Basified graphene oxide and PPO composite aerogel with basified graphene oxide for Henry reaction in solvent free conditions: a Green Approach

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General methods

High surface area graphite, with Synthetic Graphite 8427® as trademark, was purchased from Asbury Graphite Mills Inc., with a minimum carbon wt% of 99.8 and \( S_A = 330 \text{ m}^2/\text{g} \). The used carbon black samples, with surface area of 151 \( \text{m}^2/\text{g} \), were purchased from Cabot. All reagents were purchased from Sigma–Aldrich and used without any further purification. TLC was performed on Merck Kiesegel 60 F 254 plates and visualized by a 254 nm UV lamp. Column chromatographic purification of products was carried out using silica gel 60 (70–230 mesh, Merck). NMR spectra were recorded on a Bruker 400 spectrometer by using CDCl\(_3\) (\( \delta=7.26 \text{ ppm} \) in \( ^1\text{H} \) NMR spectra and \( \delta=77.0 \text{ ppm} \) in \( ^{13}\text{C} \) NMR spectra) as solvent (400.135 MHz for \( ^1\text{H} \) and 100.03 MHz for \( ^{13}\text{C} \)); mass spectral data were acquired on an electrospray spectrometer Waters 4 micro quadrupole.

Synthetic procedures

**Oxidation of Graphite.**

Graphite Oxide (GO) was prepared by Hummers’ method.\(^{[1]}\) 120 mL of sulfuric acid and 2.5 g of sodium nitrate were introduced into a 2000 mL three-neck round bottomed flask immersed into an ice bath and 5 g of carbon samples were added, with a magnetic stirring. After obtaining a uniform dispersion, 15 g of potassium permanganate were added very slowly to minimize the risk of explosion. The reaction mixture was then heated to 35 °C and stirred for 24 h. Deionized water (700 mL) was added in small amounts into the resulting black and dark green slurry for carbon black and graphite respectively, under stirring and, finally, gradually adding 5 mL of H\(_2\)O\(_2\) (30 wt%). The obtained sample was poured into 7 L of deionized water, and then centrifuged at 10000 rpm for 15 min with a Hermle Z 323 K centrifuge. The isolated GO powder was first washed twice with 100 mL of a 5 wt% HCl aqueous solution and subsequently washed with 500 mL of deionized water. Finally, powders were dried at 60 °C for 12 h. About 7.5 g of GO powder was obtained. The obtained Oxygen/Carbon weight ratio is 0.71.

**Exfoliation of graphite oxide by ball-milling**

Graphite oxide powders were introduced in 125 mL ceramic jars (inner diameter of 75 mm) together with stainless steel balls (10 mm in diameter) and were dry-milled in a planetary ball mill (Retsch GmbH 5657 Haan) for 2 h with a milling speed of 500 rpm and a ball-to-powder mass ratio of 10 to 1.
**Basification of eGO**

The basified GO (b-eGO) was prepared starting from eGO powders (360 mg) dispersed in 0.05 M NaOH solution (196 mL), 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 °C for 12 h in an oven.

The cation-exchange-capacity of the obtained GO was determined as $C_{EC_{GO}} = 7.3$ mmol/g, by the procedure reported by Matsuo et al. [2]

**General procedure for Henry reaction with b-eGO powder**

![Chemical reaction](https://via.placeholder.com/150)

The reaction was conducted in a vial. p-Nitrobenzaldehyde (0.26 mmol) and nitromethane (1.8 mmol) were added to b-eGO powder (5wt%) at room temperature. The reaction mixture was stirred at the same temperature for the time indicated. The reaction mixture was extracted with AcOEt, and the combined organic phase was dried (MgSO$_4$) and concentrated. The conversion was evaluated by $^1$H NMR. The b-eGO powder was recovered by aqueous solution

**General procedure for Henry reaction with PPO/b-eGO aerogel**

The reaction was conducted in a vial. p-Nitrobenzaldehyde (0.26 mmol) and nitromethane (1.8 mmol) were added to PPO$_{0.8}$/b-eGO$_{0.2}$ containing 5wt% of b-eGO at room temperature. The reaction mixture was kept without stirring at the same temperature for the time indicated. In presence of 99% conversion, the pure product was obtained by ethanol washing without any other purification.
Characterization techniques

Wide angle X-ray diffraction

Wide-angle X-ray diffraction (WAXD) patterns were obtained by an automatic Bruker D8 Advance diffractometer, in reflection, at 35 KV and 40 mA, using the nickel filtered Cu-Kα radiation (1.5418 Å). The d-spacings were calculated using Bragg’s law and the observed integral breadths ($\beta_{\text{obs}}$) were determined by a fit with a Lorentzian function of the intensity corrected diffraction patterns, according to the procedure described by Iwashita et al.\textsuperscript{[12]}

