A 14-a editie a SEMINARULUI NATIONAL DE NANOSTIINTA SI NANOTEHNOLOGIE
Lucrari invitate (in ordinea din program)

B. C. Simionescu, M. Pinteala, Institutul de Chimie Macromoleculara "Petru Poni" al Academiei Romane **"Institutul de Chimie Macromoleculara "Petru Poni" al Academiei Romane, Centrul de Cercetari Avansate pentru Bionanoconjugate si Biopolimeri"** (9:10-9:35)

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A. Dinescu, M. Dragoman, D. Cristea, A. Avram, R. Gavrila, F. Comanescu, INCD pentru Microtehnologie –IMT Bucuresti, **"Dispozitive nanoelectronice bazate pe grafena"** (9:35-10:00)

Abstract. Scopul nanoelectronicii este acela de a procesa, transmite si stoca informatie utilizand alte proprietati decat cele macroscopice ale materiei. Grafena, un strat monoatomic de atomi de carbon prezinta proprietati electrice, mecanice si termice exceptionale devenind in ultimii ani un material atent studiat pentru posibilele sale aplicatii in nanoelectronica, nanofotonica, senzori, etc. Dincolo de faptul ca grafena ofera posibilitati practice de testare a interactiunii electronilor in sisteme uni si bidimensionale, ea sta la baza fabricarii unor dispozitive nanoelectronice precum tranzistoare cu efect de camp, rectificatoare de foarte inalta frecventa, mixere, etc.

Scopul acestei prezentari este acela de a oferi informatii despre fabricarea si caracterizarea unor nanodispozitive pe baza de grafena realizate in IMT in ultimii 2-3 ani: FET-uri cu rezistenta diferentiala negativa, diode de grafena de inalta frecventa si fotodetectori cu structuri plasmonice integrate. Vor fi prezentate procesele tehnologice de realizare, cu accent pe configurarea grafenei la scara nanometrica (prin litografie cu fascicul de electroni si corodare in plasma), vor fi evidentiate particularitatile specifice lucrului cu grafena exfoliata sau cu grafena CVD (la nivel de placheta) si de asemenea vor fi prezentate efectele iradierii cu electroni a grafenei in cazul investigatiilor SEM ale acestor dispozitive.

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S. Astilean, Faculty of Physics, "Babes-Bolyai" University, Cluj, **"Plasmonic-Based Nanoparticles to Provide Multiple Functionalities from Molecular Sensing, Imaging Diagnosis, and Cancer Therapy"** (10:00-10:25)

Abstract. Plasmonic nanoparticles can localize light at the nanoscale by exploiting a phenomenon called surface plasmon resonance (SPR). The last decade has seen a dramatically increased interest in the field of plasmonics and related applications in medicine and life sciences, information and energy technology, environment and food safety monitoring.

In this presentation we give an overview of the current approaches in the Center of Nanobiophotonics and Laser Microspectroscopy to fabricate a large variety of plasmonic nanostructures and develop biomedical applications (http://nano.uphero.com/). The first route of fabrication involves chemical synthesis of gold or silver nanoparticles of controlled size and shape (rods, prisms, stars-shaped) enveloped in various biopolymers (chitosan, poly(ethylene) glycol, pluronic, gelatine) and exhibiting optimized optical response and bio-specificity. A second variety of nanostructures are fabricated by self- or template-assisted assembling of nanoparticles and nano-imprint lithography, aiming to operate as solid plasmonic substrates.

For instance, chitosan-coated triangular silver nanoparticles can play as dual-modal sensors via localized SPR and surface-enhanced Raman scattering (SERS), both in solution and on solid substrate, as well to perform intracellular imaging or trigger localized hyperthermia in tumoral cells

by irradiation in the near-infrared. Finally, we highlight the applicability of some selected hybrid nanoparticles to operate as highly effective biosensors, imaging and therapeutic agents.

