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CONGRESS ABSTRACTS

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β-PYRROLIC SUBSTITUTED PORPHYRINS IN DYE SENSITIZED SOLAR CELLS: SYNTHETIC BENEFITS, PROPERTIES AND FUTURE PERSPECTIVES

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Concept: The facile synthesis of β-substituted porphyrins and their photoelectrochemical properties make this class of dyes very promising for application in Dye Sensitized Solar Cells (DSSCs).
Motivations and objectives: Porphyrins are one of the most widely investigated classes of molecules in chemistry due to their chemical stability, catalytic activities, interesting optical and photophysical properties. Today, the best performance in a porphyrin-sensitized solar cell has been reached by a well-engineered meso disubstituted push-pull Zn^{II}-porphyrinate. Nevertheless such class of porphyrins can be obtained only by multistep and uneconomical synthetic routes. On the contrary β-substituted Zn^{II}-porphyrinates are of great interest because they can easily be obtained with remarkable yields using facile synthetic procedures. In addition they are featured by a significant steric hindrance which guarantees a decrease of π-staking aggregation on TiO_2 photoanode resulting highly beneficial to DSSC performances.
Results and discussion: Our investigation has shown that β-substituted Zn^{II}-porphyrinates are capable of serving as effective dyes in DSSCs, showing performances comparable to the most commonly used meso substituted push-pull Zn^{II}-porphyrinates. An in-depth EIS (Electrochemical impedance spectroscopic) investigation has proven that β-substituted Zn^{II}-porphyrinates, appears to be ascribed to a superior passivation of the TiO_2 surface against the charge recombination which involves I_3^- species of the electrolyte. This superior screening effect can be related to the higher steric hindrance of the tetraarylporphyrinic architecture of such macrocyclic systems. Furthermore, pyrrolic functionalization of the porphyrinic core appears to be beneficial in tuning the properties of these dyes. In fact, they are strongly influenced by the introduction of π-delocalized systems which exert strong steric and electronic effects on the porphyrinic ring resulting in a dramatic alteration of their optical, electrochemical and spectroelectrochemical properties. Increasing the elongation of the π-chain in β-position, by adding thienyl units, the electronic absorption spectra of Zn^{II}-porphyrinates cover a wide range of wavelengths producing a panchromatic effect in their IPCE spectra. The information extracted from our studies are helpful focusing on the development and synthesis of novel and more efficient β-substituted porphyrinic dyes which appear to be remarkable, viable and efficient alternatives to the more synthetically demanding porphyrinic dyes which exhibit the push-pull *meso* geometry.

TAILORING ASSEMBLY OF REDUCED GRAPHENE PLATELETS TO CONTROL PROPERTIES OF RUBBER NANOCOMPOSITES

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Concept: Self-assembling of reduced graphene oxide (RGO) platelets ('segregated' arrangement), as a tailored interconnected network within natural rubber and butyl rubber matrices, is proposed as a mean for obtaining nanocomposites with significantly enhanced functional properties as compared to unloaded rubber, i.e. gas barrier properties and electric conductivity, even at very low filler contents. Interestingly, the prescribed spatial arrangement of the nanoparticles results to be much more effective in improving properties than homogeneous dispersion ('not segregated' arrangement) of platelets, even at low loadings. The 'segregated' structure originates from the confinement of platelets within the interstices of the coagulated latex particles, which act as a template for the network formation. The platelets are assembled on the latex particles giving rise to spheres with a core-shell structure, with a partial or complete covering depending on graphene amount. Conversely, the 'not-segregated' structure is obtained by destroying this interconnected network by further processing the RGO nanocomposite masterbatch via twin-roll mixing, thus determining a uniform orientation of exfoliated RGO platelets.
Motivations and objectives: The aim is exploiting self-assembling of RGO platelets to provide a cost-effective method to tailor the dispersion of nanoparticles inside the host matrix, allowing to significantly decrease the percolation threshold for electric conductivity and drastically change the dependence of gas barrier on nanofiller concentration.
Results and discussion: The presence of RGO nanoplatelets radically affect the dependence of gas barrier properties on nanofiller content. An example is provided in Figure 1 for the case of oxygen permeation in nanocomposites with natural rubber matrix where the 'segregated structure (filled symbols) is compared with 'not segregated' one (empty symbols). Taking the real part of complex conductivity at the lowest investigated frequency, σ'0, as representative of the DC conductivity one can estimate the percolation threshold for electric conductivity in a nanocomposite. The optimized spatial distribution of the nanoplatelets attained in the case of 'segregated' structure, for the case of butyl rubber matrix, promotes an enhancement of σ'0 of almost two orders of magnitude suggesting the building up of conductive paths of RGO throughout the rubber phase (see filled symbols in Figure 2). Conversely, the system having a 'not-segregated' morphology displays no evident changes as compared to neat matrix (see empty symbols in Figure 2). A value of critical RGO concentration as low as Φc = 0.4 vol.% has been estimated for the "segregated" system according to the percolation theory (inset of Figure 2).

