

## Direct delamination of graphite ore into defect-free graphene using a biphasic solvent system under pressurized ultrasound

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### Supporting information

#### Interfacial energy and wettability parameter calculation:

The interfacial energy can be used to express the wettability parameter ( $\omega_{\text{water/org}}$ ) according the following equation [S1]:

$$\omega_{\text{water/org}} = \cos \theta = (\gamma_{\text{graphene/org}} - \gamma_{\text{graphene/water}}) / \gamma_{\text{water/org}} \quad \text{Eq. S1}$$

where  $\gamma_{\text{graphene/water}}$  is the interfacial tension between the graphene and water,  $\gamma_{\text{graphene/org}}$  is the interfacial tension between graphene and organic phase (dichloromethane or 1-octanol) and  $\gamma_{\text{water/org}}$  is the interfacial tension between water and the organic phase. The equation represents the ability of the graphene particle to be wetted by liquids and is directly linked to the contact angle  $\theta$ . The graphene will be adsorbed at the liquid-liquid interphase provided that  $|\omega_{\text{water/org}}| < 1$  ( $\theta = 0 - 180^\circ$ ). Contrary to that, when  $|\omega_{\text{water/org}}| > 1$  then the graphene will be localized either in water ( $\omega_{\text{water/org}} > 1$ ) or in organic phase ( $\omega_{\text{water/org}} < -1$ ).

When at thermodynamic equilibrium, the results (Table S1) show that the graphene sheets should be preferentially located at the interface of both biphasic dispersions (water / dichloromethane and water / 1-octanol).

**Table S1:** Surface tension ( $\gamma$ ) data of components and calculated values of interfacial tensions ( $\gamma_{1/2}$ ) and wetting parameters ( $\omega_{\text{water/org}}$ ).

| $\gamma$ (mN/m), 25°C                   |                   | $\gamma_{1/2}$ (mN/m), 25°C       |                    |
|---|-------------------|-----------------------------------|--------------------|
|   |                   | graphene/water                    | 4.85 <sup>d</sup>  |
|   |                   |                                   | 9.49 <sup>e</sup>  |
| water                                   | 72.7 <sup>a</sup> | graphene/<br>dichloromethane      | 1.11 <sup>d</sup>  |
|   |                   |                                   | 2.20 <sup>e</sup>  |
| dichloromethane                         | 27.8 <sup>a</sup> | graphene/1-octanol                | 1.25 <sup>d</sup>  |
|   |                   |                                   | 2.48 <sup>e</sup>  |
| 1-octanol                               | 27.1 <sup>b</sup> | water/<br>dichloromethane         | 10.59 <sup>d</sup> |
|   |                   |                                   | 20.06 <sup>e</sup> |
| graphene                                | 40.0 <sup>c</sup> | water/1-octanol                   | 11.03 <sup>d</sup> |
|   |                   |                                   | 20.84 <sup>e</sup> |
| $\omega_{\text{water/dichloromethane}}$ | -0.4 <sup>d</sup> | $\omega_{\text{water/1-octanol}}$ | -0.3 <sup>d</sup>  |
|   | -0.4 <sup>e</sup> |                                   | -0.3 <sup>e</sup>  |

<sup>a</sup> From ref. S2; <sup>b</sup> From ref. S3; <sup>c</sup> From ref. S4; <sup>d</sup> Girifalco-Good model (ref. S5); <sup>e</sup> Wu model (ref. S6).

