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Proposal for a New COST Action

COST 540

“PHONASUM”

**„PHOTOCATALYTIC TECHNOLOGIES AND NOVEL
NANOSURFACES MATERIALS – CRITICAL ISSUES“**

COST Action Proposer : Dr. Frantisek Peterka
National Centre for Nanosurfaces Engineering
Advanced Technology Group Prague
Beranovych 65
199 02 Prague 9 - Letnany
Czech Republic
Tel: + 420-233 540 099
Fax: +420-233 540 409
fpet@mbox.vol.cz

COST National Coordinator : Dr. Milos Chvojka
Ministry of Education, Youth and Sports
of the Czech Republic
Karmelitska 7
118 12 Prague 1
Czech Republic
Tel: +420-257 193 511
Fax: +420-257 193 713
milos.chvojka@msmt.cz

Rapporteur TC Materials: Prof. M H Loretto
IRC in Materials
The University of Birmingham
Edgbaston B15 2TT
Phone +44 121 414 5214
Fax +44 121 414 7890
m.h.loretto@bham.ac.uk

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Memorandum of Understanding

COST Action 540

“PHONASUM”

„PHOTOCATALYTIC TECHNOLOGIES AND NOVEL NANOSURFACES MATERIALS – CRITICAL ISSUES“

The Signatories to this Memorandum of Understanding, declaring their common intention to participate in the concerted Action referred to above and described in the Technical Annex to the Memorandum, have reached the following understanding:

1. The Action will be carried out in accordance with the provisions of document COST 400/01 "Rules and Procedures for Implementing COST Actions", the contents of which the Signatories are fully aware of.
2. The main objective of the Action is to via a concerted European effort increase the fundamental knowledge of nanocrystalline photoactive materials and development of new products, which utilize self sterilizing and self cleaning photoactive materials in commercial applications. The Action will also concentrate on the development of EU standards for the characterization of photocatalytic materials.
3. The economic dimension of the activities carried out under the Action has been estimated, on the basis of information available during the planning of the Action, at Euro 28 million in 2005 prices.
4. The Memorandum of Understanding will take effect on being signed by at least five Signatories.
5. The Memorandum of Understanding will remain in force for a period of four years, calculated from the date of first meeting of the Management Committee, unless the duration of the Action is modified according to the provisions of Chapter 6 of the document referred to in Point 1 above.

TECHNICAL ANNEX

COST 540

„PHOTOCATALYTIC TECHNOLOGIES AND NOVEL NANOSURFACES MATERIALS – CRITICAL ISSUES“

“PHONASUM”

ABSTRACT

The main objective of this Action is to increase the fundamental knowledge of nanocrystalline photoactive materials and foster the development of new products, which utilize self sterilizing and self cleaning photoactive materials. Emphasis is given to specific industrially relevant application fields such as self-cleaning and anti-microbial surfaces, water treatment, air purification and general hygienic applications. The realization of these tasks is accomplished through the development of novel highly active photocatalytic nanomaterials and coating systems with increased sensitivity in the visible region of the solar spectrum, with high environmental stability and adaptability on the various substrate systems. The Action also contributes to the development of EU standards for the characterization of photocatalytic materials.

A. BACKGROUND

The development of nanocrystalline photocatalytic materials is a rapidly growing field of science and technology. This fact relates to the unique physical and chemical properties of these materials that may be utilised for a wide range of potential applications. Specifically, upon ultraviolet irradiation these materials exhibit photocatalytic activity that enables the oxidative destruction of a wide range of organic compounds and biological species on their surface. Examples of such species include bacteria, viruses, cyanobacteria, algae and fungi and all kinds of proteins or toxic components (self-decontamination effect). In addition, these materials may also exhibit photocatalytically induced superhydrophilicity that converts the hydrophobic character of the surface to hydrophilic when exposed to UV light. This causes the formation of uniform water films on the surface of these materials, which prevents the adhesion of inorganic or organic components and thus retains clean surface of the photocatalyst. Hence these nanocrystalline photocatalytic materials may be deployed on surfaces of various substrates such as glass, ceramics or metals to provide layers that exhibit *self sterilisation* and *self cleaning* properties when they are exposed to the light. The commercial potential for such coatings are massive, including medical applications, architectural (particularly cultural heritage purposes, facade paints, indoor, wall paper, tiles, consumer goods etc.), automotive and food industries (cleaner technologies, non-fogging glass and mirrors, product safety), textile and glass industry, and environmental protection (water and air purification and disinfection).

