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Nano-Restructuration of Carbon Materials under High Temperature Heat Treatment for Environmental Application and Energy Storage

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Thermally-induced annealing by furnace in mild conditions and by fast reactor was applied to naphthalene pitch, an amorphous carbon, commercially available. The carbonaceous materials obtained with the two systems were characterized by advanced analytical tools for inferring the occurrence of structural improvements under annealing. The applicability of the produced nanomaterials for use in electrodes preparation for energy storage was discussed.

1. Introduction

Disordered and amorphous carbons originating from natural and synthetic sources (soot, pyrolytic carbon, pitches) constitute a cheap carbon feedstock sufficiently flexible to be tailored into sundry graphenic nanocarbons by a bottom-up transformation process such as thermally induced annealing. Structural transformations toward nanocarbons of different properties relevant for practical usage (fibers, composites and opto-electronic devices) can be tuned by a suitable choice of both amorphous carbon nanostructure and annealing conditions (Wang et al., 2011). The barrier towards establishing reliable and efficient methods for obtaining engineering-tailored nanocarbons is the lack of knowledge on the amorphous carbon and amorphous carbon-derived nanostructural features and their relationship with physical-chemical properties. Therein the aim of the present paper is the application to naphthalene pitch (Mochida et al., 1995], an amorphous carbon, commercially available and recently characterized in deep detail (Gargiulo et al., 2015 and 2016), of thermally-induced annealing, achievable by furnace in mild conditions (low pressure and temperature ≤ 1000 °C) and by fast reactor (under N2 at 1800°C). The naphthalene pitch represents an interesting "case study" for set-up the annealing and characterization procedures that can be then extended to cheaper waste carbonaceous materials as soot, pyrolytic carbon, coal and petroleum pitches (Apicella et al., 2017a). Advanced analytical tools were applied for the analysis of structural improved carbonaceous materials obtained from naphthalene pitch transformations under annealing. Moreover, insights on the determination of general structure-property relations linking the structural and physical-chemical features of amorphous carbon-derived materials will be given in the paper. The obtained nanomaterials can be tested for use in electrodes preparation for energy storage.

2. Experimental

2.1 Materials

AR mesophase pitch, kindly provided by Mitsubishi Gas Chemical Company, is a 100% mesophase pitch synthesized by polymerization of naphthalene (Mochida et al., 1995). AR NP has a H/C atomic ratio equal to 0.59 and a softening point of 290 °C. It is commonly named naphthalene pitch (NP).

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Carbon Black N110 (Phillips Petroleum) and Graphite (Sigma Aldrich CAS number 7782-42-5, powder, <45 µm, purity 99.99%) were also used as reference standards.

2.2 Set-up and procedures

Two systems have been used for the thermal annealing of NP, very different in terms of the process duration and environment. The employed experimental conditions are summarized in Table 1.

Table 1: Experimental condition of the annealing processes

Reactor type	AC	HSR
Environment	vacuum	N_2
Pressure	10^{-6} mbar	2 bar
Temperature	1000°C	1800°C
Heating rate	$1 \cdot 10^3$ °C/h	$2 \cdot 10^4$°C/s
Annealing time	3 h	3 s

Annealing Chamber (AC):

The annealing chamber was constituted by a steel crucible holder connected with a turbo and a rotative pump in series for reaching a high-vacuum condition [P = 10^{-6} mbar]. The crucible is surrounded by an electrical resistance embedded in an insulating material, in order to reach temperatures up to 1000°C. NP as a solid material was directly placed into the crucible inside the chamber and the pressure was decreased up to high-vacuum conditions [P = 10^{-6} mbar], which were set for 1 h. After that, the temperature was raised up 1000°C and kept constant for 3 hours. More details on the experimental system are reported in (Apicella et al., 2017b and 2017c)

Heated Strip Reactor (HSR):

