

AP10 Advanced Materials and Nanotechnology **Supported graphene films** (nanoelectronic and sensoristic applications)



Engineering, ICT and Technologies for Energy and Trasportation Department

- 1) Graphene/Ni(111), pristine, defected, N-doped:
- Synthesis by C2H4 dehydrogenation in UHV
- Characterization and reactivity towards CO







Firb2012: Futuro in ricerca



2) Graphene/Cu

- Synthesis by C60 SuMBD at 35eV

- Cage opening and formation of defected but homogeneous single layer graphene









AP10 Advanced Materials and Nanotechnology SiC as material for nanomedicine



1) SiC/SiO₂ NWs as promising biomimetic biomaterial for implantable prosthetic devices. Core/shell NWs may be suitable for tissue regeneration.

Cells adhesion and proliferation on NWs



L929 cells (96h culture)



Project funded by the Swiss foundation ITI

2) X-Ray induced photodynamic therapy for deep solid tumours treatments

H2TPACPP-functionalised nanowires and radiation on A549 cells.





Linac Varian DHX @ Parma Hospital 2° step : Irradiation



A549 cells: viability after 24, 48 and 96 hours. Cells appear elongated and spread, as typical of healthy cells.



Project funded by US National Institute of Health



AP10 Advanced Materials and Nanotechnology Nanomaterials for energy applications



I-ZEB project (Terzo Accordo–Quadro CNR-Regione Lombardia 2017-2018, n° 19366/RCC, 10/01/2017) IFP value of research project 186 keuro (funding 50%)

IFP activity: development of advanced semiconductor materials (thin films, textured coatings) for low power electronics with a focus on renewable energy.

Status of task: development of inorganic photocatalysts \rightarrow bismuth vanadate coatings (BiVO₄) were produced by plasma sputtering deposition technology using a Ar/O₂ mixture.

Targets: V and Bi₂O₃, Substrates: Si, glass, Al, Ti, FTO. Coating thickness range 400 - 600 nm. Deposition temperature: RT, post-annealing at 400°C for 2 hours.

To identify a suitable stoichiometry of coatings the power supplied to Bi_2O_3 target was changed in the range 15-30 W. The correct stoichiometry was found at 20 W, EDS measurements (in collaboration with ICMATE Milano) showed an atomic % for Bi, V and O of 16.9, 16.7 and 66.3, respectively (\approx 1:1:4).





SEM (ICMATE Milano Lab.)The coating shows a dense, uniform and smooth structure.



UV-Vis diffuse reflectance spectra: energy gap estimated 2.46 eV, according to the literature values.



AP10 Advanced Materials and Nanotechnology Nanomaterials for Energy Applications: development of advanced semiconductor materials



Photograph of BiVO₄ coatings as a function of the power supplied to Bi_2O_3 target. The deposition area is 2 cm x 7 cm.



In progress \rightarrow BiVO₄ photocurrent measurements

- \rightarrow BiVO₄/WO₃ heterojunction produced by plasma
- \rightarrow BiVO₄/WO₃ heterojunction characterization



AP10 Advanced Materials and Nanotechnology Nanomaterials for industrial devices and processes



Greencoat project 2017 (industrial task Prot. 751, 20-4-2017), IFP value of research project 10 keuro.

IFP activity: Plasma deposition of top-coatings on metal substrates to increase the surface hardness and corrosion resistance.

Status of task: organosilicon monomers (SiOxCyHz) are good process precursors for the deposition of protective coatings both anti-corrosion and anti-scratch on metal substrates. By a Plasma Enhanced Chemical Vapour Deposition (PECVD) process, it is possible to produce on the metal surface an optically transparent layer of a few nanometers of thickness with the desired characteristics. For this research activity, an appropriate layer was produced using hexamethyldisiloxane as monomer with dilution in oxygen. The deposited coating on the metal surface showed a high chemical stability, properties of water repellency and surface hardness.

