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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 2

## Experimental Techniques

### 2.1. Preparation of host layered materials

#### 2.1.1. Graphene oxide (Chapter 3)

Graphene oxide was produced from graphite powder using a modified Staudenmaier's method.<sup>[1][2]</sup> In a typical synthesis, 10 g of powdered graphite (purum, powder  $\leq 0.2$  mm; Fluka) were added to a mixture of concentrated sulphuric acid (400 mL, 95–97 wt%) and nitric acid (200 mL, 65 wt%) while cooling in an ice-water bath. Potassium chlorate powder (200 g, purum, >98.0%; Fluka) was added to the mixture in small portions while stirring and cooling. The reactions were quenched after 18 hs by pouring the mixture into distilled water and the oxidation product washed until a pH 6. The sample was then dried at room temperature.

#### 2.1.2. Natural and Synthetic Clays (Chapters 3 and 6)

The clay used in the study reported in Chapter 3 was a natural Wyoming montmorillonite (**SWy-2**) obtained from the Source Clay Minerals Repository, University of Missouri, Columbia, with a cation exchange capacity (CEC) of 78 meq/100 g clay. The clay was fractionated to  $< 2$   $\mu\text{m}$  by gravity sedimentation and purified by standard methods in clay science.<sup>[3]</sup> A sodium-exchanged sample ( $\text{Na}^+$ -SWy-2) was prepared by immersing the clay in an aqueous solution of sodium chloride (1N). The cation exchange was completed by washing and centrifuging three times with the NaCl solution. The sample was finally washed with distilled deionized water and transferred into dialysis tubes in order to obtain chloride-free clay and then dried at room temperature. A synthetic trioctahedral hectorite, Laponite RD (Lap), produced by Laporte Industries Ltd., with structural formula  $\text{Na}_{0.8}[\text{Mg}_{5.4}\text{Li}_{0.4}]\text{Si}_8\text{O}_{20}(\text{OH})_4$ , a CEC of 48.1 meq/100 g clay and average particle size of 20 nm was used for the cytotoxic measurements. The clay used in Chapter 6 was a natural Texas montmorillonite (**STx-1**), with a cation exchange capacity (CEC) equal to

80 mequiv/100g clay and particle size  $\leq 2 \mu\text{m}$ , obtained from the Source Clay Minerals Repository at the University of Missouri, Columbia and purified applying the same method as described above.

### 2.1.3. Acid activation of clay (Chapter 6)

For the preparation of acid-activated-clay (**HT**) object of the study reported in Chapter 6, natural Texas montmorillonite STx-1 (50.0 g) was ground and magnetically stirred with 250 mL of 2 M  $\text{H}_2\text{SO}_4$  (from Riedel-deHaen) at 80 °C for 2 hs in a round-bottom flask. The slurry was cooled in air, centrifuged and washed with distilled water; the operation was repeated twice. The sample contained in a dialysis membrane was placed in deionized water and the water was renewed until the pH was neutral and the conductivity was stable.<sup>[4][5]</sup> The sample was finally dried at room temperature.

### 2.1.4. Carbon nanodiscs CNDs (Chapter 4)

The nanodiscs sample (also containing a small fraction of conical structures and amorphous carbon), produced by the CB&H process<sup>[6][7]</sup> and further annealed at 2500 - 2700 °C, was purchased from Strem Chemicals, Inc. (France). The cones and soot components were removed in the oxidation procedure described below.

### 2.1.5. Preparation of Clay/Adamantylamine hybrid (Chapter 3)

The Clay/Adamantylamine hybrid object of the study reported in Chapter 3 was synthesized by the following procedure: 300 mg of  $\text{Na}^+$ -SWy-2 dispersed in 100 mL distilled deionized water were reacted with 50 mg of 1-adamantylamine (97%, Aldrich) dissolved in 20/1 (v/v) ethanol/water. This amount corresponds to 1.5 times the CEC of SWy-2 montmorillonite. 5 drops of HCl 1M were then added and the mixture was stirred at room temperature for 24 hs. The residue was separated by centrifugation, washed three times with distilled deionized water and air-dried by spreading over a glass plate (product: **SWy-2/ADMA**). A similar procedure was used for the intercalation of ADMA (30 mg) in synthetic Laponite (sample: **Lap/ADMA**).