The reactor is a special heated grid device, where the usual metal grid used as the sample holder is replaced by a pyrolytic graphite foil thermally stabilized for use up to 2500 °C (Senneca et al., 2010). The apparatus is enclosed in a stainless-steel vessel which can be pressurized up to 12 bar. The temperature of the grid is set by changing the value of the voltage at the two extremes of the strip. Due to the very high heating rate of the HSR, the strip can be considered isothermal for the entire duration of the test. About 100 mg of particles have been laid on the strip. The reactor is flushed with N_2 for 10 min with a high flow rate to remove any oxygen traces. After flushing, the pressure was increased to 2 bar. The strip has then been heated up to 1000°C and 1800°C and the total reaction time is 3 s. Due to the very small particle size, the coal particles are quickly heated up by contact with the strip and radiation from the reactor cover and can be considered isothermal with the strip. Details on equipment and heating rate profiles are provided in (Senneca et al., 2010).

2.3 Analytical techniques

The materials annealed into the two systems were preliminarily characterized with elemental analysis and Scanning Electron Microscopy (SEM). The elemental analysis was performed on a CHN 2000 LECO elemental Analyzer. SEM analysis was performed using a FEI INSPECT S.

Thermogravimetric (TG) analysis

Thermal behavior (volatility and oxidation reactivity) was studied by TG analysis performed on a Perkin-Elmer Pyris 1 TG analyzer. The pitch samples were heated from 50 to 750 °C at a rate of 10 °C min^{-1} in oxidative environment (air, 30 mL min^{-1}).

Raman

Raman spectra were measured by means of a Horiba XploRA Raman microscope system (Horiba Jobin Yvon, Japan) with an excitation wavelength of λ = 532 nm (frequency doubled Nd:YAG-solid state laser, 25 mW). The Raman spectral intensity and wavelength were calibrated with a silicon wafer by utilizing the first-order Stokes Raman of pure Si at 520 cm^{-1}. The microscope was focused onto the sample surface using the white light source and the objective with a magnification of 100. Then the white light was replaced by the laser beam and Raman spectra were recorded in the range of 900-3400 cm^{-1} (Raman shift) using a 1200 grooves/mm grating. The power of the excitation laser beam was about 1 mW. The Raman spectra were collected with an acquisition time of 30 s and an accumulation of 6 runs.

3. Results

Naphthalene pitch was treated in the two systems described in the Experimental section. The temperature of the annealing treatment initially chosen was 1000°C, which represents the temperature of an almost complete occurring of carbonization reaction, in dependence of the sample nature (Oberlin, 1984; Oberlin and

Bonnamy, 2013). During the thermal treatment, the first step is the removal of volatiles, constituted essentially by low molecular mass alkanes (C1–C3) and hydrogen (Dumond et al., 2005), with the formation of tar in the "semi-coke stage" (Oberlin, 1984). After that, the "coke stage", characterized by high carbon content, is reached by gas release only (total volatiles release is about 20% in weight). After the carbonization stage, the materials may or may not graphitize if they are heat-treated further at temperature well above 1000°C (Oberlin, 1984).

In the case of the annealing chamber (AC), the solid pitch has a time of 3 hours at 1000°C for the carbonization occurrence and the final morphology reached is reported in Figure1.

