

Supporting Information

Sonochemical Preparation of Functionalized Graphenes

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Experiment procedures:

The preparation starts with natural graphite flakes (10 mg, Aldrich) in freshly distilled styrene (15 ml, Aldrich), which is then sonicated with high intensity ultrasound using a Sonic & Materials model VCX-750, 1 cm² Ti horn at 20 kHz and 50 W/cm² at 0 °C for 2 h under Ar flow. The resulting mixture was then subjected to low speed centrifugation at 1000 rpm for 5 min. The black supernatant was then vacuum-filtered through a 0.22 µm PVDF membrane and washed with tetrahydrofuran (THF). The collected black solids were redispersed in THF and then filtered and washed with excess THF again. This dispersion-filtration-washing cycle was repeated at least 3 times to remove any residual styrene or polystyrene. The black solid is re-dispersed in THF and subjected to 3 more cycles of centrifugation (1000 rpm, 3 min) again to remove large multi-layer graphenes.

Instrumentation and Characterization:

TEM images were taken with a JEOL 2100 transmission electron microscope with an accelerating voltage of 200 kV. SEM images were taken using a Hitachi S4800 field-emission scanning electron microscope with an accelerating voltage of 10 kV. For imaging the single-layer graphene shown in Figure S10D, the accelerating voltage is 2 kV. AFM images were obtained using a tapping mode from Asylum Research MFP-3D AFM. Thermal gravimetric analysis (TGA) was conducted on TA Instruments Q600-SDT Simultaneous DSC-TGA, with a heating rate of 10 °C/min under N₂. FT-IR spectra were recorded on a Thermo-Nicolet Nexus 670 spectrometer. X-ray powder diffraction patterns were collected using Cu K α radiation (λ = 1.5418 Å) with a Seimens-Bruker D5000 instrument operating at 40 kV and 30 mA. UV-vis spectra were recorded on Cary 50 UV-vis spectrometer. Raman spectra were obtained directly from a thin film of graphene sample deposited onto a Si wafer excited with a 532 nm laser. ¹H NMR spectra were recorded on a Varian UI400 MHz spectrometer. GPC experiments were performed on a system equipped with an isocratic pump (Model 1100, Agilent Technology, Santa Clara, CA), a DAWN HELEOS 18-angle laser light scattering detector (also known as multi-angle laser light scattering (MALLS) detector, Wyatt Technology, Santa Barbara, CA) and an Optilab rEX refractive index detector (Wyatt Technology, Santa Barbara, CA). XPS spectra were collected with Kratos Axis ULTRA system.

Full citation for reference 34: Hernandez, Y.; Nicolosi, V.; Lotya, M.; Blighe, F. M.; Sun, Z.; De, S.; McGovern, I. T.; Holland, B.; Byrne, M.; Gun'Ko, Y. K.; Boland, J. J.; Niraj, P.; Duesberg, G.; Krishnamurthy, S.; Goodhue, R.; Hutchison, J.; Scardaci, V.; Ferrari, A. C.; Coleman, J. N. *Nature Nanotechnol.* **2008**, *3*, 563.

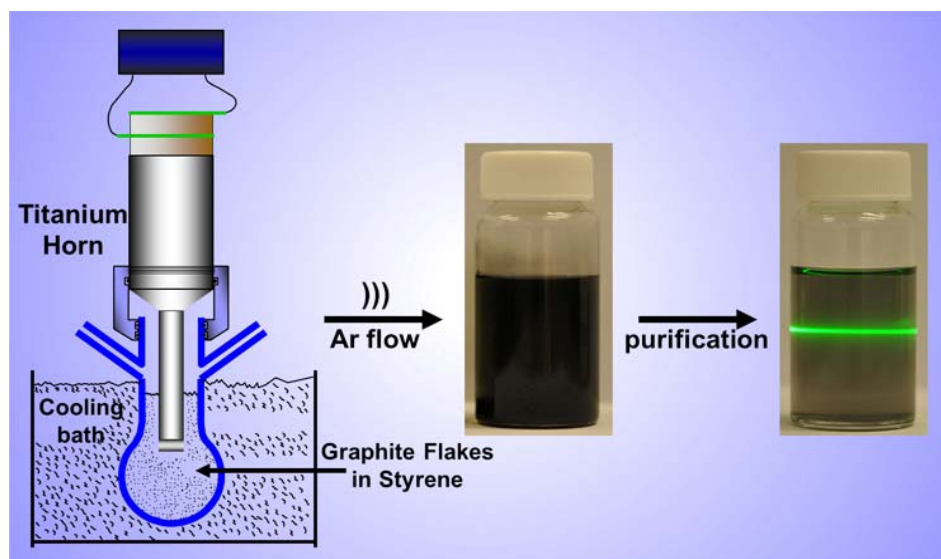


Figure S1. Experimental setup of the one-step mechanochemical process for exfoliation of graphites and sonochemical functionalization of graphenes.

