

University of Groningen

Design and Study of Pillared Graphenes and Nanoporous Carbon Materials for Energy, Environmental and Catalytic Applications

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DOI:
[10.33612/diss.192214050](https://doi.org/10.33612/diss.192214050)

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Document Version
Publisher's PDF, also known as Version of record

Publication date:
2021

[Link to publication in University of Groningen/UMCG research database](#)

Citation for published version (APA):
Thomou, E. (2021). *Design and Study of Pillared Graphenes and Nanoporous Carbon Materials for Energy, Environmental and Catalytic Applications*. University of Groningen. <https://doi.org/10.33612/diss.192214050>

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Chapter 1: Introduction

“Porous materials are like music: the gaps are as important as the filled-in bits.”¹

The technological evolution has led to breakthroughs that could never have been imagined a couple of decades ago, and at the same time has set the scientific community on a constant search for novel materials with extraordinary properties that will be able to keep up with the ever-increasing demands for efficient solutions. Among them, nanoporous materials, which have been used since ancient times, have been attracting a lot of attention throughout the last past years due to their controllable pore size, diverse geometries, surface properties and their ability to interact with molecules and atoms or adsorb them, that can be easily exploited in various fields such as catalysis, gas storage, environmental remediation, sensorics, and medical applications.

1.1. Porous materials

As suggested by the International Union of Pure and Applied Chemistry (IUPAC), porous materials can be categorized according to the width of their pores in three big categories: microporous (< 2 nm), mesoporous ($2 \text{ nm} < w < 50 \text{ nm}$) and macroporous ($> 50 \text{ nm}$).² This classification though, is not sufficient if someone bears in mind the rest of criteria by which one can differentiate porous materials such as the pore structure and shape (cylindrical, spherical, hexagonal and slit types). High surface area (m^2/g), controlled pore diameter, thermal stability and catalytic properties make porous materials outstanding candidates for gas adsorption, energy storage and heterogenous catalysis applications. The most known porous solids are:

- ❖ zeolites; microporous crystalline silicate frameworks that occur naturally;
- ❖ metal organic frameworks (MOFs); porous crystalline materials formed by metal clusters/ions linked with organic ligands;
- ❖ clays; naturally occurring aluminium phyllosilicates;
- ❖ silica nanoparticles; inorganic high pore volume nanometer sized structures, and

- ❖ carbonaceous porous sorbents (among which activated carbons); materials that are made up solely of carbon.

1.2. Carbon

Carbon is present everywhere around us. In the things we touch, the things we eat, the ones we breathe. It is a dominant element of our lives, and it is not surprising that carbon research has been the focus of thousands of researchers within the global scientific community, with major accomplishments like two Nobel prizes in Chemistry and Physics within 15 years. The first one was awarded to Harry Kroto in 1996 for the discovery of the ‘buckminsterfullerene’, a spherical hollow carbon structure made of 60 carbon atoms arranged in hexagons and pentagons.³ A couple of years later it was the turn of Andre Geim and Konstantin Novoselov to get recognition in 2010 "for ground-breaking experiments regarding the two-dimensional material graphene" for which they isolated a single flake of graphene using simple scotch tape.⁴

Carbon can be encountered in a variety of forms due to its ability to form structures with diverse properties depending on the way its atoms are covalently bonded between them in diverse hybridization states (sp , sp^2 , sp^3 and mixtures of the latter).⁵ Till the 80's, graphite and diamond were the only carbon allotropes known but over the following years a lot of new members were added to the carbon family, namely in addition to the already mentioned fullerenes and graphene, carbon dots,⁶ single and multi-wall carbon nanotubes (SWCNTs and MWCNTs),^{7, 8} nanodiamonds⁹ and graphene nanoribbons¹⁰. Apart from C-C bonds, carbon can be covalently connected with other elements in a strong and stable manner as well, allowing the formation of an almost infinite number of compounds.

1.2.1. Graphene

Graphene is a two-dimensional (2D) sheet made of sp^2 bonded carbon atoms (Figure 1.1), each of which is connected to three neighbouring ones creating this way a strong honeycomb lattice. Chemical vapour deposition (CVD) on liquid or crystalline copper, micromechanical exfoliation and liquid-phase exfoliation of graphite are the most common ways of producing high quality graphene.^{11, 12}

