Supporting Materials:

Low-temperature Exfoliation of Graphene Sheets from $FeCl_3$ and CH_3NO_2 Co-intercalated Graphite Compound

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1. Preparation of $FeCl_3$-CH_3NO_2 ternary GIC and exfoliated graphene sheets:

In a typical experiment, $FeCl_3$ (11.68 g, 0.07 moles) was dissolved in 25 mL of nitromethane in a 50 mL round-bottom flask. Subsequently, 0.2 g of graphite was added and the mixture was refluxed for 6 days. A light brown $FeCl_3$-CH_3NO_2 GIC (around 2 g) was filtered from the reaction mixture and rinsed by 10 mL of nitromethane. The product was dried in air at room temperature. A portion of the $FeCl_3$-CH_3NO_2 GIC (0.2 g) was suspended in 30 mL deionized water at ambient temperature and then immediately exfoliated by microwave radiation (700 watt) for 60 s. A monomode microwave oven (Panasonic NN-H965WFX) with rotating tray (at 3 rpm) was used to ensure homogeneous heating. Long time (>60 min) immersion of GIC in water results in inferior results because of the hydrolysis and deintercalation of $FeCl_3$ by water. The exfoliated graphene sheets were further repeatedly washed with diluted HCl (1 wt.%) to remove iron related compounds and impurities. Insufficient washing with diluted HCl (1 wt.%) result in a sample with residual $FeCl_3$. After the removal of macroscopic aggregates, a dark graphene suspension was centrifuged and re-dispersed in N-Methylpyrrolidone (NMP) for future characterization. Two control experiments were conducted for comparison purpose: (1) $FeCl_3$-CH_3NO_2 GIC (0.2g) was heated in a tube furnace at 500 ºC and then followed the same preparation procedure as the microwave treated sample; and (2) $FeCl_3$-CH_3NO_2 GIC (0.2g) was suspended in boiling water for 60 s and then followed the same preparation procedure as the microwave treated sample.

2. Characterization of $FeCl_3$-CH_3NO_2 ternary GIC and exfoliated graphene sheets by TGA-MS and XRD:

Thermogravimetric Analysis (TGA) was conducted on a TA Q-500 TGA system under an air flow of 90 ml/min. A ThermoStar mass spectrometer was connected to the TGA through a Evolved Gas Analysis (EGA) furnace for the detection of decomposed products of TGA samples. The temperature was ramped to 850 ˚C with a heating rate of 10 ˚C/min. The residual of $FeCl_3$ in the exfoliated samples was also determined by TGA in air. Powder X-ray diffraction pattern (PXRD) were recorded at a PANalytical X'pert PRO 2-circle X-ray diffractometer with a Cu Kα radiation ($\lambda \approx 1.5418$ Å). The GIC samples were ground and loaded on a silicon zero-background sample holder. The exfoliated graphene samples were dried and mounted on the same silicon zero-background sample holder. Raman spectra were recorded from 600 cm^{-1} to 3500 cm^{-1} (extended model) on a Renishaw Confocal MicroRaman spectrometer at room temperature. The GIC samples were directly loaded on a glass slide for measurements. All Raman measurements were performed by using 633 nm laser radiations. The samples were measured with a 50X lens. The energy at the sample was 0.213 mW.

As shown in the mass spectra, nitromethane evolution and decomposition were observed at temperatures below 300 ºC

