Comunicazioni

Orali

Simulazione Atomistica dello Stadio di Nucleazione Dell'aggregazione in Soluzione di Ciclodestrine Anfifiliche

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ABSTRACT

Simulazioni atomistiche di dinamica molecolare permettono di descrivere lo stadio di nucleazione nella formazione di micelle di molecole anfifiliche come le ciclodestrine chimicamente modificate.

Keywords: Simulazioni, dinamica molecolare, ciclodestrine, aggregazione, micelle

L'aggregazione supramolecolare è un fenomeno importante determinato sia dalle interazioni molecolari (mediate dal solvente), sia dalla forma delle molecole, che porta alla formazione di mesofasi non covalenti come micelle, vescicole, membrane o cristalli liquidi [1]. In soluzione, le interazioni non covalenti fra ciclodestrine native o chimicamente modificate sono cruciali per lo stadio di nucleazione dell'aggregazione che porta a queste mesofasi. Questi fattori sono importanti per ottenere un impaccamento ordinato allo stato solido, ma anche per produrre disposizioni ordinate in soluzione. Studi teorici basati su metodi atomistici di dinamica molecolare in un approccio "bottom up" come quello proposto qui forniscono dati importanti sulla formazione degli aggregati iniziali formati da molecole singole in un quadro sempre più complesso.

Ciclodestrine anfifiliche (aCD), modificate chimicamente con gruppi idrofobici e gruppi polari ai bordi opposti, possono formare diversi aggregati supramolecolari a seconda dei sostituenti [2,3]. Qui riportiamo uno studio atomistico di dinamica molecolare [4,5] dell'aggregazione di un numero crescente di molecole, fino a otto, con gruppi idrofobici tioalchili e gruppi idrofilici di glicol etilene a bordi opposti, considerando l'energia di interazione e la geometria dell'aggregato e focalizzandosi sullo stadio iniziale di nucleazione in un solvente apolare ed in acqua [6]. La coesistenza prevista di molecole isolate e di piccole micelle ed aggregati è consistente con quanto osservato sperimentalmente, suggerendo che questi aggregati formino anche Il nucleo per la crescita di aggregati più grandi. Questo studio può quindi aprire nuove prospettive nella progettazione degli aggregati e per la correlazione delle strutture con le proprietà farmaceutiche.

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Identification and Spatial Distribution of Putative Markers in Human Inflamed And Precancerous Colon Tissues Using Cluster Secondary Ion Mass Spectrometry and Multivariate Analysis

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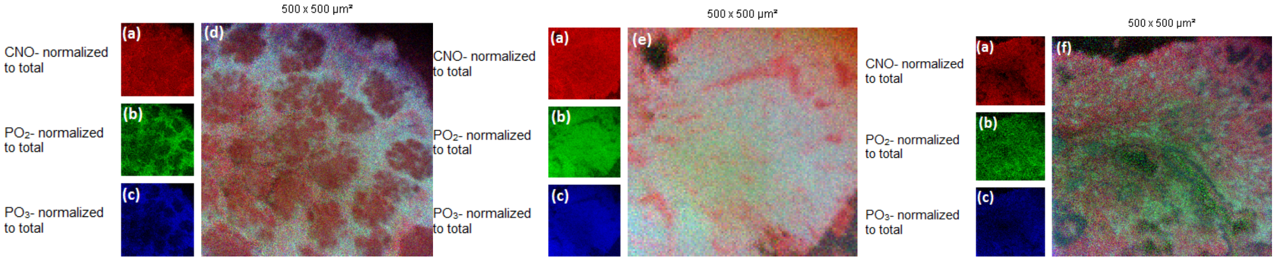
Keywords: Inflammatory bowel disease, ToF-SIMS, multivariate analysis, clustering analysis.

ABSTRACT

Colorectal cancer is one of the most prevalent and fatal cancers that causes a relevant number of mortalities worldwide. It is well known that cancer metabolism differs from that of normal tissue. As with many other cancer types also in this case a small number of markers has been identified. However, little has been reported in literature regarding the direct comparison between the inflamed and precancerous colon tissues. In fact, to prevent the development of tumour, the chemical differences between normal, inflamed and precancerous colon tissues play an important role on the knowledge of colon cancer progression. ToF-SIMS is a highly sensitive surface characterization technique that allows detecting many molecular fragments with high mass resolution such as amino acids and lipids, providing elemental and molecular surface chemical information.

We obtained intestinal mucosal samples from healthy, inflammed and dysplastic (pre-neoplastic) area during diagnostic colonoscopy. Biopsies were snap frozen and then fixed. Inorganic ions and low molecular weight fragments from biomolecules such as proteins and lipids have been identified and localized in order to evaluate the differences between human normal, inflamed and precancer (dysplasia) colon tissues. However, because of the complexity of the ToF-SIMS data we have employed clustering and multivariate analysis to reduce the size of large data sets with minimal loss of information and data noise decrease. Multivariate analysis allows to discriminate which of the molecular fragments differentiate several samples, thus giving information about the chemical modifications among different disease stage.



Normal Inflamed precancer

Figure 1: (a) CNO^- (peptide backbone, red), (b) PO_2^- (phosphate, green), (c) PO_3^- (phosphate, blue), (d) RGB overlay of normal colon tissue, (e) RGB overlay of inflamed colon tissue and (f) RGB overlay precancer colon tissue;

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New Technologies to Study the Interplay between Cancer Stem Cells and the Immune System

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ABSTRACT

The understanding of the interplay between tumor cells and the immune system mandates for new technologies enabling the description of macrophages polarization kinetics. Combining microfluidics with 3D cell culture technologies, it is possible to recapitulate the tumor milieu, offering new in vitro tools for cancer immunology research [1].

Keywords: microfluidics, 3D cell culture, cancer stem cells, immune system

Cancer stem cells (CSCs) play a critical role in the progression and chemoresistance of neoplastic diseases, which are only in part due to genetic or epigenetic modifications, and are conversely attributable to the interplay between CSCs and tumor-associated macrophages (TAMs). Although possessing high cytotoxic and antitumor activity when they express M1 polarization, TAMs are “hijacked” by tumor cells to acquire a M2 polarization, which, on the contrary, helps to preserve stemness features of cancer cells [2]. The full understanding of CSC/TAM interplay mandates for novel technologies enabling the in vitro recapitulation of the tumor microenvironment.

A robust and reproducible model for obtaining CSC-enriched cancer cell populations was optimized using either ultra-low adhesion plasticware or hydrogel formulations. Additionally, a microfluidic platform was developed to merge 3D culture protocols with accurate control over fluid-dynamic parameters, for the establishment of cell-cell interaction phenomena. The device, fabricated by soft-lithography, features a main chamber for the culture of CSCs in 3D micromass arrangement (tumorsphere) and side channels for the injection of TAMs. Micro-channel barriers separate the main chamber from the lateral ones, performing: *i)* the confinement of the gel; *ii)* the control over TAMs migration; *iii)* the control over diffusion-based mass-transport phenomena (Figure 1). The chip facilitates seeding and long-term culturing procedures; at the same time, it guarantees high reproducibility and precise quantification of the morphological and kinetic data at the single cell level (Figure 2).

Taking advantage of genetic engineering technologies, it was possible to obtain a standardized TAM model in which the M1/M2 polarization switch is accompanied by differential fluorescence emission, corresponding to different interleukin profiles. The use of the engineered TAMs within the microfluidic platform paves the way to real-time live cell imaging of the complex interplay between the tumor and the immune system.

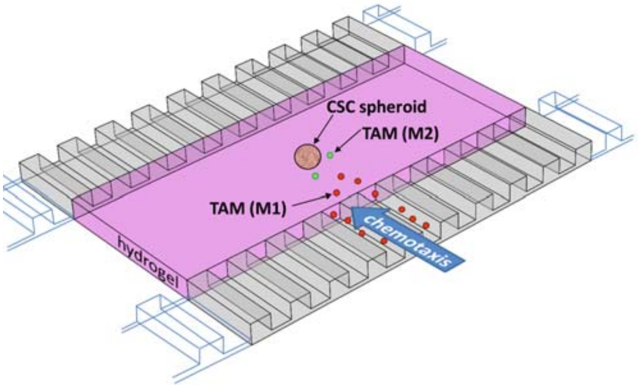

Figure 1: Working principle of the microfluidic device.