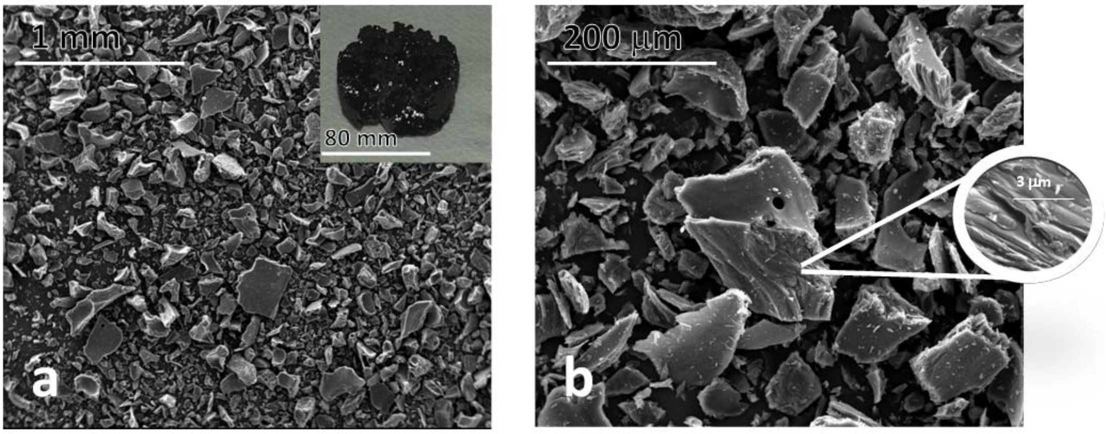

Figure 1: SEM images of NP treated in AC system at 1000°C.

The obtained material, as observable in the inset of Figure 1a, appears to be constituted of a hard block (showed in the inset of Figure1a) with some holes, with the diameter of the crucible (about 80 mm), very difficult to mill. SEM images in Figure1 revealed that, after milling, it is constituted by small flakes (of about 100µm), made of a sequence of stacked layers, as observable in the zoom at 3 µm scale reported in Figure1b.

In the case of HSR system, the time scale of the reaction is 3 order of magnitude and half lower with respect to AC (3s instead of 3 hours) and, when a temperature of 1000°C is employed, only the volatile release and the semi-coke stage occur, obtaining a fused material not removable from the graphite strip. Therefore, in the present work the carbonization process was performed at 1800°C in the HSR. The obtained material appears to be constituted by several columns (diameter of about 0.4 mm) of spongy and fragile material (as shown in the inset of Figure2a). SEM images, reported in Figure2, revealed a structure constituted of thin curved foils that, at micrometric scale (zoom at 3 µm scale reported in Figure2b) shows the presence of large spaces between the layers, indicating a high porosity of the structure.

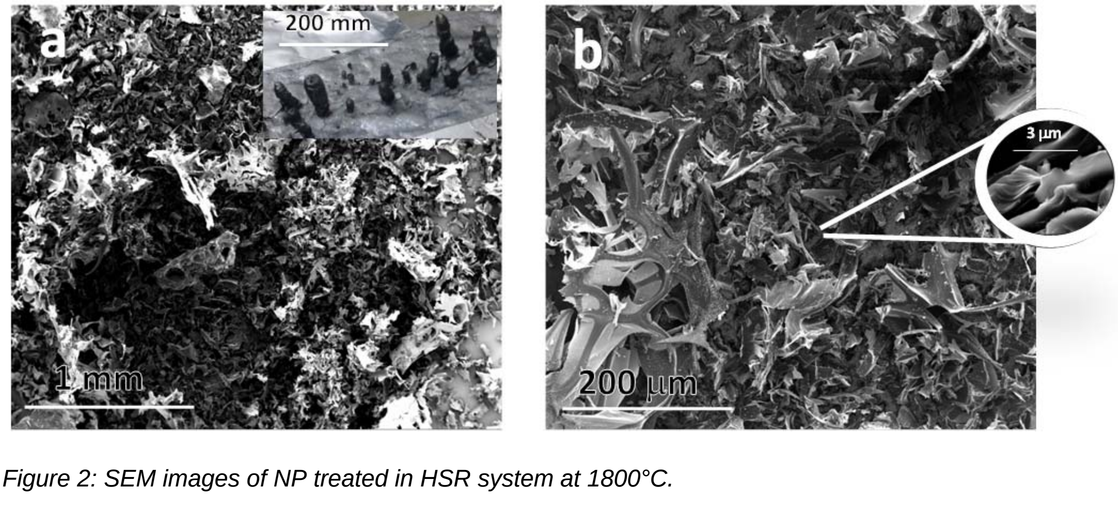

Figure 2: SEM images of NP treated in HSR system at 1800°C.

