

Introduction

Dear Participant, dear Reader of this book,

The International Workshop on Polymer/Metal Nanocomposites is a series of biennial meetings that aims to bring together physicists, chemists, and engineers from academics and industry which are active in the fields of advanced preparation techniques, new material properties and industrial applications, in computer simulations and theoretical work. The nanocomposites may consist of polymer/metal in the shape of nanoclusters, nanotubes, nanofibers, and nanowires. Contributions discussing functional properties of polymer/carbon and polymer/metal oxide composites are also welcome.

It is our pleasure to host in Toulouse, France, September 16th - 18th, 2013, the 6th edition of "Nanoworkshop" in respect to the tradition revealed first at University of Kiel, Germany (2003) and then continued in Geesthach, Germany (2005), Kobe, Japan (2007), Prague, Czech Republic (2009) and Bari, Italy (2011).

On the following pages you will find the abstracts of all oral invited lectures, topical presentations and posters presented during the Nanoworkshop 2013. The scientific programme consists of 6 invited lectures, 29 oral presentations and a poster session. The exchange of knowledge and the fruitful discussions amongst participants are important issues for the Nanoworkshop realization.

We would like to express our sincere gratitude to all authors of submitted abstracts. The high scientific level of the presented contributions largely serves the Nanoworkshop 2013 success. We are very grateful to the Members of International Organizing Committee who have kindly given their valuable time for reviewing the abstracts and have always supported us. We are very thankful to the Local Organizing Committee Members for their help and willingness to share tasks during the Nanoworkshop 2013 organization. We would also like to thank all the institutional partners for their involvement in this workshop. Last, but not least, we would like to thank Marlène Giamporcaro (SAIC, INPT) for her work and competent support all over the Nanoworkshop 2013.

We wish everyone a productive and interesting Nanoworkshop 2013, and a very pleasant stay in Toulouse.

Dr. Bernard DESPAX

Dr. Kremena MAKASHEVA

Chairs of Nanoworkshop 2013

September 10th, 2013

Toulouse

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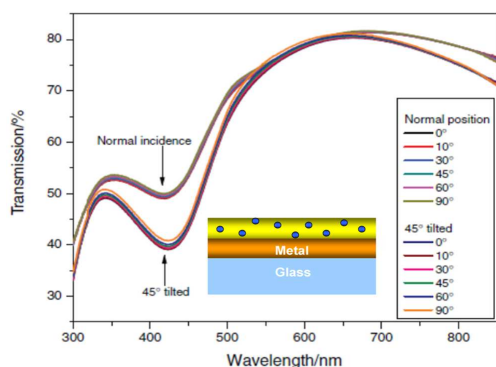
ORAL COMMUNICATIONS

Polymer-metal nanocomposite films prepared by vacuum based processes

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Polymer-based nanocomposite films consisting of metal nanoparticles in a polymer matrix have unique functional properties with host of applications [1]. The present review demonstrates how vacuum based vapor phase deposition techniques can be employed for tailoring the nanostructure and the resulting properties. Vapor phase deposition, inter alia, allows excellent control of the metallic filling factor and its depth profile as well as the incorporation of alloy nanoparticles [2] with well-defined composition. The metallic nanoparticles typically form in the polymer matrix via a self-organization process during co-deposition of the metallic and organic components due to the high cohesive energy of the metals and the low metal-organic interaction energy. Various methods such as plasma polymerization [3], evaporation [4], sputtering [5], and laser ablation [6] have been employed for the matrix component, while the metallic component has mostly been evaporated or sputter-deposited. Moreover, gas aggregation cluster sources were used to obtain independent control of filling factor and size of the embedded nanoparticles [7].



Examples presented from own work and the literature include optical composites with tuned particle surface plasmon resonances [3] for plasmonic applications [8], magnetic high frequency materials with cut-off frequencies well above 1 GHz [9], sensors that are based on the dramatic change in the electronic properties near the percolation threshold [10], and antibacterial coatings which benefit from the large effective surface of nanoparticles and the increased chemical potential which both strongly enhance ion release [6,11]. Moreover, highly deformable nanostructured elastomeric electrodes for biomedical and other applications will be addressed [12].

Figure 1. An omnidirectional transparent conducting-metal-based plasmonic nano-

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- [10] C. Hanisch, N. Ni, A. Kulkarni, V. Zaporojtchenko, T. Strunskus, F. Faupel, *J. Mater. Sci.* **46** 438 (2010).
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Real-time in situ μ GISAXS study of gold cluster growth kinetics during magnetron sputter deposition.

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The remarkable manifold chemistry of gold cluster assemblies is of great interest for fundamental research and promises various potential applications in solar cells, biosensors, reflective or antireflective coatings and especially in heterogeneous catalysis [1–4]. The adjustment of catalytic, electrical and optical properties of gold cluster assemblies is therefore a very significant issue in modern applied nanotechnology. For an efficient and controlled production of active nanostructured gold cluster surfaces, sputter deposition plays a very important role in industrial processing [5]. In order to tune the size-dependent properties, it is mandatory to understand how the metal film morphology evolves during sputter deposition.

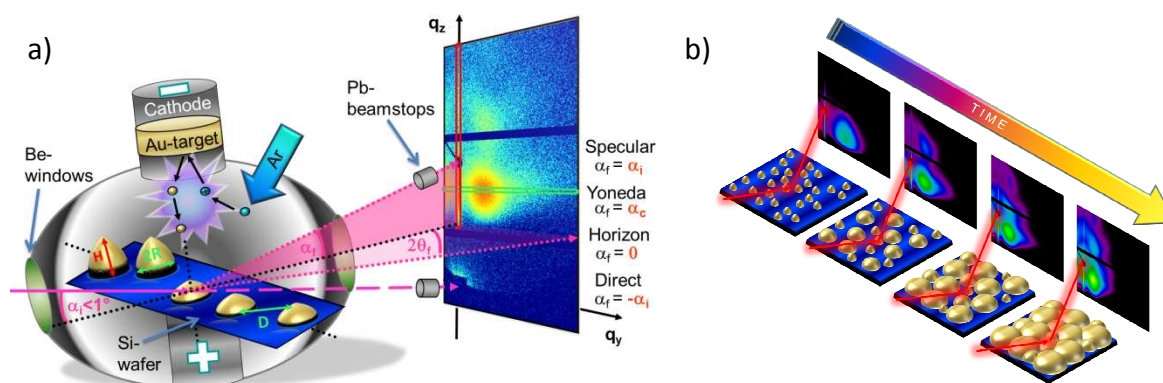


Figure 1a) Schematic representation of the in-situ sputter deposition setup. b) Selected two-dimensional detector pattern at different growth regimes and their corresponding gold clusters morphology on silicon substrate [6].

We present a real-time investigation of the growth kinetics of gold nanostructures from small nuclei to a complete gold layer during magnetron sputter deposition with high time resolution by means of in situ microbeam grazing incidence small-angle X-ray scattering (μ GISAXS) [6]. The high time resolution in the millisecond regime allows the precise determination of kinetics of initial nucleation and subsequent cluster growth during sputter deposition of a gold layer on an amorphous silicon oxide layer under conditions advancing towards industrial manufacturing. We specify the four stage growth including their thresholds with sub-monolayer resolution and identify phase transitions monitored in Yoneda intensity as a material-specific characteristic. An innovative and flexible geometrical model enables the extraction of morphological real space parameters, such as cluster size and shape, correlation distance, layer porosity and surface coverage, directly from reciprocal space scattering data. This approach enables a large variety of future investigations of the influence of different process parameters on the thin metal film morphology. Furthermore, our study allows for deducing the wetting behavior of gold cluster films on solid substrates and provides a better understanding of the growth kinetics in general, which is essential for optimization of manufacturing parameters, saving energy and resources.

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Modification of surfaces by metal and polymeric nanoparticles

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Superhydrophobic or superhydrophilic surfaces are more and more often requested for different kind of applications. Hydrophobic coatings are mainly based on teflon like materials which have normally in case of flat film static contact angle of water $\sim 115^\circ$. It has been shown elsewhere [1,2] that in case of fluorocarbon discharges under special conditions structured plasma polymer films with convenient roughness may be prepared that are slippery and superhydrophobic.

We focused in our work on preparation of fluorine free super hydrophobic coatings. To surpass the wettability limit for C:H films which is around 105° surface roughness was induced by means of metal and polymeric nanoparticles (NPs). Copper NPs were produced by DC magnetron sputtering in Haberland type [3] gas aggregation cluster source. Detail description of the cluster source can be found elsewhere [4]. In this way it was possible to prepare uniform NPs film with particle size ~ 15 nm. 200 nm thick NPs film overcoated by 7 nm C:H plasma polymer film exhibited superhydrophobic properties, i.e. contact angle of water was close to 180° .

Similar results were obtained in case of polymeric NPs produced in the same type of cluster source operated with RF magnetron where plasma polymerization in the gaseous phase occurred. NPs mean size produced in this way was ~ 150 nm. In this case one monolayer of NPs overcoated by thin C:H film was sufficient to obtain super hydrophobic coatings. However, superior properties were achieved by combination of big C:H NPs with relatively small Cu NPs. Presence of Cu NPs makes such a film also possibly antibacterial and plasmonic resonance was also observed. Short treatment of those super hydrophobic films in O₂ plasma switched them into superhydrophilic.

NPs were also used as a nanomask for lithography. This gave us possibility to produce randomly distributed polymeric nanopillars or nanoholes in polymeric or metal / metal oxide films. Possible applications of presented structures and their stability are discussed.

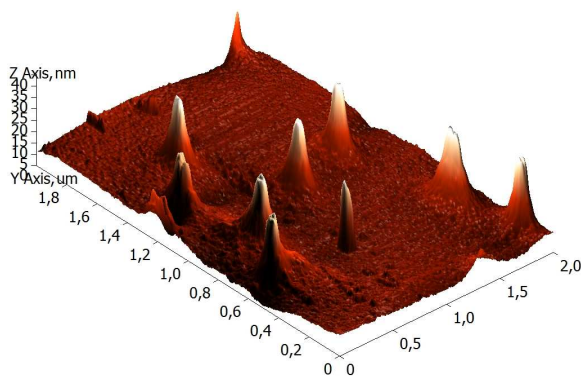


Figure 1. Polymeric nanopillars produced by lithography using C:H NPs.

Acknowledgments: This work was supported by the grant GACR 13-09853S

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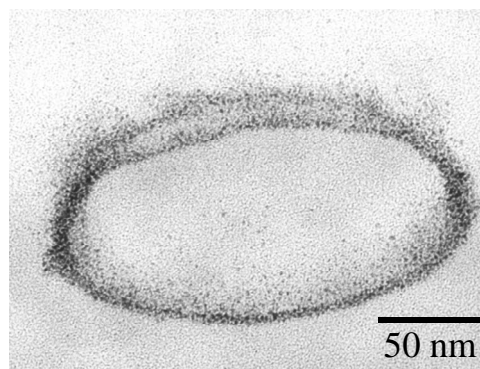
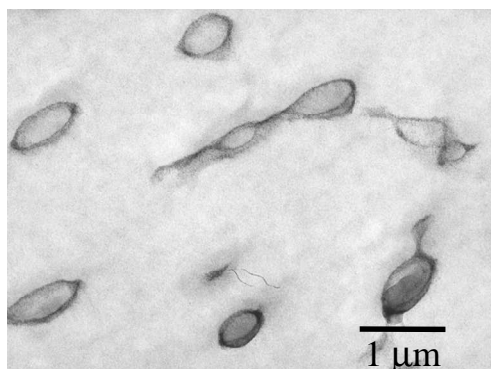
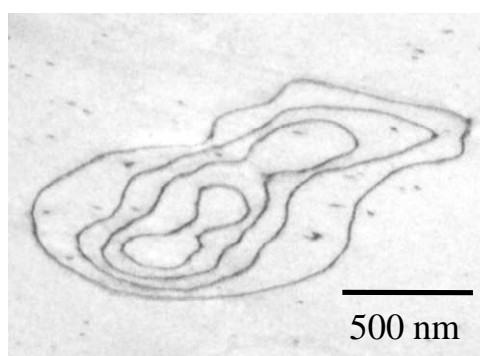
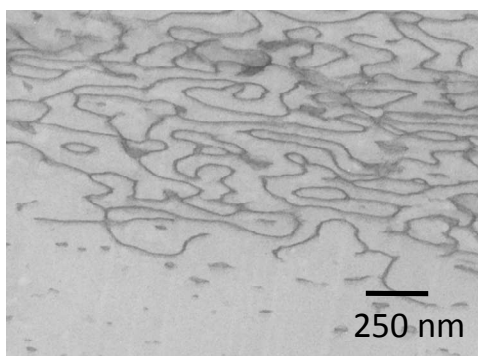
Metal(0) compounds for nanocomposite preparation

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In wet-chemical processes, inorganic particles used for nanocomposites are frequently prepared in situ by reduction of metal compounds or applied as isolated surface-modified particles. In the case of metals, however, coordination compounds with metal atoms in the oxidation state of 0 may simply be used. Upon thermal decomposition of the ligand sphere, the metal atoms readily assemble to nanoparticles which can be incorporated into polymers. Thus, for instance, dicobaltoctacarbonyl, $[\text{Co}_2(\text{CO})_8]$, contains cobalt(0) atoms which are stabilized by coordination to carbon monoxide. This complex is soluble in organic solvents but decomposes at elevated temperature to form superparamagnetic ϵ -cobalt nanoparticles in a reproducible manner if the conditions are appropriate. These particles can be dispersed well in organic polymers and keep superparamagnetic behavior in the resulting nanocomposites.

As another example, tris(styrene)platinum(0), $[\text{Pt}(\text{styrene})_3]$, dissolves readily in styrene. Hence, this solution contains de facto individual platinum(0) atoms dissolved in styrene. Upon gentle heating the platinum atoms form nanoparticles which disperse well in styrene. Subsequently or concomitantly, the solvent can be polymerized with a common radical initiator, and it is possible to obtain corresponding nanocomposites as massive bodies, films or foams. In the latter case, an excess of the radical initiator was used as foaming agent. Moreover, addition of dialkyldithiocarbamates to the initial solution led to a variety of superstructures (see images below) of the platinum particles, depending on the conditions.