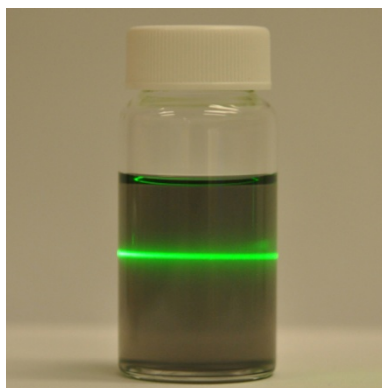


Figure S2. Sonochemical production of stable functionalized graphenes. Photograph of a graphene sample in THF after 6 months at room temperature, showing no precipitation. Tyndall effect (i.e., light scattering) is observed here using a green laser pointer through the graphene solution.

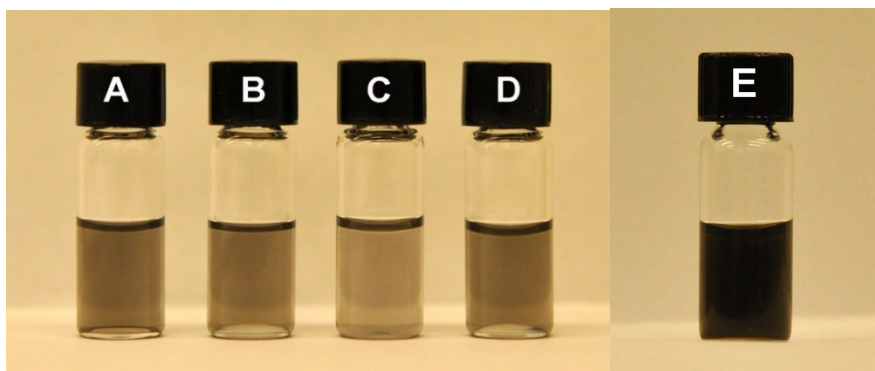


Figure S3. Soluble graphenes; photograph (taken after one week, showing no precipitation) of graphene samples suspended in different organic solvents: (A) THF, (B) chloroform, (C) toluene, (D) DMF and (E) more concentrated graphenes in DMF (~ 2 mg/mL).

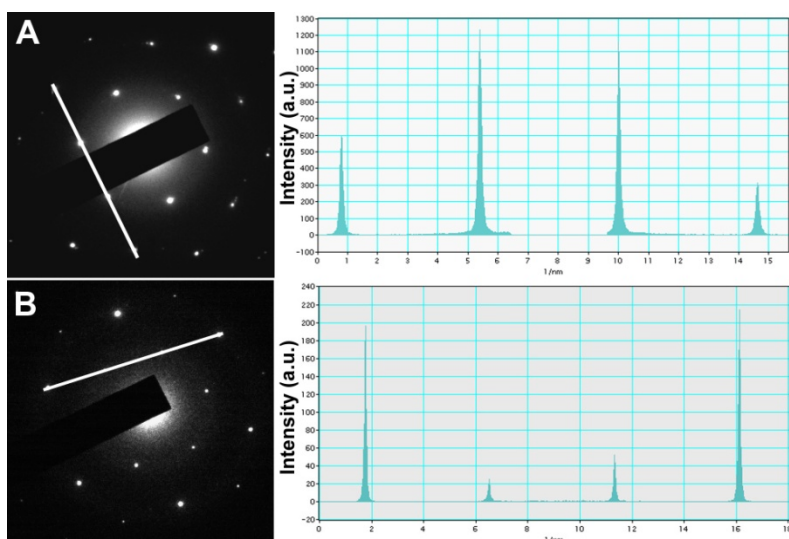


Figure S4. Evidence of single-layer graphene. (A). Selected area electron diffraction pattern and diffraction intensity of a single-layer graphene as shown in Figure 1a. (B). Selected area electron diffraction pattern and diffraction intensity of a few-layer graphene as shown in Figure 1b.