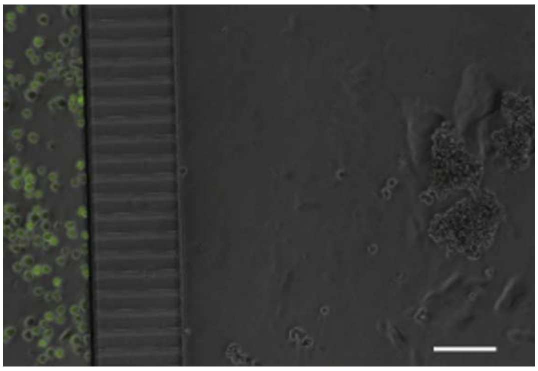

Figure 2: Co-culture of FITC-labelled TAMs and tumorspheres within the microfluidic device.

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Nanotechnology, Metals and Biomolecules: Applications of Au and Ag Nanoparticles as Sensors in Biomedicine.

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ABSTRACT

Nanoparticles in general, and in particular metal nanoparticles are among the most widely investigated systems within nanotechnology, their applications ranging from catalysis to drug delivery, from photothermal therapy to sensing [1]. Coming in a variety of shapes and dimensions, metal nanoparticles showed to be versatile, cheap and easy to synthesize, compared to bottom-down methods for creating nanostructured metal substrates.

A distinctive property of metal nanoparticles, especially in case of Au and Ag, is the occurrence of surface plasmons, i.e. coherent oscillations of surface electrons, whose frequencies fall in the visible or near-infrared region of the spectrum. Such plasmonic properties can be exploited, in Surface-Enhanced Raman Spectroscopy (SERS), for the intensity amplification of Raman spectra, a sort of molecular fingerprints with a high potential for chemical analysis, but otherwise very weak in intensity [2]. Thus, SERS can give us information about the adsorption of specific analytes on the nanoparticles surface, for sensing applications, as well as about the very nature of the biomolecule-nanoparticle interaction.

In this communication, we outline several examples out of our own work, in which metal nanoparticles are used as SERS sensors in biofluids [3] (or their model solutions[4]) or cell cultures, for bio(analysis) and diagnosis, as well as for more fundamental studies about metalloproteins [5]. In all these applications, the chemical characteristics of both the nanoparticles surface and the medium in which they are dispersed will be discussed, as they turned out to be crucial issues for controlling nanoparticle-biomolecules interaction.

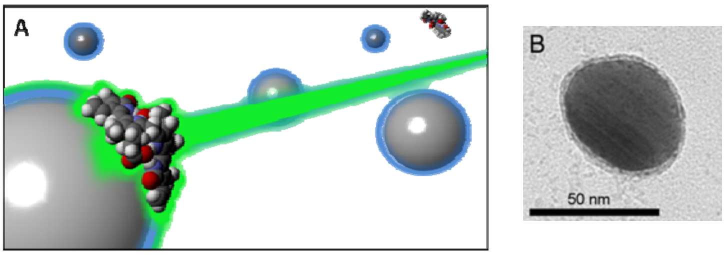

Figure 1: A) Schematic drawing depicting the SERS enhancement of an adsorbed molecule; B) a TEM image of a Ag nanoparticle coated with a layer of poly-L-lysine

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Preparation of Novel Hybrid Materials Containing Bioactive Compounds Embedded in Cardanol-Based Vesicular Nanodispersions

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ABSTRACT

Cardanol (CA) is a natural and renewable organic raw material obtained as the major by-product from the distillation of cashew nut shell liquid (CNSL). Thanks to its amphiphilic properties under alkaline conditions, was developed an environmental-friendly technology to produce engineered "green nanocarriers", without use of any organic solvents, in which CA acts as the solvent as well as being the main component of the nanodispersions.

Keywords: Green nanocarrier, Cardanol, Cholesterol, Lipophilic porphyrin, Chlorogenic acid, Cardanol-based vesicles, Natural renewable materials.

"Green" nanodispersions loaded with lipophilic or hydrophilic bioactive compounds have been produced, in which a high percentage or the entire system is derived from renewable "functional" molecules. The first example of a CA-based vesicles having an embedded lipophilic porphyrin itself peripherally functionalized with cardanol substituents (porphyrin-cardanol hybrid) was obtained [1]. Afterwards, CA-based vesicular nanodispersions have been used to encapsulate chlorogenic acids (CQAs),[2] a class of natural phenolic compounds extracted in water from two different rowanberries (*Sorbus Americana* and *Vaccinium* sp.). Stable, spherical, and regular vesicles were obtained in both the experiments (fig. 1).

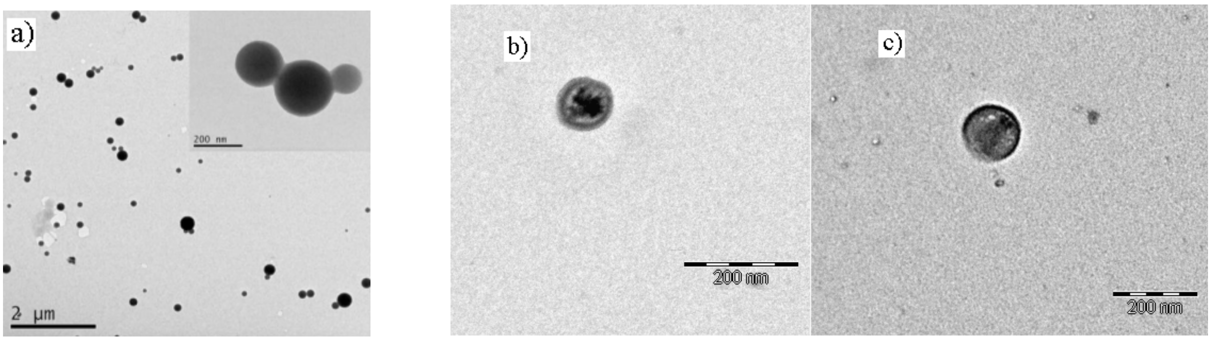
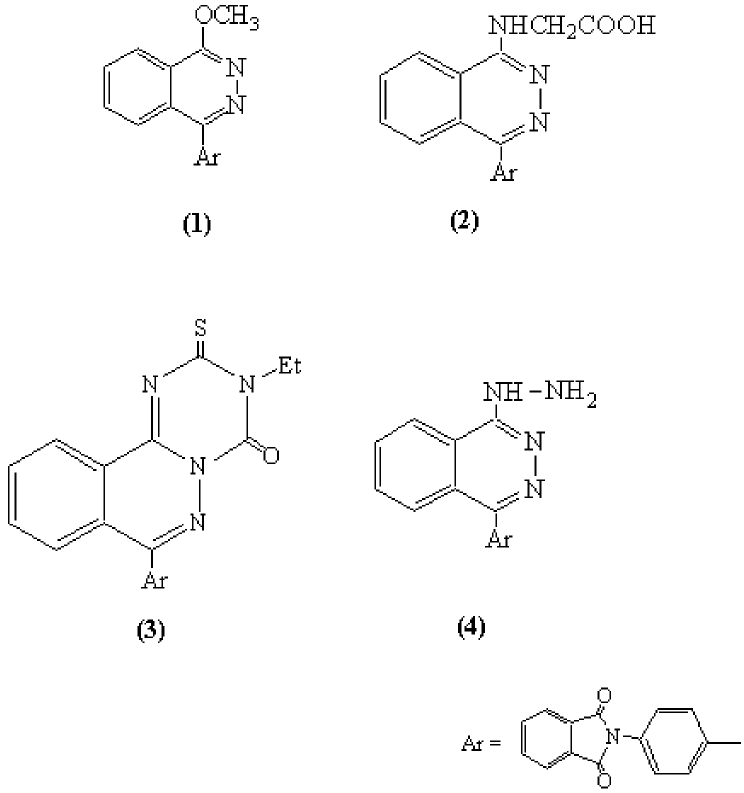


Figure 1: Transmission electron micrographs of CA-based vesicles embedded with: a) porphyrin-cardanol hybrid; b) *Sorbus Americana* extract; c) *Vaccinium* sp. extract.

