surface area (~1527 m$^2$/g) and pore volume (~3.63 cm$^3$/g). Such metal nanoparticle embedded multi-modal carbons could be used as electrocatalyst for oxygen reduction reaction, where the high surface area and pore volume would ensure easy electrolyte accessibility to the metal nanoparticle surface as well as large electro-sorption area. Also they could be used as magnetically recoverable sorbents for water purification application. The ZnCl$_2$ salt, not only helps in generating high surface area by producing secondary micropores and mesopores, but because ZnCl$_2$ boils off at the kind of carbonization temperatures used in this synthesis, it eliminates the need for acid washing. It is important to avoid post-
synthesis acid washing as it can also cause etching of the metal (Cobalt in this case) nanoparticles.

**Table 4.1:** Surface characteristic of the various synthesized porous carbons

<table>
<thead>
<tr>
<th>Synthesis Procedure</th>
<th>Sample</th>
<th>BET Surface Area (m²/g)</th>
<th>N₂ adsorption pore volume (cm³/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vacuum assisted drying</td>
<td>Salt templating alone</td>
<td>PC 0-0-2</td>
<td>2062</td>
</tr>
<tr>
<td></td>
<td>Hard templating alone</td>
<td>PC 4-1-0</td>
<td>1457</td>
</tr>
<tr>
<td></td>
<td></td>
<td>PC 22-1-0</td>
<td>979</td>
</tr>
<tr>
<td></td>
<td>Combined salt templating-hard templating</td>
<td>PC 4-1-2</td>
<td>2013</td>
</tr>
<tr>
<td></td>
<td></td>
<td>PC 22-1-2</td>
<td>2096</td>
</tr>
<tr>
<td>Heat assisted drying</td>
<td>Hard templating alone</td>
<td>PC 4-1-0</td>
<td>1257</td>
</tr>
<tr>
<td></td>
<td></td>
<td>PC 22-1-0</td>
<td>865</td>
</tr>
<tr>
<td></td>
<td>Combined salt templating-hard templating</td>
<td>PC 4-1-2</td>
<td>1954</td>
</tr>
<tr>
<td></td>
<td></td>
<td>PC 22-1-2</td>
<td>1846</td>
</tr>
<tr>
<td>Combined Hard Templating-Salt Templating-Physical Activation</td>
<td>PC 4-1-2-10</td>
<td>1908</td>
<td>4.30</td>
</tr>
<tr>
<td></td>
<td>PC 4-1-2-17</td>
<td>2517</td>
<td>4.26</td>
</tr>
<tr>
<td></td>
<td>PC 4-1-2-25</td>
<td>2404</td>
<td>3.55</td>
</tr>
<tr>
<td></td>
<td>PC 22-1-2-17</td>
<td>2579</td>
<td>3.57</td>
</tr>
<tr>
<td>Combined hard templating-salt templating with low temperature carbonization (450 °C)</td>
<td>PC 22-1-2</td>
<td>2108</td>
<td>3.24</td>
</tr>
</tbody>
</table>

Where in PC x-y-z-α, x represents the average colloidal silica size (nm) and y (=0 or 1) represents the mass ratio of silica to glucose, and z (= 0 or 2) represents the mass ratio of ZnCl₂ to glucose, α represents the flow rate for CO₂ gas for the physically activated samples. All sample solutions were dried using vacuum unless indicated otherwise.
Figure 4.2: N$_2$ sorption isotherm and pore size distribution for porous carbons synthesized through (a, b) vacuum assisted drying, (c, d) direct carbonization (heat assisted drying).
Figure 4.3: N\textsubscript{2} sorption isotherm and pore size distribution for porous carbons synthesized using single-step, combined salt templating-hard templating-physical activation approach.

Figure 4.4: N\textsubscript{2} sorption isotherm and pore size distribution for porous carbons synthesized through low temperature carbonization
Another feature of the proposed synthesis technique is that it can be used for even producing tri-modal porous carbons. For this synthesis, first glucose was added to each colloidal silica solution such that the weight ratio of silica to glucose was 1:1. Then the two colloidal silica-glucose suspensions were mixed together, followed by addition of ZnCl₂ solution (1g/mL) such that the weight ratio of glucose to ZnCl₂ was 1:2. The silica-glucose-ZnCl₂ solution was then vacuum dried, carbonized at 450 °C, followed by ZnCl₂ and silica removal. The final tri-modal carbon sample has a BET surface area of 2076 m²/g and a total pore volume of 2.95 cm³/g. The tri-modal pore size distribution for PC-4/20-1-2 is shown in Figure 4.6(b).
Figure 4.6: (a) N\textsubscript{2} sorption isotherm and (b) BJH pore size distribution for a trimodal carbon synthesized using both 4 and 22 nm sized colloidal silica (as specified by the manufacturer).

4.3.2 Electrosorption Testing

Detailed electrosorption measurements were carried out to investigate: (i) the electrosorptive performance of the thus synthesized salt-hard templated multi-modal porous carbon (PC 22-1-2, which has the highest surface area among all the synthesized salt-hard templated carbons using vacuum drying), (ii) the effect of electrode fabrication pressure on its electrosorption behavior. For understanding the effect of electrode fabrication pressure, three different electrosorption performance assessment measures are considered. First is the specific capacitance of the electrode as a function of increasing current density. Both, the absolute value of the materials’ specific capacitance as well as its retention as a function of increasing current density are considered. The capacitance is an indirect indicator of the amount of salt sorbed within the pores. It is important to note that for CDI, to achieve faster sorption, high current densities need to be used, that is why
capacitance retention measurement at high current densities is relevant. Second is the energy efficiency of the charging cycle, i.e. how much of the electrical energy supplied gets actually used for electrosorption. Third is the evolution of the EIS spectra for the electrode as a function of pressure applied during electrode fabrication. The contribution of different electrode components to the overall resistance as well as capacitive frequency response for the various electrodes as a function of electrode fabrication pressure are also evaluated. All the tests were carried out in three different configurations – pressed in the presence of 0.25M NaCl solution, pressed in the presence of MQ water and pressed under dry conditions.

Figure 4.7(a) shows the variation of specific capacitance as a function of current density for PC 22-1-2 for varying pressures applied during electrode manufacturing. There are two important things to note from Figure 4.7(a). First, for the lowest current density measured, i.e. 0.5 A/g, under various electrode pressing conditions, the specific capacitance increases only marginally with increasing electrode fabrication pressure. This can be explained on the following basis. Low current density implies slow charge-discharge conditions. And low fabrication pressure implies low electrolyte filling, which consequently increases with increased fabrication pressure. Thus, at low current densities, in spite of the low electrolyte filling (at low electrode fabrication pressure), there is enough time for the electrolyte to diffuse in the big mesopores produced from hard templating, as well as the secondary micropores and borderline mesopores produced from salt templating. Thus, the capacitance improvement with increased electrolyte filling (with increased electrode fabrication pressure) is only marginal in the case of PC 22-1-2,
as most of the pores are easily accessible through diffusion alone. Secondly, at high current density or fast charge-discharge conditions, the electrolyte diffusion is not fast enough to warrant complete area utilization offered by even the big size mesopores. Thus, increased electrolyte filling with increased electrode fabrication pressure leads to an increase in capacitance for PC 22-1-2, associated with the reduced diffusion lengths and diffusion timelines. Thus, capacitance retention shown in Figure A.7 (defined as ratio of capacitance value at any current density to capacitance value measured at lowest current density) increases with increased electrolyte filling within the pores.

