Supporting information

Green Oxidation of Carbon black by dry ball milling.

Aida Kiani,[a] Maria Rosaria Acocella,*[a]Veronica Granata,[b] Elisabetta Mazzotta,[c[Cosimino Malitesta[c] and Gaetano Guerra[a]

[a]   Dipartimento di Chimica e Biologia "Adolfo Zambelli", Università degli Studi di Salerno, Via Giovanni Paolo II 132, 84084 Fisciano, Italy.
    *Corresponding author
    Email: macocella@unisa.it
[b]   Dr. V.Granata
    Department of Physics "E. Caianello" University of Salerno
Via Giovanni Paolo II, 84084, Fisciano (SA)- Italy
[c]   Prof. E. Mazzotta, Prof. C. Malitesta
    Analytical Chemistry Lab, Department of Biological and Environmental Sciences and Technologies
    University of Salento
     Via Monteroni 73100 Lecce (Italy)

*Corresponding author

Maria Rosaria Acocella

Email: macocella@unisa.it

Number of pages:9

Number of tables: 3

Number of figures:6

EXPERIMENTAL SECTION:

1. **Materials and methods**

1.1 Materials

Carbon black samples (CB) of grade N110 containing 99.8% carbon and BET surface area 130 m^2 g^{-1}, were purchased from Cabot Company (USA).

1.2 Preparation of oCB by Ball Milling.

The ball-milling experiments were conducted at room temperature in a planetary ball mill Pulverisette 7 Premium (Fritsch GmbH, Germany).
The milling parameters were set as shown in Table S1. Silicon nitride balls with a diameter of 10 mm were used in all procedures in a Silicon nitride jar of 80ml.. Three rotational frequencies were examined: 300, 500, and 700 rpm. The 5-minute break was taken every 5 minutes before the milling resumed. Samples were designated oCB-1h, oCB-5h, oCB-9h, oCB-11h ,and oCB-13h. In order to determine the mass yield of the milled product, samples were weighed after ball milling. An Easy-GTM system (Fritsch GmbH, Germany) was used to measure the temperature of the milling beakers.

Table S1. Experimental Conditions of the Ball Milling Experiments

ball-to-powder weight ratio	150
rotation frequency [min^{-1}]	300, 500, 700
ball size [mm]	10
total balls weigt [g]	15
milling tool material	Silicon nitride
beaker volume [cm^3]	80
CB weight [mg]	100
sample notation	oCB-1h, oCB-5h, oCB-9h, oCB-11h, oCB-13h

2. **Characterization.**

2.1. BET surface areas. A Nova Quantachrome 4200e instrument was used to measure N_2 adsorption areas of carbon and milled carbon samples at liquid nitrogen temperatures (77 K).

Degassing samples at 70 °C under vacuum for 24 hours preceded the adsorption measurements. The surface area values were determined by using 32-point BET analysis.

2.2. Elemental analysis. Elemental analysis was performed with a Thermo FlashEA 1112 Series CHNS-O analyzer.

Table S2: EA of CB before and after milling for different times and RPM

| Sample	N (%)	C (%)	H (%)	O (%)	O/C
CB	0.2	97	0.6	2.2	0.02
CBM300/1h	0.5	94	0.5	5	0.05
CBM300/5h	0.9	82	1.1	16	0.19
CBM500/1h	0.7	89	0.3	10	0.11
CBM500/5h	1.3	76	0.7	22	0.29
CBM500/9h	1.2	72	0.8	26	0.36
CBM500/11h	1.2	71	0.8	27	0.38
CBM500/13h	0.9	77	1.1	21	0.26
CBM700/1h	0.23	94	0.29	5.5	0.06
CBM700/5h	0.4	91	0.72	7.9	0.09
CBM500/9h (zirconia)	0.3	83	0.7	16	0.19
CBM500/9h (stainless steel)	0.4	77	0.6	22	0.29