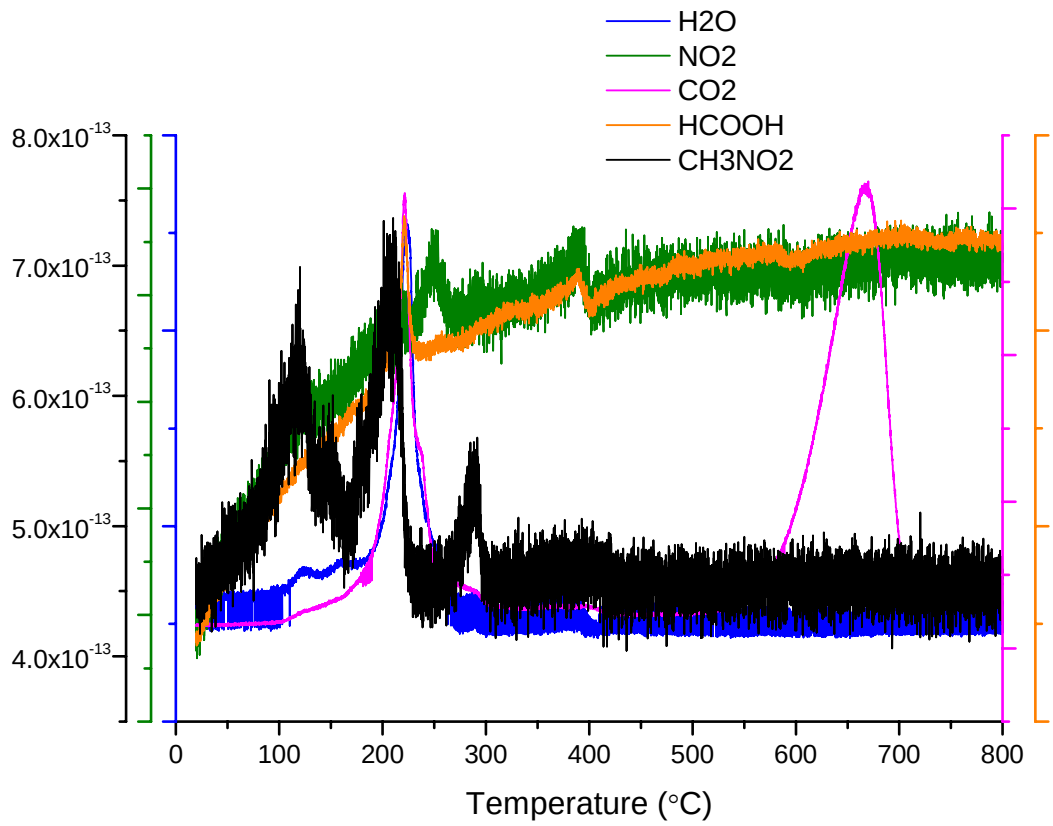

Figure S1 Mass spectra of nitromethane and its thermally decomposed products that were detected at the exhaust of the TGA furnace

The intercalation and exfoliation are confirmed by XRD. An intense peak at 2θ 14.3º corresponding to a d-spacing of 0.62 nm represents the interlayer distance of graphenes in $FeCl_3$-CH_3NO_2 GIC.[1, 2] The d-spacing of this tenary GIC is significantly smaller than 0.94 nm, the literature value of the stage 1 $FeCl_3$ intercalated graphite, which contains solid slabs of bulk $FeCl_3$ structure sandwiched between graphite planes.[3] Apparantly, the d-spacing of the $FeCl_3$-CH_3NO_2 GIC does not allow the existing of slabs of octahedrally coordinated ferric ions with a dimer structure of $Cl_3Fe_2Cl_3$. The plausisible expalnation of the shorter d-spacing could be that the sandwitched intercalant layer in $FeCl_3$-CH_3NO_2 GIC is solvated $FeCl_3$ ions instead of bulk crystall of $Cl_3Fe_2Cl_3$ dimer. If attributing the TGA weigth loss of $FeCl_3$-CH_3NO_2 GIC between

216 and 325 ℃ as the leaving of co-intercalated nitromethane, the calculated molar ratio of

nitromethane to $FeCl_3$ is about 2.5 to 1 based on the final residual iron oxide which is about 25 wt.% of the $FeCl_3$-CH_3NO_2 GIC (Figure 1). Because the excess of $FeCl_3$could not be determined, the stoichemetric ratio of nitromethane to $FeCl_3$ in the GIC cannot be accurated calculated based on the TGA data. The of crystallographic determination of the $FeCl_3$-CH_3NO_2 GIC needs further investigation with tailored synthesis conditions for the purpose of obtaining phase pure $FeCl_3$-CH_3NO_2 GIC. The small peaks between 16 to 60º are identified as iron oxide compounds from the hydrolysis of $FeCl_3$. In a sharp contrast, after microwave treatment and acid washing, the XRD pattern of the exfoliated sample does not show any strong reflection, suggesting the vanishing of pristine layered structure due to the exfoliation.