## XPS

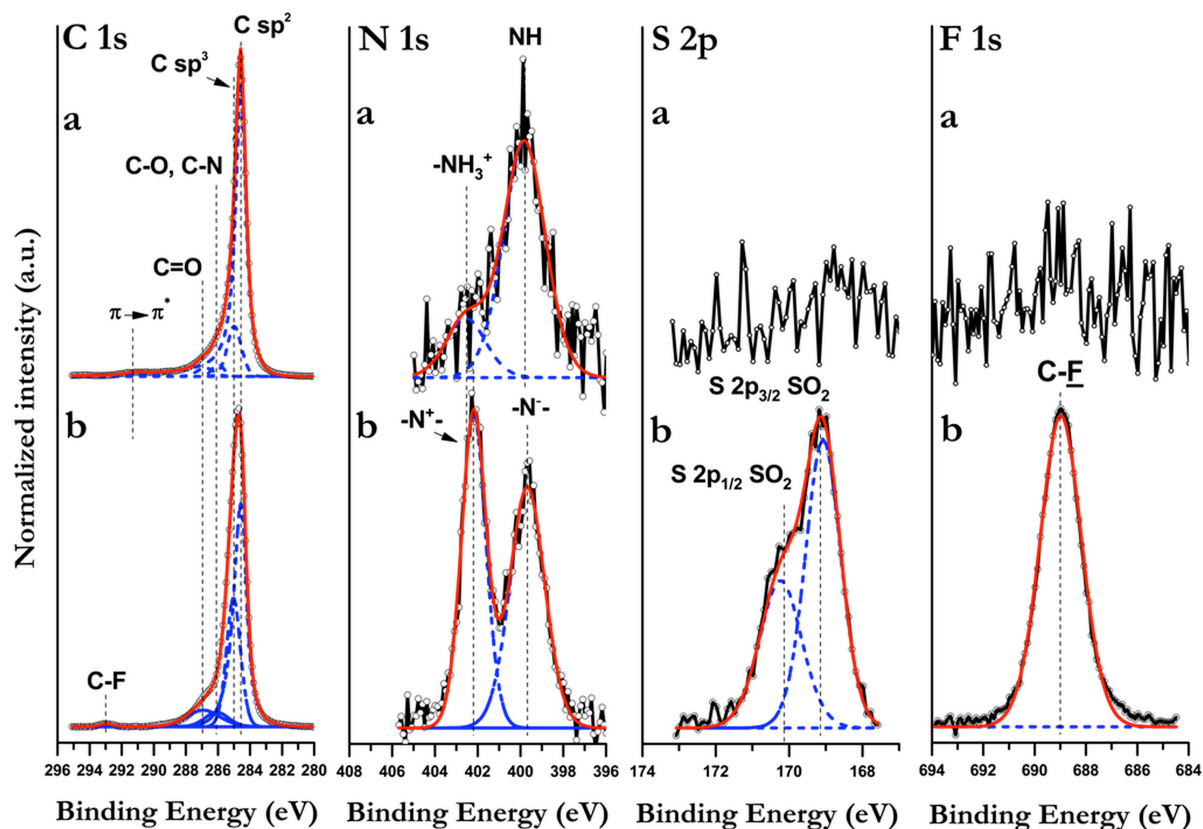


Fig. S1 High resolution core-level C1s, N1s, S2p and F1s XPS spectra of the exfoliated graphite ore without (A) and with (B) IL.

The spectrum of exfoliated graphite without IL has a dominating contribution at 284.6 eV attributed to the  $sp^2$  carbons. This peak has a characteristic broad asymmetric tail, which is shifted toward higher binding energy. The presence of defects, such as  $sp^3$  carbons,  $\underline{C}-O$  and  $\underline{C}-N$ , and  $\underline{C}=O$  moieties within the graphite structure, gives rise to the contributions at 285.0, 286.0 and 286.8 eV. Notably, the peak at 291.2 eV arises from the  $\pi \rightarrow \pi^*$  transition. The addition of  $C_4MimNTf_2$  causes clear changes in the measured core-level spectra of exfoliated graphite. In the C1s spectrum, both a clear rise in the contributions of  $sp^3$  carbons and the IL  $\underline{C}-N$  moieties contribution at 286.0 eV are observed. The presence of  $\underline{C}-F$  moieties of trifluoromethyl groups give rise to the peak at 293.0 eV. The N1s, S2p and F1s spectra corroborate these observations from the C1s spectra. While the N1s spectrum of pure exfoliated graphite has rather low contributions of primary (399.8 eV) and charged amines (402.5 eV) as a result of defects and surface contaminants, the spectrum of exfoliated graphite bearing IL molecules shows well resolved peaks of nitrogen atoms of the positively charged imidazolium ring (402.2 eV) and the negatively charged nitrogen atom of the anion

(399.6 eV). Furthermore, the incorporation of the sulphonyl groups ( $\text{SO}_2$ ) of  $\text{C}_4\text{MImNTf}_2$  within the graphite structure gives rise to the initially absent  $\text{S}2\text{p}$  signal. The  $\text{S}2\text{p}$  spectra have characteristic  $2\text{p}_{3/2}$  and  $2\text{p}_{1/2}$  spin-orbit split components at 169.1 and 170.2 eV, respectively. Similarly, the presence of trifluoromethyl moieties leads to the rise of the  $\text{C}-\text{F}$  peak at 689.0 eV in the  $\text{F}1\text{s}$  spectra.

