ACADEMIA ROMANA
Institutul de Chimie Macromoleculara
"PETRU PONI"

Centre of Advanced Research in
Bionanoconjugates and Biopolymers
IntelCentre

Contributions regarding the use of XPS in the investigation of organic and inorganic materials

PhD Thesis Summary

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To _____

This is to inform you that on **December 21st, 2015**, at **13:00**, the library of the "Petru Poni" Institute of Macromolecular Chemistry, Iasi will host the public defense of the PhD thesis entitled **"Contributions regarding the use of XPS in the investigation of organic and inorganic materials"**, elaborated by Mrs. **Adina COROABĂ**, physicist, to acquire the PhD degree.

The doctoral jury is composed of:

PRESIDENT	**Dr. Valeria HARABAGIU, senior researcher**, "Petru Poni" Institute of Macromolecular Chemistry, Iasi
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According to the Regulations on the organization and PhD thesis defense within the Romanian Academy, please find enclosed a summary of the PhD thesis. Your comments and appreciations will be highly appreciated.

You are kindly invited to attend the public presentation of the PhD thesis.

ACADEMIA ROMÂNĂ INSTITUTUL DE CHIMIE MACROMOLECULARĂ "PETRU PONI"

DIRECTOR,

Dr. Anton Airinei

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The thesis entitled **"Contributions on the use of X-ray Photoelectron Spectroscopy (XPS) in the investigation of organic and inorganic materials"** has **156** pages divided into five chapters, which include **46** figures, and **279** bibliographical references. In the following are presented some significant results discussed in the thesis, closely following the thesis content.

TABLE OF CONTENTS

ABBREVIATION LIST

^{1}H-RMN – Proton nuclear magnetic resonance

$AgNO_3$ – Silver nitrate

AgNPs – Silver nanoparticles

SA – Succinic anhydride

ATR-FTIR – Attenuated total reflection - Fourier transform infrared spectroscopy

b-PEI – Branched poly(ethylenimine)

CCL – *Candida cylindracea*

C-Dots – Carbon dots

dsDNA – Double stranded DNA

DCF – Dynamic Constitutional Frameworks

DDA – Dodecylamine

DLS – Dynamic light scattering

DMF – Dimethylformamide

EDX – Energy-dispersive X-ray spectroscopy

MP – Magnetite nanoparticles

MP-PS – Magnetite nanoparticles with polydimethylsiloxane shell

N/P – The ratio of the number of atoms of N and P

NaLS – Sodium lignosulfonate

NHS – *N*-Hydroxysuccinimide

PEG – Poly(ethylene glycol) bis(3-aminopropyl) terminated

PET – Poly(ethylene terephthalate)

PL – Photoluminescence

PLQY – Photoluminescence quantum yield

SEM – Scanning electron microscopy

siRNA – Small interfering RNA

T – 1,3,5-Benzenetricarboxaldehyde

TEM – Transmission electron microscopy

TIP – Titanium isopropoxide

TMSPMA – 3-(Trimethoxysilyl)propyl methacrylate

UV – Ultraviolet light

XPS – X-ray photoelectron spectroscopy

INTRODUCTION

X -ray Photoelectron Spectroscopy (XPS), has become an increasingly useful tool in understanding the nature of many types of surfaces. XPS method is essential for understanding important aspects of nanostructured materials, both natural and synthetic, which cannot be easily investigated using other techniques. In addition, XPS finds a great number of applications in the analysis of systems surface for biological materials, and, at the same time, plays an important role in the characterization of synthetic materials (biomaterials), materials designed in order to be used in biological environment. Bacteria and cell surfaces could be considered as complex nanostructured systems.

Using the XPS technique we can analyze polymers, pure elements, catalysts, glass, ceramics, paper, wood, makeup, teeth, bones, implants, biomaterials, viscous oils, glues and modified ionic materials. In addition, this technique can be used in the study of biological materials, with the condition that they have been previously treated in order to remove the water content.

XPS analysis technique provides information about the chemical composition of solid samples surface (metals, semiconductors, ceramics, glasses, etc.), while allowing the identification of all elements of the periodic table, except hydrogen and helium. Moreover, using XPS one can obtain semi-quantitative information regarding element concentrations exceeding 0.1% and concentration profiles in depth. Through XPS, the interaction of the analyzed material with the environment can be highlighted by identifying the chemical reactions of the elements on the surface of the sample with the environment. Also, it may determine the oxidation states, photochemical and thermal

reactions, etc. The presence of contaminants, adhesives, adsorbed molecules and their distribution on the surface of the analyzed sample can be identified. XPS technique allows detecting information about atomic orbitals and the structure of valence band levels of the elements.

The thesis entitled **"Contributions on the use of X-ray Photoelectron Spectroscopy (XPS) in the investigation of organic and inorganic materials"** has as main objective the structural characterization of nanosized and nanostructured compounds using XPS, shedding new light on the three-dimensional structure and composition of the compounds.

The thesis was organized in two parts, the first part comprising ***literature data*** and the second part of ***original results***, it was divided into three chapters. The first chapter summarizes the literature data, and the rest of the chapters are presenting the original contributions.

Chapter I briefly overviews the literature data. This chapter brings forward the data on the use of XPS in the study of nanostructured materials and biomaterials.

Chapter II contains a study on the use of XPS to determine the structure of non-viral vectors utilized for the delivery of active principles. In this chapter is presented the applicability of XPS technique in the characterization of non-viral vectors obtained by different synthesis methods such as constitutional dynamic chemistry (DCF – Dynamic Constitutional Frameworks), pyrolysis or co-precipitation.

Chapter III includes the analysis of modified surfaces and self-assembled structures using XPS.

Chapter IV presents the surface analysis of biological samples using XPS, energy-dispersive X-ray spectroscopy, attenuated total reflection –

Fourier transform infrared spectroscopy and scanning electron microscopy. In this chapter were studied fingernails from healthy donors *vs.* fingernails from patients diagnosed with psoriasis, in order to establish the degradation mechanism induced by psoriasis in human nails.

Each chapter contains conclusions and bibliography. The thesis concludes with a chapter of general conclusions (**Chapter V**) from the review of the presented material, followed by a list of published works.