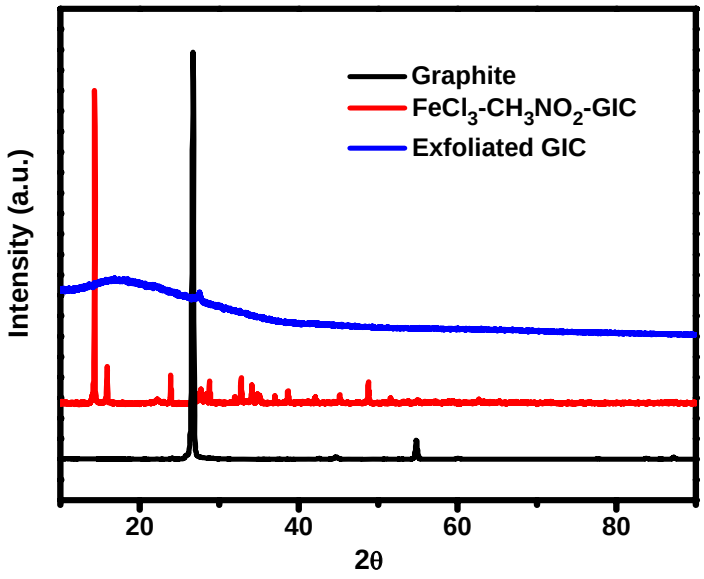

Figure. S2. Powder X-ray diffraction patterns of natural graphite, $FeCl_3$-CH_3NO_2 GIC and exfoliated GIC

3. Analysis of the G and 2D bands of Raman spectra

The Raman G band is sensitive to residual $FeCl_3$ intercalant. Shown in Figure S3 is the comparison of the G band for the as-synthesized $FeCl_3$-CH_3NO_2 GIC, exfoliated $FeCl_3$-CH_3NO_2 GIC with trace amount of residual $FeCl_3$, and exfoliated $FeCl_3$-CH_3NO_2 GIC without residual $FeCl_3$. Even trace amount of $FeCl_3$ could split the G band. After complete removal of $FeCl_3$ the G band of the resultant graphene material downshifted by 29 cm^{-1} compared to the major peak of the $FeCl_3$-CH_3NO_2 GIC. The 2D bands are also known as the fingerprint areas for graphene materials. Raman 2D bands of the exfoliated $FeCl_3$-CH_3NO_2 GIC, $FeCl_3$-CH_3NO_2 GIC, and natural graphite were fitted by using a Lorentzian function with the software Origin 8.1 SR4. The fitting was performed in the range of 2500 cm^{-1} to 2900 cm^{-1}. The 2D bands of the three samples can be fit by two Lorentzian lines. However, the shift and the symmetry of peaks are different. The peaks are marked in Figure S4.

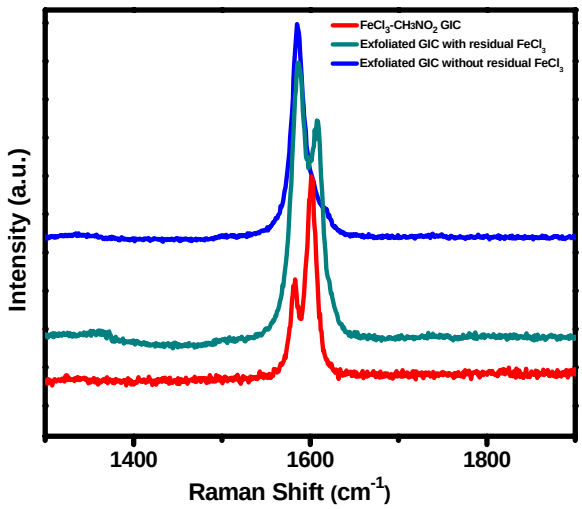

Figure S3: Comparison of G band of Raman spectra at 633 nm for microwave exfoliated GIC without residual $FeCl_3$, microwave exfoliated GIC with trace amount of residual $FeCl_3$, and $FeCl_3$-CH_3NO_2 GIC.

