

ADVANCED MATERIALS FROM CARBON BLACK MODIFICATION: A FOREVER YOUNG NANOMATERIAL

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Carbon black (CB) is a versatile carbonaceous material prone to be structurally and chemically modified in quite mild wet conditions. Recently, in our group, the potentiality of CB has been exploited producing a highly varied array of advanced materials for innovative applications in energetics (Fig.1). Among them:

- Graphene-like (GL) layers and ultrathin (GL) films;
- TiO₂/GL nanoparticles; magnetite/GL composites;
- Eumelanin/GL bioinspired conductive composites;
- Metal-Organic Framework (MOF)/GL conductive composites;
- Tailored materials by CB surface modifications: i) oxidation and functionalization with amino-groups; ii) coating with iron oxides; iii) impregnation with an ionic liquid (IL).

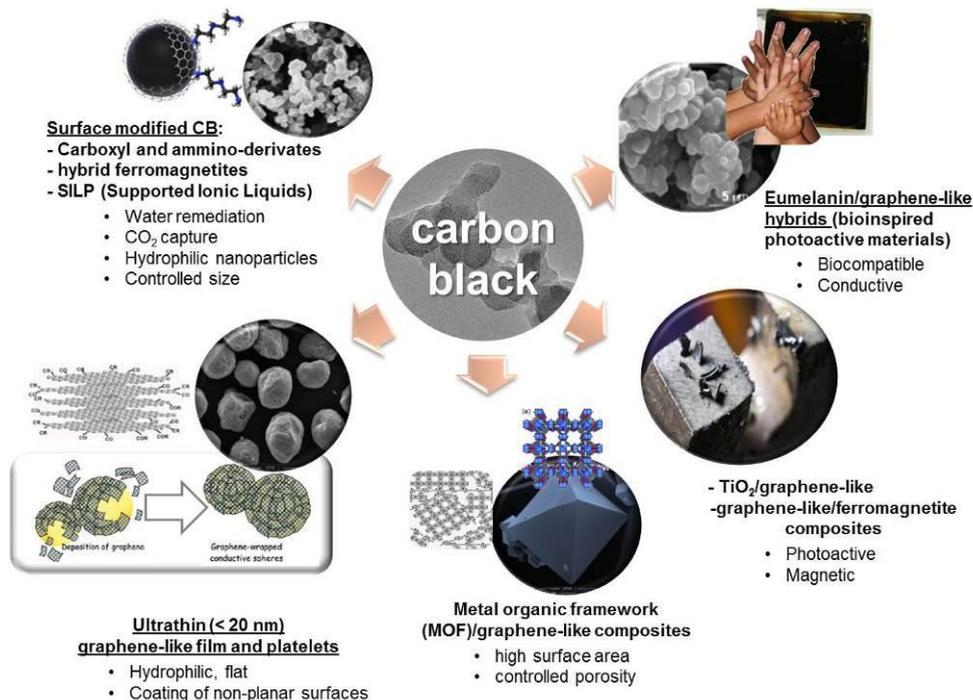


Figure 1. New-concept materials from CB.

Graphene-like (GL) layers and ultrathin (GL) films [1,2]. The production of carbon-based films simultaneously with high stability, controlled thickness, and tunable performances is an interesting challenge in material science research.

The reduction of strongly oxidized carbon black by hydrazine hydrate yields water-stable conductive graphene-like layers that undergo to self-assembling in thin film on surfaces after drying. The height of a drop-casted graphene-like film, determined by atomic force microscopy (AFM), is around 20 nm, corresponding to approximately 25 graphene-like layers. The conductivity (σ) of the film is around $2.5 \pm 0.3 \cdot 10^3$ S/cm.

Zeta potential and AFM measurements demonstrate that the morphology of the self-assembled GL films is strongly affected by the pH of the GL water suspension. In particular, at low pH (< 3.5) the film exhibits a granular surface, while at high pH (> 4) more regular morphologies are produced, with interesting observations as concerns the thickness of some peculiar surface features (Fig. 2). The assembling behavior is interpreted in terms of the forces acting in water suspension and of the role of hydrophobic or hydrophilic behaviors.

