

Electronic Supplementary Information for

Charging of Unfunctionalized Graphene in Organic Solvents

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Experimental Section

Materials:

Natural graphite flakes with a particle size of about 500 μm were purchased from Qinghao Haoyuan Graphite Company (China). This material was dried to remove the possible adsorption of water. Benzoyl chloride (98%, AR), Benzylamine (98.5%, CP), 4-Butyrolactone (97%, CP), Pyridine (99.5%, AR), N-methyl-2-pyrrolidone (98%, CP), N,N-Dimethylacetamide (98%, CP), N,N-Dimethylformamide (99.5%, AR), Cyclohexanone (98.5%, AR), and 1,2-dichlorobenzene (99%, CP) were purchased from Sinopharm Chemical Reagent Co., Ltd. Tetramethylurea (99%) was purchased from Aladdin Reagent Co., Ltd. All reagents were used as received without further purification.

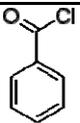
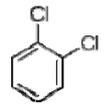
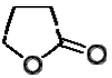
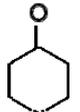
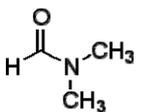
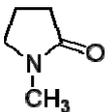
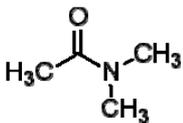
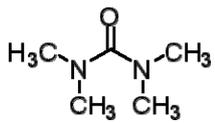
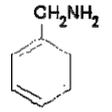
Sample preparation:

A set of identical graphene dispersions were prepared by dispersing graphite flakes in organic solvents (10 mL) at a concentration of 5 $\text{mg}\cdot\text{mL}^{-1}$. These dispersions were sonicated for 1.5 h, followed by centrifugation at 3000 rpm for 60 min. Finally, the supernatant was carefully decanted and retained for further use.

Characterization:

UV-vis spectrum was recorded on a Nicolet Evolution 300 UV-Visible Spectrophotometer (Thermo Fisher Scientific Inc., USA) using a quartz cell with a 1 cm optical path. By measuring the absorbance of graphene dispersion at 660 nm, the concentration of exfoliated graphene dispersion was calculated based on Lambert-Beer law.¹ Transmission electron microscopy (TEM) images were taken from JEM-2010F (JEOL Ltd., Japan) with an accelerating voltage of 200 kV. Samples for TEM were prepared by drop casting the graphene dispersion onto a holey carbon-coated copper grid. Atomic force microscope (AFM) images of graphene were taken on a commercial scanning probe microscope with a Nanoscope IIIa controller under tapping mode (Digital Instruments, Multimode 3000, USA). Commercial silicon cantilevers were used (Nanosensors, Type NCL-100) with a resonance vibration frequency of ~ 330 kHz. AFM measurements were made by spraying the graphene dispersions onto silicon dioxide substrates, and the solvent was then removed by annealing under Ar gas at 300°C for 4 hr. Raman spectroscopy was conducted on a Renishaw invia plus laser Raman spectrometer (Renishaw, England) with an excitation laser wavelength of 514.5 nm (5 mW) at room temperature. For Raman measurements, graphene dispersion was filtered through a Nylon filter with a pore size of 0.22 μm . Zeta potential measurements were carried out on a Zetasizer Nano ZS90 (Malvern Instruments Ltd, UK) system with irradiation from a 633 nm He-Ne laser.

Table S1. Properties of the solvents: Structure, electron donor number (*DN*), acceptor number (*AN*), viscosity (η).

No.	Solvent	Structure	DN	AN ^a	η [mPa·s, 25°C]
1	Benzoyl chloride (BzCl) ^b		2.3	13	1.24
2	1,2-dichlorobenzene (DCB)		3	11	1.25
3	4-Butyrolactone (GBL)		18	17.3	1.75
4	Cyclohexanone ^c (CYC)		18.9	12.2	2.00
5	N,N-Dimethylformamide (DMF)		26.6	16	0.80
6	N-methyl-2-pyrrolidone (NMP)		27.3	13.3	1.68
7	N,N-Dimethylacetamide (DMA)		27.8	13.6	0.95
8	Tetramethylurea (TMU)		29.6	9.2	1.40
9	Pyridine (PYR)		34.1	14.2	1.36
10	Benzyl amine (BA)		55	15	1.60

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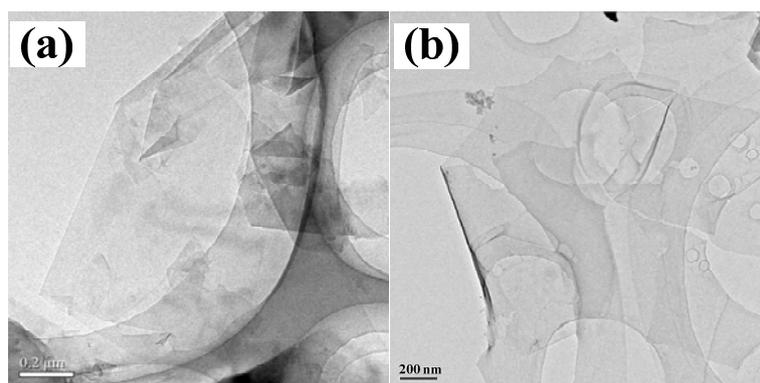


Figure S1. Bright-field TEM images of graphene flakes.

