Supplementary Information

High-Throughput, Direct Exfoliation of Graphite to Graphene via a Cooperation of Supercritical CO_2 and Pyrene-polymers

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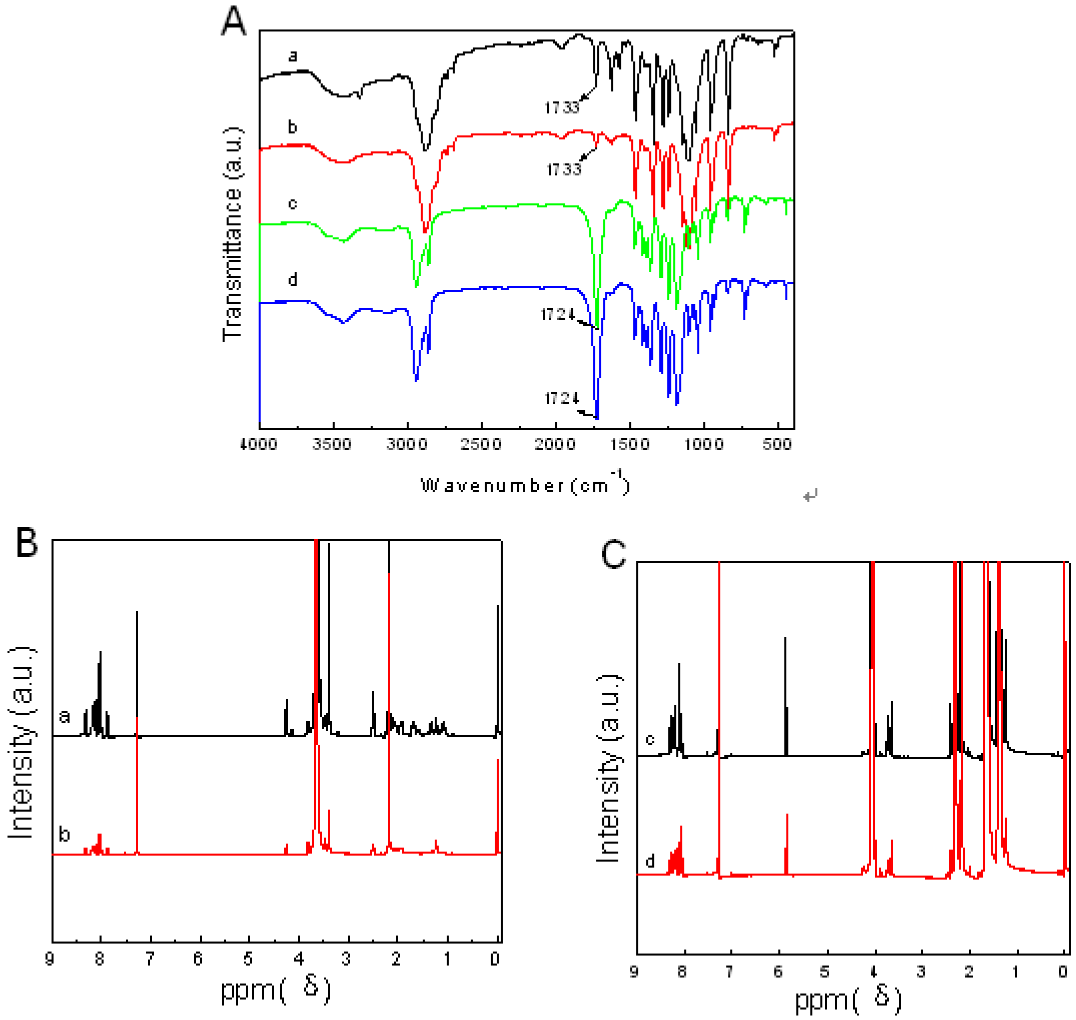
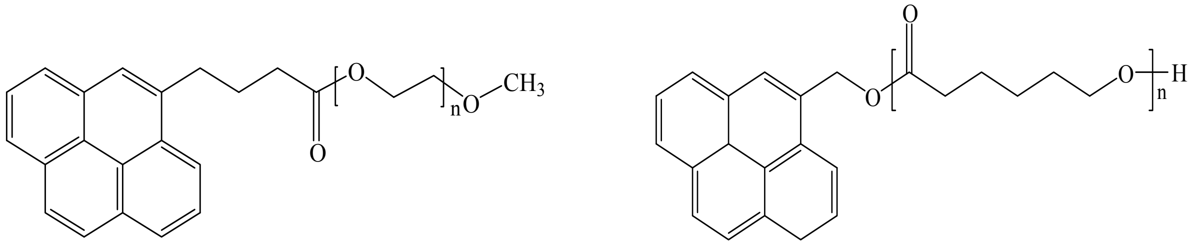