2.3. Thermogravimetric analysis. The thermogravimetric (TG) analysis was carried out on a Q500, from 10 to 800 °C at a heating rate of 10 °C, under N_2 below. Weight decreases below 100 °C were used to determine water content.
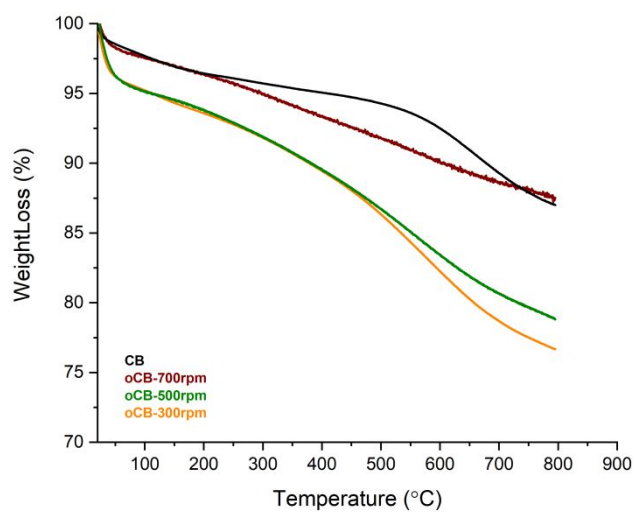
Figure S1. TGA scans of CB before and after milling for 5 hours at different speeds
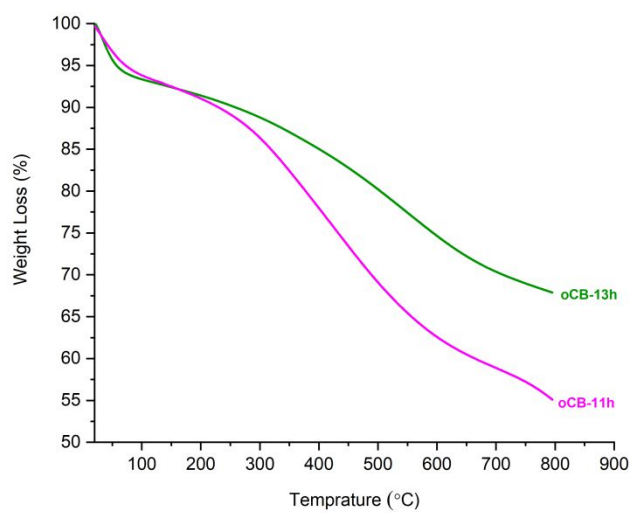
**Figure S2.** TGA scans of CB milled 11h and 13h
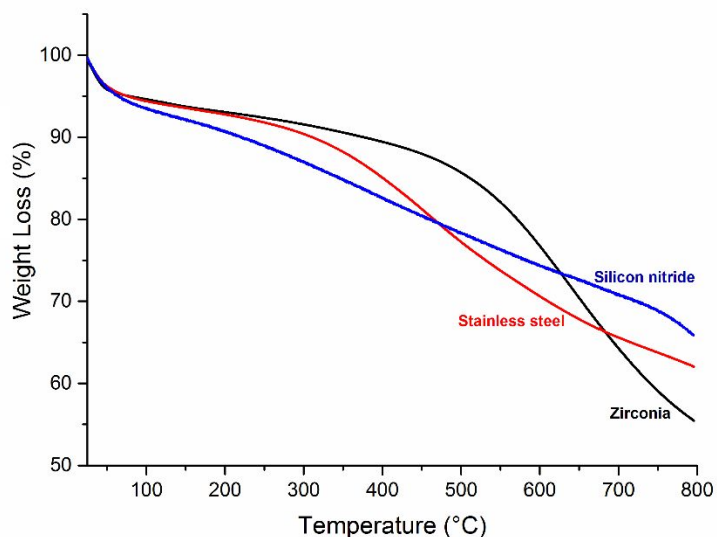
Figure S3. TGA scans of CB milled 9h with silicon nitride, zirconia and stainless steel balls.

The comparison between TGA of CB milled 9h with silicon nitride, zirconia and stainless steel balls (Fig. S3) shows the reduced ability of higher density balls, as zirconia and stainless steel, to oxidize the carbon black, as also confirmed by elemental analysis reported in Table S1. This result could be possibly due to the strong collisions with carbon material that can deeply affect the graphitic layers.

The ICP-MS analysis was performed on the sample obtained by ball milling with stainless steel balls and the amount of Cr and Ni detected are 0.006% and 0.002% respectively.

The presence of metals, even though in small quantities, might explain the better oxidation of stainless steel than zirconia .