Ellegi project 2017 (industrial task Prot. 1469, 26-07-2017), IFP value of research project 12 keuro.

IFP activity: Plasma deposition of hexamethyldisiloxane-based coatings to facilitate the sliding of plastic components on conveyor belts.

Status of task: for this research activity, an appropriate layer was produced using hexamethyldisiloxane as monomer with dilution in oxygen. The deposited coating on the surface of plastic components showed a good property of sliding.



AP10 Advanced Materials and Nanotechnology Nanomaterials for bio-medical applications



Topic sterilization/decontamination of materials by plasma methods

The plasma can be used as an efficient tool to sterilize and decontaminate surfaces without damaging them, or can be used to produce surfaces with bactericidal activity.

 Task sterilization/decontamination → low or high pressure plasmas produce oxidative sterilization/decontamination at low temperature to be used for example for medical devices and surgical instruments. On this topic, IFP obtained a project (industrial task Kenosistec Prot. 63, 22-01-2018, value of the project ~10 keuro)

IFP activity: study of low pressure plasma processes to sterilize and decontaminate inorganic compounds inoculated with different microorganisms.

Status of task: plasma processes are in progress on Bacillus stearothermophilus, Staphylococcus aureus and Candida.

Task surfaces with bactericidal activity → studying the natural bactericidal activity (due to nano-texture) of the surface
of some insects, the plasma has been used to treat the surface of different materials in order to mimic this nanotexture. Plasma treated surface inoculated with E. Coli and B. Cereus microorganisms confirmed the bactericidal
mechanism.



AP10 Advanced Materials and Nanotechnology



Istituto per le Applicazioni del Calcolo "M. Picone" - CNR



Council



2018-2022



AP10 Advanced Materials and Nanotechnology



Istituto per le Applicazioni del Calcolo "M. Picone"

Diffusion problems from a polymeric platform for drug delivery

A coupled two-layer model for drug releasing systems







Drug release from a composite spherical nano-capsule



AP10 Advanced Materials and Nanotechnology Nanomaterials for solid oxide fuel cells



Engineering, ICT and Technologies for Energy and Trasportation Department

Objective:

• SOFCs are based on *ceramic materials* and operate at high temperatures between 800-1000°C.

- •The challenges in this sector are regarding the *reduction of the operation temperature* and the direct utilization of hydrocarbons.
- This will allow to decrease degradation and make the device cost-effective by system simplification (reduced fuel processing) and use of cheap ferritic steel interconnectors.

Approach:

• The approach is to develop ceramic electrolytes for intermediate temperature operation based on ceria and gallates, use a multifunctional electrocatalytic layer at the anode to favour internal fuel processing and tailor the composition of the perovskite cathodes to speed-up the oxygen reduction process



CNR-ITAE

• The new materials and cell architectures have been validated for the direct oxidation of hydrocarbons such as methane, ethanol, bio-gas, propane, reformed diesel etc. in systems up to 2 kW power



CNR-ITAE

NR-ITA

[•] Tecnologie ad alta Efficienza per la Sostenibilità Energetica ed ambientale On-board (TESEO) Progetto PON2_00153_2939517.

[•] Intermediate temperature solid oxide fuel cells fed by bio-fuels (BIOITSOFC) prot. 2010KHLKFC. (*PRIN*)



IMPAC

- Improved Durability and Cost-Effective Components for New Generation Direct Methanol Fuel Cells.
- Improved Lifetime of Automotive Application Fuel Cells with ultra low Pt-loading.



AP10 Advanced Materials and Nanotechnology

ADVANCED MATERIALS FOR HYDROGEN GENERATION BY PEM ELECTROLYSIS



Next generation water electrolysers must achieve a good dynamic behaviour (rapid start-up, fast response, wider load and temperature ranges) to provide proper grid-balancing services and thus address the increase of intermittent renewables interfaced to the grid.

