

Supporting information

ECO-FRIENDLY AMIDATION OF OXIDIZED CARBON BLACK BY DRY BALL MILLING

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1. Materials and methods

1.1 Materials

Carbon black samples (CB) of grade N110 containing 99.8% carbon and BET surface area $130 \text{ m}^2 \text{ g}^{-1}$, were purchased from Cabot Company (USA). Sulfuric acid, sodium nitrate, potassium permanganate, and octadecyl amine (ODA) were purchased from Sigma-Aldrich. All reagents were used as received, without purification.

1.2 Oxidation of carbon black via Hummers' method

Oxidized carbon black (oCB) was prepared by Hummers' method. 12 mL of sulfuric acid and 0.25 g of sodium nitrate were introduced into a 1000 mL three-neck round-bottomed flask immersed in an ice bath and 0.5 g of carbon sample was added, with a magnetic stirring. Once a uniform dispersion was achieved, 1.5 g of potassium permanganate was added very slowly to minimize the risk of explosion. The reaction mixture was then heated to 35°C and stirred for 24 hours. Afterward, 70 mL of deionized water was gradually added to the resulting black and dark green slurry, followed by the gradual addition of 0.5 mL of hydrogen peroxide 30 wt%, The obtained sample was poured into 700 mL of deionized water and then centrifuged at 10,000 rpm for 15 min with a Neya16 centrifuge. The oCB powder was first washed twice with 10 mL of a 5 wt% HCl aqueous solution and subsequently washed with 50 mL of deionized water. Finally, the powder was dried at 60°C for 12 h. About 0.4 g of oCB sample was obtained.

1.3 Preparation of oCB via Ball Milling.

The ball-milling experiments were conducted at room temperature in a planetary ball mill Pulverisette 7 Premium (Fritsch GmbH, Germany).

The milling conditions were configured as detailed in Table S1. Each procedure utilized 8 silicon nitride balls with a diameter of 10 mm within an 80 ml silicon nitride jar. Rotational frequencies were fixed at 500 rpm for 11h. 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}]	500
ball size [mm]	10
total balls weight [g]	15
milling tool material	Silicon nitride
beaker volume [cm^3]	80
CB weight [mg]	100
sample notation	oCB_{BM}

1.4. Preparation of oCB_H/ODA and oCB_{BM}/ODA via Ball Milling.

The experiment was performed in an 80 ml silicon nitride jar with 8 silicon nitride balls, and 300 rpm rotational frequencies by using a 1/1 mass ratio of the oCB_H or oCB_{BM} and ODA for 2h. resulted powders being extensively washed only with ethanol to remove the excess amine, the products dried at 60 °C for 12 h in the oven and were recovered as black powders.

To investigate the imine formation the second part of prepared oCB_{BM}/ODA was washed extensively first with water and then with ethanol to remove the possible free amine coming from the ketone deprotection. The resulting powder dried at 60°C for 12 h in the oven.

2. Characterization.

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

2.2. 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 N₂ below. Weight decreases below 100 °C were used to determine water content.

2.3. Infrared spectroscopy. FTIR spectra were obtained at a resolution of 2.0 cm⁻¹ with an FTIR (BRUKER Vertex70) spectrometer equipped with a 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.

2.4. 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 K α radiation (1.5418 Å).

Correlation lengths (D) were determined by using Scherrer's equation

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

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

DLS analysis. All DLS analyses were performed by dispersing 1 mg of each sample into 100 mL of water to determine the dimensions using Master Sizer 2000 (Malvern Instruments Ltd., Malvern, UK).

The particle size for oCB_H/ODA is 7.9±1µm and for oCB_{BM}/ODA is 0.42±0.084 µm.

COMPARISON OF TGA AND ELEMENTAL ANALYSIS RESULTS.

Based on the elemental analysis the amount of nitrogen was evaluated and compared with the TGA weight losses.

For the oCB_H/ODA sample, the total amount of nitrogen after functionalization is 3.0. After subtraction of the nitrogen related to the starting material (0.3), the real value introduced with functionalization is 2.7%.

Therefore, for 100 mg of sample, the uptake should be 52wt%, very close to the 50wt% of weight loss detected by TGA.

For $\text{OCB}_{\text{BM}}/\text{ODA}$ sample the total amount of nitrogen after functionalization is 2.8. After subtraction of the nitrogen related to the starting material (1.1), the real value introduced with functionalization is 1.7%.

Therefore, for 100 mg of sample, the uptake should be 33 wt%, very close to the 30wt% of weight loss detected by TGA.

The same evaluation was made for the sample after washing, giving roughly 23wt% again very close to 20wt% of weight loss detected by TGA.

FTIR CHARACTERIZATION AFTER ACIDIC TREATMENT.

