Modification of carbon black by thermal treatment in air atmosphere

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Abstract. We modified carbon black (CB) with a large surface area (ENSACO 350 GRANULAR) by acetone and further thermal treatment. The pristine and the modified CB were characterized by scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS), X-ray powder diffraction (XRD) and Raman spectroscopy. The acetone treatment increases the content of oxygen-containing radicals in CB. The thermal annealing was performed at temperatures ranging from 250 °C to 1080 °C for three hours in air atmosphere. The powder XRD patterns revealed that the broad complex peak centered at about \(2\theta = 24.7\) – 24.8°, which arises from graphitic-ordered \(sp^2\)-hybridized carbon, shifts to its usual position at \(2\theta = 26.2°\) as the annealing temperature is increased. We concluded that the above results pointed to a relative decrease in the number of 3D graphitic nano-crystals and an increase in the predominantly 2D ones. The Raman studies confirmed the above conclusions.

1. Introduction
Carbon black (CB) is composed of very fine particles consisting mainly of allotropic carbon forms. These particles have irregular shape with diameters usually between 5 nm and 300 nm and may be described as a predominantly amorphous carbon whose surface is a core surrounded by nano-crystalline graphite and nano-sized multi-layered graphene [1, 2]. Additionally, the presence of such surrounding planes of \(sp^2\)-hybridized carbon determines the natural aptitude of primary CB particles to form agglomerates and even larger aggregates. The amorphous carbon core and the complexes of primary CB particles affect the hydrophilic properties of CB, making its direct application in aqueous media difficult without some initial treatment. Recently, we reported on the chemical (with acetone or hydrochloric acid) and thermal treatment of Spheron 5000 CB [3].
observed that the treatment by acetone and by hydrochloric acid resulted in a significant enhancement in the CB hydrophilic properties. Additionally, we established that the thermal modification at temperatures up to 1080 °C enhances the stabilization in predominantly 2D carbon particles, while annealing at 1150 °C leads to the formation of 3D nano-crystals, i.e., nano-graphite. Here we report results on the thermal annealing of ENSACO 350 Granular (TIMCAL Graphite & Carbon) CB initially treated by acetone.

2. Experimental
CB is hydrophobic and very difficult to press into pellets due to residual gases in the agglomerates and aggregates of CB. To minimize these effects, we treated pristine CB with pure acetone following the procedure described in detail in [3].

For thermal modification, we used acetone-treated CB; the process was carried out in an open quartz reactor tube of 30-mm inner diameter. A digital thermostat controlled the furnace temperature, and the samples were open to atmospheric air. The CB specimens (about 6 – 8 cm³ CB for each experiment) were heated to 250 °C, 510 °C, 810 °C or 1080 °C for three hours. The specimens were designated as CBN (pristine carbon black), CBA (CB treated by acetone) and CBA-250, CBA-510, CBA-810 and CBA-1080 indicating the annealing temperature.

We used a LYRA TESCAN scanning electron microscope at 5 – 10 kV accelerating voltage in secondary electron image (SEI) mode without deposition of any conducting amorphous film on the specimens.

The X-ray photoelectron spectroscopy (XPS) measurements were performed on a Kratos AXIS Supra spectrometer with a monochromatic Al X-ray source under vacuum better than 10⁻⁸ Pa at a 90° take-off angle. The C1s, O1s and Si2p lines were recorded for each specimen and, further, the C1s lines were subjected to a fitting procedure by the XPSPEK4.1 software.

A PANalytical Empyrean apparatus was employed for the X-ray powder diffraction (XRD) measurements in a θ - θ geometry using Cu Kα radiation. The Raman measurements were conducted on a HORIBA Jobin Yvon Labram HR 800 micro-Raman spectrometer with a 0.5-mW He-Ne (633 nm) laser. The laser beam was focused on a spot of about 2 μm in diameter on the studied surfaces. The spectral resolution was 1 cm⁻¹ or better.

3. Results and discussion
Oxygenation of CB in air during the thermal treatment causes a low weight-loss of CB (below 1 wt %) of the annealed CB charge, which can be related to a relatively low excretion of oxygen-containing carbon radicals and CO₂/CO molecules.

