

## **Sustainable functionalization of Carbon black via dry ball milling.**

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### **Supporting information**

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## EXPERIMENTAL SECTION:

### 1. Materials and methods

#### 1.1 Materials

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

#### 1.2 Oxidation of carbon black

Oxidized carbon black (oCB) was prepared by Hummers' method [1]. 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 samples were added, with a magnetic stirring. After obtaining a uniform dispersion, 1.5 g of potassium permanganate was added very slowly to minimize the risk of explosion. The reaction mixture was thus heated to  $35 \text{ }^\circ\text{C}$  and stirred for 24 h. Deionized water (70 mL) was added in small amounts into the resulting black and dark green slurry for carbon black, under stirring and, finally, gradually adding 0.5 mL of  $\text{H}_2\text{O}_2$  (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 powders were first washed twice with 10 mL of a 5 wt% HCl aqueous solution and subsequently washed with 50 mL of deionized water. Finally, powders were dried at  $60 \text{ }^\circ\text{C}$  for 12 h. About 0.4 g of oCB sample was obtained.

#### 1.3 Preparation of oCB/TPP<sub>1/1</sub> and oCB/TPP<sub>1/3</sub> in solution.

In this study, intercalate with TPP<sup>+</sup> was prepared according to the method described by Matsuo et al. oCB powders (50 mg) were dispersed in 0.05 M NaOH solution (10 mL), TPPBr solution (50 mg or 150 mg TPPBr (according to the ratio) in (50 mL) deionized water was added in this dispersion, and the reaction mixture was stirred at room temperature for 1 h. The slurry was centrifugated at 10 000 rpm for 15 min, and the precipitate was washed with deionized water and dried at  $60 \text{ }^\circ\text{C}$  for 12 h in an oven.

#### 1.4 Preparation of oCB/TPP<sub>BMI/1</sub> and oCB/TPP<sub>BMI/3</sub> via Ball Milling.

The ball-milling experiments were conducted at room temperature in a planetary ball mill Pulverisette 7 Premium (Fritsch GmbH, Germany). Samples were designated oCB/TPP<sub>BMI/1</sub> and oCB/TPP<sub>BMI/3</sub> according to the ratio between oCB and TPPBr respectively. 50 mg of oCB powders and 50 mg TPPBr for (oCB/TPP<sub>BMI/1</sub>), or (150 mg TPPBr in case of (oCB/TPP<sub>BMI/3</sub>) were added directly in a Silicon nitride jar of 80ml. The milling parameters were set as shown in Table S1. Silicon nitride balls with a diameter of 10 mm were used in all procedures. The rotational frequency was examined at 300rpm and for 30 minutes. In order to determine the mass

yield of the milled product, samples were weighed after ball milling after collecting as a powder from the jar and washing with water to remove the residual excess salt. the Easy-GTM system (Fritsch GmbH, Germany) was used to measure the temperature of the milling beakers. No significant increase in temperature and pressure was observed.

**Table S1.** Experimental Conditions of the Ball Milling Experiments

ball-to-powder weight ratio	150
rotation frequency [ $\text{min}^{-1}$ ]	300
ball size [mm]	10
total balls weight [g]	15
milling tool material	Silicon nitride
beaker volume [ $\text{cm}^3$ ]	80
CB weight [mg]	50
TPPBr weight [mg]	50, 150
sample notation	$\text{oCB}/\text{TPP}_{\text{BM1/1}}$ , $\text{oCB}/\text{TPP}_{\text{BM1/3}}$

## 2. Characterization.

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

**Table S2:** EA of oCB before and after milling and solution preparation

Sample <sup>a</sup>	N (%)	C (%)	H (%)	O (%)	O/C
CB	0.2	97	0.6	2.2	0.02
oCB	0.2	75.4	0.5	23.9	0.32
b-oCB <sup>b</sup>	0.2	76	0.8	23	0.30
$\text{oCB}_{\text{BM}}$	0.2	75.3	0.6	23.9	0.32
$\text{oCB}/\text{TPP}_{1/3}$	0.2	79	1.2	19.6	0.25
$\text{oCB}/\text{TPP}_{\text{BM1/3}}$	0.2	77.6	1.2	21	0.27

<sup>a</sup> Elemental composition was evaluated on anhydrous samples.