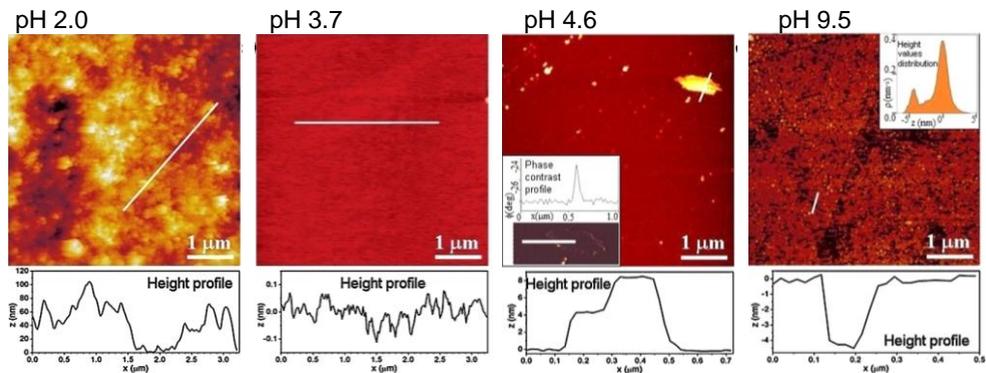


Figure 2. AFM topographic images with a line profile for each investigated sample; all the reported images correspond to a scan area of $5 \mu\text{m} \times 5 \mu\text{m}$.

The results demonstrate the possibility to tune the surface properties of GL films by simply acting on the pH of the suspension during the fabrication.

Our approach for producing morphology tuned graphene-like thin film has significant advantages over the conventional method based on graphite oxidation and reduction: i) mild conditions, ii) aqueous environments, iii) high yields, iv) use of hydrazine in water solution to restore the graphitic network. Moreover the synthetic procedure is highly compatible to an industrial scale-up process.

Thanks to GL layers low dimension, GL are particularly suitable to homogeneously coat non planar surfaces and particles, including cells.

TiO₂/GL composites; magnetite/GL composites [3]. GL layers have been used to prepare composites with TiO₂ nanoparticles. GL layers have been used in two different forms (directly in water suspension, GL, and assembled in flat

blocks/platelets, GLP) to prepare composites with TiO_2 nanoparticles in one-pot approach. The two composites formulations allowed to investigate different morphological arrangement of TiO_2/GL composites with the aim of studying the relationship between morphology and photocatalytic activity.

The photocatalytic activity of the composites were tested exploiting the selective oxidation of 3-pyridine methanol to 3-pyridine carboxyaldehyde and nicotinic acid, under de-aerated and UV/solar simulated conditions, in presence of cupric ions in aqueous solution at ambient temperature (Fig. 3).

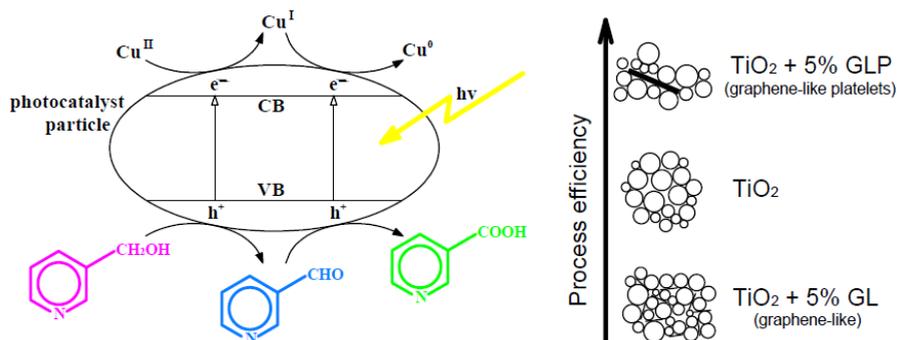


Figure 3. TiO_2/GL catalysts morphologies and efficiency of the photocatalytic process.

