

M-ERA.NET Call 2012: Funded projects

Call topic	Acronym	Full Title	Nr. Partners
Integrated Computational Materials Engineering	MC2	Multiscale Computational-driven design of novel hard nanostructured Coatings	5
Integrated Computational Materials Engineering	FASS	Physically based modelling and simulation of the mechanical behaviour of metallic thin film systems and fine grained surfaces under cyclic loading	5
Design of new interfaces, surfaces & coatings	SurfLenses	Surface modifications to control drug release from therapeutic ophthalmic lenses	7
Design of new interfaces, surfaces & coatings	BIOTERFACE	Design of BIOcompatible and customized inTERs, surFACE and coatings for Intra Ocular Lens (IOLs)	4
Design of new interfaces, surfaces & coatings	BAC-COAT	Development of bacteria formulations for seed coating and seed production	4
Design of new interfaces, surfaces & coatings	MATSENS	New materials for electrochemical sensors in microfluidic platforms: Application to molecular recognition	3
Design of new interfaces, surfaces & coatings	MAGPHOGLAS	New doped boro-phosphate vitreous materials, as nano-powders and nano-structured thin films, with high optical and magnetic properties, for photonics	3
Design of new interfaces, surfaces & coatings	HiDEPO	High deposition rate laser cladding in hydraulic applications	4
Design of new interfaces, surfaces & coatings	EnReCom	Encapsulation of Reactive Components in Coatings	3
Design of new interfaces, surfaces & coatings	IDEAS	Intelligently Designed Antimicrobial Surfaces	3
Design of new interfaces, surfaces & coatings	XOPTICS	Surface engineering and advanced coatings for the next generation of X-ray diffractive optics	4

Design of new interfaces, surfaces & coatings	APOSEMA	Advanced Nanohybrid Composites and Photonic Materials for Multifunctional Opto-Chemical Sensors	5
Design of new interfaces, surfaces & coatings	Hi2CoRe	High performance properties, for high frequency applications, by combining silver coatings and Rheo cast aluminium	4
Design of new interfaces, surfaces & coatings	NANOCOATIL	High performance nanostructured coatings using ionic liquids based on choline chloride	3
Design of new interfaces, surfaces & coatings	CarLa	Ag/Si doped carbon layer for bio-medical application	4
Hybrid composites	MACOSYS	Magnetically active anisotropic composite systems	4
Hybrid composites	CAPDESIGN	Encapsulation of polymeric healing agents in self-healing concrete: capsule design	7
Hybrid composites	GoIMPLANT	Tough, Strong and Resorbable Orthopaedic Implants	3
Hybrid composites	VOCSENSOR	Hybrid Materials for Low Cost Volatile Organic Compound Sensor System	4
Materials for Energy Systems	PCPLASTER	Phase Change Material (PCM) enhanced plaster for upgrading the energy efficiency of contemporary and historic buildings	3
Materials for Energy Systems	RADESOL	RAtional DEsign of blends for bulk heterojunction SOLar cells	4
Materials for Energy Systems	LaminaLion	Conformal layer-by-layer growth of hybrid polymer/inorganic nanolaminates for Li-ion batteries	4
Materials for Energy Systems	MOC@SUPCAP	Design of new metallic oxide-carbon hybrid composites for supercapacitors electrodes	3

MC2: Multiscale Computational-driven design of novel hard nanostructured Coatings

The goal of the MC2 project entitled “Multiscale Computational-design of novel hard nanostructured Coatings” is to develop new fundamental and technological concepts for the design of novel hard coatings, based on multi-component transition metal nitrides (TMN), with improved performance (hardness, toughness, thermal stability) under service/operation conditions used in the cutting tool industry. The core of the project concerns basic research and lies within the Integrated Computational Materials Engineering (ICME) topical priority; The selected materials under study, namely nanostructured hard coatings, add complimentary applied research character to MC2 by which the project contributes also to the “Design of New Interfaces, Surfaces and Coatings” thematic. The originality of the MC2 project lies in the implementation of an innovative multi-scale computational approach to predict phase stability and elastic properties at the single-crystal level (first-principles calculations) as well as at the polycrystal level (phase-field and kinetic Monte Carlo mesoscopic simulations, effective averaged elastic constants), to tailor the composition, growth morphology and microstructure of Ti-Al-X-N coatings with enhanced properties, where X is an alloying element such as Cr, Ta, Zr or Mo. Our task is to determine new materials, alloying compositions and nanostructural building-blocks that improve the coatings mechanical integrity (hardness, toughness, wear resistance). Due to the fact that MC2 focuses on the control of properties set by industrial needs, it goes beyond standard combinatorial studies and realizes a property-driven research method oriented towards multi-scale data mining. The present consortium offers a unique opportunity to capitalize on a common research strategy in the covered field by utilizing each partner’s expertise. It puts us in a position to break new grounds in computer-guided design of novel high temperature hard coatings and to ensure knowledge transfer to world leading European industrial end users, as exemplified with SECO Tools AB’s partnership. The complementary expertise of the different partners results in new avenues for fundamental concepts of coating design and shortens the time from concept to product. Hence, the proposal offers means to increase competitiveness of European industry relying on high temperature surface integrity such as the cutting tool industry.

FASS: Physically based modelling and simulation of the mechanical behaviour of metallic thin film systems and fine grained surfaces under cyclic loading

In this project we aim at physically based modelling and simulation supported by quantified characterisation of the mechanical behaviour of microsamples (polycrystalline metallic thin film systems and micropillars) under cyclic loads. Investigation of the physical mechanisms of fatigue in these systems is motivated by the following considerations: (i) Early stages of fatigue failure in bulk systems (inception and stage-I propagation of fatigue cracks) are governed by near-surface phenomena and can be strongly influenced by surface treatment. To understand fatigue threshold and initial crack-propagation, it is necessary to model the interplay of surfaces and interfaces (grain boundaries, GBs) with fatigue-induced dislocation patterns and cracks. (ii) Samples on the micrometer scale are amenable to full simulation of microstructural processes. This allows us to directly validate models by comparing with ‘tailored’ experiments. At the same time, larger samples in this scale range already exhibit

bulk-like behaviour. (iii) Fatigue is a multiscale phenomenon involving processes from the atomic to the continuum scale but, despite its huge technological importance, has rarely been addressed from a comprehensive multiscale modelling point of view. In simulations, the physics of fatigue still poses important challenges as material behaviour is governed by slip localisation and dislocation patterning phenomena which cannot be predicted by standard continuum or atomistic approaches. Present-day discrete dislocation dynamics (DDD) for the first time provides a physically based model of emergent dislocation patterning, but cannot access the large cumulative strains associated with failure under cyclic loads. We overcome this limitation by exploiting recently developed coarse-graining methods that map DDD onto continuum dislocation dynamics (CDD) simulations which represent the same dynamics in a continuum framework. These can be calibrated and validated by reference to the DDD models but extend to larger spatial and temporal scales. Plasticity simulations are combined with atomistic simulations that give access to dislocation nucleation at surfaces and interfaces and crack nucleation at surface heterogeneities or stress concentrations.