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### 2.1.6. Preparation of graphene oxide/adamantylamine hybrid (Chapter 3)

The GO/Adamantylamine hybrid object of the study reported in Chapter 3 was synthesized by the following procedure: 300 mg 1-adamantylamine were dissolved in ethanol (50 mL) and added dropwise to a dispersion of GO in distilled deionized water (100 mg GO in 50 mL) under vigorous stirring (pH=8). Upon addition of adamantylamine the GO solid swelled instantly. The reaction continued for 24 hs at room temperature. The GO derivative was isolated by centrifugation and washed three times with 1:1 (v/v) ethanol/water and dried in air (sample denoted as **GO/ADMA**).

### 2.1.7. Oxidation of carbon nanodiscs (Chapter 4)

The oxidization of carbon nanodiscs was achieved using a modified Staudenmaier's method.<sup>[1]</sup> In a spherical flask, 500 mg of CNDs were dispersed in a mixture of 20 mL H<sub>2</sub>SO<sub>4</sub> (95-97 %) and 10 mL HNO<sub>3</sub> (65 %) while placed in an ice-water bath (0 °C) and the system was stirred for 20 minutes. 10 g of KClO<sub>3</sub> were then added in small portions to the mixture under vigorous stirring and the reaction was completed after 18 hs. The oxidation product (**oxCNDs**) was separated by centrifugation (3500 rpm, 10 min) and washed several times with distilled water until a pH of 6 was reached. The remaining solid was spread on a glass plate and was air-dried.

### 2.1.8. Organosilane solutions (Chapters 6 and 7)

The organosilane used in the study described in Chapters 6 and 7 was 3-(2-aminoethylamino)-propyltrimethoxysilane, (EDAPTMOS), H<sub>2</sub>N(CH<sub>2</sub>)<sub>2</sub>NH(CH<sub>2</sub>)<sub>3</sub>Si(OCH<sub>3</sub>)<sub>3</sub>, from Fluka Chemicals. The formation of the octameric oligosiloxane from the hydrolytic polycondensation of the monomer occurs after dilution of EDAPTMOS in ethanol-water (v/v = 14/1) to give a solution of concentration 0.45 M.<sup>[8][9][10]</sup> 30 mL of an aqueous 0.1 M FeCl<sub>2</sub> solution (3 mmol) was reacted with 20 mL of the above solution (9 mmol) upon stirring. The colour of the ferrous chloride solution changed from pale orange to dark green, indicative of the complexation of ferrous cations with the amino functional group of the corresponding siloxane molecules. The produced Fe-EDAPTMOS complex discussed in Chapter 6 was used immediately after

its formation in order to avoid oxidation of the ferrous cations before the intercalation between clay platelets.

The Fe-EDAPTMOS-clay complexes were prepared by reacting, under stirring, a 0.5 wt% clay suspension with aliquots of the above siloxane complex solution such that the ratio  $R=[\text{Fe-EDAPTMOS}]/[\text{clay}] = 3$ . Within 1 h from the addition of iron-complex the colour of the slurry changed gradually from green to orange, indicating the oxidation of Fe(II) to Fe(III). After stirring for 6 hs the clay-organosilane aggregates were washed with water five times, separated by centrifugation and air-dried by spreading on glass plates. In order to prepare the pillared clays, the intercalated with the Fe-EDAPTMOS clay samples were calcined in air at 500 °C for 3 hs.

For the fabrication of the highly ordered  $\text{Cu}^{2+}/\text{Fe}^{3+}$  substituted POSS thin films with the LS method (Chapter 7) an additional metal organosilane solution was prepared. 30 mL of an aqueous 0.1 M  $\text{Cu Cl}_2$  solution (3 mmol) was reacted with 13.5 mL of the above described oligosiloxane solution (6 mmol) upon stirring. The colour of the copper chloride solution changed from light blue to dark purple after mixing. The produced Cu-EDAPTMOS complex was used 24 hs after its formation. Arachidic acid (AA) was used dissolved in chloroform (concentration of 0.2 mg/mL). LS films were prepared on a Nima Technology thermostated 612D LB trough at temperature of  $23\pm 0.5$  °C. Ultra-pure water with resistivity of greater than 18 M $\Omega$ -cm was used to prepare the subphase.

