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Design and development of novel layered nanostructured hybrid materials for environmental, medical, energy and catalytic applications

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CHAPTER 1

Introduction

1.1. Motivation

This thesis represents part of my research efforts aiming at the generation of new knowledge on the functionalization of carbon nanodiscs as well as the intercalation of graphene oxide and clays using a simple diamondoid derivative or polyhedral oligomeric silsesquioxanes (POSS).

The thesis also contains a study on fabrication of new complex materials by the Langmuir-Schaefer method based on metal decorated POSS.

The target of this work was the design and development of novel layered nanostructured hybrid materials for environmental, medical, energy and catalytic applications.

1.2. Graphene, Graphite oxide and carbon nanodiscs

1.2.1. Graphene

Graphene is a one-atom-thick sp^2 -bonded carbon 2D sheet consisting of carbon atoms tightly packed into a planar two-dimensional hexagonal lattice. It possesses exceptional properties, which differ from those of all the other carbon allotropes discovered so far. Its extraordinary electron mobility, combined with its high thermal and mechanical stability, chemical inertness, large surface area, elasticity and the possibility to modify electrochemically its electronic structure,^{[1][2][3]} place graphene at the top of the list of candidates for the development of new nanomaterials for a plethora of applications including molecular electronics, biosensors, environmental sensors and energy storage nanodevices.^{[4][5][6][7][8]} Graphene can be produced by five basic methods; reduction of graphene oxide, liquid exfoliation of graphite, chemical vapor deposition using a carbon source, growth by heating silicon carbide and mechanical cleavage of graphite.^[9]

1.2.2. Graphene oxide

Graphite oxide (GO) is an oxygen rich derivative of graphite decorated with hydroxyl, epoxy, and carboxyl groups (sp^3 -oxo moieties).^{[10][11][12]} These functional groups are created by strong oxidation and distributed randomly on the basal planes and edges of the GO sheets, generating aliphatic regions (sp^3 - carbon atoms) within the sp^2 -hybridized matrix, as illustrated in Figure 1.1. Due to the existence of such hydrophilic moieties, GO can swell and can be intercalated with various moieties. Both GO and intercalated GO are being considered for numerous applications such as supercapacitors,^[13] high mobility transistors,^[14] lithium batteries,^[15] hydrogen storage, adsorption of organic moieties^[16] removal of pollutants from aqueous solutions and in biomedical applications.^[8] In our experiments, we chose to use a chemical preparation approach since allows the production of product in comparatively large scale and low cost. As oxidation method we decided to use Staudenmaier method because it is a milder oxidative procedure comparing to Brodie or Hummers-Offeman methods. Moreover, Staudenmaier method leads to the formation of higher amount of distributed epoxy than carboxyl and hydroxyl groups on the surface of the graphene oxide nanosheets. The presence of these epoxy groups favor the reactions with amine ending moieties that are used for the synthesis of the hybrid materials presented in this thesis at ambient conditions.^{[17][18]}

1.2.3. Carbon nanodiscs

Carbon nanodiscs (CNDs) are a new bottom-up prepared carbon nanomaterial with well-defined size on the micron scale. They are ultra-thin quasi two-dimensional particles with diameter 1-4 μm and thickness, typically in the range 10–30 nm.^[19] They are produced through the so-called pyrolytic Kværner Carbon Black & H_2 (CB&H) Process,^[20] where hydrocarbons (typically heavy oil) are decomposed to carbon and H_2 based on the use of an industrial-scale carbon-arc plasma torch generator operating at a temperature around 2000 °C. CNDs are considered a promising material in various engineering aspects due to their exceptional electrochemical properties.^[21]

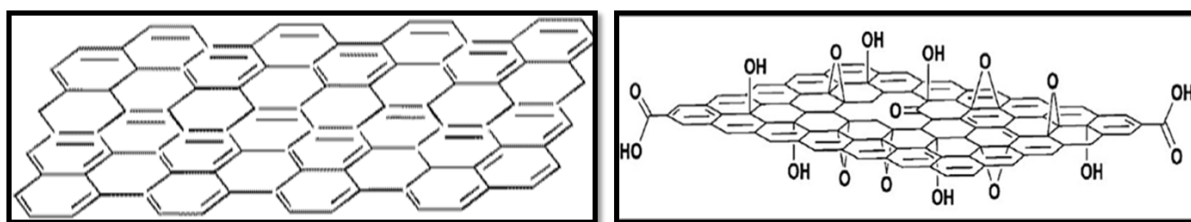


Figure 1.1. Schematic representation of graphene and graphene oxide structure

1.3. Clays

Natural clays are the product of weathering of rocks, which make up 40 % of the earth crust. They are phyllosilicates and consist of silicon oxygen tetrahedra and aluminum oxygen octahedra^[22] as sketched in Figure 1.2. Clays are used in a variety of industrial applications^[23] as absorbents,^[23] pharmaceutical additives,^{[24][25]} in fertilizers,^[26] as drilling fluids in oil drilling,^[27] in cosmetics^[28] etc. The most important properties of clays are

