Surfactant-free single-layer graphene in water

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Dispersing graphite in water to obtain true (single-layer) graphene in bulk quantity in a liquid has been an unreachable goal for materials scientists in the past decade. Similarly, a diagnostic tool to identify solubilized graphene *in situ* has been long awaited. Here we show that homogeneous stable dispersions of single-layer graphene (SLG) in water can be obtained by mixing graphenide (negatively charged graphene) solutions in tetrahydrofuran with degassed water and evaporating the organic solvent. *In situ* Raman spectroscopy of these aqueous dispersions shows all the expected characteristics of SLG. Transmission electron and atomic force microscopies on deposits confirm the single-layer character. The resulting additive-free stable water dispersions contain $400 \text{ m}^2 \text{ I}^{-1}$ of developed graphene surface. Films prepared from these dispersions exhibit a conductivity of up to 32 kS m⁻¹.

onventional wisdom dictates that graphene and water do not mix. The dissolution of graphene or non-polar hydrocarbons in water is severely hindered by the effect of the hydrophobic interaction, which is triggered by the disruptive effect of these solutes on hydrogen bonding in water^{1–3}. This results from the existence of 'dangling bonds' (hydrogen atoms of water molecules pointing to the graphene surface); water molecules close to the graphene are unable to form more than three hydrogen bonds, compared with the average 3.6 hydrogen bonds per molecule in pure water². Other than being responsible for the hydrophobic interaction, the disruptive effect of graphene promotes the nucleation of nanobubbles of dissolved gas on the graphene surface, which promotes graphene aggregation and precipitation.

After extensive research during the past decade, motivated by the large number of potential applications of graphene⁴, liquid-phase exfoliation of graphite has been achieved by sonication or highshear mixing, which often introduces structural defects on the graphene lattice⁵, and by the addition of surfactant or other surface-active species. The best dispersions are a compromise between several factors such as thickness of the material dispersed (typically between one and 20 layers), lateral size (a few hundred nanometres) and concentration⁶⁻⁹. On the other hand, graphite intercalation compounds (GICs) can be readily exfoliated down to single-layer graphene (SLG) in aprotic solvents to yield graphenide (negatively charged graphene) thermodynamically stable sol-utions¹⁰⁻¹⁴. As graphenide is a very strong reducing agent, these organic solutions are sensitive to air and moisture. On the contrary, we show here that air-stable homogeneous dispersions of SLG in water (SLG_{iw}) with no surfactant added can be obtained by mixing air-exposed graphenide solutions with degassed water.

Results and discussion

The method of preparation of a stable SLG aqueous dispersion is beautifully simple. When graphenide solutions in tetrahydrofuran (THF) are exposed to air, and then mixed with degassed water and the organic solvent evaporated off (as illustrated in Fig. 1), remarkably stable additive-free graphene aqueous dispersions can be obtained. As discussed below, Raman spectroscopy of these aqueous dispersions shows all the expected characteristics of single-layer, low-defect graphene. In degassed water graphene re-aggregation is drastically slowed down because of the small intergraphene attractive dispersive forces (a consequence of the graphene two-dimensional (2D) character) and the stabilizing electrostatic repulsion. As has been reported before, for many hydrophobic objects (for example, hydrocarbon droplets^{15,16} or air bubbles¹⁷), graphene becomes electrically charged in water as a consequence of the spontaneous adsorption on its surface of OH⁻ ions that come from graphenide oxidation and water dissociation. As two graphene flakes come together, they experience a repulsive force because of the overlap of their associated counterion clouds. Accordingly, graphene can be dispersed efficiently in water at a concentration of 0.16 g l⁻¹ (400 m² l⁻¹) with a shelf life of a few months.