The ultimate goal of the project is to provide physical foundations for computational design of fatigue resistant near-surface microstructures. To this end we develop a predictive multiscale framework for the evolution of dislocation systems interacting under cyclic loads with surfaces, cracks and GBs, and evaluate damage and failure properties. Simulations will be parameterized and validated by reference to experiments carried out on model systems, using techniques which provide information on microstructural processes on scales from nanometers up to several micrometers. Investigated systems include polycrystalline thin films and single/bicrystal micropillars of varying size and grain orientation. Cyclic plasticity of these systems will be studied using tensile and compression testing. Performing selected experiments in situ in a scanning electron microscope will facilitate direct observation of deformation and failure patterns. On even smaller scales, in-situ transmission electron microscopy will directly visualise dislocation microstructure evolution under load, dislocation nucleation and interactions at the interfaces.

The proposed effort will result in a simulation framework for modelling the physical processes behind a vast range of technological problems including the enhancement of fatigue resistance by surface treatment, and fatigue of microscale components. While work on any of these specific problems is beyond the scope of the project, we aim at establishing and expanding our contacts with potential 'users' at an early stage in order to facilitate future application and dissemination of our research findings.

SurfLenses: Surface modifications to control drug release from therapeutic ophthalmic lenses

Nowadays, most ophthalmic drug formulations are applied as eyedrops. Although this administration form is easy to use and well accepted by patients, it requires frequent applications, leads to significant drug losses (> 95%) and may cause undesirable side effects, due to the rapid drug absorption into the bloodstream. The development of more efficient drug delivery systems, that enhance the ocular bioavailability of the drugs, has been subject of an increasing interest in the last years and is regarded as a major advance in ophthalmic therapeutics. Among the several studied possibilities, soft contact lenses (SCLs) have

deserved special attention due to their high degree of comfort, biocompatibility and prolonged contact with the eye. Drug soaked SCLs demonstrated to be more efficient than eyedrops, but still lead to short release times and are not commercially available. In order to enhance their drug loading capacity and to achieve a controlled drug release, various methods have been explored. These methods may be extended to other ophthalmic lenses - the intraocular lenses (IOLs) - due to the similarity of the constituent materials and functionality.

The main objective of this project is to develop new efficient systems for the treatment of ocular diseases and post-surgical infections, based on the surface coating or modification of drug-loaded ophthalmic lens materials. Commercial SCLs, IOLs and newly synthesized lens hydrogel materials will be loaded with model drugs (e.g. fluoroquinolones, cefuroxime). Their surface will be modified/coated to create drug diffusion barriers which lead to a sustained release for an extended period of time. Tested methods will include crosslinking of the surfaces, coatings with layer-by-layer polyelectrolytes and/or with liposomes, and adsorption/grafting of specific molecules. These methods are particularly welcomed both by clinicians and industry, since they may be used in commercial lenses whose properties and production are already optimized. For the first time, the in vitro drug release kinetics will be investigated considering the tribomechanical effect inherent to eyelid sliding: a homemade apparatus allowing for simulation of tear flow and blinking will be used. Physical-chemical characterization of the hydrogels will be done to evaluate the changes caused by the surface modifications. Numerical modelling will be used to aid in the optimization of the novel delivery systems. In vitro and in vivo (with animals) biological tests will be also carried out. To achieve these purposes, an international multidisciplinary team of researchers from universities (Instituto Superior Técnico - PT, University of Coimbra - PT, University of Iceland - IS) and hospitals (Instituto de Oftalmologia Dr. Gama Pinto - PT, Instituto Oftalmológico Fernández-Vega – ES) will work in straight collaboration with industry (PhysIOL - BE, an experienced IOL manufacturer, and Altakitin - PT, which produces raw materials for medical applications, like chitosan). The project has the support of Bausch+Lomb UK (see page 5), which will supply commercial SCLs. The collaboration of the companies is fundamental for the definition of new research routes with economic viability and may have repercussions on technology transfer and on the future funding for the research centers. The participation of ophthalmologists of the two reputed Ophthalmological Institutes will be crucial for the discussion of the clinical relevance of the project outcomes and preparation of a pre-clinical validation plan. The development of a new concept for drug-delivering ophthalmic lens, besides being beneficial for improving the peoples' life quality, comfort and working ability at long term, would lead to savings for healthcare system. Collaboration between partners would enhance their cooperation potential, expertise and competitiveness at European and global level.

BIOTERFACE: Design of BIOcompatible and customized inTERs, surFACE and coatings for Intra Ocular Lens (IOLs)

This project name “BIOTERFACE - Design of Biocompatible and Customized interfaces, surface and coatings for Intra Ocular Lens (IOLs)” is focused on the research of a new biomaterial and on the design of surfaces and coating enabling fulfilling medical, chemical

and physical requirements for intraocular surgery applications (IOLs). Besides, manufacturing processes will be studied in order to improve know-how related to manufacturing possibilities; this BIOTERFACE designed coatings and interfaces as well as the deposition of the biomaterial to achieve desired results on IOLs applications.

BIOTERFACE solution will be a new set of Intra Ocular lens where the application of a new material and the surface/interface and coating on the designed lens, will increase improve functionalities of IOLs and decrease their current limitations. Besides, manufacturing processes will be analysed and adapted for this purpose.

Expected impact in relation to IOLs products is very promising because these intraocular lens are applicable to a large group of patients due to the variety of its applications. In order to understand the context, next several figures are mentioned: 200,000 patients per year are operated in Spain for refractive corneal surgery, and multifocal IOL market, only in Spain means 17.5M€ and a conservative scenario for the European market of at least 180 M€.

Besides, the world market for intraocular lenses, is estimated that it will surpass the 3.7 KM US \$ by the year 2015, with demographic data favourable in the form of ageing of the population in developed countries and economic development in countries of high development, playing a key role in driving demand.

BAC-COAT: Development of bacteria formulations for seed coating and seed production

Formulation granting prolong survival on storage and both survival and sufficient level of bio-activity in field use represents the bottleneck in the broad scale implementation of biological means in plant protection urged by the EU directive on Integrated Pest Management 2009/128/EG.