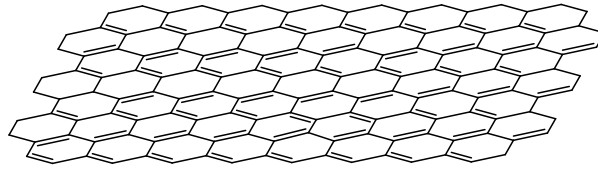


Figure 1.1. Structural representation of graphene

Its outstanding properties include a very high carrier mobility,¹³ extraordinary thermal conductivity,¹⁴ high surface area (theoretically 2630 m²/g),¹⁵ mechanical stiffness,¹⁶ impermeability,¹⁷ flexibility¹⁸ and transparency,¹⁹ which render it a perfect candidate for industrial applications in sectors like transport, (bio)medicine, electronics, photonics, energy, or desalination.²⁰⁻²³

1.2.2. Graphene oxide

Starting from graphite and choosing one of the oxidation methods developed long before graphene became fashionable by Brodie,²⁴ Staudenmaier,²⁵ and Hummers²⁶ or their more recent variations, oxygen containing functional groups (epoxy, methoxy, carboxyl) are introduced on the basal planes and edges of the carbon nanosheets (Figure 1.2). The resulting layered structure is hydrophilic and soluble in many solvents.²⁷ The presence of these groups allows for reactions (ring-opening reactions, noncovalent functionalization, cycloaddition, *etc.*)²⁸ and grafting of moieties (molecules, long chain hydrocarbons, polymers)^{29,30} that (partially) occupy the interlayer space.

1.2.2.1. Graphene Pillaring

Graphene and graphene oxide's lack of permanent porosity can be overcome through pillaring. Once a moiety has been intercalated between the layers, stability can be gained through a thermal process, which enables the preservation of the layered structure and hence of the porosity (an example of silsesquioxane pillared graphene oxide is shown in Figure 1.2). Experiments with different pillaring agents and extensive theoretical modeling,^{31, 32} have proven that with the insertion of a suitable and robust organic and/or inorganic species between the layers, demanding technological targets in gas storage or sensing can be easily reached. Apart from graphene and graphene oxide, the pillaring method can and has already been applied to other materials such as zeolites, clays and layered double hydroxides.

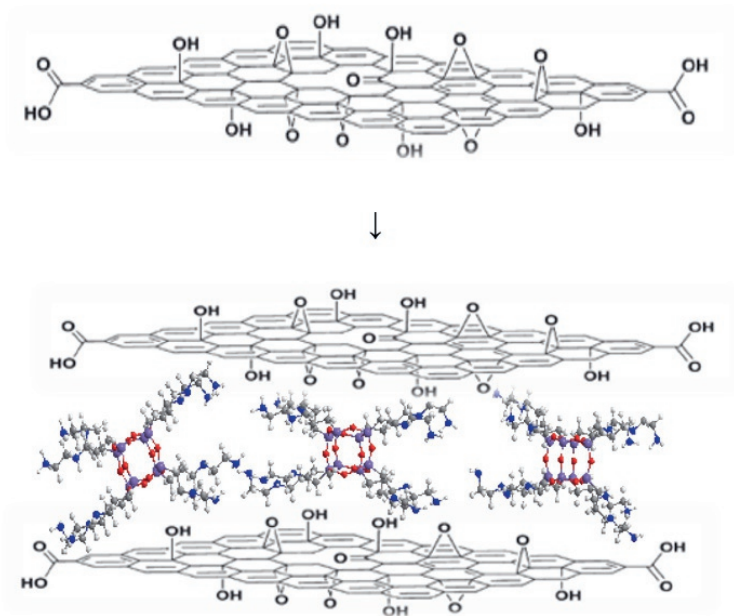


Figure 1.2. Structural representation of graphene oxide (up) and silsesquioxane pillared graphene oxide (down)

1.2.2.2. Silsesquioxanes as pillaring agents

Polyhedral silsesquioxanes (POSS) are cage-like organosilicon compounds with the chemical formula $[XSiO_{1.5}]_n$ (where $X = H$, alkyl, aryl or alkoxy) that derive from the hydrolytic condensation of organosilicon monomers.³³ They can act as pillaring agents creating a robust three-dimensional network by attaching to the graphene oxide sheets and be exploited in this way in a variety of applications ranging from hydrogen storage³⁴ to removal of water pollutants³⁵.

1.2.3. Porous Carbons

Nanoporous carbons is an important category of porous materials that combine micro and mesoporosity in their structure and have been at the centre of scientific attention for a while due to their high specific area, electrical conductivity, and chemical inertness.