Recent studies about the potential anticancer bioactivity of cardanol and cardol [3] encouraging us to develop new CA-based nanocarriers. Using a similar above-mentioned sustainable procedure, innovative nanovesicular systems CA-based have been prepared, loaded with a novel series of 1,4-

disubstituted phthalazine derivatives. On the other hand, also the heterocycles drawn in Figure 2 shown antitumor activity against MCF-7 cells showing potent cytotoxic effects.[4]



(1) (2) (3) (4)

Figure 2: (1): *2-[4-(4-Methoxyphthalazin-1-yl)-phenyl]-isoindole-1,3-dione;* **(2)**: *{4-[4-(1,3-Dioxo-1,3-dihydro-isoindol-2-yl)-phenyl]phthalazin-1-yl amino}-acetic acid;* **(3)**: *2-[4-(2-Ethyl-1-oxo-3-thioxo-2,3-dihydro-1H-2,4,10,10a-tetrazaphenanthren-9-yl)-phenyl]-isoindole-1,3-dione;* **(4)**: *2-[4-(4-Hydrazinophthalazin-1-yl)-phenyl]-isoindole-1,3-dione*

In this context, the preparation, characterization and antitumor activity of selected nanovesicles loaded with bioactive compounds will be discussed.

These findings can helpful to promote new pioneering researches such as novel “green” multifunctional anticancer tool based on nanocarrier technology.

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Spray-drying Synthesis of Pure Calcium Carbonate Nano-crystals as Anticancer Drugs Delivery Systems

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ABSTRACT

$CaCO_3$ Nano-Crystals synthesized by Spray Drying technology, have been developed as nano-carriers for anticancer drugs delivery, in order to knock down the systemic toxicity.

Keywords: Nano-$CaCO_3$, Spray-Drying, Drug Delivery

Inorganic nanoparticles are suitable for a wide range of biomedical applications in particular for drug delivery systems fabrication. In particular $CaCO_3$ is one of the most used material due its biocompatibility, bioabsorbability and the characteristic porous structure capable of trapping different bioactive compounds. The manipulation at the molecular level implies more advantageous chemical and physical characteristics than the normal size micro or macro structured materials. Several Nano-$CaCO_3$ synthetic procedures are disadvantageous providing very high temperatures (1000-1100°C), purification processes and use of surfactants [1]. We have developed a new synthesis method of $CaCO_3$ nano-crystals that provides aqueous reaction environment without organic additives and a fine control of instrument process parameters with potential scale-up. Our Spray Drying Technique produces $CaCO_3$ nano-crystals powder with defined morphology of squared (80nm X 80nm) or ellipsoidal particles (major diameter of 80-100 nm and minor diameter of 40-50 nm). Morphological characterization was obtained by TEM (figure1). Chemical characterization was determined by X-ray diffraction (XRD) analysis and Fourier transform infrared (FT-IR) spectroscopy. Nano-Crystals growth and nucleation in aqueous solutions was investigated by TEM images improving stabilization protocol and storage conditions of nano-$CaCO_3$. Their biocompatibility was established in different cancer cell lines with two nanoparticles concentrations through MTT test. Cellular uptake and intracellular localization were evaluated by Transmission electron microscope image of cancer cells showing the presence of nano-$CaCO_3$ mainly in the cytoplasm, in the nucleus and in the mitochondria.

We have developed the loading protocol of different metal-based anticancer drugs: Ag, Cu, Zn and Cis-Pt.

Nano-$CaCO_3$ functionalization with natural phospholipids is under study to improve cellular uptake and tune intracellular localization.

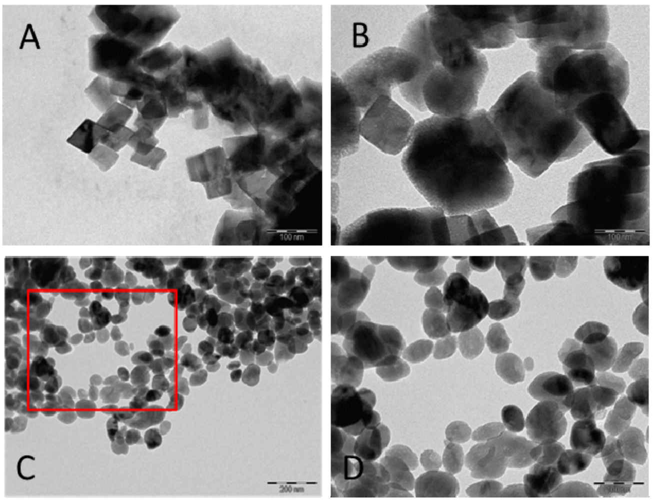

Figure 1. TEM characterization of squared $CaCO_3$ nanoparticles (A-B) and ellipsoidal $CaCO_3$ nanoparticles (C-D); in figure D is reported the magnification of previous image.

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Selective Binding of Calcium vs. Magnesium in Water by a Preorganized Metal Containing Receptor. Biological Activity of Selected Metal Complexes

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ABSTRACT

Keywords: maltol; alkaline earth; polyamines; metal complexes; DNA

Metal complexes are compounds that have ongoing important and even newer applications. For example metal complexes form the base of the most common receptor, finding multiple applications due to their intriguing properties. In this view, metal containing receptors are normally used to interact with anions or neutral species, exploiting the coordination properties of the metal center, although positively charged guests can also be hosted. In this case, the metal ion mainly serves to pre-organize the hosting area and is usually not directly involved in the interaction with the guest [1].

Recently, we developed a class of molecules based on two 3-hydroxy-2-methyl-4-pyrone units (Maltol) linked to a polyamine scaffold which exhibited anti-neoplastic activity *in vitro*. Two of these molecules, Malten and Maltonis, were further studied and characterized extending biological studies and activity also *in vivo* and they were also investigated as potential ligands for metal ions. Transition metal ions such as Cu(II) (for Malten) and Co(II) (for Maltonis) are stabilized by the polyamine functions and by the deprotonated hydroxyl oxygen atom of each maltol function. The involvement of both maltols in the coordination of the transition M(II) ion induces the formation of an electron-rich area by the four oxygen atoms of the two converging maltol units thus allowing the Cu-Malten and the Co-Maltonis metallo-receptors to bind hard metal ions [2].

In this contribution, which considers the Malten molecule and its biological activity, we extended the binding studies of the [Cu_{H-2}Malten] species as a metallo-receptor for positively charged species in water, examining the series of alkaline earth metal ions. Ultimately, we also investigated the biological potential of all of the, up to now, characterized metal complexes of Malten in terms of the ability to induce DNA structural alterations.

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Synthesis of Phenol by Means of Benzene Hydroxylation and Its Recovery in Membrane Contactors

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ABSTRACT

Two different three-compartment membrane contactors were tested in the synthesis and separation of phenol produced by direct hydroxylation of benzene using a Fenton reaction. Phenol produced in the aqueous reacting phase was extracted in the organic phase and simultaneously stripped in the basic aqueous phase. It was evidenced that the use of a third compartment containing an alkaline aqueous stripping phase permitted one to recover phenol at 100% purity.

Keywords: Phenol production, benzene hydroxylation, membrane contactors

Phenol is a very prominent chemical intermediate in industry. Nowadays it is industrially synthesized mainly by the cumene process, which presents many drawbacks, such as high energy consumption, because of multistep reactions, and the production of a large amount of acetone as by-product. On these bases, the search for new routes for phenol synthesis, as the direct hydroxylation of benzene, became more intensive in the past decade. Such a process presents various potential advantages compared to the traditional cumene process, but its selectivity is usually rather poor since phenol can be oxidized easier than benzene. The prompt removal of the produced phenol from the reacting environment represents a key point for developing such a method. On this regard, membranes can play an important role.

In our previous works [1, 2] we proposed the use of a biphasic membrane reactor, for the direct hydroxylation of benzene to phenol. A flat-sheet membrane separates an acidic aqueous phase (containing a Fe or V based catalyst and H_2O_2) and an organic phase (benzene). Benzene permeates across the membrane and reacts at the aqueous interface, while produced phenol permeates back and it is extracted into the organic phase, where it is protected by subsequent oxidations. Despite the high phenol selectivity (98%) in the organic phase, this system possesses some important drawbacks: over-oxidations with production of by-products (benzoquinone, biphenyl and tar in the reacting phase) by using Fe based catalyst or low system productivity by using V based catalysts.

Considering these results, in the present work the use of three phase membrane contactors has been tested in the one-step benzene hydroxylation to phenol. Two solid (SMC, Figure 1) or liquid (LMC, Figure 2) membranes separate three immiscible phases: the aqueous reacting phase and the organic (only benzene) phase (as in our previous work), plus a third basic aqueous phase acting as a stripping agent. Operating in this way, phenol extracted in the organic phase is simultaneously stripped in the alkaline aqueous phase [3], thus performing the process of product recovery.