ORIGINAL RESULTS

CHAPTER II. The use of XPS technique to determine the structure of non-viral vectors utilized for the delivery of active principles

DNA vector systems obtained through constitutional dynamic chemistry

Synthesis and characterization of non-viral vectors based on 1,3,5-benzenetricarboxaldehyde, poly(ethylene glycol) bis(3-aminopropyl) terminated and branched poly(ethylenimine) (T:PEG:b-PEI)

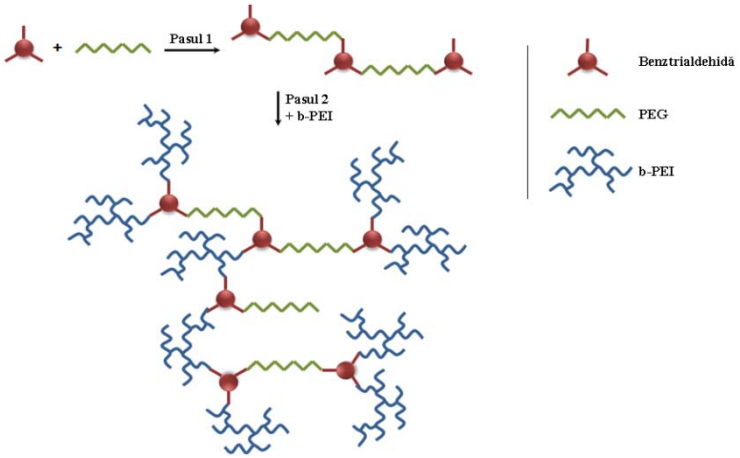

Figure 1. Scheme of the synthesis of the T-PEG-PEI vector.

The chemical structures of T:PEG and T:PEG:b-PEI conjugates, with different molar ratios, were highlighted by ^{1}H-NMR (Figure 2).

From ^{1}H-NMR spectra of T:PEG conjugates, with different molar ratios and greater than 1, it was observed that the peak corresponding to aldehydic proton, H-C=O (10 ppm), decreases while the peak corresponding to iminic proton, H-C=N-PEG (8.5 ppm) increases during the reaction of PEG amino groups with aldehydes. Also, the value of the integral of the peak corresponding to aldehydic proton (10 ppm) is consistent with the number of unreacted aldehyde groups (Figure 2A). Note that the ^{1}H-NMR spectra in D_2O remain unchanged after one month, which suggests that the PEG chains are able to protect the imine groups (susceptible to hydrolysis) formed by the reaction between aldehyde and amine groups of the PEG.

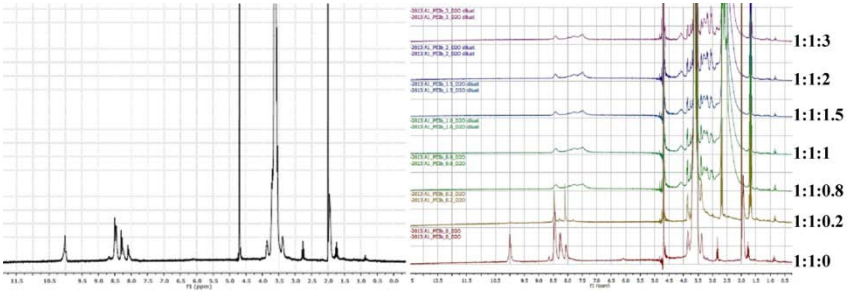

Figure 2. ^{1}H-NMR spectra for (A) T:PEG in molar ratio of 1:1, and (B) T:PEG:PEI conjugate in molar ratio 1:1:3 in D_2O.

XPS characterization of the T:PEG:b-PEI conjugates

PEG, b-PEI, and 1, 3 and 6 samples were analyzed using XPS technique to determine the chemical composition and to confirm the imine bonds formation (HC=N) during the formation of T:PEG:PEI conjugates. This type of bond is important for our study since it demonstrates that the reaction between the PEG, b-PEI and benztrialdehyde occurred in 100 % (all the C=O bonds have been consumed and have been converted to C=N).

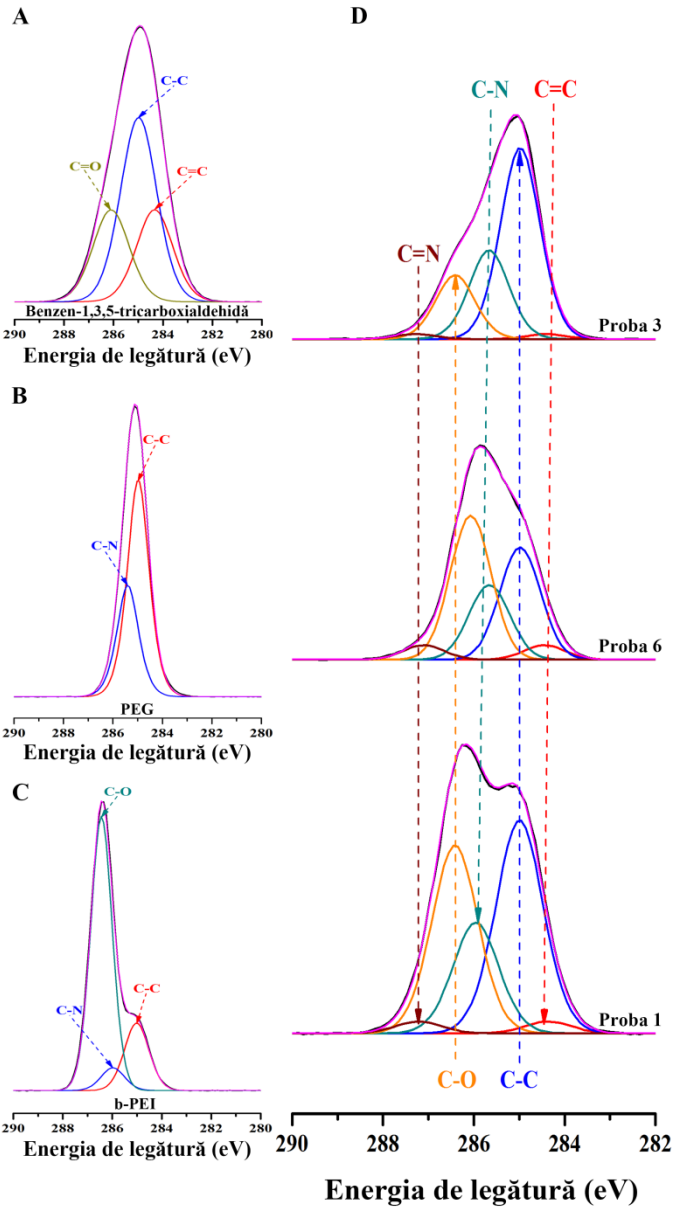

Figure 3. XPS high resolution spectra corresponding to C 1s for (A) benztrialdehyde, (B) PEG, (C) b-PEI, (D) samples 1, 3, and 6.

