Bol. Grupo Español Carbón

Engineered Carbon-based Nanomaterials for Energy, Biomass Valorization, Photocatalysis & Water Remediation

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Abstract

Carbon-based structures are the most versatile (nano)materials used in the modern fields of catalysis (e.g. photocatalysis and electrocatalysis), renewable energy (in both generation and storage) and environmental science.

The main achievements of our research group towards the development of hybrid and doped carbon-based (nano)materials for eco-sustainable catalysis, biomass valorization, energy technologies and smart devices were previously reviewed in *Boletin* nº 54 (December 2019).

In the present article, we will provide an update, focusing on our recent works.

1. Introduction

The Associated Laboratory for Green Chemistry REQUIMTE/LAQV is the largest Chemistry Network in Portugal, being recognized as a Research Centre of Excellence. Our research group from the REQUIMTE/LAQV, at the Chemistry and Biochemistry Department of Faculty of Sciences of Porto University (LAQV@FCUP) is integrated in the research group of *Materials for Sustainability and Wellness* (MatSusWell) and has been mainly contributing to the LAQV thematic lines of *Functional Materials and Energy - Clean & Renewable*. The current research activities involve the design and production of advanced multifunctional (nano)materials through sustainable methodologies for the scientific areas: i) Electrochemical Energy Conversion and Storage Technologies, ii) Photo(Electro)Catalysis, iii) Biomass Conversion into Materials, Fuels and Chemicals and iv) Wearable Technologies and Devices.

In the array of engineered (nano)materials developed by our group for the aforementioned applications, carbon (nano)materials hold a crucial role. This is due to their exceptional physicochemical properties and extensive adaptability for doping, functionalization, and combination with other components, such as transition metal complexes, noble and common metals, metal oxides, and polyoxometalates, to produce composites or hybrids.

In this article, the different R&TD activities that are being carried out at LAQV@FCUP in the field of engineered carbon-based (nano)materials for energy, biomass valorization and photocatalysis application are reviewed.

The article starts by reviewing the works developed regarding the fabrication of carbon-based electrocatalysts for energy conversion applications (fuel cells and water splitting) and smart energy harvesting and storage flexible/wearable technologies. Then, the development of bio-derived carbon materials as catalysts in biorefinery concept for energy, biomass valorization and photocatalysis is described. Finally, the last section is devoted to the development of carbon-based materials for water remediation.

2. Carbon-Based (Nano)composites for Energy Technologies

2.1 Electrochemical Energy Conversion

The ever-increasing global energy demand and the continuous consumption of fossil fuel sources has had a tremendous impact on our planet´s ecosystems and biodiversity and has posed serious challenges to energy security, pollution, climate change, and even society and political stability. So, it is imperative to develop cost-effective and environmentally sustainable solutions to meet and address these challenges. In this regard, storage and conversion of renewable energy will be a promising alternative to reduce this crisis. Some of these technologies include fuel cells (FCs), water splitting devices and CO_2 conversion into value-added products.

Within this context, our research work has been focusing on the design and preparation of novel noble metal-free composites, through eco-sustainable protocols, with enhanced electrocatalytic properties for oxygen reduction reaction (ORR) and oxygen evolution reaction (OER) in alkaline medium. Our contribution is mainly focused on the synthesis and physicochemical characterization of electrocatalysts involving carbon materials (doped or non-doped), polyoxometalates (POMs), transition metal oxides (TMO) and metal-organic frameworks (MOFs), as well as on their electrochemical performance. So far, several composites based on POMs and carbon materials (doped or non-doped) have been prepared and successfully applied towards ORR [1-3]. These include the immobilization of Wells-Dawson polyoxometalate $P_2W_{12}Mo_6$ onto nitrogen-doped multi-walled carbon nanotubes (MWCNT_N8 and MWCNT_N6), sulphur-doped multi-walled carbon nanotubes (MWCNT_S6), and sulphur-doped graphene (GF_S6) where the number (6 and 8) stands for the calcination temperatures (600 and 800 ºC, respectively). $P_2W_{12}Mo_6$@MWCNT_N8 and $P_2W_{12}Mo_6$@MWCNT_N6 showed particularly encouraging results, with onset potentials close to Pt/C, high diffusion-limiting current densities and low Tafel slopes [3]. Composites based on wheel POM KLi-P_8W_{48} have also been prepared through its immobilization on four distinct carbon materials, namely graphene flakes (GF), single-walled carbon nanotubes (SWCNT), multi-walled carbon nanotubes (MWCNT), and N-doped multi-walled carbon nanotubes (N-MWCNT) [1].