Among the various nanocrystalline photocatalytic materials that have been studied over the past 30 years research has mainly focussed on titanium dioxide photocatalysis in diverse areas ranging from water and air treatment through to self cleaning glass. Numerous papers have been published on the fundamentals of pure titania systems, and the mechanisms of oxidation and superhydrophilicity have been investigated in detail. Consequently, primarily in Japan, but also in the United States and

latterly in China, commercialisation of TiO₂ photocatalysis has been initiated in various fields. In Europe, however, although there is extensive academic knowledge in nanostructured materials and photocatalysis with several materials and processes being pioneered, the commercial potential of photocatalytic materials has yet to be realized. Currently the main commercial applications of photocatalysis in Japan are architectural tensile structures with over 50% of industrial turnover, followed by ceramics and glass. In China, wall paints already have been used, with TiO₂ dispersed in silicone-type paints. More than 3,000 patents have been issued, mainly on anatase-based photoactive form of TiO₂. The total turnover of the sale of anatase has been booming in the last years and it is expected to reach one billion Euros in 2006.

Titanium oxide, however, has several limitations, which inhibit more extensive utilization of photocatalysis in commercial applications. A major limitation is the lack of response of TiO₂ to visible light since it requires UV light below 388 nm for photoactivation. This means that current TiO₂ photocatalysts can utilize only 4% of the incoming solar energy compared to 45% of visible light. Consequently, there are also technical problems with stability of photocatalytic coatings such as drop in their photoactivity with time; weak adhesion strength of some types of layers; inhibition of photoactivity due to presence of inorganic compounds in the substrate and undesirable photocatalytic degradation of organic components of paints or plastic supporting materials.

Therefore, development of new and optimisation of existing photocatalytically active materials exhibiting activity upon visible light with surface characteristics of improved performance and of the high chemical and physical stability are needed for broader scale utilization of photocatalytic systems in commercial application. Such materials together with the development of technically applicable self aligning photocatalytic coating systems adaptable to the major substrates (polymers, glass, ceramics or metals) will represent a ground breaking step change in this field particularly in the economic viability of a range of potential processes. The first visible light systems via doping of titanium oxide with N, S and C have been already prepared recently, but no systematic investigations have been carried out to date. It is, however, expected that the soft chemical approach employing multiply doped mixed oxide heterostructures for tailored micro- and mesoporous architectures can provide a significant breakthrough in the development visible light photoactive systems. The supra-molecular engineering can additionally allow tuning of the hydrophilicity and hydrophobicity of photocatalysts. The environmental stability of nanoparticles can be also improved through hydrothermal or lyothermal processes.

In addition to the development of highly active photocatalytic materials and coating systems, there is also great need to develop suitable standards for the characterization of photocatalytic and hydrophilic properties of these materials. Standardization protocols are essential for integration of the research effort in different laboratories and to compare the performance of commercial products. Even though extensive research activities in photocatalysis have been carried out on a worldwide basis for the last twenty years, it was not until 2003 that the Japanese Standard organisation JIS has started an initiative to develop standards in photocatalysis. Based upon this JIS initiative an ISO committee has commenced with the development of respective standards for photocatalysis at the end of 2003. Therefore, any successful industrial production and commercialisation of photocatalytic systems within Europe will strongly depend also on the development of the EU standards with the further effort of their approval as ISO standards to ensure their worldwide acceptance.