![Figure 1. SEM secondary electron images of specimens CBN (a), CBA (b), CBA-250 (c), CBA-510 (d), CBA-810 (e), CBA-1080 (f).](image)

![Figure 2. Deconvoluted XPS C1s lines of specimens CBN and CBA – left-hand and right-hand panel, respectively.](image)
We did not observe a significant influence of the acetone and of the thermal treatment of the CB specimens in our scanning electron microscopy examinations (figure 1 a–e). The C 1s lines of the CB specimens investigated by XPS can be deconvoluted into several peaks: the most intensive one is situated at about 284.2 – 284.4 eV, corresponding to sp²-hybridized carbon. The next one appears around 284.9 eV and corresponds to sp³-hybridized carbon [5, 6]. Two weaker peaks arise at higher binding energies (about 286.5 eV and 287.7 eV) and should be related to –C=O/–C=OH and –C=O radicals, respectively [7]. The additional peak marked by C (figure 2) situated at 283.2 eV and observed in all carbon samples studied is usually attributed to sp³-hybridized C, as it is well known that the charging effect influences the peak top of C 1s spectra. Based on experimentally confirmed calculations, Fujimoto et al. [8] - [8-12] showed that the peak position of sp³C is lower than that of sp²C, indicating that the peak positions are largely influenced by charging effects and the assignment of sp³C in many reports could be inappropriate, depending on the analysis conditions and types of defects in the carbon materials. Therefore, we associated the peak at 283.2 eV to sp³C due to the charging effect caused by the disconnection of the pathway of electrons between sp²C and sp³C. The XPS analysis results are summarized in table 1.

The XRD patterns of all specimens (figure 3a) are similar: two broad peaks marked as D and B in figure 3a appear at 2θ values of 25° and 43°, respectively. The former peaks have a more or less pronounced shoulder at higher inter-planar distances (2θ = 22.3 – 24°). The latter one consists of two reflections with different intensity (ICSD 31170): from (-110) and (010) planes at 2θ = 42.214° (with a total intensity of about 6.90% of the intensity of d_{001} reflection (I_{001})); and from (-111) and (011) at 2θ = 44.365° (with a total intensity of 34.07% of I_{001}) [13]. We deconvoluted the XRD patterns in the 2θ = 18 – 49° region using pseudo-Voigt approximation peaks (figure 3b) and extracted B₁, B₂ and D₁ and D₂ peaks from the B and D

![Figure 3a. XRD patterns of specimens CBN (black trace), CBA (grey trace), CBA-250 (red trace), CBA-510 (green trace), CBA-810 (blue trace) and CBA-1080 (purple trace).](image)

![Figure 3b. Deconvoluted XRD pattern of CBN specimen.](image)

**Table 1.** Summarized results for the surface composition of CB samples obtained by XPS and evaluated percentage of functional groups (C=O/C=OH; C=O and O–C=O) from the total carbon.

| Experiment | Fraction sp²/sp³C | C, at% | O, at% | Si, at% | C=OH % C–O % | C=O % | O–C=O % |
|------------|------------------|--------|--------|---------|---------------|--------|---------|
| CBN        | 0.32             | 93.83  | 5.86   | 0.31    | 7.92          | 3.83   | 7.00    |
| CBA        | 0.31             | 90.50  | 9.50   |         | 8.05          | 6.25   | -       |
| CBA-250    | 0.23             | 88.01  | 11.56  | 0.44    | 4.93          | 8.83   | -       |
| CBA-510    | 0.13             | 87.51  | 11.89  | 0.61    | 13.14         | 2.26   | -       |
| CBA-810    | 0.36             | 91.44  | 8.11   | 0.45    | 10.48         | 7.98   | -       |
| CBA-1080   | 0.28             | 87.76  | 11.92  | 0.32    | 10.34         | 9.74   | -       |
reflections, respectively. Table 2 shows the summarized values of 2θ as well as the relative intensity of these peaks. The D₁ peak should be ascribed to diffraction from somewhat distorted (001) planes of the graphitic phase [13]. The D₁ can be related to a reflection from similar planes, but is most probably due to the presence of graphene oxide/reduced graphene oxide (GO/RGO) [14].