Bifunctional electrocatalyst for oxygen reactions (ORR and OER) have also been successfully developed by our group [4, 5]. Three POM@MWCNT_N6 composites based on $[M_4(H_2O)_2(As_2W_{15}O_{56})_2]^{y-}$ with $M_4 = Fe_4$, Ni_4 and Fe_2Ni_2 were successfully prepared by a simple and scalable strategy without the need for linker molecules. The prepared composites showed good, intrinsic electrocatalytic activity toward the ORR. More importantly, Fe_2Ni_2@MWCNT_N6 presented a remarkable OER performance, outperforming most of the reported results for other composites based on POMs and carbon materials and reaching an overpotential of 0.36 V *vs*. RHE (for $j = 10$ mA cm^{-2}) and a current density of 135 mA cm^{-2} at $E_p = 1.86$ V *vs*. RHE. This led to a ΔE of 0.85V *vs*. RHE ($\Delta E = E_{10}$ (OER) – $E_{1/2}$ (ORR)). Our results highlighted the role of having two different transition metals in the equatorial plane which led to a synergetic effect between the two types of metal resulting in an improvement of the electrochemical performances. At the moment, several combinations of transition metals are being explored to confirm these findings but also to unravel the overall reaction mechanisms [4].

Another set of materials that we have been developing are metal−organic frameworks (MOFs) derived carbons for application as OER electrocatalysts. This work has been done in collaboration with Dr. Luís Cunha-Silva also from *MatSusWell* group. MOFs have attracted attention due to their very interesting properties such as structural variance, compositional versatility, homogeneous distribution of metal atoms, and ordered porosity. However, these present low reactivity of metal centres due to their saturation with the coordinated linkers, limited diffusion capacities of reactants through MOF and porosity poor electron conductivity which limit their application in electrocatalysis [6]. To overcome these drawbacks, recent works have been focused on the pyrolysis of MOF sacrificial templates to produce derived nanostructured carbon materials. In this regard, our group has reported a facile synthesis of noble-metal free dual N,S-doped MOF-74-derived nanostructured carbon based materials by a 3-step strategy [7]. This approach consisted of MOF preparation, incorporation of thiourea (heteroatom source), and finally, simultaneous carbonization/doping treatment (Figure 1). One of the major advantages of this work relies of the fact that MOF-74 templates have been synthesized at RT, avoiding hard condition solvothermal processes, and contrary to the more extended pyrolysis treatments, carbonizations were performed under relatively low temperature, 500 °C. Considering their application as electrocatalysts, dual-, mono-, and undoped nanocarbons containing Co, Co/Ni, and Ni species were prepared and systematically tested to assess the influence of doping and metal composition on the OER performance. This work highlighted two synergetic effects, the first when N,S-dual-doped carbon is produced from a monometallic Co-MOF-74 template, N,S−Co@C, and the second when an undoped carbon is derived from bimetallic Co/Ni-MOF-74, Co/Ni@C. These two samples achieve remarkable OER performances with overpotentials as low as 0.41 and 0.44 V vs. RHE, respectively, being close to the state-of-art OER catalyst performance.