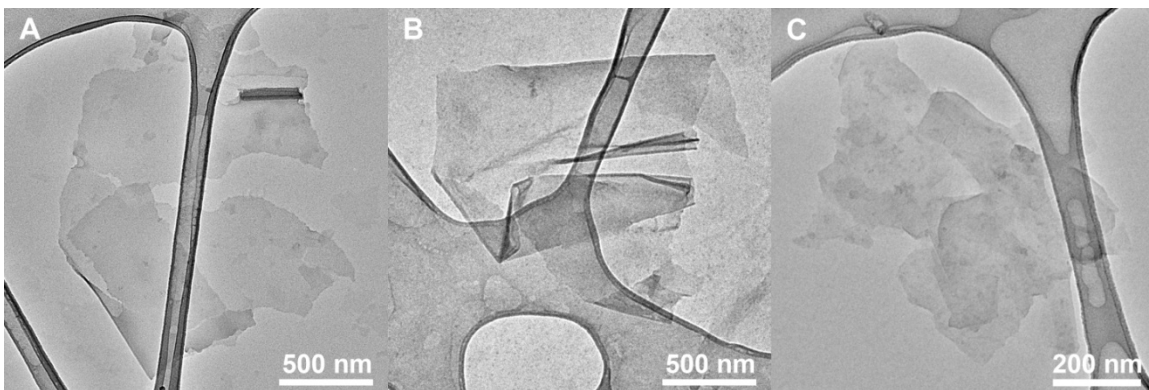


Figure S5. (A), (B) Folded and wrinkled single-layer graphene and (C) disordered few-layer graphene observed under TEM.

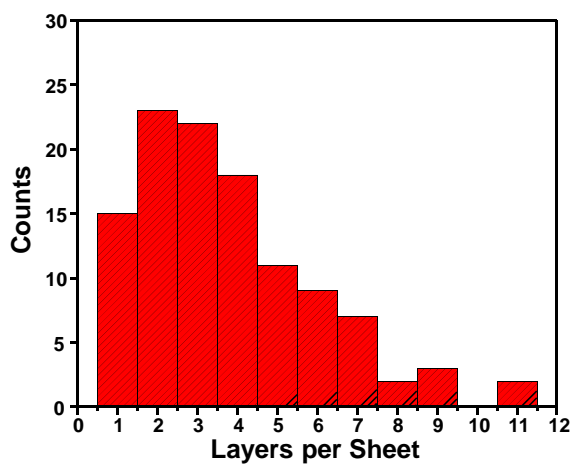


Figure S6. Histogram of the observed number of polymer functionalized graphenes as a function of the number of layers per graphene sheet.