Polymer / metallic nanowires nanocomposites for flexible conductive electrode applications

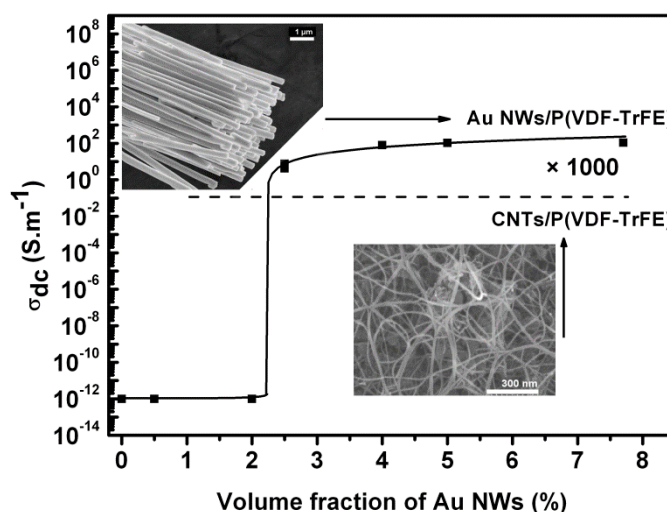
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Transparent conductive films are widely used in various devices like solar cells, liquid crystal displays or organic light-emitting diodes. Some of these applications need flexibility. The brittleness and high temperature processing used to obtain ITO layer induce difficulties for flexible applications on polymer substrate. Low content of conductive fillers in insulating polymeric matrix significantly improve the electrical properties of composite and maintain its flexibility. Percolation phenomenon is dependent on the apparent aspect ratio of the filler. Very low percolation threshold were obtained with introduction of CNTs with aspect ratio ξ higher than 100 and even 1000. Above the percolation threshold ($\phi_c < 5$ vol %), the literature shows that the conductivity value of CNTs composites levels off at an upper limit[1] of about 10^{-1} S.m⁻¹ and 10^3 Ω/\square for the surface resistivity. Metal nanowires (NW) have attracted much attention because of their higher intrinsic electrical conductivity[2].

In this work, nickel and gold nanowires were synthesized by electrochemical way giving a uniform high aspect ratio ($\xi \sim 200$). Nickel and Au NWs polymer composites were elaborated by addition of NW in a PVDF-TrFE matrix[3]. The conductivity of melt-pressed nanocomposite films has been studied as a function of NWs volume fraction and it shows a very low percolation threshold near 1 vol%. At the percolation threshold ϕ_c , the volume electrical conductivity of nanocomposites increases from 10^{-12} S.m⁻¹ to 10^2 S.m⁻¹. The influence of process on the percolation threshold value was studied with thin spray coating NW composites. Nanocomposites reach an electrical conductivity 103 times higher than the one of CNTs nanocomposites. Below 5 vol%, nanocomposites remain ductile and flexible[4]. Moreover, the surface resistivity of spray coatings has been studied as a function of AuNW volume fraction and it shows the existence of a very low percolation threshold around 2 vol%. The surface resistivity above the percolation threshold reaches a low value near 4 Ω/\square . This value is more than 1000 times lower than sprayed CNT coating.



Despite moderate aspect ratio regarding CNTs, metallic nanowires represent a very promising route to improve the electrical conductivity in polymer matrix composites for flexible electrodes applications.

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Nanocomposite based stretchable optics

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The integration of optical elements on stretchable substrates opens the way to the realization of a completely novel class of stretchable photonics systems, characterized by the ability of changing their optical properties upon modification of their shape due to tensile or compressive strain and to be highly conformable to complex surfaces [1]. Several attempts have been already made to fabricate stretchable diffracting, reflecting and focusing optical elements by depositing reflective metallic films on gratings embossed on PDMS or by embedding liquid reflecting metals into PDMS [2]. The bad adhesion of the metallic layer and the weight of the liquid metal degraded the quality of the optical elements even upon a very small deformation [2].

Here we present an effective approach to the fabrication of nanocomposite based reflective and diffractive stretchable optical components. The optically active side of a bare elastomeric (PDMS) diffraction grating, obtained by molding an existing rigid diffraction grating, is implanted with silver nanoparticles by means of Supersonic Cluster Beam Implantation (SCBI) [3,4], in order to create a nanocomposite reflective layer with a thickness of tenths of nanometers. Supersonic Cluster Beam Implantation consists in directing a beam of electrically neutral nanoparticles, accelerated by a pressure difference and focused with a very low divergence (less than 1°) by aerodynamical effects, towards the polymeric substrate in which they are implanted because of their kinetic energy. The extremely good resilience of the nanoparticles layer embedded into the polymeric substrate upon deformation of the so obtained silver-PDMS nanocomposite allows to maintain extremely good optical performances upon substantial deformation of the grating and a large number of deformation cycles [4].

Optical characterization at a single wavelength shows a good linear proportionality between the stretching of the implanted device (25% stretching) and the decrease of the diffraction angle at the first diffraction order, as expected, due to the increase of the grating pitch. The optical quality of the diffracted beams is good after hundredths of cycles of stretching. As a comparison, a PDMS grating obtained by thermal evaporation of silver atoms shows a poor optical quality prior to stretching because of the observed cracking of the rigid reflecting coating and an increase in intensity of two transversal diffracted spots with a worsening of the diffracted beams quality after few stretching cycles. AFM analysis demonstrates that the nanocomposite based grating maintains the diffractive structure of the PDMS replica thanks to the high collimation of the nanoparticles beam typical of SCBI, while the evaporated one presents many cracks in the reflective layer, mainly in the transversal direction respect to the grooves direction, and a deterioration of the grooves profile. The high deformability of the reflective stretchable grating, guaranteed by the nanocomposite layer, allows to span all the visible range wavelength at a fixed angle respect to the grating normal when illuminated with white light, simply by stretching the device up to 50%.

Thanks to its superior resilience and conformability, when the stretchable and reflective grating is applied to non-optical grade curved surfaces, optical power can be added to the outgoing light beam without any deterioration in the optical quality of the device. This allows the grating to focus the diffracted beam and to correct optical aberrations such as astigmatism, typical of many concave grating mounts. This would not be possible with stretchable reflective optical elements fabricated by standard approaches, due to the cracking of the superficial rigid metallic layer.

These results indicate that SCBI is an enabling tool for the fabrication of diffracting and reflecting optical components based on soft, stretchable and highly conformable metal-polymer nanocomposites, preserving their optical properties and qualities after extensive cycles of stretching. These highly stretchable and conformable nanocomposite based devices open the way to a completely novel class of simpler, cheaper and lighter optical systems.

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Atomistic modeling of metal-cluster implantation into a polymeric substrate

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By means of large-scale state-of-the-art atomistic simulations we investigate the implantation of a Au nanocluster(s) into a polydimethylsiloxane substrate. All the simulations are performed in realistic conditions, closely related to the actual experimental condition of supersonic cluster beam implantation.

We consider both entangled-melt and cross-linked polydimethylsiloxane amorphous structures and we show that even a single cluster impact on the polydimethylsiloxane substrate remarkably changes the polymer local temperature and pressure, in particular by generating a heat-wave propagating into the substrate as shown in figure.

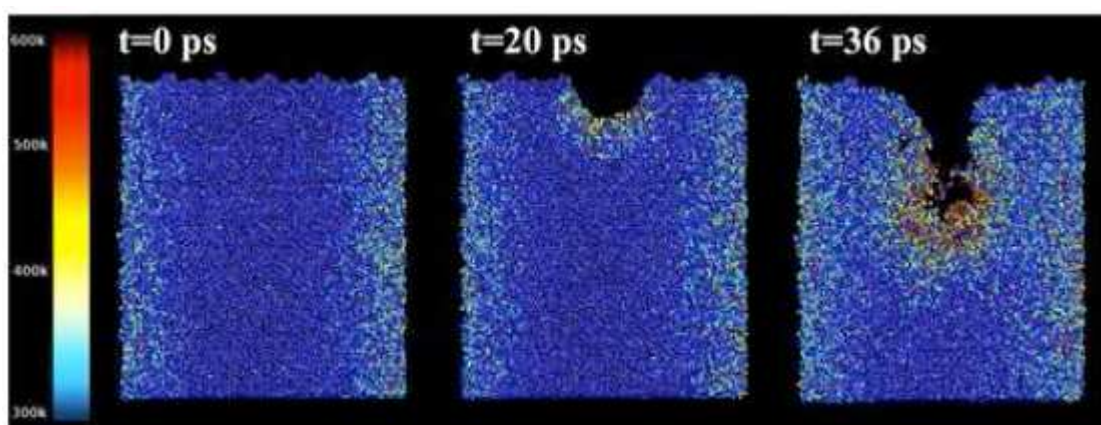


Figure caption - Time evolution of the temperature wave during the implantation of a 3nm Au cluster at 2.0 eV/atom impact energy. Each substrate atom is colored according to its local temperature: red color corresponds to a temperature of 600 K, while blue color corresponds to 300K. The cluster is not shown for sake of clarity.

Moreover, we characterize the formation upon cluster-impact of craters on the polymer surface, providing a direct atomic-scale interpretation of AFM measurements.

Finally, we carefully characterize the elastic properties of the implanted film by calculating stress-elongation curves, which are then interpreted in the framework of the rubber elasticity theory.

Present simulations suggest that the substrate morphology as well as its resulting physical properties are largely affected by the cluster impact and that most-likely such modifications favor the the penetration of the next impinging clusters.

Polyelectrolyte Dynamics in Confined Flows

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In this work, we study the dynamics of polyelectrolytes in microchannel and nanochannel flows under externally applied pressure and electric fields using both theoretical and computational approaches. Hydrodynamic interactions, acting directly within the chain and indirectly, mediated by the confinement, play a crucial role in polymer transport and migration. Emphasis is placed on properly resolving them in terms of point-force solutions to the Stokes equation.

First, we analyze the transport and separation of biomolecules (polyelectrolytes and DNA in particular) under electrokinetic flows in microscale geometries of critical dimensions on the order of the characteristic size of the molecules, i.e. radius of gyration for chains. The governing systems of field equations are discretized by finite differences on boundary-fitted overlapping grids, while the polymer is coarse-grained into a bead-spring model that follows Langevin dynamics. The objective of the work is a mesoscale-level treatment of hydrodynamic interactions in nanopores and entropic traps. We report on electrophoretic mobilities and quantify the chain transition from free flowing behavior to trapping behavior in terms of the electric field strength.

Second, we extend the kinetic theory of dilute polymer solutions under external pressure and electric fields to a) include finite chain extensibility and b) properly account for wall-induced hydrodynamic interactions due to charged polymers in an electrolyte. Focusing on cross-stream migration due to individual and combined effects of these fields, we show the effect of model refinement on the depletion layer thickness and derive migration tensors for the Green's function of Stokes flow in a Debye-Hückel electrolyte.

Finally, we examine DNA electrophoresis under pressure-driven flow in a microchannel using Brownian Dynamics. In addition to hydrodynamic interactions due to non-electric forces, we also include electrically-induced hydrodynamic interactions, which arise due to velocity disturbances generated by localized bead charges and their counter-ion clouds. All modeled bulk interactions are supplemented with the appropriate wall corrections, thus providing a uniformly valid solution for small Debye lengths. We report on cross-stream migration patterns in light of the competition among different types of hydrodynamic interactions.

LSPR properties of silver nanoparticles-Nafion membrane composite prepared by Photoreduction Process

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Surface plasmon resonance (SPR) sensor is based on the principle that the surface plasmon resonance is highly sensitive to the refractive index at the interface between metal surface and sample materials [1, 2]. In this study, we developed the preparation process using ion exchanging process to Ag⁺ form Nafion and N,N-dimethylformamide as reductant assisted with UV light irradiation for acceleration and controlling the reduction reaction. We also report the LSPR sensing properties varying refractive index of medium surrounding AgNPs.

Ag⁺-form Nafion was prepared by ion exchanging process dipping H⁺ form Nafion 115 into 0.1 mol-dm⁻³AgNO₃ (Nacalai Tesque Inc 99%) aqueous solution for 24 h. After ion exchanging, Ag⁺-form Nafion was immersed in N,N-dimethylformamide and UV irradiation (SANEI Electric, Supercure203S 200W HgXe lamp) for various minutes ranging 1 to 10 min for Ag reducing. Obtained Ag/Nafion composite was washed by distilled water twice and immersed in 1.0 mol-dm⁻³NaNO₃ aqueous solution to remove and exchange remained Ag⁺ into Na⁺ in Nafion membrane. For LSPR properties, Ag/Nafion composite sheet was put in the conventional quartz sample cell available to close system by lid. Absorbance spectra were measured ranging 300 nm to 800 nm. Various refractive index medium was prepared by dipping Ag/Nafion into various organic solvent.

AgNPs might exist in ionic cluster channel in Nafion membrane stably without any stabilizing reagent. The particle size was measured by transmission electron microscope (TEM). The mean particle size was ca. 13 nm in diameter. The obtained nanocomposite membrane has absorption bands due to local surface plasmon resonance (LSPR) in around 400 nm. A dependence on the refractive index of media surrounding AgNPs confined in Nafion membrane using absorbance spectra was shown in Figure 1. The coupling frequency (wavelength) was reflected as the peak top of the absorbance spectra. Consequently for the sensing application, the peak top value was important and sensitive to refractive index of media. We attempt to draw the absorbance spectra depending on the refractive index of medium surrounding AgNPs using Mie theory [3].

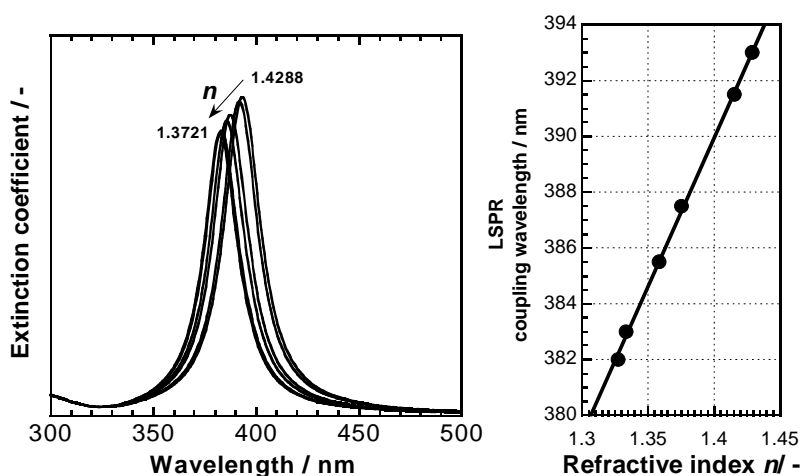


Figure 1. Variations of (a) LSPR absorbance spectra and (b) peaktop wavelength with refractive index of medium ($n = 1.3271$ - 1.4288).