## 2.2. Characterization Techniques

### 2.2.1. X-ray Diffraction (XRD) (Chapters 3, 4, 6 and 7)

The XRD patterns for Chapters 3, 4 and 6 were collected on a D8 Advance Bruker diffractometer by using  $\text{Cu K}\alpha$  (40 kV, 40 mA) radiation and a secondary beam graphite monochromator. The patterns were recorded in the 2-theta ( $2\theta$ ) range from 2 to 80°, in steps of 0.02° and a counting time of 2 s per step. Samples were in the form of films supported on glass substrates. For the preparation of the films, aqueous

suspensions of the hybrids were deposited on glass plates and the solvent was allowed to evaporate slowly at ambient temperature. For the LS Cu<sup>2+</sup>/Fe<sup>3+</sup> substituted POSS thin films reported in Chapter 7, diffraction measurements were performed on (15-20)-layer-thick films. Arachidic Acid-Metal POSS hybrid films, deposited on hydrophobic silicon wafers. The out-of-plane X-ray reflectivity data for the hybrid films were collected under ambient conditions with a Philips PANalytical X'Pert MRD diffractometer. A Cu K $\alpha$  ( $\lambda=1.5418$  Å) radiation source was used (operated at 40 keV, 40 meV), while a 0.25° divergence slit and a 0.125° antiscattering slit were employed. The 2 $\theta$  scans were performed from 0.6° to 15° with 0.02° steps and a counting time of 15 s per step.

### **2.2.2. FTIR spectroscopy (Chapters 3, 4 and 6)**

Infrared spectra reported in Chapters 3 and 4 were measured with a SHIMADZU 8400 infrared spectrometer, in the region of 400-4000 cm<sup>-1</sup>, equipped with a deuterated triglycine sulphate (DTGS) detector. Each spectrum was the average of 200 scans collected at 2 cm<sup>-1</sup> resolution by means a SPECAC variable-angle attachment. Samples were in the form of KBr pellets containing ca. 2 wt % sample. A different set up was used for the data discussed in Chapter 6 namely a Perkin–Elmer Spectrum GX infrared spectrometer, equipped with a (DTGS) detector. Each spectrum spanning the region of 400–4000 cm<sup>-1</sup> was the average of 64 scans, collected with 2 cm<sup>-1</sup> resolution. Also in this case samples were in the form of KBr pellets containing ca. 2 wt% sample.

### **2.2.3. Raman spectroscopy (Chapters 3 and 4)**

Raman spectra were recorded with a Micro – Raman system RM 1000 RENISHAW, with excitation at 532 nm (Nd – YAG). A power of 1 mW was used with a 1  $\mu$ m focus spot in order to avoid photodecomposition of the samples. The range of measurement for samples measured was 1000–2400 cm<sup>-1</sup>.

### **2.2.4. Thermal analysis (Chapters 3, 4 and 6)**

Thermogravimetric (TGA) and differential thermal (DTA) analyses were performed using a Perkin Elmer Pyris Diamond TG/DTA. Samples of approximately 5 mg were heated in air from 25 °C to 850 °C, at a rate of 5 °C/min (Chapters 3 and 4). The

measurements discussed in Chapter 4 were performed using a Shimadzu DTG 60 Thermal Analyzer. Samples of approximately 15 mg were heated in air from 25 to 600 °C, at a rate of 10 °C/min.