Unfortunately, porosimetry measurements were not applicable due to the fragility of the material and work in progress regards instead the use of microscopy for a quantitative measurement of pores distribution.

The TG and TG derivative (DTG) curves of the carbonized pitches, measured under air flow, are reported in Figure3, along with two reference standards, Carbon Black and Graphite. NP treated in AC system at 1000°C was named in the following “NP-AC 1000°C” and NP treated in HSR system at 1800°C “NP-HSR 1800°C”. It is observable that the TG profile of NP-HSR 1800°C resembles, especially in the first part, the profile of an amorphous carbon like the Carbon Black, whereas the NP-AC 1000°C profile is much more shifted toward the graphite one. Observing the DTG profiles reported in the right side of the Figure3, it is worth to note that NP-HSR 1800°C presents two peaks, one overlapped to the Carbon Black peak and the second, smaller, to the NP-AC 1000°C. The higher reactivity of NP-HSR 1800°C can be due to its much higher superficial area with respect to NP-AC 1000°C, which facilitates its reaction with oxygen, lowering its combustion temperature. By contrast NP-AC 1000°C presents an unique peak at a temperature of 780°C, which approaches the oxidation temperature found for Graphite standard (840°C).

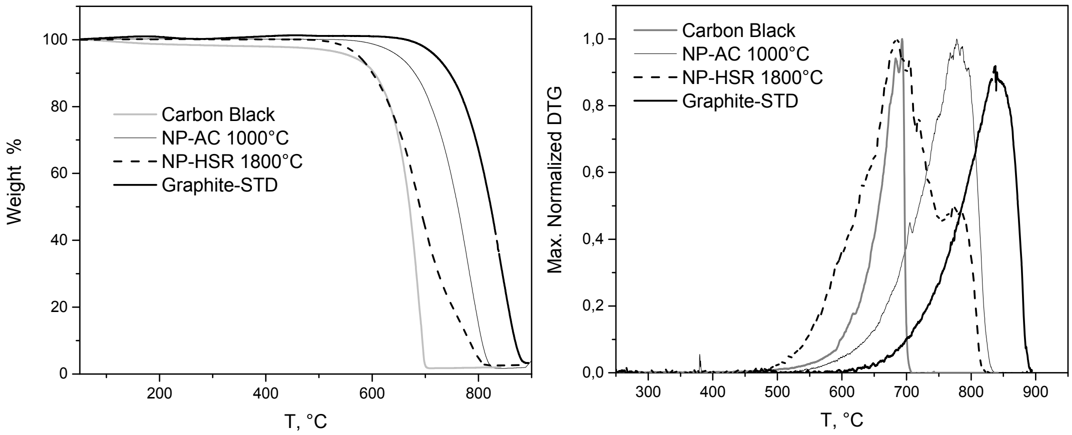

Figure 3: TG (left side) and DTG (right side) of NP treated in AC at 1000°C and in HSR at 1800°C, along with Carbon Black and Graphite standards.

Raman spectroscopy has been used to characterize the carbonaceous network of the NP annealed samples. Figure 3 reports Raman spectra of the samples produced in the two systems.

The two most remarkable spectral modes of the Raman spectra are the G peak at about 1600 cm^{-1} and the D peak at about 1350 cm^{-1}. An accurate analysis of Raman spectra by means of a systematic procedure is necessary to derive meaningful spectral parameters for carbonaceous material characterization. The deconvolution procedure and the peak attribution adopted in this work were already described in a previous study (Russo and Ciajolo, 2015). The ratio of the D to the G peak intensity, I(D)/I(G), reported in Table 2, is often used to trace carbonaceous material order/disorder.

Table 2: I(D)/I(G) ratio and FWHM (D) of NP-AC 1000°C and NP-HSR 1800°C as derived from Raman spectrum deconvolution.