Figure S1. (A) FT-IR spectra of (a) pyrene-PEG_{2K}, (b) pyrene-PEG_{5K}, (c) pyrene-PCL_{19} and (d) pyrene-PCL_{48}, (B) ^{1}H NMR spectra of (a) pyrene-PEG_{2K} and (b) pyrene-PEG_{5K}, and (C) ^{1}H NMR spectra of (c) pyrene-PCL_{19} and (d) pyrene-PCL_{48}.

For pyrene-PEG: IR (cm^{-1}): 2889 ($\nu_{C–H}$), 1733 ($\nu_{C=O}$), 1468 ($\nu_{C–H}$), 1242 ($\nu_{C–O}$), 1113 ($\nu_{C–O-C}$), 1637, 843 (pyrene). The generated ester group of pyrene-PEG was confirmed at 1733 cm^{-1} and the carboxyl group of PBA was no longer observed at 1695 cm^{-1}(Figure S1Aa, Ab).

^{1}H NMR ($CDCl_3$, δ, ppm): 7.86-8.32 (CH in pyrene), 3.60-3.82 (CH_2 in PEG), 2.17-2.22 ($COCH_2$).[1] Number–average molecular weight of pyrene-PEG determined by ^{1}H NMR (M_n, NMR): 2,300 and 5,280 respectively (Figure S1B).

For pyrene-PCL: IR (cm^{-1}): 3610-3350 ($\nu_{O–H}$), 2945 ($\nu_{C–H}$), 2866 ($\nu_{C–H}$), 1724 ($\nu_{C=O}$), 1472 ($\nu_{C–H}$), 1245 ($\nu_{C–O}$), 1637, 843 (pyrene) (Figure S1Ac, Ad). ^{1}H NMR ($CDCl_3$, δ, ppm): 8.05-8.31 (CH in pyrene), 3.64-4.09 (CH_2O in PCL), 2.26-2.34 ($COCH_2$ in PCL), 1.35-1.70 (CH_2 in PCL).[2] Number–average molecular weight of pyrene-PCL determined by ^{1}H NMR (M_n, NMR): 2,460 and 5,770 respectively (Figure S1C). The structure formula of the pyrene-PEG_{2K}, pyrene-PEG_{5K}, pyrene-PCL_{19} and pyrene-PCL_{48} are shown in Figure S2.



(a) Pyrene-PEG_{2K} and Pyrene-PEG_{5K}

n= 45 or 113

(b) Pyrene-PCL_{19} and Pyrene-PCL_{48}

n = 19 or 48

Figure S2. Molecular structures of (a) pyrene-PEG and (b) pyrene-PCL with two different molecular weights.