It is obvious that the approach to gain these tasks in fundamental knowledge as well as products and processes is clearly multidisciplinary. The topics require expertise in material science, various fields of chemistry, physics, molecular/micro biology and medicine. There is also need of closer cooperation between academia and industry in order to transfer technological know-how of

photocatalysis into the commercial products. Feedback and crossover between these activities are critical to maximize delivery on breakthroughs to the application processes, for which standardization is also required. This prompts a concerted integration of the European photocatalytic community in order to achieve these goals.

Consequently, the specific aim of this Action is to bring together European scientists and engineers from various fields and research groups in order to combine their particular knowledge, state of art equipment, experience and technical know-how in an effective way towards the design, synthesis and testing of these new nanomaterials and photoreactors. The joint effort is needed to a) gather the necessary manpower and scientific expertise to carry out the first class research needed and b) to compete with Japan and USA in the development of new products with potential large scale applications. This Action will pull together European groups with leading expertise in different nanoscale basic aspects of photocatalysis, molecular and microbiology and materials science and will combine their particular knowledge, experience and skills in an effective way towards scientific knowledge breakthroughs. The Action also aims to broaden the training and education of young European scientists to improve and develop of new skills and expertise. With co-operation of European industrial partners catalyst and materials manufacturers will closely work together with coating specialists and end users to exploit the knowledge developed by researchers looking into basics. The Action will also benefit from synergies and contacts developed by the European-Japanese Initiative on Photocatalytic Applications and Commercialisation (EJIPAC). The application step will adapt the new coating techniques to specific industrially relevant application fields including hygiene & medicine, automotive, architecture, environment, marine and textiles. As such, COST represents the most appropriate mechanism for achieving of technical & scientific objectives of this Action.

B. OBJECTIVES AND BENEFITS

The main objective of the Action is to via a concerted European effort increase the fundamental knowledge of nanocrystalline photoactive materials and development of new products, which utilize self sterilizing and self cleaning photoactive materials in commercial applications. The Action will also concentrate on the development of EU standards for the characterization of photocatalytic materials.

The realization of these tasks will be accomplished through specific objectives of this Action that are summarized as follows:

- Development of novel highly active and resistant nanoparticulate photocatalytic materials sensitive also to the visible light
- Development of technically applicable self aligning photoactive coating systems adaptable to the major substrates (polymers, glass, ceramics or metals)
- Characterization of physical and chemical properties of photocatalytic nanomaterials and coatings and design of standard photoactivity testing methods
- Utilization of new photocatalytically active nanomaterials and coating systems in specific industrially relevant application fields

The complexity of research on photocatalysis requires co-operation of scientists from various fields including scientists and engineers from physics, chemistry, medicine, materials science and engineering and process engineering, and additionally needs the involvement a number of equipment facilities. In this way, not only the participating groups will benefit directly from this Action, but there will be also considerable input into other research areas indirectly involved in the Action. Training and education activities of young scientists will enhance the development of new skills and expertise in the field of photocatalysis. European academic research integration will achieve also the appropriate critical mass of international partners with very different field of expertise to attain the objectives. The new photoactive nanostructured materials will have ecological, industrial and societal importance and may be developed to be high-added value commercial products and allow the development of innovative enterprises. The developments made in this Action will essentially strengthen the competitiveness of Europe by introducing photocatalytic nanotechnology in a multitude of application fields.

Potential direct economic benefits are generated from breakthroughs in new knowledge derived from the design and availability of multifunctional photoactive materials for the implementation of new processes and products based on smart materials. These, in turn, could have considerable impacts on many large scale productions, food packaging, self sterilising goods and tools, with larger EU independence on Japanese technology. There are many other industries that will also profit from the development of novel photocatalyst coatings. These include the building materials industry (especially materials used visibly e.g. on roof, walls, constructions made from concrete etc.), the glass industry (window glass, glass facades, automotive glazing, mirrors), the food processing industry (e.g. machinery), the textile industry (e.g. textiles for medical applications), the medicine, life-science and pharmaceutical industry (e.g. instrumentation, machinery, working benches) as well as the paint/coatings industry in general.