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3D design of embedded plasmonic architectures in dielectrics: synthesis, properties and applications

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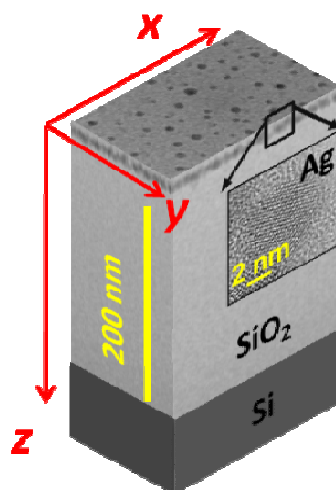
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Original hybrid metallic-dielectric substrates based on plasmonic nanostructures are presented. Their architecture consists of a single plane of silver nanoparticles embedded in a dielectric matrix (SiO₂ or SiN layer on Si substrate) at a nanometer distance from its surface. By ultra-low energy ion implantation through a stencil fabricated by focused ion beam technique, we control their size, density and location. Different patterns are conceived to simultaneously exploit near field effects, optical interference phenomenon in stratified media and localized surface plasmon resonance [1,2].

Elastic (Rayleigh) and inelastic (Raman) scattering imaging assisted by simulations are used to analyze the optical response of these layers. The reflectance contrast is strongly enhanced when resonance conditions between the stationary electromagnetic field in the dielectric matrix and the localized plasmon resonance in the silver nanocrystals are realized [2].

These novel kinds of nanocomposite systems are reproducible, preserving flatness and chemical uniformity over large surfaces [3]. They enable both fundamental studies of the properties of the nanoparticles assemblies, and offer new opportunities as substrates for enhanced optical spectroscopy and imaging of deposits, or devices based on electron or ion transfer processes. .



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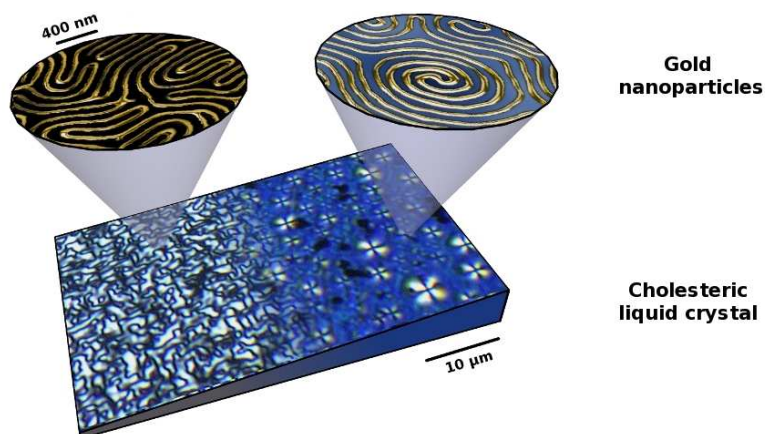
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Self-organization of gold nanoparticles in cholesteric liquid crystals

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The chiral cholesteric-liquid-crystalline structure, which concerns the organization of chromatin, collagen, chitin, or cellulose, is omnipresent in living matter [1]. A cholesteric liquid crystal (CLC) may selectively reflect the light [2] and is found in temperature and pressure sensors, supertwisted nematic liquid crystal displays, optical filters, reflective devices, or cosmetics [3]. Self-organization processes are present in many different inorganic, organic, and biological systems at various length scales and give rise to specific intrinsic physical properties [4]. Here we demonstrate the symbiotic association of gold nanoparticles (NPs) within a CLC [5], and we report the long-range growth of two-dimensional and three-dimensional self-organized arrangements of gold NPs into various cholesteric textures. The structure of these novel nanomaterials is imaged at various scales—from the macroscopic scale of centimeter-size cells to the nanoscale of self-assemblies—and we demonstrate that the NP pattern depends strongly on film thickness. We have succeeded in coating the open film onto a huge variety of substrates: a TEM copper grid coated with a polymer film, a glass plate, a plastic foil, and even the surface of water. Furthermore, we investigate how fundamental optical properties such as selective reflection are affected when CLCs are doped with gold NPs. The demonstration of the self-organization of NPs into versatile patterns induced by cholesteric structure is seen as a starting point toward an inexpensive bottom-up technique for on-demand selective positioning and patterning of NPs over large areas. Potential applications are thus envisioned in the field of soft nanotechnology and optical materials.



Gold nanoparticles may be patterned on demand into various cholesteric textures by playing with the film thickness and the interfacial properties.

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Mesostructuring of Au nanoparticles through incorporation in polymerized ionic liquids

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Over the last decade an enormous effort has been directed towards the synthesis and characterization of metal nanoparticles (NPs). Considerably less effort has focused on the functional organization of NPs into durable composites. Yet, nanotechnology has promised the fabrication of multi-component, materials with emergent / complex properties. While progress has been made in advancing our fundamental understanding of individual NP properties, information as to how they can be organized into heterogeneous functional composites is limited. Understanding long-range communication between organized arrays of NPs holds tremendous potential in the development of energy and photonic mesoscale materials. One approach for coupling NPs is through a tailored, structured scaffold that can stabilize and spatially organize them into mesoscale architectures. Ideally, the scaffold would be durable yet pliable and contain segregated hydrophobic and hydrophilic domains allowing for the selective partitioning of chemically-functionalized NPs. In addition, the scaffold would adopt a variety of architectures for varying the organization of the NPs into a range of ordered geometries. Ideally, the matrix would be stimuli-

responsive, permitting externally regulated modulation of the scaffold structure and hence internal packing arrangement of the encapsulated NPs. A dynamic scaffold would permit external regulation of the NP packing arrangement thereby offering a means to regulate their collective response.

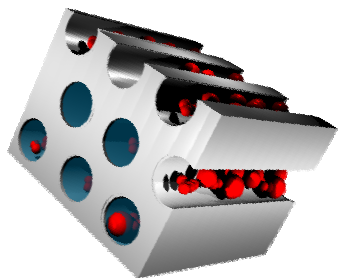


Figure 1. Schematic illustration of Au NPs organized within the aqueous channels of a hexagonal perforated lamellar (HPL) structured poly(vinyl imidazolium) chloride. Optimized packing of the Au NPs “turn-on” electronic conductivity within the polyelectrolyte.

Nanostructured polymeric ionic liquids (poly(IL)s), prepared by the polymerization of ionic liquid monomers have many of these aforementioned attributes and may serve as an ideal matrix for the mesostructuring of NPs.[1-3] Small-angle X-ray scattering (SAXS) studies have demonstrated that the poly(IL)s can adopt a rich variety of structured motifs, ranging from 1-D lamellar to 2-D hexagonal and 3-D bicontinuous cubic phases.[1] A large region of phase space has been identified in which these binary systems can adopt long-lived metastable structural states that are intermediate in character between lamellar and hexagonal, namely, hexagonal perforated lamellae (HPL) Fig. 1. The use of these hierarchically structured polymers as soft templates for the morphological control of in-situ synthesized Au NPs has also been demonstrated. Furthermore, we have shown that the polymers

can be reversibly swollen in a variety of both solvents, leading to changes in the nanostructure. The tunability of the mesophase architecture has been used to regulate the internal packing arrangement of in-situ synthesized Au NPs, leading to both color tuning and regulation of the bulk electronic properties of the composite.[2,3]

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Polymer-metal oxide nanocomposites prepared by self-assembly of nanoparticles in block copolymer films

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Nanoparticles embedded in a polymer matrix mark an important class of hybrid materials which attract high attention due to the improvement in material properties that results from the addition of nanoscopic filler particles to the polymer matrix. In particular, soft polymer films with embedded magnetic nanoparticles have attracted immense interest for wide potential applications in functional nano-devices. Among the various magnetic nanoparticles, magnetic metal oxide nanoparticles, for example maghemite and magnetite, are of interest due to their magnetic properties [1-3]. A high magnetization, low magnetic remanence and coercivity are observed for maghemite and magnetite nanoparticles.

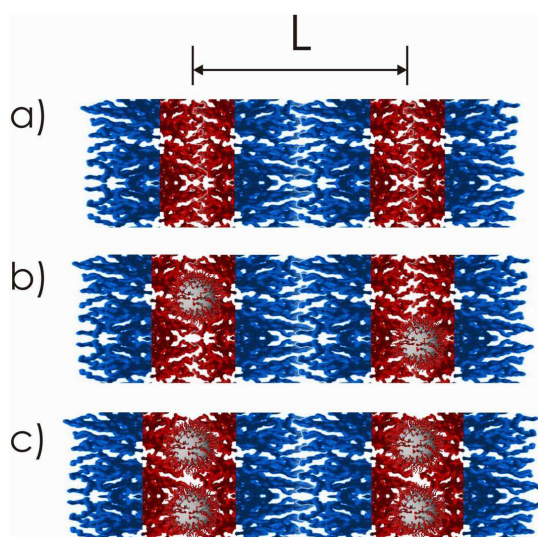


Figure 1. Sketch of the polymer and nanoparticles arrangement for the a) pure diblock copolymer matrix, b) with a low nanoparticle concentration and c) with a high nanoparticle concentration. The inter-domain distance is denoted with L . Image taken from reference [1].

In the present investigation well-aligned highly-oriented hybrid films of polystyrene (deuterated)-block-polybutyl meth acrylate symmetric block copolymer are used to guide polystyrene grafted maghemite nanoparticles within the polymer matrix [1-3]. Parallel and perpendicular lamella structured films, embedded with different nanoparticles concentrations (from 0 up to 15 wt%), are prepared by spin coating process. Both surface and buried structural information of the metal-polymer hybrid film are gained using time-of-flight grazing incidence small angle neutron scattering (TOF-GISANS). The nanoparticles are positioned in one polymer domain and a distortion of the lamella structure evolves with increasing nanoparticle concentration. The nanoparticle arrangement and possible particle assemblies within the polymer matrix is influenced by the lamella orientation.

A characterization of the magnetic properties of the nanocomposite films complements the structure-property relationship [3,4].

Acknowledgments: Y.Y. acknowledges the China Scholarship Council (CSC) for funding.

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The conductivity and permittivity of Ni-silicone rubber composites under uniaxial pressure

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The effect of uniaxial pressure on the conductivity and permittivity of a Ni-silicone rubber composite that exhibits an extremely large piezoresistivity has been investigated. The ac conductivity and the relative permittivity have been measured as a function of frequency for a sample under uniaxial forces. The dc conductivity is extremely sensitive to the applied uniaxial compression; it increases seven orders of magnitude with a uniaxial loading of 1kg (Figure 1). At high frequencies, both ac conductivity and permittivity of the composite exhibit a power law dependence on frequency, which is consistent with the prediction of the microstructural networks model. The permittivity of the composite sample increases with uniaxial force, indicating that the composite can be used to develop pressure tunable capacitors. A remarkable skin effect is observed in the frequency dependence of conductivity of the sample under uniaxial forces above 500 gram, which may have important ramifications in the design of radio-frequency and microwave applications and to some extent in ac electrical power transmission and distribution systems.

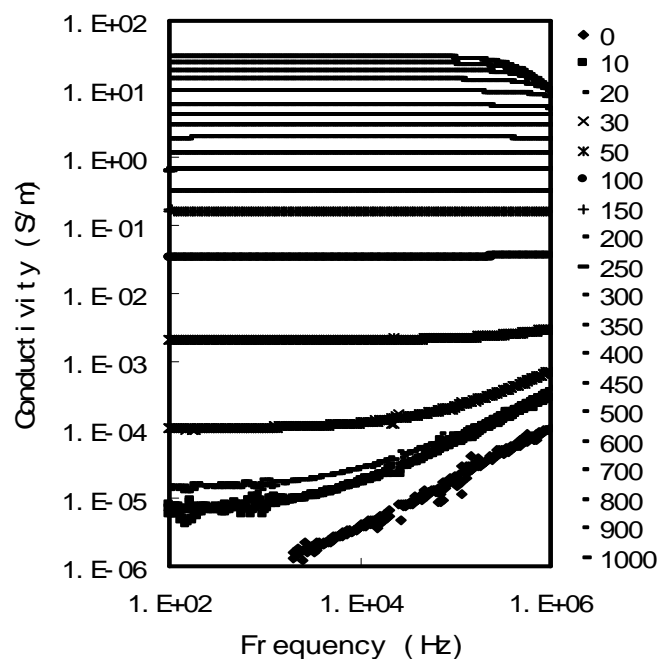


Figure 1. Frequency dependence of conductivity for Ni-silicone under uniaxial forces indicated in the figure (grams weight).

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Design, Structural Analysis and Properties of Metal Nanoparticle/Polymer Nanocomposites prepared by Ion-Doped Precursor Approach

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Research into the preparation of nanocomposites containing metal nanoparticles dispersed in polymer matrices has been triggered by the technologically important applications of these nanocomposites in optics, sensors, and nanoelectronics. The major limitation of these nanocomposite materials is the difficulty of controlling their microstructure, e.g., size, size distribution, and interparticle spacing of the dispersed nanoparticles, during synthetic processes. A technique that allows precise control over composite microstructure is, therefore, indispensable for the preparation of composite materials with desired properties. Recently, in situ synthesis of these metal nanoparticle/polymer composites by the process of dissolution and reduction of metal salts/or complexes within polymeric precursors has been proposed. The advantage of this process is the uniform distribution of the metal source and the structural homogeneity of the precursors, which provides a resultant homogeneous dispersion of nanoparticles in polymer matrix. In this contribution, our latest findings on preparation of polymer nanocomposite containing metallic nanoparticles using ion-doped precursors and control over their microstructures will be presented. This method utilizes a simple chemical treatment that provides surface-modified polymers with ion exchange capability, as well as incorporation of metal ions to form precursors with control over ion concentration. Subsequent reduction treatment causes growth of metal nanoparticles within polymer matrix, providing metal/polymer composite

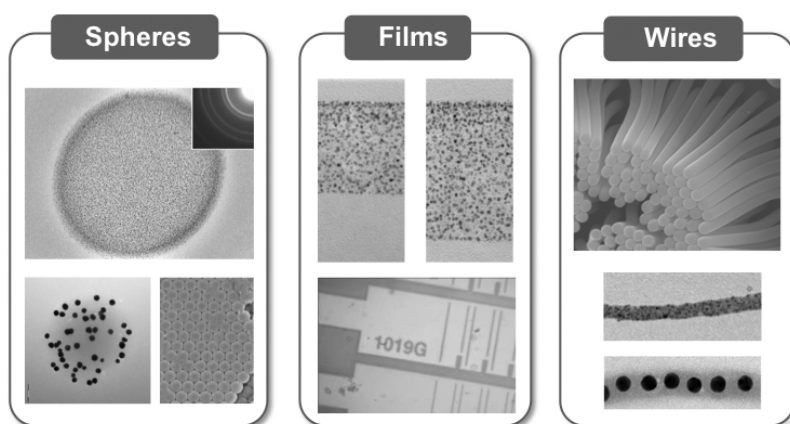


Figure 1. 3D (spheres), 2D (films), and 1D (wires) composite materials

materials with various shapes [1-5] (Figure 1). The detailed investigation concerning the reduction behavior of metal ions and the changes in chemical structure of the matrix upon annealing will be presented to provide insight into the appropriate mechanism of this process. A major long-term goal of our research in this area is to develop ways of tailoring the design and formation of new nanocomposite materials with precisely controlled microstructures. Such the control over the parameters in the nanocomposites not only is an important for fabricating high

performance nanocomposites of chosen functions but also should lead to fundamental understanding of the relationship of the physical properties to the composite microstructures.