Enhanced performance and cost-effective materials for long-term operation of PEM water electrolysers in combination with renewable power sources are developed at ITAE. The aim is to contribute to the road-map addressing the achievement of a wide scale decentralised hydrogen production infrastructure.



http://electrohypem.eu

http://www.hpem2gas.eu



AP10 Advanced Materials and Nanotechnology Hydrogen Storage Advanced Materials

AIM: The main focus is the development of new materials for Solid State H_2 storage, having low cost, simple synthesis, no sensitivity to air, H_2 storage value comparable to commercial material in non drastic T and P conditions



Volumetric analyses revealed a good H_2 sorption (~3wt%) value in particular at non drastic conditions (40bar 50° C)



cnr



AP10 Advanced Materials and Nanotechnology Advanced Materials for electrochemical devices and purification systems



1. Membranes for electrochemical systems (PEFC, AMFC, EHC, VRFB, Super-Cap)



- against 85% for N115
- ✓ Selectivity to ions V⁴⁺ di 49·10⁶ S·s·cm⁻³ against 6·10⁶ S·s·cm⁻³



- ✓ Specific capacity (123F/g) higher than reference porous separator
- ✓ Stability of 20000 cycles at 2A/g

2. Membranes for pH and metals optical sensors



Composite Nafion and s-PEEK with porphyrins 1.5



3. Membranes for waste water purification systems



PSF PVDF

 \triangleright PP

➢ PEEK

4. Membranes for Liquid Desiccant and dehumidification systems



Asymmetric membranes based on: PP, PVDF, PSF, PVA







Vanadium Redox Flow Battery (VRFB) Activity

Materials and Stack Design Optimization to improve electrochemical parameters and reduce technology costs

- Electrode materials synthesis by electrospinning tecnique
- Electrochemical characterizations from single cell up to kW stack
- Stack design and development
- Electrochemical model development
- Cell and stack fluid dynamic studies

DANGER HIGH VOLTAGE

60000 VDC

INARI





1 kW VRFB Stack





AP10 Advanced Materials and Nanotechnology

Nanomaterials for metal-air batteries

Based on the electrochemical reaction of a metal (Fe, negative electrode) with oxygen from atmospheric air (positive electrode)

$$O_2 + 2Fe + 2H_2O \xrightarrow[charge]{discharge} 2Fe(OH)_2$$

$$3Fe(OH)_2 + \frac{1}{2}O_2 \xrightarrow[charge]{discharge} Fe_3O_4 + 3H_2O$$

- Materials for the positive electrode (air):
 - Noble metal catalysts: Pd/C (sulphite complex route)
 - Cost-effective materials: Perovskites (La_{0.6}Sr_{0.4}Fe_{0.8}Co_{0.2}O₃)
- Materials for the negative electrode (Fe):
 - Fe₂O₃/C + sulphide additives (synthesized by several methods: colloidal routes, both organic and inorganic, salt fusion method).
- Alternative supports (more resistant to corrosion):
 - Carbon nanofibers (CNFs)
 - Ti-suboxide



















Development and Validation of an Innovative Solar Compact Selective-Water-Sorbent-Based Heating System — SWS-HEATING

Aim:

The SWS-Heating project will develop an innovative seasonal thermal energy storage unit based on a *novel composite sorbent material* and creative multi-modular configuration.





The SWS-Heating project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement N° 764025.



AP10 Advanced Materials and Nanotechnology Activated Bio-Char



Biomass





Carbonization

Bio-Char Activation Porous Bio-Char





Pyrolysis of local residual biomass to produce activated carbon (bio-char) with a high surface area and remarkable CO₂ adsorption properties

Beached seaweed (Posidonia Oceanica)





Elemental Analysis (wt%)									
	С	Н	Ν	0	O/C				
Biomass (Posidonia Oc.)	40.3	5.7	1.1	25.6	0.64				
Activated Bio-Char	92.7	2.1	0.6	4.6	0.05				

