Chapter 2: Characterization techniques

This chapter describes the key experimental methods used to characterize the porous carbon materials presented in this dissertation. If a specific measurement was not performed by the candidate, this is specified herein as well.
2.1. X-Ray Diffraction

X-ray diffraction (XRD) is a non-destructive analysis method based on the X-Ray photons scattering from a crystalline sample; it provides information about the crystalline phases and structure, interlayer distance and the size of the coherently diffracting domains. The XRD pattern is unique for each crystalline compound hence collecting diffraction data enables the identification of an unknown compound or phase.

The powder X-ray diffraction (XRD) patterns of the pillared graphene oxide described in Chapter 3 and of the carbon cuboid samples labelled PCC and PCC-Cu in Chapter 5, were collected on a D8 Advance Bruker diffractometer with a Cu Kα X-ray source (wavelength 1.5418 Å) and a secondary beam graphite monochromator. The patterns were recorded in a 2θ range from 2 to 40°, in steps of 0.02° and with a counting time of 2.00 s per step. The measurements were performed by Dr. Christina Papachristodoulou (University of Ioannina, Greece).

The diffraction spectra of the silsesquioxane-pillared graphene oxide samples described in Chapters 4 and of the carbon cuboid sample labelled PCC-unleached described in Chapter 5 were collected on a D8 Advance Bruker diffractometer with a monochromatic Cu Kα X-ray source (wavelength 1.5418 Å); a 1 mm divergent slit and a 3 mm antiscattering slit were used. The 2θ scans were performed from 2 to 80° with a step size of 0.02° and a counting time of 1.00 s per step.

The XRD measurements that were recorded before and after the H2S adsorption measurements reported in Chapter 5, were performed on a Panalytical X'Pert PRO powder diffractometer. About 30 mg of the selected sample was first placed on a zero-background holder and the measurements were conducted using Cu-Kα radiation (\(\lambda = 1.5406\) Å). The diffraction patterns were collected over the 2θ range of 10° to 80° with a step size of 0.02° and the time per step of 1.3 s. The measurements were performed by Dr. Georgia Basina (Khalifa University, United Arab Emirates).

2.2. Fourier Transform Infrared Spectroscopy

Infrared Spectroscopy is a widely used tool in chemistry for qualitative and quantitative identification of substances. When an infrared beam passes
Characterization techniques

through the sample, part of the radiation is absorbed, and part transmitted. Each compound absorbs, reflects, and transmits IR radiation at different frequencies resulting in a unique signal, which represents the molecular ‘fingerprint’ of the sample. The vibrational characteristics of the molecules are used for the identification of functional groups and bonds present in the structure.

Fourier transform infrared (FTIR) spectra reported in Chapters 3 and 4 were measured in the range 400–4000 cm\(^{-1}\) with a Shimadzu FT-IR 8400 spectrometer equipped with a deuterated triglycine sulfate (DTGS) detector. Each spectrum was the average of 64 scans collected at 2 cm\(^{-1}\) resolution. Samples were in the form of KBr pellets containing ca. 2 wt% sample.

2.3. Surface Area and Porosity Measurements

The morphological characteristics of porous solids and fine powders can be studied by means of gas adsorption measurements. An inert gas (usually nitrogen) is physisorbed at low temperature and the quantity of adsorbate on the material’s surface is measured over a wide range of relative pressures resulting in an adsorption isotherm. The physisorption isotherms can be grouped in 8 categories after the updated classification recommended by the International Union of Pure and Applied Chemistry (IUPAC) in 2015 (Figure 2.1).\(^1\)

Each category is indicative of the type of porosity of the adsorbent: I(a): ultramicropores, I(b): supermicropores, II & III: non porous heterogeneous planar surfaces, IV(a): large mesopores, IV(b): narrow mesopores, V: mesopores and micropores, and VI: non porous homogeneous surfaces.\(^1\)
Figure 2.1. Classification of physisorption isotherms\textsuperscript{1}

Information can be extracted about the geometrical structure of the pores from the shape of the hysteresis loop formed on the adsorption-desorption isotherms; this hysteresis loop is associated with capillary condensation. The main types of hysteresis loops are summarized in Figure 2.2.
Each type of loop is related with specific pore structures. In summary, H1 is observed for cylindrical pores, loops H2(a) & H2(b) for the so-called ‘ink bottle’ pores, which consist of a larger volume connected by a narrow neck to the next pore; H3 results for a disordered pore structure, usually aggregates of lamellar particles or networks consisting of not fully filled macropores; H4 is found if both micro- and mesopores are present, and H5 when there are open as well as restricted pores.¹