1.2.3.1. Hierarchical Porous Carbons

Hierarchical Porous Carbons (HPCs) denotes a carbon structure that possesses a labyrinthian porous network of well-defined macropores and interconnected micro- and mesopores, which provide better accessibility and a large amount of active sites distributed all over the bulk and not only the surfaces.³⁶ HPCs are usually synthesized by employing a soft or hard template method or a combination of both, which is moreover coupled with an activation process (CO_2 , KOH , *etc.*)³⁷⁻³⁹ that can induce microporosity as explained further in Chapter 6. Templating methods involve the use of suitable scaffolds that are being later removed during the synthetic procedure, leaving behind pores. Depending on the size and form of the template, the porous structure can have tailored characteristics. Thermally decaying polymers, micelles and emulsions are usually used as soft templates and simply decompose during carbonization, whereas inorganic solids (silica particles or gel, Na_2CO_3 , MgO , CaCO_3 , *etc.*) are used as hard templates, which need to be removed by chemical etching.^{36, 40-42}

1.2.3.2. Porous Carbon Cuboids

In 2014, Stefan Kaskel and co-workers⁴³ came up with a new form of ultra-hydrophilic porous carbon with cuboid shape, which is decorated with uniformly distributed N and O heteroatoms (Figure 1.3). The functional groups, in combination with the relatively high specific surface area (800-900 m^2/g), abundance of narrow micropores, low weight and great stability, render carbon cuboids very promising candidates for adsorption/molecular sieving in the gas industry.

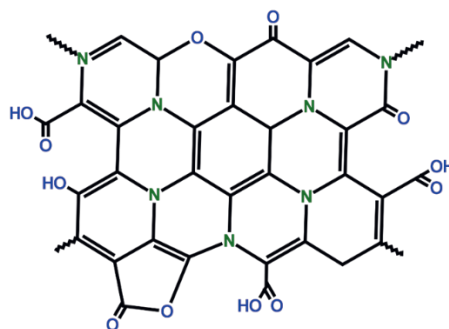


Figure 1.3. Structural representation of porous carbon cuboids

1.3. Applications

All the forementioned categories of materials have been receiving increasing attention recently due to their potential use in a plethora of applications that can meet the demands of our modern ultra-consuming world. These applications are for the most part localized in the fields of energy, environmental remediation, and catalysis.

1.3.1. Energy

Energy storage and conversion are two of the biggest challenges of our era due to the rising demands and the changes necessary to avoid even more global warming. Porous materials are being developed and studied in order to be used in hydrogen storage applications,⁴⁴ as supercapacitors,⁴⁵ in Li-ion batteries,⁴⁶ fuel cells and sensors⁴⁷.

1.3.2. Environmental remediation

With most limits of emissions being exceeded by far, a lot of effort is being made towards the development of technologies that can minimize or at least control the damage being caused to the environment by removing or separating pollutants from gas and waste streams, as well as from contaminated water. All these problems can find solutions through the development of materials that can serve as molecular sieves/adsorbents,⁴⁷⁻⁴⁹ in NO_x and H₂S removal,^{50, 51} and in assisted oil recovery among others.

1.3.3. Catalytic Applications

Porous carbons are promising candidates for the substitution of traditional catalysts and its already being studied extensively their use as catalysts or as supports for metal nanoparticles or for metal complex anchoring.^{47, 48, 52-54}

1.4. Thesis Outline

This thesis is a representative sample of the research efforts during my PhD journey towards the development of porous carbon materials with tailored properties that can be applied in energy storage, environmental remediation, and catalysis. The property that has constantly been under the spotlight all along these four years was porosity. In order to achieve high porosity materials my attempts were divided along two pathways; the

construction of ‘Parthenon like’ structures inserting columns between the sheets of layered carbon materials like graphene oxide in an attempt to create interconnected empty spaces, and the development of porous carbons cuboids and hierarchical porous carbon structures that serve as tiny waste recyclers.

As briefly described in the following paragraphs, the research conducted during this PhD project is organized in six chapters in this dissertation.

Chapter 2 explains all the characterization techniques that were employed during the preparation and characterization of the developed materials, as well as the methods used in order to determine their potential use in future applications.

Chapter 3 describes the synthesis of highly porous heterostructures with tailored properties through the creation of a silica network in the interlayer space of organically modified graphene oxide. Three distinct silica precursors were used as building blocks and the potential as sorbent of CO₂ was briefly explored for the heterostructure with the highest specific surface area.

Chapter 4 is devoted to our exploration of the use of silsesquioxane-pillared graphene oxide for CO₂ capture, where we demonstrated that modifying the silsesquioxane loading and drying method causes important variations in the adsorption capacity.

Chapter 5 gives an overview of the ability of copper-enriched porous carbon cuboids to capture H₂S gas. The properties of the sorbents were explored and their hybrid behaviour acting both as adsorbents and catalysts was investigated.

Finally, in Chapter 6 a set of hierarchical porous carbons that were developed making use of sugar and coffee wastes is presented. High specific surface areas and pore volumes were achieved, and it was shown that both can be maximized by subjecting the samples to physical activation with CO₂.

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