

<https://doi.org/10.1038/s41699-025-00525-9>

Layer-by-layer assembly yields thin graphene films with near theoretical conductivity



Oran Cassidy^{1,3}, Kevin Synnatschke^{1,2,3}, Jose M. Munuera¹, Cian Gabbett¹, Tian Carey¹, Luke Doolan¹, Eoin Caffrey¹ & Jonathan N. Coleman¹✉

Thin films fabricated from solution-processed graphene nanosheets are of considerable technological interest for a wide variety of applications, such as transparent conductors, supercapacitors, and memristors. However, very thin printed films tend to have low conductivity compared to thicker ones. In this work, we demonstrate a simple layer-by-layer deposition method which yields thin films of highly-aligned, electrochemically-exfoliated graphene which have low roughness and nanometer-scale thickness control. By optimising the deposition parameters, we demonstrate films with high conductivity (1.3×10^5 S/m) at very low thickness (11 nm). Finally, we connect our high conductivities to low inter-nanosheet junction resistances (R_J), which we estimate at $R_J \sim 1$ k Ω .

Owing to the unique physiochemical properties of graphene¹, thin films fabricated from solution-processed graphene nanosheets offer a wide array of promising device applications, such as transparent conducting films (TCFs)², supercapacitors³, memristors⁴, flexible electrodes⁵, gas sensors⁶, strain gauges^{7,8} and antennas⁹. The film conductivity is a key performance metric for many such devices, but has previously been found to display values usually no larger than $\sim 10^5$ S/m, with such high values usually found only for thick (>0.5 μ m) graphene films^{5,8,10–16}. Thinner films tend to have lower conductivity due to the effects of non-uniformity, disorder and percolation effects^{7,17–21}.

However, many printed applications require film conductivity to be maximized for minimal film thicknesses²² to avoid the need to deposit very thick films to achieve a given sheet resistance. While higher conductivities at the bulk limit for graphite (10^6 S/m) may also be achieved in thin films fabricated by CVD techniques^{23,24}, such techniques lack the ease of scalability of solution processing-based fabrication²⁵.

In solution-processed graphene films, the typically observed conductivity ($<10^5$ S/m) is generally somewhat lower than the reported in-plane conductivity of graphite ($\sim 10^5$ – 10^6 S/m)²⁶. This is due to such films being formed from a network of graphene nanosheets, where conduction is typically limited by the inter-nanosheet junction resistance (R_J)^{27,28}. This effect is even more pronounced for thin films (*i.e.*, those with thickness < 50 nm), as no conductivity larger than 1.6×10^4 S/m has been observed in such films without the use of complex post-processing strategies²¹. Such strategies include graphitization of the film through annealing at temperatures in excess of 1000 °C^{29–32}, or reduction of graphene oxide using strong reducing agents such as hydrazine or nitric acid^{21,31–35}. Although post-

processing can yield film conductivities beyond 10^5 S/m^{21,30}, many processed films exhibit conductivities no higher than 2.5×10^4 S/m^{29,31–35}.

However, high-temperature processing is undesirable for flexible device applications, as it is incompatible with polymer substrates that have low melting temperatures^{36,37}. For example, PET³⁸ starts to soften at 125–130 °C and is usually not annealed above 120 °C. In addition, aggressive chemical processing is best avoided if possible for a range of reasons including safety, cost and environmental factors^{39–41}. Hence, such strategies are unsuitable for mass-manufacture of versatile and inexpensive devices.

Emerging from the discussion above, there is a clear need for a means of fabricating solution-processed graphene thin films that exhibit high conductivity ($> 10^5$ S/m) without the requirement for aggressive processing techniques. To maximize the conductivity of any network, it is essential to minimize the junction resistance^{27,28}. In addition, at low film thickness, conductivity maximisation requires the suppression of percolation effects¹⁷ and the minimisation of disorder, specifically the misalignment of nanosheets often found in printed nanosheet films⁴². In fact, these objectives are linked as achieving a network of highly aligned nanosheets will also lead to large area junctions and so low junction resistance.

Thus, one strategy to simultaneously minimize the junction resistance and disorder would involve optimization of the network morphology, *i.e.*, developing methods to fabricate networks containing highly-aligned nanosheets which overlap their neighbours with large-area conformal junctions. The two general requirements for this to occur are, firstly, a deposition method that directs the nanosheets' basal planes to a horizontal orientation, and secondly, the nanosheets must possess sufficient mechanical flexibility to allow for

¹School of Physics, CRANN & AMBER Research Centres, Trinity College Dublin, Dublin, Ireland. ²Center for Advancing Electronics Dresden & Faculty of Chemistry and Food Chemistry, TU Dresden, Dresden, 01062, Germany. ³These authors contributed equally: Oran Cassidy, Kevin Synnatschke. ✉e-mail: colemanj@tcd.ie

the formation of conformal junctions²⁷ rather than forming jammed systems with point-like junctions⁴².

Such horizontally oriented films can best be achieved using Langmuir-type depositions, which spread nanosheets flat on top of a high surface tension liquid interface⁴³. Repeated deposition can build up films with excellent alignment and controlled thickness⁴⁴. For nanosheets to be mechanically flexible enough to readily conform to each other, it has been shown that the energy cost of creating the bends required to conform to their neighbours must be balanced by the van der Waals energy of interaction between neighbours²⁷. For this to occur nanosheets must have lateral size to thickness aspect ratios above some critical value, which depends on the mechanical properties of the material²⁷. Preparation of such high aspect ratio nanosheets cannot be achieved by well-known techniques such as liquid phase exfoliation⁴⁵ but may be facilitated by intercalation-based exfoliation techniques, where the interlayer attraction is mitigated, such as electrochemical or chemical exfoliation^{46,47}.

In this work electrochemically exfoliated graphene (EEG) ink was deposited using a customized setup for liquid interface deposition to perform a systematic study of the effect of the deposition parameters (ink concentration, nanosheet areal mass load) on the quality of the resulting films. Having found the ideal deposition parameters for fabricating a single layer to be at low ink concentrations and an appropriately large areal mass load, thicker graphene films were fabricated by further refining the liquid interface deposition technique for layer-by-layer depositions. The resulting films exhibited high conductivities in excess of 1.2×10^5 S/m at low film thicknesses (11 nm), an order of magnitude increase on the 1.6×10^4 S/m record previously established for graphene nanosheet network thin films ($t < 50$ nm) without aggressive post-processing²¹. This result is also comparable to state of the art conductivities for thicker ($t > 500$ nm) graphene

nanosheet networks¹⁵. Moreover, a TCF was demonstrated at a film thickness of 6.1 nm, showing a transparency of 82% and sheet resistance of $4.2 \text{ k}\Omega/\square$, competitive with literature values for printed graphene TCFs^{21,29,32}.