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Bifunctional polymer–metal nanocomposites: Modification of commercial polymeric ion exchangers with metal nanoparticles

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The bi-functionality of polymer-metal nanocomposites is determined on one hand by the functionality of the polymer and on the other hand by that of metal nanoparticles. In this communication we report the results obtained by modification of various ion exchange materials with mono- and bi-metallic (in this case, core-shell) Functional Metal NanoParticles (FMNPs) having biocide or catalytic properties by using InterMatrix Synthesis (IMS) technique. The bi-metallic nanoparticles (NPs) consist of a ferromagnetic core coated with the functional metal shell, which provides the final polymer-metal nanocomposite with desired additional functionality. The ferromagnetic nature of the metal core allows preventing the possible undesirable escape of FMNPs into the medium under treatment by using simple magnetic traps. This is particularly important in the case of water treatment with ion exchange materials as it prevents the post-contamination of treated water with FMNPs. It is also important for catalytic applications since the nanocatalyst can be recovered and reused.

The modification of ion exchangers with FMNPs is carried out by using IMS technique coupled with Donnan exclusion effect, which allows for production of polymer-metal nanocomposites with the most favorable distribution of FMNPs. In the case of cation exchange materials IMS technique includes the following two sequential staged: 1) immobilization of metal or metal complex ions (NP precursors) onto the functional groups of the matrix, and 2) their reduction by chemical or electrochemical means. The novel version of IMS is applied for modification of anion exchangers and the order of immobilization of NP precursors and the chemical reducing agent is inverted: 1) immobilization of the reducer anions, followed by 2) their reaction with NP precursors. This new IMS version has been shown to also provide the desired location of FMNPs close to the surface of the polymer (as it is shown in Fig. 1). This distribution substantially enhances the efficiency of their biocide and catalytic applications described in this work.

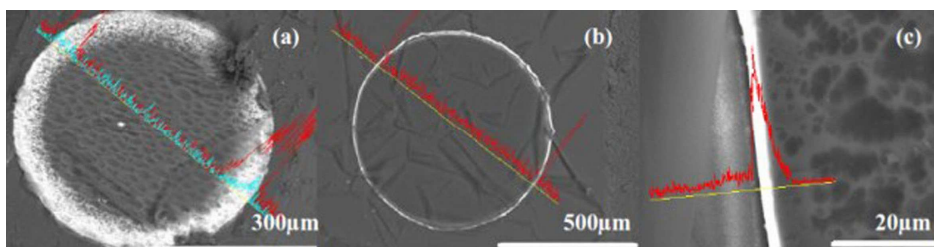


Fig 1: SEM images of cross-sectioned granules and respective LineScan EDS spectra showing distribution of: (a) Pd@CoNPs inside cation exchange and (b, c) Pd-NPs in anion exchange polymers.

Highly efficient transition metal nanoparticle generation in the gas phase by pulsed DC magnetron sputtering

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Metal nanoparticles have been of high scientific interest in the last decades as they are intermediate objects between single atoms or molecules and solid matter and have unique chemical, physical, mechanical, electrical, magnetic and optical properties, which are also explored in metal nanoparticle containing nanocomposites [1]. Gas aggregation cluster sources (GAS) following the Haberland concept are widely utilized for fabrication of various metal nanoparticles [2]. However, its utilization in industry is still rather limited. The main reason for that is the relatively low deposition rate provided by GAS which is not acceptable for most technological process.

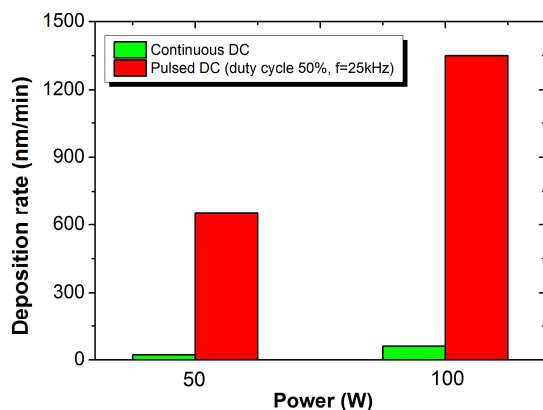


Figure 1. Deposition rate of TiO_x nanoparticles generated by a aggregation source based on continuous (green) and pulsed (red) DC sputtering.

In this work we show that a gas aggregation cluster source based on pulsed reactive DC magnetron sputtering gives rise to a huge increase in deposition rate of nanoparticles by more than one order of magnitude compared to continuous operation (e.g. TiO_x , Fig. 1). We suggest that this effect is caused by a balance between slight target oxidation (during “time-off”) and subsequent sputtering of metal oxides (sub-oxides) at “time-on” with high power impulse. It is shown that deposition rate is strongly dependent on duty cycle and discharge repetition frequency of the discharge.

The work is focused on deposition of various metal (oxide) nanoparticles (TiO_x , Al_xO_y , SiO_x). Argon was used as a working gas and additionally, a low concentration of oxygen was admixed, which is necessary for the cluster formation process [3]. The influence of the discharge repetition frequency (1 – 100 kHz) and duty cycle (30 – 95%) was investigated. By adjusting the duty cycle and repetition

frequency at constant power and oxygen admixture, a maximum efficiency of nanoparticles generation and thus deposition rate can be achieved. The prepared nanoparticles were characterized with regard to chemical composition, morphology, optical properties.

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Millisecond time resolved investigation of metal nanoparticle growth on polymer films

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Dispersed metal nanoparticles (NPs) in a polymer matrix are essential for many technologically important applications, including biological imaging, thin film technology, magnetic recording media, optoelectronics and sensors. Highly time resolved investigation of the NPs' size and shape during the metal deposition on polymer thin films would enable possible fine tune of NPs' magnetic and electric properties. Gold in its atomic state is deposited on several homopolymer and block copolymer films by utilizing a DC magnetron sputtering deposition system [1-5]. With the

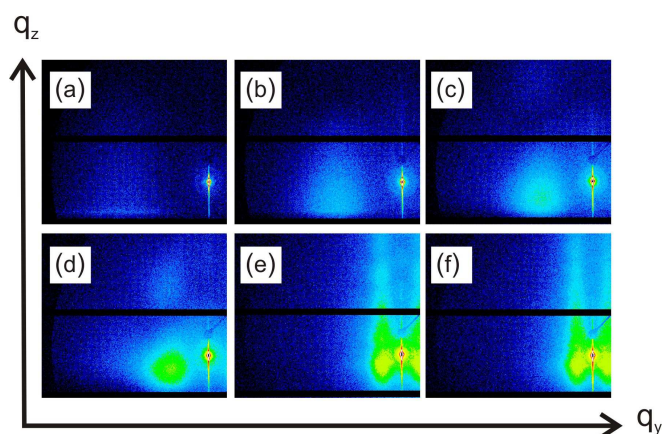


Figure 1. Composite image showing selected 2D GISAXS images during gold sputtering on a solid surface at different sputtering time viz. a) 6, b) 10.5, c) 15, d) 22.5, e) 90, and f) 150 seconds.

unprecedented time resolution of 15 milliseconds, the growth kinetics of gold NPs on the polymer surfaces is monitored using in situ real-time grazing incidence small angle x-ray scattering (GISAXS) technique (Fig. 1). Structural information including particle shape, size and size distributions are simultaneously probed as the metal is progressively deposited on the polymer surface. An exponential growth of metal particle size on all polymer surfaces is observed. Below a certain critical particle size, an initial fast particle growth is due to high particle mobility. While a slower kinetics at concentrated metal dispersion is due to the strong metal-metal interactions. The metal growth kinetics study for many chemically different homopolymer films explains the long-time debated high selectivity characteristics of metals towards one block in block copolymer based nano-templates. The possible anisotropic growth and shape selectivity of NPs are discussed.

Acknowledgments: Authors would like to thank DESY engineers and technicians for their work constructing and mounting the DC sputtering chamber on the MiNaXS beamline P03 at the PETRA III storage ring at DESY-Hamburg, Germany.

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Gold sputter deposition on polystyrene thin films: Growth retardation, doping and final metal layer formation

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Organic-inorganic hybrid multi-layer systems are widely used in modern technologies and functional applications [1]. The range of applications includes optical technology [2] and coatings [3]. The fundamental issue is the structure and morphology of the metal layer and its interaction with the underlying polymer thin film [4,5].

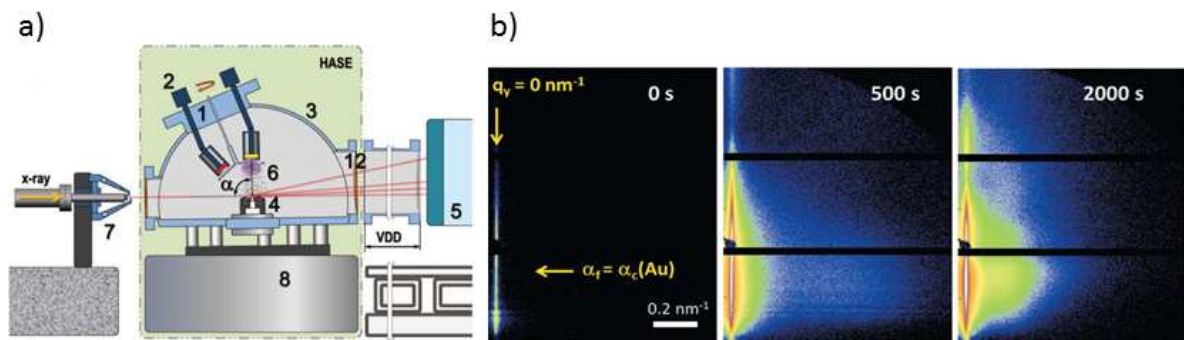


Figure 1a) Schematic representation of the in-situ sputter deposition setup [6]. b) Selected two-dimensional detector pattern of the growth of gold on polystyrene [5]. The sputter deposition time is indicated with $t=0s$ denoting the pure polymer film.

Sputter deposition is one of the most widely used methods to install nanostructured thin films in science and technology [1]. We already used the combination of stop-sputter deposition with grazing incidence small-angle X-ray scattering (GISAXS) [4,6]. This method enables to follow in detail with high statistical relevance the deposition of metals on polymers and to investigate the layer's nano- and mesostructure to obtain the relevant growth laws and correlations.

Fig. 1a) shows a sketch of the in-situ GISAXS setup used, combining a sputter chamber and a microfocused X-ray beam. In Fig. 1b) we present selected GISAXS pattern of gold sputter deposition on a polystyrene film, obtained at different deposition times during sputter deposition. Clearly, one observes changes induced by the growth of the nanoparticles. We present the detailed analysis of the layer growth and compare our findings to Au on silicon [7]. Surprisingly, a growth retardation of the gold layer is observed: Only after the installation of a gold monolayer below the surface inside the polystyrene film ("doping"), the gold layer finally develops on top of the polymer film. This doping layer is additionally confirmed by X-ray reflectivity and of crucial relevance for device tailoring.

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In situ GISAXS characterization of metal sputtering on Alq3 thin film

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Organic light emitting diode (OLED) is an important device as the next generation light source for illumination. Its low cost, easy fabrication and reasonable efficiency have attracted many research interests. The multilayer device structure emphasizes the significance of understanding the interfacial structure and properties. In most OLEDs, Tris(8-hydroxyquinolino)aluminium (Alq3) is the activating layer and different metals (Al, Au, et al.) are used as the metal electrical contact. Upon sputtering on Alq3, metal atoms can diffuse into the organic layer, modifying the both morphological and electronic structure, which are directly related to the device performance. The interaction between metal and Alq3 has been discussed by different spectroscopic techniques [1,2] and theoretical method [3] at single molecule level. Nevertheless, the growth mechanism of the metal thin film on Alq3 is scarcely studied. For this purpose, in situ grazing incidence small angle X-ray scattering (GISAXS) plays a powerful role to characterize the inorganic/organic interfacial structure during the film growth process [4,5]. In this work, we have carried out GISAXS characterization to monitor the entire process of diffusion, coarsening and growth of different metal thin film on top of Alq3 layer during the sputtering process. Considering the chemical reactivity, such as, Al and Au, we elucidate different lateral growth process from the out-of-plane scattering profile. Meanwhile, the sputtered metal/Alq3 films demonstrate good correlation to substrate roughness, illustrated by the in-plane scattering profile. The results benefit the comprehension of the development of the general metal/organic semiconductor interface structure prepared via sputtering process which is widely used in the industry.

S. Y. acknowledges the Knut och Alice Wallenberg foundation (Sweden) for financial support

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Polydivinylbenzene-supported nanoparticle catalysts that mimic the structure and morphology of inorganic catalysts for oxidation and hydrogenation

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The liquid phase oxidation and hydrogenation of alcohols catalyzed by supported metal nanoparticle catalysts are common reactions in the processing of biomass-derived compounds to value-added products. These reactions are mostly carried out at temperatures below 200 °C. Many organic polymers are stable up to this temperature, and offer versatile and readily functionalizable catalyst supports. Mesoporous polydivinylbenzene (PDVB) is of special interest, since it can be prepared by nanocasting, thereby retaining the size, shape and pore structure of conventional inorganic support materials such as carbon or metal oxides. This is important for comparing polymer-supported catalysts with classical inorganic supports, while changing as few structural parameters as possible. Therefore, PDVB-supported platinum and ruthenium catalysts are developed, and their catalytic properties investigated in the oxidation of ethanol and glycerol to the corresponding acids [1], and in the hydrogenation of 5-hydroxymethylfurfural (HMF).