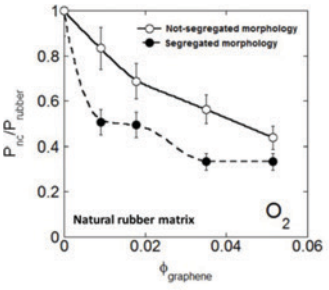

Fig. 1

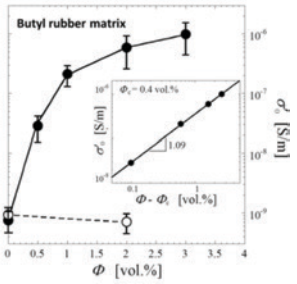

Fig. 2

cup is considered weaker part because it is made of polymer material. The design criteria in this case depend mainly on the wear due to permanent relative motion between two parts. So wear is the most important effective factor directly on the service time.

Results and discussion: The wear tests were conducted using a pin-on-disc wear tester at room temperature under dry sliding conditions (Fig. 1, left panel). The tests of flat samples against steel pin were carried out at a linear velocity of 1 m/s, normal load 30N. The results showed that the BM represents the best method to produce CNFT/UHMWPE with well dispersion and excellent wear resistance among the tested ones. The nanocomposites made by BM and EX showed a good mechanical ductile behavior (Fig. 1, right panel).

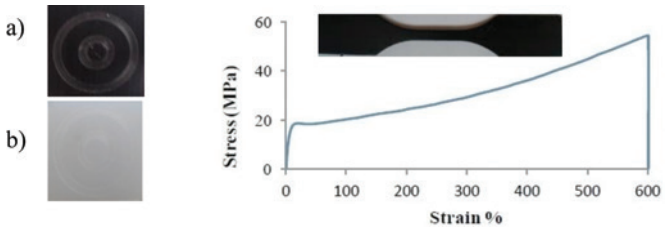

Fig. 1 - Wear tracks for (**a**) CF/UHMWPE and (**b**) UHMWPE (left panel); CF/UHMWPE tensile curve (right panel).

SYNTHESIS AND CHARACTERIZATION OF PEGYLATED GRAPHENE OXIDE FOR SORAFENIB MODIFIED RELEASE

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Concept: Graphene, a single layer of sp^2-hybridized carbon atoms arranged in a honeycomb two-dimensional (2-D) crystal lattice, has evoked enormous interest throughout the scientific community since its first appearance in 2004. Due to its unique structure and geometry, graphene possesses remarkable physical-chemical properties (including large specific surface area and biocompatibility) that enable it to be an ideal material for several applications, ranging from quantum physics, nanoelectronics, energy research, catalysis and engineering of nanocomposites and biomaterials. In the area of nanomedicine, graphene and its derivatives can be exploited for a broad range of applications, including a new generation of biosensors, nanocarriers for drug delivery and probes for cell and biological imaging. In particular, graphene oxide (GO), synthesized by intensive oxidation of crystalline graphite and then turned into a monolayer material by sonication, consists of aromatic planes and polar functional groups which consequently provide it an excellent capability to adsorb aromatic compounds via π-π stacking and hydrogen bonding. In order to improve its biocompatibility and physiological stability, some biocompatible polymer can be introduced onto GO. Among the commercially available polymers, poly(ethylene glycol) (PEG) is a very useful reagent in biology because of its minimal toxicity, biocompatibility, protein resistance, and good solubility in water or other common solvents.

Motivations and objectives: Sorafenib is a small molecule that acting as a multi-kinases inhibitor blocks tumor-cell proliferation and tumor angiogenesis. It increases the rate of apoptosis in a wide range of tumor models and is the first drug that is clinically approved for patients with advanced hepatocellular carcinoma (HCC). In the present study, we aimed to develop a GO-PEG based carrier for enhanced delivery and controlled release of sorafenib into specific cancer cells.