Results and discussion

Ink characterisation

Graphene nanosheets were prepared via electrochemical exfoliation⁴⁸ as described in the methods section. This process results in an ink containing graphene nanosheets in isopropyl alcohol (IPA) at a concentration of approximately 1 g/L. We first characterised this ink and the nanosheets therein using optical absorption spectroscopy and atomic force microscopy (AFM). An optical extinction spectrum ($\text{Ext} = -\log(T)$, where T is transmittance) measured on the graphene ink is shown in Fig. 1A. It shows the typical spectral profile characteristic of liquid dispersion of graphene nanosheets with a peak at 270 nm, associated with a band-to-band transition and a flat region at higher wavelengths⁴⁹. Previous work has showed this peak wavelength value to be associated with relatively thin nanosheets with $\langle N \rangle \sim 4$ ⁴⁹. The ink was used to deposit nanosheets on a Si/SiO₂ substrate for AFM characterisation. Fig. 1B depicts a typical AFM image with multiple graphene nanosheets. Examples of height profiles are given in the inset and the SI. The data collected by AFM allows us to extract the length and thickness values for a statistically relevant number of nanosheets (see methods). The apparent nanosheet thickness is converted to layer number (N) using the results of step height analysis^{50–53} (see methods). The resultant nanosheet length is plotted versus the layer number in Fig. 1C. It is clear that our nanosheets have N -values between 1 and 15 and maximum lateral sizes approaching $10 \mu\text{m}$. The layer number is then converted to nanosheet thickness, t_{NS} , using the crystallographic interlayer spacing

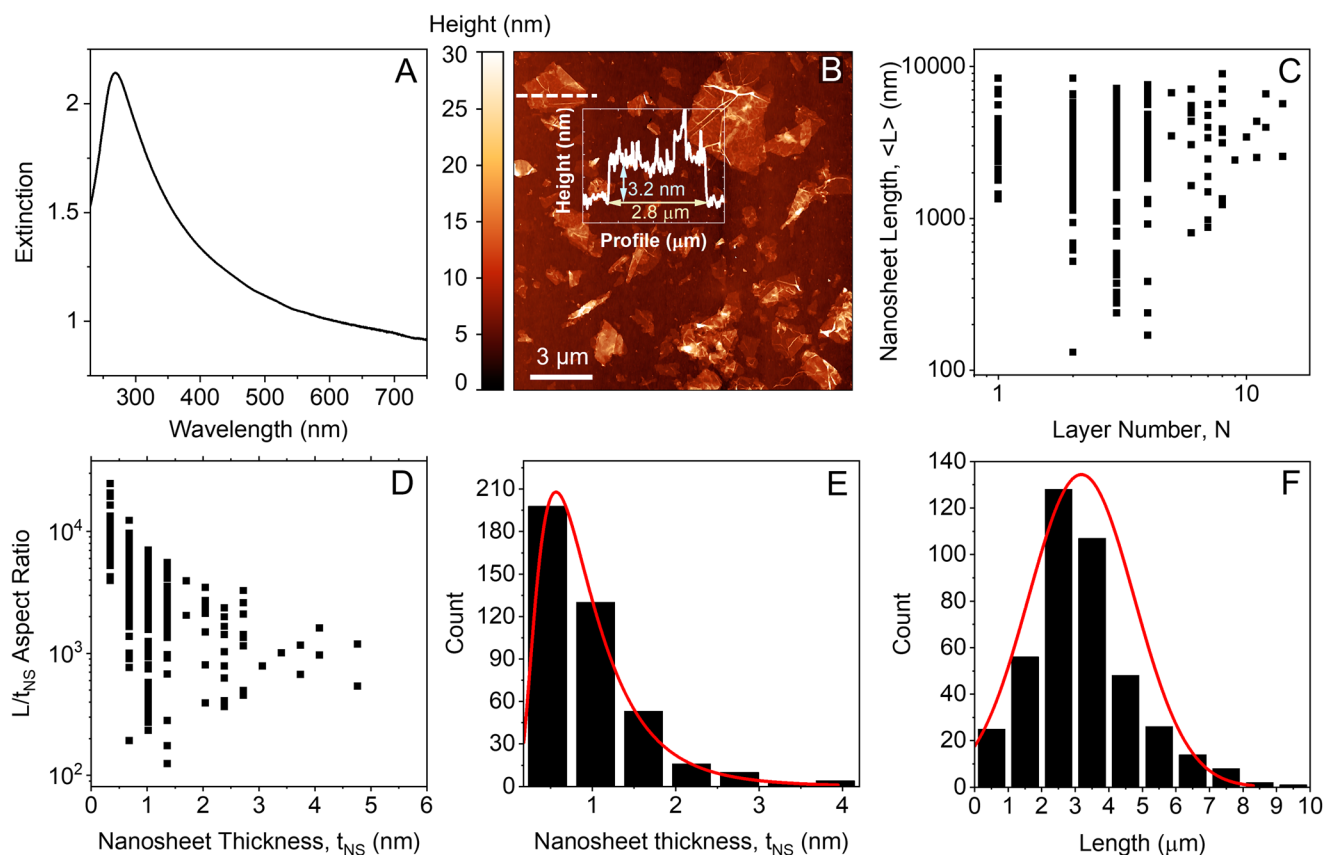


Fig. 1 | Characterization data for the electrochemically exfoliated graphene used in this study. **A** Extinction spectrum, normalized at 750 nm, of an IPA ink made using the EEG used in this study. **B** AFM image of EEG nanosheets spin coated on an Si substrate inset: line profile of a typical nanosheet with its length and thickness

shown (C) Plot of nanosheet lateral size versus nanosheet layer number and (D) lateral size/thickness aspect ratio versus nanosheet thickness for a sample of graphene nanosheets measured by AFM. **E** Histogram distribution of thickness and (F) lateral sizes of nanosheets measured by AFM.