Mesoporous PDVB networks are prepared via nanocasting [2]. A solution of monomers and radical initiator (AMBN) is impregnated into silica gel with a calculated pore filling of 80 %. Polymerization occurs in a closed reactor at 75 °C. Selective leaching of silica, filtration, washing and drying gives the desired mesoporous PDVB. The deposition of platinum and ruthenium nanoparticles is carried out by deposition-precipitation in suspension in a 1:1 solution of ethylene glycol and glycerol using K_2PtCl_4 and $RuCl_3 \cdot xH_2O$ as metal precursors, respectively. Bifunctional catalysts containing metal and sulfonic acid functionality are obtained by gas-phase sulfonation of the polymer (SPDVB). The oxidation and hydrogenation reactions are carried out in a 50 ml batch reactor in water and tetrahydropyran with an atmosphere of oxygen and hydrogen, respectively. From the comparison of supports in platinum catalysed oxidation it can be concluded that the polymer-supported catalysts outperform the inorganic catalyst supports by showing high activity and product yield. Additionally, Ru/PDVB is an active catalyst in the hydrogenation of HMF which demonstrates the versatile applicability of the polymer-supported metal nanoparticle catalysts.

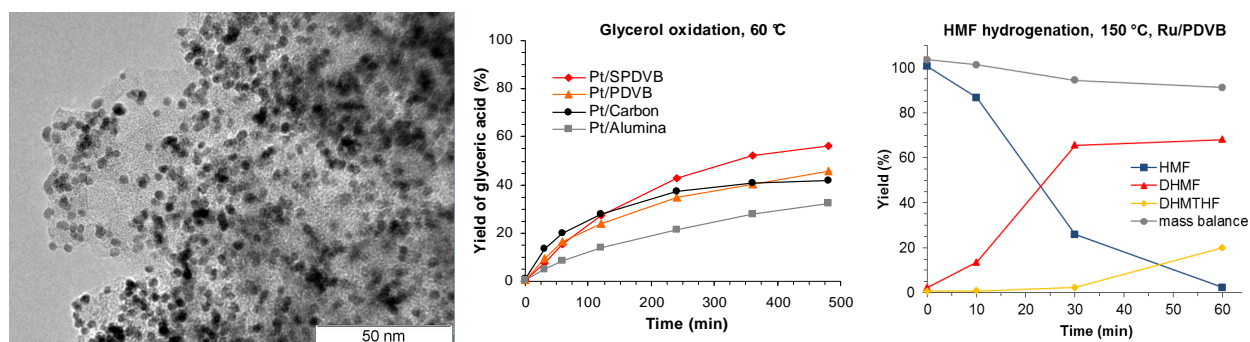


Figure: TEM image of a 5 wt% Pt/PDVB catalyst (left). Comparison of catalyst supports in the platinum catalyzed oxidation of glycerol (middle). Hydrogenation of HMF using 7 wt% Ru/PDVB (right); DHMF: di-hydroxymethyl-furan; DHMTHF: di-hydroxymethyl-tetrahydrofuran (right).

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Cold atmospheric pressure plasma deposition of organic-inorganic nanocomposite films

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Organic/inorganic nanocomposite materials have already been widely recognized as one of the most promising research areas of materials chemistry. The combined unique properties offered by both organic and inorganic components on a nanoscale level make in fact such hybrid materials attractive for a wide range of applications such as optoelectronic devices, chemical or biological sensors, and catalysts.

Nowadays, the development of new synthetic approaches to these hybrid materials is still an open issue. Recently, aerosol-assisted atmospheric pressure cold plasma processes have been addressed as an attractive route towards the deposition of hybrid nanocomposite coatings. This approach seems to be particularly convenient when for instance dispersions need to be injected directly in the atmospheric plasma. The aerosol of a dispersion of nanoparticles (NPs) in a liquid precursor can lead to the deposition of nanocomposite coatings in which the NPs are embedded in the matrix formed by the plasma polymerization of the precursor [1, 2].

This contribution deals with our recent study of the growth and structure of plasma-deposited polyethylene/zinc oxide (PE/ZnO) nanocomposite coatings with several potential applications due for instance to photocatalytic properties of ZnO. These films are deposited in a parallel plate dielectric barrier discharge (DBD) fed with He and the aerosol of a dispersion of oleate-capped ZnO NPs in liquid hydrocarbon precursors such as octane or octane/1,7-octadiene mixtures. A comprehensive study on the effect of different process parameters (e.g., atomization conditions, dispersion composition, deposition time) on the chemical composition and structure of the film will be presented.

As expected, with increasing the concentration of ZnO NPs in the starting dispersion from 0.5 to 5% w/w, the ZnO content in the coating increases. The addition of a small amount of 1,7-octadiene to octane (0.5% v/v) favors the inclusion of the NPs and hence results in an increase of the ZnO concentration of the coatings.

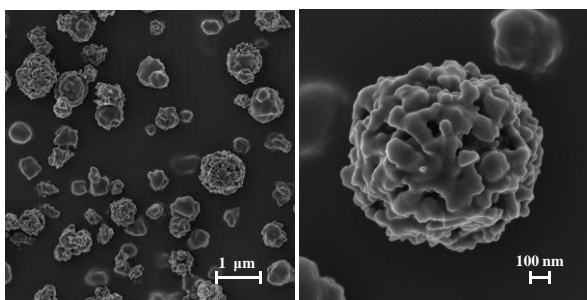


Figure 1. Representative SEM images of the plasma-deposited polyethylene/ZnO nanocomposite film.

Advancing and receding WCAs steeply increase with the NPs content in the film and reach values higher than 165° with low hysteresis indicating the formation of slippery superhydrophobic surfaces. As shown in Figure 1, SEM images confirm that this superhydrophobic character is due to the hierarchical micro-/nano-structured surface morphology of the coatings. ZnO NPs generally aggregate in almost spherical clusters that can be incorporated to a different extent into the polyethylene-like polymer as a function of the deposition process conditions.

Results on the photocatalytic activity of the deposited coatings for the degradation of organic pollutants in water under UV and visible light irradiation will be shown; the catalytic activity will be correlated with the chemical and morphological properties of the coatings.

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Nanoparticle based Nanostructured Films using Plasma Polymers

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Nanocluster and nanoparticle production in the gas phase and their deposition have been extensively studied within the last decade using cluster condensation (aggregation) source (GAS) based on planar magnetron, originally introduced in [1]. Cluster beams of various metal clusters such as Pt, Ag, Au, Cu, Al and Ti etc. were produced using this type of GAS [2]. Ag and Al clusters were embedded into C:H plasma polymer in order to prepare nanocomposite films Ag/C:H and Al/C:H.

In addition to these investigations the first studies have been performed to prepare nanoparticles of hydrocarbon plasma polymer C:H, fluorocarbon and Nylon-like plasma polymer. C:H nanoparticles were prepared in the GAS using an RF magnetron with graphite target and n-hexane mixed with the Ar gas. Fluorocarbon and Nylon-like ones were fabricated using PTFE or Nylon targets, respectively, instead of graphite. In case of Nylon a new type of hollow cathode magnetron GAS was tested.

Overcoating different types of nanoparticles with various and/or same film considerably modified roughness and especially the wettability of the coating ranging from superhydrophylic to superhydrophobic properties. In addition the experiments with human osteoblast-like MG 63 cells revealed that the creation of conveniently nano – rough TiO_x surface in the above mentioned manner may improve the adhesion of the cells.

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Nanostructured and functional polymers based materials: from macromolecules assemblies in thin films to industrial applications

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Multi functional nanostructured polymers are a key issue for the advanced development of new devices and structures. In fact, this class of materials will offer simultaneously or sequentially, the association of various functions required by materials used in advanced applications. In this frame, the search for a method to design nanostructures from a variety of materials is of growing interest and the ability to translate design methods from a laboratory to applications is of increasing significance.

In our Institute, we examine several of the most readily scalable bottom-up methods for the fabrication of such nanostructures. Different kind of nanostructuration can be of interest but we are mainly investigating the phase behavior of macromolecules assemblies in thin films especially multilayered films made of different polymers, hybrid systems that combine polymers and nanoparticles as well as thin films of polymer networks. We propose to combine versatile and straightforward methods of processing such as the layer-by-layer and plasma polymerization technique giving access to various multilayer architecture. It will be demonstrated that these latter does allow the fabrication of materials whose properties make them suitable for barrier systems. The challenge is the exact control of the polymer architecture, functionality and nanostructure in polymer materials through synthesis strategy as well as a complete understanding of the correlations between chemical structure, architecture and materials characteristics

Different kind of barrier systems [1-4] will be introduced during the paper starting from fire resistant thin films [1] up to enzyme diffusion barriers [2] as well as barriers against water (i.e. superhydrophobic surfaces). For each application, the main challenges and issues in terms of design, structure, properties and performances over the time will be discussed. Finally, it will be highlighted this approach could open doors for new kind of smart coatings that can react to an external stimulus.

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Structural, Electrical and Thermal Characterizations of Polyimide/BN Nanocomposites

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Abstract: Polyimides (PI) are a class of high performance polymers that have excellent thermal, mechanical, electrical and chemical properties. They are widely used as electrical insulating coating films in microelectronics and power electronics, such as buffer coatings, interlayer insulation, wafer-scale packages or component passivation. Because of the demands in denser and faster circuits in electronic devices, the dissipation of heat generated by electronic components focuses the interest and appears as an important issue to be resolved. Moreover, new components induce higher electric field stresses in the insulating layers. Since few years, an increase of the research regarding the electrical and thermal properties of polymer/ceramic nanocomposites attracts more and more attention in order to benefit nanometric size effects of the ceramic nanofillers. Conventionally, silica (SiO₂) or alumina (Al₂O₃) nanoparticles are used to improve respectively the electrical or the thermal properties of the polymer matrixes due to low cost. However, in the case of Al₂O₃, the thermal performances of the composites remain limited due to the low thermal conductivity of Al₂O₃. Even if more expensive, nitride-based ceramics, such as boron nitride (BN) or aluminum nitride (AlN), appears nowadays as potential solutions for the development of high thermal conductive thin polymers due to their higher intrinsic thermal conductivity. Moreover, BN and AlN present good electrical insulating properties. While AlN nanoparticles slightly oxidize at surface (thin Al₂O₃ layer of few nm) limiting the transport of phonons, BN nanoparticles remain more stable regarding potential reaction with oxygen content. Consequently, BN nanofillers appear as very attractive to improve the thermal properties of thin PI films without degrading electrical properties of the nanocomposites. In this paper, we have investigated the effects of BN nanoparticles on the current-field characteristics and on the thermal conductivity of spin-coated PI films in a wide range of filler volume contents from 0 to 60 vol.%. In this purpose, two kinds of BN nanofillers (cubic and hexagonal) with different mean sizes (40 nm and 150 nm) will be presented.

Keywords: Polyimide/Boron nitride, PI/BN, Nanodielectrics, Electrical properties, Thermal conductivity.

Thin SiCOH layers with Ag-NPs tailored interface as model system of deep artificial traps for electric charges

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Dielectric charging phenomenon remains a topic of research in many area of applications because of the necessity to control or to avoid charges accumulation in devices containing insulating parts. Considerable attention has been paid on charges accumulation in insulators in both cases: (i) when it favours the application, like for non-volatile memory devices [1] and electrets or (ii) when it represents a drawback like in the case of electrostatic adhesion in MicroElectroMechanical Systems (MEMS) [2]. Dielectric charging phenomenon still signifies great challenge, largely due to a lack of knowledge on the nature and related specific mechanisms [3]. Moreover, when the layer thickness scales down below micrometer scale, specific issues are superimposed. Adequate description of charge injection, localization and charge transport in dielectric materials at nanometer scale is a requirement to better understand the behaviour of insulating materials under electrical stress, which will certainly improve the performance and reliability of dielectric materials.

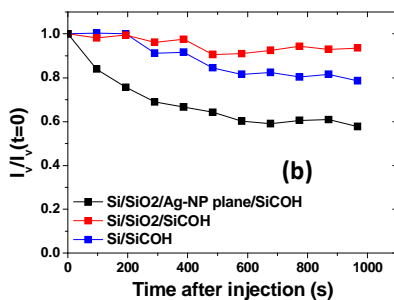
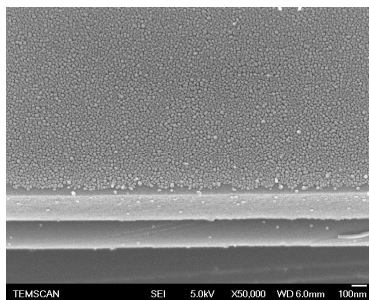


Figure 1. (a) SEM image of the plane of Ag-NPs deposited on SiO₂ layer; (b) Charge decay for different dielectric structures.

This communication presents a study on charge injection and control of dielectric charging phenomenon in thin dielectric layers with tailored interfaces. Plane of silver nanoparticles (Ag-NPs) was embedded in thin SiCOH dielectric layers (10 nm to 100 nm of thickness) at different distances from the surface. Thus, the Ag-NPs represented artificial deep traps for the charges injected from the surface. The deposition of organosilicon layers containing Ag-NPs was performed in axially asymmetric RF (13.56 MHz) discharge maintained in hexamethyldisiloxane (HMDSO)-argon mixture at low gas pressure (< 7 Pa). Pulsed injection of HMDSO ([CH₃]₆Si₂O) was used with the duty cycle as key parameter of the process. One of the discharge electrodes was Ag-made target to bear the Ag-NPs sputtering.

Different dielectric model systems were elaborated. The distance from dielectric surface to Ag-NPs plane (figure 1(a)) was measured by spectroscopic ellipsometry. The structure of organosilicon layers was analyzed by FTIR. The space-charge diagnostic was performed by Kelvin Force Microscopy, a diagnostic method derived from Atomic Force Microscopy (AFM) and giving the possibility to determine the surface potential and the quantity of charges previously injected with an AFM tip under bias voltage. Charge decay (figure 1(b)) in the model systems allows probing the dielectric charging phenomenon. The obtained results reveal that the presence of Ag-NPs close to the dielectric surface significantly modifies the electric field distribution; hence a plane of Ag-NPs can efficiently be applied to block the electrical charge injection in thin dielectric layers.

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Ag/C:H:O Nanocomposites on Textile Fibers for Sensor Applications

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Over the past decade, functional textiles have received growing interest in textile research worldwide [1]. However, so far the industry concentrated on adapting macroscopical electronic elements and attaching them onto manufactured functional garments. Our approach to sensing and acting textiles for utilization in medical, sports or home environments comprises a sensitive textile fiber (textile-electronic-fiber or e-fiber). It can be viewed as a first step to integration of electronic elements into fabrics prior to their further design and manufacture. This concept includes, for example, on-body sensor components capable of monitoring the biometric status of the user.