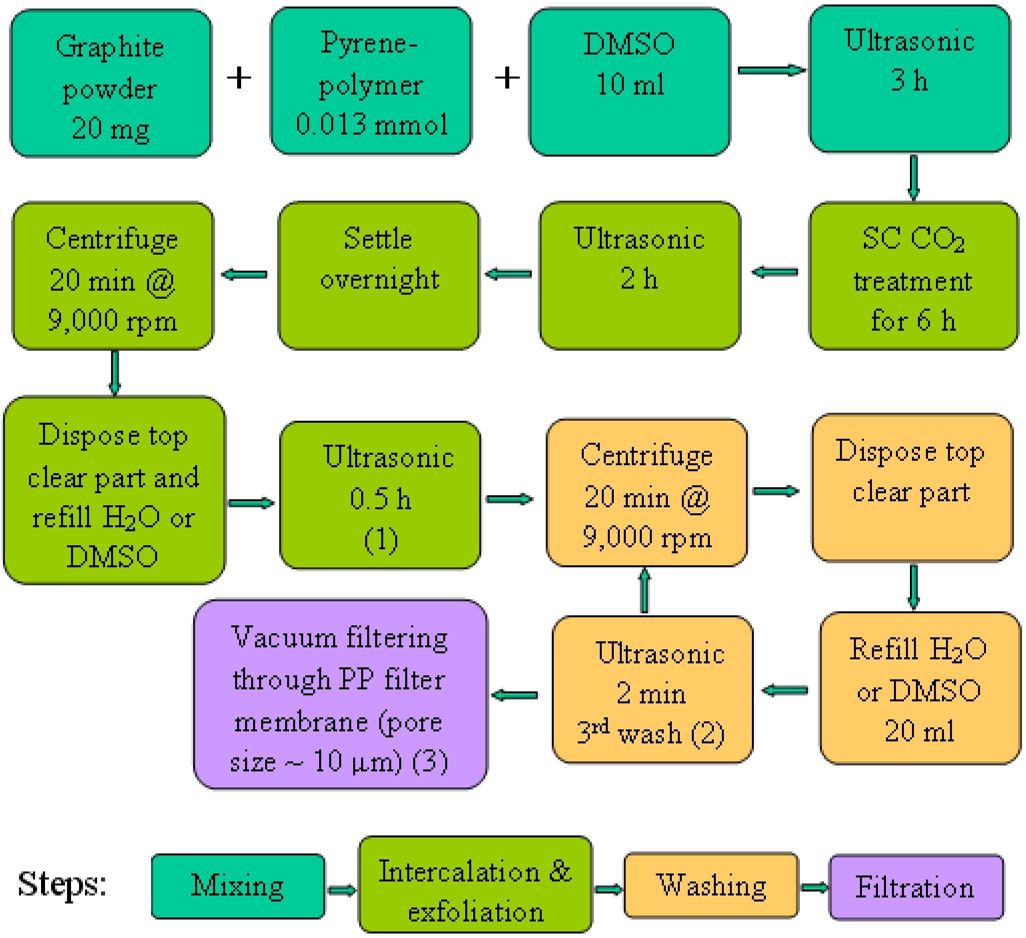


Figure S3. Process flow of intercalation and exfoliation of graphite with different steps (mixing, intercalation & exfoliation, washing and filtration) indicated in color key. (1)-(3) represent the stage 1-3, respectively.