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H. Chiriac, N. Lupu, INCD-Fizica Tehnica, Iasi **"Citotoxicitatea in vitro a nanomaterialelor biocompatibile cu temperature Curie redusa de tip Fe-ETM-Nb-B (ETM = Cr, Ti, Ta, Mn) impotriva celulelor canceroase. Hipertermia magnetica"** (10:25-10:50)

Abstract. The need for curing various incurable diseases is demanding not only new types of materials, which preferably will mimic the nature functionalities, but also the understanding of their properties in relation with their microstructure. In this context, the use of magnetic hyperthermia for curing cancer appears to be an extremely viable one. Fe oxides nanoparticles with superparamagnetic behavior (SPIONs) are extensively used in clinical tests involving magnetic hyperthermia. Among the concerns about SPIONs use in magnetic hyperthermia tests, one should mention: the preservation of the stability of Fe oxide NPs against oxidation, the limitations imposed to stop the heating of Fe-oxides (mainly Fe_3O_4) at moderate temperatures (below 47^0C), and, most importantly, the capacity to retain the temperature in the range of 41-46^0C, which requires a very rigorous control of the power of the high frequency generator.

To overcome these issues, we have developed a new type of ferromagnetic nanoparticles (the saturation magnetization is higher compared with Fe-oxides and the hysteresis losses are reduced as well), with the nominal compositions Fe79.7-xETMxNb0.3B20 (ETM = Cr, Ti, Ta, Mn; x = 12÷20 at.%), with low Curie temperatures compared with SPIONs, which can be tailored easily and precisely in the 0-700C by modifying the ETM content, with an accuracy of less than 10C, more suitable for self-regulating magnetic hyperthermia. The purpose of the present study was to evaluate in vitro the cytotoxicity of Fe79.7-xETMxNb0.3B20 alloy nanoparticles, coated or not by a biocompatible layer. The effect of Fe-ETM-Nb-B magnetic nanoparticles on tumor cells (human osteosarcoma cancer cells) was investigated prior and following particle activation by an a.c. electromagnetic field of 350 mT (f = 153 kHz) created by a home-made magnetic-induction hyperthermia unit.

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S. Tanasescu, Institutul de Chimie Fizica, Academia Romana, **"Rolul parametrilor energetici in controlul stabilitatii si reactivitatii materialelor micro si nanostructurate"** (10:50-11:15)

Abstract. Identificarea parametrilor cheie necesari pentru evaluarea beneficiilor și a riscurilor legate de producerea și utilizarea noilor materiale micro și nanostructurate este nu numai o necesitate a dezvoltării domeniului, dar și un deziderat științific. Dimensionalitatea redusă si nanostructura, in particular, sunt insoţite de modificări ale proprietaţilor fizice și chimice, pentru fiecare proprietate existând o dimensiune critică de la care pot apărea schimbari. Unul dintre factorii cheie responsabili pentru această comportare este modificarea parametrilor energetici. In lucrarea prezentă se argumentează faptul că parametri energetici au un rol esential in controlul stabilitaţii materialelor la scara nanometrica, ca și în întelegerea posibilităţilor de interacţie cu sistemele biologice. Acesta este un enorm spatiu de cercetare pentru care determinarea corelaţiilor compozitie – microstructura - proprietati termodinamice este esențială. Pentru discuţie sunt selectaţi compuși din anumite sisteme specifice: faze polimorfe oxidice importante pentru aplicaţiile lor și pentru mediul inconjurator, oxizi multicomponenţti ai metalelor tranziţionale cu proprietăti speciale magnetice sau electrice, sisteme de nanoaliaje, sisteme bio-nonbio.