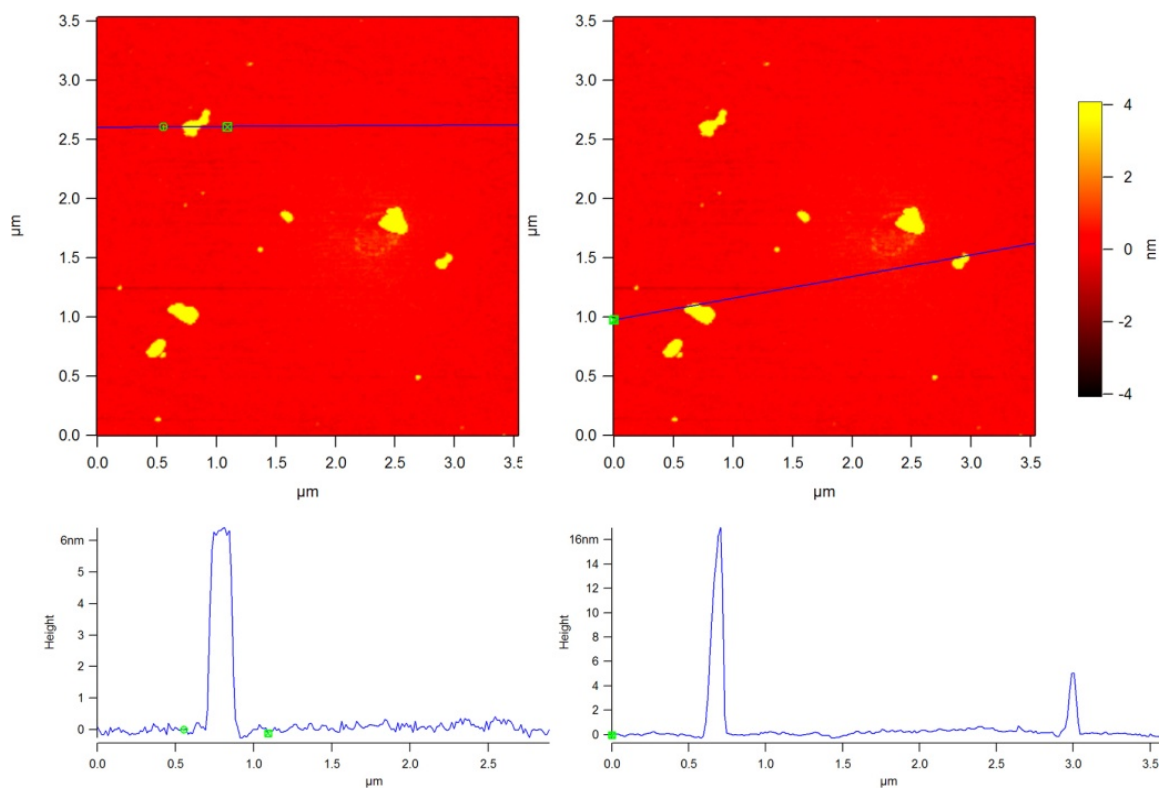


Figure S7. AFM image and height profile of few-layer graphenes on Si wafer.

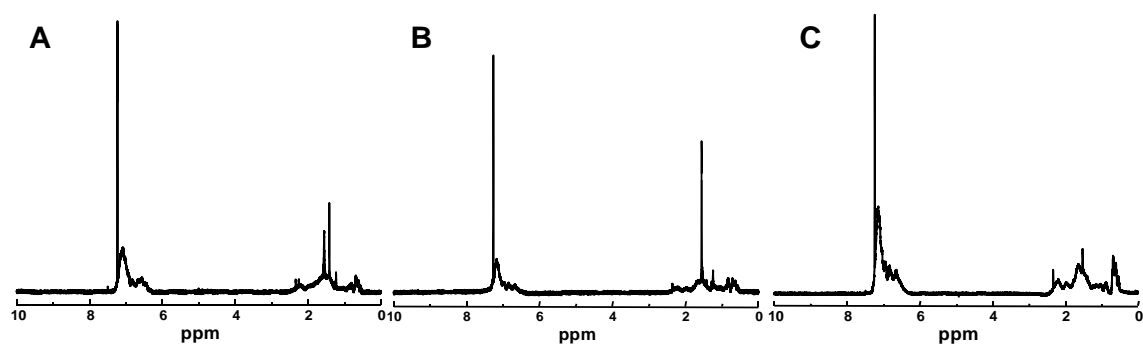


Figure S8. ^1H NMR spectra of (A) polystyrene grafted graphene (B) sonochemically synthesized graphene and (C) polystyrene standard from Aldrich.

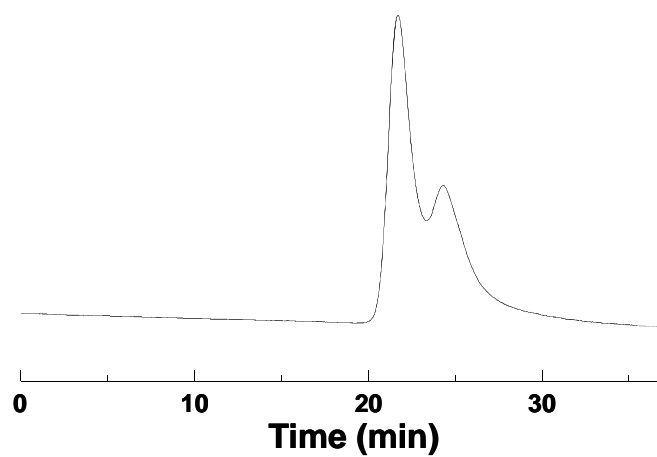


Figure S9. GPC trace of sonochemically synthesized polystyrene.