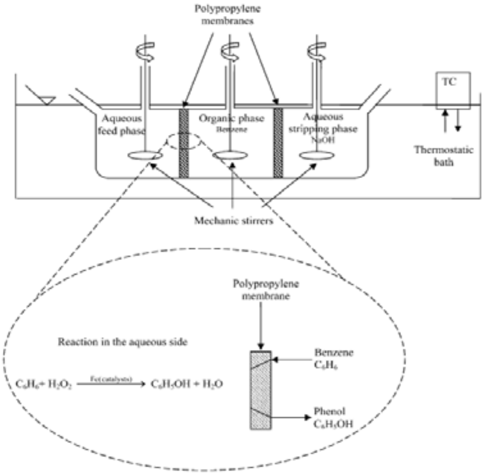

Figure 1: Scheme of the three phases SMC.

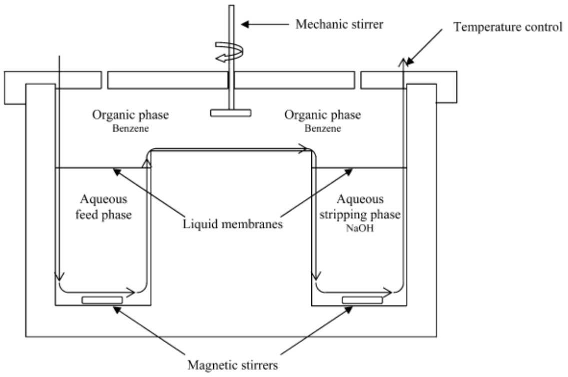

Figure 2: Scheme of the three phases LMC.

Preliminarily, mass-transport tests were carried out at 25 and 35 °C to determine the mass permeation flux of the two membrane contactor and the influence of salts dissolved in the aqueous feed phase. The obtained results evidenced better performances (86.5% of phenol recovered in the strip phase) using the SMC with 0.1 M Na_2SO_4 in the aqueous feed phase at 35 °C. Probably the worst condition of agitation of the organic phase in the case of LMC (to avoid phase mixing) is the principal cause of the observed performance.

In the catalytic tests, better results (phenol productivity 0.62 g_{ph} $gcat^{-1}$ h^{-1}) were obtained using the SMC containing 0.1 M Na_2SO_4 in the aqueous reacting phase (Table 1). These results can be explained thanks to the high phenol flux away from the reacting phase which permitted to extract a high amount of phenol in the organic and aqueous (strip) phases. The results evidenced that use of a third compartment, containing an alkaline aqueous stripping phase, permitted to perform simultaneously the process of phenol synthesis, recovery, purification (100% purity) and concentration.

Table 1. Summary of the results obtained in the catalytic tests (aqueous feed phase: pH 2.8 (0.19 mL acetic acid), 0.095 g iron(II) sulphate, NaCl or Na_2SO_4 0.1 M; organic phase: benzene; aqueous stripping phase: NaOH 0.1 M; T = 35°C; time = 240 minutes).

	NaCl		Na_2SO_4	
	SMC	LMC	SMC	LMC
$S_{ph,org}$ (%)	78.7	88.4	81.3	100
$S_{ph,strip}$ (%)	100	100	100	100
P_{ph} (g_{ph} g_{cat}^{-1} h^{-1})	0.32	0.06	0.62	0.21

$S_{ph,org}$: phenol selectivity in the organic phase; $S_{ph,strip}$: phenol selectivity in the strip phase; P_{ph}: phenol productivity.

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Riduzione Fotocatalitica di CO_2 in Presenza di Catalizzatori Compositi Gap/Tio_2

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ABSTRACT

In questo lavoro vengono riportati i risultati ottenuti nella riduzione fotocatalitica di CO_2 utilizzando fotocatalizzatori compositi GaP/TiO_2 preparati mediante mescolamento meccanico di campioni commerciali di GaP Aldrich e TiO_2 Evonik P25.

Keywords: Riduzione di CO_2, fotocatalisi, GaP, TiO_2

Il fosfuro di gallio "GaP" è un materiale semiconduttore con un valore di band gap pari a 2,3 eV che è stato usato principalmente nella fabbricazione di LED a basso costo ma è stato solo raramente usato come fotocatalizzatore perché la sua banda di valenza (VB) ha un potere ossidante basso. La posizione della sua banda di conduzione (CB), invece, è tale da poter consentire la riduzione di CO_2; infatti il suo potenziale è ca. 1.3 V più negativo di quello della coppia redox CO_2/CH_4. Nella riduzione fotocatalitica di CO_2, il GaP non è efficace da solo; infatti, nonostante gli elettroni della banda di conduzione del GaP siano in grado di ridurre il CO_2 a CH_4, la controparte ossidativa del processo non può essere soddisfatta in presenza di vapor d'acqua. Il vapore d'acqua che viene spesso scelto come trappola delle buche non può essere utilizzato perché il potenziale della (VB) del GaP non è in grado di ossidarlo a O_2. In questo lavoro sono riportati per la prima volta i risultati ottenuti nella riduzione fotocatalitica di CO_2 utilizzando dei materiali compositi formati da GaP e TiO_2, un fotoreattore batch in vetro Pyrex e una lampada allo Xenon da 1500 W. Sia il GaP che il TiO_2 puri sono risultati completamente inattivi, mentre i campioni compositi GaP/TiO_2 hanno dato luogo alla riduzione del CO_2 principalmente a CH_4. L'attività fotocatalitica dipende dalla quantità relativa tra il GaP e il TiO_2, con una formazione massima di CH_4 osservata per il campione GaP/TiO_2 1:10. Quantità maggiori o minori di GaP rispetto al rapporto 1:10 portano ad un abbassamento dell'attività fotocatalitica. L'attività fotocatalitica dei compositi può essere attribuita, a causa della posizione appropriata delle bande di valenza e di conduzione dei componenti, all'efficiente trasferimento di carica all'eterogiunzione tra il GaP e TiO_2. Questo fatto non solo consente la separazione efficiente delle coppie buca-elettone foto-prodotte, ma, come riportato in Figura 1, anche la riduzione del CO_2 (elettroni nella CB del GaP) e l'ossidazione di H_2O (buche nella VB del TiO_2). Concludendo, questi materiali compositi GaP/TiO_2 preparati in un modo molto semplice sembrano essere candidati promettenti per la riduzione di CO_2 in presenza di H_2O.

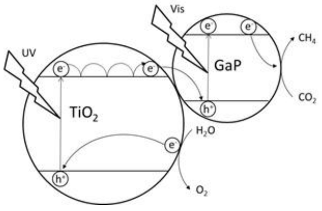

Figura 1: Schema di funzionamento dell'eterogiunzione GaP-TiO_2

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Functionalized Corroles: Structural Modifications for a Specific Application

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ABSTRACT

Corrole exhibits peculiar electronic and physical-chemical properties accounting for the increasing exploitation of such a macrocyle in several applicative fields. Its chemical versatily enables to modify quite as needed its molecular skeleton in view of a targeted practical scope. This work focuses on the peripheral functionalization of *meso*-triarylcorroles leading to potential compounds exploitable in various applications as sensors, catalysis, optoelectronics and material chemistry.

Keywords: Corroles, peripheral functionalization, expanded aromatic system, optoelectronic properties.

Corroles are tetrapyrrolic macrocycles belonging to the class of contracted porphyrins, since they lack one methine bridge compared with the parent porphyrin macrocycle. The chemistry of this macrocycle has experienced impressive advancements in the last decade; as matter of fact, the need to comply with the requirements of a specific application has prompted to corrole functionalizations, and nowadays both the meso-aryl and β-pyrrolic positions can be manipulated *ad hoc*[1] triggering their promising application in several fields, such as catalysis, medicine and material science.[2] In this context, we have been interested in the expansion of the π-aromatic system of this macrocycle, surmising a remarkable change in the optical features of the chromophore exploitable in photovoltaics devices, photodynamic therapy or chemical sensors. Among the available synthetic approaches, we carried out the structural elaboration of the corrole ring by Pd catalyzed C-C coupling reactions by the inserting alkynyl groups (Figure 1) or fusing aromatic rings on the β-positions. The main results of these studies will be presented and discussed in this contribution.

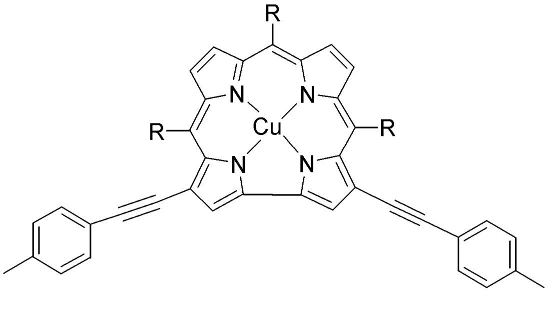

Figure 1: Example of corrole π-aromatic expansion by Sonogashira reaction.