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C. M. Teodorescu, INCD-Fizica Materialelor, **"Procese chimice la suprafeţe feroelectrice"** (12:55-13:20)

Abstract. Materialele feroelectrice, prezentând şi proprietăţi piezoelectrice sau piroelectrice sunt la momentul actual validate pentru o multitudine de aplicaţii în senzori, traductori, dispozitive micro-electromecanice şi acreditate drept candidaţi serioşi pentru micro- şi nano-electronică, în special privind memorii RAM nevolatile, supercapacitori, celule solare etc. La această multitudine de aplicaţii potenţiale, recent s-au adăugat aplicaţii din domeniul chimiei şi catalizei. S-a dovedit că apariţia curburii de benzi la suprafaţa feroelectricilor, depinzînd de sensul vectorului polarizării, pot promova aceste suprafeţe ca fiind foarte active pentru procese de oxidare, necesitând transportul de goluri spre suprafaţă, realizabil prin orientarea câmpului de depolarizare dinspre material spre exterior, sau a polarizării feroelectrice înspre interior; sau procese de reducere, necesitând transportul electronilor spre suprafaţă, caz în care polarizarea este orientată înspre exterior [1]. În industria automobilă, de exemplu, catalizatorii pentru neutralizarea compuşilor toxici din gazele de eşapament presupun procese simultane de reducere (a azotului din monoxidul de azot NO) şi de oxidare (a monoxidului de carbon CO), procese care pot avea loc în mod natural la feţe opuse ale grăunţilor feroelectrici [2]. Alte aplicaţii se referă la modul în care starea de polarizare şi activitatea catalitică pot fi modificate prin parametri externi, cum ar fi temperatura sau iradierea luminoasă, cu aplicaţii la sinteze "one pot". Vom discuta cele mai recente realizări în domeniul chimiei la suprafeţele feroelectrice, de la modele teoretice pentru curburile de benzi la suprafeţele feroelectrice libere şi la contactele metal-feroelectric până la diferite evidenţe prin spectroscopie de fotoelectroni [1,3] şi prin spectromicroscopie de fotoelectroni [2] a acestor curburi de bandă şi a evoluţiei lor atunci când metale, nanoparticule sau molecule dipolare sunt depuse sau reacţionează pe suprafeţe.

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S. Peretz[1], D. F Anghel[1], E. Vasilescu[1], M. Florea-Spiroiu[2], C. Stoian[3], Ghe. Zgherea[3], [1] "Ilie Murgulescu" Institute of Physical Chemistry, Romanian Academy, [2]University of Bucharest, Faculty of Chemistry, [3]University "Dunarea de Jos" of Galati, **"Synthesis of Fe3O4 magnetic nano and micro-particles coated with chitosan and polyacrylic acid"** (13:20-13:45)

Abstract. Nano and micro-particles have been synthesized through an original method by coating an iron oxide core with polymer layers formed by interaction between chitosan (Chi) and polyacrylic acid (PAA).

In the first stage Fe_3O_4 nanoparticles having negatively charged surface were synthesized, and then covered with a cationic chitosan layer. The size and electrical charge of the nanoparticles were determined by dynamic light scattering (DLS) and Zeta potential measurements [1]. The SEM determinations showed that iron oxide nanoparticles have a cubic shape core, which is surrounded by an envelope of chitosan, which present many pores. The X-ray diffraction pattern (XRD) spectra indicate that the coated nanoparticles have a core of pure Fe_3O_4 with a cubic inverse spinel structure, and the coating with chitosan did not change the crystal structure of the iron oxide nanoparticles [2].

In the second stage of the synthesis the chitosan coated Fe3O4 nanoparticles were introduced in a PAA solution, when complex layers were formed by the interaction between the two polymers, which led to an increase in size of the particles. The polymer coated microparticles have a quasi-spherical shape with a mean diameter of about 700 nm, and show a rough surface with pores in the form of scales. The FTIR spectra have revealed the shifting of polymers characteristic absorption peaks, due to the formation of new bonds between amino positive groups of the chitosan covered nanoparticles and the negatively charged carboxyl groups of PAA, as has been observed in other previous studies [3].
The magnetic properties of the particles were measured at room temperature by using a vibrating sample magnetometer (VSM). The saturation magnetization showed good superparamagnetic properties for the polymer coated microparticles.
Iron oxide magnetic polymer coated microparticles have potential applications for the retention of organic substances from aqueous solutions, because they exhibit good adsorption properties and can be handled externally to be easily separated from the environment.