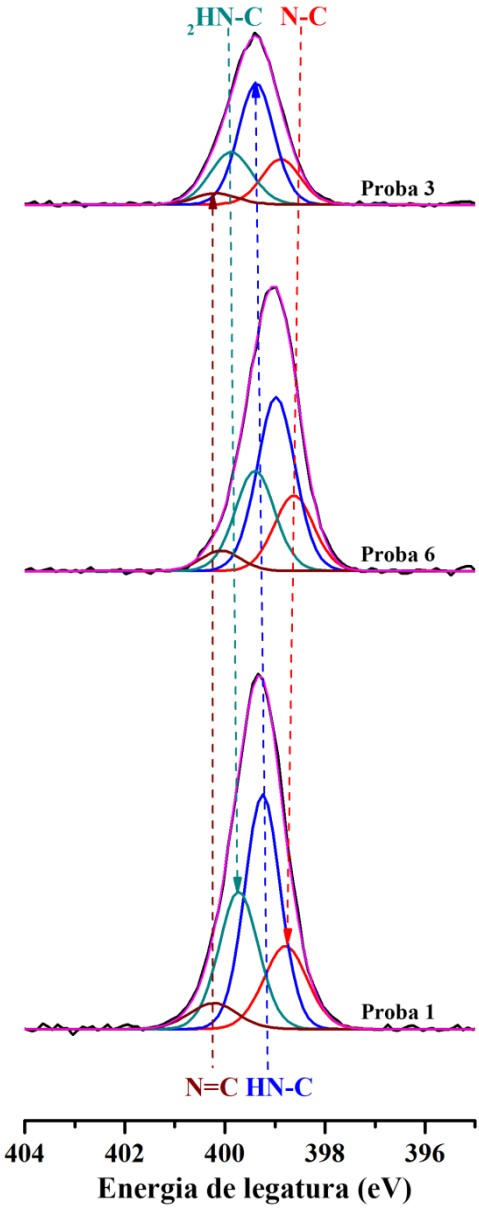

Figure 4. The deconvolution of high resolution spectra corresponding to N 1s signal for samples 1, 3 and 6.

From the deconvolution of the XPS high resolution spectra, for C 1s and N 1s, it can be clearly seen that the C=O bond, specific for the benztrialdehyde, is completely consumed and converted into the C=N bond. The results obtained from the XPS are consistent with the NMR results.

Magnetic nanoparticles with polydimethylsiloxane shell loaded with *Candida cylindracea* lipase for catalytic applications

This study presents a new core-shell nanosupport (core: magnetite, shell: hydrophobic polydimethylsiloxane) capable of charging and value lipase derived from *Candida cylindracea* (CCL). Magnetite nanoparticles (MP) preformed, with diameters between 30 and 40 nm, were coated with ester-polydimethylsiloxane (PS) using a simple method shown in Figure 5, according to reference (1).

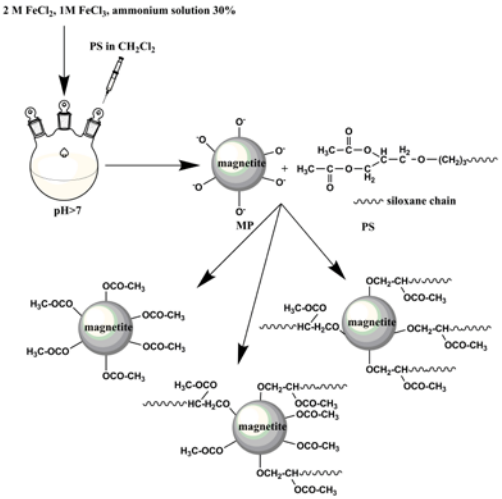

Figure 5. The reaction scheme for the preparation of magnetite-polydimethylsiloxane nanoparticles, (MP-PS) (1).

XPS characterization of magnetic nanoparticles loaded with lipase

XPS high resolution spectra of MP- PS sample (Figure 6 and Table 1) indicate the presence of Fe 2p, C 1s, O 1s, and Si 2p elements in different oxidation states. The peak specific for oxygen atoms, O 1s, varies in the 527.6-536.4 eV range, and it is decomposed into four characteristic bands, assigned to O-Fe , O-Si , O-C and O=C bonds, which confirm the existence of polydimethylsiloxane on the surface of the magnetite nanoparticles. The magnetite structure is proven by the presence of Fe 2p peak (Figure 6a, Table 1) in two oxidation states Fe^{2+} and Fe^{3+} in a ratio of about 0.5, typical magnetite report (2).

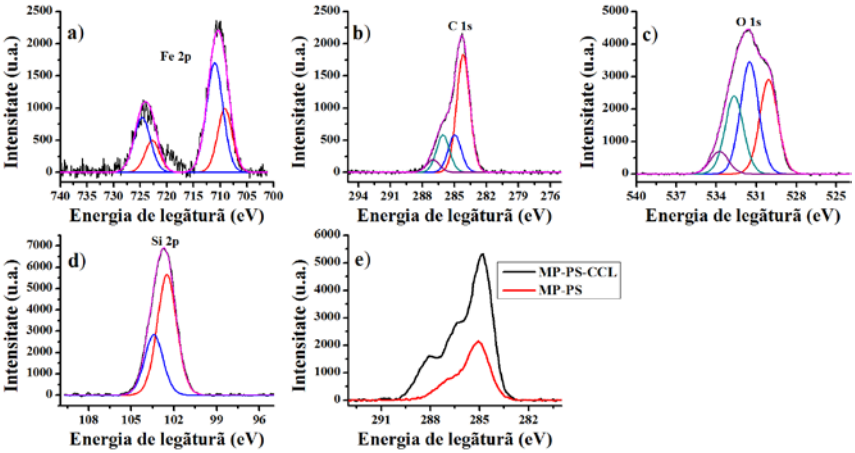

Figure 6. XPS high resolution spectra of the MP-PS nanoparticles: (a) Fe 2p; (b) C 1s; (c) O 1s; (d) Si 2p; (e) C 1s for MP-PS and MP-PS-CCL.

Table 1. Characteristics of C 1s, O 1s, Si 2p and Fe 2p elements corresponding to XPS spectrum of MP-PS (* reference peak); the data were obtained from the high resolution XPS spectra shown in Figure 6.

Element	Binding energy (eV)	Assignment	Relative concentration (%)
C 1s	284.2	C-Si	57.44
	*285	C-C/C-H	18.21
	286.1	C-O	18.21
	287	C=O	6.14
O 1s	530.1	O-Fe	30.57
	531.5	O-Si	36.39
	532.7	O-C	25.7
	533.8	O=C	7.34
Si 2p	102.5	Si-C	67.67
	103.4	Si-O	32.33
Fe 2p	709.1	Fe^{2+}	33.82
	711	Fe^{3+}	66.18

Silver nanoparticles obtained in the presence of sodium lignosulfonate (AgNPs/NaLS)

In this section of the thesis, the behavior of a water soluble (NaLS) lignin derivative is investigated, in order to reduce and stabilize the silver ions complex in the absence of any additional processes or chemicals and without a particular need for ensuring an alkaline environment. Also, in this study, a simple, cost-effective and environmentally friendly production process was applied, for preparing stable and catalytically active silver nanoparticles (3).

