Optimised exfoliation conditions enhance isolation and solubility of grafted graphenes from graphite intercalation compounds

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Supplementary figures

**Fig. S1.** TGA data (heating rate = 10°C min⁻¹, under N₂) for eicosylated graphene 1f, pristine graphite, and eicosane. A pure eicosane control decomposed predominantly below 200°C with a small amount of char disappearing about ~550°C. A very small weight loss of 1f below 210°C can be ascribed to decomposition of remaining physical adsorbed alkane. The two step weight loss of 1f observed from
210°C to 800°C is ascribed predominantly to decomposition of eicosyl chains to graphenes, although some THF may also be present (see Fig. S2). Alkyl chains grafted to graphene,\textsuperscript{1a} and SWNTs\textsuperscript{1b} synthesised by reacting with alkyl iodide, are also known to show two step weight losses from ~200°C to ~700°C, as confirmed by TGA-MS observations.\textsuperscript{1a}

\textbf{Fig. S2.} (a) TGA data (heating rate = 10°C min\textsuperscript{-1}, under N\textsubscript{2}) for eicosylated graphene 1f, 1j, 1k, and 1l. Eicosyl chains grafted to graphene showed two step weight losses from ~210°C to ~700°C, which are
the similar type of weight losses as shown in alkylated graphenes.\(^1\) (b) TGA data (heating rate = 10°C
\(\text{min}^{-1}\), under \(\text{N}_2\)) for Na-THF-GIC (synthesised with C/Na ratio = 12) after the same work-up procedure
as 1f, and Na-THF-GIC after exposure to dry \(\text{O}_2\) and filtration (without washing and vacuum drying).
Na-THF-GIC after exposure to dry \(\text{O}_2\) and filtration (but without washing and vacuum drying) showed
weight losses which are likely due to volatilisation of remaining THF and naphthalene. The weight loss
from \(~200^\circ\text{C}\) to \(~500^\circ\text{C}\) is ascribed to intercalated THF volatilisation. For comparison, a weight loss
due to intercalated alkylamine volatilisation of stage-1 Na-alkylamine-GICs is known\(^2\) to be observed
from 50°C to 500°C. After reaching \(~650^\circ\text{C}\), the trace oxygen present presumably led to some
decomposition of graphene itself\(^2\). Na-tetrabutylammonium (TBA)-GIC showed weight losses due to
intercalated TBA volatilisation at 150°C to 500°C.\(^2\) Na-THF-GIC prepared by the same work-up
procedure as 1f showed a very small weight loss at \(~200^\circ\text{C}\) to \(~500^\circ\text{C}\), which is ascribed to
volatilisation of remaining intercalated THF, since this sample did not show any characteristic
naphthalene peaks in the Raman and IR spectra. During the work-up procedure using dry \(\text{O}_2\), most of
the Na cations reacted with dry \(\text{O}_2\) producing \(\text{Na}_2\text{O}\) during charge quenching (Na-THF-GICs can be
converted into the pristine graphite), and the resulting \(\text{Na}_2\text{O}\) was removed by washing with water
several times. Most of the remaining THF between layers can be removed by drying at 80 °C under
vacuum overnight. Note that the amount of Na-THF-GIC remaining unreacted in the alkyl reacted
samples is very small (3% for 1f and 0% for 1l, see caption S3 below) and the Na-THF-GIC itself shows
a very small weight loss after appropriate washing and drying (see above). Therefore, the possible
contribution of remaining THF or other Na-THF-GIC species to the TGA weight loss of the alkylated
graphenes should be small in the current case, and in any case does not affect the clear trends observed.
Fig. S3. (a) Enlarged XRD diffractogram of eicosylated graphene 1f (blue), Na-THF-GIC obtained after filtration under air (without washing and drying) (red), and pristine graphite (dotted line). Remaining stage-1 Na-THF-GIC structure peaks are indexed as (001) lines by using two values of the characteristic period $I_c$, 1.12 and 0.72 nm, indicated as stage-1 phases A (S1 A) and B (S1 B), respectively, in the figure. The thickness of intercalate layer is calculated as 0.79 nm for phase A, and 0.39 nm for phase B, by a subtraction of the thickness of carbon layers (0.335 nm). Phase B is formed by exposing phase A to air. From these values of $I_c$, both phases are reasonably supposed to have the stage-1 structure. The content of remaining Na-THF-GIC in 1f is very small (estimated as ~3% based on the XRD peak intensity ratio of S1 A (001) in 1f (blue) to that of Na-THF-GIC (red))). (b) Enlarged XRD diffractogram of eicosylated graphene 1l (C/Na = 12), under optimum conditions. The enlarged diffractogram does not show any S1 A peaks, and shows only a very small trace at ~25.5 degrees.
**Fig. S4.** (left) Raman 2D bands (normalised by the intensity of the G peak) of pristine graphite and eicosylated graphenes 1f, 1j, 1k, and 1l. (right) (a) Lorentzian peak fitting of the 2D peak of eicosylated graphene 1l. The 2D peak of 1l have a single symmetric line profile ($R^2 = 0.989$) with a full width at half magnitude (FWHM) value of 71.9 cm$^{-1}$; this characteristic 2D peak indicates the existence of a single layer graphene sheet.$^{4-6}$ In the case of a single-layer graphene, the 2D peak is generally higher than the intensity of G peak. However, it is known that a single-layer graphene after chemical reaction shows significantly reduced and broadened 2D peak compared with non-functionalised single-layer graphene.$^5$ (b) Voigt peak fitting of the 2D peak of eicosylated graphene 1l. Voigt functions have been proposed for graphenes incorporating different environments$^7$ and here provide an even better fit ($R^2 = 0.997$), indicating possibly a combination of Lorentzian line shape with a Gaussian variation of functionalisation/defect density.
Fig. S5. SEM images of (a) pristine graphite (flake graphite G2369) and (b) eicosylated graphene 1j (C/Na = 12). The SEM image of 1j shows crumpled sheets with blunter edges, due to the exfoliation reaction and functionalisation.

Fig. S6. Concentrations of supernatant after mild centrifugation (1,000 rpm (87 g), 5 min) of eicosylated graphene 1j-dispersed DCB solution (initial concentration: 0.2, 1, and 2 mg/ml).
**Fig. S7.** UV-vis spectra of supernatant solutions after mild centrifugation of butylated graphene (1g) in DCB, dodecylated graphene (1h) in DCB, and eicosylated graphene (1j) in DCB.

**References**