<sup>b</sup> oCB after basification

A further evaluation of the functionalization degree of oCB was obtained by elemental analysis. In particular, for the oCB samples used in this paper, the O/C ratio as freshly prepared and after ball milling is the same, showing that no reduction can occur during the milling process. After the functionalization, the O/C ratio is reduced to 0.27 for oCB/TPP<sub>BM1/1</sub>.

Conversely, the oCB after basification (b-oCB) shows a slight reduction of the O/C ratio (oCB 0.32 vs b-oCB 0.30) due to the simultaneous reduction of the COOH groups and the opening of the epoxy ring in alkaline conditions, which provides two nucleophilic sites for quaternary salt functionalization. After functionalization, the O/C ratio is reduced to 0.25 for oCB/TPP<sub>1/3</sub>.

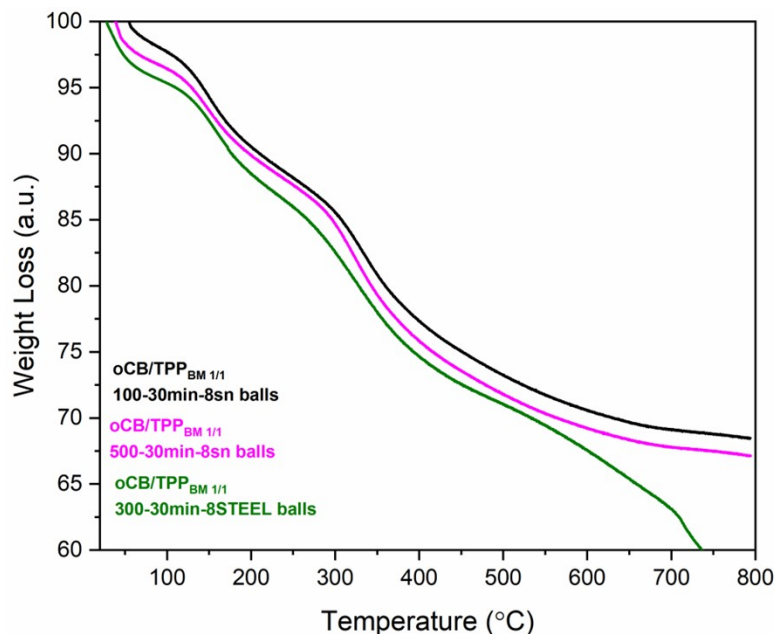
**Table S3: Mass yield**

sample	%Mass yield
oCB/TPP <sub>1/1</sub>	50
oCB/TPP <sub>1/3</sub>	50
oCB/TPP <sub>BM1/1</sub>	80
oCB/TPP <sub>BM1/3</sub>	64

**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 N<sub>2</sub> below. Weight decreases below 100 °C were used to determine water content.

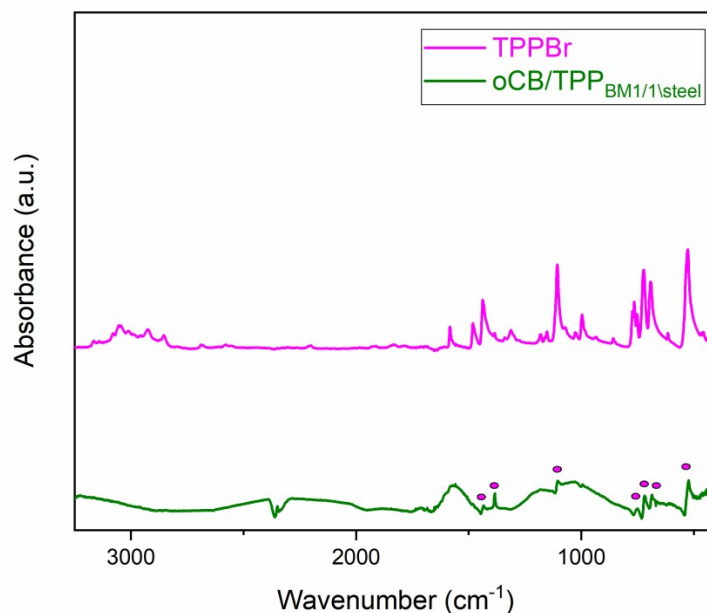
**Table S4: Optimization process for oCB/BM<sub>1/1</sub> synthesis.**