### **2.2.5. X-ray Photoelectron Spectroscopy (XPS) (Chapters 3, 4, 6 and 7)**

For the XPS measurements discussed in Chapter 3, 150 nm thick gold films supported on mica were used as substrates. All samples were dispersed in distilled deionized water and after stirring and sonication for 30 min, a small drop of the suspension was left to dry in air on the substrate. Samples were introduced via a load-lock system into a SSX-100 (Surface Science Instruments) photoelectron spectrometer, equipped with a monochromatic Al K $\alpha$  X-ray source ( $h\nu = 1486.6$  eV). The base pressure in the spectrometer was  $1 \times 10^{-10}$  Torr during all measurements. The energy resolution was set to 1.16 eV in order to minimize the measuring time. The photoelectron take off angle was 37° with respect to the surface normal. An electron flood gun providing 0.3 eV kinetic energy electrons in combination with a gold grid mounted about 1 mm above the sample was used in the case of clays and clay hybrids to compensate for sample charging. All binding energies of GO hybrids were referenced to the C1s core level of the C-C bond set to the nominal value of 285.0 eV, while in the case of montmorillonite clays, all binding energies were referenced to the Si2p core level of smectite clay at 102.8 eV.<sup>[11]</sup> Spectral analysis was performed by means of a least squares curve-fitting program (WinSpec) developed at the LISE, University of Namur, Belgium; the fit included a Shirley background subtraction and peak deconvolution employing mixed Gaussian–Lorentzian functions. For the N1s line, however, a linear background subtraction was employed since the low peak intensity did not allow for a Shirley background subtraction. The same protocol was followed for the spectra presented in Chapter 4 with the difference that the electron flood gun provided 0.2 eV kinetic energy electrons and that no gold grid was used. Similarly for the data reported in Chapter 6 an electron flood gun provided 0.1 eV kinetic energy electrons; no gold grid was used for these measurements either.

For the XPS measurements discussed in Chapter 7 (Arachidic Acid - Metal POSS hybrid films) silicon wafers (Prime Wafer) were used as substrates. The surface of substrates was made hydrophobic by modification with octadecyltrichlorosilane (purchased from Sigma Aldrich) prior to the LS film deposition.

### **2.2.6. Atomic force microscopy (Chapter 4)**

Atomic force microscopy images were obtained in tapping mode with a 3D Multimode Nanoscope, using Tap-300G silicon cantilevers with a tip radius <10 nm and a force constant of  $\approx 20\text{--}75 \text{ N m}^{-1}$ . Samples were dispersed in ethanol and deposited onto silicon wafers (P/Bor, single side polished, purchased from Si-Mat) by drop casting. Measurements were performed by Antonios Kouloumpis (University of Ioannina, Greece).

### **2.2.7. Mössbauer spectra (Chapter 6)**

$^{57}\text{Fe}$  Mössbauer spectra (MS) for powder samples were collected at room temperature 300K (26.85 °C) and 10K (-263.15 °C), using constant acceleration spectrometers, equipped with a  $^{57}\text{Co}(\text{Rh})$  sources kept at RT and a closed loop He (ARS) Mössbauer cryostat. Calibration of the spectrometers was done using metallic  $\alpha\text{-Fe}$  at RT and all isomer shift (IS) values are reported relative to this standard. The fitting of the recorded MS was done using the IMSG code. Measurements were performed by Prof. Alexios Douvalis (University of Ioannina, Greece).

### **2.2.8. High-resolution transmission electron microscopy (Chapter 3)**

High-resolution transmission electron microscopy (HRTEM) data were collected using a FEI Tecnai G<sup>2</sup> microscope operated at 200 keV. Sample was prepared by dispersing the powder form of SWy-2/ADMA hybrid in ethanol before depositing onto a honeycomb carbon film supported by a copper grid. Measurements were performed by Prof. Ke Xiaoxing (University of Antwerp, Belgium).

### **2.2.9. Surface area and porosity measurements (Chapter 3 and 6)**

The surface areas and the pore volumes of the samples in Chapter 3 were determined by a SORPTOMATIC 1900 Thermo Finnigan porosimeter, using nitrogen

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as adsorbent at 77K (-196.15 °C). Prior to the determination of the adsorption-desorption isotherms the samples were degassed at 200 °C in vacuum of  $5 \times 10^{-2}$  mbar for 20 hs. The specific surface area of the samples was calculated by applying the BET equation using the linear part ( $0.05 < P/P_0 < 0.15$ ) of the adsorption isotherm and assuming a closely packed BET monolayer, with  $\alpha_m(N_2) = 0.162 \text{ nm}^2$  at 77 K. In Chapter 6 the same protocol was used but with the relative pressure range  $0.01 < P/P_0 < 0.30$ .