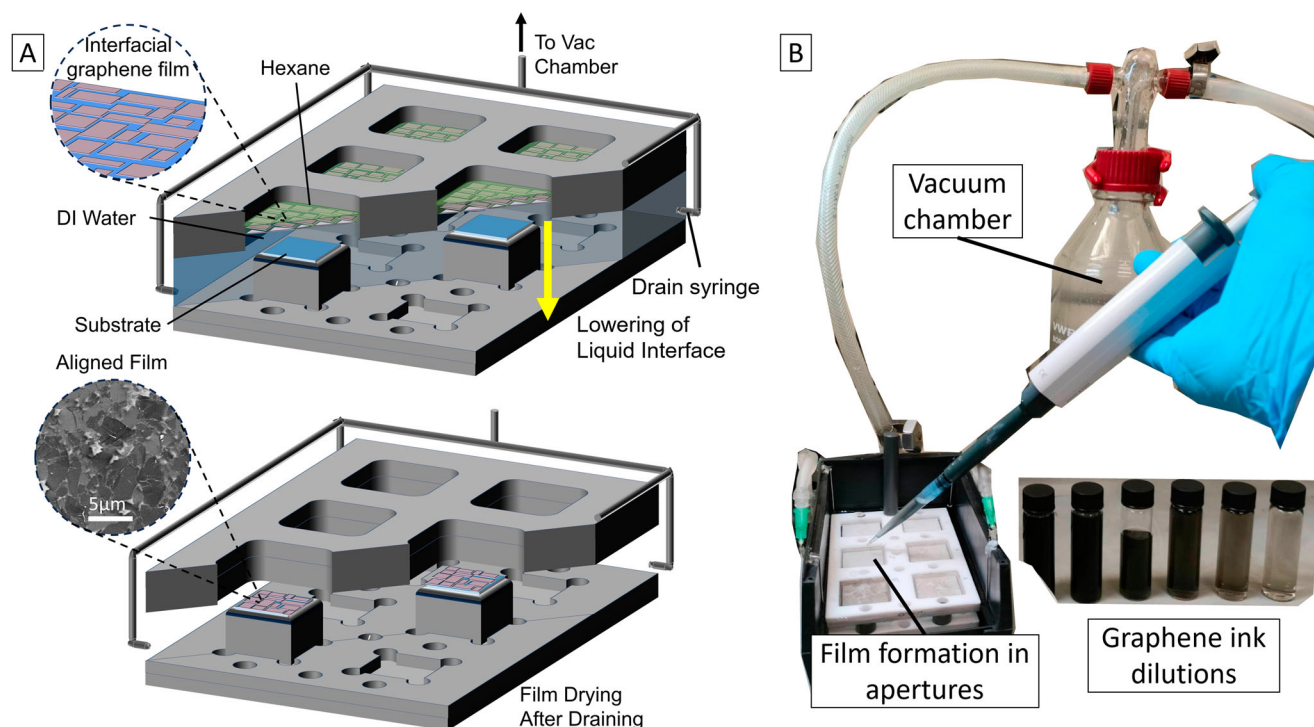


Fig. 2 | Schematic and photograph of the Langmuir-type setup used for the deposition parameter optimization. **A** Schematic of the method of liquid interface deposition used in this study, shown in cross section for clarity. A high surface tension interface is created between DI water and distilled hexane, the ink is injected into the interface to form a film of aligned nanosheets, and the water is then

evacuated by vacuum to transfer the nanosheet film onto substrates below the interface. Inset below: SEM image of a typical film, showing a high degree of flat nanosheet alignment. **B** Image of the setup used in the study, showing the apertures into which substrates are placed, a film is formed, and then water is evacuated via tubing placed below the water line into a vacuum chamber to transfer the films.

($t_{\text{NS}}(\text{nm}) = 0.34 \text{ nm} \cdot N$)⁵⁴ and this data is plotted in Fig. 1D as aspect ratio ($AR = L/t_{\text{NS}}$) versus t_{NS} . The average aspect ratio observed was 4540 ± 180 (ranging from 125–24660), while ~90% of our nanosheets have an $AR > 1000$. A histogram of nanosheet thickness is shown in Fig. 1E, which shows t_{NS} to range from 0.35 nm–4.9 nm with a mean nanosheet thickness, $\langle t \rangle_{\text{NS}} = 0.97 \pm 0.03$ nm. Similarly, the nanosheet length histogram is given in Fig. 1F and is consistent with $\langle L \rangle = 3.18 \pm 0.08$ μm. This appears to be typical of electrochemically exfoliated graphene, as previous studies report measured nanosheet thicknesses ranging from 0.8–7 nm, and lateral sizes ranging from 1 to 40 μm^{48,55,56}.

Liquid-liquid interfacial deposition

An excellent way to achieve thin but highly aligned films of nanosheets is via the liquid interface deposition method^{43,44}. This method exploits the large interfacial tension between two immiscible solvents, such as the water-hexane system shown in Fig. 2A. To achieve this, an ink containing graphene nanosheets is injected into the interface whereby the high interfacial tension then drives the graphene nanosheets to lie flat along the interface. This yields a highly aligned close-packed film of nanosheets, which can then be transferred onto any desired substrate by moving the substrate through the interface. In practise, we achieve this by steadily lowering the interface by removing water from below the waterline as indicated in Fig. 2A. After deposition, the films are annealed at 120 °C under inert gas for 1 h. A custom made, readily available setup was developed to accomplish this for fabricating multiple samples at once, using simple mill-cut PTFE parts as pictured in Fig. 2B and detailed in Supplementary Section 1.3.

Optimization of monolayer deposition

To quantitatively assess the quality of the produced films, we have developed a number of metrics using results from both optical and electrical characterisation techniques. Firstly, optical transmission scans were acquired on

deposited films using a high-grade commercially available transmission scanner. These scans yield values for transmitted intensity (expressed in signal intensity) for a large array of spatially resolved pixels. After calibration (detailed in Supplementary Section 1.4), these signal intensity values can be converted to absolute transmittance and then to optical extinction via $\text{Ext} = -\log(T)$. The resultant extinction values are averages over the visible range (i.e., 380–750 nm).

Shown in Fig. 3A is an optical transmission scan for a relatively poor-quality film. Although the spatial variation of extinction can be analysed⁵⁷, the simplest form of analysis is to use a random sample of extinction data from the image presented in Fig. 3A to plot a histogram as shown in Fig. 3B (see supporting information section S1.4.1 for further details). Such histograms provide information about the distribution of local thicknesses within the film (as $\text{Ext} = \epsilon t_{\text{film}}$, where ϵ is the film extinction coefficient and t_{film} is the local film thickness). The histogram in Fig. 3B implies the presence of regions of different thickness across the film, as indicated by the different colours of dashed rectangles in Fig. 3A which are colour-correlated with the coloured bands in Fig. 3B. These correspond to regions of uncovered substrate (green), regions of thick aggregated material (blue), and flat homogeneous regions of nanosheets (orange).

However, for better quality, more homogeneous films, such as that represented by the extinction map in Fig. 3C, the extinction histogram (Fig. 3D) follows a bimodal Gaussian distribution. In this example, regions of covered and uncovered (i.e., around the edge) substrate can be distinguished from the transmission scans, which correspond to the black, and red bins in Fig. 3D, respectively. This allows the extraction of the number of sampled pixels associated with uncovered substrate (red), $\Sigma_{\text{substrate}}$, and the number of sampled pixels associated with the graphene film (black) Σ_{film} . In addition, we can obtain the mean substrate optical extinction, $\langle \text{Ext} \rangle_{\text{substrate}}$ which allows us to correct the extinction associated with the film for the optical effect of the substrate. Furthermore, the total length of all boundaries between domains of uncovered substrate and film, which is a measure of the