C. SCIENTIFIC PROGRAMME

To achieve the aims of the Action the Scientific Programme is based on three interlocking Working Groups (WGs). In addition, a common activity group working across these WGs will ensure that the Action takes full advantage of past and on-going research in this area and maintain and develops its links throughout programme. The first Working Group (WG1) will concentrate on the preparation of novel nanoparticulate photocatalyst materials and coatings. The mechanistic and analytical methods in WG2 will be used to characterise physical and chemical properties of these new materials together with in-situ investigations of the photocatalytic processes occurring on the surfaces. Important fundamental problems shall be also solved in WG2 that is also driven towards the establishment of EU-standards for photocatalytic activity in all its variations. The results from WG1 and WG2 will have a direct input for WG3 to produce a range of coating methods and procedures for utilization of new photocatalytically active nanomaterials and coating systems in specific industrially relevant application fields. This truly integrated approach will provide a route to addressing real breakthrough in the development and application of photocatalytic technology. The Working Groups are summarized in the following sections.

WG 1: New Photocatalytically Active Nanomaterials and Coatings

The main aim of this WG is the preparation of new highly active photocatalytic nanomaterials and coating systems with increased sensitivity in the visible region of the solar spectrum, with high environmental stability and adaptability on the various substrate systems.

To achieve enhanced activity of photocatalytic materials in the visible region highly innovative approaches will be used:

- Development of binary and ternary metal oxide sols and nanocrystalline layers (mainly TiO_2 , ZnO , $\text{Ti}_x\text{Zn}_y\text{O}_z$) doped with nitrogen, sulphur or carbon to match their spectral response.
- Alternatively, the titania and $\text{Ti}_x\text{Zn}_y\text{O}_z$ hybrid architectures will be electronically coupled with polyoxometalate clusters or metallic particles and multiply doped with transition metal cations.

Soluble nanopowders obtained from the above liquid nanocomposite precursors will add a high value to the development of new photoactive and visible light supported coating systems. To increase their environmental stability lyo- or hydrothermal processing will be used as a second step after sol-gel processing or thermodynamically controlled precipitation for obtaining narrow size distributed systems with tailored particle diameters. Additionally, using colloidal approaches, controlled fixation of nanoparticles (lower nm range) on carrier particles in the 100 nm range will be carried out to tailor the specific architecture of these systems. Nano and micropatterning of the photocatalytic layers to tune the final morphology and interface chemistry of immobilized nanostructures will be investigated. The mesoporosities will be created either photoelectrochemically or by using block-copolymer strategies. Embossing and etching will create micro patterned antireflective layers. Laser post-treatments will be employed for rapid thermal sintering of large scale coatings and to tune the internal and interfacial structures of the photoactive deposits. Application of chemical surface complexations and inclusion of electrically polarized nanocrystals (permanent/switchable) into the photocatalytic layers will be also tested with respect to the improvement of the bulk charge carrier separation.

The methods and technologies for adaptation and optimisation of self-organising gradient coating systems for different classes of base materials with a special consideration of the material specific requirements will be also developed in this WG. Further consideration will be laid on the ease of application and the automation of the coating process. The work will be structured based on the type of substrate:

- **Polymers** - Low temperature applications on plastics and additional features of the coatings e.g. enhancement of the scratch resistance or of the UV-stability of the interfaces.
- **Metals** – Wet coatings for metallic surfaces with special regard to passivation and bonding mechanisms. Additional effects such as the electric conductivity of the substrate on the photocatalytic activity will be examined. Development of photocatalytic coatings using electrodeposition as an alternative method.
- **Glass & Ceramics** – Protection of the active components against catalyst poisons from the substrates, e.g. sodium ions will be achieved. The coating of highly porous substrates will be enabled by the adaptation of the matrix materials.
- **Fibrous materials** - Coatings with a special regard on the optics and haptics of fibrous materials will be provided. The development of alternative fixation techniques of

nanoparticulate photocatalysts on fibres and protection of fibres against degradation will be the main focus.