## XRD

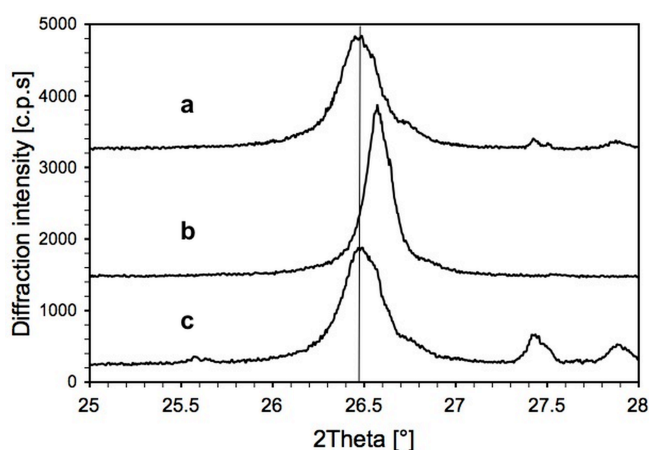


Fig. S2 XRD patterns of  $\text{C}_4\text{MImNTf}_2$  assisted and dispersed graphite-graphene after 30 min of pressurized sonication of graphite ore in  $\text{H}_2\text{O}-\text{CH}_2\text{Cl}_2\text{-IL}$  (a), graphite ore in  $\text{H}_2\text{O}-\text{C}_8\text{H}_{17}\text{OH-IL}$  (b), and powdered natural graphite in  $\text{H}_2\text{O}-\text{CH}_2\text{Cl}_2\text{-IL}$  (c).