In BAC-COAT we are planning to address this challenge and develop principally new surface coating solutions for the protection of biocontrol microorganisms based on self assembly of mineral nanoparticles and poly(electrolyte) complexes that fulfil the following requirements, constituting a pre-requisite for successful and sustainable application of biological solutions for plant protection:

- increased life time and storage stability (≥ 6 months)
- tailored material properties to ensure controlled release, rapid activation and plant colonization when brought to the field and
- are compatible with conventional processes and equipment for seed production

The project will reveal crucial chemical and biochemical mechanisms in development of this type of coatings and identify the approaches permitting to achieve improved biocompatibility and also to understand possible differences in formation, stability and functionality of such coating for different types of microorganisms such as gram-positive and gram-negative bacteria and also spore-forming and non-spore-forming bacteria.

The project will make its principal impact in development of sustainable materials and processes for the highly requested field of bio control addressing the market of large-scale plant cultures such as rice, maize, and potato. The developed technologies will find their direct implementation at the companies involved into this application, CaptiGel AB, Sweden – the producer of materials and Saatbau Linz GmbH – the producer of formulated seeds. The

project can contribute in perspective to overtaking of large fractions of the multi-billion dollar market of plant protection.

MATSENS: New materials for electrochemical sensors in microfluidic platforms:

Application to molecular recognition

MATSENS proposal is focused on the development of new electrode surfaces and recognition elements in order to get the next generation of sensitive and low-cost electrochemical biosensors integrated in a portable and user-friendly microfluidic platform.

In this sense, materials science and nanotechnologies are useful to improve the electrode surface that will act as electrochemical transducer. Thus, (micro)electrodes will be manufactured in different designs and materials by using thin- & thick-film technologies. Moreover, the electrode surface will be modified with different nanostructures (by using nanoimprint lithography - NIL), nanomaterials (such as metal nanoparticles), polymer layers, etc... in order to enhance the sensitivity and selectivity of the sensors. The methodologies for the fabrication of the electrodes and carry out the modifications have to be the simplest possible, low cost, environmental-friendly and easily scalable to industrial level. Hence, the production of the new materials for the electrodes has to fulfill these requirements, too. The development of an electrochemical biosensor will also involve the immobilization of biological materials (such as enzymes, antibodies, antigens...) as recognition element in the surface of the electrodes. Different immobilization methodologies will be evaluated in order to the construction of the sensing element. Thus, the use of new materials and micro-/nano-technologies is going to improve the immobilization of the biological elements enhancing the stability, life-time, sensitivity and selectivity of sensor. Moreover, the biosensor will be integrated in a microfluidic platform in order to improve and make easy the use of the new device as Point-of-Care system. In this sense, microfluidic technologies will also enable the use of very small sample volume as well as the possibility of integrating multisensing elements at the same platform.

As proof-of-concept the new smart materials and methodologies will be evaluated in the construction of a microfluidic multi-biosensor focused on the simultaneous determination of different cardiovascular blood metabolites such as total and free cholesterol, glucose and lactate; which can open new market opportunities for the companies involved.

MAGPHOGLAS: New doped boro-phosphate vitreous materials, as nano-powders and nano-structured thin films, with high optical and magnetic properties, for photonics

The purpose of the proposal are the i) design, ii) modeling, iii) development, iv) prototyping of a) nano-structured layers with functional surfaces, b) interdependence between nano-structure and chemical-physical properties and c) ancient and recent thermal history and d) rest of related process parameters for a total new class of boro-phosphate nano-structured materials (nano-structured functional doped boro-phosphate glass) via chemical route, comprising sol-gel, coprecipitation and coacervate obtaining techniques together with new physical

techniques, meaning fs laser pulse deposition and treatment and RF magnetron sputtering. The vitreous matrix will comprise as network formers phosphorus and boron oxide, as modifiers and chemical durability increasers CaO or MgO together with ZnO. For the opto-electronic and magnetic properties small components as dopants will be added, comprising Fe₂O₃, V₂O₅, Bi₂O₃, 1d, 3d, 5d elements or/and rare earth. This complex nano-matrix composition is all new and original. The project proposes as a main research direction, the achievement of a new class of vitreous advanced nano-functional layers and multilayers, with complex magnetic and optical properties, by non-conventional methods. The new chemical and physical methods comparatively to the classical melting of glass have decisive advantages as: rigorous stoichiometric control, high purity of raw materials and of final nano-materials, fine adjusting of the composition in solution and after heat treatment, gain of new well-defined properties controlled by the process parameters, decreasing by hundred degrees of the thermal treatment temperatures, lack of the noxes releasing and high work security. This proposed project makes an original connection between two domains of materials with special emphasis, boro-phosphate new nano-structured glasses and laser physics regarding functional thin films and nanostructured materials. For the first time we make and treats the solid film deposition for this new class of materials using laser and magnetic fields. These new nano-materials will be processed with pulse laser (high brightness and very short pulse laser) of 15 TW and the pulse duration of 20-25 fs, which have been recently acquired in INFLPR.

Phosphate and borate glasses are important materials as substrate because they can incorporate high amount of rare earth ions, making them ideal to host material for making compact high gain waveguide lasers and amplifiers for telecommunications window [1-3]. Phosphate glasses demonstrate changes to the glass structure after fs-laser writing that are not good for the fabrication of wave guiding devices. The present researches will focus on how boro-phosphate glasses, as well as specific composition of doped boro-phosphate glass will amplify and improve the properties of special structures induced by using focused femtosecond laser pulses. The project will study the fundamental relationships between the initial composition of boro-phosphate glasses and the structural changes associated with refractive index modification that could be resulting from fs-laser irradiation focusing the results on new prototypes of Faraday rotators and ultra-fast opto-magnetic switching devices design and manufacturing.

HiDEPO: High deposition rate laser cladding in hydraulic applications

Manufacturing and overhauling of hydraulic cylinders is increasing business in Europe. This is attributed primarily to the growth of renewable energy applications such as wind turbines and wave energy systems where the hydraulics play important role. Hydraulics are also widely employed in mining and construction, oil & gas drilling and other energy applications. Due to demanding operating conditions (wear, corrosion, static and dynamic loads), hydraulics is frequently surfaced with various wear and corrosion resistant coatings manufactured by hard chrome plating and thermal spraying to extend their service life and performance. Consequently, surface engineering is key technology in hydraulic cylinder manufacturing and overhauling as the failure of a cylinder renders likely the entire hydraulic-

bearing machine inoperable which leads to high financial losses, pollutant emissions to environment and compromised human safety. Due to insufficient coating properties obtained by conventional surfacing techniques, several premature failures of key hydraulic components have been reported particularly in marine and offshore applications. For instance, in oil & gas drilling, piston rod failures of riser tensioning systems due to insufficient coating properties can lead to losses more than 550 000 USD per day. Piston rods composed of solid Ni-based super alloys and duplex stainless steels are good alternatives in many conditions but they are cost prohibitive. Laser cladding is promising new surfacing technique for hydraulic applications. This method combines the strength and availability of low cost steels with excellent corrosion resistance and good adhesion of metallic coatings based on fusion bond. Drawback of current laser cladding technologies based on coaxial powder feeding and 3-6 kW laser devices is, however, low cost-efficiency.