Ternary nanocomposites consisting of POMs, metal nanoparticles and a carbon matrix have also been developed by decorating four different MOF-74-derived nanocarbons with the sandwich-type polyoxometalate $[Co_4(H_2O)_2(PW_9O_{34})_2]^{10-}$ [8]. This work demonstrated for the first time the POM "bulk" deposition strategy as a useful tool to prepare highly active OER electrocatalysts and revealed the dramatic effect that the nanocarbon doping and metal composition has on the resultant POM loading, electrocatalytically active area and OER performance.

2.2 Smart Energy Harvesting and Storage Flexible/Wearable Technologies

The fascinating growth of wearable electronics and Internet of Things markets, combined with the global clean energy demand, have prompted the quest for sustainable self-chargeable smart technologies merging energy harvesting and storage functionalities [9, 10]. Thermally-chargeable supercapacitors open

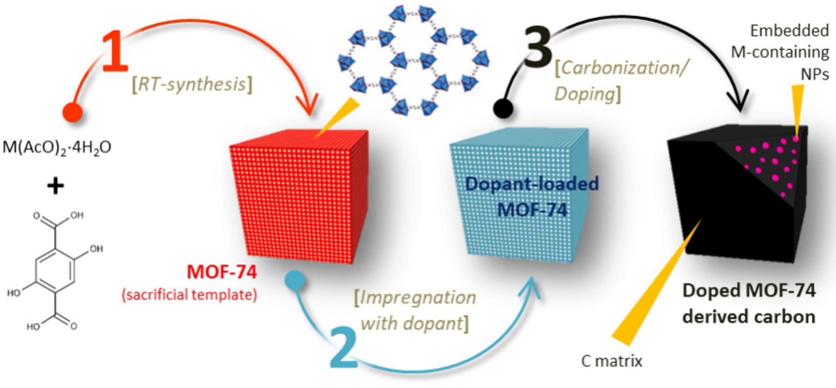

Figure 1. Scheme for the 3-step strategy used to produce electrocatalysts consisting of noble-metal-free doped carbons derived from an MOF-74 template. M = Co, Ni, or Co/Ni, and dopant = dicyandiamide, sulphur, or thiourea. Reproduced from ref 7 with the permission of American Chemical Society.

promising prospects as a 2-in-1 power source to feed low energy consumption electronic sensors and illumination systems for a wide array of applications, ranging from healthcare and fashion to defense and transportation. These systems can harness the ubiquitous wasted thermal energy from the human body, environment or industry, convert it into electrical energy, and subsequently store it [10].

LAQV@FCUP has been coordinating an R&TD project in this field since 2022, entitled *BoostEnergy4Tex – All-In-One Energy Harvesting & Storage Smart Textiles: Boosting the New Generation of Safe and Sustainable Self-Powered Wearable Electronics* (PTDC/CTM-TEX/4126/2021), in collaboration with the research unit IFIMUP – Institute of Physics for Advanced Materials, Nanotechnology and Photonics at FCUP, the Technological Centre for the Textile and Clothing Industry of Portugal – CITEVE, and the textile company TINTEX Textiles S.A. [11]. In BoostEnergy4Tex project, innovative multifunctional thermally-chargeable supercapacitor (TCSC) technologies are being developed on textile and plastic substrates using advanced 3D porous hybrid nanostructures combining carbon nanomaterials and metal sulfides as active electrode nanomaterials and non-toxic redox-active polyelectrolytes. Members of LAQV@FCUP and IFIMUP@FCUP have jointly developed a pioneer TCSC technology both on textile and flexible PET substrates through scalable eco-friendly processes and engineered architectures (multilayer and planar) [12-14]. MWCNTs were used as active electrode nanomaterial and polyvinyl alcohol (PVA) doped with orthophosphoric acid was applied as non-toxic solid-gel electrolyte. The sandwich-type all-textile-based TCSC could efficiently harness temperature gradients in the range of 6–25 K, reaching the highest Soret coefficient (S) reported so far for fabric-based TCSCs ($S = 1.85$ mV K^{-1}), which was ~10× higher than the Seebeck coefficient of thermoelectric materials (e.g., 190 μV K^{-1} for Bi_2Te_3) [13]. To test the practical performance of the textile TCSC device (6 × 6 cm^2 active area), it was attached to a hand pulse and the top electrode was heated with a hair dryer at low speed and low heat mode to simulate the outdoor environment under warm temperature conditions (Figure 2A). The practical test demonstrated the potentiality of the device to harness small temperature gradients, opening promising prospects for wearable electronic systems.