Figure 4.7(b) shows the energy efficiency of the charge cycle, calculated using equation 2, as a function of increasing pressure applied during electrode fabrication, under the three different pressing conditions. An important thing to note from Figure 4.7(b) is that the energy efficiency increases with increasing electrode fabrication pressure, reaching to a maximum value at an optimum pressure, after which it starts falling. The charge cycle energy efficiency increases as a result increase in energy stored during charging. The energy stored during charging increases as a result decrease in ohmic drop during charging which is a result of decrease in resistance with increasing electrode fabrication pressure. The existence of an optimum pressure beyond which the cycle efficiency starts falling can be easily explained on the basis of collapse of big size pores beyond a certain electrode fabrication pressure.189

The EIS results for electrodes prepared by pressing in the presence of electrolyte, MQ water and dry conditions, at increasing pressure are presented in Figure 4.7(c, d, e).
The break-up of the total resistance \( R_t = \Delta V_{ohm,d} / I \), where \( \Delta V_{ohm,d} \) is the ohmic drop during discharging, computed from the galvanostatic charge-discharge curves, into different components is presented in Figure 4.7(f, g, h). The total resistance can be divided into two main components – (i) \( R_s \) - series resistance comprising of electrolyte resistance, intrinsic resistance of carbon film, contact resistance at the interface of carbon film/current collector,\(^{183}\) (ii) \( R_i \) – ionic resistance attributable to ion migration within the carbon film and carbon pores. The series resistance, \( R_s \), is given by the first intersection point of the Nyquist spectrum in the high-frequency region. The ionic resistance, \( R_i \), is basically the difference between total resistance \( (R_t) \) and series resistance \( (R_s) \). An important thing to note from the resistance break-up plot is that the ion migration resistance decreases with increase in pressure. This again could be attributed to the increased filling of electrolyte within the pores as a result of applying increasing pressure during electrode fabrication. Increased electrolyte filling results in reduced diffusion length and time required for ion migration to the pore wall for forming the electrochemical double layer, thus resulting in low ionic resistance. Apart from analyzing the resistive behavior, the impedance spectra can also be used to determine the capacitive response as a function of modulation frequency. A sample normalized capacitive frequency response (calculated using equations 4, 5, 6) for electrode pressed in the presence of electrolyte is given in Figure A.8. The frequency at which the normalized capacitance becomes half, for the various electrode fabrication configurations, is given in Figure 4.7(i). As can be seen in Figure 4.7(i), the frequency corresponding to 50% capacitance retention, increases with increase in electrode fabrication pressure, as a result
of higher utilization of the available area as a result of increased electrolyte filling, in line with the results from the GCD measurements.

As mentioned before, all the tests were carried out in three different configurations – pressed in the presence of 0.25M NaCl solution, pressed in the presence of MQ water, pressed under dry conditions. Among the three pressing configurations, the electrosorptive performance is the highest for pressing in the presence of electrolyte, followed by pressing in the presence of MQ water, followed by pressing under dry conditions. Although, application of pressure ensures better electrosorption, but it would also result in higher energy/operational costs as well, because of the need to apply continuous pressure or compression on the electrode assembly. For such systems, it is proposed that the pores be at the least filled once with the solvent medium (in this case MQ water). Then when such electrodes (with MQ water filled within the carbon pores) come in contact with the electrolyte solution, the ion diffusion into the solvent filled pores becomes enhanced due to concentration gradient, same as the ion diffusion in bulk, higher than ion diffusion in air filled pores. The electrodes prepared by dry press procedure, exhibit both low capacitance as well as high resistance leading to poor electrosorption performance. The break-up of resistance into different components suggests that $R_e$ is almost the same for all three pressing configurations. Whereas, $R_i$ is slightly lower for the electrolyte pressing case as compared to the MilliQ pressing case, resulting in its slightly superior electrosorption performance, probably because of the presence of ions within the carbon particles and carbon pores for the electrolyte press case. On the other hand, the ions need to diffuse through the solvent, present between the
carbon particles and within carbon pores, for the MilliQ press case. The \( R_i \) for the electrolyte press case as well as the MilliQ press case is much lower than the dry press case. This can be easily explained on the basis of diminished ion diffusion through the compact carbon particles and within empty carbon pores for the dry press case.

4.4 Conclusions

In summary, this work reports a novel low energy intensity, single-step, one-pot approach to synthesize multi-modal porous carbons, which combine meso- and microporosity in a simple material platform. Our approach integrates salt templating with hard templating to produce multi-modal porous carbons with high surface areas, and large pore volumes. The technique offers tight control and tunability of mesoporosity. The superior flexibility of the proposed synthesis technique was also demonstrated by carrying out example synthesis involving (i) use of multiple salt templates resulting in the synthesis of metal nanoparticle embedded high surface area multi-modal carbons, (ii) use of multiple hard templates resulting in tri-modal carbons, (iii) low temperature (450 °C) carbonization afforded by the presence of Lewis acid salt (such as ZnCl\(_2\)), (iv) ease of combination with physical activation approaches. The synthesized multi-modal carbons show good performance as electrode materials for electrosorption or capacitive deionization, wherein, pressure applied during electrode fabrication was also found to play a favorable role towards enhanced electrosorption.
Figure 4.7: Electrode fabrication pressure dependent variation of (a) specific capacitance, (b) Cycle energy efficiency, (c, d, e) EIS spectrum, (f) total resistance (Rt), (g) series resistance (Rs), (h) ionic resistance (Ri), (i) capacitive frequency response (frequency corresponding to 50% capacitance retention, calculated from the EIS measurement), for electrodes pressed in the presence of electrolyte, MilliQ and under dry
condition for varying pressure applied during electrode fabrication. The electrodes were made with the previously determined best performing PC 22-1-2 and measurements were performed with 0.25M NaCl electrolyte.
CHAPTER 5. FACILE STRATEGY FOR IMPROVING STABILITY OF PHOTOELECTRODE: CARBON LAYER PROTECTED CUPROUS OXIDE NANOWIRE ARRAYS FOR EFFICIENT WATER REDUCTION