To better understand the stability of the $\text{oCB}_{\text{H}}/\text{ODA}$ and to confirm the covalent functionalization by using the mechanochemical approach, further characterization of the product was performed by FTIR after acidic treatment in acetic acid (pH=4.5). As reported in Figure S1, after washing with acetic acid, the $\text{oCB}_{\text{H}}/\text{ODA}$ FTIR profile is superimposable with that one coming from ethanol treatment, without showing any release of ammonium salt. (yellow profile vs the red one)

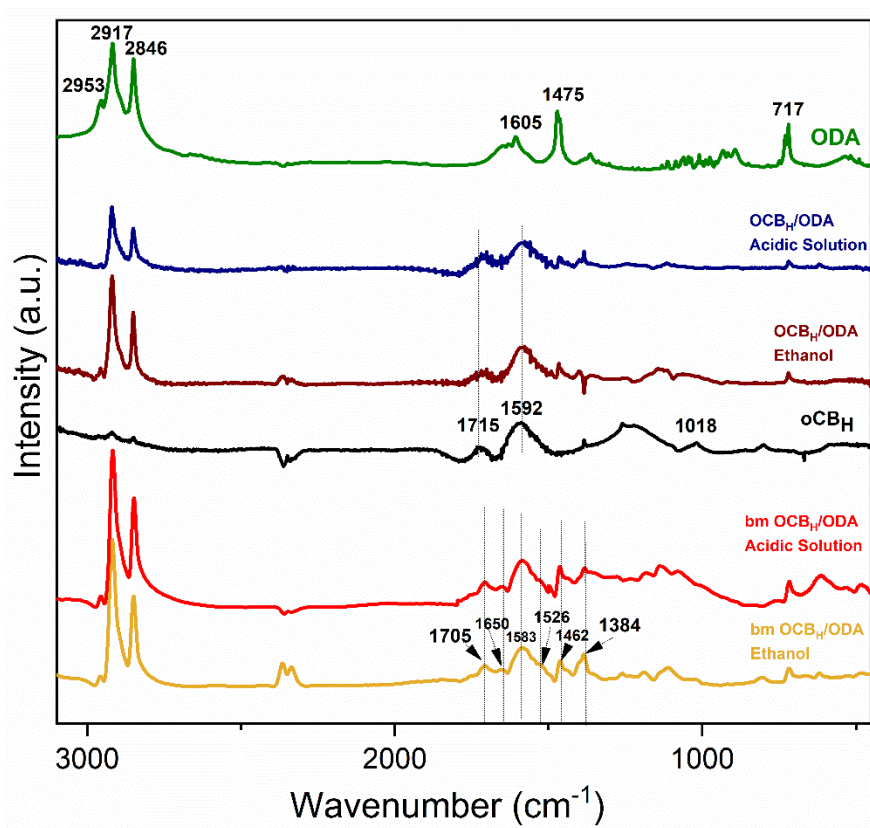


Figure S1. FTIR spectra of bm $\text{oCB}_{\text{H}}/\text{ODA}$ (yellow) washed with Ethanol, bm $\text{oCB}_{\text{H}}/\text{ODA}$ (red) washed with acidic solution, oCB_{H} (black), $\text{oCB}_{\text{H}}/\text{ODA}$ (wine) washed with Ethanol, $\text{oCB}_{\text{H}}/\text{ODA}$ (blue) washed with acidic solution, and ODA (green)

Additionally, the EA of oCB_H/ODA after acidic treatment was compared with the one freshly prepared with the standard procedure. As reported in Table S2, the percentage of all the elements are almost the same.

Table S2. Elemental analysis of the oCB_H/ODA samples.

Entry	Sample	N (%)	C (%)	H (%)	O (%)	O/C	H/C	N/C
3	oCB _H /ODA	3.0	79.7	6.3	11.0	0.14	0.08	0.04
4	oCB _H /ODA*	2.9	79.0	6.1	12	0.15	0.08	0.037

*oCB_H/ODA was washed with an acetic acid solution at pH 4.5 and then in water and ethanol to finally remove the possible free alkylammonium ions and free amine, respectively.

For the sake of comparison, a new adduct was prepared by simply mixing ODA and oCB_H in the minimum amount of ethanol.

The FTIR spectrum shows that the simple mixing does not introduce new vibrations in the region between 1580 and 1720 cm⁻¹, leaving an almost unchanged pattern for the COOH and C=C groups, while the characteristic vibrations of the alkyl chains at 2953, 2917, 2846, and 717 cm⁻¹ are visible.

After the acidic treatment in acetic acid solution at pH=4.5, a significant reduction of the bands at 2953, 2917, 2846, and 717 cm⁻¹ is observed, due to the weak interactions that can possibly be formed between the amine and the functional groups present on the carbon surface.

It has to be noted that for both samples an additional pH=2 treatment was performed in the attempt to remove the amines, showing that only for the oCB_H/ODA simply mixed the amine vibrations almost disappeared.