XPS characterization of AgNPs/NaLS nanoparticles

The structure of AgNPs nanoparticles and the interactions established between AgNPs and NaLS were examined by XPS.

The high resolution spectra of Ag 3d shows two strong signals at 368.8 and 374.8 eV, representing about 95 % of the total concentration of silver species added to the synthesis process (Figure 7). The spectra also show two satellite signals placed at 369.8 and 375.8 eV, respectively. The peaks corresponding to Ag 3d from AgNPs/NaLS systems located at 368.8 and 374.8 eV are shifted to higher binding energies than those of metallic silver (367.9 and 373.9 eV). However, the peaks situated at 368.8 and 374.8 eV are presenting a 6 eV separation, equal to that of metallic Ag 3d, which confirms the presence of Ag^0 (metallic) in AgNPs/NaLS system (4). This observation is supported by the literature, which shows that the peak at 368.8 eV binding energy is characteristic to silver nanoparticles (5,6). The presence of satellite peaks are due to the existence of a proportion of very small nanoparticles, possible subnanometric dimensions, that can foster optical transitions, leading to enhanced luminescence and Raman scattering phenomena (7). Moreover, the presence of subnanometric nanoparticles is a key factor in achieving high polydispersities observed in DLS measurements.

XPS high resolution spectra of C 1s, O 1s, and S 2p registered for AgNPs/NaLS reveals that there is a general shift of peaks, by 0.4-0.7 eV, towards higher binding energies compared with the corresponding peaks from NaLS, which confirms the existence of metal-polymer interactions in AgNPs/NaLS systems. It should be noted also that the synthesis temperature does not lead to significant changes in the XPS spectra.

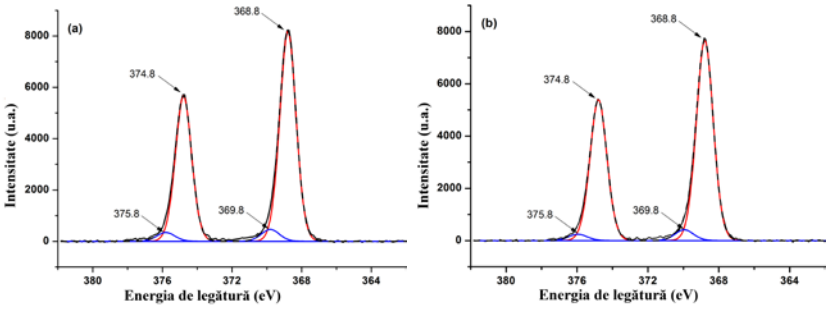

Figure 7. XPS high resolution spectra of the Ag 3d for AgNPs/NaLS prepared at 25 °C (a), and 70 °C (b).

CHAPTER III. XPS analysis of modified surfaces and self-assembled structures

Polyethylene terephthalate films (PET) surface modified with collagen

The purpose of this study was surface functionalization of PET film treated with UV light, as an alternative to other existing unconventional methods. PET surfaces were irradiated at two different time periods to attach collagen molecules for patch applications.

XPS characterization of untreated and modified collagen films

Chemical surface modifications induced by the UV treatment and the collagen immobilization were determined by XPS analysis (Figure 8). From the wide scan spectra of both untreated and grafted collagen films, the specific elements can be observed: C 1s, O 1s, and N 1s (Table 2).

Table 2. The elemental composition (atomic %) obtained by XPS analysis.

Sample	O	C	N	O/C	N/C
Untreated PET	25.24	74.76	-	0.34	-
PET-UV 24h-collagen	20.92	68.36	10.72	0.3	0.15
PET-UV 48h-collagen	20.12	67.64	12.24	0.29	0.18

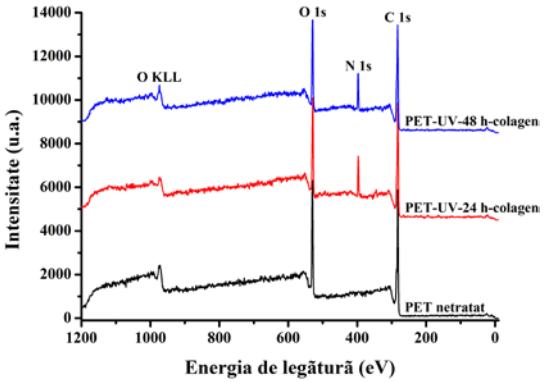

Figure 8. XPS analysis of untreated PET films and films with collagen immobilized on the surface.

The collagen adsorption on the surface of PET films was shown by XPS analysis. The appearance of N 1s peak in XPS wide scan spectra demonstrates the adsorption of collagen at the surface of treated films and also the adsorbed amount of collagen is in close connection with the irradiation time.

Functional silsesquioxane-based hierarchical assemblies for antibacterial/antifungal coatings

The combination of sol-gel reactions with molecular self-assembly process induced by the evaporation of the solvent, and the nucleation of silver

nanoparticles allows the formation of new types of methacrylate silsesquioxanes-based hybrid nano-composites containing titanium and/or silver nanoparticles.

The two levels of hierarchical morphologies (nanowires and nano-rod confined with semi-cylindrical shells of micrometer-sized type structures) were awarded as the result of combining self-assembly mesophases, controlled phase separation, sol-gel transitions, and stabilized silver nanoparticles by electrostatic interactions.

XPS characterization of the methacrylate silsesquioxane-based hybrid nanocomposites containing titanium and/or silver nanoparticles

XPS analysis shows that there are no interactions between the silver and the amino groups from dodecylamine, probably due to the protonation of these groups, which results in a reduction in the number of binding sites. The shifts of the binding energy values for C=O of both silsesquioxanes-based polymers compared to the standard value for C=O units were assigned to electrostatic interactions between the oxygen atoms and the surface of the silver nanoparticles.

In Table 3 are presented the deconvolutions of XPS high resolution spectra.

Table 3. XPS high resolution spectra deconvolution for POSS-Ag and POSS-AgTi (BE: binding energy (eV); RC: relative concentration (%)).