Results and discussion: Herein, we developed a GO-PEG nanocarrier for enhanced delivery and controlled release of sorafenib into specific cancer cells. GO-PEG was first synthesized dispersing GO in bi-distilled water followed by adding PEG_{2000}-NH_2. For the preparation of sorafenib loaded GO-PEG a solution of sorafenib in DMSO was added to an aqueous GO-PEG dispersion at pH 8.4, and the obtained solution was kept under magnetic stirring at room temperature overnight. The empty and drug-loaded GO-PEG were characterized in terms of size, zeta potential, polydispersity, morphology and drug loading capacity. The release kinetic studies, carried out in an appropriate medium mimicking the physiological environment, confirmed that this system permits a controlled release of sorafenib.

RECYCLING OF YTTRIA-STABILIZED ZrO_2 (YSZ) FOR CERAMIC TILE GLAZES AND PIGMENTS

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Concept: Thermal spraying overspray of yttria stabilized ZrO_2 (YSZ) powders have been characterized by means of grain size laser technique, scanning electron microscopy, X-ray fluorescence, X-ray diffraction and colour measurement. Two different powders, APS5 and APS6, coming from two different thermal spray process has been analyzed. The results showed that only APS6 is strongly polluted with metallic element as Ni, Co and Cr. Both powders have been sieved, in order to separate the pollutant particles, and each fraction has been characterized, to verify the content of metallic pollutant particles. The sieved fraction with the lower grain size results suitable to substitute zirconium oxide into ceramic frits, glazes and pigments formulation. Frits, glazes and pigments produced with standard and recycled zirconium oxide have been analyzed by means of scanning electron microscopy, X-ray diffraction, chemical durability and colour measurement. The final results demonstrate that the less polluted thermal spraying overspray of yttrium stabilized zirconia powders can replace zirconium oxide for the production of frits and glaze to obtain super-white surfaces, whereas the most polluted powders can be used for the formulation of at least five pigments for ceramic body.

Motivations and objectives: Thermal spraying overspray powders are a relevant waste for the coating industry because of their great amount, up to 70-90% of the starting powder, and the presence of hazardous element as Ni, Co, Cr. The recycle of these powders is even more strategic considering the increasing costs of the raw materials, as in the case of zirconia. On the other hand the high cost of zirconia is a strong limit in the tile manufacturing industry. The aim of this study is to employ thermal spraying overspray powders into the formulation of ceramic frits, glazes and pigments, in order to avoid hazardous waste disposal and save high priced raw material. This study is a part of the activity done under the LIFE ReTSW-SINT project.

Results and discussion: The main results of this study, suggest that the colour of the waste yttrium stabilized zirconia is strictly related with the content of metallic pollutants. We found out also that the pollutant content is concentrated mainly at the fraction of the powders with the highest grain size. For this reason the fractions of waste powders with the lower grain size has been employed in super-white glaze whereas the others fractions for pigment formulations. APS5 waste powder is suitable to replace Zirconium Oxide in frits for white glazes formulation, in the amount of 100 wt%, whereas APS6 waste powder is suitable and more advisable than APS5 to replace a part of the pigment in the amount of 5wt% for five colours: green, grey, beige, yellow and brown, as shown in Figure 1.

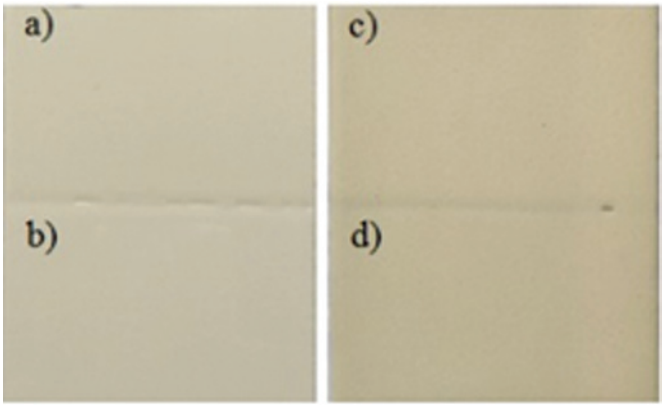

Fig. 1 - a) Standard white glaze; **b**) APS5 white glaze; **c**) Standard yellow pigment; **d**) APS6 yellow.