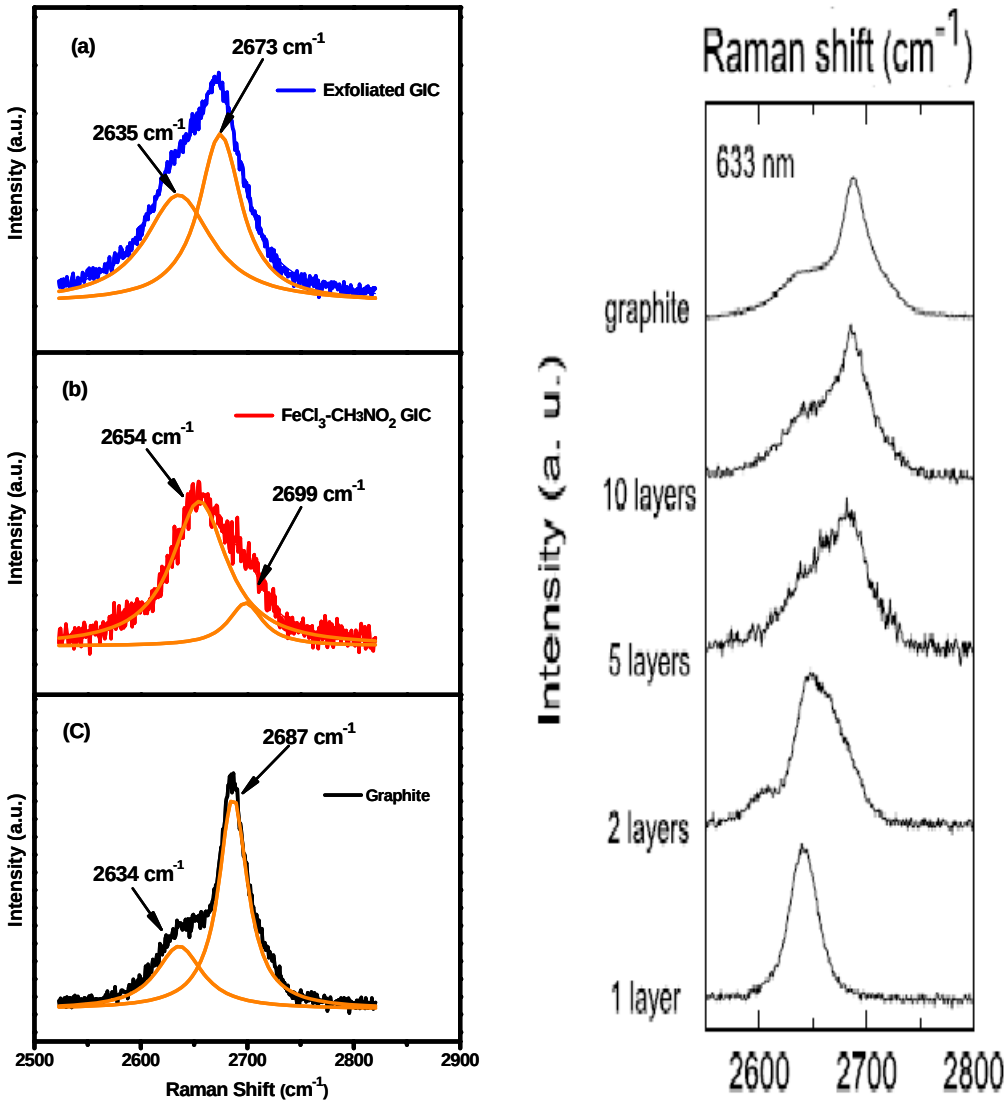

Figure S4: Left panel is the Comparison of 2D band of Raman spectra at 633 nm for (a) exfoliated GIC, (b) $FeCl_3$-CH_3NO_2 GIC, and (c) natural graphite and the right panel is the literature reported correlation of layer numbers to the 2D band shapes. (the figure is extracted from figure 2 of A. C. Ferrari, J. C. Meyer, V. Scardaci, C. Casiraghi, M. Lazzeri, F. Mauri, S. Piscanec, D. Jiang, K. S. Novoselov, S. Roth and A. K. Geim, Phys. Rev. Lett., 2006, 97, 187401) .

4 Electron Micrographic studies on the exfoliation process:

The intercalation and exfoliation process is further demonstrated by the scanning and transmission electron microscopy studies (SEM and TEM). As shown in Figure S5a, GIC preserves the layered structure but with much expansion of volume. The expansion of volume is indicated by the transparency of this thick particle under the electron beam: the holey carbon TEM grid is visible under a particle with a thickness about 1 micron. The expansion along the c-axis of the intercalated sample is consistent with the XRD measurement. Conventional heating of the GIC in a tube furnace to 500 ºC only slightly expands the graphite (Figure S5b). The evaporation and decomposition of nitromethane leaves cracks in the graphite particles but have not exfoliated the graphite to thin graphene materials. All particles preserve the original morphology of the natural graphite and no graphene sheet is observed in the sample heated in the tube furnace. The microwave treated sample has a completely different morphology. This sample consists of thin flakes spanning from submicrons to a few microns (Figure S5c). Representative TEM images of graphene sheets are shown in Figure S5d. The graphene sheets are highly transparent to the electron beam. Some parts of the edge (indicated by circles) are darker than the center because of the folding of the edges.[4]