Sample	I(D)/I(G) ratio	FWHM (D), cm^{-1}
NP-AC 1000°C	0.96	137.9
NP-HSR 1800°C	1.02	79.1

However, in their pioneering work Tuinstra and Koenig (1970) showed that I(D)/I(G) varied inversely with La. Ferrari and Robertson (2000) found that the relationship found by Tuinstra-Koenig equation is no longer valid for small crystallites (La < ~2 nm) and showed that in such case the D band intensity is proportional to the area of the aromatic domains. Thus in a narrow La range, centered around 2 nm, the same I(D)/I(G) ratio corresponds to two different La values. Nevertheless, to overcome this ambiguity and to probe the graphitization/carbonization process by Raman spectroscopy, the full width at half maximum of the D band (FWHM(D)) is often chosen as a more meaningful structural order parameter (Vallerot et al., 2006): FWHM(D) decreases as the structural order increases. NP-AC 1000°C is characterized by a FWHM (D) around 140cm^{-1}much broader in comparison to that of NP-HSR 1800°C whose Raman spectrum presents also a well-structured second order The Raman features indicate a higher structural order reached by NP-HSR 1800°C with respect to NP-AC 1000°C.

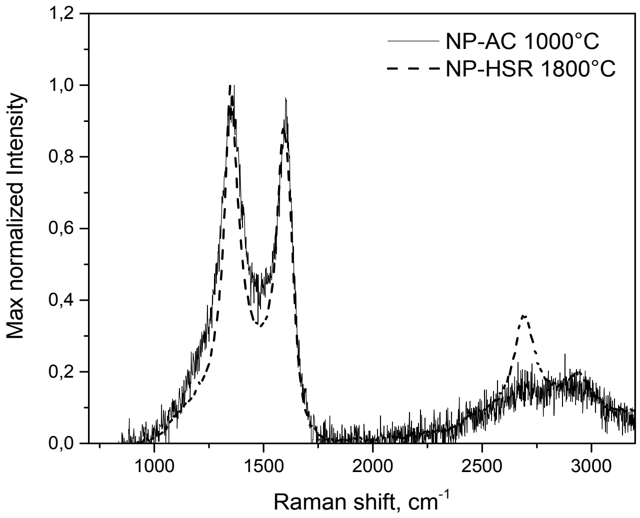

Figure 4: Normalized intensity Raman spectra of NP treated in AC at 1000°C and in HSR at 1800°C.

In order to test the two materials for the use of electrodes preparation for energy storage, it is mandatory to verify their capability of forming stable suspensions in organic solvents (Di Blasi et al., 2015).
Preliminary tests revealed that only the NP-HSR 1800°C was well dispersed in isopropanol, which is the solvent commonly used in electrodes preparation (Di Blasi et al., 2015). Work in progress regards the test of NP-HSR 1800°C performance after its deposition on electrodes through isopropanol dispersion and also the trial of other organic solvents for dispersing NP-AC 1000°C.

4. Conclusions

In the present work two annealing processes, in mild conditions, have been performed to improve the structural order and therefore the technological interest of an amorphous carbon, the naphthalene pitch. It was found that the temperature and the annealing times are important to address morphological, structural and mechanical properties of the obtained materials. A temperature of 1800°C is necessary for carbonizing in a very short time (3 sec) the material, obtaining a spongy, porous and fragile material (NP-HSR 1800°C), easily prone to be milled and dispersed in organic solvents for deposition on electrodes and electrochemical application. It appears also to be more reactive, due to its high superficial area, but instead presents a higher degree of nanostructural order with respect to the material obtained in furnace. In furnace, it is possible to use lower temperature for carbonization occurring (1000°C) but much longer times are necessary (3 hours) and a material much harder is obtained (NP-AC 1000°C), difficult to be milled and dispersed in solvents. Work in progress regards the test of mechanical properties of the material produced in furnace for exploring its possible applications.

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