Other versatile wearable/flexible supercapacitor technologies are being produced on textiles and plastics using oxidized/heteroatom-doped and hybrid/composite carbon-based electrode nanomaterials assembled with redox-active polyelectrolytes to boost both the energy density and power density outputs, while ensuring long cycle life [15-17]. In particular, multifunctional electrochromic and glow-in-the dark/fluorescent supercapacitors can be highlighted for real-time monitoring of energy usage and reflective/safety electronic clothing in low visibility environments, respectively (Figures 2B and 2C) [18]. A dual-functional textile supercapacitor featuring energy storage and fluorescence features was produced with a sandwich-type structure using a new redox-active PVA/H_3PO_4 electrolyte containing Mn(II)-doped ZnS fluorescent pigment and MWCNT-coated textile electrodes [18]. The hybrid supercapacitor demonstrated superior energy storage performance compared to the analogous device with an undoped electrolyte. Specifically, it achieved 20% higher operating potential (1.64 V vs. 1.37 V), 48% higher energy density (1.63 W h kg^{-1} vs. 1.10 W h kg^{-1}), and 74% higher power density (641.6 W kg^{-1} vs. 369.2 W kg^{-1}). Moreover, it exhibited exceptional cycling stability (100%) after 8000 charge/discharge cycles. The device displayed a strong yellow-orange fluorescence under UV light irradiation, while maintaining the energy storage capability. Finally, it could feed a thermometer/timer electronic sensor for approximately 12 min after a 10 s charging period, and an LED for 1 min 13 s after being charged for 5 s.

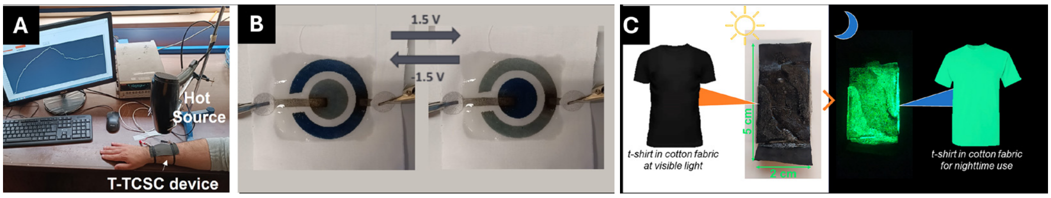

Figure 2. A) Thermally-chargeable textile supercapacitor. B) Electrochromic textile supercapacitor. C) Glow-in-the-dark textile supercapacitor.

3. Bio-derived carbon materials as Catalysts in biorefinery concept for Energy, Biomass Valorization & Photocatalysis

Growing global concerns about climate change, environmental pollution and declining availability of petroleum reserves are increasing the worldwide search for alternative renewable and cost-effective resources that ensure sustainable development. In this context, biomass has emerged as the most promising solution to substitute fossil fuels as it is the most abundant and renewable natural resource. An increasing research attention in recent years has been focused on lignocellulosic biomass conversion and biorefinery for production of multiple bio-based products to add profit and promotes sustainability to the agricultural industry and rural economy.