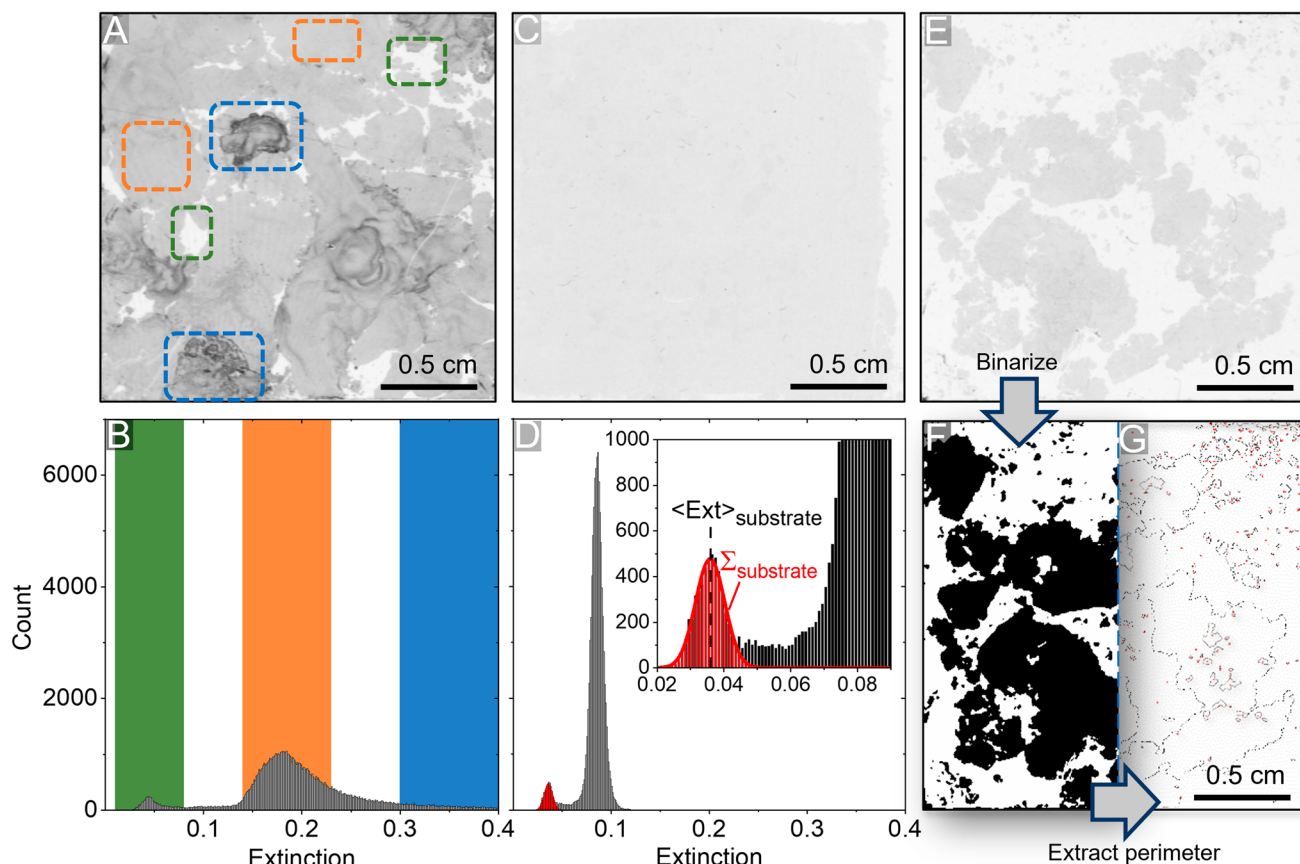


Fig. 3 | Methods for extracting figures of merit of film quality from optical scans.

A An optical scan of one of the films fabricated in the study. The differing regions observed in the film are highlighted, **green** showing uncovered substrate where breaks in the film formed, **orange** showing homogeneous film coverage, and **blue** showing regions of material aggregation. **B** A histogram of extinction values calculated for a sample of 100000 pixels from the image in (A). **C** Image of another film with more homogeneous film quality without full substrate coverage. **D** Image extinction histogram from the image in (C). Shown in the inset is how the substrate's

extinction, $\langle \text{Ext} \rangle_{\text{substrate}}$ is determined, such that it may be subtracted from the average extinction in the image to yield the average film extinction $\langle \text{Ext} \rangle_{\text{film}}$. Also shown, how the substrate pixel sum $\Sigma_{\text{substrate}}$ is determined by integration of the histogram curve, which is used to determine film coverage. **E** shows how the film perimeter is determined for a sample image, by binarization of the image between film and substrate domains as shown in (F) and then using particle analysis to find the sum of the perimeter of the boundary between the two regions, the result of which can be seen in (G).

amount and distribution of gaps in the film, may be determined by binarization and subsequent particle analysis on the scanned film. The binarization is achieved by applying ImageJ's thresholding feature to the image (Fig. 3E), below which the dark pixels (film) are defined as 0, and the light pixels (substrate) are defined as 1, giving a binary image (Fig. 3F). ImageJ's particle analysis feature may then be used to extract the total perimeter of all domains in the binary image—the film perimeter, in pixels. Further detail on this procedure is provided in Supplementary Section 1.4.2.

From the transmission scans we can obtain three different metrics for the quality of deposited films. These are the relative film coverage, the film thickness homogeneity, and the relative length of the perimeter dividing regions of film from bare substrate. These parameters can be generated quickly and easily from transmission scans and will be useful in allowing us to systematically optimize the homogeneity of the deposition process. We now describe how each metric is extracted and their physical meanings.

The **relative film coverage** is determined using the integral of the peaks corresponding to exposed substrate ($\Sigma_{\text{substrate}}$), and the film (Σ_{film}), respectively. The coverage metric was taken from the ratio of both values $\left(1 - \frac{\Sigma_{\text{substrate}}}{\Sigma_{\text{film}}}\right)$. This quantifies the relative amount of the substrate covered by graphene, with the maximum, 1, indicating a film with complete coverage.

The **film thickness homogeneity** was produced from the extinction histograms. As described in further detail in Supplementary Section 1.4.1, the mean film extinction and its standard deviation can be generated from the scans. The homogeneity is calculated from the ratio of the mean film

extinction, $\langle \text{Ext} \rangle_{\text{film}}$, and its standard deviation, $\Delta \text{Ext}_{\text{film}}$, which is equivalent to the ratio of mean film thickness and the corresponding standard deviation $\left(\frac{\langle t \rangle_{\text{film}}}{\Delta t_{\text{film}}}\right)$. This metric gives a relative value of variation in optically measured thickness across the film, with a larger value indicating a more homogeneous film thickness distribution.

Finally, the film-substrate perimeter length is obtained after binarization (Fig. 3E–G). To this end, perimeter lengths (in metres) were divided by the total area of the film (in m^2) to give a **relative film perimeter length (m/m^2)**. This quantifies the granularity of the film – a small perimeter length indicates a continuous film without small holes.

For a systematic optimization of the deposition process, using the electrochemically exfoliated graphene ink, we assess the quality of films produced while varying the two main deposition parameters: the ink concentration and areal mass loading of nanosheets injected into the interface. To this end, 36 films were deposited, using 6 different concentrations (0.54–0.02 g/L) and 6 different nanosheet aerial mass loads (3–21 g/m^2) for each ink concentration. The optical transmission scans of each film are shown in Fig. 4A. Note that each box in the 6×6 grid corresponds to a film with an area of $\sim 4 \text{ cm}^2$.

From the grid in Fig. 4A, it can be seen that various regions of the parameter space (e.g., top and left) yield patchy, inhomogeneous films. Visually, only the bottom right seems to yield uniform, homogeneous films. Below, we interrogate our various metrics to demonstrate this quantitatively.