(Paper published in ACS Nano)\textsuperscript{193}

5.1 Introduction

Since the pioneering work by Honda and Fujishima,\textsuperscript{194} enormous efforts have been focused on exploring suitable semiconductor materials as efficient photoelectrodes in photoelectrochemical (PEC) water splitting system for hydrogen generation. Within a PEC water splitting cell, the equilibration of the semiconductor's Fermi level with the redox potential of the electrolyte solution results in a band bending and thus generation of an electrical field, which drives the photogenerated minority charges from the semiconductor (i.e., electrons for a p-type semiconductor and holes for an n-type semiconductor) toward the semiconductor/water interface, where water is either oxidized to oxygen with n-type semiconductor (photoanode) or reduced to hydrogen with p-type semiconductor (photocathode).\textsuperscript{195-199} In terms of hydrogen generation, p-type semiconductors are advantageous over n-type ones. The electrons can be directly injected into the electrolyte on the p-type semiconductors, and thus directly reduce water to hydrogen at the p-type semiconductor/water interface while with n-type semiconductors, the photo-generated electrons have to migrate through an external circuit before being utilized for water reduction on the counter electrode, which involves a potential energy loss.\textsuperscript{200-203}

Unfortunately, of the current known natural crystal structures of semiconductors, p-type ones are much less than n-type (e.g., \(\text{TiO}_2\), \(\text{ZnO}\), \(\text{Fe}_2\text{O}_3\), \(\text{WO}_3\)).\textsuperscript{204-209} As one of the few metal oxides that naturally show p-type conductivity,\textsuperscript{210} cuprous oxide (\(\text{Cu}_2\text{O}\)) is thought of by many as
the most promising candidate as efficient photocathode material for the following reasons: (1) it has a band gap of \( \sim 2.0 \) eV, which guarantees efficient visible light absorption;\(^{211,212}\) (2) its conduction band lies 0.7 eV negative of the hydrogen evolution potential, which allows Cu\(_2\)O to drive off water reduction reaction as photocathode;\(^{213}\) \(^{41}\) (3) the natural abundance of copper on earth crust makes the large-scale fabrication of Cu\(_2\)O photoelectrode potentially competitive.

However, the practical application of Cu\(_2\)O in PEC process is still limited by two main drawbacks: (1) its mismatch of the intrinsic carrier diffusion length (usually 20-100 nm)\(^{214,215}\) with the light absorption depth near the band gap (approximately 10 \( \mu \)m);\(^{216}\) and (2) its poor stability due to self-photocorrosion in electrolyte solution.\(^{217}\)

One-dimensional (1-D) nanostructures (e.g., nanowire, nanorod, nanotube) are known to have the capability of independently modulating semiconductor's actual carrier diffusion length and light absorption depth and have been emerging as a promising solution to the problem of the mismatch between short carrier diffusion length and long light absorption depth, which commonly occurs with many semiconductors.\(^{205,218-221}\) The synthesis of 1-D Cu\(_2\)O was not reported until recently when Li’s group\(^{222}\) synthesized Cu\(_2\)O nanowires with a chemical oxidation method, and when Reisner’s group reported fabrication of Cu\(_2\)O nanowires via electrochemical anodization.\(^{44}\) On the other hand, it has been identified that the Cu\(_2\)O photocorrosion occurs at the Cu\(_2\)O/electrolyte interface, so protective layer coating naturally comes as a rational strategy to keep the semiconductor from directly contacting the electrolyte solution.\(^{40,41,44}\) For this strategy to be successful, the protective layer must meet the following criteria: (1) it must be dense enough so that it can block the aqueous electrolyte solution from accessing the semiconductor surface; (2) it must be thin enough so that it does not negatively
interfere with the light absorption of the semiconductor; (3) it must be conductive so that it can transmit minority carriers from the semiconductor into the electrolyte solution.

Although significant research efforts have been invested in coming up with a scalable, facile, cheap, and environmental friendly method to synthesize coating-layer protected and thus highly stable Cu$_2$O based photocathode, they are met only with limited success. Recently, Paracchino et al. made a considerable stride in increasing Cu$_2$O photocathode's resistance to photocorrosion through atomic layer deposition of multiple protective layers, but the inherent complexity of the fabrication process significantly limits its possibility of scaling up.$^{40,41}$ Our group also reported an in situ Cu$_2$O protection strategy with CuO film as a protective layer, but it is not suitable for 1-D nanostructures.$^{45}$ Also a spin-coating based procedure for coating a layer of metal oxide co-catalyst (NiO-Ni(OH)$_2$) on pre-synthesized Cu$_2$O was also suggested recently for improving the photostability of Cu$_2$O photocathode.$^{44}$

Carbon material is known to have superior conductivity, non-toxicity, and high strength and the feasibility of solution-based carbon precursor inspires the idea of forming a thin carbon coating layer on 1-D nanostructures to protect otherwise non-stable semiconductor-based photoelectrode.$^{35,223}$ In this study, we propose and demonstrate a solution based carbon precursor coating (i.e., glucose solution) combined with subsequent carbonization to be an effective strategy to form a thin protective carbon layer on radial Cu$_2$O nanowire arrays (NWAs). The Cu$_2$O NWAs were grown in situ during the carbonization/annealing step from Cu(OH)$_2$ NWAs which are synthesized directly on a Cu mesh using electrochemical anodization method. The thus-synthesized material serves as an efficient and extraordinarily stable photocathode for PEC
water splitting. Also since the protective layer is a metal/co-catalyst free pure carbon layer, coated using a simple solution based approach instead of costly vapor deposition, it makes the overall synthesis highly cost effective and easily scalable. We believe the proposed approach has the potential to address the stability issue of many non-stable photoelectrodes, and thus can make a significant contribution in the field of energy conversion.

5.2 Experimental Section

5.2.1 Preparation of C-x-/Cu NWAs/Cu mesh photocathode

The Cu mesh (Alfa Aesar, 100 mesh, 0.11 mm as wire diameter) was anodized in an alkali solution (3 M NaOH) for 30 min under 10 mA cm\(^{-2}\) to form Cu(OH)\(_2\) NWAs/Cu mesh. The temperature of the electrochemical cells was maintained at 25 °C for all experiments. The as-anodized Cu(OH)\(_2\) NWAs/Cu mesh was annealed at 550°C at N\(_2\) atmosphere for 4 hour with or without glucose coating. The glucose solution was prepared using deionized water only.

5.2.2 Structural Characterization

The morphologies of the C-x-/Cu NWAs/Cu mesh photocathodes were characterized by scanning electron microscopy (SEM, FEI, Quanta 600) and transmission electron microscope (TEM, Tecnai T12). The crystalline structure of the samples was analyzed by X-ray diffraction (XRD) (Bruker D8 Discover diffractometer, using Cu Kα radiation (1.540598 Å)). The chemical compositions and status were analyzed by X-ray Photoelectron Spectroscopy (XPS) with an Axis Ultra instrument (Kratos Analytical) under ultrahigh vacuum (<10\(^{-8}\) torr) and by using a monochromatic Al Kα X-ray source. The adventitious carbon 1s peak was calibrated at 285 eV and used as an internal standard to compensate for any charging effects. The diffuse reflectance
UV-vis adsorption spectra were recorded on spectrophotometer (Shimadzu, UV 2550), with fine BaSO$_4$ powder as reference. All digital photos were taken by a Cannon EOS 7D.

