Nanostructured Carbon Materials

Carbon Materials with Tuned Properties

Tuning the Surface Chemistry and Textural Properties

Modification of textural properties and surface chemistry of carbon nanotubes (CNTs) was carried out by a solvent-free methodology involving a ball-milling mechanical treatment and thermal treatment for the incorporation of different heteroatoms (N, S, P, and B). The synthesis of N-doped glucose-derived carbons has been investigated. Glucose-derived carbon/carbon nanotubes hybrid materials were prepared and the introduction of P-functionalities was explored.

Introduction

Due to the ability of carbon atoms to bond with each other (forming linear, planar, and tetrahedral arrangements), the production of several carbon materials (carbon nanotubes (CNTs), carbon nanofibres (CNFs), ordered mesoporous carbons, graphene-based materials, carbon gels) with distinct properties is possible. Taking advantage of the unsaturated carbon atoms at the edges of the graphene layers and at basal plane defects, various types of surface functional groups containing O, N, S, B or P can be incorporated on the surface of carbon materials either by in-situ doping during synthesis, or by post-doping in the presence of heteroatom-precursors.

By combining recent advances on the development of nanostructured carbons with their tunable texture and surface chemistry, innovative materials were developed to meet the requirements of the targeted applications in catalysis, adsorption and energy storage.

Current Development

Mechanothermal approach for heteroatom doping We extended a recently developed solvent-free post-doping methodology involving a mechanical step using a ball-milling and subsequent thermal treatment under N_2 flow to incorporate B, P, or S onto the surface of CNTs (Fig.1), using easily available precursors such as sodium thiosulfate, sodium dihydrogen phosphate, and boric acid [1].
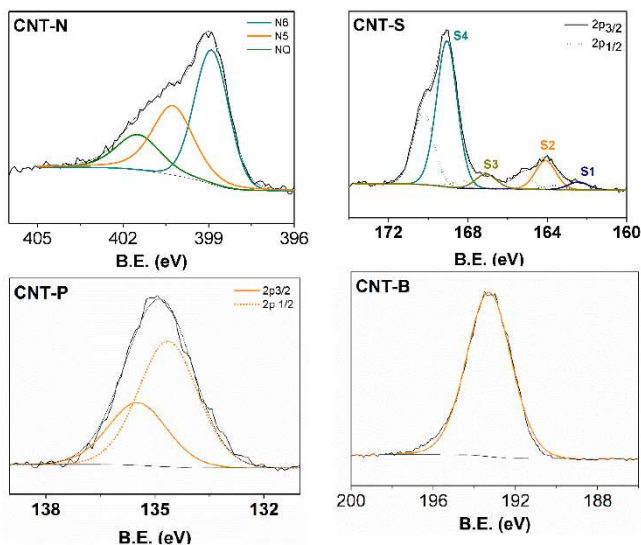
Different functionalities were identified in the samples: $Na_2S_2O_3$ (S1, B.E. = 162.4 eV), elemental S (S2, B.E. = 164.1 eV), Na_2SO_3 (S3, B.E. = 167.1 eV), and Na_2SO_4 (S4, B.E. = 169.1 eV); the P2p spectrum of sample CNT-P1 showed phosphorous in the form of metaphosphates (PO_3^-); and the B1s spectrum of the CNT-B sample showed a single peak at 193.0 eV, which is commonly assigned to boron oxide (B_2O_3).

The N, S-co-doping of commercial CNTs was also performed by a solvent-free mechanothermal approach using thiourea. CNTs were mixed with the N, S-dual precursor in a ball-milling apparatus, and then thermally treated under inert atmosphere between 600 and 1000 °C. The influence of the temperature applied during the thermal procedure was investigated. Textural properties of the materials were not significantly affected either by the mechanical step or by the heating phase. Concerning surface chemistry, the developed methodology allowed the incorporation of N (up to 1.43%) and S (up to 1.3%), as pyridinic (N6), pyrrolic (N5), and quaternary N (NQ) groups, and C–S–, C–S–O, and sulphate functionalities [2].

