Oxidized Carbon Black as activator of transesterification reactions in solvent free conditions

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Materials

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. All reagents were purchased from Sigma–Aldrich and used without any further purification. TLC was performed on silica gel 60 F254 0.25 mm on glass plates Merck and non-flash chromatography was performed on silica gel (0.063-0.200 mm) (Merck).

Synthethic procedure

Oxidation of Graphite

Graphite Oxide (GO) and oCB were prepared by Hummers’ method [S1]. 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 thus 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 H2O2 (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 and oCB powders were 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 and 6.5 g of oCB powders were obtained. The obtained Oxygen/Carbon weight ratio is 0.71 for graphite oxide and 0.77 for oxidized carbon black.

Oxidation of Carbon Black in H2O2/H2SO4 solution

Oxidation of commercial Carbon Black was carried out in 5/1 H2O2/H2SO4 solution. 500 mg of Carbon Black were added into 500 ml of H2O2 30 wt% in water with a magnetic stirring. Then H2SO4 was slowly dripped into the uniform dispersion. After 24 hrs the mixture was diluted in 1.5 L of deionized water and then centrifuged at 10000 rpm for 10 min with an Awel centrifuge. The isolated oCB powders was washed with 500 mL of deionized water. Finally, powders were dried at
60 °C for 12 h. About 1.3 g of oxidized CB (so-CB) powders were obtained with Oxygen/Carbon weight ratio 0.85

**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.

**Synthetic procedure for transesterification reaction**

The reaction was carried out in a flask. Ethyl 3-phenylpropanoate (1 mmol, 178.2 mg, 176 ul) and benzyl alcohol (2 mmol, 216.3 mg, 208 ul) were added to the catalyst (5 wt% compared to the ester) at 80°C. The reaction was stirred at the same temperature for the time indicated. The reaction mixture was extracted with AcOEt, and the combined organic phase was dried (Na2SO4) and concentrated. The residue was purified by column chromatography (silica gel, petroleum ether/EtOAc, gradient) to obtain the pure product.

**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 (βobs) were determined by a fit with a Lorentzian function of the intensity corrected diffraction patterns, according to the procedure described by Iwashita et al. S2

The instrumental broadening (βinst) 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, β = βobs – βinst. The correlation lengths (D) were determined using Scherrer’s equation.
\[
D = \frac{K\lambda}{\beta \cos \theta}
\] (1)

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

**FIGURE S1.** X-ray diffraction patterns (Cu K\(\alpha\)) of the high-surface-area graphite (HSAG), of the derived GO, and eGO obtained by ball-milling of GO.

GO sample exhibiting a 001 reflection (d001=0.84 nm) with half-height width larger than for the 100 reflection (\(\beta_{001} = 2^\circ\) and \(\beta_{100} = 0.5^\circ\)), and hence higher correlation length parallel (D100 = 30 nm) than perpendicular to the graphitic layers (D001 = 4.5 nm). (C) exfoliated graphite oxide (eGO) maintaining essentially only the order parallel to the graphitic layers (D100 = 30 nm).
FIGURE S2. X-ray diffraction pattern of CB samples before and after oxidation with Hummers procedure and H$_2$O$_2$/H$_2$SO$_4$ mixture.

No substantial variation was detected before and after oxidation of CB with both methods.

*FTIR spectroscopy*

FTIR spectra were obtained at a resolution of 2.0 cm$^{-1}$ 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$^{-1}$ using a He-Ne laser. 32 scans were signal averaged to reduce the noise.

*BET surface areas.*

Surface areas of carbon and oxidized carbon samples were measured by nitrogen adsorption at liquid nitrogen temperature (77 K) with a Nova Quantachrome 4200e instrument. Before adsorption measurements, samples were degassed at 60 °C under vacuum for 24 h. The surface area values were determined by using 11-point BET analysis.
Elemental analysis

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

TABLE S1. Elemental analysis of oxidized carbon black (oCB) and of graphite oxide and graphene oxide samples.

| Starting material | Oxidation method | Sample Name | C (wt%) | H (wt%) | O (wt%) | S (wt%) | O/C (wt/wt) |
|------------------|------------------|-------------|---------|---------|---------|---------|-------------|
| CB               | Hummers          | oCB-1       | 50.3    | 2.3     | 41.7    | 5.4     | 0.83        |
| CB               | H$_2$O$_2$/H$_2$SO$_4$ 5/1, v/v | oCB-2       | 55.4    | 1.7     | 36.6    | 6.1     | 0.66        |
| Graphite         | Hummers          | GO          | 56.1    | 1.2     | 39.8    | 2.7     | 0.71        |
| Graphene Oxide   | Hummers          | eGO         | 59.4    | 0.6     | 37.1    | 2.6     | 0.62        |
| Graphite         | H$_2$O$_2$/H$_2$SO$_4$ 10/1, v/v | –           | 88      | 0.7     | 11.6    | -       | 0.13        |

*Elemental composition of anhydrous samples: The error in C and O content is close to 1 wt% while the error in H content is close to 0.1 wt%; water contents (as evaluated by TGA, after equilibration at room temperature in air with a relative humidity of 45%) was in the range 10-15 wt%, for all the examined samples. Graphite has a surface area of 330 m$^2$/g.