Functional groups			**POSS-Ag**	**POSS-AgTi**
C 1s	C-C/C-Si	BE	285	285
		RC	70.69	71.45
	C-N/C-O	BE	286.5	286.4
		RC	16.21	14.66
	C=O	BE	287.8	287.4
		RC	6.62	6.09

	O-C=O	BE	289	288.9
		RC	6.48	7.8
O 1s	O-Ti	BE	-	530.9
		RC	-	13.42
	HO-Si	BE	531.5	531.5
		RC	16.53	27.27
	Si-O-Si	BE	532.5	-
		RC	56.61	-
	Si-O-Si/ Ti-O-Si	BE	-	532.6
		RC	-	46.18
	O-C	BE	533.7	533.8
		RC	18.09	13.13
	O-C=O	BE	534.9	-
		RC	8.77	-
Ag 3d	Ag^0	BE	368.7	368.6
		RC	96.82	85.70
	Ag^+	BE	374.7	374.6
		RC	3.18	14.30
Si 2p	O-Si-C/ Si-O-Si	BE	101.8	101.2
		RC	9.97	18.33
	Si-O-Si	BE	102.6	-
		RC	90.03	-
	Si-O-Si/ Ti-O-Si	BE	-	102.2
		RC	-	81.67
S 2p	SO_4^{2-}	BE	168.3	168.3
		RC	100	100
N 1s	N-Ti-O	BE	-	398.9
		RC	-	13.05
	Ti-O-N	BE	-	400.1
		RC	-	77.92
	N-C	BE	399.4	399.2
		RC	64.4	9.03
	N-O	BE	400.7	-
		RC	35.6	-
Ti $2p_{3/2}$	O-Ti din TiO_2	BE	-	459.1
		RC	-	81.61
	Si-O-Ti	BE	-	458.2
		RC	-	18.39

From the deconvolution of the XPS high resolution spectrum corresponding to the Ag 3d signal two components were observed, chemically different, for both silsesquioxane-based nanocomposites containing titanium and/or silver.

The component from lower binding energy (368.6 – 368.7 eV) is attributed to the emission of electrons in metallic silver (Ag^0 – 96.82 % and 85.70 % for POSS-Ag and POSS-AgTi, respectively), and the component from higher binding energy (374.7 and 374.6 eV for POSS-Ag and POSS-AgTi, respectively) is specific to silver ions and indicates that only a small fraction of unreduced Ag^+ remains on the surface of the sample (Ag^+ – 3.18 % and 14.30 % for POSS-Ag and POSS-AgTi, respectively).

Through the XPS technique the structure and properties of POSS-Ag and POSS-AgTi compounds were evidenced. Due to the presence of carbonyl groups, the silsesquioxane-based hybrid nanocomposites influence the final shape and size of silver nanoparticles, and the formation of metallic silver provides a good antibacterial and antifungal activity. The large amount of chemically adsorbed nitrogen on the surface of TiO_2 (77.92 %) limits the catalytic performance of POSS-AgTi compound.

CHAPTER IV. Surface analysis of biological samples by XPS, EDX, ATR-FTIR, and SEM – Structural characterization of healthy *vs.* psoriatic nails

This study is focused on understanding the mechanism of degradation induced by psoriasis in human fingernails. Imaging and spectroscopic methods, such as XPS, EDX, ATR-FTIR, and SEM have provided information on the

chemical structure, elemental composition and surface morphology of healthy and psoriatic nails.

Due to the formation of inter- and intramolecular hydrogen bonds (Figure 9A) and the existence of disulfide bonds (thanks to the presence of cystine) (Figure 9B), keratin has a helix form which gives greater stability to the nail (8).

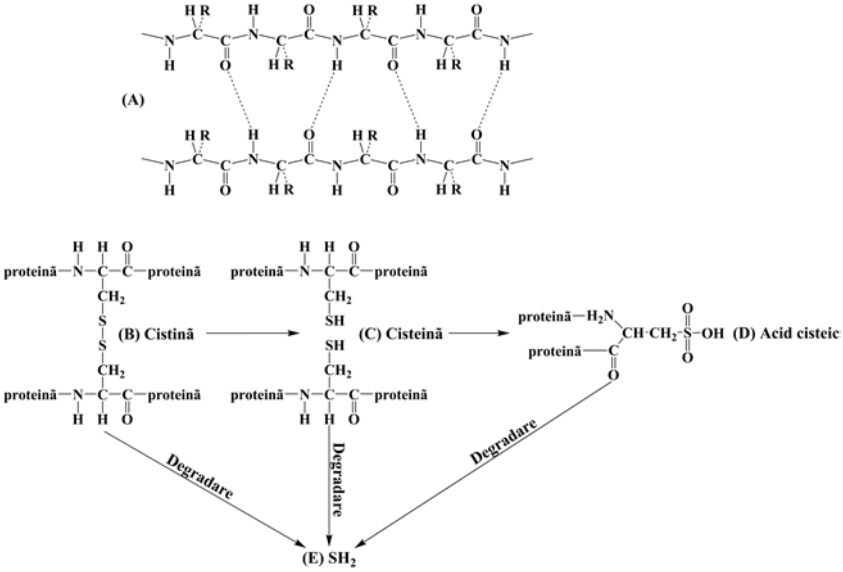

Figure 9. (A) The formation of hydrogen bonds. The mechanism of degradation of disulfide bonds (B) Cystine, (C) Cysteine, (D) Cysteic acid, (E) The degradation process.

X-ray photoelectron spectroscopy (XPS)

Through the XPS technique (which allows analysis down to a 10 nm depth) the following elements have been identified, for both healthy and psoriatic nails: C, N, O, S, and Ca (Table 4). As a consequence of the disease, a

slight increase in the C content and a decrease of the N and S contents can be observed.

Table 4. The experimental results obtained by XPS analysis for elemental composition of both healthy and psoriatic nails, in men and women (% atomic concentration).

	C	N	O	S	Ca
Healthy nails (%)	81.11±0.66	5.13±0.41	11.69±0.34	1.17±0.17	0.90±0.05
Psoriatic nails (%)	83.45±0.58	2.51±0.14	12.77±0.34	0.41±0.07	0.86±0.06
Unpaired *t* test (*p* value)	0.0288(*)	0.0003(***)	0.3446	0.0035(**)	0.5645

For all data has been calculated the mean ± SEM (standard error of the mean). Unpaired *t* test was used and a value of $p<0.05$ was considered significant.