WG 2: Characterization and Standardization

The primary aim of this WG is to determine physical and chemical properties of photocatalytic nanomaterials and coating systems prepared in WG1 and design of standard methods of testing of their photocatalytic and superhydrophilic activity.

The characterisation of the structural, mechanical and optical properties will be performed by advanced surface analytical techniques in collaboration with time-resolved and in-situ studies: SIMS and XPS surface analysis; scanning probe and analytical electron microscopies for surface morphology and general structural analysis; laser scattering analysis of particle sizes in suspensions; accelerated ions-based analysis for composition profilometry; mechanical property tests; EPR, EXAFS and quantum modelling calculations for understanding visible light-active compositions. Time-resolved spectroscopies (EPR, IR/Raman, laser photolysis) together with photo-electrochemical tests will study *in situ* which electronic states, radicals and molecular components are key elements in the sterilisation process; space-resolved studies on lithographed nanopatterned planar models will address the relevance of active species diffusion in pores; *in situ* X-ray diffraction, EXAFS and Raman techniques will study how nanocrystals appear and material components evolve and aggregate as coatings are formed. Microbiology work will determine molecular routes to gene modification and cell killing or viability changes under photocatalytic processing. This will clarify and optimise dopant characteristics, texture effects and preparation variables of the coatings, and will aid to optimize their efficiency for cell destruction.

To determine the photocatalytic activity of nanomaterials and coatings standard model test systems of self-sterilizing and self-cleaning properties of surfaces will be developed focussing on the standardisation of the European Photocatalysts market. The main effort will be focused on the development of methods and tools, for use by partners in this Action and later also by the external world, which enables testing the photoactivity and superhydrophilicity efficiency of photocatalytic materials and coatings in ways enabling comparison between the results of different groups. These tools should be relatively easy to apply and suitable for future commercialization. The development of standardization methods will be focussed on the characterization of photocatalyst performance in the following areas: degradation of organic substances in air and water, antibacterial effects and self-cleaning effects. The aim is to propose them as European-wide standards for quality control within this technology area. Versatility will be attempted, with the aim to cover the different situations addressed (in respect to germs to eliminate, substrate type, kind of radiation used, etc.). Also, simple photocatalytic reactions will be defined which may be proven to show correlation with the sterilisation processes, being thus proposed as simpler alternative tests of photocatalytic activity of these coatings. It is also anticipated to propose these novel EU standards to the ISO committee to ensure their worldwide acceptance.

WG 3: Photocatalytic Cleaning and Sterilization Applications

The aim of this WG is to bring together the newly developed knowledge in WG1-2 and to utilize new photocatalytically active nanomaterials and coating systems and technologies in specific industrially relevant application fields, especially in the areas of self-cleaning surfaces, anti-microbial surfaces, anti-fogging, water treatment, air purification and general hygienic applications. The main focus will be concentrated on the following applications:

- **Medical and Hygienics:** Application of the newly developed photocatalytic materials and coating systems with relevance in the medical and hygienic sector will provide surfaces with photocatalytic sterilisation and cleaning behaviour. The enhanced products will be thoroughly tested with a special respect on the evaluation of the anti-microbial effects, the degradation of toxins and biofilms (e.g. antifouling in water tanks or cisterns). Further aims are the development of medical instruments with better sterilisability. The new surfaces will also be applied in food industry or on surfaces for daily use (frequently touched surfaces FTS such as e.g. phones, handrails). The hygienic aspect of photocatalytically active textiles (personal hygiene as well as medical applications) will also be examined. Coating development for organic filter membranes, medical textiles, re-usable surgical equipment, medical devices (e.g. catheters) and surgical implants (e.g. pace makers) will be performed.
- **Architecture and Interior Applications:** The application of the newly developed coating systems on substrates and surfaces with relevance for the architectural sector (e.g. protection of facades, windows, roofs, inaccessible outer spaces of buildings) will provide surfaces with photocatalytic cleaning and anti growth effects (e.g. biofilms, moss or lichens). For interior use the application of the photocatalytic coatings on household appliances, sanitary ceramics, tiles and mirrors, and the reduction of soiling and formation of biofilms will be examined. Special attention will be paid to the identification of optimal wavelength, intensity and duration required to achieve desired photocatalytic effect.
- **Water and Air Purification Applications:** The newly developed visible light active photocatalytic materials and coatings will be utilized for development of photocatalytic reactor systems with application for decontamination of polluted water (e.g. degradation of pesticides, organic dyes, or water sterilization) and treatment of air (e.g. VOCs, CFCs, or odorous substances). Kinetics and mechanisms of photocatalytic degradation of various pollutants in water and air will be studied in order to determine intrinsic activity of a photocatalyst (coatings or nanoparticles) and to determine the effect of the characteristic of the pollutants on photocatalytic degradation efficiency.

D. ORGANISATION

The Action will be organised on the basis of three Working Groups. Where necessary, subgroups will be formed depending on the size of the activity. Each Working Group and sub-group will have an appointed co-ordinator. These will report to the Action's Management Committee that will coordinate the research work, including the short-term scientific missions, the workshops and publications. Once a year the Action will organize a joint Working Group Meeting. A website will be set up for communication within the Action, to convey the aims and objectives of the Action to the scientific community, and for disseminating results. The Action will also benefit from synergies and contacts developed by the European-Japanese Initiative on Photocatalytic Applications and Commercialisation (EJIPAC).

This estimate is valid under the assumption that all the countries mentioned above but no other countries will participate in the Action. Any departure from this will change the total cost accordingly.

G. DISSEMINATION PLAN

Dissemination of the results of the Action is specifically targeted to the contributing members of the COST-Action as well as to other researchers in the field, other researcher frameworks and Institutes and Academia and, if appropriate, industrial companies. Generally, this will be in the form of interim and final reports, standard publications in peer-reviewed journals and at national and international conferences and symposia. Once a year the Action will organize a joint Working Group Meeting. Relevant results will be posted on a public Website of the Action available for a general audience.

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ADDITIONAL INFORMATION

NOT PART OF THE MOU

LIST OF EXPERTS

There are about 25 potential participants from 12 European countries who have already expressed their interest in the Action or may be interested but have not been contacted during the pre-proposal planning. Experts, who have been consulted during the drafting of the proposal and have already expressed interest in the Action, are:

Name of expert (Country)	Affiliation and Contact Address
Dr. Frantisek Peterka (Czech Republic) PROPOSER	Centre for Nanosurface Engineering Advanced Technology Group Prague Beranovych 65 199 02 Prague 9, Czech Republic Tel: + 420 233 540 099 Fax: +420 233 540 409 E-mail: fpet@mbox.vol.cz
Dr. Erich Kny (Austria)	ARC Seibersdorf Research GmbH A-2444 Seibersdorf, Austria Tel: +43 50550 3300 Fax: +43 50550 3366 E-mail: erich.kny@arcs.ac.at