Bio-char Adsorption-Desorption measurements					
Surface Area m ² /g	2938				
Adsorbed CO ₂ mmol/g	4.8				
Pore volume cm ³ /g	0.91				
Horvath Kawazoe Median pore width nm	1.16				

SEM Analysis









AP10 Advanced Materials and Nanotechnology Nanohybrid materials for the production of DME via CO₂ hydrogenation







Structured catalysts with enhanced transport and surface to volume ratio properties for the development of intensified reactors for catalytic conversion of CO_2 into usable fuels and chemicals (methanation case)



Cordierite Structured support 500 CPSI

Channel	Wall	Bed	Bed	Open	Geometric
Inner Size	thickness	density	porosity	frontal	surface area
d _p (mm)	t (mm)	(kg/m³)	(%)	area ε	GSA (cm²/cm³)
0.83	0.32	771	72.5	0.52	25.29

■ MO-B catalyst allowed saving about 40-50% of catalyst employed in packed-bed system. **High surface-to-volume ratio** and **good interphase mass transfer** were able to ensure high methanation activity with low amount of catalytic phase.

 \Box CH₄ productivity increased by increasing space velocity, reaching the maximum at 400°C and 50,000 h⁻¹: **10.7** L_{CH4}/g h.

Future perspective

- Advanced materials for catalytic conversion of CO₂ into usable fuels and chemicals are needed to scaling down the conventional processes for small-scale application and integration with distributed renewable energy production.

- New environmental friendly and competitive cost solutions for power plants and carbon-intensive industry, new markets and job creation for innovative industrial sectors



Catalyst loading: 0.5 g/cm³ (60% of packed bed)

□ Well uniform and high-resistance coated layers

Adhesion tests results, pointed out *good resistance* of the coated layers, with negligible weight loss (0.3-0.5%) after two sonication baths.







2.1 Advanced materials for industrial processes

Development of sustainable methods for machining **Ti alloys and Inconel** materials for aeronautic and aerospace applications: replacement of conventional lubrorefrigerants, with reduction of environmental impact.

Wear and friction properties of materials for mechanical applications (main focus on **brake systems**): redesign of pads materials, for environmental impact reduction.

Detail oxide nanomaterials for gas sensing: early detection and monitoring of poisonous and hazardous chemicals, allow advancing on environmental security and healthcare.





2.2 Enhanced materials and nanotechnologies for energy and environment

Oxidic nanostructures embedded into a polymer for flexible, versatile coatings of easy fabrication and low environmental impact for application in renewable/alternative energy technologies: use of wasted mechanical energy, energy consumption and carbon emissions reduction



2.3 Advanced materials and nanotechnologies for bio-medical use

Nanocomposite materials (oxide-polymer) for biomedical applications, endowed with reduced rigidity compared to metals and ceramics, with enhanced osseointegration properties with respect to polymers: cost reduction compared to commercially available materials.





AP10 Advanced Materials and Nanotechnology Low-Dimensional materials: quantum and 2D



- ♦ advanced synthesis
- hanoscale characterization
- ♦ material modelling



control over the fundamental quantum-mechanical properties of materials

2D MoS₂: promising candidate for transistors, memory devices, photodetectors, solar cells, electrocatalysts for HER, lithium ion batteries.

Synthesized by Ion Jet Deposition (IJD)

Synthesized by Chemical Vapor Deposition (CVD)



Advanced synthesis in vacuum: no need for post-deposition treatments





AP10 Advanced Materials and Nanotechnology Low-Dimensional materials: quantum and 2D



 Graphene nanoribbons and C-based nanostructures: suitably designed precursor molecules determine different structures and different electronic properties.



Graphene nanoribbons produced by surface assisted polymerization of di-bromopyerene





Corrugated C-nanostructures produced by surface assisted polymerization of Bromo-corannulene

 Epitaxial semiconductor Quantum Dots: 0-dymensional systems integrated into a semiconductor platform for the realization of electro-optical devices as QD lasers, QD single photon emitters, QD sensors.