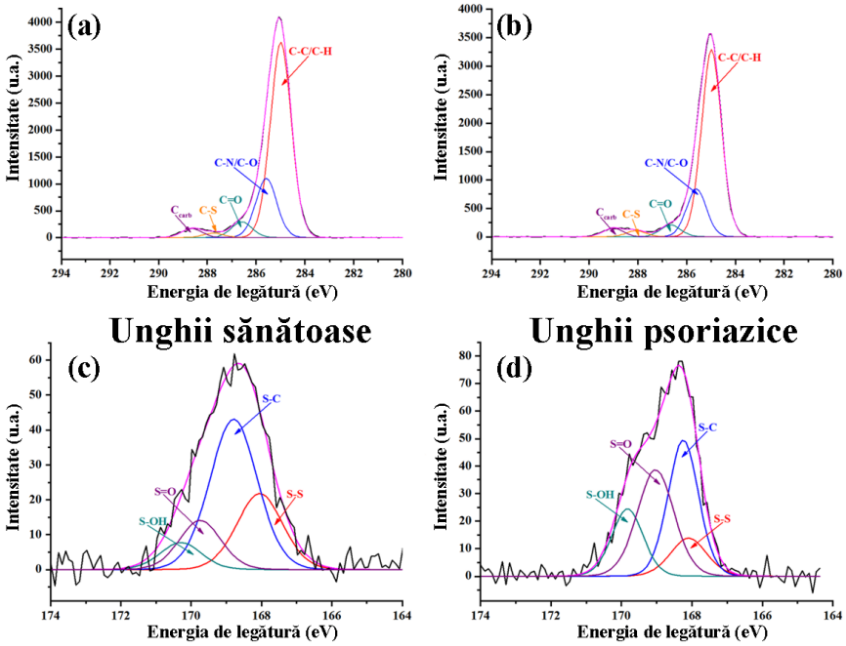

Figure 10. Deconvolution of C 1s and S 2p signals.

Table 5. The deconvolution of C 1s and S 2p signals for both healthy and psoriatic nails, in men and women (% relative concentration).

Element	Assignment	Binding energy (eV)	Healthy nails (%)	Psoriatic nails (%)
C 1s	**C-C/C-H**	285.0	62.80±0.80	71.45±0.49
	C-N/C-O	285.6	25.45±0.54	18.09±0.29
	C=O	286.6	6.17±0.48	4.51±0.10
	C-S	288.0	2.95±0.17	2.45±0.07
	C_{carb} (CO_3^{2-})	288.8	2.63±0.12	3.50±0.05
S 2p	**S-S**	168	25.56±0.33	12.00±0.19
	S-C	168.5	51.27±0.31	35.66±0.17
	S=O	169.4	14.73±0.22	33.87±0.09
	S-OH	170.0	8.44±0.13	18.47±0.09

For all data has been calculated the mean ± SEM (standard error of the mean).

The presence of cysteic acid structural units is highlighted through the existence of S=O and S-OH bonds. In psoriatic nails, the content of the S=O and S-OH bonds is increasing with the decrease of the S-S bond content. Thus, we can say that the deterioration of the nail affected by psoriasis is also produced by the breaking of disulfide bridges specific to cystine, favoring the appearance of a higher cysteic acid concentration. The -S-S- disulfide bridges are chemically reduced to –SH groups (cystine disulfide bridge is broken, thereby forming cysteine) and, subsequently, some of them are converted to sulfate groups.

Attenuated total reflection - Fourier transform infrared spectroscopy (ATR-FTIR)

The ATR-FTIR spectra for both types of nails, after the deconvolution of the 1700-1600 cm^{-1} band, were decomposed into nine different components assigned as follows:

- β-sheet: peaks #1, #2, #3, #4, and #8;
- random coil: peak #5;
- α-helix: peak #6;
- β-turn: peaks #7, and #9 (9,10).

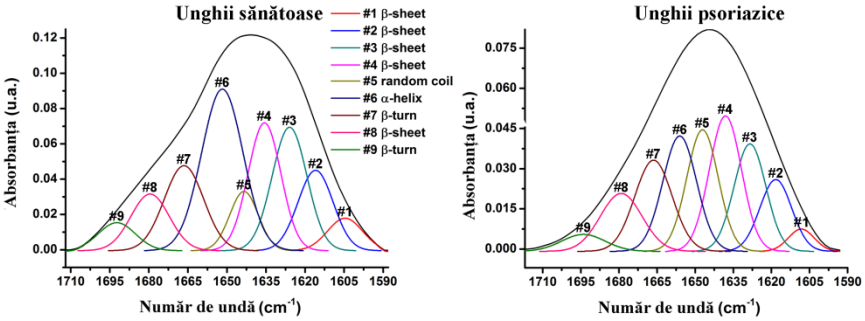

Figure 11. Deconvolution of absorption band specific to amide I region.

From the ATR-FTIR spectra it was observed in the psoriatic nail a significant reduction of α-helix content associated with the increase of β-sheet and random coil content, regardless of age or sex. Nails are hard α-keratins, which have plenty of α-helix (8) and a decrease in the α-helix content destabilizes the nail protein (9). On the other hand, the increased β-sheet is due to erroneous folding of keratin in amyloid-like fibrils – intermolecular β-sheets involved in protein aggregation (11,12). The damage caused by nail psoriasis is associated with the α-β transition followed by a β-sheet-mediated protein aggregation. Moreover, the increased content of random coil is a measure of the protein distortion (9).

Through the non-invasive techniques, such as XPS, EDX, ATR-FTIR, and SEM, it was showed how the molecular structures of keratin and cystine are damaged and how this degradation is linked to the loss of elemental composition.

CHAPTER V. General Conclusions

From the material presented in this paper, the following general conclusions can be formulated:

- 1,3,5-benzenetricarboxaldehyde: poly(ethylene glycol) bis(3-aminopropyl) terminated-branched poly(ethylenimine) (T:PEG:b-PEI) non-viral vectors were synthesized, obtaining a "library" of compounds based on 1,3,5-benzenetricarboxaldehyde modified with PEG and b-PEI in various molar ratios.

- Non-viral vectors are able to load the plasmidic DNA, resulting in polyplexes with sizes between 39 and 126 nm, depending on the molar ratio of T:PEI:PEG.

- XPS analysis revealed that the C=O bond, specific to aldehyde group, is completely consumed and converted to C=N imine bond. XPS results were consistent with the results obtained from NMR analysis.

- Strongly fluorescent C-Dots were prepared by a controlled pyrolysis process (180 °C, 30 min) in one step of *N*-Hydroxysuccinimide in a simple experimental model.

- Detailed XPS analysis of C- Dots showed the C-Dots graphitic nature and the abundance of different functional groups located on the surface.

- Magnetite nanoparticles were obtained with a diameter of 30-40 nm, coated with polysiloxane and used as hydrophobic substrate for the immobilization of *Candida Cylindracea* lipase.