The specific surface area, pore volume and pore size distribution can be extracted from the adsorption measurements. The most widely used procedure for evaluating the specific surface area is the Brunauer-Emmett-Teller (BET) method², which is an extension of the Langmuir theory for monolayer formation, and makes use of the following equation:

\[ \frac{p}{V(p^0 - p)} = \frac{1}{V_m C} + \frac{C - 1}{V_m C} \left( \frac{p}{p^0} \right) \]

where V is the volume adsorbed, V_m is the volume of a monolayer, p the equilibrium pressure, p^0 the saturation pressure and C is a constant related to the enthalpy of adsorption in the first adsorbed layer (BET constant).
The nitrogen adsorption-desorption isotherms for the pillared graphene oxide described in Chapter 3 and the porous carbon cuboids presented in Chapter 5, were measured at 77 K on a Sorptomatic 1990 Thermo Finnigan porosimeter. Specific surface area values were determined by the Brunauer–Emmett–Teller (BET) method. The measurements reported in Chapter 5 were performed by Dr. Vasilis Kostas (University of Ioannina, Greece).

Low-pressure nitrogen sorption measurements for the silsesquioxane-pillared graphene oxide samples of Chapter 4 were carried out using an Autosorb 1-MP instrument from Quantachrome equipped with multiple pressure transducers for highly accurate analyses and an oil-free vacuum system. Ultra-high purity N₂ gas (99.999 %) was used for the adsorption measurements. Prior to the measurement, each sample was transferred to a 9 mm quartz cell and activated under dynamic vacuum at 100 °C for 20 h (until the output rate was less than 2 mTorr/min) to remove all volatile species. After activation, the sample was weighed to obtain the precise mass of the solids and the cell was transferred to the analysis port of the gas sorption instrument. The measurements were performed by Dr. Giasemi K. Angeli (University of Crete, Greece).

The nitrogen adsorption-desorption isotherms for all the hierarchical porous carbon samples described in Chapter 6 were recorded on a Micromeritics ASAP2420 apparatus at 77 K before processing to the activation step. The specific surface area was evaluated with the BET method. The samples were degassed under reduced pressure at 120 °C for 15 h prior to the measurements.

The nitrogen adsorption-desorption isotherms for the carbon cuboid sample labelled PCC-unleached of Chapter 5, and the activated hierarchical porous carbon samples of Chapter 6, were recorded at 77 K on a Autosorb iQ gas sorption system from Quantachrome Instruments. The samples were degassed under high vacuum for respectively 10 h at 100°C (PCC-unleached) and 120 °C (activated hierarchical porous carbon) before performing the measurements. The measurements were performed by Dr. Konstantinos Spyrou (University of Ioannina, Greece) and the analysis by myself.
2.4. X-Ray Photoelectron Spectroscopy

Based on the photoelectric effect, X-ray photoelectron spectroscopy (XPS) is a surface-sensitive quantitative spectroscopic technique that is applied to acquire useful information about the surface elemental composition (up to a depth of ~10 nm), as well as the chemical environment and electronic state of each element present.\(^3\) The material is irradiated with an X-ray beam and the kinetic energy and number of the electrons emitted are analysed in order to acquire the spectra.

