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Research Article

Green Oxidation of Carbon Black by Dry Ball Milling

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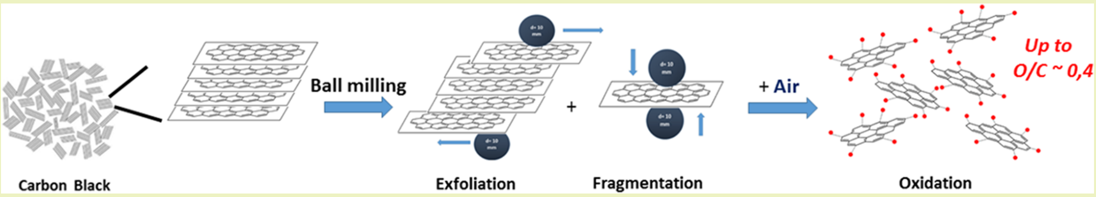

ABSTRACT: A sustainable and green method is presented in this paper to produce highly oxidized carbon black using dry ball milling. The mechanical energy by colliding milling balls is able to easily break and build chemical bonds providing new oxygenated functional groups. The reaction is performed in the presence of air and in solvent-free conditions achieving, for the first time, a high degree of functionalization comparable to that obtained under harsh conventional conditions. With different milling times, it is possible to control the degree of oxidation. The procedure is environmentally friendly, respecting important green metrics, no solvent or additional reagent is required, and the product can be collected without any assistance from a solvent.

KEYWORDS: *mechanochemistry, sustainability, carbon black, oxidation*

INTRODUCTION

Graphite-based materials are widely used for many applications, mainly as fillers in polymer matrices, because of their ability to improve the mechanical and physical properties.[1−3] In the past decades, they attracted considerable attention for their possible application in many fields such as catalysis,[4−8] energy storage[9−12] and conversion,[13,14] water remediation,[15,16] and supercapacitors.[17]

For many of these applications, the introduction of oxygenated functionalities is necessary to guarantee the improvement of their ability for the corresponding purpose, i.e., starting from oxidized carbon materials, highly ordered intercalation compounds can be achieved,[18,19] and changing the polarity can prevent filler aggregation, the affinity for metal ions or the wettability.

Several procedures have been developed to functionalize carbon materials by introducing amino- or oxygen-containing groups, but most of them suffer the involvement of expensive procedures and toxic reagents.

Mainly regarding oxidation, very harsh and dangerous conditions have to be used to obtain a high functionalization degree. Specifically, Staudenmaier,[20] Hofmann,[21,22] and Hummers methods[23] require caution in handling, the use of hazardous chemicals, and an extensive washing step to remove metal oxides. Furthermore, an additional procedure widely used for providing a high O/C ratio is the treatment with the sulfonitric mixture,[24] but the strongly acidic conditions do not meet the environmental sustainability requirements.

Recently, a procedure with H_2O_2/H_2SO_4 in the ratio 5/1 was used to efficiently oxidize carbon black providing up to a 0.6 O/C ratio that was found to be helpful as a catalyst for transesterification reaction.[7] Although the functionalization degree was high, the procedure was still not green.

The first green approaches were reported in the literature using only hydrogen peroxide solution.[25,26] Still in this case, the O/C ratio did not exceed 0.08 and was also strictly dependent on the surface area of the starting materials.

An alternative green route to provide the introduction of oxygenated functionalities on the carbon black surface is represented by ozone[27,28] or UV/ozone treatment[29] on carbon black powder or gasified carbon black.[30] Although these procedures can be performed in solvent-free conditions, oxidation can be achieved up to a 0.48 O/C ratio only in the presence of preactivation of carbon materials (steam activation and acid wash),[27] up to 0.16 O/C by preheating the sample to make more efficient the surface modification,[29] or by adding a high volume of ozone to provide an acceptable oxidation degree (up to an 11% surface oxygen concentration).[28] Furthermore, the energy required to produce ozone in all cases and even more on gasified carbon black reduces the energy efficiency metric increasing the energy demand required for the process.[31]

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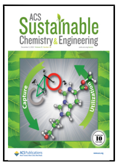