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O. Gingu, C. Teisanu, G. Sima, D. Coman, M. Mangra, Facultatea de Mecanica, Universitatea din Craiova

"Aplicatii actuale si viitoare ale materialelor nanostructurate obtinute prin tehnologia metalurgiei pulberilor" (13:45-14:10)

Abstract. Lucrarea prezinta stadiul actual al cercetarilor intreprinse la Universitatea din Craiova in domeniul obtinerii de materiale nanostructurate prin tehnologia metalurgiei pulberilor. Sunt vizate aplicatii de inalta performanta din domeniul ingineriei tesuturilor si industriei opto-electronice, cum ar fi: materiale biocompozite cu matrice din hidroxiapatita ranforsata cu particule de titan respectiv materiale bimetalice Ag-Cu nanostructurate. Tehnologia metalurgiei pulberilor ofera oportunitati deosebite in ceea ce priveste obtinerea de materii prime sub forma de nanopulberi sau particule de pulberi micronice nanostructurate care, ulterior, sunt procesate prin metode avansate de sinterizare: sinterizare cu descarcare in plasma, sinterizare cu incalzire in camp de microunde, sinterizare in doi pasi. Evidentierea performantelor materialelor elaborate s-a realizat prin: microscopie electronica cu baleiaj, analiza spectrala in volum si de suprafata, spectroscopie Raman, analiza termogravimetrica, analiza dilatometrica. Tehnologii avansate de post-procesare au fost aplicate materialelor nanostructurate obtinute, cum ar fi micro-procesarea cu fascicule laser.

Dezvoltari viitoare in domeniul metalurgiei pulberilor vizeaza tehnologia de formare prin micro-injectie de pulberi metalice/ceramice/compozite in vedera obtinerii de produse cu dimensiuni min. 1-10 mm, forma geometrica complexa/neregulata si cu tolerante dimensionale de ordinul micronilor. Avantajul major al acestei tehnologii consta in utilizarea de presiuni medii (0-50 bar) pentru injectarea feedstock-urilor la temperaturi de max. 1200C fata de varianta clasica de injectie de pulberi care foloseste presiuni de 100-150 bar la temperaturi de 200-3000C. Reconstructia osoasa de mici dimensiuni, la nivel cranian si corp vertebral, precum si fabricarea de spume metalice de forma neregulata reprezinta cateva din aplicatiile tehnologiei de micro-injectie de pulberi metalice/ceramice/compozite.

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C. Kusko, R. Tomescu, M. Kusko, INCD pentru Microtehnologie –IMT Bucuresti, **"Componente plasmonice neliniare"** (15:00-15:25)

Abstract. Lucrarea exploreaza posibilitatea utilizarii componentelor bazate pe ghiduri plasmonice neliniare cu functionalitati avansate in prelucrarea si procesarea optica a informatiei. Caracteristica fundamentala prezentata de ghidurile de unda plasmonice este confinarea puternica a campului electromagnetic pe dimensiuni cu mult mai mici decat lungimea de unda. Aceasta caracteristica duce la intensificarea campului electromagnetic in ghidul de unda, fapt care favorizeaza aparitia efectelor neliniare [1]. Pe langa aceasta, ghidurile de unda plasmonice prezinta regimuri de functionare interesante in care dispersia este anomala, apar moduri cu viteza de grup redusa (slow modes) sau viteza de grup prezinta sens contrar vitezei de faza. Aceste caracteristici favorizeaza intensificarea efectelor neliniare conducand la fenomene de bistabilitate, auto-oscilatii sau comutatie optica.

In mod specific, aceasta lucrare va investiga un rezonator circular plasmonic care prezinta o neliniaritate de tip Kerr [2]. S-a demonstrat numeric si teoretic ca acest sistem prezinta instabilitai de tip Ikeda care conduc la aparitia unui regim de auto-oscilatie. Prin simulari numerice s-au pus in evidenta auto-oscilatile care prezinta durate de ordinul sutelor de femtosecunde. S-a calculat teoretic regimul de bistabilitate al rezonatorului si s-au identificat regimurile de functionare ale acestuia ca functie de puterea undei incidente: regim stationar, regim de auto-oscilatie, regim haotic. De asemenea, s-a investigat acordabilitatea acestui sistem pentru a genera pulsuri cu frecvente diferite. Acest sistem poate prezenta aplicatii in generarea de radiatie de terahertz sa ca ceas optic cu pulsuri de ordinul sutelor de femtosecunde in circuite optice integrate.