## HRTEM of the graphenes produced in the water/1-octanol system

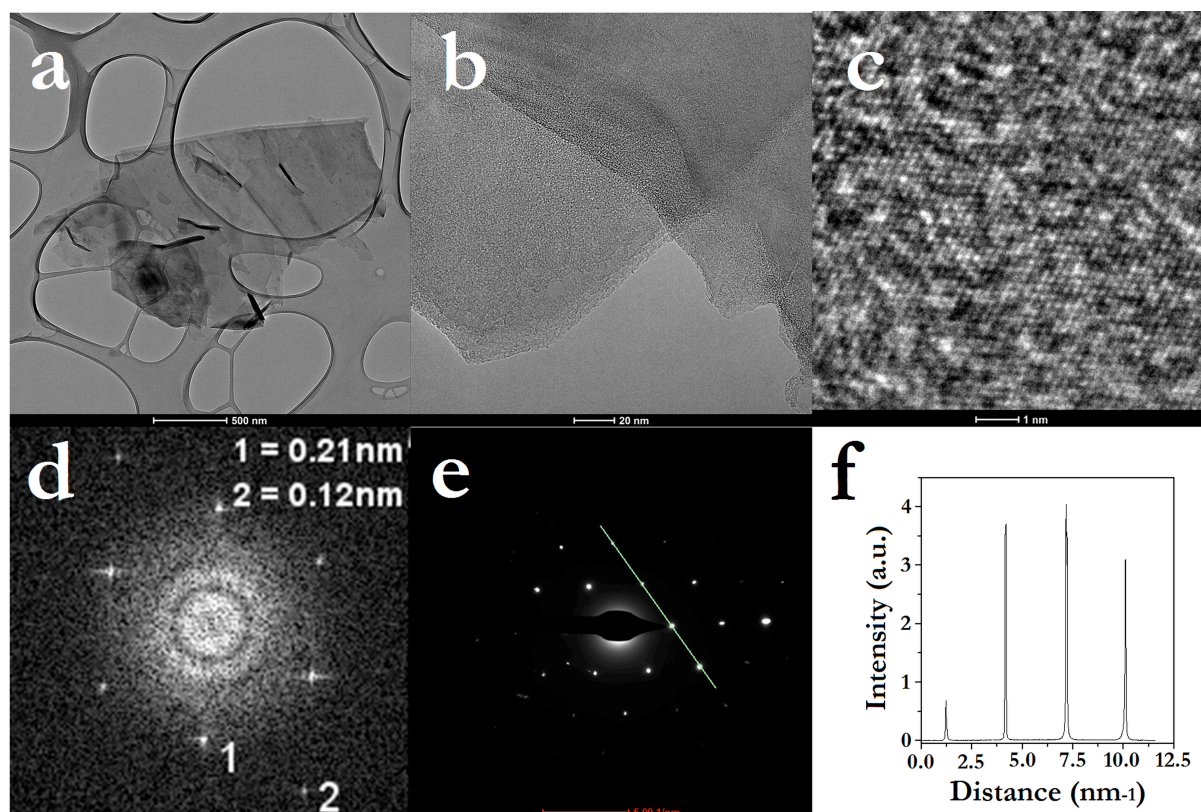


Fig. S3 Electron microscopy of graphene sheets produced after 30 min of pressurized sonication of graphite ore in the  $\text{H}_2\text{O}-\text{C}_8\text{H}_{17}\text{OH}$  (95/5) system with 0.3 wt.% of  $\text{C}_4\text{MImNTf}_2$ : TEM images of few-layer (a) and monolayer graphene (b). HRTEM image of a few-layer graphene (c), taken from (a). Two-dimensional FFT analysis of a few-layer graphene (d), taken from (a). Electron diffraction patterns of monolayer graphene (e), taken from (b). Diffracted intensity taken along the (1-210)-(0-110)-(-1010)-(-2110) axis (f), for the pattern shown in (e).

## Raman spectroscopy

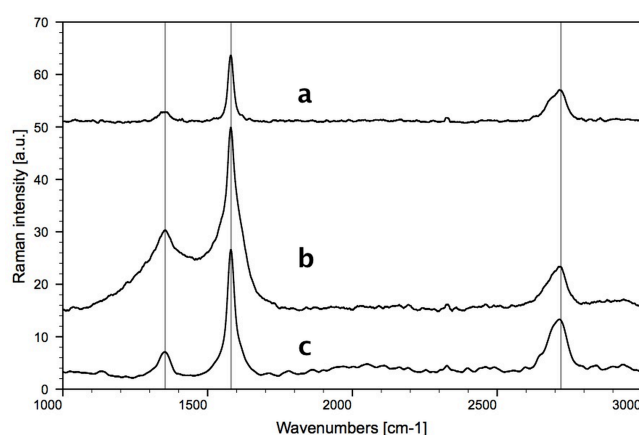


Fig. S4 Raman spectra of pristine graphite ore (a) and graphene dispersions produced after 50 min sonication in H<sub>2</sub>O-CH<sub>2</sub>Cl<sub>2</sub> (b), and after 30 min sonication in H<sub>2</sub>O-CH<sub>2</sub>Cl<sub>2</sub>-IL (c).

Table S2 The summary of experimental runs and relative intensities of Raman D and G bands ( $I_D/I_G$ ) of the prepared graphene/graphite dispersions and the pristine graphite ore.

| Material for exfoliation | Time of sonication [min] | Water / org. phase [vol. / vol.]                            | C <sub>4</sub> MI <sub>m</sub> NTf <sub>2</sub> [wt. %] | $I_D/I_G$ |
|--------------------------|--------------------------|---|---|-----------|
| Graphite ore             | 10                       | H <sub>2</sub> O / CH <sub>2</sub> Cl <sub>2</sub> (95 / 5) | 0   | 0.15      |
| Graphite ore             | 30                       | H <sub>2</sub> O / CH <sub>2</sub> Cl <sub>2</sub> (95 / 5) | 0   | 0.17      |
| Graphite ore             | 50                       | H <sub>2</sub> O / CH <sub>2</sub> Cl <sub>2</sub> (95 / 5) | 0   | 0.16      |
| Graphite ore             | 10                       | H <sub>2</sub> O / CH <sub>2</sub> Cl <sub>2</sub> (95 / 5) | 0.3   | 0.14      |
| Graphite ore             | 30                       | H <sub>2</sub> O / CH <sub>2</sub> Cl <sub>2</sub> (95 / 5) | 0.3   | 0.14      |
| Graphite ore             | 50                       | H <sub>2</sub> O / CH <sub>2</sub> Cl <sub>2</sub> (95 / 5) | 0.3   | 0.13      |
| Graphite ore             | 30                       | H <sub>2</sub> O / CH <sub>2</sub> Cl <sub>2</sub> (95 / 5) | 0.3   | 0.13      |
| Natural graphite powder  | 30                       | H <sub>2</sub> O / CH <sub>2</sub> Cl <sub>2</sub> (95 / 5) | 0.3   | 0.16      |
| Graphite ore             | 30                       | H <sub>2</sub> O / 1-octanol (95 / 5)                       | 0.3   | 0.17      |
| Pristine graphite ore    | -                        | -   | 0   | 0.15      |