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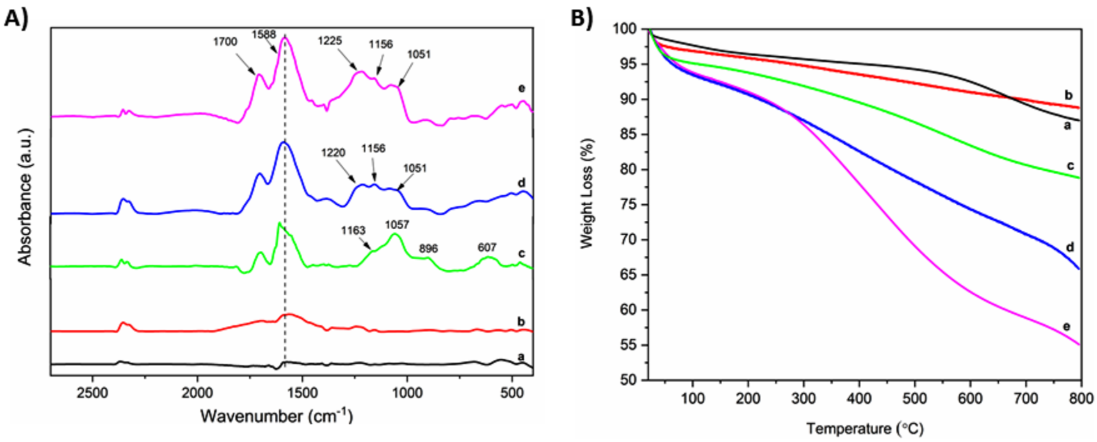

Figure 1. FTIR spectra (A) and TGA scans (B) of starting carbon black CB (a) and milled carbon black after 1 h oCB-1 (b), 5 h oCB-5 (c), 9 h oCB-9 (d), and 11 h oCB-11 (e).

Moreover, plasma treatment[32,33] might also be an alternative to perform the reaction in milder conditions, but advanced equipment and high power input are again incompatible with the environmental concerns.

Most of the procedures reported meet the needs of the conventional chemical synthesis in which the energy dispersion and the transport to make the reaction work are possible by the action of the solvent. The presence of a solvent reduces the reactants' total concentration, requiring the use of challenging conditions to assure a high functionalization degree.

A new and alternative technology to introduce different functionalities into carbon materials is based on mechanochemistry. According to IUPAC, mechanochemistry is defined as a tool to promote "a chemical reaction by direct absorption of mechanical energy",[34] and making it possible to work on the solid state in solvent-free conditions can represent a new concept for doing green chemistry meeting the requirement of environmental sustainability.

Ball milling is an efficient mechanochemical approach that reduces the particle size of carbon samples and can break or build chemical bonds by colliding milling balls.

The effectiveness of ball milling performance depends on the nature and dimension of balls, the weight ratio of the balls/sample, rotation rate, milling time, and temperature.

Although this approach was efficiently used for producing edge-carboxylated graphite[35] in the solid state without using hazardous chemicals or high-surface area graphite oxide,[36] graphite functionalization with sulfur,[37] and production of N-doped graphene[9] and sulfur carbon nanotubes,[38] it is still a relatively new concept that can represent an innovative technology for doing chemistry with respect to environmental sustainability.

Recently, the ability of ball milling to increase the oxygen functionalities on different biochar materials was described, even though, with the functional groups already present, the authors suggest that ball milling does not create new functional groups, but the reduction of particle size can better expose the oxygen groups on the biochar surface.[39]

Among various graphite-based materials, carbon black is one of the most widely used materials for industrial applications and, as a waste product coming from the incomplete combustion of petroleum products, is cheaper and readily available. Because of the need to functionalize it for all possible applications, a green and scalable approach should be useful.

Based on the impressive results of using ball milling with a variety of carbon materials, this approach was extended to carbon black.

A previous paper[40] reported the possibility of oxidizing carbon black by using ball milling, but a rather poor amount of oxygen was achieved (8.7 wt % and an O/C ratio of ∼0.1).