isomorphic substitution, *i.e.* the possibility for ions of smaller valence to substitute ions of the clay platelets;

cation exchange capacity, which is the total capacity of a soil to hold exchangeable cations;

ability to swell when dispersed in polar solvents, a reversible process, which is determined by their charge density;

porosity which is affected by the drying process after dispersion;

and finally the Brønsted and Lewis acidity, present due to the active acid sites on the clay platelets.^[29]

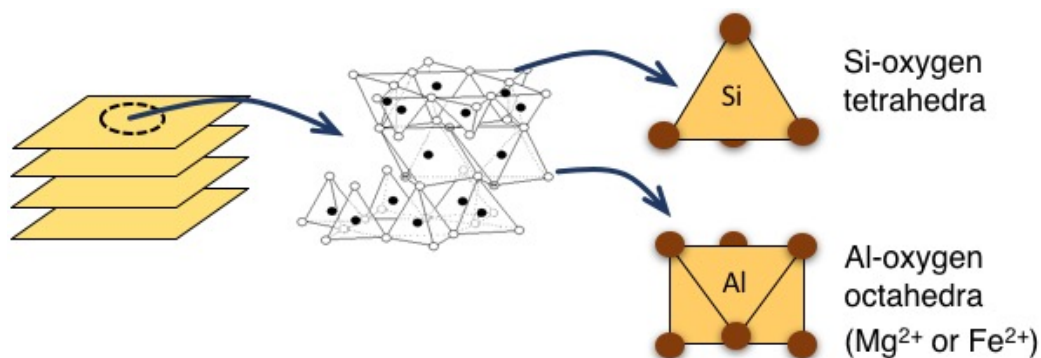


Figure 1.2. Schematic representation of the clay structure

1.3.1. Pillared Clays

The main disadvantage of clays is their lack of permanent porosity. A normal clay swells upon hydration but its interlayer shrinks again after dehydration. To create a structure in which the platelets are kept permanently at a certain distance, clays can be pillared with a variety of pillaring species such as organic cations (organo-clays), organometallic pillars, metal oxide sols (*e.g.* imogolite), metal complexes, polyoxocations and mixed pillaring species^{[30][31]} as schematically shown in Figure 1.3. The produced pillared structures can be used in numerous applications such as in catalysis,^[32] in biomedicine,^[8] in environmental remediation^[33] *etc.*

1.4. Polyhedral oligosilsesquioxanes (POSS)

Silsesquioxanes belong to the family of silicone resins.^[34] They are described with the general formula $\text{RSiO}_{3/2}$ tend to form three dimensional (3D) cage-like highly symmetric frameworks known as polyhedral oligosilsesquioxanes (POSS). Several structures are known for silsesquioxanes, including random, ladder, partially condensed and cage (*e.g.* T8, T10 and T12) types.^[35] These cubic, hexagonal,

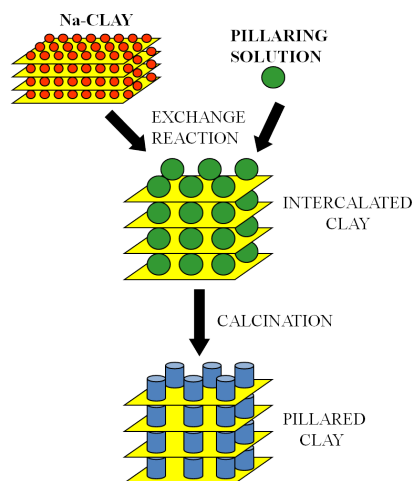


Figure 1.3. Schematic representation of pillaring procedure.

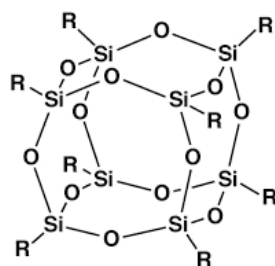


Figure 1.4. Molecular structure of a cubic polyhedral oligomeric silsesquioxane (POSS).

octagonal, decagonal, dodecagonal or even open cage like structure are derived from hydrolytic condensation reactions of trifunctional organosilicon monomers.^[36] The example of a cubic POSS is shown in Figure 1.4.