The pH values after the transfer of graphene to water are very revealing. While the system that results from the mixture with non-degassed water (Fig. 1b, left vial) has a pH close to 11, stable graphene suspensions have a pH close to neutrality, between 7 and 8 (Fig. 1b, right vial). As the same amount of OH⁻ is produced in both cases after graphenide oxidation, the remarkable difference in pH is attributed to the adsorption of OH⁻ on the suspended graphene flakes. This hypothesis is supported by the electrophoretic mobility and zeta potential ζ of the graphene flakes. Negative ζ values ($\zeta = -45 \pm 5$) were observed at neutral pH conditions; to the contrary, charge reversal was observed in an acidic pH environment ($\zeta = +4 \pm 2$ at pH 4). It could be argued that this ζ variation results from the reduction of pH below the pK_a of functional groups that are dissociated at basic pH. To discard this hypothesis, we measured ζ of water-dispersed graphene in the presence of tetraphenylarsonium chloride, Ph₄AsCl, which contains a hydrophobic cation known to adsorb readily on hydrophobic surfaces¹⁸. As reported in Table 1, we observed a progressive increase in ζ with increasing concentration of the hydrophobic cation, with charge reversal at sufficiently large cation concentrations. Control experiments (Supplementary Methods) show that stable dispersions can be obtained in degassed water between pH 4.5 and 11, whereas all the experiments in non-degassed water lead to immediate re-aggregation.

Several hypotheses have been advanced to explain the ionic adsorption on hydrophobic surfaces often observed; favourable entropy changes as a result of the partial release of an ionic

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Figure 1 | **Preparation of SLG**_{iw}. **a**, KC₈ is solubilized in THF under inert atmosphere as single-layer graphenide polyions^{11,12,14}. Graphenide ions are then oxidized back to graphene in THF by air exposure and immediately transferred to degassed water. On air exposure, graphenide reduces oxygen to the superoxide anion³⁷ (which eventually yields the hydroxide anion), whereas graphenide turns to neutral graphene¹³, with some minor functionalization (*vide infra*). Graphenide dedoping (oxidation) is ascertained from ultraviolet-visible (UV-vis) absorption. Additionally, the oxidation of graphenide solution into graphene can be monitored visually because the emptying of occupied states in graphene conduction bands leads to allowed absorption transitions and a darkening of the solutions (Supplementary Movie 1). The stability of SLG_{iw} is determined by the interaction between the individual graphene plates. In regular laboratory conditions, gases dissolved in water (about 1 mM) adsorb on the graphene surface, which induces a long-range attractive interaction between the dispersed objects and promoting aggregation (bottom left, gas bubbles and ions are not to scale). On the contrary, if water is degassed (removing dissolved gases) water ions readily adsorb on the graphene surface, which confers a certain charge to the dispersed objects. The repulsive electrostatic interaction favours the stability of the dispersed material. **b**, The left vial contains a mixture of graphene in THF after the addition to water that was not degassed. The aqueous dispersion is not stable and black aggregates visible to the eye begin to form a few minutes after mixing. The right vial contains a stable dispersion of graphene in degassed water after THF evaporation. No evidence of aggregation is observed after several months of storage at room temperature. **c**, UV-vis absorption spectrum shows an absorption peak at 269 nm (4.61 eV), the exact wavelength reported for the absorption of a single layer of graphene on a substrate³⁸

hydration layer on adsorption¹⁹, asymmetry of water ions²⁰, dispersion interactions related to ionic polarizability and the ionic-induced decrement of water-polarization fluctuations²¹ are some examples discussed in the literature. For the particular case of graphene, adsorption is also likely to be promoted by its conducting character.