Here, we report the ability of carbon black to be functionalized by using planetary ball milling in solvent-free conditions at room temperature achieving, for the first time, a high degree of oxidation comparable to that obtained by the Hummers method. The reaction is entirely green, carbon black can be used as a raw material without any further treatment, no solvent or additional reagent is required, and the product is easily collected from the jar without any solvent assistance.

■ RESULTS AND DISCUSSION

Commercial carbon black (CB), exhibiting a surface area of 130 m^2/g, has been oxidized by using planetary ball milling (Pulverisette 7 Premium line, Fritsch) with 8 silicon nitride balls with a diameter of 10 mm.

The first experiment was performed in air, present after closing a jar of 80 mL, with 100 mg of CB, using 500 rpm as revolution time and stopping the reaction after 1, 5, 9, and 11 h. For all the experiments, a 98% mass yield was recovered irrespective of the milling time.

The temperature inside the milling beakers was monitored. Within 90 min of milling, the temperature was increased to 34 °C from room temperature and was quite stable because of the milling procedure, including a 5 min milling pause after each 5 min milling run.

The effectiveness of the procedure and the functional groups produced by the ball milling action were studied by comparing FTIR spectra of CB and the powders obtained after different milling times named oCB-1, oCB-5, oCB-9, and oCB-11, respectively after 1, 5, 9, and 11 h (b−e, Figure 1A).

While the CB spectrum does not show any vibration, after 5 h of grinding, it starts to change significantly. Specifically, the appearance of peaks at 607 and 896 cm^{-1} related to peroxide and epoxide groups and 1057 and 1163 cm^{-1} associated with ether and alcohol groups were observed[19] (Figure 1A-c).

As the milling time is increased, the peroxides and epoxides disappear, and the peaks at 1220−1225 cm^{-1} from vinyl-ether stretching are more apparent, as well as the peak at 1588 cm^{-1} from the carbon double bond and the peak at 1700 cm^{-1} from the carbonyl group (Figure 1A-d,e). No additional information is coming from the WAXD pattern before and after milling because of the amorphous nature of carbon black (see the Supporting Information).

In order to improve the oxidation degree, a further experiment was performed prolonging the reaction time to 13 h, but no change in the FTIR spectra was detected. Moreover, additional characterizations (i.e., elemental analysis and TGA, see the Supporting Information) show an even lower efficiency.

As shown in Figure 1B, TGA scans confirmed the different levels of oxidation of the samples according to milling times. The weight loss largely increases with the oxygen content and results in a decrease in thermal stability.

The surface area of the samples was defined using BET analysis (Figure 2).

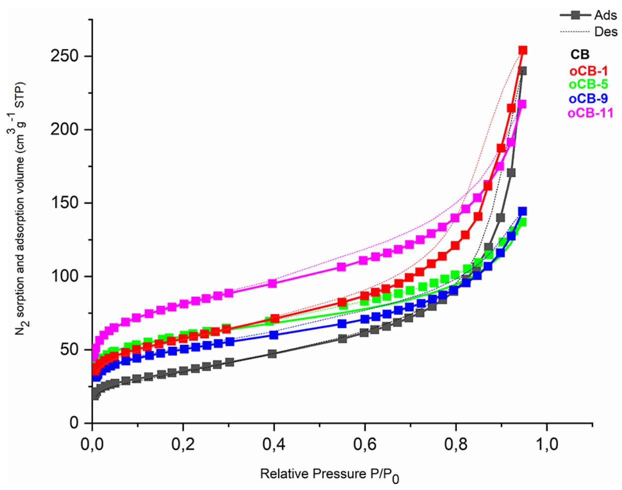

Figure 2. N_2 adsorption−desorption isotherms of CB and ball-milled samples.

After milling the powder for 1 (oCB-1) and 5 h (oCB-5), the surface area is increased from 130 to 205 and 213 m^2/g, respectively (Table 1), as a result of particle fracturing and exfoliation induced by ball impacts. It has to be noted that the negligible change in the surface area present in oCB-5 with respect to oCB-1 is a result of the balance between the particle fracturing and the agglomerate formation of the functional groups starting to form. Prolonging the milling time to 9 h (oCB-9), the surface area shows a slight decrease to 180 m^2/g due to the agglomeration effects for the good interactions between the functional groups present.[41] Moreover, going on for 11 h, the surface area starts again to increase for the further reduction of the particle size.