5.2.3 Photoelectrochemical measurements

The PEC performance of the prepared C-x-/Cu NWAs/Cu mesh photocathodes were evaluated using a three-electrode configuration with C-x-/Cu NWAs/Cu mesh, Ag/AgCl, and Pt gauze as working electrodes, reference electrode, and counter electrode, respectively. The electrolyte used was 1.0 M Na$_2$SO$_4$ solution. The photoresponse of the prepared photoelectrodes was measured under a chopped irradiation from a 300 W Xe lamp (PLS-SXE300) (light on/off cycle: 5 s). The intensity of light source was calibrated with a Si diode (Newport) to simulate AM 1.5 illumination (100 mW cm$^{-2}$). The scan rate for the linear sweep voltammetry was 2 mV s$^{-1}$. The PEC stability of the materials was evaluated by measuring the photocurrent densities produced under chopped light irradiation (light on/off cycles: 10 s) at a fixed electrode potential of 0 V vs RHE. The impedance measurements were performed using a PGSTAT302N Autolab Potentiostat/Galvanostat (Metrohm) equipped with a frequency analyzer module (FRA2). The electrochemical impedance spectra were done at an excitation signal of 10 mV amplitude. The impedance vs frequency spectra were acquired at fixed sample potentials. Afterward, impedance vs potential measurement at fixed frequencies of 5k Hz was performed.
5.3 Results and Discussion

Figure 5.1: Photocathode design and synthesis strategy of C/Cu$_2$O NWAs/Cu mesh: (a) electrochemical anodization of Cu mesh in 3 M NaOH solution; (b) Cu(OH)$_2$ NWAs on the Cu mesh; (c) glucose coating on the Cu(OH)$_2$ NWAs; (d) carbonization of the glucose; (e) carbon layer protected Cu$_2$O NWAs. (I) Cu(OH)$_2$ NW; (II) glucose layer on the Cu(OH)$_2$ NW surface; and (III) carbon layer protected Cu$_2$O NW.

Figure 5.1 presents the design and synthesis strategy of the carbon layer protected Cu$_2$O NWAs on Cu mesh (C/Cu$_2$O NWAs/Cu mesh) as a photocathode. Cu mesh was selected as the base material for the photocathode based on the following considerations: (1) it is a conductive substrate; (2) it can serve as a precursor of Cu$_2$O NWA directly; (3) the unique open area of the mesh benefits the flow of electrolyte and the mesh structure provides extra lateral surface in comparison to a Cu sheet/foil.$^{224,225}$ The Cu mesh (100 mesh with the wire diameter being 0.11 mm, Figure A.10) was first electrochemically anodized with a galvanometric model in 3 M NaOH aqueous solution (Figure 5.1(a)). The galvanometric anodization curve, with a constant current density of 10 mA cm$^{-2}$, is presented in Figure A.11. Under these anodization conditions, uniform Cu(OH)$_2$ NWAs were formed on the Cu mesh surface (Figure 5.1(b)). Although CuO is p-type semiconductor, unlike Cu$_2$O, it cannot be employed as photocathodes for hydrogenation because their conduction band edges are more positive than the H$^+/H_2$ reduction potential and H$_2$
formation is therefore thermodynamically unfavorable.\textsuperscript{226,227} In view of the desirable 1-D NWA structure, it is imperative to maintain the NWA architecture of the anodized Cu(OH)$_2$/Cu mesh while converting it to Cu$_2$O. In the current synthesis, a solution-based glucose coating of the Cu(OH)$_2$ NWAs/Cu mesh (Figure 5.1(c)) and subsequent annealing of the glucose/Cu(OH)$_2$ NWAs/Cu mesh under inert environment (Figure 5.1(d)) was applied to achieve the delicate conversion of the Cu(OH)$_2$ to Cu$_2$O along with the simultaneous formation of a thin carbon film as a protective layer (Figure 5.1(e)). In more detail, the anodized Cu(OH)$_2$ NWAs/Cu mesh was first soaked into an aqueous glucose solution, dried at ambient condition, and then annealed at 550 °C in N$_2$ atmosphere to form carbon layer coated Cu$_2$O NWAs. The concentration of the glucose solution was varied so as to control the thickness of the final carbon layer on the Cu$_2$O NWAs. For the convenience of discussion, we denote the carbon layer coated Cu$_2$O NWAs/Cu mesh samples with C-x-/Cu$_2$O NWAs/Cu mesh, where x represents the glucose solution concentration (mg ml$^{-1}$). The conversion of Cu(OH)$_2$ to Cu$_2$O is presumably achieved by dehydration of Cu(OH)$_2$ to CuO, followed by removal of oxygen from the lattice of CuO to form Cu$_2$O at high temperature in inert N$_2$ atmosphere.\textsuperscript{228,229} At the early stage of the annealing, the glucose dehydrates and crosslinks, and as the reaction continues, aromatization and carbonization take place, resulting in a firm carbonized shell covering the NW surfaces, which protects and guarantees the integrity of the original morphology of the starting Cu(OH)$_2$ NWAs.

This synthesis procedure is simple and facile and, due to its solution based carbon precursor coating process, it can be employed to nanostructures with other morphologies as well. The rationally designed and synthesized C/Cu$_2$O NWAs/Cu mesh is expected to work as an efficient and stable photocathode for water splitting application because (1) the Cu$_2$O NWAs
with a high surface area provide more contact with electrolyte, (2) their high aspect ratio facilitates carrier diffusion, and (3) the carbon layer (Figure 5.1-III) serves as a protective film, preventing the electrolyte from contacting Cu$_2$O NWAs, (4) the carbon layer also inhibits electron hole recombination,\textsuperscript{230,231} facilitating electron transfer into the electrolyte solution where H$_2$ is generated.

**Figure 5.2:** Digital photographs, scanning electron microscopy and transmission electron microscopy images of the Cu(OH)$_2$ NWAs/Cu mesh (a1-a6); Cu$_2$O NWAs/Cu mesh (b1-b6); and C-3-/Cu$_2$O NWAs/Cu mesh (c1-c6).

Figure 5.2 a, b, and c present the digital photographs, scanning electron microscopy (SEM) and transmission electron microscopy (TEM) images of the Cu(OH)$_2$ NWAs/Cu mesh, Cu$_2$O NWAs/Cu mesh without carbon layer, and C-3-/Cu$_2$O NWAs/Cu mesh. The digital photograph of the Cu(OH)$_2$ NWAs/Cu mesh (Figure 5.2(a1)) showed a blue color, which agrees well with the typical color of Cu(OH)$_2$. Both X-ray diffraction (XRD) (Figure A.12) and X-ray photoelectron spectroscopy (XPS) (Figure A.13) measurements also confirmed the pure Cu(OH)$_2$ phase, with no Cu$_2$O and CuO being identified. The SEM images in Figure 5.2(a2-a5) show that the Cu mesh substrate was uniformly covered with a dense layer of the Cu(OH)$_2$ NWAs. Annealing the naked (i.e., nonprotected) Cu(OH)$_2$ NWAs/Cu mesh in N$_2$ atmosphere at
550°C converted it to Cu$_2$O NWAs/Cu mesh, which showed a shiny red color (Figure 5.2(b1)), while for the glucose/Cu(OH)$_2$ NWAs/Cu mesh (Figure 5.1-II), the annealing under otherwise same conditions produced C-x-/Cu$_2$O NWAs/Cu mesh, which showed a dark red color as exemplified by the C-3-/Cu$_2$O NWAs/Cu mesh (Figure 5.2(c1)).