Fig.1. X-ray photoelectron spectra recorded for doped carbon nanotube (CNT-N) (N1s), CNT-S (S2p), CNT-P (P2p) and CNT-B (B1s) [1].
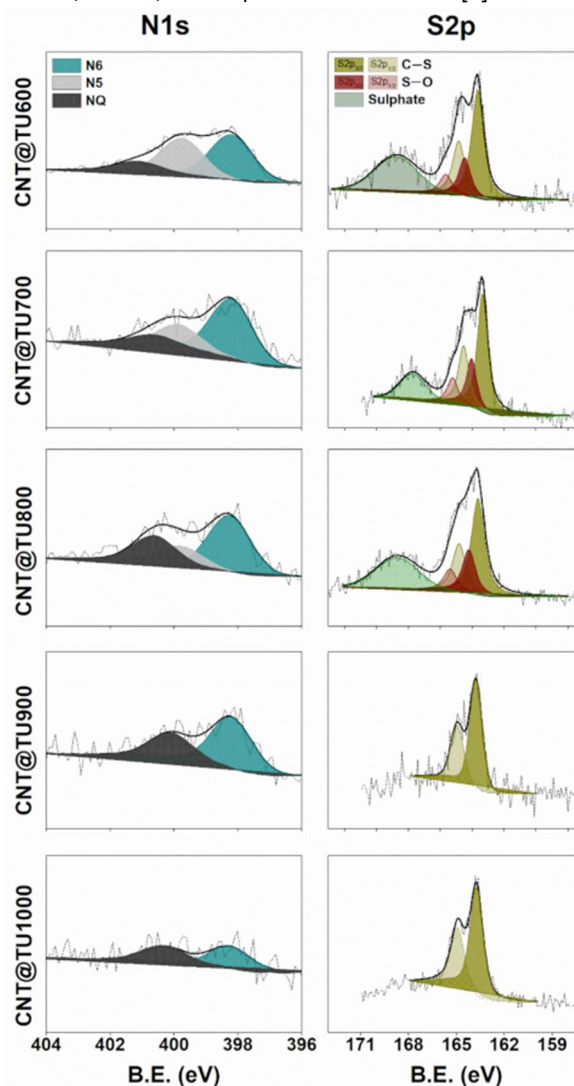

Fig.2. The N1s and S2p XPS spectra for the N, S-co-doped CNT samples [2].

Glucose-derived carbon materials Nitrogen-doped biomass-derived carbon materials were prepared by hydrothermal carbonization of glucose, and their textural and chemical properties were subsequently tailored [4]. Carbonization and physical activation were applied to modify the textural properties, while nitrogen functionalities were incorporated via different N-doping methodologies (ball milling and conventional methods) using melamine. Regardless of the doping method used, samples presented highly developed microporosity with specific surface areas up to 1943 m^2 g^{-1}. Similar amounts of nitrogen were incorporated into the carbon structures. However, significant differences were observed in the nitrogen functionalities according to the doping method applied: ball milling appeared to originate preferentially quaternary and oxidized nitrogen groups, while the formation of pyridinic and pyrrolic groups was favoured by conventional doping.