- XPS analysis revealed the nature of magnetic nanoparticles (MP-PS) and the presence of siloxane and CCL enzyme on the surface of MP-PS nanoparticles.

- Aqueous suspensions of silver nanoparticles coated with sodium lignosulfonate through an environmentally friendly, simple and cheap process have been obtained.

- The AgNPs/NaLS nanoparticles presented colloidal stability for more than 2 months. The systems were characterized by XPS, XRD and DLS.

- It was first proposed the obtaining of silver nanoparticles through an ecological process (using sodium lignosulfonate), simple (just by shaking the components) without external temperature supply and without raising the pH printed by the presence of sodium lignosulfonate. AgNPs will be tested for the establishment of their antimicrobial properties.

- The structure of macromolecular compounds from the surface of wood samples was chemically modified by the treatment with succinic anhydride.

- The results obtained by XPS analysis showed an increased O/C ratio for chemically modified wood that could be explained by the fact that oxidation occurred during the chemical reaction.

- Changes in the chemical composition set out by the XPS analysis are consistent with the results reported in the literature.

- An increased value of C4, O1 peak areas and of O/C, C4/C2 and O1/O2 ratios signify the occurrence of oxidation reactions during chemical modification process.

- PET films were activated by UV radiation (to produce reactive functional groups), and then were immersed in a solution of collagen.
- Collagen adsorption on the PET film surface was shown by XPS analysis.
- The N 1s peak appearance in XPS wide scan spectra demonstrates the collagen adsorption on treated films surface and also the adsorbed amount of collagen is in close connection with the irradiation time.
- The formation of hierarchical assemblies has been attributed to a combination of self-assembly of mesophases, phase separation, sol-gel transition and stabilization of silver nanoparticles through electrostatic interactions.
- Through XPS technique the structure and the properties of POSS-Ag and POSS-AgTi compounds was evidenced.
- Due to the presence of carbonyl groups, silsesquioxane-based hybrid nanocomposites influence the final shape and size of silver nanoparticles, and the formation of metallic silver provides good antibacterial and antifungal activities.
- The large amount of chemically adsorbed nitrogen on the surface of TiO_2 (77.92 %) limits the catalytic performance of POSS-AgTi compound.
- XPS, EDX, ATR-FTIR and SEM methods were used to characterize the effects induced by psoriasis in human fingernails.
- All obtained results were consistent and complementary and have shown that:

- psoriasis causes the disulfide bonds degradation from the cystine structural units to thiol groups, some of which are later converted into sulphite groups or completely degraded;

- psoriasis produces a significant decrease in the α-helix content with a simultaneous increase in the β-sheet and random coil contents. These alterations cause the destabilization of the nail matrix and induce changes in the surface morphology in terms of uniformity, density and roughness.

- Through XPS, EDX, ATR-FTIR and SEM non-invasive techniques it was showed how the molecular structure of keratin and cystine are damaged and how this degradation is linked to the loss of elemental composition.

- It can be said that the apparent beneficial effects of topical treatments lasts only a short period of time due to the formation of aggregates mediated by the intermolecular β-sheets. These aggregates cannot be broken and the reconstruction of the keratin structure cannot be achieved.

- The techniques used in our study help in the development and optimization of non-invasive diagnostic methods and new treatments.

SCIENTIFIC ACTIVITY

The original results presented in this thesis were published in 7 scientific articles in international journals, including 6 published and one submitted for publication and presented as communications (7) and posters (8) at various scientific meetings.

A. Papers published in ISI indexed journals declared for the thesis

1. **A. Coroaba**, T. Pinteala, A. Chiriac, A.E. Chiriac, B.C. Simionescu, M. Pinteala, Degradation mechanism induced by psoriasis in human fingernails – a different approach, *Journal of Investigative Dermatology* **2016**, *136*, 311-313 **IF 7.216**.

2. I.-A. Turin-Moleavin, F. Doroftei, **A. Coroaba**, D. Peptanariu, M. Pinteala, A. Salic, M. Barboiu, Dynamic constitutional frameworks (DCFs) as nanovectors for cellular delivery of DNA, *Organic & Biomolecular Chemistry* **2015**, 13, 9005-9011, BACK COVER, **IF 3.562**.

3. M. Drobota, M. Aflori, L.M. Gradinaru, **A. Coroaba**, M. Butnaru, S. Vlad, D.S. Vasilescu, Collagen immobilization on ultraviolet light-treated poly(ethylene terephthalate), *High Performance Polymers* **2015**, 27, 646-654, **IF 1.286**.

4. I.-E. Bordianu, G. David, B. Simionescu, M. Aflori, C. Ursu, **A. Coroaba**, G. Hitruc, C. Cotofana, M. Olaru, Functional silsesquioxane-based hierarchical assemblies for antibacterial/antifungal coatings, *Journal of Materials Chemistry B* **2015**, *3*, 723-727, **IF 4.726**.

5. A. Durdureanu-Angheluta, M.-E. Ignat, S.S. Maier, L. Pricop, **A. Coroaba**, A. Fifere, M. Pinteala, A. Chiriac, Lipolytic biocatalyst based on recyclable magnetite-polysiloxane nanoparticles, *Applied Surface Science* **2014**, *292*, 898-905, **IF 2.711**.

6. R. Bodirlau, C.-A. Teaca, D. Rosu, L. Rosu, C.-D. Varganici, **A. Coroaba**, Physico-chemical properties investigation of softwood surface after treatment with organic anhydride, *Central European Journal of Chemistry* **2013**, *11*, 2098-2106, **IF 1.329**.

7. L. Ignat, M. Pinteala, **A. Coroaba**, M.-E. Ignat, Investigations on a green, facile, and efficient synthesis of silver nanoparticles by using sodium lignosulfonate aqueous solutions. *Colloids and Surfaces A: Physicochemical and Engineering Aspects* **2015**, ID COLSUA-S-15-02181, trimisă spre publicare, **IF 2.752**.

B. Papers published in ISI indexed journals related to the thesis topic

1. C.-M. Uritu, C.D. Varganici, L. Ursu, **A. Coroaba**, A. Nicolescu, A.I. Dascalu, D. Peptanariu, D. Stan, C.A. Constantinescu, V. Simion, M. Calin, S.S. Maier, M. Pinteala, M. Barboiu, Hybrid fullerene conjugates as vectors for DNA cell-delivery, *Journal of Materials Chemistry B* **2015**, 3, 2433-2446, **IF 4.726**.

2. C.S. Stan, C. Albu, **A. Coroaba**, M. Popa, D. Sutiman, One step synthesis of fluorescent carbon dots through pyrolysis of N-hydroxysuccinimide, *Journal of Materials Chemistry C* **2015**, *3*, 789-795, **IF 4.696**.