Molecular Beam Epitaxy of InGaAs-based nanoislands:



AFM: QD ensamble



HR-TEM: single QD



properties dependent on surface states: molecular sensor



optical emission at **telecom** wavelength: lasers / single-photon emitters



AP10 Advanced Materials and Nanotechnology Electronic Materials

High band-gap semiconductor for high power electronics UV detection and quantum photonics



3C-SiC as an emerging material for quantum photonics Single photon emission Optical resonant microstructures



Ga2O3 as an emerging material for power devices Development of e-Ga2O3 epitaxy by Vapor Phase Epitaxy Material characterization (structural, optical, electrical) Device prototyping (realized: UV-photodetector)





mm-long rolled-up semiconductor µicrotubes with nmthin walls



applications as µfluidics channels for sensing, photonic integrated compononents, catalytic µicrotubular engines



AP10 Advanced Materials and Nanotechnology Electronic Materials



Metal oxide nanostructures



Mesoporous ZnO nanobelts and by thermal decomposition of ZnS(en)0.5 precursors



ZnO nanorods





fiber by wet chemistry

voltage

ZnOnanorods-based

piezosensor



ZnO tetrapods by vapor phase

CdZnTe-based X- and gamma-ray detectors



CdZnTe is the best material for room temperature operating, spectroscopic x- and gamma- ray detectors

XDRONE



materials





32000 pixels imaging detector

²⁴¹Am Spectrum Experimental Acquisition



Linear array detectors for X-ray scanners



AP10 Advanced Materials and Nanotechnology Advanced catalysts and materials for sustainable chemistry and energy





Development of novel and advanced materials/catalysts for process intensification and/or new alternative processes compared to traditional ones.

- Formulation of new materials with chemical and physical properties and functionalities tailored for specific applications
- Lowering costs and enhancing performances of currently used materials
- Development of properties of resistance to severe operating conditions
- Toxicity mitigation of common materials



AP10 Advanced Materials and Nanotechnology Advanced catalysts and materials for sustainable chemistry and energy



From combustion pollutants and raw materials and precursor to engineered materials





AP10 Advanced Materials and Nanotechnology Advanced catalysts and materials for sustainable chemistry and energy



Heterogeneous Catalysis for Energy & Environment





AP10 Advanced Materials and Nanotechnology Magnetic materials and multiferroics





RawMaterials



694 692 690 688 6 Binding Energy (eV)

Intensity (a.u.)



AP10 Advanced Materials and Nanotechnology Organic & Hybrid materials





SQUARE ASSEMBLY



FLOWER ASSEMBLY



Aminoacid Glutamate self-assembly on Ag(100) surface. Biosensing, biomedicals





AP10 Advanced Materials and Nanotechnology NANOFLUIDS



Engineering, ICT and Technologies for Energy and Trasportation Department

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WHAT ARE NANOFLUIDS?

- \geq COLLOIDAL SUSPENSIONS OF NANOPARTICLES IN COMMON FLUIDS
 - BASE FLUIDS: water, oil, ethylene glycol, refrigerants
 - NANOPARTICLES: oxides (ceramics), metals, carbon nanotubes



MAIN ACTIVITIES

- THERMOPHYSICAL PROPERTIES MEASUREMENTS
 - colloidal suspension stability
 - transport properties (λ , μ , α)
- TRIBOLOGICAL PROPERTIES MEASUREMENTS
 - evaluation of anti-friction and anti-wear properties ٠
- PERFORMANCE EVALUATION IN ENERGY SYSTEMS

POTENTIAL APPLICATIONS

HVAC&R DEVICES

- domestic refrigerators
- residential air conditioning units
- compressor lubrication