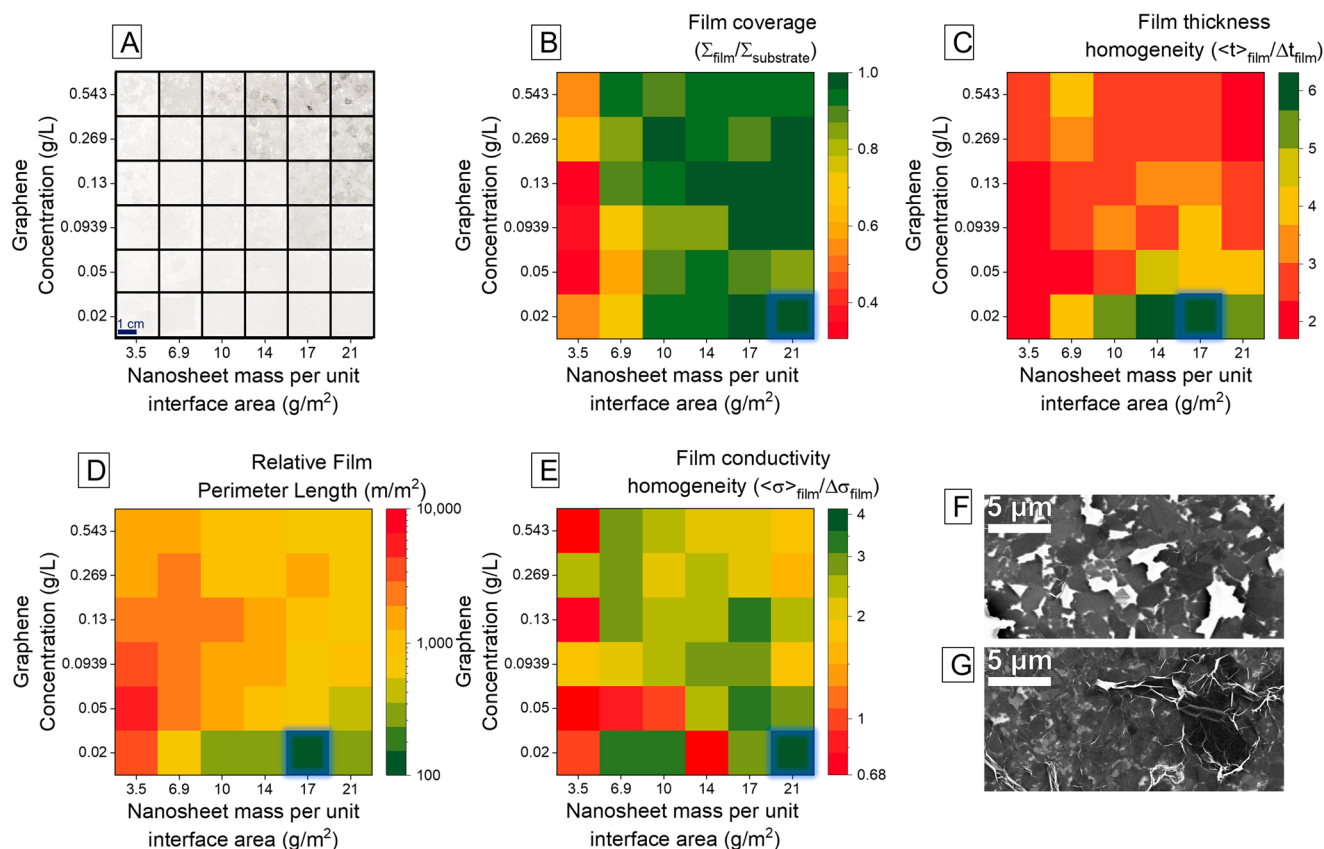


Fig. 4 | Heatmaps of film deposition parameters showing optimal concentration and mass load for homogeneous film formation. **A** Graph showing optical scans of the films formed for the ink optimisation study, with the ink concentrations (g/L) and areal mass load of nanosheets on the interface (g/m²) shown. **B** Heatmap of film coverage of each of the films formed, showing that lower areal mass loads lead to incomplete films. **C** Heatmap of film thickness homogeneity (ratio of the mean film thickness and film thickness standard deviation, extracted from ratio of mean extinction $\langle \text{Ext} \rangle_{\text{film}}$ and extinction standard deviation $\Delta \text{Ext}_{\text{film}}$), showing high areal mass load, low ink concentration to yield films with best thickness homogeneity. **D** Heatmap of relative film perimeter, showing that only high areal mass load and

low concentration yields films with completely contiguous films. **E** Heatmap of film conductivity homogeneity (ratio of the mean film conductivity $\langle \sigma \rangle_{\text{film}}$ and the average uncertainty in film conductivity $\Delta \sigma_{\text{film}}$) measured by the transmission line method, showing that high areal mass load, low ink concentration yields films with the best film conductivity homogeneity. **F** SEM image of a film with medium concentration and low areal coverage (0.0939 g/L 6.9 g/m²), showing discontinuities on the microscale, and **(G)** SEM image of a film with high concentration and high areal coverage (0.543 g/L 21 g/m²), showing the formation of aggregated, inhomogeneous structures on the microscale.

Heatmaps of the metrics described above are shown in Fig. 4B–D. A full coverage of the substrate tends to be achieved at injection masses of ~17–21 g/m² over all concentrations (Fig. 4B), while the film thickness homogeneity (Fig. 4C) and length of nanosheet film perimeter (Fig. 4D) are best for the injection of 17 g/m² at the lowest concentration (0.02 g/L). We note that lower concentrations are not suitable for our deposition process as mixing of the graphene with the water sub-phase is observed for too high ink injection volumes as required for complete substrate coverage at concentrations below 0.02 g/L. This is discussed in further detail in Supplementary Section 2.

In further analysis, a set of 18 gold contacts were evaporated on each deposited film to assess the spatial homogeneity of the conductivity of the fabricated films across different areas of the substrate. This represents a fourth metric for the film quality in addition to the ones extracted from transmission scans. We extract the “film conductivity homogeneity” and the contact resistance using the transmission line method (see Supplementary Section 1.6 for additional details). The average film conductivity, $\langle \sigma \rangle_{\text{film}}$, and its respective average uncertainty, $\Delta \sigma_{\text{film}}$, are used to calculate the conductivity homogeneity metric as the ratio between the two values $\frac{\langle \sigma \rangle_{\text{film}}}{\Delta \sigma_{\text{film}}}$. This gives a relative value of the variation in conductivity across the film, similar to the thickness homogeneity metric, with larger values indicating more homogeneous conductivity across the film area. The heatmap corresponding to the conductivity homogeneity metric is shown in Fig. 4E. This

clearly shows the lowest concentration and highest mass per unit area to yield the best film.

Based on the metrics, the region of high areal mass load and low ink concentration consistently yields films with the most desirable values for each metric. Conversely, films produced by low areal mass load appear to have low coverage, non-contiguous film domains, poor homogeneity in thickness, and are least conductive. An SEM image in Fig. 4F shows the microstructure of such a film, produced using a graphene ink concentration of ~0.1 g/L, injected to an aerial mass load of 6.9 g/m²—numerous holes and gaps are apparent between the individual nanosheets. Films produced by high concentration, while having relatively high coverage and contiguous film domains, appear to have even poorer thickness homogeneity and subpar conductivity homogeneity. An SEM image in Fig. 4G shows the microstructure of a film, produced using a graphene ink concentration of ~0.5 g/L, injected to an aerial mass load of 21 g/m²—shows the appearance of aggregated structures, made of folds and creases in the nanosheets.