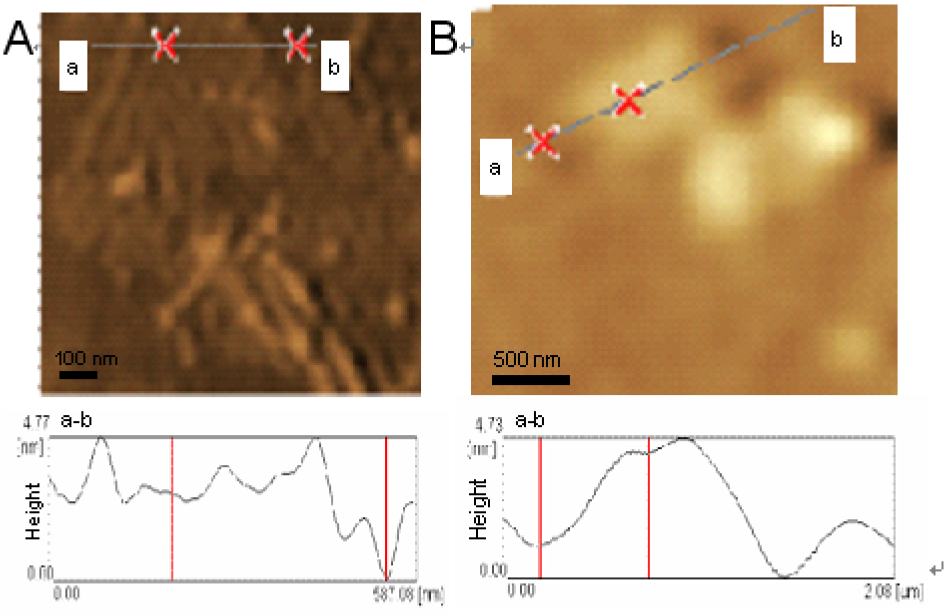


Figure S4. Tapping mode AFM images and topographic height profiles of graphene sheets by non-covalent functionalization of pyrene-PEG$_{2K}$ (A) and pyrene-PCL$_{19}$ (B) on Si surface, respectively.

The topology profiles (Fig. S4) show that the average height of the obtained graphene sheets is approximately 2~4 nm, suggesting that the graphene sheets consist of two or three atomic layers thickness structure feature. And the residual pyrene-polymers adsorbing on graphene surface can also contribute to the higher thickness observed for the AFM images.

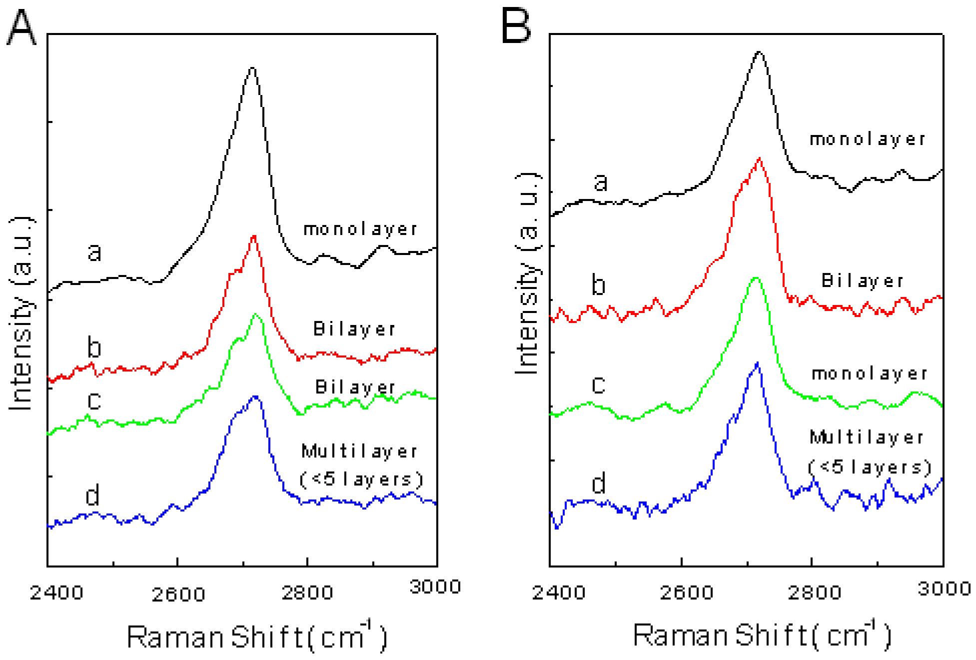


Figure S5. 2D Raman spectra for individual graphene sheets deposited from solution on holey carbon TEM grids. The shape of the 2D peak allows to identify the number of layers per graphene sheet.[3] (A) 2D Raman spectra of graphene sheets by non-covalent functionalization of pyrene-PEG$_{2K}$ (a,b) and pyrene-PEG$_{5K}$ (c,d), respectively. (B) 2D Raman spectra of graphene sheets by non-covalent functionalization of pyrene-PCL$_{19}$ (a,b) and pyrene-PCL$_{48}$ (c,d), respectively.