Metal/plasma polymer nanocomposite coatings attract a long-term interest in research due to a wide range of possible applications as a result of a great potential in tuning their mechanical, electrical and optical properties in various different directions according to the special requirements of any particular application [2,3]. These nanocomposite films have already been identified as a suitable type of material for sensor applications (e.g. for sensing of strain or relative humidity). Several plasma-based deposition techniques have been explored in order to incorporate metal nanoparticles into a plasma polymer matrix, e.g. simultaneous magnetron sputtering from metal and polymer targets or metal evaporation during PECVD [4]. Plasma technology offers a controlled film growth at high surface diffusion and low temperatures. Despite the fact that the deposition of metallic coatings onto textile fibers (i.e. metallization) has already been industrially established [5], deposition of nanocomposite coatings is not yet fully industrialized.

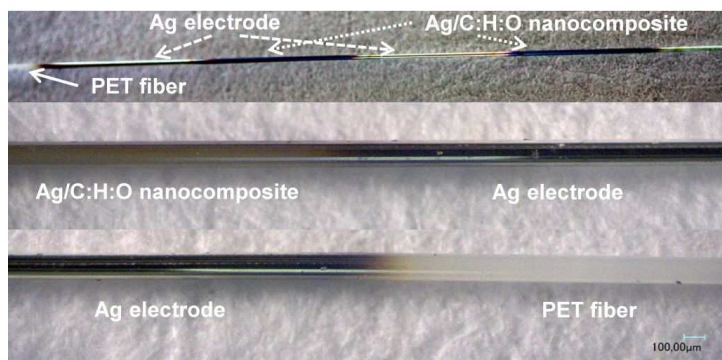


Figure 1: View by optical microscope of monofilament PET textile fiber coated by structured Ag electrode and Ag/C:H:O nanocomposite film.

In this contribution, we present a study of vacuum deposition process of nanocomposite silver/oxidized hydrocarbon plasma polymer thin films (Ag/C:H:O) by simultaneous PECVD of ethene and sputtering of silver target. Our study will address the most important parameters that affect the deposition and properties of the Ag/C:H:O coatings. Also, aging of the nanocomposite coatings and the influence of an aqueous environment on changes in their internal structure and properties are discussed. Finally, we show transfer of the nanocomposite films from plane substrates onto monofilament PET textile fibers (Figure 1).

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Polymers –Metal Composite Membranes: Synthesis, Characterization and Applications as Gas Filter

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The molecular structure of the polymer films can be engineered chemically as well as physically at the nano level through several routes and processing. Nano level metal cluster doping in polymer controls gas diffusion through polymeric membranes. The polymers are passive materials, having long molecular chains, entangled, cross-linked, short range ordered and distributed free volume. These can be converted thin film form of the order of nm to um, solution casting method. The Nano structure of thin films of polymers can be modified by doping, heat treatment, irradiation, leaching, SHI and etching. The properties of these polymer films are modified and can be characterized by XRD, AFM, FTIR, Raman, Ellipsometry, DTA and Positron Annihilation.

These nano engineered films called as membranes can be used as gas filters, gas sensors, ion filters, artificial skin. The talk will present important results for our laboratory and others to justify the theme.

Nanocomposite vectors for cancer diagnosis and therapy

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In the context of increased interest for nanomedicine, nanocancer diagnosis and therapy strategies to detect and eradicate cancers have emerged during the last few years. Among these strategies, iron oxide magnetic nanoparticles represent a potential multifunctional clinical tool that can provide cancer cell detection by magnetic resonance imaging (MRI) contrast enhancement as well as targeted cancer cell therapy. However, our knowledge about how engineering of targeted iron oxide nanoparticles influence their ability to efficiently cross all natural barriers before they concentrate in tumors still deserves serious investigations in adequate models of cancers. Furthermore, uptake mechanism of targeted iron oxide nanoparticles by cancer cells and their intracellular fate still remains poorly documented, although these data are essential for setting-up efficient anti-cancer therapeutic strategies. In our talk, after presenting general considerations concerning nanomaterials used in nanomedicine, we will present a hybrid system (termed MG10-IONP-DY647) composed of an iron oxide nanocrystal decorated with a peptidic ligand of a receptor (CCK2R) that is over-expressed in several types of human malignant tumors. We will show that MG10-IONP-DY647 recognize cells expressing the CCK2R with a very high specificity and, once bound to CCK2R, internalize via a mechanism involving recruitment of β -arrestins, clathrin-coated pits and dynamin. MG10-IONP-DY647 are then directed to lysosomes. Trafficking of CCK2R internalized following binding of nanoparticles is slightly modified in comparison to CCK2R internalized in the presence of unconjugated ligand. However, accumulation of nanoparticles in lysosomes increases as a function of peptide density at nanoparticle surface. Interestingly, even at high concentrations, nanoparticles did not stimulate inflammasome. Tumoral endocrine cells which had accumulated nanoparticles via active internalization through the targeted receptor and which were subsequently submitted to an alternative magnetic field died through a mechanism which does not involve a perceptible temperature rise. This mechanism of cell death is under active investigation.

Preparation and characterization of nanomagnetic particles Chitosan composite for enzyme immobilization

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Abstract

Nanomagnetic Chitosan composite beads were prepared, characterized and applied for enzyme immobilization. Effect of Chitosan molecular weight, de-acetylation degree, Chitosan concentration, medium pH and medium temperature on the particle size and particle size distribution was studied. The nanomagnetic Chitosan beads were further activated with glutaraldehyde and immobilized with beta-galactosidase enzyme. The activation process was proved using FT-IR and TGA analysis. The immobilized enzyme was further used in lactose hydrolysis process. The efficiency of the hydrolysis process was correlated to the nanomagnetic particles content and the porosity of the composite beads. The immobilized enzyme characters were estimated and compared with the free counterpart such as optimum pH and temperature profile. The kinetics of the immobilized enzyme were also studied and discussed. The stability of the immobilized enzyme against operational conditions was also investigated.

Use of the Enhanced Fluorescence of (Conducting Polymer)/(Metallic Nanoparticle) Composites for the Development of Rapid Diagnostics Tests

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After we have identified an enhanced luminescence in certain kind of (conducting polymer)/(metal nanoparticle) composites, in what we dubbed as the ELINOR effect [1], we have learned how to vary the corresponding fluorescence of these composites in a controlled manner by appropriate changes in the preparation conditions [2]. Since conducting polymer chains can be considered as polycations, they can pair with single nucleotide chains (s-DNA) through a nonspecific Coulombian interaction, and these composites can then be used as convenient fluorescent markers of DNA/RNA. We have exploited this property for the development of a simple and rapid molecular diagnostic test for genetic and infectious diseases based on the use of polyaniline/gold nanocomposites.

To test a patient for the presence of a given infectious agent, we begin by anchoring the corresponding primer (i.e., a short segment of the corresponding s-DNA that uniquely identifies the organism) on a solid substrate. A single drop (of a previously heated small amount) of the genomic material extracted from the patient under investigation is placed atop the primer and then covered by a drop of the fluorescent nanocomposite solution. After being rinsed with running water and thoroughly dried, the substrate is placed on a fluorescence microscope. Only in the case of a positive test, when the DNA of the infectious agent is in fact present in the genomic material, there is enough nucleotide material retained in the substrate to interact with the composite, resulting in a marked fluorescence (while only a basal luminescence would be observed in the negative case). The test can be performed in a few minutes, and so the ELINOR procedure appears as a promising platform for a variety of rapid diagnosis test of a molecular nature, where no previous nucleotide amplification step is required.

To evaluate the reliability of the test, we applied the ELINOR procedure in a double-blind analysis to identify the presence or absence of different infectious organisms (human papilloma virus 18 – HPV 18, leishmaniosis – in material extracted either from human patients or from dogs, and human t-lymphotrophic virus – HTLV) in samples that had been previously classified by polymerase chain reaction (PCR), the usual golden standard in biotechnology studies. The corresponding results are shown in Table 1, where the sensitivity (S) of the test is defined as the ratio between the number of positive results and the known number of infected samples, while the specificity (s) is the ratio between the number of negative tests and the number of truly non-infected samples.

Infectious Agent	S	s
HPV 18	83.3	93.3
Leishmaniosis (human patients)	88.3	71.3
Leishmaniosis (domestic dogs)	86.5	90.0
HTLV	91.5	80.0
Table 1: Sensibility (S) and specificity (s) of the ELINOR test in the identification of different infectious agents.		

The corresponding results seem very promising when compared to the corresponding values of available commercial tests for these diseases, which usually take longer and are more complex and expensive than the ELINOR methodology.

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Plasmonic Bionanocomposites

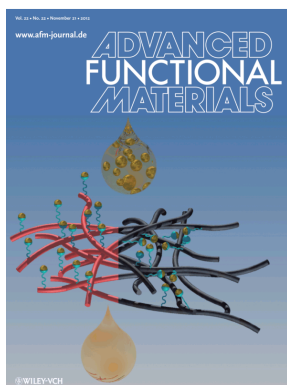
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Plasmonic nanocomposites are artificial structures with exotic properties originating from their plasmon resonance. Recently, this topic attracted much attention due to its great potential for a host of applications ranging from optics to energy. In the present approach, we apply this concept for two extreme purposes which are directly correlated to each other, namely; transparent conductor and perfect absorber based plasmonic metamaterials [1-3].

Biological materials are inherently and naturally multifunctional. The knowledge about smart combinations of various functions in materials that appeared in the biological evolution might inspire design of novel artificial plasmonic



bionanocomposites. Recently, we adopted this principle to bridge the gap between "Filtration and Plasmonics" while introducing plasmonic bionanocomposites [5,6] as a novel group of stimulus-responsive nanostructured hybrid materials with unique properties. In the Nanoworkshop 2013 we would like to share with you our recent results of the tuneable plasmonic bionanocomposites where the filling factors of the integrated nanoobjects is controlled for the first time by the protein filling factor.

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Preparation of Ag coatings for antibacterial and plasmonic applications

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Polymer-metal nanocomposites as well as metallic nanocoatings on top of polymeric films are of great scientific and engineering relevance since they are used in advanced optical, electrical and medical applications [1,2]. In particular, Ag-polymer nanocomposites or nanocoatings have been shown to exhibit excellent properties that can be exploited for applications such as antibacterial coatings, plasmonic devices or sensors [3-5].

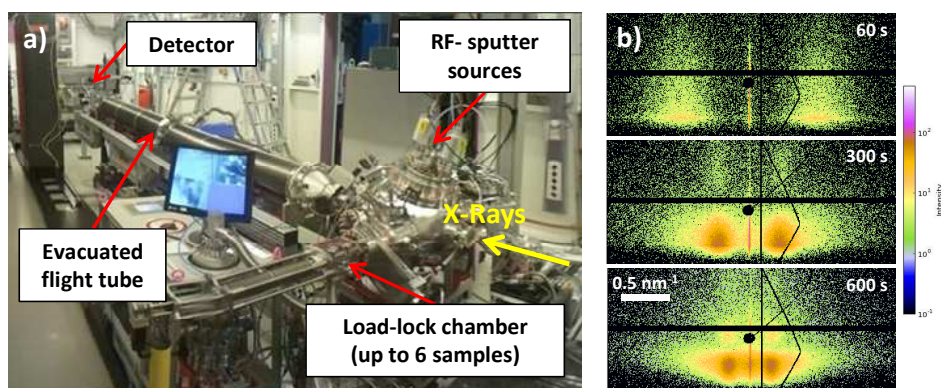


Figure 1. a) Picture of the RF-sputter chamber used for the experiments at the P03/MiNaXS beamline [9]. b) Selected two-dimensional detector patterns of the growth of Ag on Si

Among the different methods used to prepare such nanocoatings, sputter deposition is a widely employed technique in industry and research, presenting a major advantage in comparison with wet chemical approaches that is the absence of residual solvents in the prepared thin films.

Nevertheless, in order to fully control the desired final properties of the

nanocoatings, that are very sensitive to the morphology developed on the surface during the growth as well as to the arrangement of the metal nanoclusters on top of the polymer, it is mandatory to achieve a profound understanding of the growth kinetics of Ag. In this sense, micro Grazing Incidence Small Angle X-ray Scattering (μ GISAXS) [6] is a very powerful and valuable tool for the in-situ characterization of the growth kinetics allowing to extract morphological information of the surfaces that are developing with time resolution on the order of the millisecond [7].

In this work we present important μ GISAXS results concerning the time evolution of the structures developed during the RF-sputtering of Ag. A portable in-situ RF-sputter deposition chamber [8] that can be couple to the P03/MiNaXS beamline [9] at the PETRA III storage ring (DESY, Hamburg, Germany) has been designed and manufactured for the performance of in-situ μ GISAXS measurements.

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Fine tuning the silver release properties of polymeric or ceramic silver nanocomposite coatings using thin barriers

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Due to its broad band antimicrobial activity silver containing coatings are of great potential interest for medical applications, e.g., for coating of implants or catheters. Due to the large surface area, coatings containing silver in nanoparticulate form are especially suitable for this purpose. Silver nanoparticles (Ag NPs) release ions only in the presence of oxygen and protons [1]. Thus, one of the approaches to tune the silver ion release process is by embedding the Ag NPs in a matrix or by covering them with a coating as the water diffusion through the matrices or the coating is crucial for the silver ion release. There is significant interest in fine tuning the Ag ion release properties to optimize performance and to reduce the negative effects on human cells, in particular cytotoxic effects of the silver [2]. An important issue concerning Ag ion release is its kinetics; fast or slow release, high or low dose, short or long-term action.

One way to prepare such nanocomposite coatings is by physical vapor deposition using techniques like sputtering or plasma polymerization. These deposition techniques provide a precise control of the microstructure of the nanocomposite coating compared to other techniques. Further advantages are purity of the films, since it does not require additional materials, e.g., precursors, and the absence of finishing steps such as post annealing for sol gels. Sputtering or plasma polymerization even allows deposition at room temperature, enabling the coating of sensitive materials like polymers.

As a polymeric model system we studied the silver ion release properties and the water uptake of silver/polytetrafluoroethylene (Ag/PTFE) nanocomposites coated either by sputtered Teflon barriers or by a SiOxCyHz-polymer which was grown from the precursor hexamethyldisiloxane (HMDSO) in an radiofrequency (RF)-plasma. The concentration of the silver ions released from the nanocomposites after immersion in water was measured using inductively coupled plasma mass spectrometry (ICP-MS). The silver release potential was influenced by the barrier properties and showed a direct effect of the oxygen content in the case of the HMDSO coatings. Electrochemical impedance spectroscopy (EIS) measurements performed by our partners show a strong water diffusion dependence on the oxygen content in the coating films. This indicates that by tailoring the properties of the plasma polymerized coatings film, one can fine tune the silver ion release properties of Ag/polymer nanocomposites.