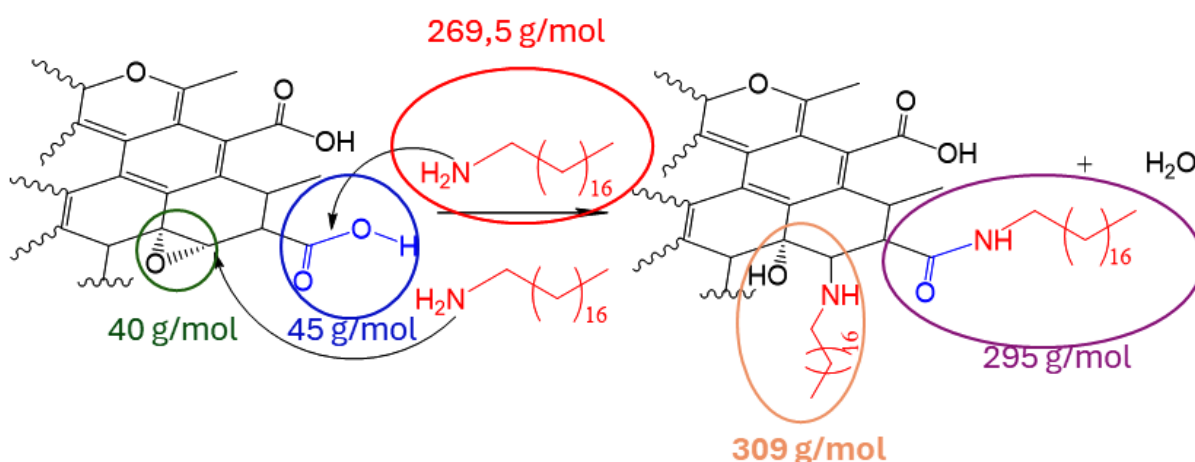
GREEN MEETRICS CALCULATIONS

In order to compare our reaction with those reported in the literature for which the yielding mass has not been mentioned, we need to assume that all the product can be completely recovered after the reaction and that the increased weight after functionalized could be evaluated based on the degree of functionalization reported by the authors in the TGA profile.

Starting from these assumptions, it is possible to compare the amidation by heating with the mechanochemical process starting from oCB_H and oCB_{BM}.

The evaluation of Atom efficiency, RME, and PMI were performed based on the possible mechanism of functionalization and the reagent ratio reported for each procedure:

A) Treatment under vacuum followed by heating at 180°C for 3 h (2 h for the reaction to work and 1 h more to remove the excess amine) on a mixture of 1 to 5 ratio of oCB and octadecyl amine.



Being unknown the molecular weight of oCB, we can consider the functional groups involved in functionalization to make a reasonable evaluation of Atom efficiency (AE).

$$AE = \frac{(309 + 295) \text{ g/mol}}{[(45 + 40) + (269.51) * 2] \text{ g/mol}} * 100 = 97\%$$

The evaluation of RME and PMI taking into account the mass of the product and the total mass reagent used, considers the excess of reagent used for the functionalization: oCB/ODA ratio is 1/5.

In order to compare our reaction with those reported in the literature for which the yield mass has not been reported, we needed to assume the reaction is performed on 100 mg of oxidized carbon material and the product can be completely recovered after the reaction. Therefore, based on the degree of functionalization reported by TGA the mass yield was hypothesized to calculate RME and PMI

$$RME = \frac{\text{mass of the product}}{\text{total mass of reagents}} * 100$$

$$\text{RME} = \frac{277\text{mg}}{100\text{mg} + 500\text{mg}} * 100 = 46\%$$

$$\text{PMI} = \frac{\text{total mass in process}}{\text{mass of product}} * 100$$

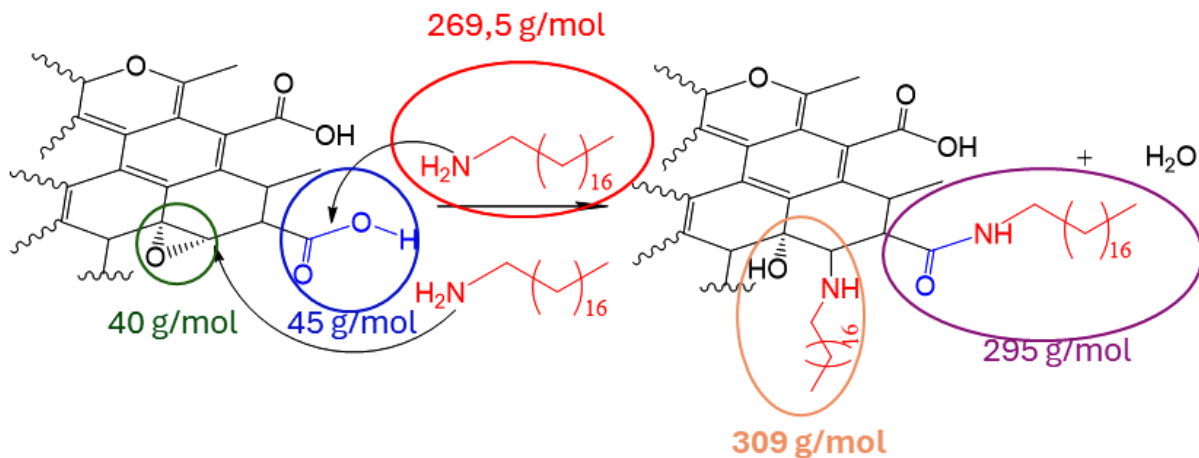
$$\text{PMI} = \frac{600\text{ mg}}{277\text{ mg}} * 100 = 2.16$$