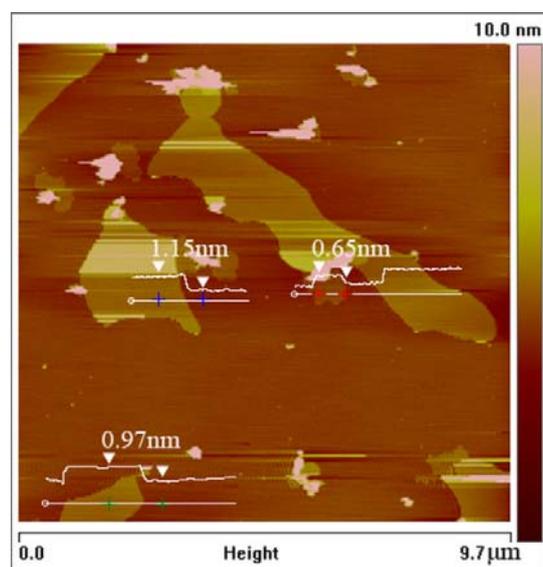


Figure S2. AFM images of a number of graphene flakes and their thicknesses, showing that they are of a few layers.

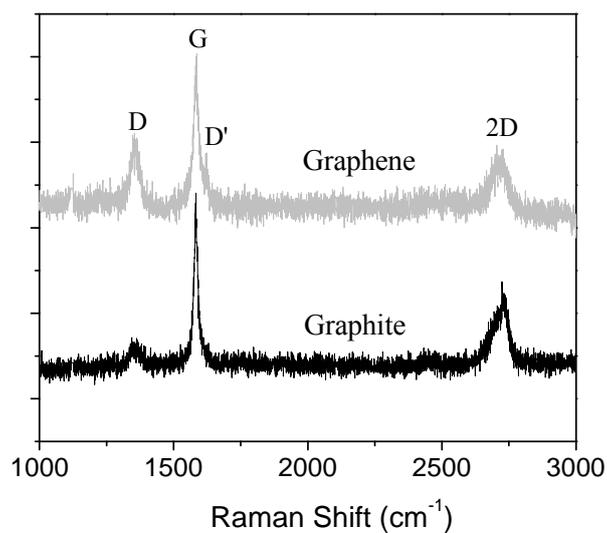


Figure S3. Raman spectra for bulk graphite and graphene.

Raman spectra for the starting graphite material and the as prepared graphene are shown in Figure S2. Raman features at approximately 1355 and 1620 cm^{-1} are disorder-induced bands, called D and D' bands, respectively. They are usually observed when there is a symmetry-breaking perturbation on the hexagonal sp^2 bonded lattices for graphite, such as structure defects or flake edges.² Since the Raman excitation beam has a spot size of $\sim 2\text{ }\mu\text{m}$ and this size is comparable to the sizes of the most graphene flakes, the beam can always “see” a large quantity of graphene flake edges. As a result, the D band in Figure S2 appears a little bit broader on graphene than that on graphite, and the splitting of the D' band from the G band can be observed. We suggest that the D band as well as the D' band split from the G band result mainly from the flake edges. The lack of broadening of the G band supports that the D band comes from edges, but not from structural defects inside graphene planes.

The shape of 2D peak varies with the number of layers in graphene flakes,³ as recognized as a single narrower and sharper peak for monolayer, a band with four component peaks for bilayer, a broadened band for less than five layers, and finally a graphite-type band with two component peaks for more than 5 layers. For more than 5 layers the Raman spectrum becomes hardly distinguishable from that for bulk graphite. The slightly broader 2D peak observed in Figure S2 for graphene than that for graphite indicates the presence of graphene flakes of a few layers in the present graphene samples.⁴

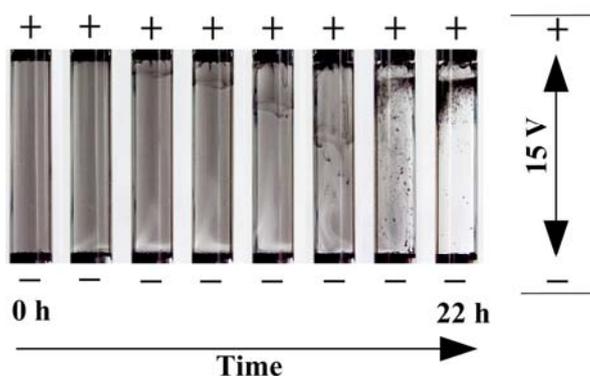


Figure S4. Electrophoresis of graphene dispersed in NMP.