Glucose-derived carbon/carbon nanotube hybrid materials The influence of CNTs as additives in biomass-derived carbons was investigated. Glucose-derived carbon/carbon nanotube (CNT) hybrid materials were prepared by hydrothermal carbonization of glucose in the presence of CNTs and subsequent carbonization, physical activation (CO_2), or chemical activation (KOH) [5]. The proportion of CNTs added during the hydrothermal polymerization of glucose was varied. Both the thermal treatment applied and the addition of CNTs lead to changes in the textural and chemical properties of the activated carbons. It was observed that samples bearing CNTs exhibit a higher number of nucleation centers for glucose oligomers to polymerize, and consequently, the behavior of the hydrothermal carbon toward activation differs according to the activating agent employed. Moreover, the initial chemical speciation dominated by acidic groups shifts to more basic functionalities (quinones and carbonyl groups) with the addition of CNTs. Interestingly, it was observed that chemically activated samples with proportions of CNTs above 2 wt % developed mesoporous systems and did not present the sphere-like morphology commonly observed for HTCs. In contrast, they display solid and continuous structures yielding lower surface areas and oxygen contents (Fig.3). Regardless of the thermal treatment applied, carbonization or activation, an increase in the proportion of CNTs also causes changes in the surface oxygen speciation, which becomes enriched in more basic functional groups.
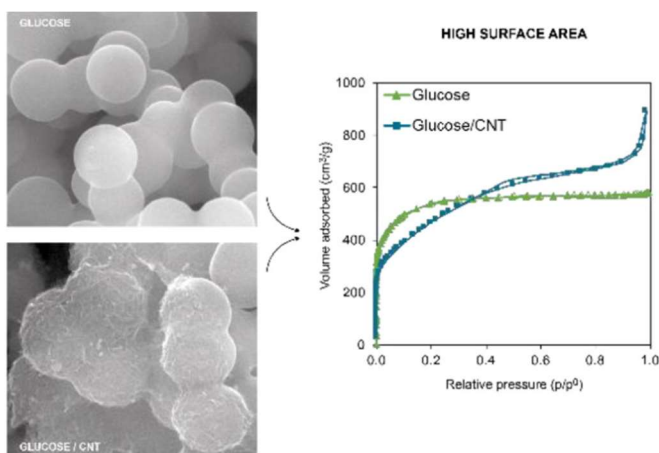
P-doped carbon hybrids were prepared by hydrothermal carbonization of glucose in the presence of CNT followed by chemical activation with phosphoric acid, using two different methods: I) by chemical activation with phosphoric acid and ii) by addition of phosphoric acid during the hydrothermal polymerization of glucose in the presence of CNT [6]. The role played by phosphoric acid on the final textural and chemical properties of the samples was thoroughly investigated by varying the temperature of activation. Temperatures higher than 700°C were needed to chemically activate the samples, while 800°C is the optimum temperature to generate the largest amount of micropores. In addition to oxygen functional groups such as carboxylic acids, anhydrides, lactones, phenols and carbonyl quinones, several phosphorus functional groups are also detected. At 700 °C, only C-O-P-O3 and C-P-O3 groups are observed; meanwhile, C3-P=O and C3-P groups appear at 800 °C and 900 °C, respectively. The P-doped hybrid treated at 800 °C resulted in a porous carbon material with a specific surface area of 806 m^2 g^{-1} and with a high phosphorus content (6.6%).

Future Work

Biomass-derived precursors, such as cellulose, chitosan, starch, lignin and tannins or raw biomass like wood, fruit shells and peels, can be processed by hydrothermal carbonization to obtain carbon materials. In an ongoing project in collaboration with Instituto Superior Técnico (Lisboa, Portugal) we are developing novel cork-derived carbons by more environmentally friendly and inexpensive routes.

Related Sustainable Development Goals

Outputs

PhD Theses
Raquel P. Rocha, Carbon Catalysts for Liquid Phase Reactions, PDEQB, FEUP, 2018.
Margarida Linhares, Nitrogen-doped graphene as metal-free carbon-nanocatalysts, PDEQB, FEUP, 2018.

Master Dissertations
Miguel Â.C. Granja, Functionalized phosphorous carbon materials derived from biomass for supercapacitor application, MIEQ, FEUP, 2018.

Selected Publications
[1] O. Salomé G.P.Soares et al., Journal of Carbon Research, C, 5(2), 30 (2019).
[2] Raquel P. Rocha et al., Catalysts 11(5), 578 (2021).
[3] Raquel P. Rocha et al., Catalysis Today 418, 114136 (2023).
[4] Rafael G.Morais et al., Beilstein J. Nanotechnol. 10, 1089 (2019).
[5] Natalia Rey-Raap et al., ACS Appl. Mater. Interfaces 11, 6066 (2019).
[6] Natalia Rey-Raap et al., Electrochimica Acta 354, 136713 (2020).