Table 1. Elemental Analysis, Surface Area, and Water Content (%) of CB and Ball-Milled Samples[a]

sample	N (%)	C (%)	H (%)	O (%)	O/C	surface area (m^2/g)[b]	% H_2O[c]
CB	0.2	97	0.6	2.2	0.02	130	2
oCB-1	0.7	89	0.3	10	0.11	205	3
oCB-5	1.3	76	0.5	22	0.29	213	5
oCB-9	1.2	72	0.8	26	0.36	180	6
oCB-11	1.1	71	0.5	27	0.38	291	7

[a]Elemental composition of anhydrous samples. [b]The surface area was calculated according to the Brunauer−Emmett−Teller theory. [c]Water content as determined by thermogravimetry.

The morphological analyses, shown in Figure 3, are in agreement with the BET data. In fact, the starting material shows the typical agglomeration of carbon black that moves to the different morphologies after ball milling (FeSEM, Figure 3). Specifically, as a result of fragmentation and exfoliation, the sample grain size decreases after 1 h of milling, while some aggregation appears after 5 h. This aggregation becomes stronger after 9 h because of a higher oxidation degree. Prolonging the milling time up to 11 h again, particle size reduction is observed (Figure 3, FeSEM oCB-11).

Elemental analysis performed on oCB-1, oCB-5, oCB-9, and oCB-11 samples also confirms that the oxidation degree rises with an increasing milling time (Table 1). It has to be noted that the O/C ratio obtained after 11 h is up to ∼0.4. This result is extremely impressive since it is possible to achieve a comparable oxidation level to that obtained by Hummers' method with a straightforward mechanical activation.

Furthermore, as for the O/C, increased hydrophilicity was observed prolonging the milling time (Table 1), as also shown from the dispersibility test in pure water of the oCB samples (Figure 4). Moving from CB to oCB-1, a slight increase of dispersibility is observed (0.02 vs 0.11 O/C ratio), which is definitely more pronounced for oCB-5, oCB-9, and oCB-11 with 0.29, 0.36, and 0.38 O/C ratios, respectively.

The surface chemistry of carbon black samples, before and after milling treatment, has been further analyzed by XPS.

With the aim to assess the oxidation degree of the surface of milled samples, the atomic ratio O/C has been evaluated. Obtained results are reported in Figure 5.

It can be observed that the oxygen content significantly increases after the first hours (namely, 1 and 5 h) then reaching a plateau value after a 9 h milling treatment. Although these results are in agreement with FTIR data, a certain reduced surface oxidation degree seems to emerge with respect to the elemental analysis values. This apparently contradictory result could be explained considering that, as a result of fragmentation and exfoliation induced by milling treatment and with the proceeding of the oxidation process, some products (i.e., CO_2) could be formed and detached from the surface of CB, thus resulting in an apparent reduced oxidation with respect to the bulk of the material.

For gaining information about the nature of oxidized carbon species and their relative distribution, high-resolution C 1s has been fitted in starting CB and in milled CB samples. Results are collected in Table S3 (see the Supporting Information) reporting the identified C 1s components, along with their position in terms of binding energy. Representative high-resolution C 1s fitted spectra are shown in Figure 6, referred to starting CB and to CB milled for 11 h for evidencing carbon signal modification arising from milling treatment.

A significant increase of all oxidized carbon species is readily appreciable, especially C−O and C═O, in agreement with FTIR results.