Maybe there are doubts about the driving force of the movement shown in Fig. 1. That is, the movement shown in the electrophoresis of graphene dispersion could be due to gravity. We present two pieces of evidence that this is not the case. First, as stated in the main text, “Such dispersion could be stable for months”. Without adding an electric field, the dispersion was stable with no sediment. Second, we exchanged the cathode and anode sides of the applied electric field and repeated an electrophoresis experiment on NMP dispersion. As shown in Fig. S4, the anode is now on the top and the cathode on the bottom of the dispersion container. When an electric field was applied, the liquid near the cathode started to be clear, and graphene sheets moved up to the anode. This process continued until most of the graphene sheets gathered at the anode side. Such phenomenon was different from that in Fig. 1. This observation indicates that the graphene sheets in NMP were negatively charged, and the migration was derived by electric field instead of gravity.

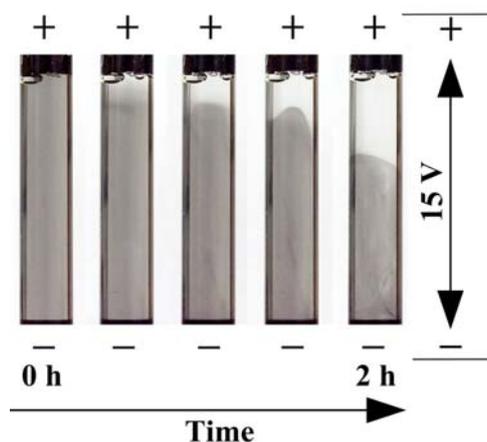


Figure S5. Electrophoresis of graphene dispersed in BzCl.

Figure S5 shows the electrophoresis of graphene dispersion in BzCl. When an electric field was applied, the liquid near the anode started to be clear, and a black and white interface gradually formed. As time passed by, the interface was moving towards the cathode side, leaving behind a clear solvent. This observation indicates that the graphene sheets in BzCl were positively charged.

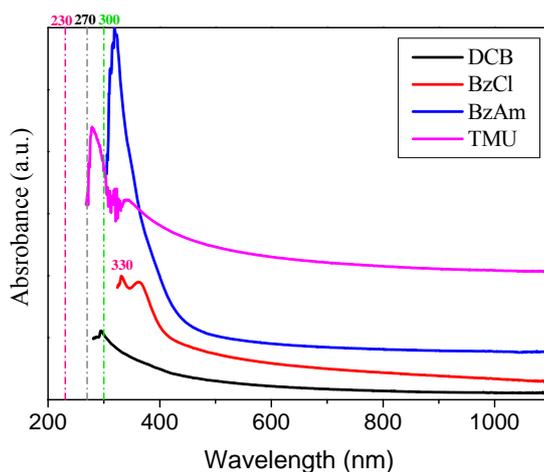


Figure S6. UV-vis absorption spectra of graphene dispersions.

The UV-vis absorption spectrum of graphene oxide (GO) dispersion has two characteristic features that can be used as a means of identification: a maximum at 231 nm (attributed to $\pi \rightarrow \pi^*$ transitions of aromatic C=C bonds) and a shoulder at ~ 300 nm (ascribed to $n \rightarrow \pi^*$ transitions of C=O bonds).⁵ After reduction, the maximum at 231 nm redshifts to about 270 nm,⁶ and the peak at ~ 300 nm disappears. We choose two solvents (DCB, BzCl) that make graphene positively charged, and other two solvents (BzAm, TMU) that make graphene negatively charged, to characterize the UV-vis absorption spectrum. As shown in Figure S6, the spectra were partly plotted, because it was impossible to compensate their strong absorption in the UV wavelength range; there were no peaks of GO features observed; the redshift of absorption peaks for all the four graphene dispersions were noticed, and two solvents exhibit 2 peaks. For the BzCl dispersed graphene, the peak at 330 nm may be attributed to the formation of the anion of BzCl.⁷ As previously reported for the edge-functionalized graphene, a red shift, due to the charge transfer between the carbon atoms of graphene and the edge functional groups, were observed for both electron-donating and electron-withdrawing functional groups.^{8,9} Such an effect may happen through the interaction between graphene sheet and the solvent molecules in the dispersions.

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