2.4. Infrared spectroscopy. FTIR spectra were obtained at a resolution of 2.0 cm^{-1} with an FTIR (BRUKER Vertex70) spectrometer equipped with deuterated triglycine sulfate (DTGS) detector and a KBr beam splitter using KBr pellets. The frequency scale was internally calibrated to 0.01 cm^{-1} using a He–Ne laser. The noise was reduced by signal-averaging 32 scans.
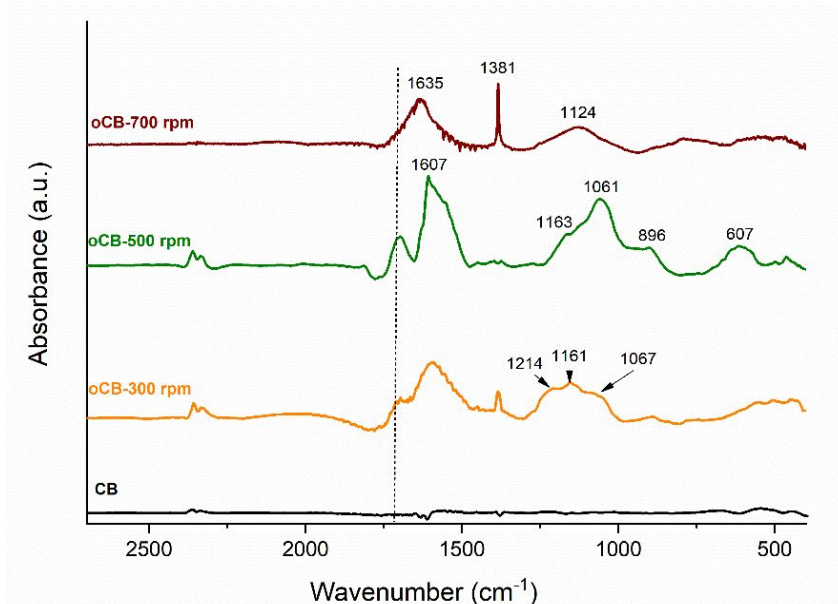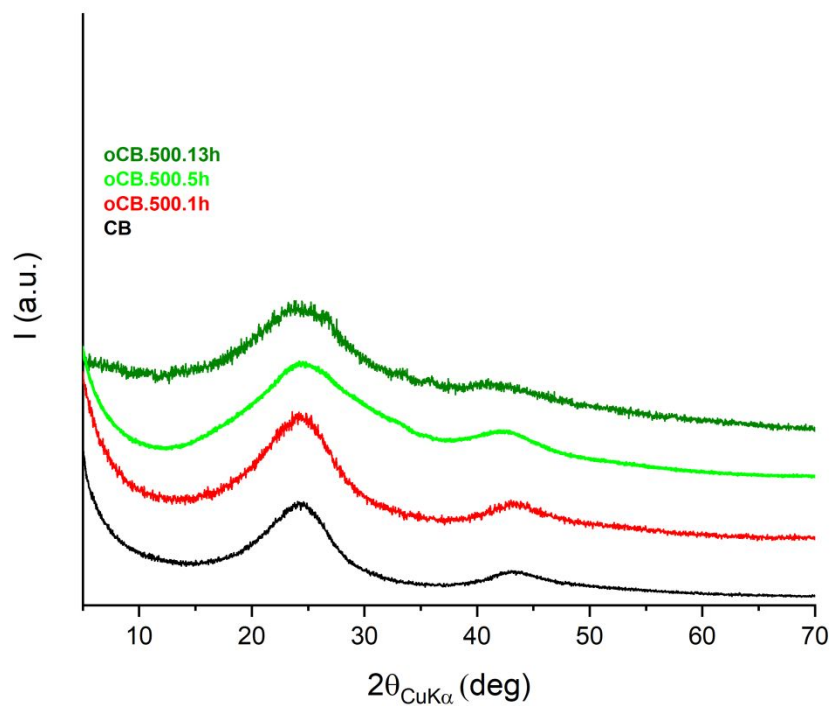
Figure S4. FTIR spectra of CB before and after milling for 5 hours at different speeds