In the attempt to further improve the oxidation degree, additional experiments were performed by changing the speeding rate being essential both the right impact and shear forces to provide high and effective dynamic energy. By reducing the speeding rate to 300 rpm, some oxidation occurs, reaching a 0.19 O/C ratio, although it is significantly lower than the value obtained by using 500 rpm (0.29 O/C ratio). On the contrary, increasing the speeding rate up to 700 rpm

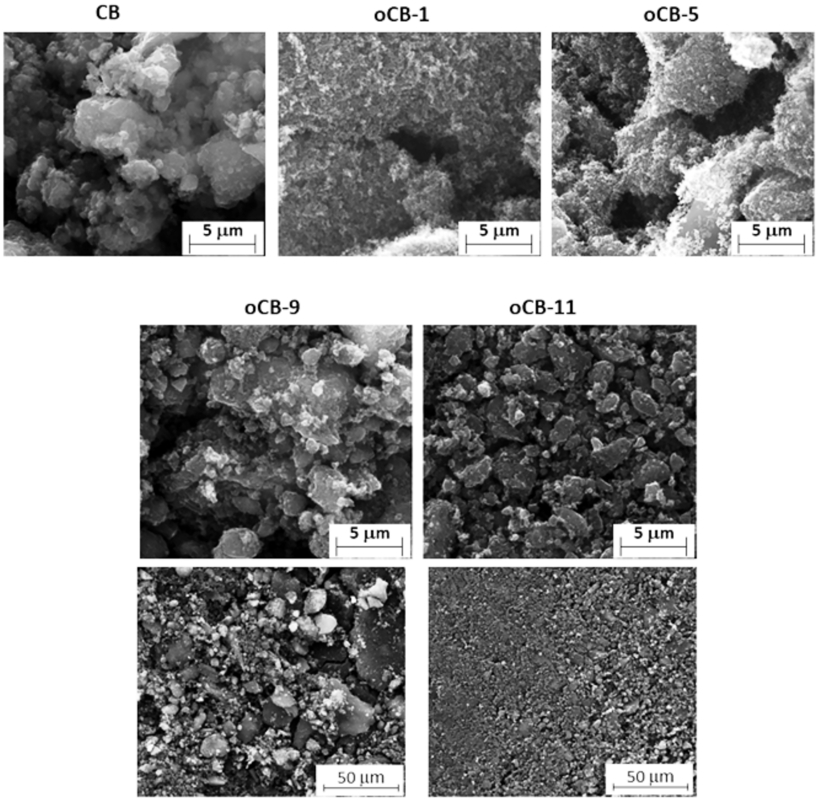

Figure 3. FeSEM micrographs of Cb, oCB1, oCB-5, oCB-9, and oCB-11.

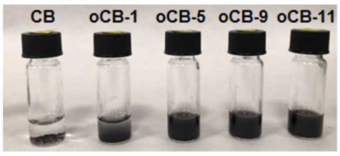

Figure 4. Suspension in 5 mg/mL water solution, after 5 min of sonication and 24 h of storage.

does not help the oxidation, poorly affecting the oxygen content and achieving just a 0.09 O/C ratio. Further experiments were also performed using zirconia and stainless-steel balls, and in both cases, the reaction proceeds with a lower degree of oxidation (see the Supporting Information).

In order to demonstrate the effectiveness of ball milling oxidation, a comparative study between two green procedures, the mechanical solid-state oxidation and the oxidation by H_2O_2 in solution, was performed. For the sake of comparison, the