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Porphyrin and Zn Oxide: A Marriage for Smart Chemical Sensors

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ABSTRACT

Porphyrins coated ZnO is an interesting material where the exposure to light and gas may cooperate to modulate the respective sensitivities. The porphyrin layer uncompletely coats the semicondutor surface in order to keep both ZnO and porphyrins in contact with the analyte. It is known that UV light may prompt the chemical sensitivity of ZnO replacing the high temperature condition. We show that thanks to the photoinjection of electrons from the porphyrin to the ZnO, the same effect can be obtained with visible light.

Keywords: Porphyrins, Zinc oxide, nanostructures, chemical sensors

The development of smart and reliable chemical sensors has become increasingly important for several application fields, ranging from medical to environmental applications. A chemical sensor is in fact a device that transforms chemical information, ranging from the concentration of a specific sample component to the total composition analysis, into an analytically useful signal. Porphyrins are useful materials for chemical sensors development, since in these devices the porphyrins play the role of receptor, the component that interacts with the chemical environment and for this reason it mostly influences the performances of the device. Since 1995 we have been involved in the preparation of different kind of porphyrin based chemical sensors, for the detection of analytes both in liquid and in the gaseous phase. A critical step in the development of such a devices is the deposition of porphyrins as solid layer, because in this process it is necessary from one side to preserve the recognition properties of the single molecules and from the other side take eventually advantage of the additional interaction pathways that the supramolecular organization can offer. This latter feature could be furtherly improved by the development of hybrid sensing materials, where the recognition properties of porphyrin aggregates are boosted by the coupling with both inorganic or organic substrates. We have been interested in this approach, developing hybrid materials where porphyrins have been deposited onto ZnO nanorods. The preparation of porphyrin-functionalized ZnO nanorods can be done by two different methods. Initially our work dealt on the development of gas sensors based on carboxylic group-substituted free-base porphyrin coated ZnO nanorods. We have developed a light-induced technique with enhanced gas sensing properties based on porphyrin/ZnO hybrid organic-inorganic material. It was found that the exposure to visible light affects the conductivity of porphyrin-coated ZnO nanorods, in such a way to induce a higher selectivity to amines than to alcohols. Recently, we have reported the light-enhanced gas selectivity of metalloporphyrin-coated ZnO nanorods prepared by one-pot procedures. We will present the results obtained in the application of metalloporphyrin-decorated ZnO nanocomposites, which can open up new perspectives for the widening of porphyrins applications in the sensor field.

Photoabatement of Water Pollutants iIn Turbid Suspensions by Means of Photoactive Fluorinated Transparent Coatings

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The abatement of organic pollutants in liquid phase promoted by photoactive titanium dioxide has been widely studied in the last decade. Despite the high photodegradative rates guaranteed by slurry TiO2, industrial use is strongly limited by the catalyst recovery cost. To overcome this obstacle powder TiO2 was immobilized into a multilayer ionomeric-perfluorinated matrix.

In order to obtain the correct interaction between the activated TiO2 and the polluted aqueous solutions the polymeric matrix must be characterized by high chemical resistance, high transparency towards UV light, good wettability and good permeability to oxygen and water vapor. Since perfluorinated polymers are perfectly illustrated by the above properties we undertaken the study on the interaction between perfluorinated material and photoactive semiconductors [1-3]. An appropriate perfluorinated multilayered coatings was applied directly on the UV source and employed as substrate for immobilization of theTiO2 photocatalyst.

A double-layer of TFE/perfluorodioxole copolymer and a dispersion of TiO2 in an ionomeric copolymerTFE /perfluorosulphonylvinylether acted as photoactive coating (PAC). The strong acidity of the ionomeric side chains conferred hydrophilicity to the whole polymer, allowing a good interaction with the polluted aqueous solutions. The PAC photoactivity was evaluated for each organic pollutant and compared to the abatement performances observed with dispersed TiO2.

All photodegradation tests were described through pseudo-first order kinetics. Results showed that the TiO2 containing coating had higher photocatalytic activity than dispersed titanium dioxide, even at low pollutant concentration (Image 1). Further tests, conducted in presence of a solid suspension, proved the photoactive coating to be effective even in turbid solutions. Indeed TiO2 activation and pollutant diffusion took place at the two opposite sides of the coating. Moreover, any costly separation of the catalyst from the purified water was avoided since the catalyst was immobilized in the fluorinated polymeric matrix, thus potentially allowing the development of the methodology to a simple and efficient continuous apparatus.

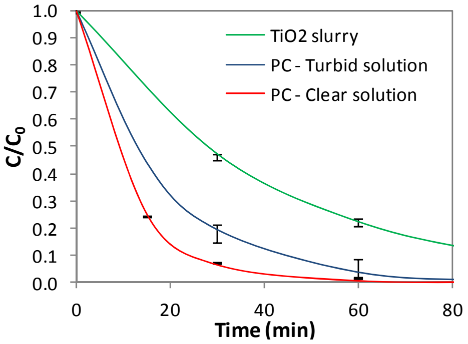

Image 1. Degradative efficiency of PAC compared to the performances guaranteed by slurry TiO_2

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Production of Graphenes from Kraft Lignin Pyrolysis

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ABSTRACT

Single and multiple layer graphenes were produced by vacuum pyrolysis of kraft lignin, a product derived from paper pulping process. Graphenes were produced on different silica supports such as Si/SiO_2 wafers and high surface silica. The characterization of the materials was made by IR, Raman and EPR spectroscopy together with SEM and AFM techniques. The reactivity of the radicals on graphene was studied by EPR. A unusually stable silicon peroxy radical was found and characterized in detail.

Keywords: Graphenes, Kraft lignin, pyrolysis, EPR

Kraft lignin is obtained as a byproduct of the paper pulping process. In the Kraft process the insoluble lignin polymer present in wood is decomposed into smaller units under high temperatures (170-180 °C) in the presence of strong alkali solutions (sodium hydroxide) and sulfides. The pyrolysis of lignin, i.e. the treatment at high temperature in the absence of oxygen, leads to the elimination of sulfur and oxygen present in the polymer, thus leaving carbon as a residue. The pyrolysis of Kraft lignin proceeds in two steps according to the pyrolysis temperature. In the temperature range 200-400 °C carbon dioxide was produced together with volatile sulfur compounds [1] and in the range 500-600 °C carbon monoxide was produced from phenols decomposition. Hydrogen production starts at 500 °C, indicating that, starting from this temperature, carbon defects are cured. Samples pyrolyzed at different temperatures were analyzed by microraman spectroscopy. The removal of inorganic salts and alkali from lignin led to detrimental production of graphene under the same conditions. Via vacuum pyrolysis, graphene and pyrolytic carbon was obtained onto high surface silica too. In that case the reactivity with oxygen, related to the simultaneous presence of both silica and carbon was extensively studied by EPR spectroscopy. This has led to the detection of stable silicon peroxy radicals, usually considered unstable at ambient temperature [2]. Defects present on graphenes and pyrolytic carbons, especially those related to the presence of radicals, are interesting from the point of view of chemical reactivity and can be detected and followed easily by EPR. Reactions with reactive species such as nitrogen oxides will be presented, together with magnetic properties measured at different temperatures.

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Catalytic Growth of Engineered CNT Structures

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ABSTRACT

The research of new engineered structures based on carbon nanotubes (CNTs) enhancing the already extensive features of these nanostructured materials, nowadays, is affecting an increasing number of researchers [1, 2]. The aim of the present work is the synthesis of CNT-based nets by chemical vapor deposition (CVD) of methane on trimetallic Co-Mo-Mg catalyst.

Keywords: CNTs, nets, CVD

Tri-metallic Co-Mo-Mg catalyst is synthesized by the sol-gel method according to the procedure reported elsewhere [3]. The weight of the components is determined in order to have molar ratios Mo/Co=30, Mo/Mg=3. CNT synthesis is carried out using CH_4 as carbon source at 900°C for 30min. CNT morphology is investigated by means of Scanning Electron Microscopy and Transmission Electron Microscopy. Under growth condition of the present work, C yield almost linearly increases with CH_4 partial pressure from 0.34 to 1.00 atm. A threshold limit value (0.34 atm) has to be reached to form filamentous product. In a very strictly range of CH_4 partial pressure (0.34-0.55 atm) CNT-based nets appear as shown in Figure 1a. Overcoming the above-mentioned range, net morphology disappears and mainly bundles form (Figure 1b).