E= PMI-1

E= 1.16

B) Ball milling treatment for 2h, room temperature, on a mixture of 1 to 1 ratio of oCB_H and octadecyl amine.

Considering the possible formation of amine by ring opening of the epoxides present on the carbon surface, and the amidation reaction the AE is:



$$\text{AE} = \frac{(309 + 295) \text{ g/mol}}{[(45 + 40) + (269.51) * 2] \text{ g/mol}} * 100 = 97\%$$

Considering the mass yield of the reaction (130 mg), and the reagent ratio 1 to 1 for oCB_H and ODA used for the reaction, the RME and PMI are

$$\text{RME} = \frac{130 \text{ mg}}{100 \text{ mg} + 100 \text{ mg}} * 100 = 65\%$$

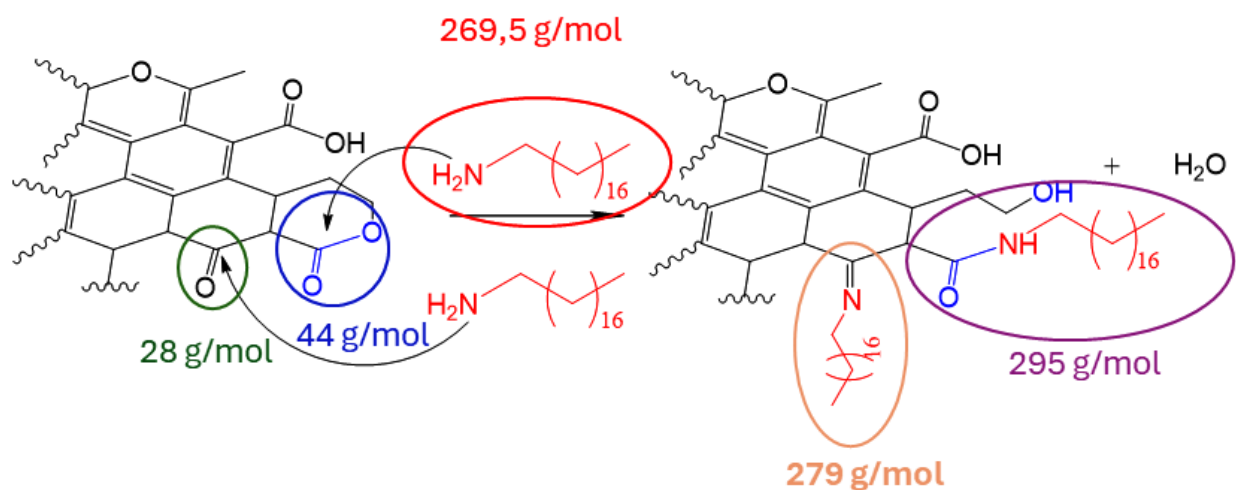
$$\text{PMI} = \frac{200 \text{ mg}}{130 \text{ mg}} * 100 = 1.54$$

Being E= PMI-1

$$E=0.54$$

C) Ball milling treatment for 2h, room temperature, on a mixture of 1 to 1 ratio of oCB_{BM} and octadecyl amine.

The evaluation of AE was performed based on the possible reactions of imination and amidation that occur with ketones and lactones, respectively, in the presence of ODA.



$$\text{AE} = \frac{(279 + 295) \text{ g/mol}}{[(44 + 40) + (269.51) * 2] \text{ g/mol}} * 100 = 94\%$$

Considering the mass yield of the reaction (115 mg), and the reagent ratio 1 to 1 for oCB and ODA used for the reaction, the RME and PMI are

$$\text{RME} = \frac{115\text{mg}}{100\text{mg} + 100\text{mg}} * 100 = 57.5\%$$

$$\text{PMI} = \frac{200\text{ mg}}{115\text{ mg}} * 100 = 1.7$$

Being E= PMI-1

E=0.7