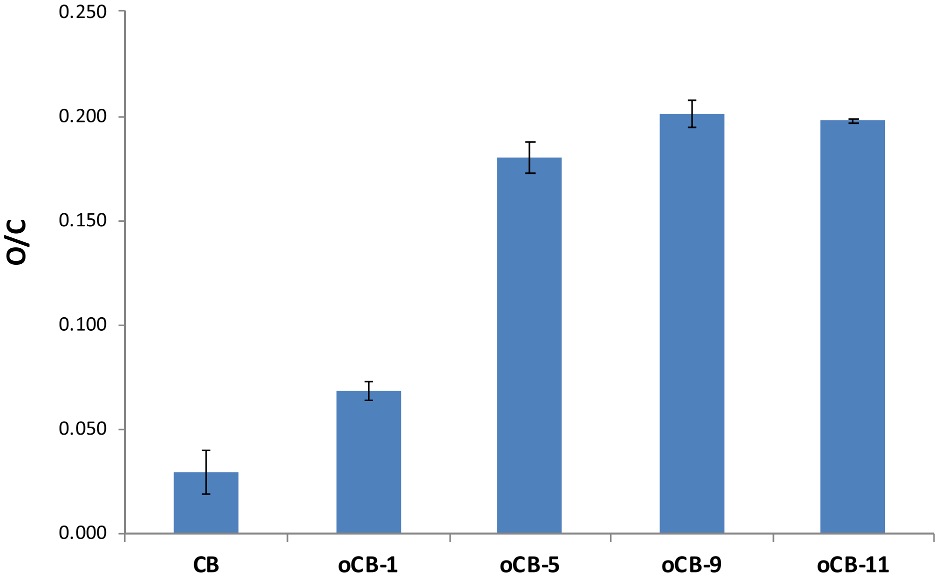

Figure 5. Atomic ratio O/C evaluated by XPS analysis of high-resolution signals of O 1s and C 1s on CB, oCB-1, oCB-5, oCB-9, and oCB-11 samples. Error bars are referred to the average values obtained from triplicate measurements on different areas of each sample.

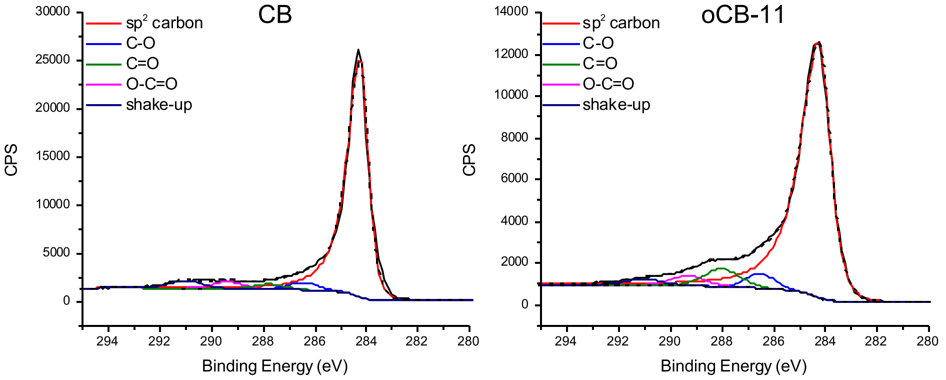

Figure 6. XPS-fitted C 1s high-resolution signals of starting CB and CB milled for 11 h.