Raman spectroscopy emerges as the most useful way to probe the thickness of exfoliated flakes because the features of graphite and graphene directly reflect changes in electronic structure from the stacking of successive layers.[3] Their spectra show common features in the 800-3,000 cm^{-1} region: the D peak, which lies at ~1,350 cm^{-1}, is due to the breathing modes of sp^2 atoms and requires a defect for its activation. The D band is not Raman active for pristine graphene but can be observed where symmetry is broken by edges or in samples with a high density of defects. The G peak is observed around ~1,580 cm^{-1}, which corresponds to the Raman active doubly degenerate zone center E$_{2g}$ phonon (in-plane optical mode) of sp^2 hybridized carbon. The 2D peak at ~2,700 cm^{-1} is a second-order two-phonon mode.

Gupta et al. and Ferrari et al. pointed out that Raman spectroscopy can clearly distinguish a single layer, from a bilayer from few (less than 5) layers.[3] In bulk graphite, the

2D peak is comprised of two components, the intensities of which are roughly 1/4 and 1/2 that of the G peak for the low and high shift, respectively. For monolayer graphene, the 2D peak is a single park at the lower shift. While it splits in four bands in bilayer graphene. Fig. S5 shows the Raman spectra for individual sheets deposited from solution (stage 3) onto holey carbon TEM grids using a 514.5 nm excitation laser. The spectra shows that most of the samples comprise of single-, bi- or tri-, and multilayered graphene sheets (<5 layers), further confirm that our method can successfully exfoliate bulk graphite.