The SEM images (Figure 5.2(c2-c5)) and TEM image (Figure 5.2(c6)) of the C-3-/Cu$_2$O NWAs/Cu mesh clearly show that there were no significant morphological changes and the NWA structure remained during the annealing process. More importantly, the C-3-/Cu$_2$O NWAs/Cu mesh showed smooth surfaces with no obvious fractures (Figure 5.2(c6)), which stood in a sharp contrast with the Cu$_2$O NWAs/Cu mesh whose images showed abundant presence of isolated fractures (Figure 5.2(b4-b6)), which would be very undesirable for PEC application of Cu$_2$O given its already high tendency toward photocorrosion. The comparison implies that the carbon layer helps to keep the integrity of NWAs during the annealing presumably due to the high strength of the carbon layer. The cross-sectional SEM image of the C-3-/Cu$_2$O NWAs/Cu mesh in Figure A.14 reveals that the length of the Cu$_2$O NWs was around 7~10 μm, which is close the Cu$_2$O's maximum light absorption depth near the band gap (approximately 10 μm), and thus guarantees an efficient light absorption. As mentioned previously, the thickness of the carbon layer of the C-x-/Cu$_2$O NWAs/Cu mesh can be easily tuned simply by varying the starting glucose concentration. A series of the C-x-/Cu$_2$O NWAs/Cu mesh samples were prepared with different glucose concentrations (i.e., 1, 2, 3, 4, 5, 10 mg ml$^{-1}$) and clearly all of the C-x-/Cu$_2$O NWAs/Cu mesh samples showed much better integrity of the original NWA structure than non-carbon protected Cu$_2$O NWAs/Cu mesh (Figure 5.2 and Figure A.15).
It is noted that the C-x-/Cu$_2$O NWAs/Cu mesh samples prepared at low glucose concentrations (*i.e.*, 1 and 2 mg ml$^{-1}$) showed some fractures on the carbon surfaces (Figure A.15(a, b)) while any further increase of the glucose concentration beyond 2 mg ml$^{-1}$ led to continuous carbon coatings on the NWAs surfaces with no fractures visible (Figure 5.2(c), Figure A.15(c-e)). These results suggest that the minimum glucose concentration for forming a continuous carbon coating layer in the current system is 3.0 mg ml$^{-1}$. The relationship between the glucose concentrations and average carbon layer thickness, calculated based on the TEM measurements, is summarized in Figure 5.3, which clearly shows that the average carbon layer thickness increased with increasing glucose concentration, in an almost linear manner.

Figure 5.3(b) shows the XRD pattern of the C-3-/Cu$_2$O NWAs/Cu mesh. As can be seen, besides three peaks for elemental Cu coming from the Cu mesh substrate, others are all attributed to Cu$_2$O phase with a strong (111) orientation, without CuO or Cu(OH)$_2$ being identified. The XPS of C 1s core level for the C-3-/Cu$_2$O NWAs/Cu mesh sample is presented in Figure 5.3(c). The experimental curves were well fitted with Gauss peaks model after Shirley background subtraction. The strong C-C peak at 285.0 eV implies the formation of a carbon layer on the Cu$_2$O NWAs surface while the much lower intensity of C-O, O-C=O and CO$_3^{2-}$ peaks are attributed to the left over oxygen functional groups within the carbon layer. From XPS measurement, no evidence was observed for the formation of Cu-C bond and elemental Cu was not detected in the NWAs (Figure A.16).
The optical properties of the Cu$_2$O NWAs/Cu mesh and C-3-/Cu$_2$O NWAs/Cu mesh were measured using UV-vis diffuse reflectance spectra (DRS) and are presented in Figure 5.3(d). Compared with the Cu$_2$O NWAs/Cu mesh (red solid line in Figure 5.3(d)), the C-3-/Cu$_2$O NWAs/Cu mesh (black dashed line in Figure 5.3(d)) showed an enhanced absorption in the long wavelength region ranging from 600 to 800 nm, which is due to the strong absorption of the carbon layer in this region and which agrees well with the color change of the samples (Figure 5.2(b1, c1)). However, a decreased absorption in the short wavelength region ranging from 300
to 600 nm was also observed, which implies the carbon layer reduces the optical absorption of the Cu$_2$O NWAs to some extent within this range. This phenomenon was observed on all C-x-/Cu$_2$O NWAs/Cu mesh samples prepared in this study, with thicker carbon layers leading to higher reduction in optical absorption of the Cu$_2$O NWAs within the short wavelength region, to which Cu$_2$O is photocatalytically responsive due to its band gap (Figure A.17). Thus, from a combined viewpoint of lower light absorption (in short wavelength region) for thicker carbon coatings and surface fractures for thinner carbon coatings, there seems to exist an optimal carbon thickness which would give maximum PEC performance for such carbon layer coated Cu$_2$O NWAs photoelectrode.

The DRS measurements were transformed using the Kubelka-Munk function and plotted against the energy of light (inset in Figure 5.3(d)), from which the same band gap values of 2.03 eV for the Cu$_2$O NWAs/Cu mesh and C-3-/Cu$_2$O NWAs/Cu mesh were estimated, indicating that no band gap narrowing occurred with the carbon layer coating and thus implying that there was no carbon elements doped into the Cu$_2$O lattice. The results agree well with the results from the XPS measurement.

To evaluate the PEC performances of the Cu$_2$O NWAs/Cu mesh and C-x-/Cu$_2$O NWAs/Cu mesh photocathodes, linear sweep voltammetry (LSV) measurements were performed in 1 M Na$_2$SO$_4$ electrolyte under AM 1.5G (100 mW cm$^{-2}$) illumination using a three-electrode electrochemical system, with the Cu-mesh based photoelectrode, Ag/AgCl electrode, and Pt mesh as working electrode, reference electrode, and counter electrode, respectively. During the LSV scan, the illumination was chopped with a frequency of 0.2 Hz so that the dark and the light
Figure 5.4: Photoelectrochemical performance of (a1) the Cu$_2$O NWAs/Cu mesh and (b1) C-3-/Cu$_2$O NWAs/Cu mesh under illumination of chopped AM 1.5G (light on/off cycle: 5 s), the insets in (a1) and (b1) plotted the photoconversion efficiencies vs applied bias potentials for Cu$_2$O NWAs/Cu mesh and C-3-/Cu$_2$O NWAs/Cu mesh respectively, and respective photocurrent density decay at 0 V vs RHE in chopped light illumination (light on/off cycle: 10 s) for stability evaluation (a2,b2).