Raman spectroscopy has been used as a powerful tool to study graphene samples, to determine the number of layers, the stacking sequence in the case of multiple layers, doping, and the amount and nature of defects²². The Raman spectrum of SLG_{iw} (Fig. 2 and Table 2) shows typical features of SLG, such as a narrow, symmetrical, intense 2D (also called G') band of full-width at halfmaximum (FWHM) below 30 cm⁻¹. Good fits of the 2D, D, G and D' peaks are obtained using single Lorentzian lines (Fig. 2b-d). It is interesting to compare the Raman spectrum of SLG_{iw} with those of other aqueous dispersions, such as sonication-aided sodium cholate (SC) suspensions prepared according to Lotya et al.⁹ (spectrum (iv) in Fig. 2a). The quality of the exfoliation is readily apparent from the much sharper and more-intense 2D band for SLG_{iw} (spectrum (iii)), whereas the D band is only slightly enhanced compared with sonication-aided dispersions (spectrum (iv)). Finally, the stability of these aqueous dispersions is addressed in Fig. 2e (and Supplementary Fig. 1) in which the

Table 1 Zeta potential of graphene	e flakes dispersed in water.
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ζ (mV)	
-45 ± 5	
-21 ± 4	
-10 ± 4	
+5 ± 2	
	ζ (mV) -45±5 -21±4 -10±4 +5±2

temporal evolution of the Raman 2D band is presented. No apparent change can be seen after a few months of storage. Similarly, light-scattering experiments show no change over a period of a few months (Supplementary Fig. 2). As air re-dissolution in water is known to happen on a short timescale (hours at most), the stability of SLG_{iw} with time shows that, once adsorbed, the OH⁻ ions are not displaced by dissolved gas.

Single layeredness. Neutron-scattering spectroscopy and atomic force microscopy (AFM) have shown that graphenide dissolved in THF demonstrates full exfoliation down to single layers^{11,12,14}. The question is whether re-aggregation happens on transfer to degassed water. A key Raman signature of SLG is the intensity, shape and width of the 2D (G') band. Multilayer, AB-stacked (Bernal) few-layer graphene shows a 2D band with a complex shape fitted by a number of Lorentzian lines²³. Turbostratic graphite, that is, graphite with uncorrelated graphene layers, shows a single Lorentzian 2D band with a FWHM of 50 cm^{-1} (ref. 23). On the contrary, the intense 2D band of supported SLG can be well fitted by using single Lorentzians of FWHM between 20 and 35 cm⁻¹ (ref. 24), and suspended graphene shows a 2D FWHM of $24 \pm 2 \text{ cm}^{-1}$ (ref. 25). Therefore, the observed 2D band at 2,681 cm⁻¹ (at 2.33 eV) with an intensity twice that of the G band, a pure Lorentzian shape and a FWHM of 28 cm⁻¹ strongly support that SLG_{iw} contains mainly, if not only, SLG. For the experiment performed in the liquid state on an ensemble of flakes of all sizes and orientations, the whole of the sample distribution is represented in this 28 cm⁻¹ linewidth. The other characteristics of the Raman spectra (Table 2) are all in agreement with the literature for SLG. AFM data (vide infra) further confirm the single layeredness with the thickness centred below 0.5 nm (Fig. 3a and all images of Supplementary Fig. 3) in

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Figure 2 | Raman spectroscopy of SLG_{iw}, **a**, Raman spectra of SLG_{iw} dispersion (i), water (ii) and graphene after the subtraction of water (iii) at 2.33 eV. Graphene spectra were obtained by subtraction of the spectrum of pure water from that of the graphene dispersions measured in the same cuvette, normalized on the bending peak of water (asterisk). For comparison, a spectrum of a sonicated SC few-layer graphene dispersion (iv) is shown (prepared according to the experimental details in Lotya *et al.*⁹). **b**-**d**, Typical fits of the 2D (**b**), D (**c**), and G + D' (**d**) peaks of SLG_{iw} at 2.33 eV. The slight asymmetry in the fit of the 2D line results from imperfections in the water background subtraction. **e**, The Raman 2D band as a function of time (at 1.94 eV) shows excellent time stability; the corresponding full spectra are presented in Supplementary Fig. 1.

favourable deposition conditions, that is, when no crumpling and folding is observed (Supplementary Fig. 11b).