<p>Dr. Anne Beeldens (Belgium)</p>	<p>Belgian Road Research Center, Bld. de la Woluwe 42 B-1200 Brussels, Belgium Tel: +32-2-766 03 46 Fax: +32-2-767 17 80 E-mail: a.beeldens@brrc.be</p>
<p>Dr. Jaromir Jirkovsky (Czech Republic)</p>	<p>J. Heyrovsky Institute of Physical Chemistry Academy of Sciences of Czech Republic Dolejskova 3 182 00 Prague 8, Czech Republic Tel: +420 266 053 737 Fax: +420 286 582 307 E-mail: jirk@jh-inst.cas.cz</p>
<p>Prof. Tapio Mäntylä (Finland)</p>	<p>Tampere University of Technology Institute of Materials Science Laboratory of Ceramic Materials and Surface Engineering, PO Box 589 33101 Tampere, Finland Tel: +358 3 3115 2326 Fax: +358 3 3115 2330 E-mail: tapio.mantyla@tut.fi</p>
<p>Prof. Lubomir Spanhel (France)</p>	<p>Institut de Chimie de Rennes Université de Rennes 1 263 AVE du Général Leclerc CS 74205 35042 Rennes Cedex, France Tel: +33 2 23 23 62 59 Fax: +33 2 23 23 56 11 E-mail: Lubomir.Spanhel@univ-rennes1.fr</p>

<p>Dr. Chantal Guillard (France)</p>	<p>Laboratoire d'Application de la Chimie a l'Environnement Universite Claude Bernard Lyon 1 UMR CNRS 5634 Batiment J. Raulin, 43 bd du 11 novembre 1918 69622 Villeurbanne Cedex, France Tel: +33 4 72 43 29 79 Fax: +33 4 72 44 84 38 E-mail: chantal.guillard@univ-lyon1.fr</p>
<p>Prof. Detlef Bahnemann (Germany)</p>	<p>Institute for Technische Chemie Universitat Hannover Callinstrasse 3 D-30167 Hannover, Germany Tel: +49 511 762 5560 Fax: +49 511 762 2774 E-mail: bahnemann@iftc.uni-hannover.de</p>
<p>Dr. John Colreavy (Ireland)</p>	<p>CREST Dublin Institute of Technology Camden Row, Dublin 8, Ireland Tel: +353(0)1 4027940 Fax: +353(0)1 4027941 E-mail: John.Colreavy@dit.ie</p>
<p>Prof. Claudio Minero (Italy)</p>	<p>Department of Analytical Chemistry University of Torino Via Pietro Giuria 5 I-10125 Torino, Italy Tel: +39 011 670 7632 Fax: +39 011 670 7615 E-mail: claudio.minero@unito.it</p>
<p>Dr. Jose Carlos Conesa (Spain)</p>	<p>Institute of Catalysis and Petrochemistry Spanish Council for Scientific Research (CSIC)</p>

	<p>Campus de Cantoblanco 28049-Madrid, Spain Tel: +34 91-5855475 Fax: +34 91-5854760 E-mail: jconesa@icp.csic.es</p>
<p>Dr. John Kiwi Dr. Cesar Pulgarin (Switzerland)</p>	<p>Laboratory for Environmental Biotechnology Swiss Federal Institute of Technology EPFL-ISTE/LBE CH C3435 (Batiment CH) Station 6 CH-1015 Lausanne, Switzerland Tel: +41 21 693 47 20 Fax: +41 21 693 47 22 E-mail: john.kiwi@epfl.ch E-mail: Cesar.Pulgarin@epfl.ch</p>
<p>Prof. Peter Robertson (United Kingdom)</p>	<p>The Robert Gordon University Faculty of Design & Technology Clarke Building, Schoolhill Aberdeen AB10 1FR, United Kingdom Tel: +44 1224 262352 Fax: +44 1224 262222 E-mail: peter.robertson@rgu.ac.uk</p>
<p>Assoc. Prof. Dr. Aydin Dogan (Turkey)</p>	<p>Anadolu University Faculty of Engineering and Architecture Materials Science and Engineering Department 26470 Eskisehir, Turkey Tel: +90 (222) 321 3550 / 6306 Fax: +90 222 323 9501 E-mail: adogan@anadolu.edu.tr</p>