Thermogravimetric analysis

TGA analysis was carried out on a TG 209 F1, manufactured by Netzsch Geraetebau, from 20 to 800 °C, at a heating rate of 10 °C, under N$_2$ flow, after pretreating samples in an oven at 100 °C for 12 h.
**FIGURE S3.** TGA analysis of the starting Carbon Black (CB) and of its derived oCB-1 and oCB-2. The TGA of eGO is shown for comparison.

*Scanning electron microscopy*

The morphology of the samples was inspected by scanning electron microscopy (SEM) LEO, model EVO 50.
FIGURE S4. SEM images of oCB, with O/C molar ratio of 0.83

The micrometric morphologies presented in amorphous oCB sample obtained by Hummers oxidation is quite similar to that one obtained with the $\text{H}_2\text{O}_2$/H$_2$SO$_4$ mixture.

$^1$H-NMR analysis

All $^1$H NMR and $^{13}$C NMR spectra were recorded with a DRX 400 MHz instrument, by using CDCl$_3$ (δ = 7.26 ppm in 1H NMR spectra and δ = 77.0 ppm in $^{13}$C NMR spectra) as solvent (400.135 MHz for $^1$H and 100.03 MHz for $^{13}$C).

For the products 3aa, 3ad, 3ae, 3ca, the $^1$H-NMR and $^{13}$C-NMR match with those reported in literature.[S2-S5]

**butyl 3-phenylpropanoate**; Purified by flush column chromatography (silica gel, Hexane/EtOAc = 95/5); colorless oil; $^1$H NMR (400 MHz, CDCl$_3$) δ 7.30-7.27 (m, 2H), 7.21-7.18 (m, 3H), 4.07 (t, $J$ = 6.6 Hz, 2H), 2.95 (t, $J$ = 8.0 Hz, 2H), 2.62 (t, $J$ = 8.0 Hz, 2H), 1.62-1.55 (m, 2H), 1.37-1.30 (m, 2H), 0.92 (t, $J$ = 7.4 Hz, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$): δ=14.0, 19.4, 30.9, 31.3, 36.2, 64.6, 126.5, 128.5, 128.7, 140.8, 173.2. MS(EI) m/z (relative intensity) 206 [M+].

**Cyclohexyl 3-phenylpropanoate**; Purified by flush column chromatography (silica gel, Hexane/EtOAc = 95/5); colorless oil; $^1$H NMR (300 MHz, CDCl$_3$) 1.2–1.8 (m, 10H,), 2.59 (t, $J$ = 7.8 Hz, 2H), 2.94 (t, $J$ = 7.8 Hz, 2H), 4.7–4.8 (m, 1H), 7.1–7.3 (m, 5H); $^{13}$C NMR (75 MHz, CDCl$_3$) 23.77, 25.46, 31.14, 31.66, 36.28, 72.56, 126.01, 128.14, 128.26, 140.49, 172.05; MS(EI) m/z (relative intensity) 232 [M+].

**3-phenylpropionic acid phenyl ester**; Purified by flush column chromatography (silica gel, Hexane/EtOAc = 95/5); colorless oil $^1$H NMR (400 MHz, CDCl$_3$) δ 2.87 (t, $J$=7.6 Hz, 2H), 3.06 (t, $J$=7.6 Hz, 2H),
6.98–7.01 (m, 2H), 7.17–7.33 (m, 8H); \(^{13}\text{C}\) NMR (100 MHz, CDCl\(_3\)) \(\delta\) 30.9, 35.9, 121.5, 125.7, 126.4, 128.3, 128.5, 129.3, 140.0, 150.6, 171.3. MS(EI) m/z (relative intensity) 226 [M+].

**4-allyl-2-methoxyphenyl 3-phenylpropanoate;** Purified by flush column chromatography (silica gel, Hexane/EtOAc = 95/5); colorless oil; pale yellow oil; \(^1\text{H}\) NMR (300 MHz, CDCl\(_3\)) 7.31–7.18 (m, 5H), 6.86–6.68 (m, 3H), 6.02–5.89 (m, 1H), 5.01–5.04 (m, 2H), 3.87 (s, 3H), 2.98–2.88 (m, 2H), 2.77–2.55 (m, 2H). \(^{13}\text{C}\) NMR (100 MHz, CDCl\(_3\)) 172.9, 146.1, 143.8, 140.5, 137.4, 131.8, 128.4, 128.2, 126.2, 121.1, 115.4, 114.2, 111.1, 55.8, 39.8, 35.9, 30.9. MS(EI) m/z (relative intensity) 296 [M+].
FIGURE S5. $^1$H NMR and $^{13}$C NMR of 3ab
FIGURE S6. $^1$H NMR and $^{13}$C NMR of 3ac
FIGURE S7. $^1$H NMR and $^{13}$C NMR of 3ad
FIGURE S8. $^1$H NMR and $^{13}$C NMR of 3af
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