An enhanced photocatalytic activity of TiO_2/GLP , with respect to the neat TiO_2 , has been observed and attributed both to the broader variety of free-radical species stabilized within the delocalized π -electron systems of the TiO_2/GLP , as indicated by EPR analyses and to a reduction of the hydroxyl radicals formation.

Thanks to their good water stability, GL are also suitable to produce magnetite/GL composites.

Eumelanin/GL (EUGL) bioinspired conductive composites [4]. Organic Bioelectronics applications are largely dictated by the chemical nature of the materials that transduce signals across the biotic/abiotic interface. Among the available materials for functional biocompatible interfaces, the human pigment eumelanin (EU) is currently gaining increasing interest. The low conductivity of these pigments is limiting the implementation of eumelanin-based devices. Among the different strategies under investigation to improve electrical performance of eumelanin thin films, a clear-cut approach lies in hybridization with suitable conductive counterpart. A biocompatible substrate featuring typical eumelanin properties, including adhesion and water stability, but exhibiting improved electrical conductivity with respect to the natural pigment was prepared by interfacing the eumelanin and GL layers.

The hybrid was obtained by inducing the polymerization of eumelanin precursors (5,6-dihydroxyindole, DHI and 5,6-dihydroxyindole-2 carboxylic acid, DHICA) in

aqueous media containing GL layers.

The hybrid material EUGL exhibits: i) strong adhesion to polar and apolar surfaces, ii) water stability, iii) biocompatibility allowing Murine Embryonic Stem Cell (ESC) and Rat Microglial Cell (MC) culture and iv) improved electrical conductivity more than 4 orders of magnitude greater than that of the parent eumelanin compound (Fig. 4).

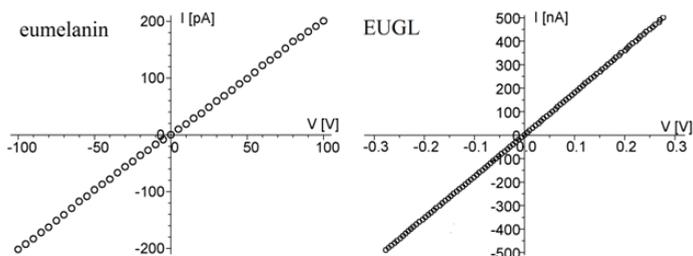


Figure 4. I-V dc curves of eumelanin and EUGL

The properties of the hybrid may expand the scope of eumelanin in bioelectronics paving the way to true biocompatible organic electrochemical transistor-like interfaces capable to translate cellular activity in electrical signals.

Metal-Organic Framework (MOF)/GL conductive composites [5]. Metal-organic frameworks (MOF) are coordination networks characterized by a high crystallinity and uniform porosity, obtained by the assembly of metallic centers and organic linkers through strong covalent bonds. MOF have attracted a lot of attention in the last years due to their structural properties and their versatility for technological applications. The electrical properties of MOF were very rarely studied due to their insulating nature. The preparation of composites combining MOF and carbon-based materials has been proposed as a solution to overcome the weak points of MOF and to expand their field of applications.

A new class of copper-based metal-organic framework/GL (MGL) composites were produced starting from a copper-based MOF. The selected MOF, HKUST-1, combines high surface area, water stability, simple preparation and low costs. MOF composites were produced at different GL content. The main features of HKUST-1 in the composites are preserved, indicating that the interaction of the HKUST-1 units with the carboxylic functionalities of GL layers does not interfere with the HKUST-1 crystal growth. Moreover the incorporation of GL layers introduces a new porosity in the composites suggesting a distortion in the porous structure of the materials. Electrical measurements revealed a strong increase of the dc conductivity in the samples as a function of GL layers content (Fig. 5).