For silver/titania nanocomposite coatings, the strong surface segregation tendency of the silver has to be taken into

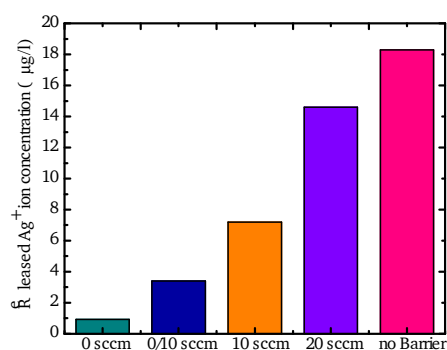


Figure 1. Silver release after 7 days in water of a Ag/Teflon nanocomposite through plasma polymerized barriers prepared under different oxygen flow conditions.

account. We demonstrate that the silver surface segregation tendency depends strongly on the preparation conditions of the coatings, in particular the total pressure during reactive sputtering. For a wide range of sputtering conditions, it is largely impossible to suppress silver segregation and to deposit an effective titania barrier onto the Ag/titania composite. Only at sufficiently low total pressure conditions a sputtering process can be established that allows the deposition of an effective titania barrier enabling good control on the silver release properties.

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Antifouling Properties of Reverse-Osmosis Filtration Membranes with Silver Nanoparticles

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The reverse osmosis process is an efficient water purification technology with comparatively low energy consumption. While numerous fouling control strategies have been suggested, unwanted biofilm formation remains a major challenge for membrane plant operators. The thin film composite membranes used for this process consist of a nonwoven support material, a polysulfone layer, and a very thin (< 50 nm) aromatic polyamide skin which acts as the selective layer. One promising approach to prevent biofouling is the deposition of toxic, e.g. silver nanoparticles. The strong antibacterial impact of silver nanoparticles has been shown; however, critical factors for the applicability of toxic nanoparticles are the long-term upkeep of the silver ion release rate as well as the preservation of the membrane filtration performance.

Silver nanoparticles were deposited onto the selective side of the membranes (polyamide layer) by magnetron sputtering and vacuum evaporation. Particle size and shape distributions were determined by Scanning Electron Microscopy (SEM). Vertical cross sections were prepared by Focused Ion Beam (FIB) technology and investigated by transmission electron microscopy (TEM). Optical properties were measured by UV-Vis and NIR-spectroscopy.

To test the desalination efficiency of the silver coated membranes, e.g. the permeate flux and salt rejection, a membrane coupon-tester was used. The coupon testing device operates at a reverse osmosis standard pressure for brackish water (15-20 bars). Critical values were set for both the flux and salt rejection which decide on the applicability of the modified membranes. The antimicrobial effect was verified by inducing a reproducible microbial stress on the membranes with a chemostat. In an effort to simulate the fouling potential of seawater, a mineral medium was used to cultivate typical water-borne bacteria *Pseudomonas* species. A flow-cell with parallel insets for up to five membrane samples was connected to the chemostat. The low concentrated bacteria broth passed through the flow-cell at a defined rate to induce biofilm formation on the membrane samples. After a selected time period, the formed biofilm was quantified off-line using confocal laser scanning microscopy (CLSM) and SEM.

POSTER COMMUNICATIONS

Morphological Changes of Reactive Polymers Surface after Modification with Metal Nanoparticles

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Intermatrix synthesis (IMS) technique coupled with the Donnan Exclusion Effect (DEE) can be successfully applied for the modification of reactive polymers with Functional Metal Nanoparticles (FMNPs). This IMS-DEE version of IMS technique results on the most favourable distribution of FMNPs near the surface of the obtained polymer-metal nanocomposite materials (PMNCMs) (see Fig. 1a). This type of FMNPs distribution in PMNCM is particularly important in their practical applications in such fields as catalysis and electrocatalysis. At the same time modification of the surface of reactive polymers results in dramatic changes of their surface.

In this communication we report the results obtained by the modification of reactive polymers such as, ion exchange materials with mono- or bi-metallic Functional Metal NanoParticles (FMNPs) having biocide, catalytic or electrocatalytic properties. The bi-metallic FMNPs consist of a ferromagnetic core coated with a functional metal shell, which provides the final polymer-metal nanocomposite with desired functionality. The ferromagnetic nature of the metal core allows the prevention of possible undesirable escape of FMNPs into the medium under treatment by using simple magnetic traps.[1]

The modification of polymeric ion exchangers of gel type with FMNPs by using IMS-DEE technique has been shown to result in the appearance of worm-like structure on the surface of the final PMNCM (see Fig.1b). This changes in the morphology of PMNCM leads to the appearance of nanoporosity what enhances their mass-transfer characteristics. The IMS-DEE technique consists of: 1) immobilization (sorption) of metal or metal complex ions (FMNP precursors) onto the functional groups of the polymer, and 2) their chemical or electrochemical reduction. [2, 3]

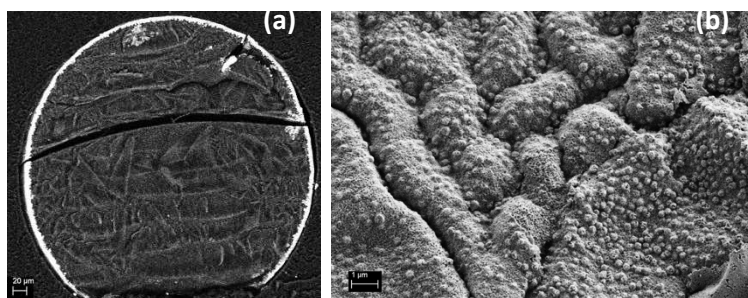


Figure 1. SEM images of PMNCM obtained by modification of cationic resin Purolite® C100E with Pd-FMNPs. (a) PMNCM bead cross-section and (b) PMNCM bead surface.

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Development of reusable catalytically-active silver nanocomposites on a polyurethane foam basis

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During the last century, catalysis has played a central role in chemistry and over the last decade, heterogeneous catalysts have attracted increasing interest because of their general advantages [1] that have been boosted thanks to the use of nanomaterials[2,3]. However, even if the use of Metal Nanoparticles (MNPs) seems to open a new window through the development of new-age catalytic species, some environmental and health safety risks, sometimes referred as nanotoxicity and nanosafety must be intensively considered [4].

The synthesis of polymer-metal nanocomposites[1,5-7], obtained by the incorporation of MNPs in polymeric matrices, has demonstrated to be an attractive approach because it is possible to prevent their escape to the reaction medium, thus providing an easy separation of the catalyst from the reaction mixture which, in turn, allows the possibility to reuse the catalytic species without losing efficiency. Under this context, the Intermatrix synthesis (IMS) based on the in-situ synthesis of MNPs in polymeric matrices, provides a novel route of synthesis with the main feature of taking advantage of the dual function of the matrix itself, that serves as both the medium for the synthesis of MNPs and as a stabilizer that prevents their uncontrollable growth, aggregation and escape to the media. [8]

In this work we report the IMS of silver nanoparticles (AgNPs) in polyurethane foam, which has been chosen as a suitable polymeric matrix because of its high stability against chemical degradation and because it is also one of the most cost-effective, food-grade polymers available, what makes it really suitable for industrial applications.

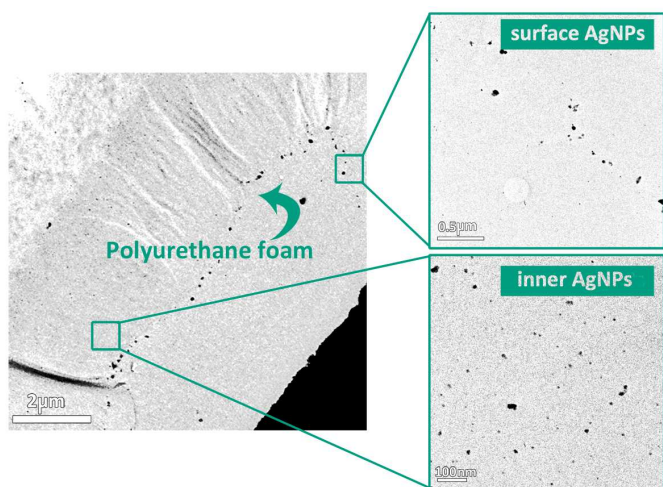


Fig. 1. Transmission Electron Microscope images of ultrathin slice of Ag-MNP- polyurethane foam nanocomposite.

By this procedure, small non-aggregated AgNPs were obtained all over the matrix (Figure 1).

In order to evaluate the catalytic activity of the developed PMNCs, a model catalytic reaction was carried out in different flow condition experiments: the reduction of p-nitrophenol to p-aminophenol in the presence of NaBH₄ and metallic catalyst. The possibility to reuse catalytic nanocomposites was also evaluated in 5 consecutive cycles, and, for all of them, no loss in the efficiency was found.

Finally, the leakage of the catalytic species to the media was evaluated during the experiments and under extreme aging conditions (4h in an ultrasonic bath), and any AgNPs were found outside the matrix, what agrees with the results obtained for the catalytic experiments.

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Optical signature of delta-layer of silver nanoparticles embedded in silica matrix elaborated through Low Energy Ion Beam Synthesis or combined silver sputtering and Plasma Enhanced Chemical Vapour Deposition

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Noble nanoparticles embedded in dielectric matrix present a huge interest for plasmonic devices. The plasmonic coupling of this kind of structures with light enhances the range of useful optical phenomena, like Surface Plasmon Resonance (SPR) and Surface-Enhanced Raman Scattering (SERS), all of them having potential applications in areas such as ultra-sensitive chemical and biomolecular detection and analysis, photonic switches, etc. The main advantage of these assemblies is the possibility to manipulate, localize and enhance the electromagnetic field at the structure surface [1].

In this work, we present a study on the optical signature of silver nanoparticles (Ag-NPs) embedded in silica matrix. The measurements were achieved with different spectroscopic techniques. The attained results were exploited to obtain a model of these complex systems. A delta-layer of Ag-NPs was embedded in thin films (thickness from 30 to 100 nm) near the free surface. Two different approaches were used to elaborate the nanocomposite structures. The first one was Low Energy Ion Beam Synthesis (EL-IBS) using a modified implanter to work in the low energy range (0.65 ÷ 20 KeV) [2]. The second approach combined silver sputtering and Plasma Enhanced Chemical Vapor Deposition (PECVD) by using the plasma of axially asymmetric RF (13.56 MHz) discharge. The discharge was maintained in hexamethyldisiloxane

(HMDSO)-oxygen-argon mixtures at low gas pressure (< 7 Pa) [3]. The two elaboration methods allowed obtaining a wide variety of experimental conditions in order to better understand the optical response of these plasmonic structures containing Ag-NPs delta-layer.

The optical properties of the composite layers were analyzed by spectroscopic ellipsometry, optical reflectance spectroscopy and Raman spectroscopy. The various analysis methods allowed large wavelength range coverage. Besides, the size and density distribution of Ag-NPs were measured by transmission electron microscopy. From the correlation of optical measurements with images obtained by electron microscopy we developed a non destructive method, based on spectroscopic ellipsometry, for diagnostic of plasmonic structures.

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Limitation of charge injection in polyethylene by a nano Ag/SiCOH barrier

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The necessity to produce green electrical energy has been demonstrated and multiple ways are viable and effective. However, the implantation of these new energy production sites, like offshore wind farms, is often far away from consumption areas and the energy must be transported over long distances. In this context, energy transport under direct current form exhibits many advantages [1]. Insulated cables used for buried or submarine energy links are made for over 30 years with polyethylene as insulation in case of Alternative Current energy transport. In case of High Voltage Direct Current (HVDC) cables, the background is much more limited. One of the key issues is prevention of space charge build up, which is at the origin of field distortion inside the cable and of early dielectric breakdown and ignition of electrical discharge [2].

The aim of our research is to control and limit the injection of charges in dielectric materials. Our strategy consists in depositing a layer acting as "deep electron trap" at the interface of polyethylene with the semiconducting material of the cable. The layer is created by combining silver sputtering and Plasma Enhanced Chemical Vapor Deposition (PECVD) by using an axially asymmetric RF (13.56 MHz) discharge. The plasma is maintained in hexamethyldisiloxane (HMDSO)-argon mixtures at low gas pressure (< 7 Pa). The RF electrode is Ag-made target to support the sputtering process [3]. Thus, the final interface structure is composed of silver nanoparticles embedded in a matrix of polymeric organosilane SiCOH.

Distribution profiles of charge density in the dielectric are measured by Pulsed Electro Acoustic method (PEA). The method permits to localize and quantify, in the volume, charge injected as a function of time along with electric field distribution [4]. This communication presents the first results on the capability of nano Ag/SiCOH layers to prevent charge injection in low density polyethylene (LDPE). The residual charge density is significantly reduced when the coating is deposited. Results with different layer configuration for applied fields in the range 10-50kV/mm will be presented and the role of silver nanoparticles as trapping centers will be discussed at the workshop.

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NOTES

Deposition of SiO₂/TiO₂ nanocomposite thin films by Atmospheric Pressure Townsend Discharge

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Cold Atmospheric Pressure Plasma Enhanced Chemical Vapour Deposition (AP-PECVD) has already demonstrated its potential for homogeneous thin film deposition. A new challenge is the deposition of nanocomposite thin films in AP discharges in order to obtain multifunctional properties.

This contribution is focused on the study of the growth of nanocomposite coatings based on titanium oxide (TiO₂) nanoparticles embedded in a silica-like (SiO₂) matrix, using a parallel plate dielectric barrier discharge (DBD) at atmospheric pressure. The gas mixture is made of nitrogen (N₂) as the main gas, a mixture of hexamethyldisiloxane (HMDSO) and nitrous oxide (N₂O) for the deposition of the SiO₂ matrix, and nanoparticles of TiO₂, which are introduced in the gas mixture by nebulizing different stable colloidal solutions.

The discharge works in the homogeneous regime, namely the Atmospheric Pressure Townsend Discharge. The gas mixture is injected longitudinally to the dielectric plates, allowing gas phase and surface analyses as a function of the mean residence time, which gives additional information on the thin film deposition mechanisms. The DBD is characterized through electrical and optical diagnostics and the characterization of the coatings is performed using Fourier transform infrared spectroscopy, X-ray photoelectron spectroscopy, Raman spectroscopy and scanning electron microscopy.

Preliminary results show that TiO₂ nanoparticles can be incorporated in the thin film through this process. Moreover, similarly to low-pressure dusty plasmas, the electrostatic forces play a dominant role on the transport of the nanoparticles in the discharge. As a result, an appropriate tuning of the applied voltage waveform (shape, amplitude and frequency) has a direct impact on the distribution of the nanoparticles in the thin film. This allows to elaborate coatings with several potential applications for instance due to the oxygen barrier properties of the SiO₂ matrix and the UV-protection properties of TiO₂.