Biochar is a carbon-rich solid material formed during thermochemical conversion of lignocellulosic biomass, algae biomass, animal wastes, municipal solid wastes and other organic carbonaceous materials with limited supply of oxygen [21]. By-product streams from biorefineries can be converted

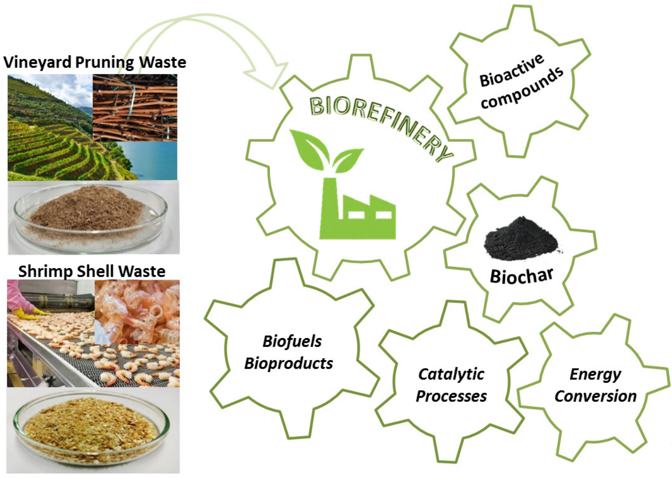

Figure 3. Biorefinery concept from Vineyard pruning waste and Shrimp shell waste [19, 20].

into carbon materials with catalytic applications, thus maximizing the use of resources and reducing waste. The bio-based carbon materials is increasingly recognized for its potential as a catalyst and catalyst support in environmental, catalytic and energy-related applications and they can be integrated into biorefinery processes to increase the overall efficiency of the process. The use of biochar-based catalysts in biomass upgrading is a breakthrough to increase the economy of biorefinery concept approach as previously observed by our group [22], in which valorisation of biochar allows obtaining additional environmental credits, which benefits the system, and is environmentally highly recommended in line with a biorefinery concept. Biochar-based catalysts can be tailored to exhibit specific surface properties and functionalities, making them suitable for applications such as wastewater treatment, soil remediation, and biofuels/bioenergy production. The physicochemical properties can be fine tuning through various activation and functionalization approaches aiming at enhancing the biochar´s catalytic or adsorption properties. Heteroatom doping can enhance the catalytic activity and selectivity of biochar-based nanomaterials by creating additional active sites and modifying the electronic structure of the carbon matrix. The engineering of biochar-based nanomaterials by functionalizing of the surface with ligands, metals, metal oxides, the production of hybrid or composite materials is a very interesting topic due to their wide range of applications, including soil improvement, water purification, carbon sequestration, energy storage, and catalysis [23] offering unique opportunities to address a wide range of challenges in this areas [21]. In the context of *BioreVinery* project (PTDC/BII-BIO/30884/2017), we also used in an integrated valorisation approach (Figure 4) the solid by-product of extraction technologies to produce biochar materials and consequently biochar-based catalysts [23-24]. We reported for the first time a protocol for the preparation of novel -SO_3H functionalized biochar and transition metal N-doped biochar based catalysts from biochar obtained from vineyard pruning waste. The biochar was activated through CO_2 in order to improve the textural properties (>700 m^2/g, BET). Then, the activated biochars were functionalized by: (i) addition of -SO_3H groups by functionalization with H_2SO_4, $ClSO_3H$ and 2-(4-chlorosulfonylphenyl)-ethyltrimethoxysilane (SO_3H-BioC); [25] (ii) incorporation of Ni, Co, Fe and Cu metal phases via incipient wetness impregnation/ball milling (M-N/BioC), (Figure 4) [26].

The SO_3H-BioC derived catalysts were applied in different catalytic reactions including the production of alkyl levulinates, as fuel additives, from 5-Hydroxymethylfurfural (HMF) and, in Prins-Ritter or Ritter reactions for the synthesis of bioactive