Sample	Procedure	TGA	%Mass yield
oCB/TPP <sub>BM1/1</sub>	<b>100rpm/30min/ 8SN balls / SN jar</b>	14	78
oCB/TPP <sub>BM1/1</sub>	<b>300rpm/30min/ 8SN balls / SN jar</b>	<b>15</b>	<b>80</b>
oCB/TPP <sub>BM1/1</sub>	<b>500rpm/30min/ 8SN balls / SN jar</b>	14	82
oCB/TPP <sub>BM1/1</sub>	<b>300rpm/30min/ 8Steel balls / Steel jar</b>	13	84



**Figure S1.** TGA scans of oCB/BM<sub>1/1</sub> in different conditions: with silicon nitride balls at 100rpm ( black ) and 500 rpm (pink), with steel balls at 300 rpm ( green).

**2.3. Infrared spectroscopy.** FTIR spectra were obtained at a resolution of 2.0 cm<sup>-1</sup> 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<sup>-1</sup> using a He–Ne laser. The noise was reduced by signal-averaging 32 scans.



**Figure S2.** FTIR of oCB/TPP<sub>BM1/1</sub> with steel balls ( 300 rpm, 30 minutes)

**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 $\alpha$  radiation (1.5418 Å).

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

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

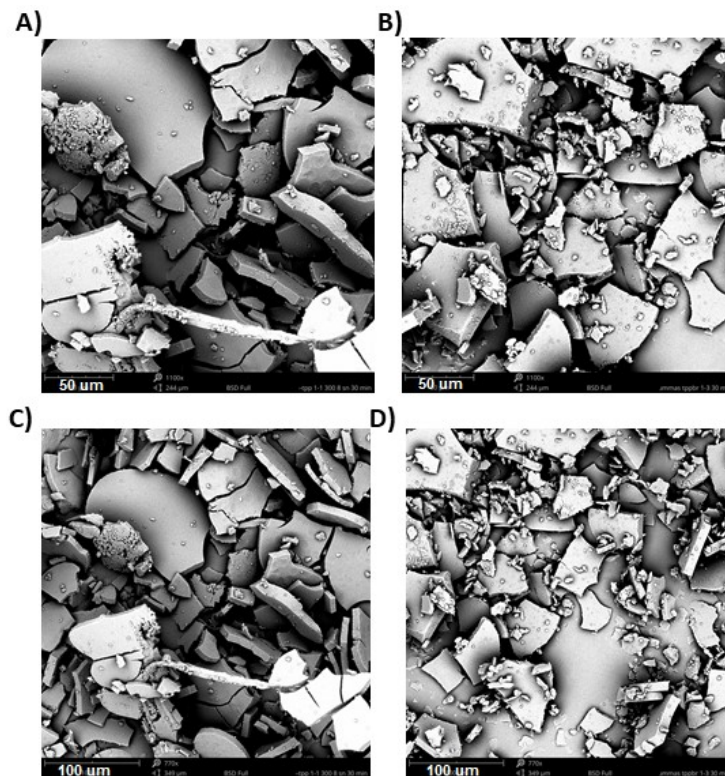
where  $\lambda$  is the wavelength of the incident X-rays and  $\theta$  is the diffraction angle, assuming the Scherrer constant  $K = 1$ .

### 2.5. UV-vis Spectroscopy and Release Properties of oCB/TPP<sub>BM1/1</sub>.

UV-vis spectra were recorded using a PerkinElmer Lambda 800 UV-vis spectrophotometer. The TPP<sup>+</sup> release from oCB/TPP<sub>BM1/1</sub> in neutral (10wt% NaCl) and acid (0.05 M HCl) aqueous solutions was measured as a function of the soaking time. A nitrocellulose filter containing 8 mg of oCB/TPP<sub>BM1/1</sub> was soaked in 20 ml of aqueous solution at room temperature under stirring. Aliquots of solution were sampled by syringe at different times, and the concentration of released TPP<sup>+</sup> was evaluated by a UV-vis spectrophotometer.