Team
José L. Figueiredo, Emeritus Professor; M. Fernando R. Pereira, Full Professor, Group Leader; O. Salomé S.G.P. Soares, Auxiliar Researcher; **Raquel P. Rocha**, Contract Researcher; Rafael Morais, contract researcher; Natalia Rey-Raap, Former Post-doctoral researcher; Miguel Granja, formed master student.

Funding

Fig.3. SEM images of glucose-derived carbon and hybrid material with CNT; and corresponding N2 adsorption-desorption isotherms [5].

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Carbon Materials from Plastic Solid Waste

Carbon-based materials can be synthesized from various precursors, including mixed municipal solid waste materials. Plastics, considering simulated and waste precursors, have been used to produce carbon nanotubes (CNTs). The main application is for oxidation reactions, either for wastewater treatment via catalytic wet peroxide oxidation (CWPO) of micropollutants or for reactions under biphasic systems, targeting oily wastewaters and removal of fuel contaminants (nitrogen and sulfur compounds).

Introduction

Carbon-based materials display several advantages in oxidative processes. Their ability to form oxidizing species (such as hydroxyl radicals) from oxidant sources (such as hydrogen peroxide) has been widely studied, and they are proven catalysts for oxidation reactions in the liquid phase, either as catalysts on their own or in hybrid forms [1]. In recent years, special attention has been given to developing catalysts from waste precursors [2], giving value to materials labeled as residues and allowing them to achieve circular economy goals. In this sense, many organic wastes have been tested as a source for preparing carbonaceous catalysts (mainly hydrochars, activated carbons, and biochars), especially from agro-industrial residues (plants, animal manure, sewage sludge, food waste, bagasses, and so on). Another residual source for the preparation of carbon-based materials is plastic solid waste (PSW). PSW offers advantages compared to typical biomass residues, such as the high carbon content [3] of typical polymers and their well-defined structures, yielding carbonaceous catalysts with relatively well-controlled structures. Thus, PSW can be used as a carbon source in the synthesis of several carbon materials, with special emphasis on carbon nanotubes (CNTs) via chemical vapor deposition (CVD). The CVD of a polymer source requires a two-step process: (i) cracking of the solid material into carbon-rich gaseous fractions and (ii) deposition of the carbonaceous gas into metallic catalysts for CNT growth. The CVD process also allows the introduction of heteroatoms by including other precursors during the growth period, such as acetonitrile [4], allowing *in-situ* doping of the CNT. The strategy can be interesting in increasing the catalytic activity towards the process studied. Furthermore, CNTs with magnetic properties can also be produced, given that suitable catalysts are used [2].

This topic's main objective is synthesizing carbon nanotubes from plastic solid waste precursors, tackling the issue of PSW accumulation. The aim is to use those materials as catalysts for oxidation-based treatments, focusing on three types of streams: (i) wastewaters containing contaminants of emerging concern, (ii) oily wastewaters containing lipophilic contaminants, and (iii) fuels containing nitrogenated and sulfonated compounds.

The term 'oily wastewater' comprises any wastewater containing an oil fraction that could cover petroleum and its derivatives, but also fats, vegetable oils, and others [5]. In some cases, the oil fraction can be of interest in the case of compounds with high-added value. Thus, selective oxidation processes can be interesting in the removal of undesired compounds while allowing recovering both oily and water fractions [4]. Selective removal of undesired compounds through oxidation is also studied for removing nitrogenated and sulfonated compounds from fuels in oxidative denitrogenation and desulfurization [1]. Some heteroatoms are inherently found in petroleum and petroleum-based fuels; among them, S and N are the most abundant (up to 8 *wt.*% and 1.8 *wt.*%, respectively). Some N and S- compounds are not reactive towards typical industrial processes (such as hydrodesulfurization), and the oxidation-based process comes as a complement to allow compliance with legislation regarding the presence of those compounds [1]. The CNTs discussed earlier are suitable catalysts for oily wastewater and fuel treatment due to their ability to tune their surface to display amphiphilic characteristics for contact with both water and oily phases.