Effect of nanoparticle injection in magnetized low-pressure plasmas

A new way to form nanocomposite thin films

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Although dust particles in plasmas have been observed not long after the discovery of plasmas themselves, the phenomenon was mostly left unstudied until the last decades. The occurrence of solid, nano- or micrometric particles in plasmas has been chiefly considered unwanted, as it caused significant changes in the electrical properties of the discharge, interfering with the plasma processes (1). However, dusty plasmas have become attracting with the advent of technologies based on nanomaterials and nanocomposites (2) indeed, they represent a new efficient way to deposit nanocomposite thin films by forming both simultaneously matrix and nanoparticles that progressively stack on the surfaces.

Dusty plasmas are widely studied in capacitively coupled plasmas, as the experimental conditions are likely to induce gas phase polymerization mechanisms. Although the working pressure is not in the good range for powder growth, dusty plasmas can also be obtained in Multipolar Microwave Plasma excited at Distributed Electron Cyclotron Resonance (MMP-DECR) (3). For example, we will report the growth of graphite-like nanoparticles and the deposition of nanocomposite thin films consisting of those nanoparticles embedded in a hydrogenated amorphous carbon matrix (Figure 1) (4).

A key role of the magnetic field has been revealed to obtain nanoparticles in this kind of plasmas. Then, we will discuss a new way under development based on the direct injection of nanoparticles in the plasmagene phase. For example, a laser ablation chamber was coupled to the plasma chamber to form various kinds of nanocomposite thin films. Depending on the gas mixtures in the plasma chamber, their magnetic confinement allows forming highly crystalline nanoparticles or core-shell structure that cannot be easily obtained directly by PE-CVD.

Then, in contrast with the classical routes that need several steps (synthesis of nanoparticles and matrix, mixing and thin film deposition), nanocomposite thin film can be formed in one single process in cold plasmas.

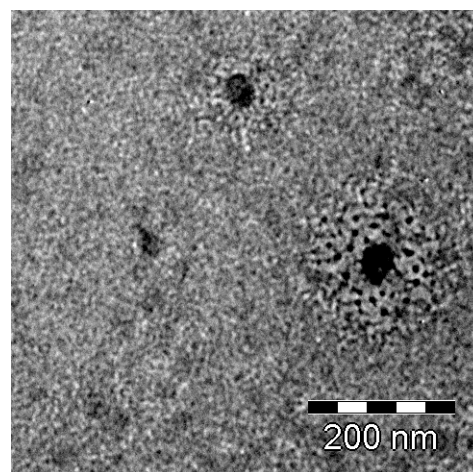


Figure 1. TEM of nanocomposite thin film obtained in C_2H_2 MMP-DECR.

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Growth processes of Zirconium metal-organic layers deposited by MMP-DECR reactor using zirconium tert-butoxide/O₂ mixture.

Role of substrate temperature and polarization.

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ZrO_xCyHz metal-organic thin films were deposited by low pressure microwave DECR plasma of zirconium tetra-Tert-Butoxide (ZTB) as metal-organic precursor mixed with oxygen as oxidant gas. X-Ray Photoelectron Spectroscopy (XPS), Fourier Transform Infrared Spectroscopy (FTIR), and Spectroscopic ellipsometry were used to investigate the deposited films. Moreover the plasma phase was probed by Optical Emission Spectroscopy (OES). The plasma was created in a Microwave Multipolar reactor excited by Distributed Electron Cyclotron Resonance (MMP – DECR). The films were deposited for temperatures ranging from -5°C to 110°C, the total gas pressure was 1mTorr (0.133 Pa), the microwave power was fixed at 400W and the oxygen ratio varied from 60% to 95%. Moreover, an RF Bias (From 0.0V to -100.0 Volts) was applied to the Sample holder to control the ion bombardment of the substrate. The influence of sample temperature, polarization and gas mixture ratio [O₂/ZTB+O₂] on deposition rate, density, chemical bonds, atomic composition and micro – and meso-structure of the deposits are presented.

At high temperature (110°C) and room temperature and 80% of O₂ in the mixture, microstructure analysis shows a columnar growth, while at low temperature (-5°C) the columns disappear. At fixed temperature an increase of polarization enhances the columnar growth but for high values of polarization (80V) the columns are removed.

Correlation between process parameters and structure of the deposited films will be presented. The understanding of columnar growth allows the control of the optical and barrier properties of the deposited films.

Dielectric Properties of Multilayer Graphene/Epoxy Nanocomposites for Various Filler Contents

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Abstract: Graphene is a carbon-based allotrope material which, since very few years, appears as very exciting due to incredible physical properties such as a high electron mobility (250,000 cm²/Vs), a high thermal conductivity (5,000 W/mK) and a high Young's modulus (1 TPa). Obtained from the exfoliation of graphite pristine in the form of multilayer graphene (MLG) nanoplatelets, it focuses an increasing attention when mixed to a polymer matrix to produce MLG/polymer nanocomposites. Up to now, few studies have mainly reported on the effects on the thermal conductivity of various MLG/polymer nanocomposites. However, no study has been led on their dielectric properties. In this paper, we propose to study the impact of MLG on the room temperature electrical conductivity, the dielectric permittivity and loss tangent of an epoxy nanocomposite with different nanoflakes filler contents below and above the electrical percolation threshold, which will be determined.

Keywords: *Graphene, Multilayer graphene nanoplatelets, Epoxy Nanocomposites, Electrical percolation threshold.*

Magnetic properties of Bi Doped $\text{Pr}_{0.6}\text{Sr}_{0.4}\text{MnO}_3$ manganite

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Abstract: Observation of colossal magneto-resistance (CMR) in perovskite manganites has been investigated by several researchers mainly due to their distinctive structural, electrical, thermal and magnetic properties. Of late, these materials have draw attention due to its potential applications such as magneto-caloric effect (MCE) which is defined as the changes in adiabatic temperature or isothermal magnetic entropy of a magnetic material when it is magnetized. In particular, $\text{Pr}_{1-x}\text{Sr}_x\text{MnO}_3$ (PSMO) series has been investigated extensively essentially to understand the physics behind phenomenon such as CMR, electro-resistance and MCE [1-3]. It is important to mention that Bi doped $\text{Pr}_{1-x}\text{Sr}_x\text{MnO}_3$ compounds exhibit high MCE values and have technological importance as refrigerating materials. Recently, we have published comparative studies of Bi-doped compounds $\text{Pr}_{0.7-x}\text{Bi}_x\text{Sr}_{0.3}\text{MnO}_3$ and $\text{Pr}_{0.6-x}\text{Bi}_x\text{Sr}_{0.3}\text{MnO}_3$ and it was seen that for the former compounds, the transition temperatures (TMI and TC) increase with Bi-concentration. On the other hand, for the latter compounds the transition temperatures (TMI and TC) decrease with Bi-concentration. In literature there few reports on Mn doped PSMO compounds and most of the reports pertain to Mn site. Little work seems to have been done on Bi-doping in the Pr-site. It is worth observing that Bi^{3+} (1.17 Å) and Pr^{3+} (1.126 Å) ions have nearly same ionic radii. Keeping this in mind, in this communication, we report some preliminary results of magnetic studies of Bi-doped PSMO compounds $\text{Pr}_{0.6-x}\text{Bi}_x\text{Sr}_{0.3}\text{MnO}_3$. From the temperature dependent magnetization behaviour, we observe that the ferro-to-para magnetic transition temperature, TC decreases with Bi-doping. From the M-T and M-H results for these compounds show that there is contribution of anti-ferromagnetic interaction since the ZFC and FC are quite distinct thereby indicating inhomogeneity in long range ferromagnetic order [4,5].

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Surface modification of polystyrene substrates for use in ELINOR rapid diagnostic tests of Human Papiloma Virus infection

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Polyaniline/Gold (Pani/Au) nanocomposites were synthesized by wet chemistry methods in ethanolic solution and the pH of the solution was adjusted to 3. At these conditions, when excited at 350nm the composite exhibits a strong fluorescent emission at 480nm. Since proton-doped polyaniline chains behave as polycations, the composite can be used as a convenient biosensor for the presence of DNA/RNA chains, due to the nonspecific electrostatic interaction between the phosphate groups of the oligonucleotides and the amine groups in the polyaniline chains. In the present work, we describe the surface modification of polystyrene (PS) to be used as substrates in the ELINOR rapid test for detecting the presence of the Human Papilloma Virus 18 (HPV18) in human patients.

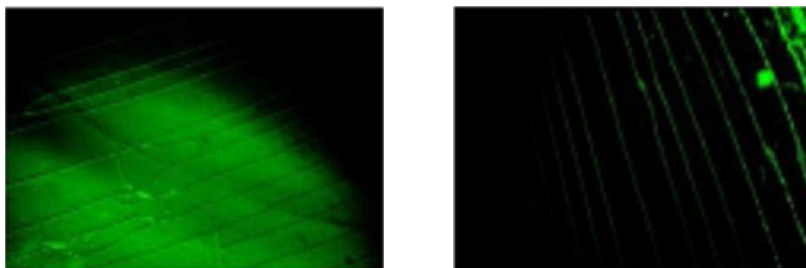


Fig. 1: ELINOR test for HPV18. Positive (left) and negative (right) cases.

To anchor the HPV18 primer to PS substrates, we start by modifying their surface to create carboxylic anchoring sites, which were identified by Raman spectroscopy. Plasma Glow (PG) was then used to increase the hydrophilicity of the surface (a decrease from 94° to 54° was observed for its water contact angle). PG was chosen over UV/O₃ for the surface treatment because it is a simple and efficient method that suppresses auto-fluorescence effects that could mask the Pani/Au emission. A subsequent treatment with acrylic acid (AA) was adopted to increase the number of functional sites, and then we used N-(3-dimethylaminopropyl)-N'-ethylcarbodiimide hydrochloride (EDC) to activate the carboxylic sites prior to the linkage of N-hydroxysuccinimide (NHS) and ethylenediamine (EDA). Finally, EDC and imidazole were used to activate the HPV18 primer to allow its anchoring to the substrate. Following the protocol for the ELINOR test [1], polymerase chain reaction (PCR) certified positive or negative HPV18 samples from human patients were dripped for the eventual coupling to the primer. Then a small amount PANi/Au was added and the excess material was washed and finally dried. By using a fluorescence microscope, we noticed the signature of an intense Pani/Au green fluorescence signal on the positive samples, when compared to negatives [Fig. 1]. This simple and rapid (t < 5 min) diagnostic method has shown a sensitiveness of 83,3% and a specificity of 93,3% towards HPV18 recognition.

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Description of the biocide effect on microorganisms of very thin layers containing nano-silver deposited on stainless steel by means of a radio frequency discharge

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Nanosilver-containing coatings can be achieved using different chemical or physical methods, including plasma processes. Among them, a process combining silver sputtering and plasma polymerization of hexamethyldisiloxane (HMDSO) was developed to produce organosilicon thin films, containing silver nanoparticles, deposited on stainless steel [1]. Saulou et al [2] recently demonstrated the antimicrobial properties of these nanosilver-containing organosilicon thin films against the model yeast *Saccharomyces cerevisiae*, since a log reduction value of 1.9 was reported for sessile cells after 24 h contact in saline solution, compared to control conditions with the matrix alone. In relation with the antimicrobial properties of nanosilver containing films and the cell adhesion, an analysis of biofilm formation was performed indicating an important inhibition of biofilm formation. Besides high resolution TEM (HRTEM), STEM, energy dispersive x-ray microanalysis spectroscopy (EDS) and electron microdiffraction on the model yeast revealed the formation of electron-dense nodules. Some sulfur-containing silver clusters preferentially located at the cell wall periphery were detected, together with nodules composed of silver, sulfur and phosphorus all over the cell. In both silver-based treatments, nitrogen and silver signals overlapped, confirming the affinity of silver entities for proteinaceous compounds. Moreover, in the case of nanosilver, interactions of silver with phosphorus-containing subcellular structures were indicated.

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Environmental Effects on Mechanical Properties of Layered Silicate Epoxy Nanocomposites

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Epoxy resins and their particulate filled composites are widely used in the aerospace, automobile, coating and microelectronic industries. In engineering service environments, moisture absorption is a commonly encountered phenomenon, which usually accompanying with the temperature effect. The water molecules absorbed into epoxy can be classified into two types. The first involves diffusion of water molecules inside the micro gaps between polymer chains that is usually bonded to hydroxyl groups in the epoxy network. The second involves capillary transport into the gaps and flaws at the interfaces. In general, polymers tend to absorb significant amounts of water when exposed to high humidity conditions. The absorbed moisture has many detrimental effects on the composite performance. Therefore, investigation of water aging of polymer/fibre composites is useful because these materials are usually designed for use in construction or transportation industry and they will be exposed to wet environments.

Nanocomposites containing the organo-montmorillonites were prepared at clay mineral levels of 1.5, 3 and 5 weight% by mechanical stirring. The epoxy resin was preheated at 85 °C in order to reduce the viscosity. The required amount of clay was added slowly while stirring with a mechanical stirrer. The mixture was further stirred for 2 h. The mixture was then degassed at 85 °C for 2 h. The curing agent TETA was added and the mixture was gently stirred in order to avoid the formation of bubbles. After degassing, the solution is cast in the mold. X-ray diffraction was performed on nanocomposites by PHILIPS PW-1730 (CuK α radiation at a scan rate of 1°/min in 2 θ range from 3 to 15°) to study the clay dispersion.

The effect of clay on water absorption of epoxy clay nanocomposites is discussed. The specimens are immersed in distilled water at 80 °C using constant temperature bath. It is noted that the clay is more hydrophilic than the epoxy matrix. The results show that diffusivity is decreased and the equilibrium moisture uptake is found to increase with the amount of layered silicate added. It is theorized that the decreased diffusivity might be ascribed to the restricted motion of polymer chains, which are associated with the clay particles. The increase in total water uptake is ascribed to the attraction of the clay particles to moisture. Decrease of 32.82% in diffusivity and increase of 7.47% in equilibrium moisture uptake for 5 wt.% clay nanocomposites are observed. Mechanical tests are performed on epoxy clay specimens in water at 80 °C for 100 h. A diminution in the mechanical properties after immersion in water is observed for all clay loadings.

Table 1 Water uptake characteristics of epoxy and its clay nanocomposites

Material	Diffusivity (mm ² /sec)	Equilibrium water content (%)
Epoxy	5.95629 x10 ⁻⁶	2.96
Epoxy + 1.5% clay	5.41491 x10 ⁻⁶	3.03
Epoxy + 3% clay	4.70946 x10 ⁻⁶	3.11
Epoxy + 5% clay	4.0012 x10 ⁻⁶	3.18

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