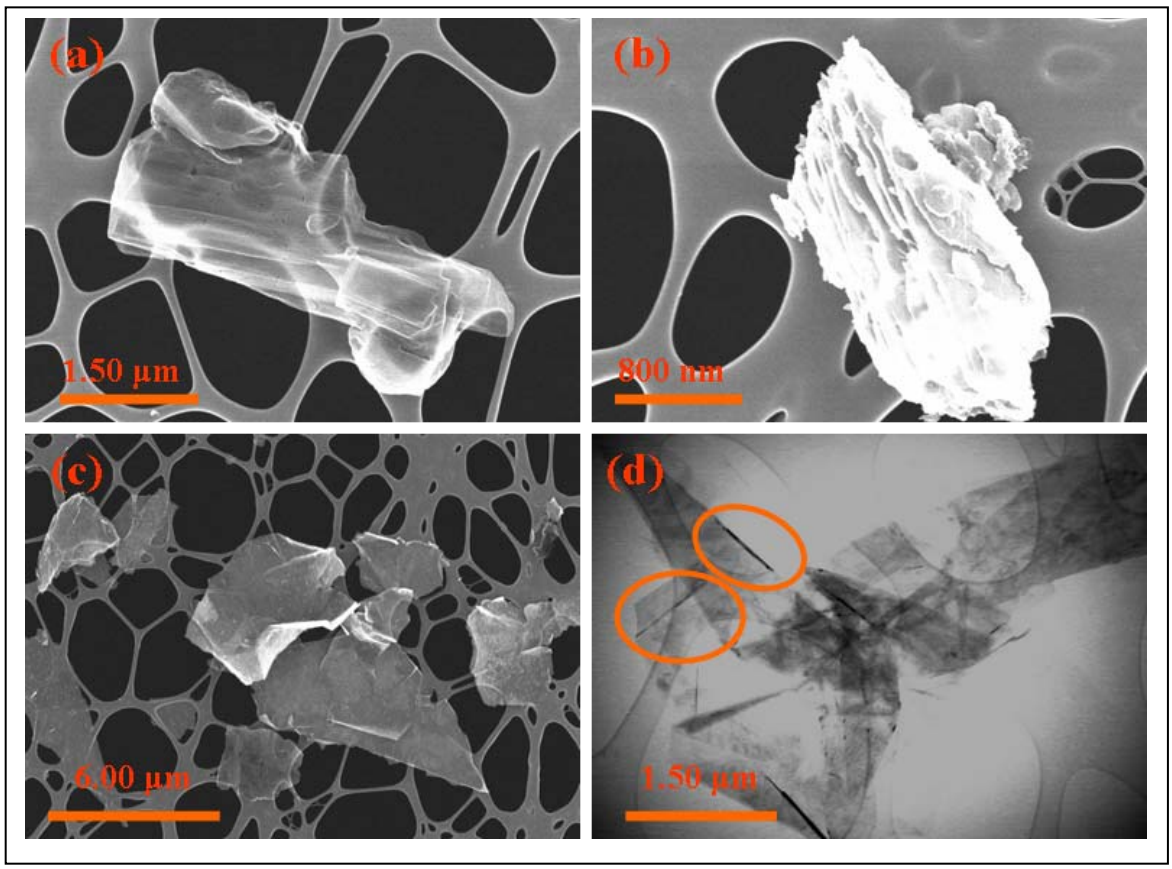

Figure S5. Electron microscopy of $FeCl_3$-CH_3NO_2 GIC and treated GIC: (a) SEM image of $FeCl_3$-CH_3NO_2 GIC; (b) SEM image of conventionally heated GIC; (c) SEM image of graphene sheet exfoliated by MW treatment; (d) TEM image of graphene sheets exfoliated byMW treatment

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2. J. G. Hooley, *Carbon*, 1972, **10**, 155-&.
3. W. Rudorff and W. Ostertag, *Angewandte Chemie-International Edition*, 1963, **75**, 725-&.
4. X. Xie, L. Ju, X. F. Feng, Y. H. Sun, R. F. Zhou, K. Liu, S. S. Fan, Q. L. Li and K. L. Jiang, *Nano Lett.*, 2009, **9**, 2565-2570.