The increase of reaction temperature (T_R) and of contact time (t_c) are also studied.

On the basis of characterization data, reaction mechanism will be discussed.

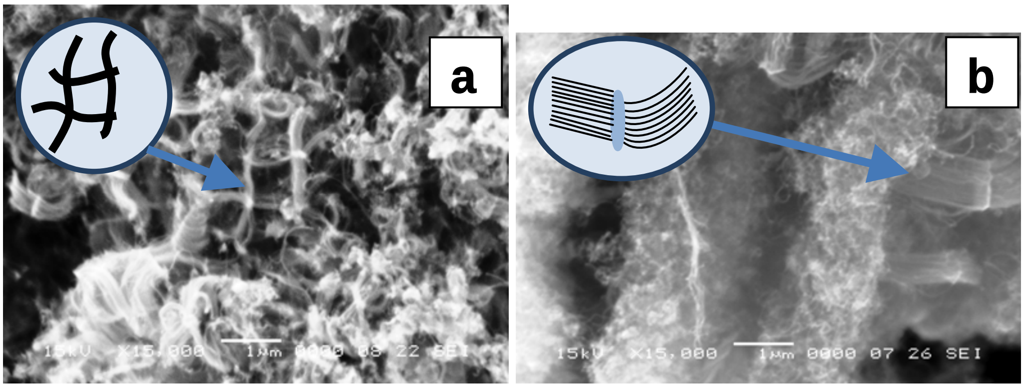

Figure 1: SEM images of CNTs at different CH_4 partial pressure (a, b)

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Novel Method for the Synthesis of Nano-Sized Zeolite

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ABSTRACT

The reduction of zeolite crystal size has been a major research field for the past 10 years as the decrease of dimension leads to substantial changes in the properties of the materials. The aim of this work is to develop a new strategy for the synthesis of nanosized SAPO-34, using carbon nanotubes as nanoreactors where nanoparticles grow.

Keywords: nanomaterials, carbon nanotubes, zeolites.

SAPO-34 obtained by traditional hydrothermal processes have crystallites of average size ranging from a few microns to a few tens of microns. The synthesis of nanoparticles of zeolite leads to several advantages such as an enhancement of the catalytic activity to the increase of the surface/volume ratio and adsorption properties [1, 2].

The innovative idea is to use carbon nanotubes (CNTs) as '*nanoreactors*' for the nanozeolites growth.

On CNTs, previously oxidized to ensure the presence of suitable functional groups (-COOH, -COH,), is adsorbed the appropriate template agent (eg. TEAOH), molecule around which zeolite grows. In this way TEAOH is not free in solution, but adsorbed on CNTs in a fan-shaped configuration (Figure 1). This particular configuration makes the system CNTs/TEA$^+$ apolar .

As it is known, the interactions between water and non-polar surfaces are not favorable: apolar molecules tend to contract reducing the surface area in contact with water (hydrophobic effect), rearranging in order to occupy the smallest space.

Then agglomerates of CNTs/TEA$^+$ dispersed in the aqueous phase are formed and, due to the configuration assumed by the template agent upon interaction with the CNTs, the available space where the formation reaction of zeolites can take place is very small, and molecules of nanometric dimensions are obtained (figure 2).

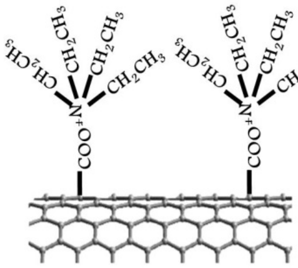

Figure 1: System CNTs/TEA$^+$.

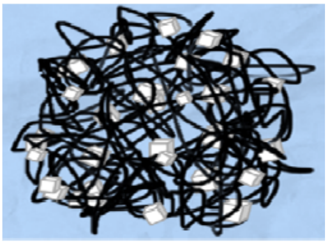

Figure 2: Example of synthesized material.

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Nanocompositi Polimerici Termicamente Conduttivi a Base di Nano-Lamelle di Grafene

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ABSTRACT

Keywords: Graphene nanoplatelets; conducibilità termica; nanocompositi, miscelazione dal fuso

Un grande interesse è oggi rivolto ai nano-compositi polimerici termicamente conduttivi, per la loro potenzialità nel sostituire componenti tradizionalmente realizzati in metallo, sfruttando la leggerezza, resistenza a corrosione e la facile processabilità tipiche dei materiali polimerici.

In particolare, si mira in quest'ambito allo sfruttamento di nano-particelle termicamente conduttive (nanotubi di carbonio, grafeni, nitruro di boro) da disperdere all'interno della matrice polimerica per ottenere un apprezzabile aumento della conducibilità termica rispetto ai polimeri tal quali, notoriamente buoni isolanti termici.

I nanotubi di carbonio (CNT) sono stati largamente utilizzati come particelle per aumentare la conducibilità termica in matrici polimeriche, con risultati variabili, limitati dallo scarso contatto termico tra le particelle [1]. Più recentemente, i *graphene nanoplatelets* (GNP) sono diventati una valida alternativa ai nanotubi di carbonio, grazie alla geometria lamellare, che permette un maggiore contatto tra le particelle [2-4]. Tuttavia, il raggiungimento di un sufficiente grado di dispersione di GNP in matrici polimeriche è critico, specialmente nel caso di preparazioni per miscelazione dal fuso.

In questo lavoro, finanziato dai progetti di ricerca europei Nanocool e Graphene Flagship ICT, sono stati seguiti diversi approcci per migliorare la dispersione delle particelle e la costituzione di un assetto percolativo per queste ultime e in ultima analisi incrementare la conducibilità termica dei relativi nanocompositi:

- Combinazione di GNP con grafiti micrometriche, con evidenza di sinergia tra particelle nanometriche e particelle convenzionali, per l'ottenimento di materiali ad elevata conducibilità termica
- Pre-dispersione di GNP in additivi liquidi (es. plastificanti, oligomeri) da utilizzare come master nella miscelazione dal fuso in polimeri termoplastici
- Funzionalizzazione non covalente di GNP con derivati reattivi del pirene (es. amino pirene) per la dispersione in polimero mediante processi di miscelazione reattiva in polimeri termoplastici.

Le conducibilità termiche conseguite saranno infine confrontate con i target prestazionali richiesti dai principali settori di applicazione industriale (radiatori e intercooler per motori, recuperatori termici da fumi di combustione di biomasse, sistemi elettronici con scambio termico intensificato, ecc.).

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Modified Porphyrinoids as Functional Materials

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ABSTRACT

Porphyrinoid derivatives have been widely used in several applications. The close relationships between the structure of the macrocycles and their inherent properties, with the consequent possibility of tuning both by subtle synthetic modifications, prompted us to focus our attention to expanded porphyrinoids, in particular on β–fused porphyrinoid derivatives.

Keywords: expanded porphyrinoids, dye-sensitized solar cell, chemical sensors

In the last decade great attention has been focused on the preparation of porphyrin derivatives characterized by an expanded aromatic system, because these molecules show novel optical and electronic properties, making them particularly interesting for potential applications in fields [1] ranging from PDT to chemical sensors, and especially in dye-sensitized solar cell (DSSC) [2]. In fact, the extension of the porphyrin core aromaticity causes a decrease in the HOMO-LUMO gap that leads to improved harvesting of solar energy in a broad spectral region. Moreover, these chromophores not only are characterized by a batho- and hyper-chromically shifted absorption profile in comparison to the single porphyrinoid units, but, would offer a convenient handle to modulate their optical properties by varying the number and the nature of porphyrinoid units. Within this scenario, we have developed a one-pot reaction to prepare β-fused homo-porphyrin system (figure 1) that has been tested for DSSC and CSPT (computer screen photoassisted technique). Up to date, we are optimizing the preparation of hetero systems characterized by the fusion of different macrocycles.

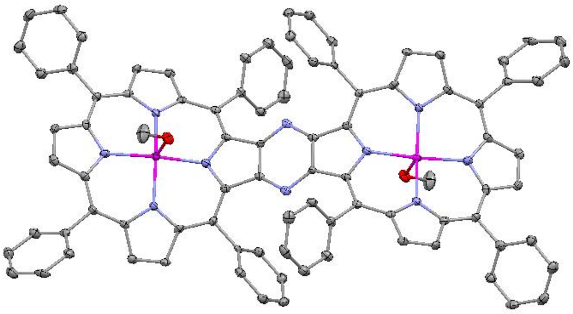

Figure 1: Bis-porphyrin structure.