The objective of this proposal is to develop novel high deposition rate laser cladding techniques, unique know-how associated with their optimum function and advanced coating solutions for surfacing large hydraulic components. This will allow for higher performance repairs and coatings with improved properties. Significant enhancements in deposition rates and cost-efficiency are achieved by utilizing the state-of-the-art high power diode lasers (HPDL) at the power range of 6-20 kW and developing novel hybrid cladding techniques based on preheated coaxial wire and strip feeding.

By the development of innovative, environmentally-friendly and sustainable surfacing technologies, participating SMEs enlarge their business potential, access new markets and become more competitive in global market. By adopting new production methods, end-users reduce their maintenance costs, increase the efficiency of their processes and material efficiency by replacing solid high alloyed metal products with low-alloy steels surfaced with layer of high performance laser coatings. Environmental and safety impact will be enhanced by developing alternative coatings and manufacturing techniques to environmentally hazard hard chrome plating processes which are widely employed in hydraulic applications.

EnReCom: Encapsulation of Reactive Components in Coatings

The project EnReCom will investigate the possibility to develop a two component coating system, masked as a one component system. The reactive component will be micro-encapsulated, which will protect the reagent during formulation and storage time until application. The shells will be designed to such an extent that they break upon the mechanical stress during high shear coating application (roller coating, spray-coating), releasing the reactive component for crosslinking, adhesion promotion reactions and the like. Reactive components that could be encapsulated comprise catalysts, crosslinkers, initiators, siccatives, enzymes, active pigments, sol-gel reagents, etc. The result is a one component coating system with the performance of a two component system; there are no pot-life issues associated with these one component systems, significantly reducing waste.

IDEAS: Intelligently Designed Antimicrobial Surfaces

The World Health Organisation (WHO) has identified the increasing use of systemic antibiotics, which is generating strains of lethal microbes that are resistant to conventional treatment, as a major global threat. Alongside the EU commission, the WHO has declared that preventing and combating microbial infections is one of the most important problems facing the world in the next few years and has called for increased research and development. It is estimated that over 16 million patients worldwide suffer from chronic wounds each year and over 40% of these will become infected, resulting in a delayed healing process. (Epsicon 2007).

Recent research has shown that physical and chemical nano-features and nano-patterns on surfaces can be highly effective at reducing initial adhesion of bacterial cells to different materials. There is now an opportunity to translate basic research into applied research and innovation in surface and interface materials of relevance in the healthcare sector.

The IDEAS project aims to exploit the properties of physical and chemical nano-patterns and topographical functionalisation to reduce microbial attachment and biofilm formation on key materials used throughout the healthcare industry and, in particular, in the advanced wound-dressings sector. There is a need for new technologies to enable antimicrobials, antibiotics and pharmaceuticals to be topically applied in wound dressings and other medical devices to accelerate wound healing, thus combating hazardous biofilms formation and also reducing the threat of creating resistant bacteria.

As a consortium led by an industrial health care specialist and two surface nanotechnology coatings companies, we aim to create a knowledge-based toolkit developed specifically to facilitate the intelligent design of advanced antimicrobial surfaces and interfaces.

With this toolkit, the three industrial organisations involved in this project will be able to develop new highly competitive healthcare products with reduced bacterial attachment properties and antimicrobial activities.

XOPTICS: Surface engineering and advanced coatings for the next generation of X-ray diffractive optics

The proposed project is aimed to develop and further refine crucial fabrication steps of high-end X-ray diffraction optics. The nowadays X-ray optics has to fulfill very tight specifications regarding the surface finish, surface roughness and sub-surface crystal quality. The surface figure has to be better than $\lambda/20$ measured by reflected wave distortion at HeNe laser wavelength. The surface roughness has to be lower than 0.1 nm RMS. And the sub-surface damage (SSD) to the crystal lattice introduced by surface manufacturing technique has to be removed. The conventional surface cutting, milling, grinding, lapping and polishing techniques are suitable only for planar or symmetric surfaces. However the latest developments in the X-ray diffraction optics involve fabrication of complicated symmetric and asymmetric channel-cuts where the active surfaces are not accessible by conventional surface manufacturing and polishing techniques. In the last thirty years the ultra-precision manufacturing using diamond tools was established as a promising manufacturing technique. This technique coined as single point diamond turning (SPDT) can manufacture precise interfaces with very low figure error and surface roughness less than 1 nm RMS. This project targets the refinement of SPDT manufacturing technique intending to reach the lowest possible SSD. The manufacturing optimization cycles will be supported by measurements and

numerical simulations of residual stress introduced by SPDT. In order to make the SPDT compatible with the fabrication of the latest high-end X-ray optics additional polishing steps has to be developed especially for the nested surfaces. The aim of this project is to refine the existing polishing techniques in combination with SPDT. A special goal is the development of new polishing approaches. Especially we will address the combination of SPDT manufacturing with ion beam polishing and nanosecond laser remelting technologies. Furthermore we will develop wear and oxidation resistant functional coatings that will suppress X-ray scattering at low incidence/exit angles.

APOSEMA: Advanced Nanohybrid Composites and Photonic Materials for Multifunctional Opto-Chemical Sensors

The overarching goal of this M-era.Net project is the development, fabrication and application of (i) innovative nanofiber hybrid composite materials incorporating photonic (fluorescence & mid-infrared) and molecular (recognition & enrichment) functions integrated into a combined optical sensor platform for the development of rapidly responding photonic sensor devices, and of (ii) novel superlattice photonic materials based on the III/V material system (AlGaIn)/(AsSb) for the fabrication of interband cascade laser (ICL) gain media operating at room temperature in the mid-infrared wavelength range up to 6 μm .

Among the most promising applications of advanced optical sensor systems is the non-invasive analysis of exhaled breath enabling disease detection, disease diagnosis, and therapy progression monitoring. To date, there is no sensor technology available that enables simultaneous continuous analysis of both volatile organic constituents (VOCs) and diatomic molecules with sufficient discriminatory power. Chronic obstructive pulmonary disease (COPD) is present in approx. 10% of the total adult population and predicted to become the third most common cause of death and disability worldwide by 2020[1]. Atherosclerosis (AC) is the most frequent disease in the western world (prevalence of 25-30% in the population aged 45–75 years) and thus is the “no. 1 killer” in Germany accounting for 15% of deaths[2]. Here, we propose a highly innovative sensing platform taking advantage of novel coatings based on nanostructured hybrid composites, and of photonic materials providing the basis for novel laser technologies facilitating combined and miniaturized opto-chemical sensors, which simultaneously enable molecular enrichment, fluorescence sensing, and mid-infrared sensing for the real-time detection of O₂, CO₂, NO, and of volatile organic species (e.g. ethane, pentane, isoprene, carbondisulfide), which are considered relevant biomarkers for diagnosing COPD and AC in exhaled breath.