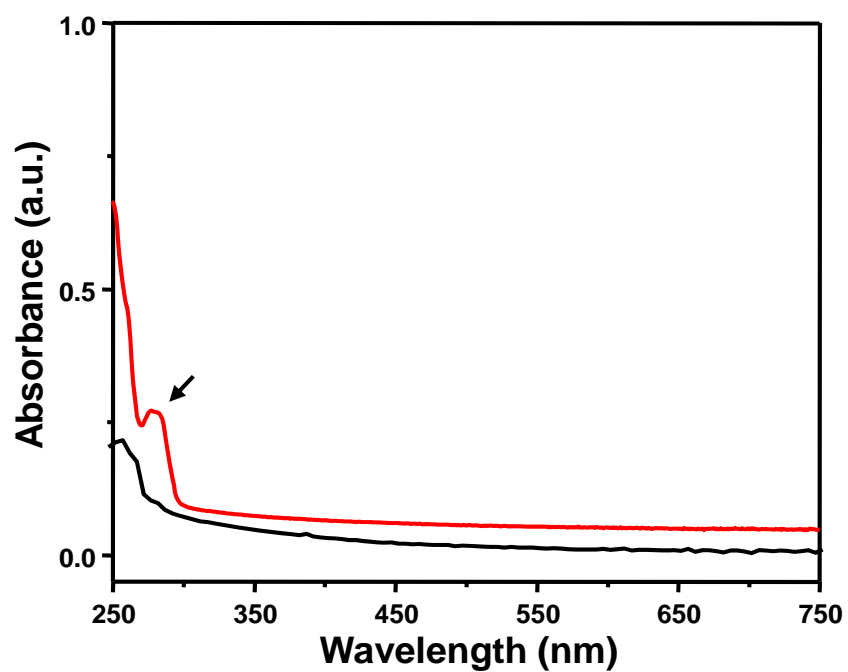


Figure S10. UV-vis spectra of polystyrene functionalized graphene (red) and sonochemically synthesized polystyrene in THF (black).

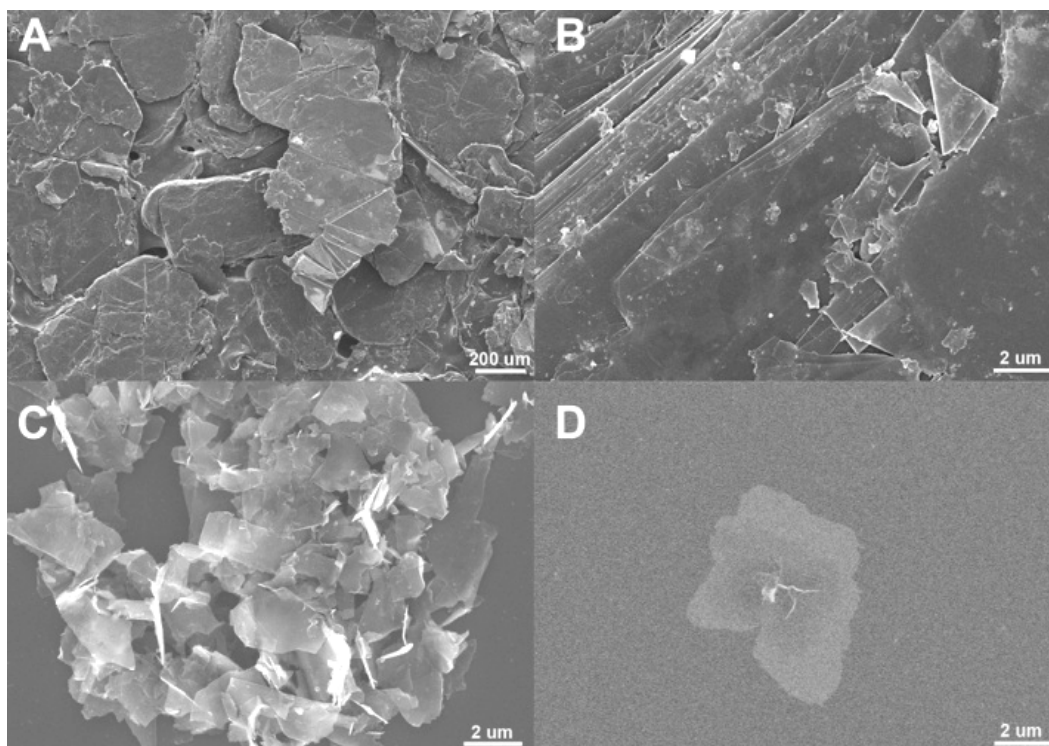


Figure S11. (A) and (B) SEM images of graphite flakes before sonication. (C) SEM image of graphite after sonication recovered as a precipitate after centrifugation. (D) SEM image of a single-layer graphene with a wrinkled morphology.