Characterization of the optimized film

Having found the optimal deposition parameter space for homogeneously covered films, an advanced characterization of the best film was carried out (0.02 g/L, 21 g/m²), a photograph is shown in Fig. 5A, the black rectangles are gold electrodes. The substrate-corrected film extinction histogram (Fig. 5B) demonstrates a $\Delta \text{Ext}_{\text{film}}$ of 8.3×10^{-3} , indicating a thickness variation

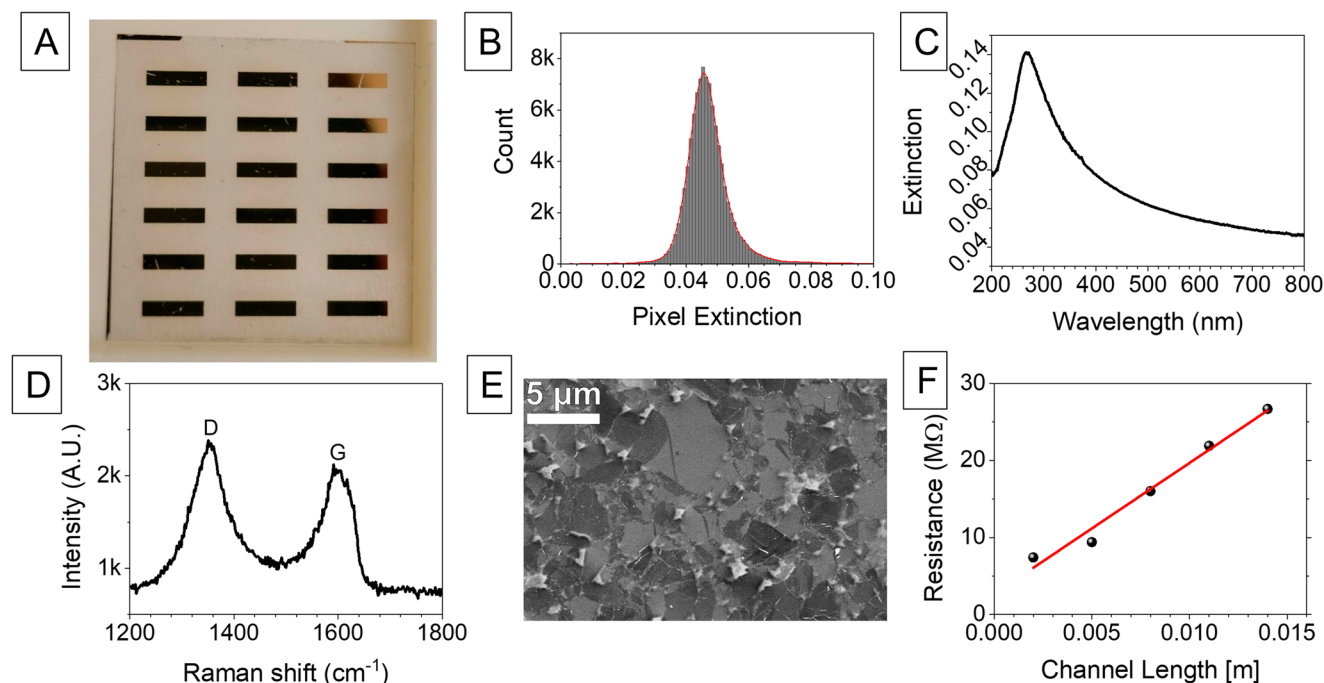


Fig. 5 | Characterization data of an optimized graphene film. **A** Optical image of optimal film (0.02 g/L, 21 g/m²) with top contacted Au electrodes shown. **B** Extinction histogram from the optical scan of the optimal film. **C** Extinction spectrum measured for a similarly fabricated single layer film on fused silica.

D Raman spectrum measured for the optimal film – note the D/G ratio indicating presence of defects (**E**) SEM image taken for this film, showing superior coverage of the substrate and microscale ordering. **F** A transmission line of measured resistances for this film.

($\frac{\langle \text{Ext}_{\text{film}} \rangle}{\Delta \text{Ext}_{\text{film}}}$) of 0.21, a relative measure of the roughness of the film equivalent to $\frac{\langle \text{Ext}_{\text{film}} \rangle}{\Delta \text{Ext}_{\text{film}}}$. Using samples of the graphene film of varying thickness, achieved by repeated interface deposition of the material onto masked glass substrates – film thicknesses are extracted from AFM height profiles (Supplementary Fig. 6A, C) and the film extinction is extracted from transmission scans (see Supplementary Fig. 6B) in order to determine the extinction coefficient as $(1.65 \pm 0.03) \times 10^7 \text{ m}^{-1}$ (see Supplementary Fig. 6D). Using this extinction coefficient, the mean thickness for this film can be determined as $2.9 \pm 0.1 \text{ nm}$.

An extinction spectrum corresponding to a film very similar to the one in Fig. 5A is shown in Fig. 5C. For the purpose of wavelength dependent extinction measurements, we deposited a film using the same conditions for the one shown in Fig. 5A, but on fused silica. We measure an average extinction of $(59 \pm 9) \times 10^{-3}$ between 380 and 750 nm, which is similar to the average extinction extracted from the transmission scan $(47 \pm 9) \times 10^{-3}$.

In addition, we performed Raman spectroscopy on the deposited film (Fig. 5D). The spectrum displays peaks at 1350 cm^{-1} and 1580 cm^{-1} , which respectively correspond to the D and G bands characteristic of graphene⁵⁸. The D/G band intensity ratio (1.15) observed is consistent with a considerable number of basal plane defects, and is comparable to the value observed for reduced GO (~ 1.1 – 1.5)⁵⁹, which is reported in the literature for similar preparation protocols of EEG by anodic exfoliation^{55,56}, indicating that defects are introduced during the exfoliation process.

We further study the microstructure of the optimized film using SEM imaging (Fig. 5E). The image shows a homogenous and close packing of the nanomaterial, with slight overlap between the individual nanosheets. This confirms the high degree of nanosheet alignment associated with this deposition method.

By depositing multiple gold electrodes (Fig. 5A) we can use the transmission line method to measure both film conductivity, σ , and contact resistance, R_c . For a uniform film, we expect a well-behaved linear dependence between the measured resistance, R , and the electrode spacing, L : $R = 2R_c + L/(\sigma w t_{\text{film}})$, where w is the electrode width. Fig. 5F demonstrates that this is indeed the case with linear fitting yielding $\sigma = 84 \pm 20 \text{ S/m}$ and $R_c = 900 \pm 700 \text{ k}\Omega\text{-m}$, respectively. We note that this conductivity of a

single layer of nanosheets is relatively low compared to thicker graphene films which can have conductivities approaching 10^5 S/m ²⁷.

Layer-by-layer deposition of densely packed graphene nanosheet films

Having found optimal deposition parameters for a single layer, the method was further refined for depositing films layer-by-layer to increase the film thickness. For this purpose, we configured the setup as described in detail in Supplementary Fig. 8. In short, using a rotating stage helps with reproducibility due to more homogenous ink injection. Hence, we change the geometry of the setup from the square cavities shown in Fig. 2 to a circular cavity shown in Fig. 6A. Note that this changes the absolute injection volume to achieve the same aerial mass load.