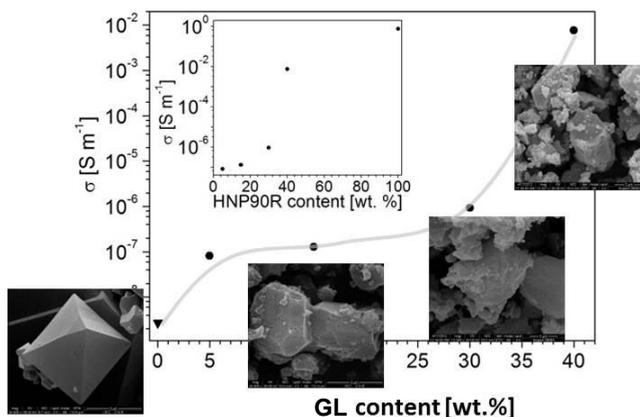


Figure 5. Electrical conductivity and SEM images of HKUST-1 and MGL composites.

The conductivity and the new porosity distribution arising by GL incorporation, together with high specific surface area of the composites, impart new properties to the pristine HKUST-1. The production of electrically conducting porous phases is expected to be of great interest for possible applications in molecular sensing and selective electrode materials as well as proton exchange membrane fuel cells.

Tailored materials by CB surface modifications: i) oxidation and functionalization with amino-groups; ii) coating with iron oxides; iii) impregnation with an ionic liquid (IL) [6,7]. Carbon Capture and Storage (CCS) through CO_2 adsorption with solid sorbents is one of the most promising options for post-combustion CO_2 capture strategies. Tailored materials for CCS applications were produced tailoring the CB surface by: i) oxidation (CB_{ox}) and functionalization with amino-groups, ii) coating with magnetite (FM) and iii) impregnation with an ionic liquid (IL). The CB-based adsorbents exhibit good thermal stability (up to 200 °C in the case of amino-functionalized material and SILP and up to 500 °C in the case of magnetite composite) useful for the designing of practical application. The CO_2 capture performances, tested in a lab-scale fixed bed micro-reactor, were (with the exception of CB_{ox}) significantly higher than a 13X zeolite (up to 4 time more in the best case).

The role of the microporosity of CB acting as supporting material for the CO_2 active phase was also investigated. It was shown that the use of a microporous supporting material limits the accessibility of CO_2 toward the absorbing material (IL or FM) in all cases and in the exploited experimental conditions (CO_2 1–15% vol. and atmospheric pressure), lowering the number of available binding sites for CO_2 .

A deep study was conducted of CB/FM composites [6]. Five different CB/FM composites differing for the CB:FM ratio were produced and the performances toward CO_2 capture were tested. It was established that when the amount of CB in

the composite is higher than 14.3% and up to 60% the CO₂ uptakes is remarkably increased with respect to the pure FM.

The best adsorbing composite (50% of CB load) was tested in a sound assisted fluidized bed. Sound assisted fluidization considerably enhances the CO₂ uptake (about 20 mgCO₂/g). The composite can undergo several adsorption and desorption of CO₂ cycles without modification in adsorption properties, demonstrating its suitability for practical applications (Fig. 6).

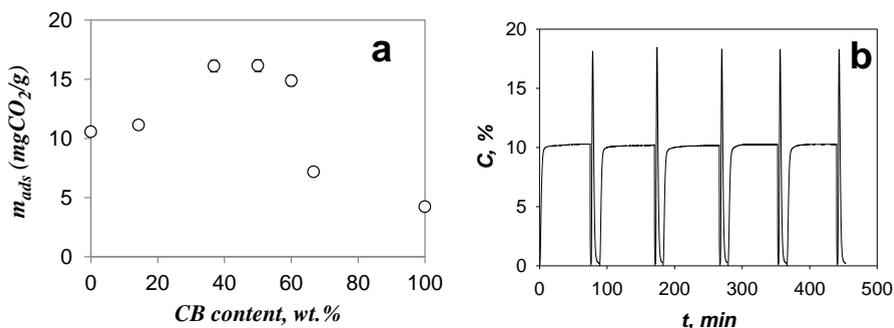


Figure 6. (a) Absorbed CO₂ as a function of nominal CB loading. (b) CO₂ outlet concentration profiles during cyclic adsorption and desorption in the fluidized bed.

The obtained results are interesting in prospect of a cyclic operation in two interconnected fluidized bed, since the time needed to adsorb almost the total CO₂ uptake is comparable to that necessary to completely regenerate the adsorbent.

Acknowledgments

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