### 2.6 SEM microscopy.

The SEM images were acquired by Phenom pro X Thermofischer, at different magnifications.



**Figure S3.** SEM images of oCB/TPP<sub>BM1/1</sub> (A and C) and oCB/TPP<sub>BM1/3</sub> (B and D) at 50  $\mu\text{m}$  and 100  $\mu\text{m}$  respectively.

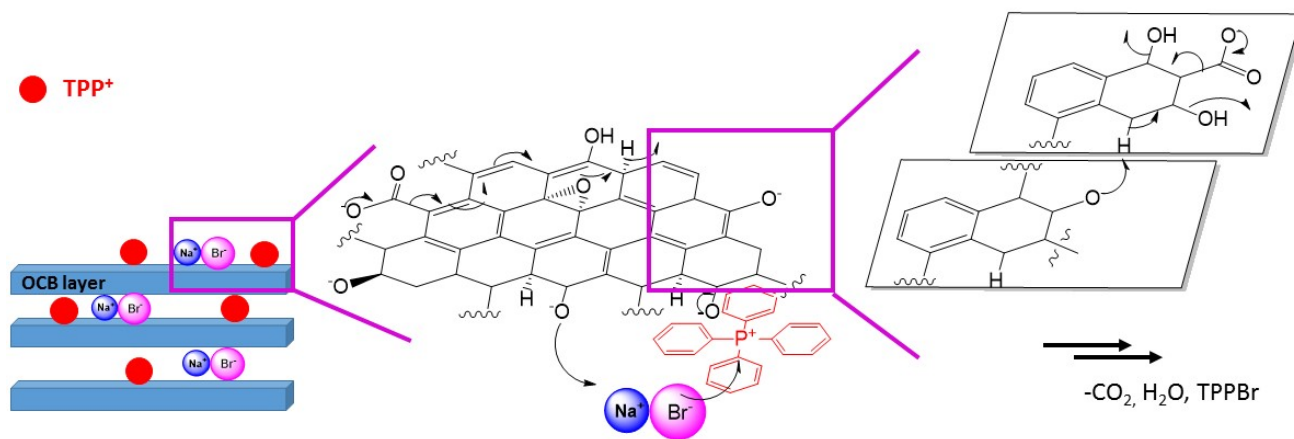
SEM images reveal the same flake morphology in both samples, with reduced size for the one milled with more salt.

### POSSIBLE DEGRADATION MECHANISM AND RESTORING TPPBr SALT

The instability of oCB/TPP adduct provided by reaction in alkaline solution, shown in Figure 3 of the manuscript, can be explained considering the natural evolution of basified carbon materials in a more thermodynamically stable system with restoring the aromatic structure as previously reported in a precedent paper. [2]

Moreover, the formation of the TPPBr salt is possible due to the NaBr residue after basification that tends to settle between the graphitic layers and even after extensive washing, is very difficult to remove. The ability of Salts to be enclosed in the graphitic structure as clusters is widely reported in the literature. [3,4]

A scheme of a possible degradation mechanism and restoring TPPBr salt is reported in Figure S4.