We note that issues with the colloidal stability of our graphene ink were observed over extended storage periods. To address this, we employed mild centrifugation on the stock dispersion ($c_{\text{ink}} = 1 \text{ g/L}$) to remove aggregates. UV-Vis was then used to determine the concentration of the remaining supernatant, which was subsequently diluted to 0.02 g/L to match the optimal ink concentration.

For multilayer deposition, each layer was deposited using the optimised protocol, as described above. In addition, we perform thermal annealing after the deposition of each layer to improve the adhesion between adjacent nanosheet layers. In addition, we soak the deposited and annealed films briefly in acetone, to remove organic residues on the nanomaterial surface. Following this protocol, these steps can be repeated for as many layers as desired. Transmission scans for films of deposition numbers from 1–16 (Supplementary Fig. 8) were measured to allow for a systematic analysis. A sample of the resulting extinction histograms is shown in Fig. 6B. The curves show a systematic shift towards higher extinction with each deposition as well as a broadening with increasing deposition number.

In further analysis, we extract the mean extinction of these films, $\langle \text{Ext}_{\text{film}} \rangle$ as well as their standard deviation, $\Delta \text{Ext}_{\text{film}}$. The extinction increases linearly with deposition number, indicating that each deposition sequentially adds layers of approximately equal thickness. In addition, $\Delta \text{Ext}_{\text{film}}$ serves as a measure for the roughness across the deposited

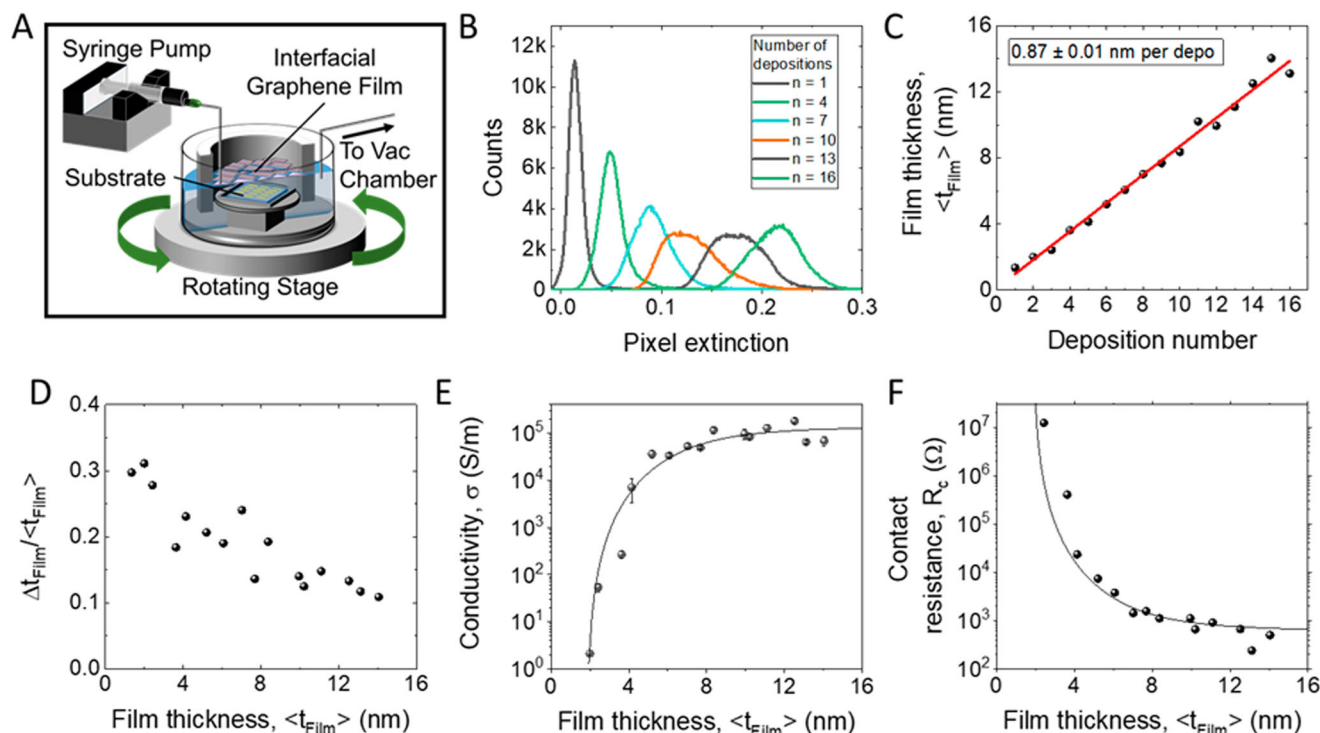


Fig. 6 | Multilayer deposition using monolayer-enriched graphene ink utilizing the protocols developed in this study. **A** Schematic of the setup used to deposit multiple layers of graphene, with film formation aperture shown in cross section. Upon deposition of a layer, films were dried, thermally annealed, and then washed in acetone before adding subsequent layers by repeating the same process. **B** Extinction histograms of a selected sample of multilayer films from the study. **C** Average film thickness versus deposition number, showing a linear scaling that indicates that a layer of nanosheets that are on average bilayer are added with each deposition, which

is supported by the distribution in Fig. 1B. **D** Ratio of standard deviation thickness to mean film thickness for each film, showing a reduction in relative roughness with deposition number. **E** Graph of film conductivity versus film thickness, indicating the networks fabricated by this material and method approach a bulk conductivity of 1.3×10^5 S/m. **F** Graph of average contact resistance across the films versus deposition number. The solid line in H is related to the solid line in G via $R_c = 8.4 \times 10^7 / \sigma$.

nanosheet film. $\Delta \text{Ext}_{\text{film}}$ follows a sublinear increase with layer number, saturating above about 10 layers. As shown below, that $\Delta \text{Ext}_{\text{film}}$ increases slower than the mean extinction means the films become relatively more uniform with increasing deposition number.

The mean film extinction was converted to the average film thickness using the extinction coefficient mentioned above. As plotted in Fig. 6C, the mean film thickness shows a linear increase with deposition number. From the slope, we can extract that approximately 0.87 nm are added with each deposited layer, consistent with each layer consisting of nanosheets each with an average N of ~ 3 . In addition, we converted $\Delta \text{Ext}_{\text{film}}$ to standard deviation of thickness Δt_{film} and calculated the ratio of Δt_{film} to the mean film thickness, $\Delta t_{\text{film}} / \langle t_{\text{film}} \rangle$, as shown in Fig. 6D. This parameter is a measure of the relative roughness of the films and falls steadily with increasing deposition number. For the thickest film, this data implies the standard deviation of the thickness distribution to be $\sim 10\%$ of the mean thickness.

Finally, we use set electrodes to measure the I/V characteristics on each film, similar to the measurements used for the optimization of the single layer deposition (see further above, and in the SI, section S1.6 for additional details). This allows the determination of the film conductivity and contact resistance for films of each layer number. These parameters are plotted as a function of film thickness in Fig. 6E, F.