XPS analysis in Chapters 3, 4 and 5 was performed using a Surface Science SSX-100 ESCA instrument with a monochromatic Al K\(\alpha\) X-ray source (\(h\nu = 1486.6\) eV). The pressure in the measurement chamber was maintained at 1x10\(^{-9}\) mbar during data acquisition. The electron take-off angle with respect to the surface normal was 37°. The XPS data were acquired by using a spot size of 1000 \(\mu\)m in diameter and the energy resolution was 1.3 eV for both the survey spectra and the detailed spectra of the core level regions. All XPS spectra were analysed using the least-squares curve-fitting program Winspec (developed at LISE laboratory of the University of Namur, Belgium). Deconvolution of the spectra included a Shirley baseline\(^4\) subtraction and fitting with a minimum number of peaks consistent with the chemical structure of the sample, taking into account the experimental resolution. The profile of the peaks was taken as a convolution of Gaussian and Lorentzian functions. All binding energies derived from deconvolution are reported \(\pm 0.1\) eV. For the spectra reported in Chapter 3 the binding energies are referenced to the C1s photoemission peak centred at a binding energy of 284.8 eV.\(^5\) The uncertainty in the peak intensity determination is 2 % for all core levels reported. For the analysis I was helped by Dr. Orest de Luca (University of Groningen, the Netherlands). For the spectra of the silsesquioxane-pillared graphene oxide samples shown in Chapter 4 the Au4f\(_{7/2}\) core level was used as a reference binding energy.\(^5\) For the measurements, evaporated polycrystalline 150 nm thick gold films supported on mica (grade V-1, TED PELLA), prepared by sublimation of 99.99% gold (Schöne Edelmetaal B.V.) as detailed in Mendoza \textit{et al.}\(^6\) were used as substrates where freshly prepared samples were drop casted. All the data were normalized to the number of scans and corrected for the sensitivity factor of the spectrometer. The analysis was performed by Dr. Konstantinos Spyrou (University of Ioannina, Greece).
XPS measurements on the porous carbon cuboids detailed in Chapter 5 were performed under ultrahigh vacuum conditions with a base pressure of $5 \times 10^{-10}$ mbar in a SPECS GmbH instrument equipped with a monochromatic Mg Kα source ($h\nu = 1253.6$ eV) and a Phoibos-100 hemispherical analyser. Samples were suspended in water, drop casted on Si wafers, and after they were dry, they were left in high vacuum overnight to outgas, before being transferred to the main chamber for XPS measurement. The energy resolution was set to 1.18 eV, and the photoelectron take-off angle was 45° with respect to the surface normal. Recorded spectra were the average of three scans with the energy step set to 0.05 eV and a dwell time of 1 s. All binding energies were referenced to the C1s core level at 285.0 eV. Spectral analysis included a Shirley background subtraction and peak deconvolution employing mixed Gaussian–Lorentzian functions in a least-squares curve-fitting program WinSpec. The analysis was performed by Dr. Konstantinos Spyrou (University of Ioannina, Greece).

2.5. Thermal Analysis

Thermal analysis techniques reveal the phase transitions of a sample, which are almost always accompanied by a mass loss, as a function of temperature. They can provide qualitative and quantitative information regarding the thermal stability, decomposition, as well as the exothermic and endothermic character of the phase transitions taking place.

Thermogravimetric (TGA) and differential thermal (DTA) analyses for Chapters 3 and 5 were performed using a Perkin Elmer Pyris Diamond TG/DTA. Samples of approximately 5 mg were heated in air from 25 to 850 °C, at a rate of 5 °C/min.

Thermogravimetric analysis (TGA) for Chapters 4 and 5 was performed with a TA-Instruments Discovery TGA 5500. Samples of approximately 5 mg were heated in air from 25 °C to 850 °C, at a rate of 5 °C/min. The measurements were performed by Jur van Dijken (University of Groningen, the Netherlands).
2.6. Scanning Electron Microscopy

Scanning electron microscopy (SEM) is a method for obtaining detailed imaging of the morphology of a surface at high magnification. A finely focused beam of electrons is used to probe the surface of the solid sample and the backscattered and secondary electrons are detected. Asperities on the surface modulate the intensity of the signal being emitted from the scanned area and the intensity variations recorded while scanning over the surface are used to construct the image. Since the impinging electrons can also interact inelastically and the excited atoms decay emitting X-rays typical of the specific element, most SEM setups are equipped with X-ray detectors, which allow elemental analysis and mapping, in addition to revealing the surface morphology. All samples analysed by SEM must be conductive to avoid charge build-up; insulating samples are coated with a thin metallic film before analysis.

The SEM micrographs of the graphene based heterostructures described in Chapter 3 were collected using a JEOL JSM-7401F field emission scanning electron microscope (FE-SEM). A low acceleration voltage was applied (~2 kV), and the working distance was set to 3 mm. A powder sample was mounted onto the round brass substrate using double-coated conductive carbon tape. The measurements were performed by Lamprini G. Boutsika (National Centre for Scientific Research “Demokritos”, Greece).

SEM analyses on the silsesquioxane-pillared graphene oxide samples described in Chapter 4 were carried out using a JEOL JSM-6390LV microscope equipped with an Oxford Instruments detector for energy dispersive X-ray spectroscopy (EDS). The measurements were performed by Konstantinos G. Froudas (University of Crete, Greece).