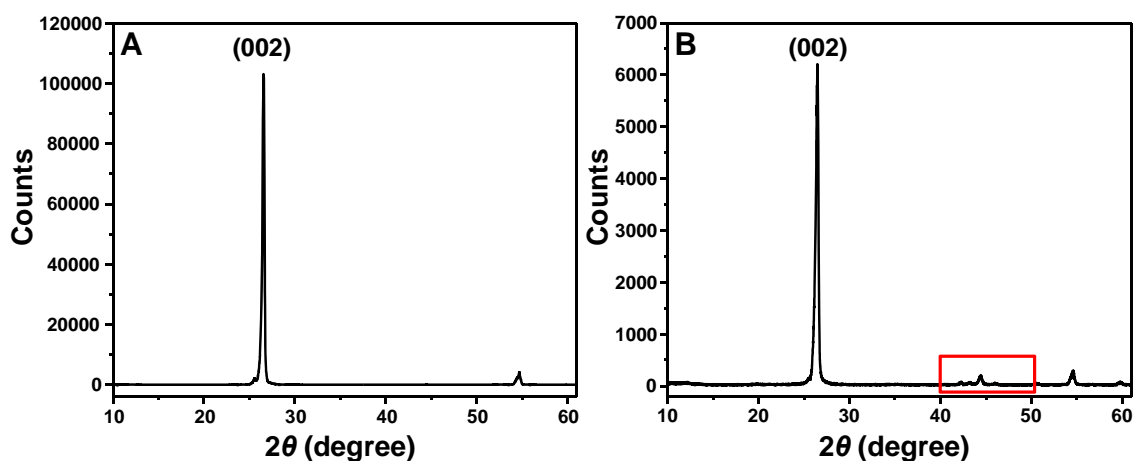


Figure S12. XRD spectra of (A) pristine graphite flakes (as shown in the SEM of Figure S11A and B) and (B) graphite after sonication recovered as a precipitate after centrifugation (as shown in the SEM of Figure S11C). After sonication, the graphite indeed has become thinner and the lateral sizes of the pieces become smaller; as a consequence, the intensity of the (002) peak decreased from ~ 10300 to ~ 6300 counts and the FWHM of the (002) peak increased from 0.25° to 0.34° .

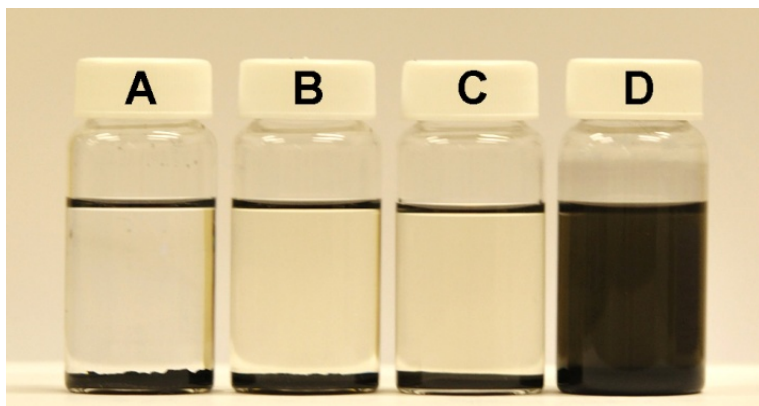


Figure S13. Control experiments with non-polymerizable solvents. Photograph (taken after 1 day) of graphene samples after sonication in different organic solvents: (A) toluene, (B) ethylbenzene, (C) 1-dodecene, and (D) styrene. Stable suspensions are only formed by sonochemical functionalization with styrene.