Consequently, the focus of this project is the development, optimization, and application of innovative materials facilitating the proposed sensing functions, i.e., (i) polymer nanofiber composite materials with integrated noble metal nanoparticles and fluorophores coated into substrate-integrated hollow waveguide (iHWG) sensing structures for simultaneously providing molecular recognition/enrichment, fluorescence detection, surface enhanced infrared absorption (SEIRA), and potentially surface plasmon coupled fluorescence emission (SPCE) functions, and (ii) superlattice structures as basis for active lasing material for advanced ICL technology providing monolithically integrated components within the Sb-containing materials for additional photonic functions such as wavelength filtering or beam

conditioning.

In summary, combining IR and fluorescence sensing schemes into a single device based on advanced photonic materials with integrated molecular recognition functionality along with novel photonic materials for tunable ICLs is a unique concept far beyond the current state-of-the-art, thereby facilitating advanced opto-chemical sensors for next-generation breath diagnostics.

Hi2CoRe: High performance properties, for high frequency applications, by combining silver coatings and Rheo cast aluminium

Different types of filters, waveguides and horn antennas are used by the telecommunication and measurement technology industry today (in e.g. radars, mobile phone systems, and industrial microwave applications). All these components are partly consisting of hollow three-dimensional structures, which often are casted in aluminium. The precision is usually very high and should be kept in the range of a few micro meters. To obtain such a precision mechanical pre-treatment is necessary. This can be achieved by using Rheo cast technology. In order to minimize in the electromagnetic losses the components are coated with silver by electroplating. The electric conductivity and the smoothness of the silver coating are essential since the high frequency electromagnetic signals are only conducted in the upper few micro meters or less of the coating. At the same time the geometry of the components is very complicated to electroplate, having high aspect ratio (ratio between depth and width) and a lot of small blind holes.

The present consortium have realised that the main constraint in producing high quality waveguides and likewise components, will soon become the quality of the silver plating including proper pre-treatment of the precise Rheo casted components. Therefore, the consortium wants to conduct a project with the purpose of realising highly functional silver coatings on complex shaped, Rheo cast, aluminium components for telecom applications by the use of bipolar pulse plating, optimised with the help of computer modelling.

NANOCOATIL: High performance nanostructured coatings using ionic liquids based on choline chloride

Recently it has been demonstrated the possibility of forming of ionic liquids from eutectic mixtures of quaternary ammonium salt such as choline chloride (2-hydroxy-ethyl-trimethyl ammonium chloride) with hydrogen bond donor species such as amides, glycols or carboxylic acids. These media, also known as “deep eutectic solvents (DES)” exhibit good air and water stability. They are potentially recyclable, biodegradable and with no harm on human health. Unlike the conventional ionic liquids, the use of DES for a large range of metal surface treatments through electrochemical and electroless processes may be an attractive alternative due to their easy synthesis and manipulation, at a lower cost. They are much safer to use in the workplace than existing aqueous based processes, are stable in use and have a lower

environmental impact. The solvents are also environmentally benign and many are biodegradable. Therefore, the sustainability of the new metal finishing ionic liquid electrolytes is greatly superior to both current aqueous systems and alternative ionic liquids. Based on previous excellent experimental results, the present project intends to develop several novel nanostructured coatings, respectively: (i) corrosion resistant Cr/Ni/Co alloys with Mo, V and also metal carbon nanotube (Me-CNT) composites and (ii) ordered nanoporous/nanotubes oxide layers onto valve metal surfaces (e.g., Al, Ti, Nb, Ta) with an enhanced growth rate. Main applications of these coatings are in metal finishing and electronic industries, involving choline chloride based ionic liquids. Through a careful selection of IL based electrolyte composition and operating conditions various nano-morphologies could be obtained, suitable for different final applications. The main advantage of the development and promotion of the use of these new electrochemical media refers not only to the accumulation of new scientific information but also allows the minimization of production costs, of industrial waste quantities, with positive effects on environment and health.

The present proposal strongly addresses new processing routes and new solutions to develop nanostructured coatings with tailored properties through optimization either cathodic or anodic reaction. It is expected a significant impact on the development of novel corrosion resistant metallic coatings on one side and of ordered nanoporous anodic oxide layers with a large sectorial use, including metal finishing, electronic, automotive and renewable energy (e.g., PEM fuel cells) industries. Corrosion is a problem that affects in a large extent the manmade structures where metal are extensively used for reinforcement or casing a vast number of products and constructions. Corrosion prevention is a never ending task with large costs for private and national economies. The introduction of new surfaces either with increased corrosion resistance, less costly, produced in more environmentally friendly conditions or absent of more toxic metals will have a big impact in industry and economy of efforts in corrosion hindrance.

European industry will benefit from the development of innovative technological applications with less environmental impact that can create novel products with better corrosion resistance, new metal finishing protocols and technology. The European scientific system, in particular the institutions proposing this project will benefit from the work in cutting-edge scientific areas, developing of new methodologies in ionic liquids applications, improving their scientific knowledge to give them a better contribution over industries and to allow the formation of young scientists in a scientific area of great importance.

CarLa: Ag/Si doped carbon layer for bio-medical application

The CarLa project is a common undertaking of POLAND and ROMANIA concerning one aim where each scientific partner conducts biological and mechanical tests of new Ag/Si doped carbon layers deposited onto medical Ti alloy using six different methods in order to provide to the market products in a form of antimicrobial medical implants with good mechanical properties and ability to accelerate the osteointegration process. The role of industrial partners in the project is to verify the modified implants under industrial conditions. According to the Global Biomaterials Market report (2009-2014) published by the World

Market and Markets, every year around the world about 100,000 artificial heart valves, 200,000 pacemakers and 1 million orthopedic implants are implanted. The increase is due to the use of biomaterials social demand increase from 8% to 15%. Growth factors are: aging population, increased public awareness, shorter approval process of biomaterials and complications after the implantation.

This last problem is widely discussed in literature. It was proved that most of post-implantation complications are caused by the infections and/or disorders induced by toxic reactions as a result of release of alloy elements from the implant. The most typical are: difficulties in wound healing, increase of bacterial and fungal infection risk, slowdown of osteogenic cells adhesion, slack of prosthesis due to bone disappearance around implant or allergic dermal eczema. It is estimated that allergy problem in implantology will be increasing for the next generations. Accordingly the post-implantation complications have not only clinical but also economic consequences. Clinical consequences are: longer period of antibiotic therapy and repeated surgical procedures, disability or even death. Economic effects are directly related to elongation of clinical procedures and generate additional costs (several billion € annually throughout Europe).