Table 1. Examples of materials produced from LDPE, HDPE, PP and PS with distinct catalyst.

Source @catalyst	Yield (%)	S_{BET} ($m^2\,g^{-1}$)	Outer diameter (nm)	Water contact angle (°)
LDPE@ Ni/Al$_2$O$_3$-WI	32	72	15	22
LDPE@ NiFe/Al$_2$O$_3$-WI	49	153	16	19
LDPE@ NiFe/Al$_2$O$_3$-CP	48	134	12	54
LDPE@ NiFeAl-CP	55	151	15	63
LDPE@ Fe/Al$_2$O$_3$-SG	33	235	32	130
HDPE@ Fe/Al$_2$O$_3$-SG	28	189	29	126
PP@ Fe/Al$_2$O$_3$-SG	27	242	26	123
MIX@ Fe/Al$_2$O$_3$-SG	28	194	33	114
MIX@ NiFe/Al$_2$O$_3$-SG	55	148	N.M.	110

Current Development

This work has been carried out under a collaboration with Prof. Helder T. Gomes (IPB – Polytechnic Institute of Bragança, Portugal). Several materials have been prepared, considering polymers as precursors in the growth of CNTs. The initial approach was to evaluate different CVD catalysts using pure low-density polyethylene (LDPE). The catalysts evaluated were based on Ni and Fe supported on Al$_2$O$_3$, or a mixture of Ni, Fe, and Al, with no support, using distinct synthetic routes (wet impregnation – WI or coprecipitation - CP). It was found that the catalyst greatly influences the obtained CNT, with bimetallic catalysts surpassing monometallic catalysts. Some characteristics of the CNTs obtained can be seen in Table 1. It is evident that the Ni-based catalyst resulted in a much lower yield and surface area compared to bimetallic catalysts. Similarly, the synthesis route of the catalyst (wet impregnation versus coprecipitation) influenced the water contact angle of the

final materials. Other catalysts synthesized by sol-gel (SG) were also considered.

The use of different polyolefins was also evaluated, such as high-density polyethylene (HDPE) and polypropylene (PP), and a mixture of the three polyolefins (LDPE, HDPE, and PP), and it was found that the resulting materials have some similar properties (oxidation behaviour, water contact angle, surface chemistry, among others), but also differ in yield and in surface area (Table 1). On the other hand, when polystyrene (PS) was used as a precursor, an evident impact was observed in the obtained CNT, especially on some characteristics, such as the surface chemistry (pH_{PZC}), presence of defects (D/G ratio from Raman), and water contact angle (not shown here). The next step was to evaluate the use of real solid plastic waste as the carbon source for synthesizing CNTs. The first attempt was using residual LDPE obtained from the local waste management company, followed by a mixture of polyolefins. The use of real waste did impact some CNT properties, such as the yield and the surface area, among others (characterization is still undergoing). Some images of the mentioned materials are displayed in Fig. 1. Finally, some effort has also been put towards purifying CNT samples (*i.e.*, removing metal particles) and towards changing the surface chemistry of the materials by incorporating surface groups, specifically oxygenated ones.

The materials have been tested in distinct streams, namely in wastewaters containing nitrogenated compounds, treated by catalytic wet peroxide oxidation (CWPO), and for the oxidative removal of nitrogenated and sulfonated compounds by oxidative denitrogenation (ODN) and desulfurization (ODS).

In CWPO reactions, two model nitrogenated compounds have been under investigation, specifically acetaminophen [2] and quinoline [3]. In both cases, the complete degradation of the target compound was achieved regardless of the catalyst used in under 6 h of reaction, with total organic carbon (TOC) removals in the range of 42-70% for acetominophen and 49-75% for quinoline.

In ODN reactions conducted under a biphasic system (water-oil) aiming at selectively removing quinoline, the CNTs produced were highly active, with complete removal of quinoline from the oily phase in 15-60 min. The surface chemistry of the CNT was found to be relevant, with materials with higher incorporation of acidic groups allowing a higher quinoline removal. Similar results have been observed for pyridine. The CNTs are not only active but also stable, with removals higher than 98% being obtained for up to 6 cycles. The effect of several parameters affecting ODN was evaluated (pH, O/W ratio, catalyst concentration, temperature, hydrogen peroxide concentration, and CNT surface chemistry).