Deposits were also made from SLG_{iw} (Fig. 3). Figure 3a and Supplementary Fig. 3 show AFM topographic images on mica. As is evidenced in Fig. 3a flakes of one layer only (~0.34 nm height) are consistently obtained, which corroborates Raman analysis on the bulk solution. AFM results are confirmed by transmission electron microscopy (TEM). Figure 3b (and Supplementary Figs 4 and 5) reveals the crumpled geometry of larger flakes after deposition. Crumpling is a general phenomenon of flat surfaces and has been observed in, for example, graphene oxide paper²⁶. Electron diffraction analysis (Supplementary Fig. 4) confirms the graphitic structure of the deposited material, and the degree of exfoliation of the flakes can be estimated by the careful analysis of folded edges. Unfortunately, the crumpled and multiply folded nature of the deposited material prevents a precise determination of the thickness of each flake. Nevertheless, the uniformity of the TEM image contrast reveals homogeneous exfoliation, and the abundance of folds that show only one (002) graphite fringe in the high-resolution TEM (HRTEM) image definitely confirms the Raman spectroscopy and AFM findings of extensive monolayers in the produced material.

Lateral-size distribution. Lateral size can be estimated from dynamic light scattering (DLS), Raman spectroscopy of annealed films, AFM, SEM and TEM. By using DLS, we obtained a lateral size close to 800 nm. The size measured by this technique, performed in the liquid state, corresponds to the mean lateral size of a large number of objects in the macroscopic scattering volume. Raman spectroscopy of films annealed at 800 °C (with all sp³ defects removed) allows one to estimate a lateral size of ~350 nm from the I_D/I_G intensity ratio. Microscopy techniques are more problematic because large flakes tend to crumple and fold, as observed on Fig. 3b and Supplementary Fig. 11. However, statistics on favourable cases lead to mean lateral sizes of a few hundred (200 nm for few-layer graphene nanometres by AFM (Supplementary Fig. 11) on 320 objects and 100 nm for SLG by SEM on 400 objects). As the contribution of the particles (flakes) to the measured size in DLS is weighted by the intensity of scattering (intensity distribution), larger particles have a larger weight on the calculated average than smaller particles. For this reason the measured size is significantly larger than those obtained from AFM or SEM micrographs, which are calculated from a number distribution (each particle has equal weighting). Thus,

Table 2	Raman characterization:	peak positions (cm $^{-1}$), FWHM (cm $^{-1}$) and	l relevant intensity ratios at 2.33 eV.
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Excitation energy (eV)	D		G		D'		2D		I _D ∕I _G	I _D ∕I _{D′}	I _{2D} /I _G
	Position	FWHM	Position	FWHM	Position	FWHM	Position	FWHM			
2.33	1,345	27	1,586	21	1,620	16	2,681	28	1.5	9.0	2.0

Similar results for different excitation energies are presented in Supplementary Table 1



Figure 3 | Characterization of deposits from SLG_{iw}. Deposits were made by dip coating. **a**, Topographic images on mica by AFM show the homogeneous thickness of the deposited graphene flakes. Insets show the height profile along the dashed lines—a similar thickness is obtained for the great majority of flakes observed. **b**, TEM micrograph of a flake deposited from the liquid solution over the TEM grid. Inset: HRTEM of a folded flake. The number of graphite (002) fringes visible at the edge allows a direct measurement of the local number of graphene layers (monolayer fold). Supplementary Fig. 5 shows additional results of the TEM characterization of the flake borders.

 SLG_{iw} samples contain a distribution of sizes from a few tens of nanometres to a few micrometres with a submicronic mean size.