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Enhancing Electrocatalytic Oxygen Reduction on Pt-free Electrocatalysts in Microbial Fuel Cells

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ABSTRACT

The current need for new solutions for waste management and clean energy production can find a concrete answer in the technology of microbial fuel cells (MFCs) MFCs allows the production of electrical energy, using as fuel several agro-industry or urban wastewater, eliminating at the same time some of the problems linked to their disposal [1]. MFCs performance is greatly affected by the cathode side, where oxygen is the electron acceptor. The use of platinum as catalyst for the oxygen reduction reaction (ORR) significantly contributes to device cost, thus representing one obstacle to the commercial development of MFCs [2]. Aim of this work is to identify innovative and cost-effective Pt-free electrocatalysts to be used as cathode in lab-scale MFC prototypes. Iron-based catalysts supported on either carbon Vulcan or carbon nanotubes (CNTs) were prepared. The combination of carbon supports with electronically conducting polymers (i.e., polyindole) and ceramic oxides (i.e., zirconium oxide) was also investigated to boost catalytic activity, while reducing the adsorption of contaminant species. Morphology of the prepared catalysts was analyzed using scanning electron microscopy (SEM) and transmission electron microscopy (TEM). Specific surface area and pore structure was investigated by means of Brunauer-Emmett-Teller (BET) and pore distribution analysis. Figure 1a shows a TEM image of a typical iron catalyst supported on CNTs. Reaction kinetics, activity reproducibility, and stability was evaluated by cyclic voltammetry (CV). Polarization and power density curves (Figure 1b) acquired in single chamber air breathing MFCs assembled with prepared electrocatalyst as cathodes indicated high and stable performance, demonstrating the potential ability of Pt-free cathodes to substitute platinum catalyst for ORR in MFCs.

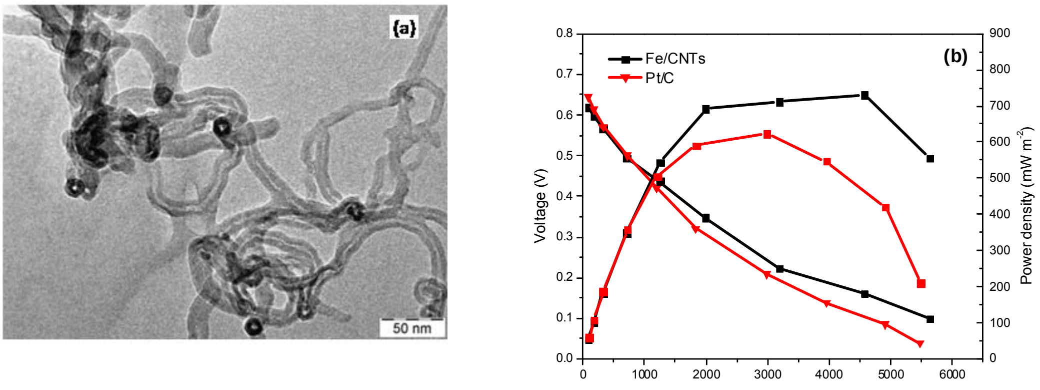

Figure 1: (a) TEM image of Fe/CNTs; (b) polarization and power density curves in MFC operating mode.

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On the Relationship Between ^{195}Pt Chemical Shift and the Structural Features of Pt Coordination Compounds

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Keywords: Platinum compounds, ^{195}Pt NMR spectroscopy

ABSTRACT

Coordination chemistry of platinum represents a research area of increasing importance for basic and applied sciences. Studies on platinum compounds comprise synthesis and reactivity, catalysis and mechanistic studies, intermetallic and drug binding studies. In this respect, heteronuclear NMR spectroscopy represents an irreplaceable tool for structural elucidation, relaxation studies, dynamics, kinetics and mechanistic studies.[1]

In the framework of our recent studies on coordination chemistry of platinum, we have obtained a library of compounds bearing fluorine and/or phosphorus containing ligands.[2-5] The presence of such nuclei, which are higher γ-nuclei with respect to ^{195}Pt, allows for indirect detection of ^{195}Pt and registration of very informative HMQC spectra. In particular, more data regarding the uncommon +1 and +3 oxidation states of Pt are now available.

In this presentation, the ^{195}Pt NMR features of several phosphido Pt complexes will be discussed including the relationship between ^{195}Pt chemical shift and the structural features of the Pt complexes.

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Synthesis and application of organic dyes for DSSCs

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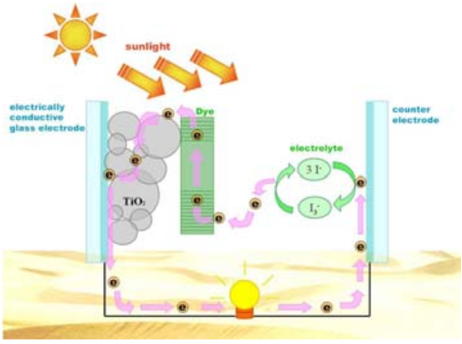
ABSTRACT

Dye sensitized solar cells (DSSCs) represent one of the most promising next-generation photovoltaic devices. These devices have been attracting considerable attention due to high performance and low-cost production. Dyes as photosensitizers are one of the most important components influencing the photovoltaic performances of DSSCs, because they determine the photoresponse range of the device and initiate the primary steps of the photon absorption and the subsequent electron transfer process. In addition to conventional Ru-complex sensitizers, metal-free organic dyes have also been utilized as sensitizers in DSSCs, and the photovoltaic performance of DSSCs based on organic-dye sensitizers has been improved by careful molecular design. [1,2]
We have designed and synthesized three novel organic dyes containing two donor moieties bonded to the dibenzofulvene core Fig.1, with several thiophene spacer-linker forming a 2D-π-A push-pull system, to improve solar-cell performance of the solar cells. The DSSCs based on the TK3 dye showed high power conversion efficiency of 7.45%.



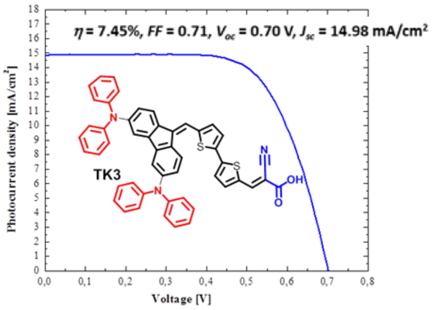


Figure 1: Schematic energy flow in operational DSSC. **Figure 2:** TK3 structure and DSSC parameters.

Keywords: dibenzofulvene dyes, photosensitizers, DSSC.

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Catalytic Activity of Recyclable Polymer Supported Palladium Nanoparticles in Oxidation and Hydrogenation Reactions in Aqueous Medium

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ABSTRACT

Polymer supported palladium catalyst (in the following *Pd-pol*), obtained by copolymerization of the metal coantaining monomer [1] Pd(AAEMA)$_2$ [AAEMA$^-$ = deprotonated form of 2-(acetoacetoxy)ethyl methacrylate] with ethyl methacrylate (co-monomer)and ethylene glycol dimethacrylate (cross-linker), exhibited excellent activity and selectivity for the oxidation of benzyl alcohols to aldehydes in water, for the selective hydrogenation of quinolines to 1,2,3,4-tetrahydroquinolines under mild temperature (80°C) and H_2 pressure (10 bar) in aqueous medium and for the nitroarene reduction in water (figure 1). Both the activity and selectivity could be maintained up to twelve reaction runs. No metal leaching into solution occurred during duty. TEM analyses carried out on the catalyst showed that the active species were supported palladium nanoparticles having a mean size of 4 nm, which did not aggregate with the recycles.

Keywords: water solvent, quinoline hydrogenation, nitroarene reduction, benzyl alcohol oxidation, polymer supported Pd nanoparticles, recyclable catalyst

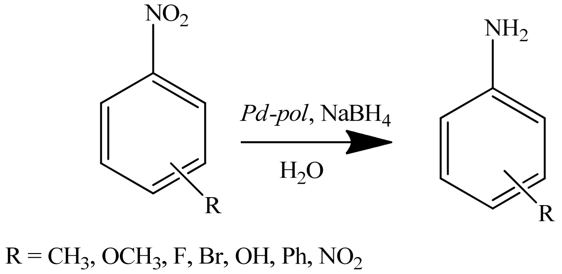

Figure 1: nitroarene reduction

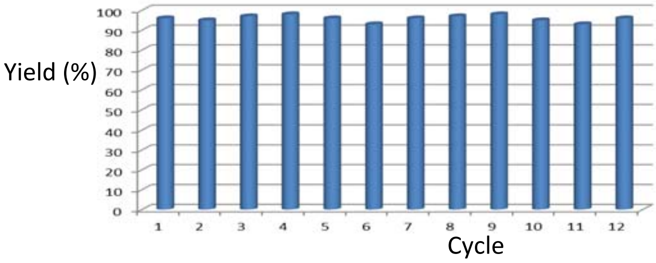

Figure 2: recyclability of *Pd-pol* catalyst

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Alfalfa Stems Hydrolysis for Sugars Production

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ABSTRACT

Hydrolysis of alfalfa stems was performed with microwave and subsequently with enzymes. A single mode microwave oven was used for the pretreatment. Good conversion yield of polysaccharide into sugars was obtained (80%) with low unwanted products. SEM characterization was performed during the different steps of conversion in order to better understand the action of enzymes onto specific plant structures.