Taking above into consideration it is profitable to conduct proposed research and worked out new solution which being proposed on the market give patients better/safer products and lower cost of clinical treatment. In this connection the main objective of the project is manufacturing of Ag/Si doped C coatings onto the titanium alloy medical implants. The innovation of proposed solution is based on simultaneous introduction to the carbon coating two elements with different properties. This will result in the improvement of the existing solutions and also broaden the range of their possible uses. The presence of silver in the coating will ensure a broad spectrum of antimicrobial action, though protecting the implant against the disadvantageous influence of bacteria and fungi causing biofilm associated infections, local inflammation and other implant-tissue reactions. The addition of silicon will lead to the enhancement of mechanical properties of the coating and promote osteointegration. This will result in shortening the healing process of patients and allow using of proposed solution for the modification of the long-term implants surfaces.

Despite of the fact that the subject of doping of carbon coatings by different elements is on the European scientific map and many research results can be found in this field, there is a lack of reports concerning the mechanical and biological properties of Ag/Si doped carbon layers synthesized with use of the technologies proposed in CarLa. The results of this project will bridge the gap in the state of the art of submicron structures modifications.

The high scientific level of the proposed project, the novelty of the scientific problem to be undertaken, and well-composed team of professionals with complementary expertise and big experience in the work entrusted to them, ensures that the project will be implemented in a timely manner and at the highest level of science and its results will be published at top rank journals and be implemented into the market.

MACOSYS: Magnetically active anisotropic composite systems

The widespread acquaintance of liquid crystals is based on today's liquid crystal display technology (LCD). There are also other important devices (less well known to the public)

relying on liquid crystals like optical switches, photo-elastic-modulators, tunable lasers, tunable filters, etc. These devices for functioning take the use of the anisotropy (orientational dependence) in the optical and electric properties of liquid crystals.

Liquid crystals are magnetically anisotropic too, however, in general, the magnetic anisotropy is much smaller than the anisotropy of the electric properties. It has been predicted theoretically in early 70's that the magnetic sensitivity of liquid crystals can be greatly increased by doping them with magnetic particles. This assumption has been confirmed experimentally in the 80's. Moreover, very recently (after 2010), new discoveries have been made regarding the optical response of such liquid crystals doped with nanoparticles to very low magnetic fields .

Our project proposal targets these novel findings at very low magnetic fields (especially regarding the relevant experimental conditions), and the major problem that prevents the real application of these liquid crystals (e.g., as magneto-optical devices), namely, the aggregation of the nanoparticles. In our project we also propose a novel class of materials – self-standing films of cross-linked liquid crystalline elastomers doped with magnetic nanoparticles potentially having unique magneto-optical and magneto- mechanical properties.

The key questions targeted by the project proposal (and the hypothesis how the experiments may answer the question) are:

- under which conditions is the application of the small bias magnetic field crucial for the optical response of ferronematics at low magnetic fields? (a possible answer expected from the experiments with and without the bias magnetic field);
- how the initial pretilt angle relates to the bias magnetic field and to the response (both optical and dielectric) to low magnetic fields? (a possible answer expected from the experiments by changing the direction of the bias magnetic field and that of the pretilt angle);
- besides the restoring elastic interactions, which other factors/interactions give contribution to the aggregation of nanoparticles in ferronematics? (studies of the aggregation process for different type of nanoparticles, for homogeneously as well as for periodically distorted initial state of the nematic liquid crystal host material);
- can the magnetic field induced shift of the phase transition temperature be considerably enhanced? (to our expectations in ferronematics based on bent-core nematics);
- can one produce a magnetically sensitive, optically anisotropic self standing film? (by doping liquid crystalline polymers with magnetic nanoparticles prior the aligning and cross-linking process).

On the one hand, the increased sensitivity of ferronematics to magnetic fields regarding their optical and dielectric responses, as well as the enhancement of the magnetically induced shift in the phase transition temperature – which are the main objectives of the project proposal – could certainly trigger further experimental and theoretical research in the expanding field of magnetoactive composite materials.

On the other hand, but not less importantly, these objectives of the project, together with a better understanding of the aggregation process of nanoparticles (another key objective of the proposal) are directly related to the questions/problems that have prevented ferronematics from the realization of practical applications in various magneto-optical or magneto-

mechanical devices. Therefore, the present project proposal has a considerable importance from the viewpoint of potential technological applications too.

CAPDESIGN: Encapsulation of polymeric healing agents in self-healing concrete: capsule design

We consider that € 40–120 million of the maintenance costs for concrete bridges, tunnels and retaining walls in the European Union could be saved by application of self-healing concrete. For self-healing concrete with polymeric healing agents (e.g. PUR, PMMA), the bottleneck for valorization is however the encapsulation technique since the capsules have to possess multifunctional properties. The capsules with embedded healing agent (i) have to protect the healing agent for a long time, (ii) have to release the healing agent when cracking occurs and (iii) should not influence the fresh concrete workability and the early and long term mechanical properties. More important, we are looking for capsules which can easily be mixed in concrete and/or can survive the placement technique (e.g. projection). In that way, the concrete production / application process is not too much affected and the processing costs will not rise. The contradictory requirements make it however difficult to find a suitable encapsulation material: on the one hand, we want no breakage during concrete preparation / application, but on the other hand, we strive for immediate breakage of the capsules when a crack appears. Since no commercial products seem to be appropriate, the challenging objective of CAPDESIGN will be to develop, optimize and test new capsules for applications in self-healing concrete.

In addition, an innovative and specific placement technique by projection / injection of the capsules in association with concrete will be developed. Its main objective is to provide a greater durability of the capsules during the concrete placement.

The benefit of capsules which can survive mixing / application is that (i) the cost of self-healing concrete can be reduced, (ii) companies can be more easily persuaded to produce self-healing concrete, (iii) self-healing concrete can be valorized. Of course, as self-healing concrete does require much less repair, the application of self-healing concrete will lead to a lot of economic, environmental and social benefits, for example a reduction of traffic jams, an increased safety level, etc.

GoIMPLANT: Tough, Strong and Resorbable Orthopaedic Implants

The aim of the project is to develop resorbable, tough, strong and biocompatible hybrid composite implants meeting patients needs. The mechanical strength of proposed composite materials will reach 270 MPa, fracture toughness more than $1 \text{ MPa}\cdot\text{m}^{1/2}$ and they will be resorbable in a time up to 24 months. The present materials of choice for implants are titanium alloys or stainless steel, which frequently require to be removed in a second operation. This is an additional risk and cost for patients. Resorbable implants are currently made from polymers. Their mechanical strength is not satisfactory, and inflammatory processes are a significant risk factor. The new implants will conquer a large fraction of the market of orthopaedic implants, which will reach 250 billion euro in 2015 .

The key success factors of this project are three innovative technologies: synthesis technology of Calcium Deficient Hydroxyapatite Nanoparticles (CDNHAP), technology to produce hybrid nano composite granules from PLA polymer and CDNHAP, and Ultra-High Pressure Warm Isostatic Compaction (UHPWIC).