## HRTEM of natural powder graphite exfoliated in the water/dichloromethane system

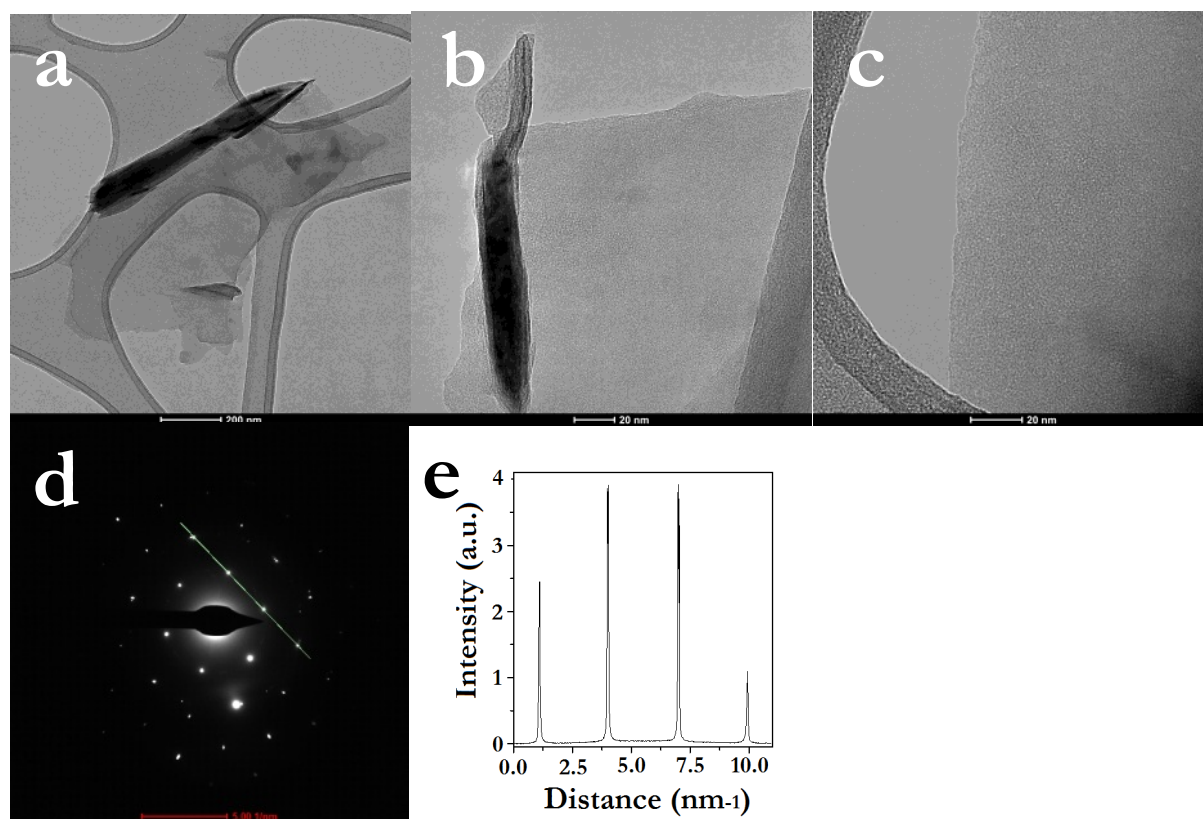


Fig. S5 Electron microscopy of graphene sheets after 30 min sonication of powdered natural graphite in  $\text{H}_2\text{O}-\text{CH}_2\text{Cl}_2$  (95/5 vol.) containing 0.3 wt.% of  $\text{C}_4\text{MImNTf}_2$ . TEM images of few-layer (a,b) and monolayer graphene (c). Electron diffraction patterns of monolayer graphene (d), taken from (c). Diffracted intensity taken along the (1-210)-(0-110)-(-1010)-(-2110) axis (e), for the pattern shown in (d).

### References

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