currents could be simultaneously monitored. It is worth mentioning that in the field of water splitting, the photocurrent going through external circuit is widely used as a reliable surrogate for hydrogen and oxygen gas measurement in evaluating the performance of various semiconductors, including Cu$_2$O.$^{222,239-242}$ The results show that the C-3-/Cu$_2$O NWAs/Cu mesh photocathode generated a photocurrent density of -3.95 mA cm$^2$ (Figure 5.4(a1)) at 0 V vs reversible hydrogen electrode (RHE) (the potential often chosen as a metric to evaluate the
performance of photocathode as it corresponds to the water reduction potential),\textsuperscript{44,243,244} which is the highest among all samples tested in this work. To the best of our knowledge, this value is the highest ever reported for Cu$_2$O materials without the use of any co-catalyst,\textsuperscript{45,245} and it is much higher than -2.28 mA cm$^{-2}$ generated on the bare Cu$_2$O NWAs/Cu mesh (Figure 5.4(b1)). A digital photo of hydrogen gas bubbles generated on the C-3-/Cu$_2$O NWAs/Cu mesh photocathode is presented in Figure A.18. A possible mechanism for the improved photocurrent density on the C-3-/Cu$_2$O NWAs/Cu mesh photocathode will be presented in a latter section.

The photoconversion efficiencies of the Cu$_2$O NWAs/Cu mesh and C-3-/Cu$_2$O NWAs/Cu mesh photocathodes were calculated with the equation of $\eta = J_{P_{max}}V_{P_{max}}/P_{in}$,\textsuperscript{196,246} where $J_{P_{max}}$ and $V_{P_{max}}$ are the current density (mW cm$^{-2}$) and photovoltage (V vs. RHE) at the maximum power point and $P_{in}$ (mW cm$^{-2}$) is the incoming light flux (100 mW cm$^{-2}$ in our case). The insets in Figure 5.4 (a1, b1) present the plots of the photoconversion efficiencies vs applied bias potentials for the Cu$_2$O NWAs/Cu mesh and C-3-/Cu$_2$O NWAs/Cu mesh photocathodes respectively. The Cu$_2$O NWAs/Cu mesh exhibited an optimal conversion efficiency of 0.28% while the C-3-/Cu$_2$O NWAs/Cu mesh achieved a much higher optimal conversion efficiency of 0.56\% at the potential of 0.21 V vs RHE.

The PEC performances of all C-x-Cu$_2$O NWAs/Cu mesh samples are presented in Figure A.19 and summarized in Figure 5.5. The photocurrent densities of the C-x-/Cu$_2$O NWAs/Cu mesh first increased with increasing glucose concentrations and thus with increasing carbon layer thickness and reached a peak at the glucose concentration at 3 mg ml$^{-1}$ and at correspondingly carbon layer thickness of 20 nm (\textit{i.e.}, C-3-/Cu$_2$O NWAs/Cu mesh) before declining.
monotonically thereafter. The deteriorating PEC performance on the C-x-/Cu$_2$O NWAs/Cu mesh samples with thicker carbon layer can be ascribed to a stronger optical blocking by the carbon layers which reduces the light absorption of the Cu$_2$O NWAs within the wavelength range between 300-600 nm, as discussed earlier.

The stability of the photocathodes under illumination was evaluated with chronoamperometric measurements at 0 V vs RHE in chopped light with the same intensity and with a frequency of 0.1 Hz over 20 min, a condition which is widely used as a semi-standard for comparing photostability of semiconductor.$^{40,41,45}$ The photostability was quantified as the percentage of the photocurrent density at the end of the last light cycle ($J$) compared with that at the end of the first light cycle ($J_0$) within the 20 min measurement period.$^{40,41,45,210}$ As shown in Figure 5.5 and Figure A.19, all C-x-/Cu$_2$O NWAs/Cu mesh samples exhibited considerably improved photostability, increasing almost linearly with the carbon layer thickness before reaching a plateau at 80.7% with a carbon layer thickness of 20 nm (i.e., C-3-/Cu$_2$O NWAs/Cu mesh). A close comparison of the photocurrent density decay curves of the C-3-/Cu$_2$O NWAs/Cu mesh and Cu$_2$O NWAs/Cu mesh photocathodes is presented in Figure 5.4 (a2, b2). Compared with the photostability of only 12.6% for the non-carbon protected Cu$_2$O NWAs/Cu mesh photocathode, the C-3-/Cu$_2$O NWAs/Cu mesh photocathode showed a remarkably improved photostability of 80.7% (almost 600% increase). This demonstrates the protective role of the carbon layer coating and thus exemplifies that the carbon layer protection strategy is indeed an effective strategy for combating the photo-corrosion problem of unstable semiconductors. The photostability measurement was also performed for a longer period of time (i.e., 1 hour) and the results were presented in Figure A.20. As can be seen, after 1 hour illumination, the Cu$_2$O
NWAs/Cu mesh almost lost its photoactivity completely, while the C-3-/Cu$_2$O NWAs/Cu mesh maintained 75% of its original photoactivity. Furthermore, the SEM images of the Cu$_2$O NWAs/Cu mesh and C-3-/Cu$_2$O NWAs/Cu mesh after 1 hour illumination were presented in Figure A.21 and clearly some metallic copper particles were found on the surface of the Cu$_2$O NWAs/Cu mesh sample, but no copper particles could be identified on the C-3-/Cu$_2$O NWAs/Cu mesh sample, which partially confirms the enhanced photostability with the carbon protective layer.

**Figure 5.5:** Photocurrent densities (measured at 0V vs RHE) and photostability of the C-x-/Cu$_2$O NWAs/Cu mesh photoelectrodes as a function of glucose concentration and thus carbon layer thickness.

Increasing the carbon layer thickness beyond 20 nm didn’t result in any further improvement in photoelectrodes’ photostability and thus an optimal carbon thickness of 20 nm was identified in the current study (C-3-/Cu$_2$O NWAs/Cu mesh). And since among all the samples tested in this study, the C-3-/Cu$_2$O NWAs/Cu mesh gave the highest photocurrent density as well, it is the optimal photoelectrode for water splitting application.
The electrochemical impedance spectroscopy (EIS) is a powerful tool for studying material’s PEC properties.\textsuperscript{247} The EIS measurement was carried out covering the frequency of $10^5$–0.1 Hz interval using an amplitude of 10 mV at a bias potential of 0 V \textit{vs} RHE. Figure 5.6 presents Nyquist plots for the Cu$_2$O NWAs/Cu mesh and C-3-/Cu$_2$O NWAs/Cu mesh in dark and under illumination. It is known the semicircle in a Nyquist plot at high frequencies is characteristic of the charge transfer process and the diameter of the semicircle is equal to the charge transfer resistance (R$_{ct}$).\textsuperscript{248} The C-3-/Cu$_2$O NWAs/Cu mesh showed a lower R$_{ct}$ value than the Cu$_2$O NWAs/Cu mesh both in dark and under illumination, which is presumably due to the good conductivity of the carbon layer on the Cu$_2$O nanowire surface. The carbon layer thus facilitates the electron transfer from Cu$_2$O to the electrolyte, resulting in an overall reduced charge transfer resistance, which also explains the better PEC performance of the C-x-/Cu$_2$O NWAs/Cu mesh.