Table 2. Summarized results by deconvolution of Raman spectra: intensity ratios of D and G bands (I_D/I_G) and of 2D and G bands (I_{2D}/I_G); and XRD patterns: intensity ratios of D₁ and D₂ (I_{D1}/I_{D2}); of B₁ and D₂ (I_{B1}/I_{D2}); and of B₂ and D₂ (I_{B2}/I_{D2}) peaks of all specimens.

| Experiment | I_D/I_G | I_{2D}/I_G | D₁ | D₂ | B₁/ | B₂/ |
|------------|---------|------------|-----|-----|-----|-----|
| CBN        | 48      | 26         | 23.19 | 57  | 25.59 | 42.53 | 7 | 44.02 | 18 |
| CBA        | 48      | 23         | 22.35 | 26  | 25.15 | 42.28 | 7 | 44.10 | 22 |
| CBA-250    | 45      | 30         | 23.41 | 64  | 25.75 | 42.50 | 7 | 44.21 | 24 |
| CBA-510    | 54      | 18         | 23.70 | 67  | 25.75 | 42.46 | 14 | 44.48 | 29 |
| CBA-810    | 46      | 31         | 23.51 | 68  | 25.74 | 42.80 | 24 | 44.39 | 21 |
| CBA-1080   | 47      | 38         | 24.29 | 97  | 25.77 | 42.77 | 22 | 44.27 | 29 |

The Raman spectra of the specimens CBN, CBA, CBA-250, CBA-510, CBA-810 and CBA-1080 (figure 4a) are very similar to those of nano-sized graphite and a mix of graphene oxide (GO) and reduced graphene oxide (RGO) [15, 16]. It is dominated by two broad bands (D and G) situated at about 1330 cm⁻¹ and 1590 cm⁻¹, respectively. It is worth noting that two overtones (2D and 2D’) are also distinguishable (figure 4a). Peaks G and D’ are merged in all specimens, but the presence of the D’ band can be suggested in all specimens. Moreover, it is clearly distinguishable in CBA-810 and CBA-1080 as a shoulder at the higher-energy side of the G band. To distinguish the different features in the CB samples’ Raman spectrum, we deconvoluted the Raman spectra of all specimens (table 2). In figure 4b we show the results of deconvolution of the 2D band of specimen CBA-1080 only, as this band is most clearly manifested there. Additionally, the combination bands at 1880 – 2100 cm⁻¹ are also visible but not indicated in figure 4b. It seems that our specimens consisted of complex phases (nano-sized graphite, GO and RGO), and the nano-sized graphite dominated in the CBN specimen, while the GO/RGO phases predominated in the CBA specimens.

According to the XPS results, the chemical treatment by acetone (CBA samples) unambiguously increased the content of the –C=O / –C–OH and –C=O radicals and removed the carboxylate (–O–C=O) radicals. It seems that the thermal treatment has a monotonic influence on the CB: the relative
intensity $I_D/I_G$, i.e. the relative intensity of $D_1$ peak in the XRD patterns increases with the annealing temperature. It is shifted to the $D_2$ peak (table 2), i.e. the $d_{(001)}$ inter-planar distance of the oxidized hexagonal planes decreases, while the inter-planar distance of the “graphitic” planes ($D_2$ peak) remains practically constant. The relative intensity of $B_1$ increases with the increasing annealing temperature (table 2). This relationship can be ascribed to a decreasing number of defects in the hexagonal planes. The presence of oxygen-containing radicals (and the total oxygen content) increases with the annealing temperature. The Raman spectra measurements confirmed these conclusions (table 2). The graphene-like (transformed from 3D to 2D particles) structure is most clearly pronounced in CBA-1080 as the $I_D$ band in the Raman spectrum is about 40% of $I_G$. The highest relative intensity of the G-band and the lowest intensity of the 2D band in the Raman spectrum of CBA-510 pointed to the presence of the most strictly ordered 3D graphitic phase.

4. Conclusions
The treatment of CB with acetone removes the -O-C=O radicals. The thermal treatment increases the oxygen content in CB as the annealing temperature is increased. The $d_{(001)}$ inter-planar distance of the hexagonal planes of GO/RGO decreases, i.e. the number of oxygen/oxygen-containing radicals situated between the hexagonal planes relatively decreases. The number of defects in the hexagonal planes decreases – the relative intensity of peak $B_1$ related to (-110) and (010) planes decreases with the increasing annealing temperature. The annealing at 510 °C preserved the 3D graphitic ordering in the nano-crystalline particles. The thermal treatment at 810 °C and at 1080 °C for three hours in air atmosphere enhances the formation of graphene-like (predominantly 2D) phases in the CBA-1080 specimen.

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