Polyhedral oligomeric silsesquioxanes appear as highly promising candidates for the synthesis of hybrid nanomaterials suitable for a wide range of applications such as for polymer nanocomposites;^[37] in catalysis,^[38] energy storage;^{[39][40]} environmental applications^[41] and biomedicine.^{[42][43][44]}

1.5. Langmuir Blodgett/Langmuir Schaefer techniques

The Langmuir–Blodgett (LB) technique that was introduced by Langmuir and Blodgett (yielding Irving Langmuir the Nobel prize in Chemistry in 1932), is a useful tool to

prepare thin molecular films, ranging from one to several tens or even hundreds of molecular layers.^[45] In general, it is applied to amphiphilic molecules where a polar (hydrophilic) and a non-polar (hydrophobic) part is present.^[46] These molecules can form stable Langmuir films at the air/water interface, which can subsequently be transferred onto chosen substrates.^{[47][48]} The deposition of the LB films takes place in a water trough equipped with moving barriers. The amphiphilic molecules (surfactants) are spread on the water surface, whereupon the hydrophilic part stays in contact with the water surface while the hydrophobic part points away from the water surface, thus preventing the molecules from dissolving. Then the barriers of the trough are closed, forcing the molecules to change from a 2D gas state at the air/water interface first to the liquid and finally the solid phase. During this compression the surface pressure is increased while the area per molecule is decreasing, as shown in Figure 1.5. When the solid phase is reached and stabilized, a substrate is dipped onto the surface vertically and the molecules are deposited on both sides of the substrate. In 1938 Schaefer introduced a variation of the technique where the dipping of the substrate is horizontal, known as Langmuir Schaefer method (LS). LB and LS techniques enable the fabrication of single molecule films with control over the packing density of molecules. They also enable the creation of multilayer structures with varying layer composition.

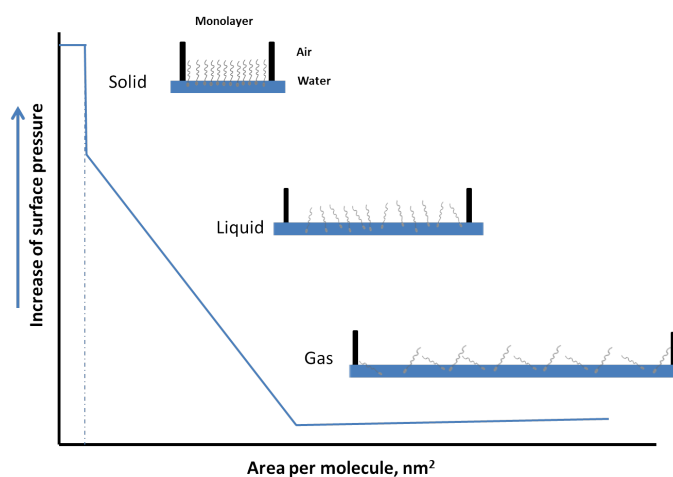


Figure 1.5. Surface pressure versus area isotherm (schematic curve).

1.6. Outline of the thesis

The research work described in this thesis is organized in seven chapters as follows:

Chapter 2 describes the experimental techniques that were used to prepare and to characterize the studied materials; the methods employed to determine possible future applications for the produced materials are also illustrated.

Chapter 3 reports the synthesis of multi-functional pillared layered materials synthesized by intercalation of cage-shaped adamantylamine molecules into the interlayer space of graphite oxide and layered aluminosilicate nanoclays. The produced hybrid materials were characterized for what concerns their structure and composition; they were found to exhibit an antiproliferative activity for cells, as well as a high adsorption power for small organic pollutants from aqueous solutions.

Chapter 4 presents the oxidation of carbon nanodiscs towards the formation of a hydrophilic analogue, the detailed characterization of the pristine and produced material as well as a study of the cytotoxicity properties of the final product.

Chapter 5 is dedicated on our review article "Carbon Nanostructures Containing Polyhedral Oligomeric Silsesquioxanes (POSS)" giving an overview of the synthesis and properties of carbon nanostructures containing organic-inorganic cage-like polyhedral oligomeric silsesquioxane (POSS) nanoparticles.

Chapter 6 describes the intercalation of iron-decorated POSS in natural and in acid activated clays, the characterization of the pristine and produced pillared materials as well as a study of their catalytic properties in the decomposition of isopropanol.

Finally, Chapter 7 reports the fabrication of metal (iron and copper) decorated POSS thin films. The LS films were produced using either the Langmuir –Schaefer method or a combination of this method with self-assembly.

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