\textbf{Figure 5.6:} Nyquist plots ($Z_{re}$ vs. $Z_{im}$) for the Cu$_2$O NWAs/Cu mesh and C-3-/Cu$_2$O NWAs/Cu mesh photocathodes in dark and under illumination.
5.4 Conclusion

In this work, a facile strategy based on coating a thin protective carbon layer was proposed to combat the photo-corrosion problem of unstable semiconductors. The proof-of-concept test successfully showed that the thin carbon layer protected Cu$_2$O nanowire arrays not only exhibited remarkably improved photostability but also showed significantly improved water splitting performance.
CHAPTER 6. CONCLUSIONS AND FUTURE WORK

6.1 Conclusions

This dissertation work focused on developing synthesis techniques for producing multi-modal porous carbons and carbon layer coated metal oxide nanostructure composites for addressing important environmental and energy issues.

Overall, two major class of synthesis techniques were developed for producing multi-modal porous carbons, and these carbons were tested for three different environmental applications, in particular, CO$_2$ capture, reducing membrane fouling in wastewater reuse and capacitive deionization. The first synthesis approach integrates ice templating with hard templating and physical activation to produce HPCs with interconnected porous structure, large surface area, and pore volume. The technique offers tight control and tunability of porosity (macro- meso- and microscale) in terms of both size and extent. It also offers the ability to make HPC monoliths of desired shape and size. The hierarchical carbons thus synthesized showed excellent performance as sorbents for amine based CO$_2$ capture. The synthesized hierarchical porous carbons were also found to give exceptional irreversible fouling abatement for low pressure membranes used for pre-treatment in wastewater reuse. Comparison between coupled ice-hard templated hierarchical porous carbons and only hard templated mesoporous carbons revealed that macropores produced from ice templating play a favorable role towards biopolymer removal. Among the various carbons tested, the carbons with larger size mesopores and higher mesoporosity content gave higher biopolymer removal and fouling control. For HPCs, pre-
deposition of sorbents gave better biopolymer removal and thus better fouling control as compared to traditional sorbent-feed mixing approach. A novel ultra-low pressure membrane involving hierarchical porous carbon pre-deposited on a large pore size (0.45 μm) membrane support was also found to outperform the microfiltration ceramic membrane in terms of fast, energy efficient and high EfOM removal capacity.

The second synthesis technique for producing multi-modal porous carbons reported in this dissertation is a low energy intensity, single-step, one-pot approach, that integrates salt templating with hard templating to produce multi-modal (meso and micro) porous carbons with high surface areas, and large pore volumes. The technique offers tight control and tunability of mesoporosity. The superior flexibility of the proposed synthesis technique was demonstrated by: (i) using multiple salt templates resulting in the synthesis of metal nanoparticle embedded high surface area multi-modal porous carbons, (ii) using multiple hard templates resulting in tri-modal porous carbons, (iii) low temperature (450 °C carbonization afforded by the presence of Lewis acid salt (such as ZnCl₂)), (iv) ease of incorporation of physical activation step in the overall synthesis. The synthesized multi-modal porous carbons showed good performance as electrode materials for electrosorption or capacitive deionization, wherein, pressure applied during electrode fabrication was also found to play a favorable role towards enhanced electrosorption.

Another objective of this dissertation work was related to our group’s interest in developing protective coating layer for photoelectrochemical electrode materials. In this regard, the dissertation work explored the synthesis and effectiveness of a carbon layer protective coating for nanostructured cuprous oxide based photoelectrodes for water splitting. A solution-
based carbon precursor coating and subsequent carbonization strategy was proposed to form a thin protective carbon layer on Cu$_2$O nanowire array structure. A proof of concept was provided by using glucose as carbon precursor to form protective carbon coating onto cuprous oxide “Cu$_2$O” nanowire arrays which were synthesized from copper mesh. The carbon layer protected Cu$_2$O nanowire arrays exhibited remarkably improved photostability as well as considerably enhanced photocurrent density.

### 6.2 Future Work

1. For the ice templating-hard templating approach, although the tunability of the technique to control the mesoporosity was well established, the ability to play around with the macroporosity was not explored which could be the basis of future work. Similarly, for the amine based CO$_2$ capture part, only first generation PEI-HPC composites (involving PEI impregnated within HPCs) were tested. Future work could involve synthesis and testing of second generation composites involving PEI covalently bonded to carbon pore walls. The covalently bonded PEI could lead to enhanced cyclical CO$_2$ sorption performance because of reduced PEI evaporation upon regeneration.

2. For the membrane fouling project, a pilot scale study could be performed to determine the long term performance of pre-deposited HPC-Membrane hybrid systems. It would also help in figuring out any scale up issues associated with the proposed technology. Another interesting study could be to explore the effect of carbon material’s chemistry, in particular,
the effect of increasing its hydrophilicity, on its biopolymer removal and fouling reduction ability.

3. For the coupled salt-hard templating synthesis approach, it would also be useful to establish the effects of varying the silica/glucose and ZnCl$_2$/glucose mass ratios on the porosity of the thus synthesized carbons. For the CDI project, it would help to study the CDI performance using a full scale continuous flow set up rather than the batch set up, which for now was sufficient for exploring the effect electrode fabrication conditions on its electrosorption ability. Again the effect of carbon chemistry on its CDI performance would also be worth exploring.
Figure A.1: SEM images where the sample was cut and polished via microtome as described previously. The SEM images reveal (a) a fishbone like structure in the glucose-silica composite that is also seen in the (b) carbonized HPC material. HR-SEM images show (c) the macroporous walls of the glucose-silica hybrid material, in which the (d) colloidal silica can clearly be seen.
Figure A.2: TEM images of KCU-C x-y samples. Scale bars for all images are 200 nm for the larger images and 20 nm for the inset images. a) KCU-C 4-1 b) KCU-C 4-2 c) KCU-C 8-1 d) KCU-C 8-2 e) KCU-C 20-1 f) KCU-C 20-2.
Figure A.3: (a) N$_2$ sorption isotherms and (b) BJH pore size distributions, for KCU-C 4-1 samples that underwent physical activation for 0, 1, 3 and 4 hours at a CO$_2$ flow rate of 50 cc/min. The curves show how the 2-4 nm shoulder present in the KCU-C 4-1 sample increases with increased activation time. This increased shoulder correlates directly with the increased surface areas for increasing activation times seen in Table A.1 (below).

Table A.1: BET surface area and mesopore volume of KCU-C 4-1 samples under various physical activation times. As the activation times increase, the surface area and pore volume increase.