The instrumental broadening ($\beta_{\text{inst}}$) was also determined by fitting of Lorentzian function to line profiles of a standard silicon powder 325 mesh (99%). For each observed reflection, the corrected integral breadths were determined by subtracting the instrumental broadening of the closest silicon reflection from the observed integral breadths, $\beta=\beta_{\text{obs}} - \beta_{\text{inst}}$. The correlation lengths ($D$) were determined using Scherrer’s equation.

\[
D = \frac{K\lambda}{\beta \cos \theta} \tag{1}
\]

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

FTIR spectroscopy

FTIR spectra were obtained at a resolution of 2.0 cm\textsuperscript{-1} with a 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\textsuperscript{-1} using a He-Ne laser. 32 scans were signal averaged to reduce the noise.
FIGURE S1. IR spectrum of high molecular weight PPO aerogel Cpol=10% (blue) and IR spectrum of aerogel PPO/bGO 80/20 Cpol=10% (red).

Thermogravimetric analysis

The thermogravimetric (TG) analysis was carried out on a Q500, manufactured by TA Instruments, from 20 to 200 °C at a heating rate of 10 °C, under N\textsubscript{2} flow. The water content was determined from the weight decrease below 100 °C.
**Figure S2.** TGA of graphite oxide (GO), GO after milling (eGO) and after basification of graphene oxide (b-eGO).

*SEM image.*

**FIGURE S3.** SEM images of the morphology of the monolithic pristine PPO aerogel (A) and of the hybrid PPO/b-eGO aerogel obtained after scCO₂ solvent extraction (B). Some b-eGO particles dispersed in the hybrid aerogel are indicated by red circles.
Elemental analysis

Elemental analysis was performed with a Thermo FlashEA 1112 Series CHNS-O analyzer, after pretreating samples in an oven at 100 °C for 12 h.

**TABLE S1. Results of elemental analysis on the starting graphite and the derived oxidized samples.**

| Sample | C (wt%) | H (wt%) | N (wt%) | O (wt%) | S (wt%) | O/C |
|--------|---------|---------|---------|---------|---------|-----|
| Graphite | 99.8 | 0.1 | 0.1 | 0.0 | 0.0 | 1/ |
| GO | 56.1 | 1.2 | 0.1 | 39.8 | 2.7 | 0.71 |
| eGO | 59.4 | 0.6 | 0.1 | 37.1 | 2.6 | 0.62 |
| b-eGO | 53 | 1.2 | 0.1 | 45.7 | 0 | 0.86 |
| b-eGOb | 61.5 | 0.9 | 0.1 | 37.5 | 0 | 0.61 |

*Elemental composition of the anhydrous samples: water contents of nearly 5 %wt. and 6 %wt. are evaluated by TGA for GO and eGO, respectively.

b-eGO after 1 week

The adopted basification procedure leads to an increase of the oxygen content with respect to the GO, possibly mainly due to opening of epoxide groups on the GO layers as promoted by hydroxyl ions.

**1H – 13C NMR spectra.**

NMR spectra were recorded on Bruker 400 and 300 spectrometer by using CDCl₃ (δ=7.26 ppm in ¹H NMR spectra and δ=77.0 ppm in ¹³C NMR spectra) as solvent (400.135 MHz and 300.135MHz for ¹H and 100.03 MHz and 75 MHz for ¹³C); mass spectral data were acquired on an electrospray spectrometer Waters 4 micro quadrupole. All the spectra match those reported in literature [3-10]
FIGURE S4. $^1$H NMR and $^{13}$C NMR of 2-bromo-1-(2,4-dinitrophenyl)-2-nitroethanol
2-bromo-1-(2,4-dinitrophenyl)-2-nitroethanol

$^1$H-NMR (300MHz, CDCl$_3$) syn: δ 3.94 (br s, 1H); δ 6.26 (br s, 1H); δ 6.55 (d, 1H, J= 1,6 Hz); δ 8.34-8.36 (d, 1H, J= 8.8 Hz); 8.59-8.62 (dd, 1H, J$_1$=8.8 Hz; J$_2$=2.4 Hz); 8.97-8.98 (d, 1H, J= 2.4 Hz); anti: δ 3.94 (br s, 1H); δ 6.12-6.14 (d, 1H, J= 5.2); δ 6.36-6.37 (d, 1H, J=5.2 Hz); δ 8.03-8.05 (d, 1H, J= 8.8 Hz); 8.53-8.56 (dd, 1H, J$_1$=8.8 Hz; J$_2$=2.4 Hz); 8.92-8.93 (d, 1H, J= 4 Hz)