### 2.2.10. Catalytic measurements (Chapter 6)

The catalytic decomposition of isopropanol took place in a bench-scale flow reactor. The reactor consisted of a silica tube (1 cm in diameter) with a sealed-in quartz bed onto which 0.20 g of the catalyst was placed. The system was heated in a tubular furnace with a temperature control system accurate to within  $\pm 1$  °C. Analysis of reactants and products was carried out by sampling  $1 \text{ cm}^3$  of the gases in a Fisons GC-9130 gas chromatograph equipped with a flame ionization detector. The column used for analysis was a DB-WAX, 30 m x 0.32 mm, and with film thickness 0.5  $\mu\text{m}$ , supplied by J&W scientific. Helium used as carrier gas in the gas chromatograph. Another line drove Helium through a saturator bottle ( $40 \pm 1 \text{ cm}^3 \text{ min}^{-1}$ ) containing the isopropanol (at constant temperature), whose vapour was then driven to the reactor. Under the experimental conditions the partial pressure of isopropanol was 33 mmHg. Measurements were taken in the range of 90 to 200 °C in 5 or 10 °C intervals. Before the catalytic experiments were started, the catalyst was heated at 500 °C for 2 hs under Helium flow to remove adsorbed water from the pores. No signs of catalyst 'die off' were observed on the time scale of our experiments. The products detected were propene, diisopropyl ether and water. From the percentage degree of total conversion of isopropanol we calculated the reaction rate at each reaction temperature. Moreover the selectivity for each of the two main products, propene and diisopropyl ether, at various degrees of total conversion of isopropanol was also determined. Measurements were performed by Prof. Athanasios Ladavos (University of Patra, Greece) and Prof. Dimitrios Petrakis (University of Ioannina, Greece).

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### 2.2.11. Study of cytotoxicity in vitro (Chapters 3 and 4)

For the cytotoxicity study reported in Chapter 3: (a) Cell lines and cell culture used with **GO**, **GO/ADMA**, **LAP** and **LAP/ADMA** were Human lung cancer cells (A549) and normal human fetal lung fibroblasts (MRC-5), provided by Dr. Evangelos Kolettas, Laboratory of Physiology, Faculty of Medicine, University of Ioannina. All different cell lines were cultured in Dulbecco's Modified Eagles Medium (DMEM) enriched with 10% fetal bovine serum (FBS), 100 IU/mL penicillin, 100 µg/mL streptomycin and 1.4 mM L-Glutamin, at 37°C, with 5% CO<sub>2</sub>. All materials were provided by Costar and PAA. (b) MTT assay: Cell growth inhibitory ability of the substances, expressed by the average IC<sub>50</sub> value (substance's concentration required for 50% inhibition of cell growth), was analyzed using the MTT assay (3-(4,5-Dimethylthiazol-2-yl)-2,5-diphenyltetrazolium bromide). Briefly, 3×10<sup>3</sup> A549 cells and 5×10<sup>3</sup> MRC-5 cells were cultured overnight on 96-well plates and culture media containing different concentrations (ranging from 1 to 850 µg/mL) of **ADMA**, **Lap**, **Lap/ADMA**, **GO** and **GO/ADMA** were added. All substances were dissolved in sterilized water (solvent). The 96-well plates with culture media containing different volumes of sterilized water (solvent), equal to volumes of solutions added to the test wells, were considered as control. After incubation for 48 hs, 50 µL of MTT were added in each well from a stock solution (3 mg/mL), and incubated for additional 3 hs. The yielded purple formazans were re-suspended in 200 µL of DMSO, using a multi-channel pipette. The solution was spectrophotometrically measured (540 nm, background absorbance measured at 690 nm subtracted) using a microplate spectrophotometer (Multiskan Spectrum, Thermo Fisher Scientific, Waltham, USA). All the experiments were performed at least in triplicate. IC<sub>50</sub> values were determined by the curve of percentage of inhibition versus dose. Measurements were performed by Dr. Ioannis Verginadis and Dr. Anastasia Velalopoulou (University of Ioannina, Greece).