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V. Musat, A.Tabacaru, M. Ibanescu Busila, N. Tigau, Centrul de nanostructuri si materiale functionale (CNMF), Universitatea Dunarea de Jos Galati, **"Hybrid ZnO-Based nanostructured materials with photoluminescent and antimicrobial properties"** (15:55-16:20)

Abstract. Even ZnO is a well known electronic and photocatalytic material due to the wide, direct band gap energy and a large exciton binding energy, the construction of hybrid materials based on ZnO nanoparticles (NPs) opens up new perspectives and broadens its applicability through two pathways: the control of down sizing below 10 nm to the level of QDs (which is important, knowing its high growth rate) and the reduction of the recombination rate of excited photoelectron-hole pairs (knowing its relatively high recombination rate) with a subsequent shift of the optical absorption to the visible region therefore enabling more efficiently utilize solar energy.

Based on the great potentiality of organosilane species to establish stable covalent bonds by ZnO surface grafting, with direct influence on its particle size, morphology and electronic features, the choice of organosilane surfactant was part of our strategy to explore the tuning of ZnO optical properties taking into consideration the nature of end group bound to silicon. We investigated the effect of several representatives of organosilanes class, as 3 (trimethoxysilyl)propylmethacrylate(MPS), 3-glycidyloxypropyl trimethoxysilane (GPTMS) and vinyltrimethoxysilane (VTMS), also in addition with chitosan, for building new hybrid nanostructured materials and biocompatible materials with high potential applicability in optoelectronics (HLED) and photocatalysis, as well as for antimicrobial (functional textile), intelligent food packaging and

fluorescent probes in biomedical applications. Their syntheses were conducted through a simple and non-expensive modified precipitation method, in some cases associated with sol-gel method, while their characterization was performed by means of X-ray diffraction (XRD), high-resolution scanning electron microscopy (HRSEM) and transmission electron microscopy (HRTEM), Fourier Transform Infrared spectroscopy (FTIR), thermogravimetric (TGA) and elemental analysis, optical transmission, reflectance and photoluminescence spectra, photocatalytic and antimicrobial tests. A decrease of band gap energies, from 3.49 eV for unmodified ZnO NPs until 3.37 eV for organosilane modified-ZnO NPs, considering the effect of the organosilane surfactant on the nanoparticles size reduction was observed and discussed, giving a new insight into the relationship between the nanoparticle size reduction promoted by an organic surfactant with electron injection into ZnO bands and the value of band gap energy.

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T. Sandu, INCD pentru Microtehnologie –IMT Bucuresti, **"From biological cells to semiconductor and metallic nanoparticles: the same recipe with different flavors"** (16:20-16:45)

Abstract. The use of the same boundary integral equation method allows the treatment of different systems with different sizes on different frequency scales of the electromagnetic field. Thus, the radiofrequency behavior of biological cells, the surface optical phonons in semiconductor nano- and microparticles, and the collective electronic response in metallic nanoparticles can be described as electrostatic resonances that depend on the shape of the systems and are essentially scale invariant. We will analyze not only the similarities but also the differences between the resonances of these systems. The differences come mostly from the frequency-dependent dielectric constant leading to different effects. For biological cells and, more generally, for any heterogeneous dielectric system the radiofrequency resonance is a Maxwell-Wagner relaxation that can be thought as an impedance matching in a lumped-circuit view. In nanoparticles made of polar semiconductors the infrared response of surface optical phonons is readily observed in Raman spectra. In metallic nanoparticles, on the other hand, the response is done by collective excitations (plasmons) of free electrons with large light scattering and absorption cross-sections and huge field enhancements. Finally, examples and applications will be given for each separate case.