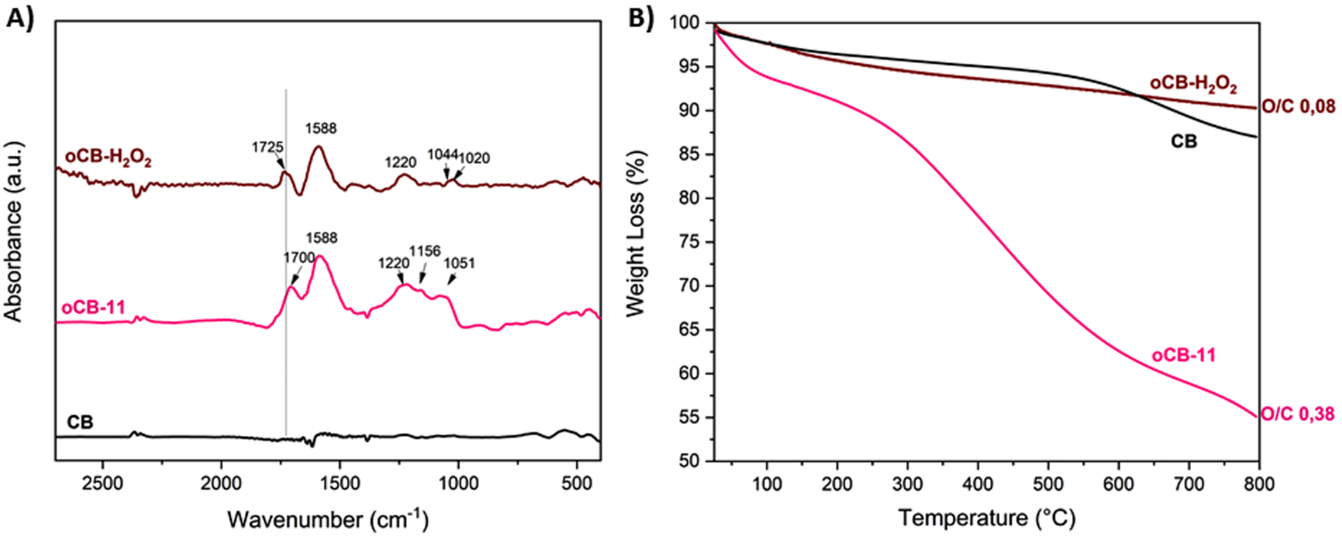

Figure 7. FTIR spectra (A) and TGA scans (B) of CB, oCB-11, and CB oxidized by H_2O_2.

oCB-11 and CB oxidized for 24 h at 60 °C in the presence of H_2O_2 (oCB-H_2O_2) were chosen.

As a result of the FTIR analysis (Figure 7A), substantial differences are revealed, not only in the nature of the functional groups but also in the degree of oxidation. More precisely, while the bands at 1220 and 1051−1020 cm^{-1} corresponding to ether and vinyl ether, respectively, are present in both spectra, the 1156 cm^{-1} vibration associated with the alcoholic group is missing for oCB-H_2O_2. Moreover, the nature of the carbonyl group is deeply different, being the 1725 cm^{-1} vibration related to the carboxylic group for oxidation by H_2O_2 and the 1700 cm^{-1} band for oCB-11 possibly due to unsaturated lactones and ketones. The remarkable difference in the oxidation degree was further confirmed by TGA scans like those shown in Figure 7B. In contrast to oCB-H_2O_2, which shows little degradation and high thermal stability with an O/C ratio of 0.08, oCB-11 shows a higher weight loss due to its high oxygen content, with an O/C ratio close to 0.4 comparable to that obtained by reactions performed under harsh conditions.

To demonstrate the efficiency and sustainability of the milling oxidation, in addition to the H_2O_2 method, the ozone oxidation procedures, deemed ones of the greenest, were also compared by considering the metrics of the green chemistry in terms of atom economy (AE), *E*(nvironmental)-factor, Ecoscale, and the amount of CO_2 production associated to the process (greenhouse gas equivalents). In particular, while the AE and *E*-factor are the simplest and most popular green metrics used to compare different synthetic routes, the Ecoscale and greenhouse gas equivalents are relatively new metrics to define the sustainability and the environmental impact of the process.[31]

Specifically, the atom economy, being related to the amount of reagents incorporated into the final product, indicates the conversion efficiency of the chemical process, and it is extremely useful to predict the amount of waste that the process will generate, while the *E*-factor is the effective amount of waste produced in the process.

The Ecoscale, instead, is a semiquantitative tool to select organic preparation considering yield, cost, safety, conditions, and purification. This approach is based on assigning a range of penalty points to these parameters on the maximun value of 100 and is particularly important going from the laboratory to industrial scale.[42]

The inclusion of the energy required for each process needs to be also evaluated because the energy consumption generates waste mainly as carbon dioxide. Therefore, the energy demand plays a fundamental role, ever more important nowadays, in comparing different synthetic approaches, and the related metrics can be based on energy demand and waste generated in CO_2 equivalents.[31]

Taking into account the chosen parameters, an initial assessment was performed on the AE of reactions 1−3 (Scheme 1). Based on the stoichiometry of the reactions, while oxygen in ball milling completely reacts with CB providing only the oxidation product (oCB) (3) and reaching 100% AE, in the presence of ozone (1), only two oxygen atoms per ozone molecule are directly consumed during the oxidation, providing not only oCB but also O_2 and CO_2 as byproducts[43] substantially reducing the AE of the reaction. Oxidation by H_2O_2 similarly reduces the atom economy.