COOLING SOLAR COLLECTORS

- flat plate ٠
- direct absorption (DAC)
- evacuated tubular



HEAT PIPES

- heat pipe for CPU cooling
- screen mesh heat pipe
- flat plate heat pipe

PEM FUEL CELLS



- PEM FUEL CELL COOLING SYSTEMS
 - domestic refrigerators •
 - residential air conditioning units
 - compressor lubrication





AP10 Advanced Materials and Nanotechnology Advanced Activity Measurement of Photocatalytic Materials



Engineering, ICT and Technologies for Energy and Trasportation Department

HETEROGENEOUS PHOTOCATALYSIS

CHEMICAL REACTIONS CATALYZED BY LIGHT AND (NANOCRYSTALLINE) SOLID PHOTOCATALYSTS

- Oxidation and reduction processes of organic and inorganic species in air and water
- Needs of specific instruments for the study of photocatalytic materials performance



PHOTOCATALYTIC SAMPLE SUPPLY AIR PROCESSED

MAIN ACTIVITIES

DEVELOPMENT OF SPECIALIZED ANALYTICAL SYSTEMS FOR PHOTOCATALYTIC ACTIVITY MEASUREMENTS

 Advanced measurement of photocatalytic air depollution with a state-of-the-art, specifically developed analytical system

 Activity studies of nanostructured photocatalysts in air and water for special photocatalytic materials development

 Study of water-based photocatalytic oxidation processes of natural products



POSSIBLE APPLICATIONS

DEVELOPMENT OF HIGH EFFICIENCY PHOTOCATALYSTS OPERATING IN UV AND VISIBLE LIGHT

- Air and water depollution by special photocatalytic materials
- Photocatalysis-based advanced oxidation processes (AOP) for waste water

treatments

Water-based and solar driven chemical processes for sustainable chemistry

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AP10 Advanced Materials and Nanotechnology Materials for photonic sensing



Plasmonic substrates for rapid surface enhanced Raman detection of proteins, hormones, DNAs, disease biomarkers in trace amounts in biological fluids. [Coordinator: P. Matteini; Ref: *Sci. Rep.* **8** 1033 (2018)]

Photonic components, such as:

Whispering gallery mode resonators as transducers for the detection of analytes of biomed interest [Coordinator: S. Pelli] or broadband ultrasound [Coordinator: S. Soria]
Optical fiber nanotips for intracellular sensing and monitoring of the effect of new drugs [Coordinator: S. Pelli, Ref: US PATENT pending]





AP10 Advanced Materials and Nanotechnology Materials for photonic theranostics



Consiglio Nazionale delle Ricerche Engineering, ICT and Technologies for Energy and Trasportation Department

Hybrid particles for intracellular delivery of DNA probes, such as so-called molecular beacons, which acts as theranostic agents capable to sense and to silence m-RNA [Coordinator: A. Giannetti; Ref: J. Contr. Release, 280, 76 (2018); Biosens Bioelectron, 88, 15, (2017)]

Bionic contrast agents for photo-acoustics/ thermics in association with biomolecular ligands or cellular vehicles, i.e. autologous cells that constitutively migrate to a tumor microenvironment [Coordinator: F. Ratto; Ref: Adv. Funct. Mater. 26, 7178 (2016)]

Optically responsive patches for welding of connective tissue and controlled drug release [Coordinator: P. Matteini; Ref: PATENT US2015086608]





materials

Alginate

Graphene oxide/alginate hydrogel

for articular cartilage regeneration

AP10 Advanced Materials and Nanotechnology Tissue Engineering



Consiglio Nazionale delle Ricerche Engineering, ICT and Technologies for Energy and Trasportation Department

> AFM images of biomimetic substrates functionalized with graphene's derived nanomaterials

05 cm **Biomimetic Nanomaterials** scaffolds design functionalization and development 0.48 µm D Histological Cell adhesion sections over scaffolds representing functionalized **Cell Biology** cartilage matrix with deposition graphene's of human derived mesenchymal nanomaterials stem cells for bone cultured within the Alginate regeneration Graphene oxide/