3. T. Coman, E.-L. Ursu, V. Nica, V. Tiron, M. Olaru, C. Cotofana, M. Dobromir, **A. Coroaba**, O.-G. Dragos, N. Lupu, O.F. Caltun, C. Ursu, Improving the uncommon (110) growing orientation of Al-doped ZnO thin films through sequential pulsed laser deposition, *Thin Solid Films* **2014**, *571*, 198-205, **IF 1.759**.

4. I.-D. Carja, D. Serbezeanu, T. Vlad-Bubulac, C. Hamciuc, **A. Coroaba**, G. Lisa, C. Guillem Lopez, M. Fuensanta Soriano, V. Forrat Perez, M.D. Romero Sanchez, A straightforward, eco-friendly and cost-effective approach towards flame retardant epoxy resins, *Journal of Materials Chemistry A* **2014**, *2*, 16230-16241, **IF 7.443**.

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C. Participations at national/international conferences

- Oral communications

1. **A. Coroaba**, Mecanismul de degradare indus de psoriazis în unghii, *Seminariile CHRONEX-RD – Conferința finală a proiectului POSDRU 133377, Universitatea de Medicină şi Farmacie „Grigore T. Popa”*, December 3-5 2015, Iasi, Romania.

2. **A. Coroaba**, Noi metode investigative în psoriazisul unghial, *Seminariile CHRONEX-RD, Universitatea de Medicină şi Farmacie „Grigore T. Popa”*, June 12 2015, Iasi, Romania.

3. **A. Coroaba**, B. Minea, A. Chiriac, C. Solovan, B.C. Simionescu, M. Pinteala, Noninvasive tools to investigate nail psoriasis: ATR-FTIR, EDX, and SEM used on human fingernails, *Congresul Național de Dermatologie*, November 5-8 2014, Timisoara, Romania.

4. M. Aflori, M. Drobota, **A. Coroaba**, S.I. Dunca, D.S. Vasilescu, Effect of surface modification Of PET by plasma on collagen and/or silver nanoparticles immobilization for biocompatibility and antibacterial activities improvement, *10th International Conference on Physics of Advanced Materials*, Universitatea “Al. I. Cuza”, September 22-28 2014, Iasi, Romania.

5. C.-D. Varganici, **A. Coroaba**, R. Bodirlau, C.A. Teacă, L. Roşu, D. Roşu, Studiul proprietăților structurale şi termice ale lemnului modificat chimic, *Zilele Academice Iesene, A XXIV-a Sesiune de comunicări ştiințifice a Institutului de Chimie Macromoleculară „Petru Poni” Iaşi – Progrese în Ştiința Compuşilor Organici şi Macromoleculari*, October 3-5 2013, Iasi, Romania.

6. L. Ignat, M.-E. Ignat, A. Durdureanu-Angheluta, **A. Coroaba**, F. Doroftei, D. Timpu, M. Pinteala, Green synthesis of silver nanoparticles with sodium lignosulphonate, *Zilele Universității „Al. I. Cuza” din Iaşi, Conferința Facultății de Chimie*, October 25-27 2012, Iasi, Romania.

7. E. Pâslaru, B. S. Munteanu, **A. Coroaba**, G. E. Hitruc, M. C. Baican, C. Vasile, (Bio)active layers deposition by electrospraying, *Zilele Universității „Al. I. Cuza” din Iaşi, Conferința Facultății de Chimie*, October 25-27 2012, Iasi, Romania.

- Posters

1. **A. Coroaba**, B. Minea, A. Chiriac, B. Simionescu, M. Pinteala, ATR, energy-dispersive X-ray spectroscopy (EDX), and scanning electron microscopy (SEM) analyzing psoriatic fingernails, *24th EADV Congress*, October 7-11 2015, Copenhagen, Denmark.

2. A. Irimia, T. Zaharescu, F. Doroftei, **A. Coroaba**, C. Vasile, Effect of gamma irradiation on cellulose-based materials, *COST Action FP 1205*, March 10-11 2015, Iasi, Romania.

3. **A. Coroaba**, A. Chiriac, C. Solovan, B. C. Simionescu, M. Pinteala, ATR-FTIR, a non-invasive tool to investigate keratin from human fingernails, *Zilele Universității "Al. I. Cuza", Conferința Facultății de Chimie*, October 31 – November 1 2014, Iasi, Romania.

4. G. David, C. Zgardan, **A. Coroaba**, L.E. Ursu, L. Clima, Biopolymer – based nanoparticles for gene and/or drug delivery, *NanoBio- Europe Congress*, June 2-4 2014, Münster, Germania.

5. C.-M. Uritu, L. Ursu, **A. Coroaba**, M. Pinteala, Evaluation of DNA binding to hyperbranched polyethyleneimine (PEI) on siloxane core, *European Workshop Polymer Science at Nanoscale*, October 22-23 2013, Iasi, Romania.

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magnetite nanoparticles, *The 5th International Congress and the 31st Annual Scientific Session of Romanian Society for Cell Biology*, June 5-9 2013, Timisoara, Romania.

8. C.-M. Uritu, A. Durdureanu-Angheluță, **A. Coroaba**, M. Pinteala, Heparin-magnetite particles for targeted drug delivery applications, *The 23rd Conference of Institute of Macromolecular Chemistry "Petru Poni" Iasi „Iasi Academic Days ZAI 2011"*, September 29 – October 1 2011, Iasi, Romania.

D. Member in research projects

1. PNII-RU-TE-2014-4-2976 project, *New approaches in designing polymer surfaces with controllable pattern for applications in biomedicine and high technologies*, Coordinator: "Petru Poni" Institute of Macromolecular Chemistry, Iasi; Project director: Dr. Andreea Irina Barzic – PhD student (October 2015-present).

2. POSDRU/159/1.5/S/133377 project, *Program of excellence in multidisciplinary doctoral and postdoctoral research in chronic diseases*, beneficiary "Grigore T. Popa" University of Medicine and Pharmacy Iasi, project co-financed by the European Social Fund Operational Programme "Human Resources Development" for 2007-2013 – PhD student (July 2014 – November 2015).

3. PN-II-ID-PCCE-2011-2-0028 project, *Biologically inspired systems for engineered structural and functional entities*, "Petru Poni" Institute of Macromolecular Chemistry, Iasi; Project director: Dr. Mariana Pinteală – research assistant (2012-present).

4. Sectoral plans project, *Assessing the Romanian research potential in chemistry and drafting the national strategy for international cooperation*,

Coordinator: “Petru Poni” Institute of Macromolecular Chemistry, Iasi (2011-2012).

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