Two requirements are necessary to formulate SLG liquid dispersions: the production of SLG and its transfer to the liquid matrix. The practical value of the obtained dispersion is ultimately governed by its stability. Three factors converge to promote the stability of SLG_{iw}, as can be ascertained from the graphene-graphene energy of interaction (Fig. 4): the adsorption of OH⁻ ions on graphene, the reduction of hydrophobic interaction in the absence of dissolved gases and the relatively weak van der Waals interactions between SLG by virtue of their 2D character. The stability of SLG_{iw} is governed by the difference between the repulsive electrostatic interaction and the destabilizing attractive forces (dispersion and hydrophobic). Graphene flakes experience attractive hydrophobic interaction in water as a consequence of their disruptive effect on the water hydrogen-bond network^{1,2} (a discussion of graphene hydrophobicity is given in Supplementary Note 1). It has also been argued that, in the presence of dissolved gases, long-range capillary attraction appears because of nanobubbles adsorbed on hydrophobic surfaces or a zone of depleted density close to the interfaces. When gases are removed thoroughly, the range of this interaction is substantially reduced, as has been observed by the direct measurement of surface forces in a number of studies^{27,28}. Attractive dispersion interaction is another destabilizing contribution to the interflake interaction. The van der Waals interaction energy (per unit area), W_{vdW} , between flakes of thickness a at a separation D can be estimated as:

$$W_{\rm vdW} = -\frac{A_{\rm Ham}}{12\pi} \left(\frac{1}{D^2} - \frac{2}{(D+a)^2} + \frac{1}{(D+2a)^2} \right)$$

where A_{Ham} is the Hamaker coefficient for the particular combination of materials (graphene–graphene in water). For thick objects, $W_{\text{vdW}} \simeq 1/D^2$ and the value of *a* is inconsequential. To the contrary, the effect of a finite thickness is notorious when *D* is comparable to or larger than *a* (ref. 29). There are two important consequences of this attractive force. First, few-layer objects are less stable than SLG: the increasing dispersion interaction substantially reduces the energy barrier to flake aggregation when the thickness of the dispersed flakes increases (Fig. 4b). More interestingly, the secondary attractive potential energy minimum—normally observed as a consequence of the prevalence of dispersive over electrostatic interaction at large separations—is not present for SLG because of the fast decay of the attractive interaction (Fig. 4c). Hence, loose flocculation, a factor responsible for the instability of many micrometre-sized object dispersions, is absent in the case of charged SLG_{iw}. A more detailed discussion about graphene interflake interaction is presented in the Supplementary Discussion.

Reports of 'graphene' dispersions abound. Nonetheless, these studies actually describe suspensions with a distribution of flake thickness that ranges from 1 to 20 graphene layers in the best cases^{6,9,30}. Stable dispersion of SLG_{iw} has not been reported. By dispersing graphite with the help of mechanical energy, one goes against thermodynamics to break apart the efficient packing of graphene in graphite. Hence, the resulting dispersion has to be a statistical distribution of thicknesses with single-layer flakes that form the tail of that distribution. As we start from fully exfoliated graphenide flakes^{11,12,14}, all that is needed is an energy barrier to circumvent graphene re-aggregation. Degassed water affords that barrier without the need for any additive, apart from the OH⁻ ions. Although a large number of reports claim exfoliation of graphite into graphene, Raman characterization of those dispersions in situ is rare. One of the very few Raman spectra in liquid of a graphene dispersion shows a symmetrical, Lorentzian-shaped 2D band with a FWHM of 44 cm⁻¹, attributed to turbostratically packed fewlayer graphene³¹. SLG_{iw}, on the contrary, shows a clear Raman signal of SLG in a liquid. At first sight, the D band appears large. However, one is not measuring a single flake but a large number of them, of all sizes and orientations. Thus, edges naturally have a large contribution although they do not fully account for the intensity of the D band, as some sp^3 defects have been created in the process. However, as quantified according to Cançado et al.³², the defect concentration in SLG_{iw} amounts to 300-600 ppm only (Supplementary Table 1 and the details of the calculation in Supplementary Methods). Further proof of the low number of defects is given by X-ray photoelectron spectroscopy analysis of the films, which shows minor widening on the high-energy side of the C 1s peak (Supplementary Fig. 8). Actually, the minute (and controllable³³) number of defects in SLG_{iw} represents an opportunity for further functionalization, for example, with responsive or biologically relevant functions. Finally, the exceptional exfoliation level of SLG_{iw} and low defect level is reflected in the conducting properties of materials made from it: conductive coatings prepared by filtering SLG_{iw} show average conductivities of 10 and 35 kS m⁻¹ after annealing at 200 and 500 °C, respectively (Supplementary Figs 6 and 7). The best device exhibited a sheet resistance of 2,100 Ohm sq⁻² (at 60% transparency), a value to be compared with the best of their kind within RGO films, which