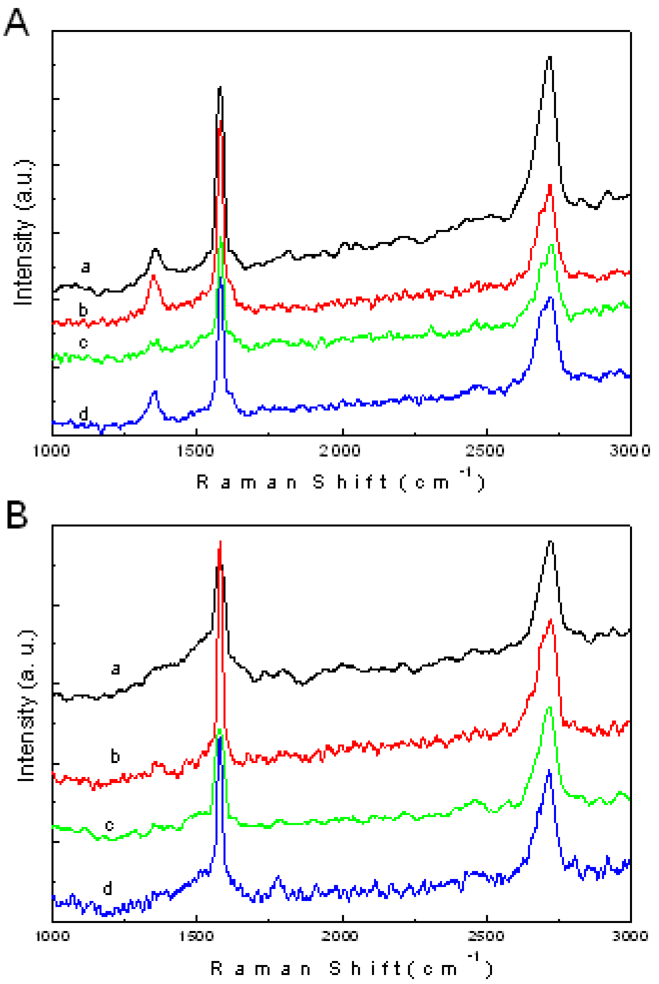


Figure S6. Raman spectra of individual graphene sheets deposited from solution on holey carbon TEM grids. (A) Raman spectra of graphene sheets by non-covalent functionalization of pyrene-PEG$_{2K}$ (a,b) and pyrene-PEG$_{5K}$ (c,d), respectively. (B) Raman spectra of graphene sheets by non-covalent functionalization of pyrene-PCL$_{19}$ (a,b) and pyrene-PCL$_{48}$ (c,d), respectively.

Table S1. I_D/I_G intensity ratios of the samples shown in Figure S6. The I_D/I_G intensity ratios were calculated by the ratios of peak areas of D- and G- bands. The peak areas of D- and G-bands were obtained by baseline corrections and being fitted with Lorentzian function.

Sample	I_D/I_G	Sample	I_D/I_G
Aa	0.23	Ba	0.04
Ab	0.25	Bb	0.09
Ac	0.11	Bc	0.03
Ad	0.24	Bd	0.02

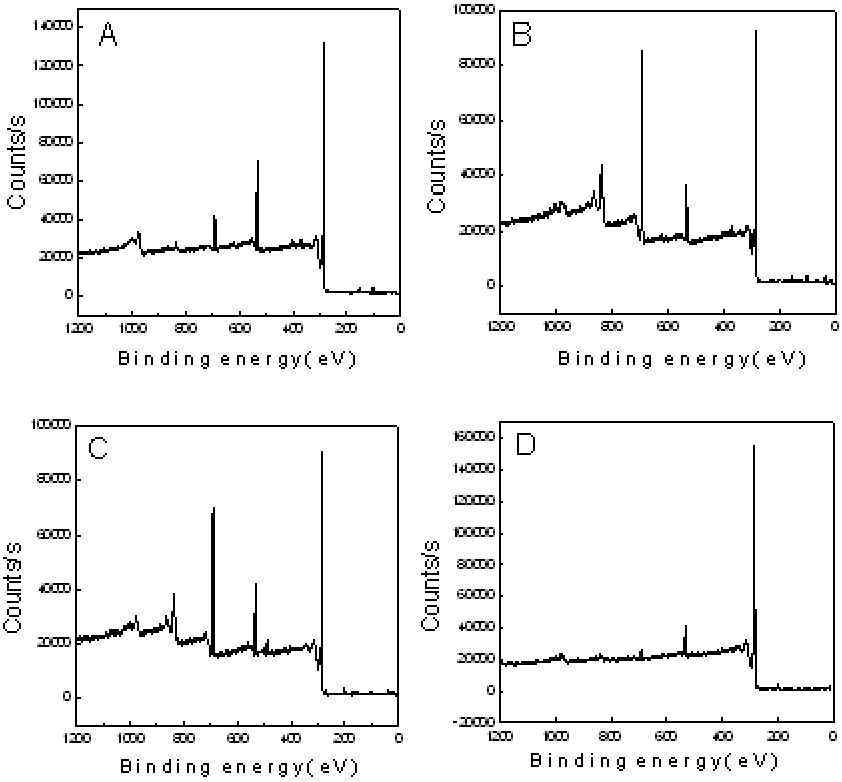


Figure S7. XPS survey scans of the four vacuum filtered graphene films, which were prepared by non-covalent functionalization of pyrene-PEG$_{2K}$ (A), pyrene-PEG$_{5K}$ (B), pyrene-PCL$_{19}$ (C) and pyrene-PCL$_{48}$ (D), respectively.

Table S2. Elemental analysis of the four vacuum filtered graphene films (A-D) determined by XPS.

Sample	% Composition/Atomic		
	C	O	S
A	83.96	15.76	0.28
B	89.58	10.28	0.13
C	88.34	11.4	0.27
D	93.39	6.39	0.22

References

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