2.5. Wide-angle X-ray diffraction. Wide-angle X-ray diffraction (WAXD) patterns were obtained by an automatic Bruker D2 phaser diffractometer, in reflection, at 35 KV and 40 mA, using nickel-filtered Cu Kα radiation (1.5418 Å).
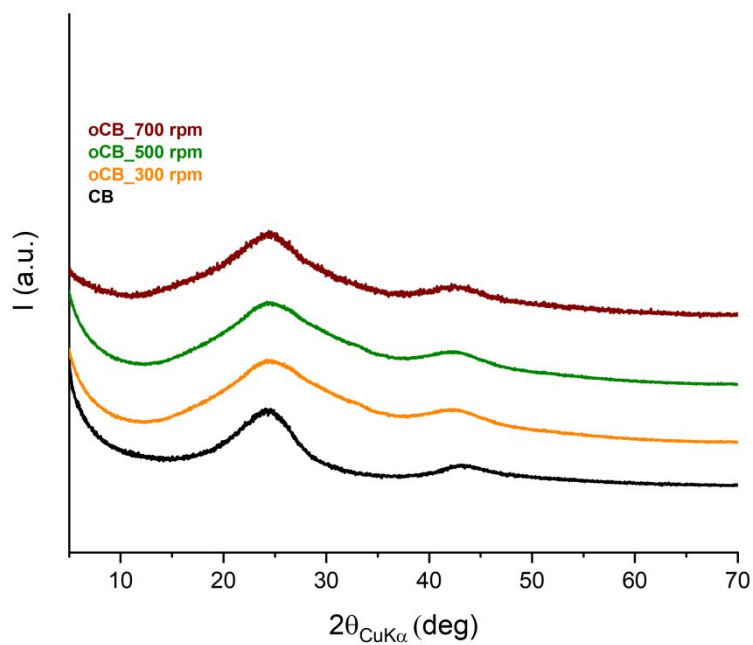
Correlation lengths (D) were determined by using Scherrer's equation

$$D = \frac{K\lambda}{\beta \cos\theta}$$ (1)

where λ is the wavelength of the incident X-rays and θ is the diffraction angle, assuming the Scherrer constant K = 1.

Figure S5. X-ray diffraction patterns of CB before and after milling at 500 rpm at different time.

Figure S6. X-ray diffraction patterns of CB before and after milling for 5 hours at different speeds

2.6. XPS.

X-ray photoelectron spectroscopy (XPS) measurements were recorded with an AXIS ULTRA DLD (Kratos Analytical) photoelectron spectrometer using a monochromatic AlKα source (1486.6 eV) operated at 150 W (10 kV, 15 mA). Base pressure in the analysis chamber was 5.3×10^{-9} Torr. Survey scan spectra were recorded using a pass energy of 160 eV and a 1 eV step. High-resolution spectra were acquired using a pass energy of 20 eV and a 0.1 eV step. The hybrid lens mode was used for all measurements. In each case, the area of analysis was about (700×300) μm^2. During the data acquisition, a system of neutralization of the charge has been used. Processing of the spectra was accomplished by CasaXPS Release 2.3.16 software. The binding energy (BE) scale was referenced to the Au 4f7/2 peak at 84.0 eV. For the analysis of high-resolution spectra, all peaks were fitted using the Shirley background and GL(30) line shape (a combination of Gaussian 70% and Lorentzian 30%). For quantitative analysis, the relative sensitivity factors present in the library of CasaXPS for the areas of the signals were used. The graphitic carbon component was fitted with a Voigt line shape exhibiting a higher binding energy tail [1]. Surface charging was corrected considering the binding energy (BE) of sp^2 C 1s ($= 284.3$ eV) as obtained for not milled CB sample.

Table S3. Binding Energy (BE) value for C 1s components was identified by fitting the XPS high-resolution C 1s spectrum of starting CB and oCB-1, oCB-5, oCB-9, and oCB-11 samples. Data are presented as mean (± s.d) obtained from triplicate measurements on different areas of each sample.

	BE (eV)				
	CB	oCB-1	oCB-5	oCB-9	oCB-11
C sp²	284.3±0.00	284.3±0.06	284.3±0.00	284.2±0.00	284.3±0.06
C-O	286.5±0.06	286.4±0.06	286.4±0.15	286.4±0.10	286.5±0.06
C=O	287.7±0.00	288.0±0.06	288.0±0.17	287.8±0.07	288.0±0.00
O-C=O	289.3±0.12	289.5±0.06	289.2±0.06	288.9±0.21	289.1±0.26
shake-up	291.0±0.06	291.1±0.06	291.0±0.06	290.8±0.14	290.8±0.21

References

[1] F. Scalera, A. G. Monteduro, G.Maruccio, L. Blasi, F. Gervaso, E. Mazzotta, C. Malitesta, C. Piccirillo *Sustainable Materials and Technologies* **2021,** 28, e00260