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Figure 4 | Graphene interflake interaction. a, The interplate interaction energy *W* can be estimated by adding up the different contributions, as discussed in the Supplementary Information. A non-monotonic *W* versus *D* behaviour, with the energy barrier slowing down the aggregation, is obtained from the competition between attractive and repulsive interactions; the larger the energy barrier the more stable the graphene dispersion will be. **b**, The attractive component quickly increases with the number of layers of the dispersed objects, shifting from 2D to 3D objects, which reduces the energy barrier that assures the dispersion stability. **c**, The secondary minimum, observed at large separations for few-layer flakes, is responsible for the flocculation and poor dispersibility of thin graphite. This minimum is not observed for SLG. The flake lateral size is 0.5 µm at 298 K.

exhibit sheet resistances of 840 and 19.1 kOhm sq⁻² for flakes of respective mean sizes 7,000 and 200 μ m² (ref. 34). The average flake area in our films is below 1 μ m², which should translate into quite resistive films if it were not for the quality of the flakes. The equivalent bulk conductivity of this film is 32 kS m⁻¹, which reveals exciting perspectives for conductive coatings and composite applications of graphene films. State-of-the-art scalable graphite dispersions yield few-layer graphene with a maximum concentration of 0.07 g l⁻¹ and an exfoliation yield below 0.1% (Paton *et al.*⁶) whereas the process described here leads to single layers, a maximum concentration of 0.16 g l⁻¹ or 400 m² l⁻¹ and a yield of 4%.

Conclusions

The implications of this work are fourfold. (1) Graphene can be efficiently dispersed in water as true single layers, with no additives, at a concentration of 400 $\text{m}^2 \text{l}^{-1}$ and with a shelf life of several months. This remarkable feat results from the graphene 2D character. Hence, the method might well be used to produce additive-free aqueous dispersions of other 2D materials. (2) As has been the case for graphene obtained by the mechanical exfoliation of graphite, the intensity, shape and width of the Raman 2D band are proposed as very sensitive quality parameters of the graphene aqueous dispersions and composites. (3) With true SLG_{iw}, a vast amount of potential applications can be readily envisioned, such as drug carriers, toxicology studies, biocompatible devices, composites, patterned deposits that exploit the superior electrocatalytic performance of carbon surfaces in general and of graphene in particular, impregnation of 3D architectures for supercapacitors and other energyrelated applications. (4) SLG_{iw} brings new experimental evidence as to the hydrophobic surface/water interaction.

Methods

Preparation of graphenide solution. Potassium graphite (KC₈) was prepared by a standard procedure, that is, by reacting a slight excess of potassium with natural graphite (Nacional de Grafite; its characterization is given in the Supplementary Information together with Supplementary Fig. 10) at 250 °C in an evacuated Pyrex tube for 48 hours³⁵. Under inert atmosphere, 108 mg of KC₈ were then dispersed in 18 ml of distilled THF and this mixture was tightly sealed and mixed for six days with a magnetic stirrer (900 revolutions per minute (r.p.m.)). After stirring, the solution was left to stand overnight to allow undissolved graphitic aggregates to form and settle at the bottom. The mixtures were centrifuged in 10 ml glass vials at 3,000 r.p.m. for 20 min. The top two-thirds of the solution were extracted with a pipette and retained for use.