$^{13}$C-NMR (300MHz, CDCl$_3$) syn: 148.7, 139.2, 133.4, 128.5, 121, 84.31, 69.4; anti 146.7, 138.5, 133.4, 128.5, 121.2, 81.7, 72.2; ESI-MS m/z 336.94(M$^+$), 334.94 (M$^+$); Anal. Calcd for C$_8$H$_6$BrN$_3$O$_7$ C 28.59; H 1.80; Br 23.78; N 12.50; O 33.33. Found : C 28.6; H 1.70; Br 23.6, N 12.7; O 33.4.
FIGURE S5 $^1$H NMR and $^{13}$C NMR of 2-bromo-2-nitro-1-(2-cyanophenyl)ethanol

$^1$H NMR (250MHz, CDCl$_3$) syn: δ 3.40 (br s, 1H); δ 6.29-6.30 (dd, 1H, J$_1$=3.5 Hz; J$_2$=1.0 Hz,) δ 7.21 (s, 1H); δ 7.57; 8.07 (m, 2H; 7.68-7.69; 7.77-7.78 (m, 2H);) anti : δ 3.37 (br s, 1H); δ 6.07-6.10 (dd, 1H, J$_1$=8...
Hz; J=0.25 Hz) δ 7.21 (s, 1H); δ 7.53; 8.04 (m, 2H); 7.65-7.66; 7.73-7.74 (m, 2H). $^{13}$C-NMR (400 MHz, CDCl$_3$): Syn: 140.6, 134.6, 133.7, 130, 125, 117, 114, 80.4, 74.2,140.6, 134.1, 133.7, 130.9, 123, 116, 112, 79.66, 72.5: anti 140.6, 134.1, 133.7, 130.9, 123, 116, 112, 79.66, 72.5. ESI-MS m/z 269.96 (M$^+$), 271.96 (M$^+$); Anal. Calcd for C$_9$H$_7$BrN$_2$O$_3$ C 39.88; H 2.60; Br 29.48, N 10.33, O 17.71 Found :C 40.01, H 2.50, Br 29.00, N 10.33, O 18.06

**FIGURE S6** $^1$H NMR and $^{13}$C NMR of 2-bromo-2-nitro-1-(4-cyanophenyl)ethanol

2-bromo-2-nitro-1-(4-cyanophenyl)ethanol: H-NMR (300MHz, CDCl$_3$) syn: δ 3.30 (br s, 1H, OH); δ 5.46-5.47 (d, 1H, J=2,4 Hz); δ 6.05- 6.06 (d, 1H, J=3 Hz); δ 7.58-7.60 (d, 2H, J=6,3 Hz); 7.73 (m, 2H); anti: δ 3.30 (br s, 1H, OH); δ 5.39-5.41 (d, 1H, J=6,3 Hz); δ 5.88-5.90 (d, 1H, J=6,3 Hz); δ 7.55-7.57 (d, 2H, J=6 Hz.) 7.71 (m, 2H).

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$^1$H-NMR and $^{13}$C NMR of 2-bromo-2-nitro-1-(2-trifluoromethylphenyl)ethanol

2-bromo-2-nitro-1-(2-trifluoromethylphenyl)ethanol: $^1$H-NMR (300MHz, CDCl$_3$) syn: $\delta$ 5.85 (d, 1H, J= 0.6 Hz, CHO=OH) $\delta$ 6.16-6.17 (d, J= 2.7 Hz, 1H, CHBr); $\delta$ 7.62-8.00 (m, 4H) ; anti: $\delta$ 5.79-5.82 (d, 1H, J= 7.8 Hz, CDCl$_3$) 1,131, 133.2, 127.8, 130, 114, 80.8, 74.14; anti: $\delta$ 141, 133.1, 128.8, 130, 118, 85.4, 75.9; ESI-MS m/z 269.96 (M$^+$), 271.96 (M$^+$); Anal. Calcd for C$_9$H$_7$BrN$_2$O$_3$: C 39.88; H 2.60; Br 29.48, N 10.33, O 17.71. Found: C 39.95, H 2.75, Br 29.65, N 10.45, O 17.2
Hz, CHOH) δ 6.14 (d, 1H, J=0.6 Hz, CHBr); δ 7.62–8.00 (m, 4H). $^{13}$C-NMR syn: 143.2, 137, 132, 130.6, 128.3, 125, 80.7, 69.6; anti: 145, 135.6, 131, 130, 128,124.6, 125.4, 79.7, 70.19 ESI-MS m/z 269.96 (M$^+$), 314.95.

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