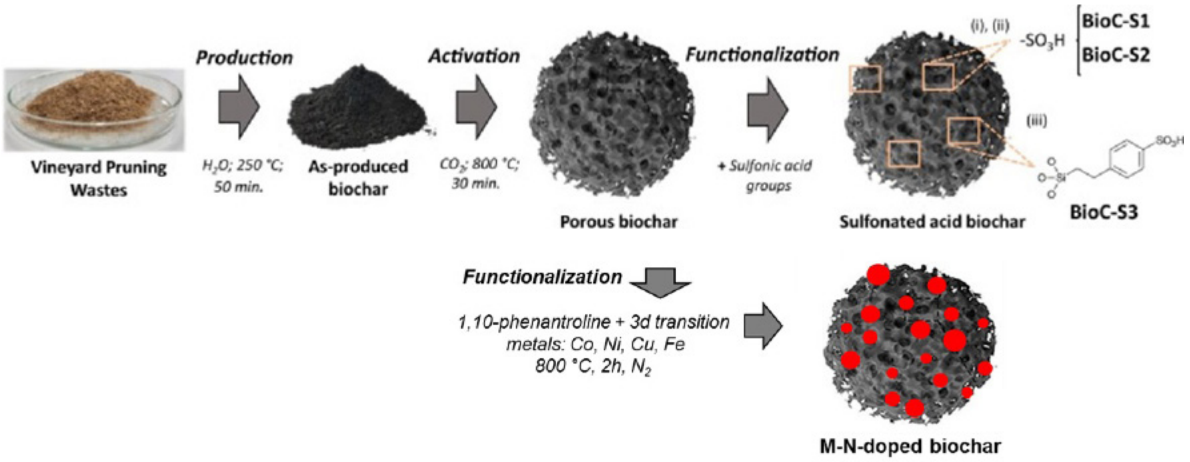

Figure 4. Preparation of novel -SO_3H functionalized biochar and transition metal N-doped biochar based catalysts. Adapted from ref. 23, 24 with the permission of MDPI.

chromenols and other amides (using different alcohols and nitriles and 2-phenylethanol as model substrate) [27, 28]. The observed remarkable activity and selectivity in these catalytic reactions established a promising catalytic route to valorise biomass platform molecules into biopolymers, bioactive compounds and biofuels. The results of catalytic one-pot conversion of HMF to ethyl levulinate (EL), in ethanol, without other co-solvent suggest that the highest acid site density play the paramount role to the rate-limiting ethanolysis step. The maximum yields of EL were obtained at 130–145 °C (84–98 % after 6 h), establishing a facile one-pot process for the production of EL [27].

The versatility of N-doped biochar-supported metal catalysts (M/N-BioC) derived from vineyard pruning waste, to promote circular bioeconomy, was also evaluated in catalytic transfer hydrogenation (CTH) of furfural(FF), and electrocatalytic oxygen reduction and evolution reactions (ORR and OER). The solid biochar was produced by hydrothermal carbonization. The followed nitrogen-doping (using 1,10-phenanthroline) and metal functionalization included the pyrolysis of the treated sample in nitrogen atmosphere and resulted in well dispersed metal particles. The catalytic results suggest that the metal composition and the nitrogen source play vital roles to promote the hydrogenation step of FF towards furfuryl alcohol (FA), achieving the highest conversion (80.0 %) and selectivity (87.6 %) over the Co/N-BioC catalyst, establishing a promising catalytic route to valorise biomass platform molecules using these bio-based catalysts. These M-N-Bioc materials have also been used as electrocatalysts in ORR and OER as an example of other alternative and emergent catalytic applications and showed good electrocatalytic activity for both reactions in alkaline medium with Co/NBioC showing the best performance for both reactions. Regarding ORR, it showed a nO_2 value close to 4, which indicates a direct process of O_2 to H_2O, an E_{onset} of 0.86 V *vs.* RHE and a j_L of -3.48 mA cm^{-2}. It was also remarkably insensitive to methanol crossover (93 % of current retention) which constitutes an advantage for methanol-based fuel cells. As for OER, the Co/NBioC showed an overpotential of 0.48 V vs. RHE and a maximum current density of 42.6 mA cm^{-2}. The bifunctionality anticipates its use in an unitized regenerative fuel cell that ultimately will offer a competitive advantage over the conventional precious metal catalysts.