<table>
<thead>
<tr>
<th>Sample name</th>
<th>CO$_2$ activation time (h)</th>
<th>BET surface area (m$^2$/g)</th>
<th>N$_2$ adsorption pore volume (cm$^3$/g)</th>
</tr>
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<tbody>
<tr>
<td>KCU-C 4-1</td>
<td>0</td>
<td>1316</td>
<td>2.3</td>
</tr>
<tr>
<td>KCU-C 4-1-1</td>
<td>1</td>
<td>1703</td>
<td>2.6</td>
</tr>
<tr>
<td>KCU-C 4-1-3</td>
<td>3</td>
<td>1935</td>
<td>2.9</td>
</tr>
<tr>
<td>KCU-C 4-1-4</td>
<td>4</td>
<td>2096</td>
<td>3.0</td>
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Figure A.4: Filtration experiment set-up
Figure A.5: (a) N$_2$ sorption isotherm and, (b) pore size distribution based on N$_2$ sorption - for the various PCMs, before and after sorption (AS). The sorption test was carried out in batch mode with 30 mg/L PCM dose and a contact time of 24 hours.
Table A.2: Surface characteristic of PCMs

<table>
<thead>
<tr>
<th>PCM</th>
<th>Total Surface Area (m²/g)</th>
<th>% Surface Area available after sorption</th>
<th>Total Pore Volume (cm³/g)</th>
<th>% Pore Volume available after sorption</th>
<th>Pore Size Maxima Before Sorption (nm)</th>
<th>Pore Size Maxima After Sorption (nm)</th>
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<tbody>
<tr>
<td>SA Super</td>
<td>903±42</td>
<td>32</td>
<td>0.80±0.06</td>
<td>48</td>
<td>2.3</td>
<td>3.2</td>
</tr>
<tr>
<td>MPC-12</td>
<td>1206±40</td>
<td>69</td>
<td>3.52±0.10</td>
<td>77</td>
<td>15.0</td>
<td>14.7</td>
</tr>
<tr>
<td>MPC-4</td>
<td>1277±81</td>
<td>58</td>
<td>4.52±0.29</td>
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<tr>
<td>HPC-12</td>
<td>1364±37</td>
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<td>3.61±0.08</td>
<td>68</td>
<td>14.0</td>
<td>13.7</td>
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<tr>
<td>HPC-4</td>
<td>1173±91</td>
<td>60</td>
<td>4.32±0.22</td>
<td>74</td>
<td>36.0</td>
<td>35.0</td>
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</table>

Figure A.6: N₂ sorption isotherm and pore size distribution for porous carbons synthesized using hard templating alone and combined salt templating-hard templating. Two different colloidal silica solutions having silica nanoparticle size of 8 nm and 12 nm were used. For samples involving salt templating, a mass ratio of glucose:ZnCl₂ of 1:2 was used.
Table A.3: Surface characteristics of the porous carbons synthesized using colloidal silica solutions having silica nanoparticle size of 8 nm and 12 nm

<table>
<thead>
<tr>
<th>Synthesis Procedure</th>
<th>Sample</th>
<th>BET Surface Area (m$^2$/g)</th>
<th>N$_2$ adsorption pore volume (cm$^3$/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vacuum assisted drying</td>
<td>PC 8-1-0</td>
<td>1234</td>
<td>2.22</td>
</tr>
<tr>
<td></td>
<td>PC 12-1-0</td>
<td>1180</td>
<td>2.39</td>
</tr>
<tr>
<td>Hard templating alone</td>
<td>PC 8-1-2</td>
<td>1804</td>
<td>3.60</td>
</tr>
<tr>
<td>Combined salt templating-hard templating</td>
<td>PC 12-1-2</td>
<td>1816</td>
<td>3.53</td>
</tr>
</tbody>
</table>

Figure A.7: Variation of capacitance retention with current density for electrodes made with PC 22-1-2, for varying pressures applied during electrode fabrication. The electrodes were pressed in the presence of electrolyte, i.e., 1M H$_2$SO$_4$. 
Figure A.8: Sample normalized capacitive frequency response for PC 4-1-0 as a function of different pressures applied during electrode fabrication
Figure A.9: SEM images of electrodes pressed in the presence of electrolyte at various pressures (a) Before pressing, (b) Pressed at 2 bar, (c) Pressed at 4 bar, (d) Pressed at 6 bar. After pressing the electrodes were rinsed with MilliQ water to drain out the electrolyte, followed by drying under vacuum.
Figure A.10: (a) Digital photograph and (b) SEM image of the Cu mesh.
Figure A.11: Galvanometric anodization curve with a constant current density of 10 mA cm$^{-2}$ for the Cu mesh anodization

Figure A.12: XRD pattern of the Cu(OH)$_2$ NWAs/Cu mesh.
Figure A.13: XPS of survey (a), Cu 2p core level, and O 1s core level of the Cu(OH)$_2$ NWAs/Cu mesh.
Figure A.14: Cross-sectional SEM image of the C-3-/Cu$_2$O NWA/Cu mesh.

Figure A.15: SEM and TEM images of the C/Cu$_2$O NWAs/Cu samples prepared with different glucose concentrations: (a1-a6) 1 mg ml$^{-1}$; (b1-b6) 2 mg ml$^{-1}$; (c1-c6) 4 mg ml$^{-1}$; (d1-d6) 5 mg ml$^{-1}$; (e1-e6) 10 mg ml$^{-1}$. 
Figure A.16: (a) XPS survey of the C-3-/Cu₂O NWAs/Cu mesh, (b) core level of Cu 2p and (c) core level of O 1s.
Figure A.17: UV-visible diffuse reflectance spectra (DRS) of the Cu$_2$O NWAs/Cu mesh and C-x-/Cu$_2$O NWAs/Cu mesh.

Figure A.18: Digital photograph of hydrogen gas bubbles generated on the C-3-/Cu$_2$O NWAs/Cu mesh under illumination.
Figure A.19: PEC performances and stability measurement of (a1,a2) C-1-/Cu₂O NWAs/Cu mesh; (b1,b2) C-2-/Cu₂O NWAs/Cu mesh; (c1-c2) C-4-/Cu₂O NWAs/Cu mesh; (d1-d2) C-5-/Cu₂O NWAs/Cu mesh; (e1-e2) C-10-/Cu₂O NWAs/Cu mesh.
**Figure A.20:** Stability measurement (a) Cu$_2$O NWAs/Cu mesh and (b) C-3-/Cu$_2$O NWAs/Cu mesh under illumination of chopped AM 1.5G (light on/off cycle: 10 s) at 0 V vs RHE for 1 h.

**Figure A.21:** SEM images of the Cu$_2$O NWAs/Cu mesh (a1-a4), and C-3-/Cu$_2$O NWAs/Cu mesh (b1-b4) after 1 h photo-stability measurement under illumination of chopped AM 1.5G (light on/off cycle: 10 s) at 0 V vs RHE.
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