ODS reactions were carried out under a biphasic system (acetonitrile-oil) aiming at removing dibenzothiophene. Over 90% of dibenzothiophene was removed in less than 4 h of reaction under the best-case scenario. A controlled decomposition of hydrogen peroxide was found to be a key factor in increasing the removal of DBT, such as in the case of purified CNT samples.

Selective oxidation has also been carried out to recover oily and water phases from oily wastewater. CNTs were produced from pure precursors (ethylene and acetonitrile), varying the time feed of each precursor, leading to the formation of CNTs where undoped and N-doped sections
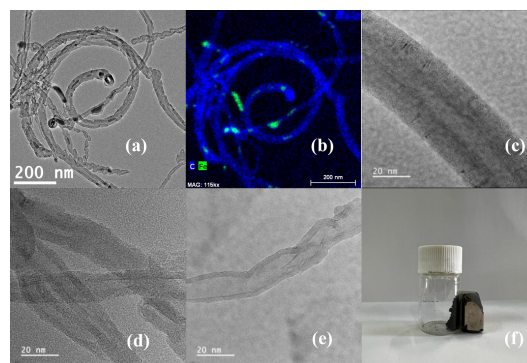

Fig 1. Some examples of CNT samples synthesized from (a, b) pure LDPE (LDPE@Fe/Al2O3), (c) a mixture of LDPE, HDPE, PP (pure source) (MIX@ Fe/Al2O3), (d) pure PS (PS@NiFe/Al2O3), (e) residual LDPE (LDPER@NiFe/Al2O3) and (f) magnetic response of LDPE@Fe/Al2O3.

were spatially isolated, giving a Janus structure to those CNT samples. It was found that nitrogenated moieties were directly associated with the materials activity, regardless if the reactions were carried out under an aqueous phase or a biphasic system. However, under a biphasic system, the ability of the material to form and stabilize a Pickering emulsion (i.e., an emulsion stabilized by a solid particle) was found to be the key characteristic in TOC removal. Thus, the material that allowed the emulsion with the smallest droplet size, which was achieved by adjusting Janus balance, was the material with the highest activity in biphasic reactions.

Future Work

In the near future, the efforts will be directed to synthesizing other CNT samples from real plastic solid waste, initially in separate fractions (HDPE, PP, PS, and so on) and later on using a mixture of polymers, approximating the composition of PSW. Time will also be devoted to exploring the correlation between different polymer sources and the characteristics of the CNTs. That step also passes through the evaluation of the cracking products of real PSW. The comparison of the catalytic activity displayed between samples derived from pure and waste precursors will also be addressed in the near future, mainly for ODS/ODN and CWPO reactions.

Furthermore, systems comprising simultaneous desulfurization and denitrogenation will also be studied, and the modeling of the reactions will be carried out.

Related Sustainable Development Goals

Outputs

PhD Thesis

F. F. Roman. Amphiphilic carbon-based materials for one-pot denitrogenation and desulfurization of liquid fuels. PDEQB, FEUP, ongoing.

A. S. Silva. Optimization of municipal solid waste management systems towards sustainability. PDEQB, FEUP, ongoing.

Selected Publications

[1] F.F. Roman et al., Catalysts 11, 1239 (2021)
[2] J.L. Diaz de Tuesta et al., Catalysis Today 419, 114162 (2023)
[3] F.F. Roman et al., Catalysts 13, 1259 (2023)
[4] F.F. Roman et al., Catalysis Today 420, 114001 (2023)
[5] F. F. Roman et al., Química 45, 162 (2021)

Team

Adrián M. T. Silva, Professor; **Joaquim L. Faria**, Professor; **Fernanda F. Roman,** PhD Student **Adriano S. Silva,** PhD Student