Transfer of graphene from THF to water. Under ambient atmosphere, the centrifuged graphenide THF solution was left exposed to air for 1 min and then added carefully to previously degassed deionized water (MilliQ water, 18.2 Mohm cm) and left open to let THF evaporate for two days. For degassing, the water was subjected to

agitation with a rotating Teflon stirrer under a reduced pressure of 0.2 mbar for 30 min. The final concentration of gases for graphene stabilization is not critical, but it should be maintained as low as possible. In our experimental protocol, we can estimate the final concentration of oxygen and nitrogen in the water for SLG_{iw} preparation (by using Henry's law) to be 5×10^{-8} mol 1^{-1} (O₂) and 10^{-7} mol 1^{-1} (N₂). Then the air pressure was gently increased back to atmospheric pressure. The degassed water (7 ml) was transferred to a 20 ml glass vial; the graphenide solution was exposed to air for 1 min and then added dropwise to the degassed water with gentle stirring using a stainless-steel needle. The vial was left open in a dust-free environment to allow THF evaporation at room temperature while stirring gently with a steel needle every hour for the first ten hours and occasionally thereafter to yield a slightly dark dispersion of graphene in water. Different graphenice solution and water. The dispersions were characterized using absorption spectroscopy, Raman spectroscopy and DLS. The yield of dispersed SLG versus starting graphite was 4%.

Electrophoretic mobility. The electrophoretic mobility of graphene in SLG_{iw} was measured using a Zetacompact Z8000 (CAD Instrumentation). An electric field of 8.95 V cm⁻¹ was applied and the graphene mobility was measured by direct particle tracking. As a result of the large concentration of graphene in SLG_{iw}, the suspensions were diluted 100 times before the measurements. The ζ of the graphene flakes was calculated from their electrophoretic mobility by applying the Smoluchowski equation³⁶.

Raman spectroscopy. Raman spectroscopy was performed on an Xplora spectrometer from Horiba-Jobin-Yvon at an excitation energy of 2.33 eV (532 nm laser wavelength) using a macrosample holder that contained a cuvette filled with SLG_{iw} (1 cm pathway). The peak positions were calibrated using the T_{2g} peak of silicon (520.5 cm⁻¹) and the G band of highly ordered pyrolytic graphite (1,582 cm⁻¹).

DLS. The size and state of aggregation of the SLG in SLG_{iw} were determined by DLS (ALV 5000 CGS). The autocorrelation function of the scattering intensity, $g^2(q;\tau)$, is exquisitely sensitive to the size of the particles in the dispersion. No significant changes were observed in $g^2(q;\tau)$ after several weeks of storage of SLG_{iw} at room temperature, as is shown in Supplementary Fig. 2. The mean lateral size obtained was 0.8 µm.

AFM deposits. Deposits were obtained by dip coating a freshly cleaved mica substrate in SLG_{iw} by itself or containing 1 mM AsPh₄Cl salt. The positively charged AsPh₄Cl salt ions adsorb on the graphene flakes, which confers them a positive charge (as verified by ζ measurements), improving adsorption. The deposits were rinsed with 0.1 M HCl and distilled water followed by blow drying with dry N₂ gas. Topography micrographs were measured using an AFM Icon (Bruker).

TEM. SLG_{iw} was dropcast on holey carbon grids for TEM characterization. Structural and morphological characterization of the material was performed on an FEI Tecnai F20 ST TEM operated at 120 kV of accelerating voltage to reduce the beam damage on the graphene while preserving the resolution to image (0,0,2) graphite fringes for the measurement of the local thickness on folded edges. Local elemental analysis was performed *in situ* in the TEM using an energy-dispersion X-ray spectrometer.

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Author contributions

G.B. prepared and characterized SLG_{iw}. K.H. and C.D. recorded the AFM images. L.O. and V.M. made the TEM analysis. G.B., E.A., A.P. and C.D. planned the experiments, analysed the experimental data and wrote the manuscript.

Additional information

Supplementary information is available in the online version of the paper. Reprints and permissions information is available online at www.nature.com/reprints. Correspondence and requests for materials should be addressed to C.D. and A.P.

Competing financial interests

The authors declare no competing financial interests.