SEM images of the porous carbon cuboids depicted in Chapter 5 were recorded using a JEOL instrument (JSM-6510LV with a LaB₆ filament) equipped with an EDS detector (Oxford Instruments, x-act) operating at an accelerating voltage of 20 kV and using high vacuum (10⁻⁵ bar). All samples were in the form of a powder; they were placed on a double-sided carbon tape to be stabilized and were measured without coating.

The SEM images of the carbon cuboid samples labelled PCC-unleached, before and after the H₂S adsorption measurements reported in Chapter 5,
were obtained on a Quanta 250 FEG-FEI microscope, using a Schottky field emission gun as the electron source, with a spatial resolution of ~1 nm at 5-10 kV. Elemental analysis and phase mapping were also conducted using this microscope, equipped with an Apollo silicon drift detector, integrated with the EDAX Genesis software. The measurements were performed by Dr. Georgia Basina (Khalifa University, United Arab Emirates).

The SEM images of PCC-unleached reported in Chapter 5, were recorded using a Zeiss Gemini 500 Scanning Electron Microscope at the Cornell Centre for Materials Research. The measurements were performed in Dr. Emmanuel P. Giannelis group (Cornell University, United States of America).

The SEM measurements on the hierarchical porous carbons described in Chapter 6, were performed with a FEI Philips FEG-XL30s microscope by Dr. Liqiang Lu (University of Groningen, the Netherlands).

2.7. CO$_2$ adsorption measurements

The evaluation of the graphene-based materials synthesized in Chapters 3 and 4 as carbon dioxide sorbents was performed by monitoring their ability of capturing CO$_2$.

CO$_2$ adsorption isotherms at 0, 10 and 20 °C reported in Chapter 3 were measured on an Intelligent Gravimetric Analyser (IGA–Hiden Ltd.). Before exposure to CO$_2$ the samples were outgassed overnight in 250 °C under high vacuum (10$^{-8}$ mbar) until the mass was observed to remain constant. The measurements were performed by Dr. Andreas Sapalidis (National Centre for Scientific Research “Demokritos”, Greece).

Low-pressure carbon dioxide sorption measurements on the silsesquioxane-pillared graphene oxide samples described in Chapter 4 were carried out using an Autosorb 1-MP instrument from Quantachrome equipped with multiple pressure transducers for highly accurate analyses and an oil-free vacuum system. Ultra-high purity CO$_2$ gas (99.999%) was used for the adsorption measurements. Prior to the measurement, each sample was transferred to a 9 mm quartz cell and activated under dynamic vacuum at 100 °C for 20 h (until the output rate was less than 2 mTorr/min) to remove all volatile species. After activation, the sample was weighed to
obtain the precise mass of the solids and the cell was transferred to the analysis port of the gas sorption instrument. The measurements were performed by Dr. Giasemi K. Angeli (University of Crete, Greece).

2.8. Anion exchange chromatography

To determine the sugar (monomer) composition in the biomass derived samples of Chapter 6, High-performance anion exchange chromatography (HPAEC) was performed on a Dionex Ultimate 6000 system (Thermo Scientific, Sunnyvale, CA, USA) equipped with a CarboPac PA-1 column (2 mm x 250 mm ID) in combination with a CarboPac PA-1 guard column (2 mm x 50 mm ID) and PAD detection. The system was controlled using Chromeleon 7.2.9 software (Thermo Scientific, Sunnyvale, CA, USA). The samples were freeze dried and milled (powder) prior to the analysis. The dry samples were dissolved in MilliQ water (concentrated liquid sugar beet root wastewater: 9.2 mg/mL, and molasses: 38 mg/mL), centrifuged and diluted 6-40x and injected on the Dionex HPAEC system on the Oligomer method, which is described as follows. Elution of oligomers (0.3 mL min⁻¹) was performed with a multi-step-gradient using the following eluents: A: 0.1M NaOH and B: 1M NaOAc in 0.1M NaOH. After 12 min equilibration with 100 % A a linear gradient over 35 min up to 38 % B was performed, followed by 8 min wash with 100 % B. Quantification was performed based on the pure fructose/sucrose and glucose standards. The measurements were performed by Dr. Edita Jurak (University of Groningen, the Netherlands).
References