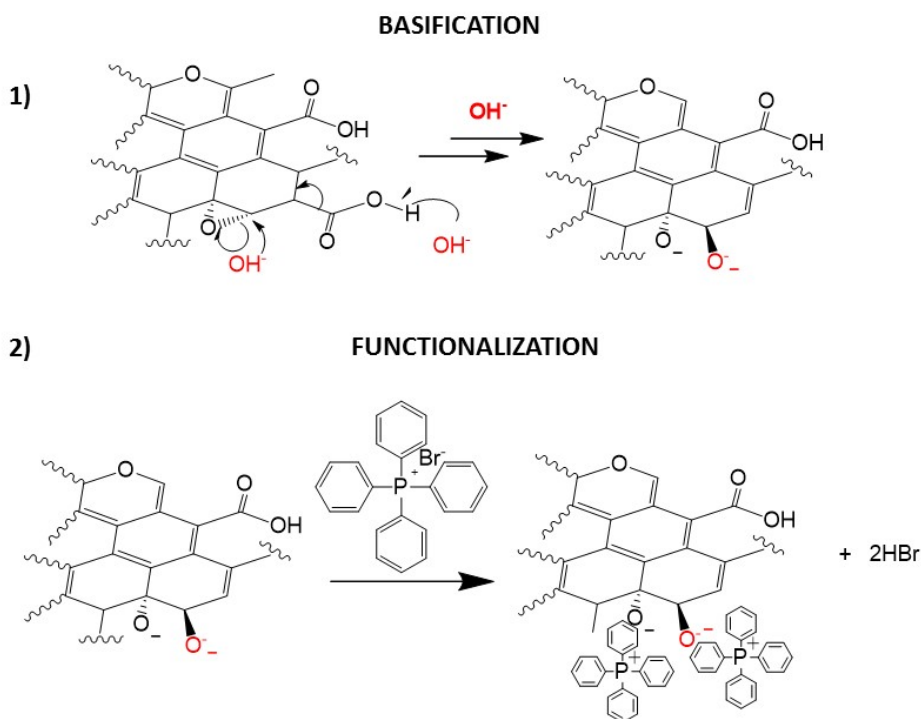


**Figure S4.** Scheme of possible degradation mechanism and restoring TPPBr salt

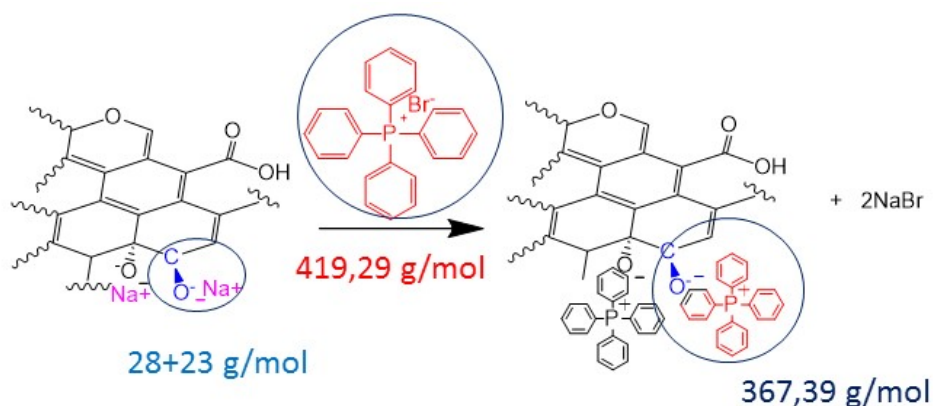
### GREEN MEETRICS CALCULATIONS

#### oCB/TPP<sub>1/3</sub> in solution.

The evaluation of Atom efficiency was performed based on the possible mechanism of functionalization in alkaline conditions:



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).



$$AE = \frac{367.39 \text{ g/mol}}{(28 + 23 + 419.29) \text{ g/mol}} * 100 = 78\%$$

The E(nvironmental)-factor, PMI, and MP were evaluated following the equation (2) (3), and (4)

$$E = \frac{\text{Total mass waste}}{\text{Mass of product}}$$



(2)

The alkaline solution provided by the reaction was obtained by mixing 50 ml of water with 10 ml of 0.05 M NaOH solution (d= 1.084 g/ml).

The reaction provides 25 mg of product as powder, corresponding to 50% of mass yield.

$$E = \frac{(50 + 18,4) \text{ mg}}{25 \text{ mg}} = 2,7$$

$$\text{PMI} = \frac{\text{Total mass in process (incl wqter)}}{\text{Mass of product}}$$