Scheme 1. Representative Scheme of the Oxidation with Ozone (1), H_2O_2 (2), and Ball Milling in the Presence of Air (3)

$$\begin{aligned} &\mathrm{CB} + \mathrm{O_3} \longrightarrow \mathrm{oCB} + \mathrm{O}\cdot + \mathrm{CO_2} \\ &\mathrm{O}\cdot + \mathrm{O_3} \longrightarrow \mathrm{O_2} \end{aligned} \qquad (1)$$

$$\mathrm{CB} + \mathrm{H_2O_2} \longrightarrow \mathrm{oCB} + \mathrm{H_2O} \qquad (2)$$

$$\mathrm{CB} + \mathrm{O_2} \longrightarrow \mathrm{oCB} \qquad (3)$$

As reported in Table 2, it is quite clear how the ball milling oxidation is more convenient and more environmentally friendly. In fact, although the *E*-factor seems to be equal for ozone and ball milling oxidation, the Ecoscale, evaluated based on the classification previously reported,[42] can significantly change for ozone depending on the procedure used[27−30] but is never higher than the ball milling procedure.

Table 2. Comparison between Ball Milling and H_2O_2 and Ozone Oxidation Procedures Based on Green Metrics

procedure	*E*-factor	Ecoscale[a]	energy demand (kW)	CO_2 production (kg)[b]	oxidation efficiency (O/C)
ozone	0	93−96	15−60	6.5−26	0.10−0.48[c]
H_2O_2	0.73	90	19.2	8.3	0.08
ball milling	0	99	13.2	5.7	0.38

[a] The Ecoscale was evaluated based on the classification reported in ref 42 [b] The CO_2 production was evaluated based on the energy demand in kW/h for each process and converted into CO_2 following the conversion factor reported by EPA (2020) AVERT, US Environmental Protection Agency, Washington, DC. [c] This value can be obtained only with activated carbon.

The most interesting is the aspect related to the energy consumption and greenhouse gas equivalents as CO_2 emission. To evaluate the energy consumption correlated to the compared procedures, the analysis of the energy consumption in terms of kW/h was performed, taking into account the values associated with the equipment for the reactions. Specifically, an average value of 15 kW/h was estimated for ozone generator equipment based on the literature reports[44,45] for the time indicated from each ozone oxidation procedure (from 1 to 4 h),[27−30] and for the H_2O_2 oxidation, 0.800 kW/h was assumed as a reference value, as reported from the Heidolph data sheet, for keeping the reaction at 60 °C for 24 h. To compare the energy efficiency of the ball milling procedure, a maximum value of 1.2 kW/h related to the maximum speed possible (800 rpm), as reported by the technical data sheet of a planetary ball milling Pulverisette 7 premium line, was considered for 11 h, the time required to reach the maximum oxidation degree. (O/C 0.38). It is quite clear that even with assuming the maximum sorption of energy, the ball milling procedure is still more convenient than the ozone oxidation for energy consumption as well as total CO_2 emission.

Therefore, in all the metrics reported, ball milling assures the achievement of the best values representing a more environmentally friendly procedure to provide a high oxidation degree of carbon black.

CONCLUSIONS

Ball milling is a powerful, environmentally friendly synthetic technology to obtain highly oxidized carbon black in the presence of air. Mechanical grinding is able to create new oxygenated functional groups whose nature and relative quantity can change depending on the reaction time.

The powders obtained were fully characterized by FTIR, TGA, BET surface area analysis, FeSEM, and XPS.

The reaction proceeds in solvent-free conditions without adding any other reagent and without any further treatment of the raw materials. The powders can be easily collected by a jar without solvent assistance with a yield mass of up to 98%.

Prolonging the milling time makes it possible to reach an oxidation degree of up to ∼0.4 O/C comparable to that obtained by other conventional procedures performed in harsh conditions.

A comparative study was also performed between the milling oxidation, the H_2O_2 method, and the ozone oxidation procedures, by considering the metrics of the green chemistry in terms of the atom economy (AE), *E*(environmental)-factor, Ecoscale, and the amount of CO_2 production associated to the process (greenhouse gas equivalents). Ball milling has shown to be the most environmentally friendly procedure able to provide a high oxidation degree of carbon black.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acssuschemeng.2c05638.

> Experimental section containing description of materials and methods, FTIR, TGA WAXD, and XPS characterization of the products (PDF)

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Author Contributions

The manuscript was written through contributions of all authors.

Notes

The authors declare no competing financial interest.

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