More recently, in the context of *Shell4BioA* (EXPL/BII-BIO/0436/2021) [19], shrimp shells have been used as renewable source for biochar production, as they contain high content of heteroatoms (mostly nitrogen, but also a considerable amount of sulfur and phosphorus) which can be retained during the biochar preparation. Since shrimp shells are mainly composed by proteins, calcium carbonate ($CaCO_3$) and chitin, there is a high commercial value for these natural compounds for multiple applications [29]. Moreover, the $CaCO_3$ present in their structure acts as a self-template, contributing to the formation of pores and enhancing the biochar's surface area. Different M-supported shrimp shells based biochars have been prepared and used in CTH of FF, reductive amination of ketones and ORR and OER electrocatalytic reactions.

Given the need to reduce the consumption of non-renewable resources and global concerns over climate change it is crucial to find ways to make biomass utilization more efficient [30, 31]. In this context, the quest for new advanced technologies using renewable energy resources like solar energy, wind power and hydropower in energy sector has been increasing significantly in recent decades [31, 32]. The platform chemical HMF, usually obtained by oxidation of lignocellulose derived six-carbons sugars can be furtherly oxidized to a variety of useful entities as 2,5-diformylfuran (DFF), 5-formyl-2-furancarboxylicacid (FFCA), 2,5-furandicarboxylicacid (FDCA), among others [33]. Transformation of the hydroxyl of HMF into a corresponding aldehyde group, is of interest in a context of circular economy and recycling because the target product - DFF can be widespread used as monomer of furan-based biopolymers and intermediate of pharmaceuticals, antifungal agents, as well as in photography, analytical chemistry etc [34]. Several approaches for HMF oxidation have been explored. One of them is classic heterogeneous catalysts using organic solvents, and temperature (up to 165 ºC). The low DFF yield and selectivity, poor stability of the catalysts, demanding of noble metals, organic solvents, and drastic conditions (high pressure and temperature) make the process ineffective, expensive, and polluting. Even the use of ionic liquids to avoid catalyst deactivation due to adsorption of FDCA and by-products increases the costs and turns the process less sustainable [35]. In our group, magnetic composite photocatalysts based on the assembly of carbonaceous materials and semiconductors stand out as new advanced solar assisted photocatalytic solutions for the efficient and sustainable oxidation of biomass-derived platform molecules. The project *FotoBioTrans – Photocatalytic Transformation of biomass-derived compounds into valuable products*, (EXPL/CTM-CTM/0790/2021) coordinated by LAQV@FCUP was focused on design and production of a new generation of magnetically recyclable, light responsive, high-performance and high-selectivity carbonaceous material/natural biopolymer/semiconductor photocatalysts for the oxidation of biomass-derived platform molecules (HMF) to valuable products (Figure 5). To achieve the goal, multicomponent composites containing: carbon rich fraction of fly ash (sourced from a bituminous coal-fired thermal power plant, located in Abrantes, Portugal), natural polymer and semiconductors NPs (metal oxides) were prepared by cost-effective, environmentally friendly approaches.

The new generation of multi-component composites was applied for the photocatalytic oxidation of HMF. It was found that the substrate conversion and product distribution depend mainly on the type of semiconductor and the solvent used. TiO_2 and BiOBr-containing catalysts, using water as a solvent, led to non-selective oxidation resulting in HMF degradation. In contrast, the material containing the $MnFe_2O_4$ semiconductor facilitated the formation of DFCA. When acetonitrile was used as the solvent, HMF was selectively protoxidized to DFF.