$$\text{PMI} = \frac{(50 + 18.4 + 50 + 150) \text{ mg}}{25 \text{ mg}} = 10.7$$

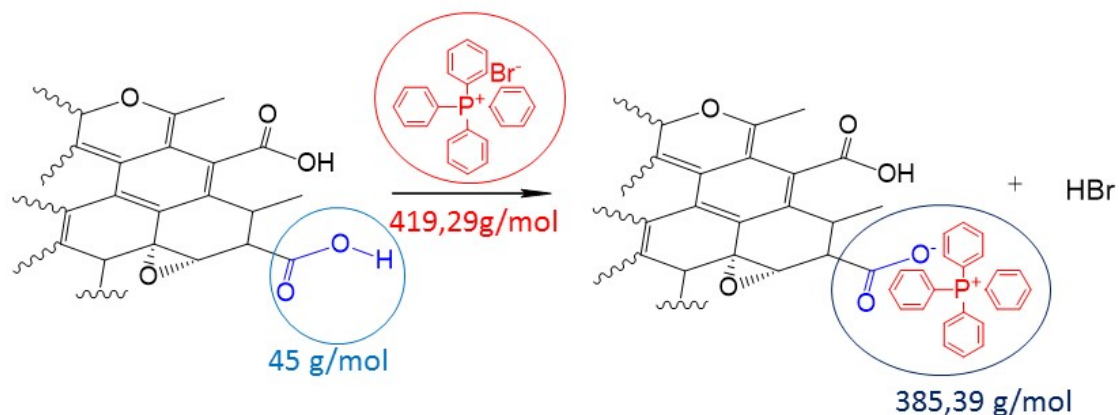
(4)

$$\text{MP} = \frac{\text{Total mass (Incl solvents)}}{\text{Mass of product}} * 100$$

$$\text{MP} = \frac{25 \text{ mg}}{(50 + 18.4 + 50 + 150) \text{ mg}} * 100 = 0.09 * 100 = 9\%$$

**oCB/TPP<sub>1/1</sub> ball milling.**

Atom efficiency was evaluated based on the possible mechanism of functionalization promoted by ball milling. By assuming that the ionic exchange is faster for –COOH groups:



And being unknown the molecular weight of oCB we can consider just the COOH before and after functionalization.

$$AE = \frac{385,39 \text{ g/mol}}{(45 + 419,29) \text{ g/mol}} * 100 = 83\%$$

The reaction is performed in the presence of 100mg of oCB and 100 mg of TPPBr, affording the product as a powder in 80% mass yield

The E(nvironmental)-factor, PMI, and MP were evaluated following the equation (2) (3), and (4)

Total mass waste<sub>2</sub>

$$E = \frac{\text{Mass of product}}{\text{Total mass waste}_2}$$

The reaction is performed in a solvent-free condition. No waste is produced.

$$E=0$$

Total mass in process (incl water)

$$PMI = \frac{\text{Total mass in process (incl water)}}{\text{Mass of product}}$$

$$PMI = \frac{100 \text{ mg} + 100 \text{ mg}}{80 \text{ mg}} = 2.5$$

$$PMI = \frac{100 \text{ mg} + 100 \text{ mg}}{80 \text{ mg}} = 2.5$$

Mass of product (4)

$$MP = \frac{\text{Mass of product}}{\text{Total mass (Incl solvents)}} * 100$$

$$MP = \frac{80 \text{ mg}}{100 \text{ mg} + 100 \text{ mg}} * 100 = 40\%$$

## References

- [1] Hummers, W. S.; Offeman, R. E. Preparation of Graphitic Oxide. *J. Am. Chem. Soc.* **1958**, *80* (6), 1339–1339. <https://doi.org/10.1021/ja01539a017>.
- [2] Cascone, E.; Longo, S.; Acocella, M. R. Basified Graphene Oxide and PPO Composite Aerogel with Basified Graphene Oxide for Henry Reaction in Solvent-Free Conditions: A Green Approach. *ACS Omega* **2022**, *7* (29), 25394–25402.
- [3] Hwang, T.; Cho, M.; Cho, K. Interlayer Design of Pillared Graphite by Na-Halide Cluster Intercalation for Anode Materials of Sodium-Ion Batteries. *ACS Omega* **2021**, *6* (14), 9492–9499.
- [4] Kim, H.; Hong, J.; Yoon, G.; Kim, H.; Park, K.-Y.; Park, M.-S.; Yoon, W.-S.; Kang, K. Sodium Intercalation Chemistry in Graphite. *Energy Environ. Sci.* **2015**, *8* (10), 2963–2969.