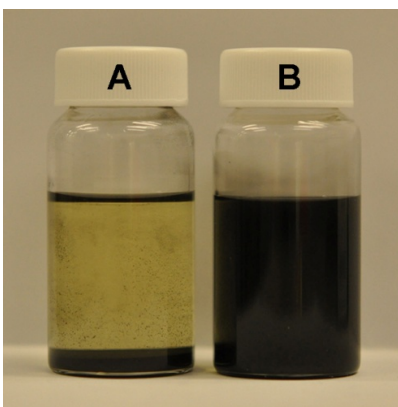


Figure S14. Effect of styrene concentration on functionalization of graphene. Photograph of graphene samples after sonication in: (A) 1 M styrene in 1-dodecene, and (B) styrene after ~24 hours. Sonication in pure styrene is much more effective in producing a permanent suspension.



Figure S15. Photograph of poly(4-vinylpyridine) functionalized graphene sample suspended in DMF. Image was taken after one week.

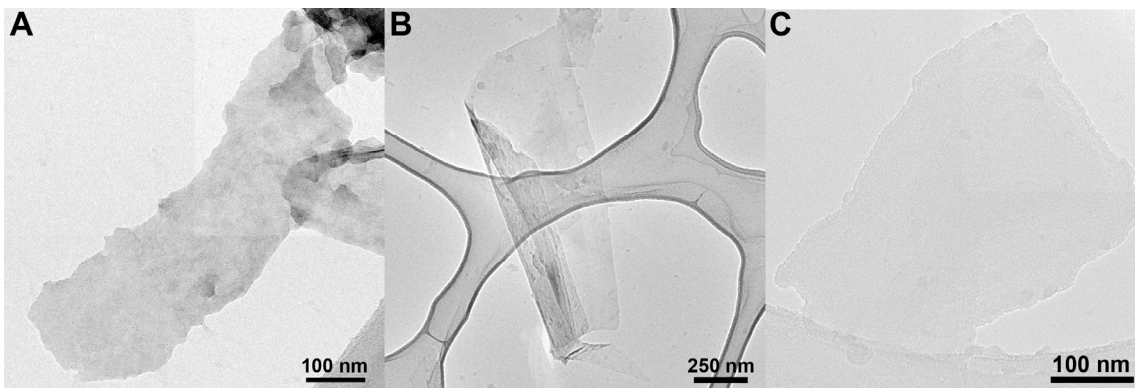


Figure S16. (A) A single-layer graphene, (B) a partially folded single-layer graphene and (C) a few-layer graphene observed under TEM from sonication of graphites in 4-vinylpyridine.

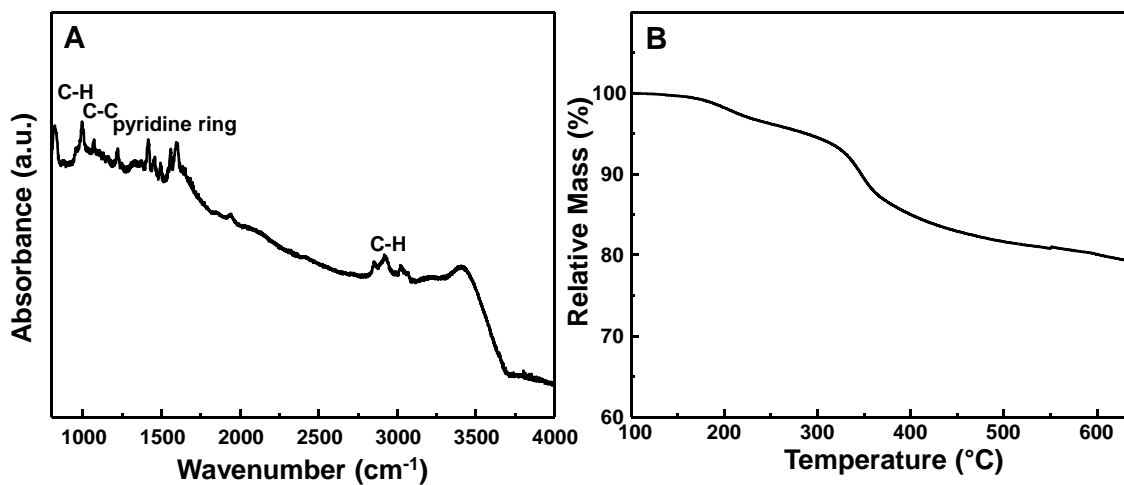


Figure S17. (A) FT-IR spectrum of poly(4-vinylpyridine) functionalized graphene in KBr pellet. (B) TGA of poly(4-vinylpyridine) functionalized graphene (under Nitrogen, heating rate at 10 °C/min).