The CDNHAP nanoparticles developed by us are exceptionally bio-compatible. Preliminary tests have shown that they are also non-toxic to test cells. The synthesis process relies on precisely controlling the hydrothermal synthesis time in a high power microwave reactor, with precision of 30 sec. Further, we developed a granulation method, where the PLA molecules are tightly bonded with the HAP nanoparticles during the granules formation process. The method will be further improved using a freeze granulation process, to ensure scale up of the production. Finally, the granules will be compacted into 100% dense bulk hybrid nanocomposites under pressures up to 1 GPa at a temperature up to 450K. The temperature will be adjusted to prevent PLA decomposition. The technology will permit to obtain hybrid nanocomposites with nano-HAP content from 50% up to 95%, depending on the specific orthopaedic application. The compaction conditions will be optimised, so that during densification the bio-compatible nanostructure is preserved. As a consequence, high strength will be combined with ductility.

The project partners already filed several patents to protect the CDNHAP technology and the granules formation technology. The CDNHAP powder was registered under the trade name GoHAP. Further patents will be filed. These measures are taken to accelerate the technology commercialisation.

VOCSSENSOR: Hybrid Materials for Low Cost Volatile Organic Compound Sensor System

We are proposing to develop low cost, high sensitivity, mobile volatile organic compound (VOC) sensor system that can be easily installed and used in home, laboratory, factory to provide better living environment and protect human from VOC exposure and explosion. Volatile organic compound means any organic compound having an initial boiling point less than or equal to 250°C measured at a standard pressure of 101,3 kPa (Directive 2008/50/EC). The system can detect and monitor any excess harmful VOC in the environment and send out warning signals to alert people through visible and/or audible alarm; smart cell phone or computer message (Directive 2004/42/EC).

The proposed mobile VOC sensor system using inexpensive components of LED light sources, sensing chip, light to electricity detector (analog to digital), signal acquisition that can be interfaced with smart cell phone or computer to send out warning signal or display the level of VOC. The innovation and core technology of this system is the sensing chip that is made from the thin film of novel hybrid material of conducting polymers and nanoparticles. The morphology of the hybrid film is changed upon the exposure to the vapor of volatile organic compounds that in turn changes the absorption behavior of the hybrid. The change in the absorption provides different current signal that is transferred into the warning signal. The warning signal can be either in visual or audio to alert people for prompt remediation action. The proof-of-concept of this novel technology has been demonstrated by Prof. Wei-Fang Su's group of National Taiwan University. The results indicate that various VOCs can be detected

within few minutes of time, confirming the regulations and directives at the occupational health safety administration of European Agency for Safety and Health at Work (EU-OSHA). The proposed program will base on this initial result and aims the further development with increased sensitivity of ppm range, less than minutes response time by using new hybrid materials and adding automated data acquisition system for reliable VOC sensor readouts. This Project comprises research, technology and product development of VOC sensor system and encourages unique European-Taiwan co-operation in new areas of mutual benefit. The program will be led by National Taiwan University and in-depth collaboration with well established researchers from Nanordic Oy of Finland (SME), University of Szeged of Hungary and Ingenieros Asesores of Spain (SME). A number of stimulation actions of trans-national cooperation will be taken place and expedited research results to achieve the goal. The consortium will provide a significant technological knowledge base; the facility and infrastructure sharing and will offer additional opportunities for the development. This project will bridge the current gap existing between pure sensor development academia and end users companies of manufacturing and final environmental monitoring. The duration of the program will be 36 months with total funding budget of 578,125EUR requested.

PCPLASTER: Phase Change Material (PCM) enhanced plaster for upgrading the energy efficiency of contemporary and historic buildings

The improvement of the energy efficiency of buildings is currently one of the highest priorities of the energy policy of the European Union. Member States must take measures to encourage existing building owners to renovate their properties by upgrading the building shell's thermal performance. In this effort, advanced building materials, such as phase changing materials (PCMs), have a major role to play. PCMs are used in many different applications, taking advantage of their capacity of absorbing or releasing energy in the form of latent heat during the melting or solidifying process, respectively. The principle of latent heat storage can be applied to any porous building material, but current research primarily concerns gypsum wallboards, cementitious composites and insulation materials. A PCM-enhanced plaster is a heat storage medium combining an appropriate PCM with a cementitious or non-cementitious matrix to produce a low cost thermal storage material with structural and thermostatic properties. Although important research efforts have been conducted in the recent past to boost the penetration of PCM-enhanced plasters in the building material market, their applicability remains restricted to specific application fields.

The objective of the proposed project is the development of a novel cementless PCM-enhanced plaster with improved physical, chemical, mechanical and thermal properties, which will be appropriate for the southern European climatic conditions. The proposed PCM-enhanced plaster will be thermally efficient, reliable and durable in use, and it will come at a low cost. The project also aims for improvements in the production process and lifecycle performance and impacts of PCM-enhanced plasters.

The aforementioned objective will be satisfied by means of combined R&D activities at both university and industry levels. The thermal and mechanical properties of the PCM plaster will

be experimentally and numerically investigated. The research will also aim to define appropriate thermophysical and hygric properties for PCM-enhanced plasters for the southern Europe boundary conditions throughout the year. A parametrical analysis will result in the development of a series of PCM-enhanced lime plasters. Pilot applications and field measurements will be conducted in order to verify the numerical results and the efficiency of the new products, focusing on their thermal and physico-mechanical properties. The compatibility of the PCM-enhanced plasters with existing building materials will also be investigated, as this is of paramount importance in restoration and renovation projects. A Life Cycle Analysis performance of selected PCM-enhanced plasters will also be conducted; a feasibility study will be additionally carried out to determine whether the new product will be able to enter the market at a competitive level.

Building integration of the PCM-enhanced plaster is expected to lead to reduced energy consumption. This will support the European community in meeting its strategic policy targets of reduction in primary energy use in the building sector. The proposed research will cover both fundamental and applied aspects and will enable the establishment of a durable collaboration and dialogue between RTD performers, material researchers/producers and industrial end-users. The active integration of a PCM-enhanced plaster manufacturer in the proposal guarantees the relevance of the research.

RADESOL: RAtional DEsign of blends for bulk heterojunction SOLar cells

Within the research and technology field of organic electronics, organic photovoltaics (OPV) - based on either small molecule or polymer active materials – have recently shown substantial progress concerning performance of the solar cells produced and fundamental insights in device physics, architectures, lifetime and processing technology. The relevance of this emerging technology for future renewable energy production lies mainly in its potential to reduce the production cost per GigaWatt production volume in a substantial way. Processing of the required materials as inks using existing printing techniques and the limited demands on the production environment (no cleanrooms needed) allow for a cheap high-volume production of solar cells of medium efficiency. As only very thin films are used for the active layers (in the range of 100 nm) and various classes of organic materials can be applied, the cost advantages of such technology become even more clear.