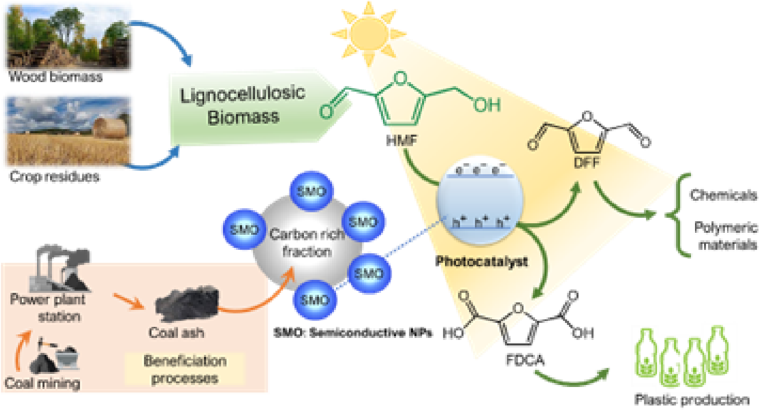

Figure 5. PhotoBioTrans project concept.

4. Carbon based materials for water remediation

The intensification of urbanisation and industrial activities significantly exacerbates the distribution of toxic contaminations into the aqueous environment. Especially synthetic dyes are dangerous organic compounds for the environment as over 10–15 % and 12 % of the dyes are estimated to be lost during dyeing and manufacturing/processing operations respectively. Approximately 20 % of these lost dyes are released into industrial wastewater, causing environmental problems [36, 37]. In our group, different composites or hybrids based on carbonaceous materials have been applied for the PhotoFenton water treatment processes. Several strategies were developed to prepare the materials with semiconductive nanoparticles, NPs (metal oxides or sulphides) with enhanced photo-activities under visible or UV-A light: (i) wet chemical methods; [38, 39] and (ii) in situ immobilization of TiO_2 nanoparticles over AC [40]. The catalytic activity of the novel catalysts S-GF/CuS/Fe_2O_4 [39] and GF/CuS/Fe_2O_4 [38] was evaluated in the oxidative degradation of dyes 4-Nitrophenol (4-NPh) and Rhodamine B (RhB) respectively in the presence of H_2O_2 and under UV-A light irradiation (low power lamp 15W). In both cases the tricomponent composites showed enhanced activities in dyes degradation due to the synergistic effect between the components. This effect was markedly clear for the S-GF/CuS/Fe_3O_4 nanocomposite [39], which showed a 20 % and 32 % increase in the 4-NPh degradation in comparison with S-GF/CuS and S-GF/Fe_3O_4 respectively, and 41 % and 55 % increase in comparison with the Fe_3O_4 and S-GF, respectively. Moreover, S-GF/CuS/Fe_3O_4 led to 61% degradation of 4-NPh (Fenton) vs. 95 % (photo-Fenton) process indicated that the radiation has a positive effect on 4-NPh degradation. Similarly, tri-component composite GF/CuS/Fe_3O_4 was able to complete RhB degradation in water (photoFenton) during 60 min [38]. The rate constant of RhB removal over GF/CuS/Fe_3O_4 was 2.1, 5.1 and 15.0 times higher than those of GF/CuS, GF/Fe_3O_4 and pristine Fe_3O_4, respectively confirmed the synergy between the components. The GF/CuS/Fe_3O_4 catalyst could be efficiently reused for at least three cycles.

TiO_2/AC composites were produced by the in-situ immobilization of TiO_2 nanoparticles over activated carbon (AC) derived from spent coffee grains with different ratio TiO_2:AC. The materials were tested as adsorbents (dark) and photocatalysts in a combined adsorption+photocatalytic process (solar irradiation) for methylene blue (MB) removal from ultrapure water, and from a secondary effluent (SecEf) of an urban wastewater treatment plant [40]. It was shown that the presence of AC in the composites increased the photoactivity of TiO_2, due to the high surface area of AC effectively concentrated MB around the deposited TiO_2. The best photocatalytic performance was found for the catalyst with 29 %wt of AC which was able to remove 98.1 % MB during 60 min under simulated solar light irradiation. When the assays were performed using a SecEf as water matrix, all the materials led to a MB discolouration percentage similar to that obtained in the assays with ultrapure water. Moreover, it was shown that the catalyst, besides allowing higher MB removal, also contributed to the overall improvement of the quality of SecEf.

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