For the cytotoxicity study reported in chapter 4: (c) Cell lines and cell culture used with **oxCNDs** were the human embryonic kidney cell line Hek293T and the human adenocarcinoma HeLa cell line, which were obtained by Dr. E. Mastrobattista

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(Utrecht University). The cells were cultured in high glucose D-MEM medium with 10% fetal bovine serum and 1% Penicillin/ Streptomycin. The cells were maintained at 37 °C in a humidified 5% CO<sub>2</sub> incubator for 24 hs. After that stage the sterilized and diluted compound was added in different concentration. (d) XTT toxicity tests: In vitro cytotoxicity studies were performed using the XTT (2,3-Bis(2-methoxy-4-nitro-5-sulfophenyl)-2H-tetrazolium-5-carboxanilide inner salt) colorimetric method <sup>[12]</sup> according to the literature.<sup>[13]</sup> Briefly, cells were seeded into flat bottomed 96-well plates at a concentration of 20.000 for Hek and 10.000 for HeLa cells per well. After 24 hs of incubation the medium was replaced and dispersed **oxCNDs** in D-MEM at concentrations of 2-1000 µg mL<sup>-1</sup> were added. Cell-seeded wells with only D-MEM growth medium were used as controls. The mitochondrial redox function, translated as cell viability of all cell groups was assessed by the XTT assay at selected time point of 48 hs post-incubation. The absorbance was measured for each well by a spectrophotometric [SpectraMax M3] at 490 nm plate reader. The experiment was repeated in triplicate. Measurements were performed by Karolin Romhild (University of Groningen, The Netherlands).

### 2.2.12. Adsorption of chlorophenols (Chapter 3)

a) Swelling of materials: 10 mg of **GO** or **GO/ADMA** were swelled for 20 hs in methanol under stirring in glass vials. Then, distilled deionized water was added to a final MeOH/H<sub>2</sub>O = 70/30 (v/v). 10 mg of **SWy-2** or **SWy-2/ADMA** were swelled for 20 hs in distilled deionized water (pH=4.5) under stirring in glass vials. After 20 hs methanol was added so the final volume ratio MeOH/H<sub>2</sub>O = 70:30 (v/v). This methanol/H<sub>2</sub>O mixture was chosen for both materials, since the goal of this experiment was to compare the performance of the clay and GO-based materials. (b) Adsorption: The solutes used were 2,4,6-trichlorophenol (2,4,6-TCP) pentachlorophenol (PCP) and 2,4-dichlorophenol (2,4-DCP) purchased from Aldrich (purity 97%). Stock solutions of 0.8 mM 2,4-DCP, 2,4,6-TCP and PCP were prepared in MeOH/H<sub>2</sub>O [70:30 v/v]. Adsorption experiments were performed in batch. 2,4-DCP, 2,4,6-TCP or PCP were added, at concentrations ranging between 7 µM and 70 µM, in

10 mg of swelled dispersions of the pristine and hybrid materials. The pH of the reaction mixture was adjusted using NaOH to pH=5.3 for both 2,4-DCP and 2,4,6-TCP and pH=4.5 for PCP to ensure the presence of protonated form of the phenols since the  $pK_a$  of 2,4-DCP is 6.79, the  $pK_a$  of 2,4,6-TCP is 6.23 and the  $pK_a$  of PCP is 4.7.<sup>[14]</sup> Screening experiments showed that the adsorption was completed in 90 min. Thus measurements were performed after 2 hs of incubation to ensure adsorption equilibrium. Then the samples were centrifuged and UV-Vis spectra of supernatants were measured in quartz cuvettes 6Q, 1x1cm. Controls were run for chlorophenol solutions every 2 hs with no solid material in the reaction mixture. The UV-Vis spectra were recorded using a Perkin-Elmer Lambda-35 double beam spectrometer. Quantification of the chlorophenols was done using the peaks at 280 nm for 2,4-DCP, at 290 nm for 2,4,6-TCP and at 210 nm for PCP. By comparing the UV-vis spectra for solutions with known phenol concentrations with the corresponding spectra recorded on our materials we calculate the concentration of chlorophenols adsorbed. Measurements were performed by Eleni Seristratidou (University of Ioannina, Greece).

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