At this moment power conversion efficiencies (PCEs) above 10% can be envisaged for OPV and progress in device engineering has allowed for a first evaluation in real life, for the time being rather as a test-case in consumer electronics. To contribute substantially to resolving the TeraWatt energy challenge, many questions still need to be addressed, e.g. at the level of fundamental understandings, the development of the most effective device architectures, the use and role of specific interfaces and charge transport layers and implementation of the most economic production technology.

The project proposal has as a main objective to achieve a more profound understanding on the molecular scale of the nanomorphology-performance relationship in active layer blends for bulk heterojunction (BHJ) organic solar cells and thus focuses specifically on the relationship between the molecular structures and supramolecular organization within the active layer and the device physics responsible for the solar cell performance. As such, the research activities

involved concentrate on the synthesis of active organic materials, the study of the physicochemical properties of the active layer (components and blend), the morphological structure of the blend and the electro-optical characterization of devices prepared from these blends. As a direct impact of the project, a rational design of materials and active layers for OPV can be expected, providing a springboard for efficiency improvement of organic solar cells. The four partners (UHasselt, VUB, NTNU and IT) from three European countries (Belgium, Norway and Portugal) have all well-documented research activities in the field of organic electronics and more in particular OPV. The numerous contributions of said research groups relate to all the different aspects needed to make fundamental progress in the field. A highly complementary and interdisciplinary team is gathered in the consortium and a high level of synergy in the research activities can be achieved. As a direct benefit of the project, the scientific know-how within the European organic electronics community will be reinforced. The objective of the proposal comprises a very critical and fundamental aspect toward further progress in the performance of organic solar cells. Furthermore, all partners are strongly integrated in the existing research networks around OPV, with key research groups in Belgium, the Netherlands, UK, Sweden, Denmark, Germany, France and Spain. Indirectly, the results of this research will certainly disseminate into collaborations with research partners in these countries.

LaminaLion: Conformal layer-by-layer growth of hybrid polymer/inorganic nanolaminates for Li-ion batteries

For the application of durable micro-storage for autonomous systems and implants, 3D thin-film batteries are leading candidates. Lithium ion batteries have the highest energy density of all known systems and are thus the best choice for these rechargeable micro-batteries. Since liquid electrolyte based batteries present safety issues and limitations in size and design, pure solid state devices are considered particularly for miniaturization. The thin-film concept provides the means for good ionic conductance through reduction of the distance for Li-ion diffusion. Combined with the large surface area of a 3D structured surface (e.g. etched pillars or nanowires) an acceptable battery capacity is maintained as the total electrode volume is preserved by the increase in effective surface. Remaining technological issues are (i) the mechanical strain induced in the rigid solid stack during charge/discharge which limits the life time of the battery and (ii) pinholes in the films which limits their minimum thickness and as such the battery power (ionic conductance). The main objective of this project is to develop a mechanically flexible solid electrolyte in the form of a conformal thin-film stack which is to be used for 3D thin-film solid-state lithium-ion batteries. The success of this objective is measured through the durability (cycle life time) of a 3D thin-film micro-battery demonstrator. The second objective is to obtain pinhole-free thin-films constituting a thin-film electrolyte stack with total thickness down to 100nm or less to achieve good ionic conductance. The success of this objective is measured through the performance of the 3D thin-film micro-battery demonstrator. These objectives will be achieved through the application of ALD/MLD processes. Our final goal is a functional battery stack with fast charging/discharging kinetics and long cycle life time.

MOC@SUPCAP : Design of new metallic oxide-carbon hybrid composites for supercapacitors electrodes

The objective of the MOC@SUPCAP project is to develop a novel class of hybrid composite electrodes with high performance targeted for the next generation supercapacitors, namely asymmetric supercapacitors, based on cheap and reliable fabrication methods.

Needs addressed: Supercapacitors (SC) are energy storage devices, essential to support the peak loads/consumption in renewables production and that can complement batteries due to their higher power density. SC exhibit unique features such as high power density, and fast charge/discharge rates, sustaining up to millions of cycles. However, they lack energy density when compared to batteries. This drawback can be mitigated by developing new electrode materials combining higher specific capacitance and therefore enhanced power and energy densities.

The answer resides in developing new composite electrodes with highly porous hierarchical structures, combining enhanced double layer capacitance, typical of carbon-based materials with the pseudocapacitance behaviour of transition metal oxides. Composite electrodes composed of transition metals oxides (NiO₂, Co₃O₄, MnO₂ and V₂O₅) and carbon (like cloth/fibre and graphene) are a promising route when tailored as porous hierarchical two-dimensional (2D) or three-dimensional (3D) structures. The preparation of these structures should, however, be simple and flexible, allowing fine tuning of the surface properties in order to fulfil the requirements of electrodes for high performance SC.

The innovative contribution lies in the design and fabrication of deposited tailor made transition metallic oxides on C based substrates to obtain high performance composite electrodes. The metallic oxides will be obtained by simple, flexible and low-cost routes (electrodeposition and wet chemical synthesis methods) which are easily scaled-up. For example, the production of structured oxides by pulsed cathodic electrodeposition is a novel approach to this process that is already widely used in the industry for the production of coatings.

Results: A new class of hybrid composite electrodes based on assemblies of carbon materials (for enhanced double layer response) and porous transition metals oxides (for high faradaic contribution) will be developed. The combined advantages of carbon with those of transition metals oxides will enable more effective supercapacitors, able to work with environmentally friendly aqueous electrolytes. Furthermore they can be easily assembled in asymmetric devices, which combine a battery electrode with a supercapacitor electrode. A specific capacitance above 500 Fg⁻¹, an operating voltage larger than 1.5 V and high cycling stability will be targeted as sought-after characteristics of the designed hybrid composite electrodes.

The MOC@SUPCAP project outputs are:

- more efficient composite supercapacitor electrodes consisting of carbon and transition metallic oxides, with additional ability to undergo various redox processes;
- the implementation of cheaper fabrication processes capable of producing novel classes of nanostructured porous oxides/carbon composite materials;
- to foster new Hi-Tech applications, combining the traditional electrodeposition or wet chemical methods of producing metallic oxides with new advanced materials such as

graphene;

- advanced physical, chemical and electrochemical characterisation and fundamental knowledge on electrochemical behaviour of such electrodes using transient mathematical models, predicting efficiency, performance and lifetime.

The project addresses some of the most important concerns of current times: sustainable energy production and efficient energy storage for a cleaner environment while contributing to sustainable economic growth, boosting of new markets, creation of jobs and social well being. The proposal is thus, by no doubt, in the scope of the call topic "Materials for Energy Systems".