Keywords: Alfalfa, Hydrolysis, Sugars, SEM, Microwave.

Second-generation bioethanol is one of the most promising fuels obtained from renewable sources. The possibility of obtaining fermentable sugars from biomass, without interfering with the food chain, makes this fuel a sustainable source. Alfalfa stems are considered as a waste, since they are not used for the forage. Because of that alfalfa stems are interesting for the production of second generation bioethanol. Surprisingly, even if alfalfa is widely used worldwide as a forage, very few studies consider alfalfa stems as feedstock. We carried out an optimization of the hydrolysis process with both acids (sulfuric and phosphoric acid) and with water only. The single-mode microwave oven gave energy balance of the process at the different process conditions. Subsequently solid residuals were hydrolysed with enzymes, at different times, in order to attain higher sugar yields. HPLC and SEM characterization (figure 1) were performed at different stages of hydrolysis. Through SEM images the enzymatic hydrolysis was correlated to the decomposition of anatomical parts of the plant. The optimal process conditions were found with sulfuric acid and subsequent enzymatic hydrolysis, giving a maximum yield of 80% (figure 2) of sugars related to cellulosic content.

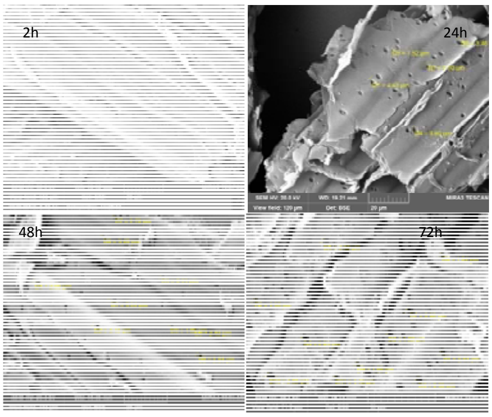

Figure 1:SEM alfalfa

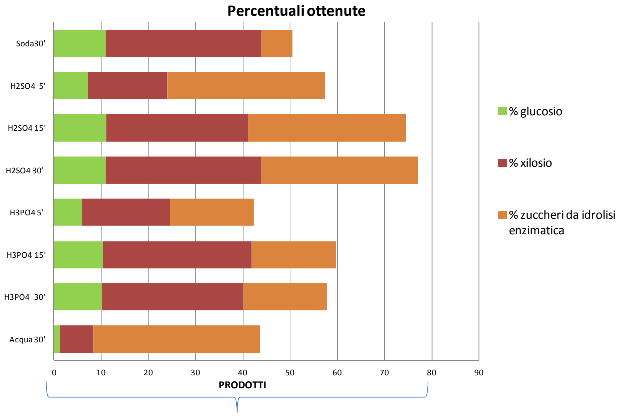

Figure 2: yields of sugars

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Palladium-Rush iIn Bio-Transfer Hydrogenolysis Reactions.

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ABSTRACT

The selective cleavage of the C-O bonds in biomass derived compund such as glycerol, 2-phenylethylacetate, furfural and 5-(hydroxylmethyl)-furfural is reported. The reactions were carried out in absence of added hydrogen by using the reaction solvent (2-propanol) as hydrogen source in the presence of coprecipitated Pd/Fe_3O_4 catalyst

Keywords: transfer hydrogenolysis, coprecipitated palladium catalysts, biomass valorization

The use of renewable biomass for bulk chemicals production provides a viable route for the modern chemical industry to alleviate its historical dependence on fossil resources and to reduce, at the same time, CO_2 emissions [1]. Compared to fossil fuel components, which are mostly unfunctionalized hydrocarbons, biomass feedstocks are over-functionalized with -OH and -CO groups and thus they contain a large amount of oxygen. As a consequence, C-O bond hydrogenolysis is of particular significance since it allows the production of important high value chemicals from biomass derived intermediate compounds [2]. Surely, one of the main targets is currently to make the hydrogenolysis a self-sustainable process and to reduce the costs related to hydrogen purchase, transport and storage and to minimize safety problems in industrial hydrogenation processes. Catalytic transfer hydrogenolysis (CTH) reactions [3] represent an interesting alternative to the direct use of molecular hydrogen.

This contribution documents the past and contemporary advances in the transfer hydrogenolysis of biomass-based substrates, with particular emphasis on promising coprecipitated palladium catalysts. The catalytic results are interpreted in terms of metal-metal interaction that modifies the electronic properties of palladium [4] thus enhancing its catalytic properties in the transfer hydrogenolysis of glycerol [5], 2-phenyethylacetate, furfural and 5-(hydroxylmethyl)-furfural [6].

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Developments of New Hg(II)-Imprinted Polymer Beads: Adsorption Performances And Morphological Characterization

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ABSTRACT

Environmental problems associated with water pollution, are today a serious problem that has attracted great attention of the global community. In particular, the release of various harmful heavy metal ions owing to industrial and agricultural processes represent today the main cause of pollution [1]. Mercury is one of the most hazardous elements for human health for its relatively solubility in water and living tissues. Common methods used for mercury separation from water samples include, liquid-liquid extraction [2], solid-liquid extraction [3], flotation [4] and membrane filtration [5] Moreover, many synthetic polymers opportunely functionalized by impregnation [6], grafting of commercial sorbents [7] or of home-made polymers [8] were prepared. However, a good selectivity is difficult to achieve with the previously mentioned materials. For this reason, highly selective Hg(II) imprinted polymers were prepared using different synthesis approaches and a correlation between the adsorption behavior and morphological characteristics of all polymers was made. Finally, selectivity studies using a mixture of different metal ions, were carried out.

Keywords: ion imprinted polymer, mercury detection, diphenylcarbazone

The aim of this study was to prepare a water compatible ion imprinted polymer selective for mercury using different simple and easy synthesis approaches in the presence and in absence of a non polymerizable ligand such us Diphenylcarbazone (DPC) in order to understand the influence of this compound in the adsorption behavior of the polymers. For polymers preparation two synthesis strategies were used: a dynamic bulk polymerization and a precipitation polymerization. Reaction mixture includes HgCl2 (1 mmol), 4-vinylpyridine (4 mmol), ethylene glycol dimethacrylate (20 mmol) as template, functional monomer and cross-linker respectively. In particular a first polymer (IIP1) was prepared by dynamic bulk polymerization without DPC. Successively the same synthesis approach was used in presence of DPC (1 mmol) to prepare IIP2. Finally, to understand the influence of morphological characteristics on the binding behavior and selectivity performance of polymers, a precipitation approach was used to prepare a new polymer (IIP3).

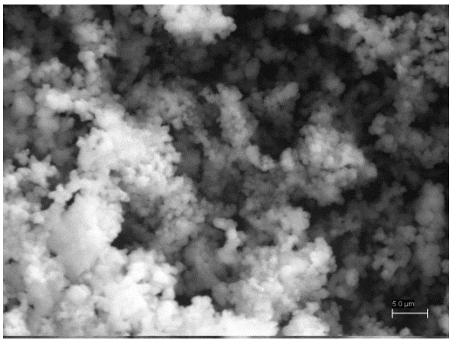

Figure 1: SEM image of IIP1

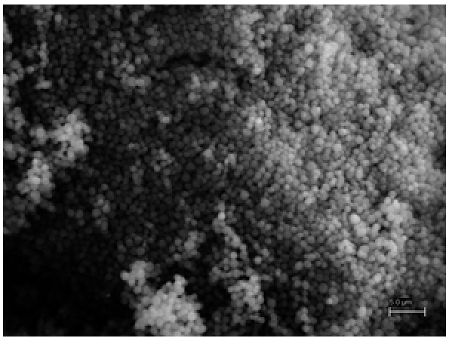

Figure 2: SEM image of IIP3

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