For the optimised multilayer deposition setup, the first two layers had near-negligible conductivity, contrary to the conductivity for single layers in the initial optimization study. This may be due to a variety of reasons. One aspect is that we observe a concentration change of the ink after prolonged storage times. We assume that partial aggregation of higher layer numbers occurs over time, and therefore a slight change of the concentration and the monolayer content in the dispersion. Hence, a

smaller effective mass load was used for the same injection volume. Additionally, a mass load below a complete film is in fact desirable for depositing multiple layers, as the lack of close-packing avoids the nanosheet folds observed in Fig. 5E. Such folds contribute to the formation of pores in a multilayer network, and hence reduce its conductivity. As such, individual layers deposited with the aged material were homogenous according to the transmission scans, but below the percolation threshold (see SI, section S1.7 for further details and AFM images).

The film conductivity (Fig. 6E) is relatively low for the thinnest (low layer number) films but increases rapidly with increasing thickness, before saturating at 1.3×10^5 S/m for thicknesses above 8 nm (layer numbers above 10). Such thickness-dependent behaviour is as expected for thin films due to surface effects. For example, the Fuchs-Sondheimer model⁶⁰ shows the resistivity of perfectly flat thin films to increase with decreasing thickness as $\langle t_{\text{film}} \rangle^{-1}$ because of surface scattering of electrons. A number of models^{61,62} have shown that for thin films with roughness or disorder on the nanoscale, the resistivity increases with decreasing thickness can be even faster, than $\langle t_{\text{film}} \rangle^{-1}$ (see SI section S3). Such models describe the resistivity as the sum of a bulk-like resistivity (associated with thick films) and a term describing the increase in resistivity with decreasing thickness. In the case of solution deposited films of nanoparticles, De et al.¹⁷ have shown similar behaviour: the conductivity of thin films falls off with decreasing thickness. This paper describes the data in terms of two regimes: a bulk-like regime above some threshold thickness (t_x) and a percolative regime, below t_x . For printed graphene films, Caffrey et al.⁷ have comprehensively mapped out these regimes, accurately determining t_x , demonstrating thickness-independent conductivity for $\langle t_{\text{film}} \rangle > t_x$ and fitting the conductivity to a percolation scaling law for $\langle t_{\text{film}} \rangle < t_x$. However, accurately performing such fitting requires a prohibitively large number of conductivity versus thickness data points.

To avoid this requirement, we show in the SI (S3) that one can apply the thin film strategy of adding bulk-like and thickness-dependent resistivity terms used in the Fuchs-Sondheimer model⁶⁰ to a system where the behaviour is percolative at low thickness. This yields the following semi-empirical equation for film conductivity, σ , as a function of mean film thickness, $\langle t_{\text{Film}} \rangle$:

$$\sigma = \sigma_B \left[1 + \frac{1}{4} \left[\frac{t_x - t_c}{\langle t_{\text{Film}} \rangle - t_c} \right]^n \right]^{-1} \quad (1)$$

Here, σ_B is the thickness of a thick (bulklike) film, t_c is the percolation threshold (the thickness below which no conduction occurs), t_x is defined as the thickness where the film conductivity reaches 80% of the bulklike value ($\sigma(t_x) = 0.8\sigma_B$) while n is the percolation exponent. We find this equation fits the data extremely well with fit parameters of $t_x = 12$ nm, $t_c = 2$ nm, $\sigma_B = 1.4 \times 10^5$ S/m and $n = 3$. This fit implies the transition to bulk-like conductivity to occur at a film thickness of 12 nm. This is a relatively low value of t_x , compared to others in the literature. The lowest reported value we know of is that of Caffrey et al.⁷ who reported $t_x = 120$ nm. Nevertheless, values of t_x lower than 12 nm would be useful, especially for films of semiconducting nanosheets (e.g. MoS₂) in transistor applications. This is because the on/off ratio in such devices is expected to fall with increasing network thickness due to screening effects. Future work will attempt to decrease t_x by enhancing the deposition method to further reduce disorder in these networks.

The main advantage of this work is that it yields solution-processed graphene films with combinations of reasonably high conductivity and relatively low thickness that surpass any previous reports. It should be noted that measured conductivities for solution-graphene films comparable to the conductivities reported here— $(1.3 \pm 0.2) \times 10^5$ S/m at 11.1 ± 0.2 nm—have only previously been achieved for significantly thicker films (e.g., 1.2×10^5 S/m at a thickness of 500 nm)¹⁵ or for thin (<50 nm) films using aggressive post-processing techniques (2.5×10^5 S/m at 15 nm after 65% HNO₃ treatment)²¹. For published thin films similar to those here (i.e., $t < 50$ nm without high temperature or chemical post-processing), the record conductivity is an order of magnitude lower (1.6×10^4 S/m at a thickness of 15 nm)²¹. As such, this method demonstrates its utility for fabricating films with state-of-the-art conductivities at extremely low thicknesses. One of the thinner films (6.1 ± 0.2 nm) fabricated in this study exhibited a transmission of 82% and conductivity of $(3.6 \pm 0.6) \times 10^4$ S/m, which corresponds to a sheet resistance R_s of 4.5 kΩ/□. This is competitive with the lowest sheet resistance of a lightly-processed graphene TCF device found in the literature (measured transmission of 85%, R_s of 4.1 kΩ/□)²¹. For further comparison to existing graphene films reported in the literature, see Supplementary Table 1.

It has recently been shown that the conductivity of bulk-like nanosheet networks is given by an equation⁶³ which can be rewritten as:

$$\sigma_B = \left[\frac{(1 - P_{\text{Net}})}{\sigma_{\text{NS}}^{-1} + 2t_{\text{NS}}R_j} \right] \quad (2)$$

Where P_{Net} is the network porosity, σ_{NS} is the conductivity of the individual nanosheets, t_{NS} is the mean nanosheet thickness (~ 1 nm here) and R_j is the mean junction resistance. For highly aligned films such as these we can approximate $P_{\text{Net}} \sim 0$, allowing us to write

$$R_j \approx \frac{(\sigma_B^{-1} - \sigma_{\text{NS}}^{-1})}{2t_{\text{NS}}} \quad (3)$$

We can take σ_{NS} to be the in-plane conductivity of graphite which has been reported in the range $\sim 10^5$ – 10^6 S/m²⁶. Although we do not know the

exact conductivity of the graphite used here, we can calculate the maximum possible junction resistance by taking the upper limit of graphite conductivity as our value for σ_{NS} . Then, taking $\sigma_B = 1.4 \times 10^5$ S/m and $t_{\text{NS}} = 1$ nm, we find $R_j < 3$ kΩ. However, because the graphene used here is quite defective, its conductivity is likely somewhat below this maximal value. For example, if we take a more realistic value of $\sigma_{\text{NS}} = 2 \times 10^5$ S/m, this would imply a junction resistance of ~ 1 kΩ. This compares to a measured 3.3 kΩ value for R_j measured for a spray-cast graphene network²⁸ and indicates that the liquid interface deposition technique yields networks with more conductive junctions when compared to other printing techniques.

Finally, we show data for the contact resistance as a function of film thickness in Fig. 6F. Here we see a very sharp decrease in contact resistance with increasing film thickness before saturating at thicknesses above 8 nm. This is essentially the inverse of the behaviour displayed by the conductivity. In fact, as displayed by the solid line in Fig. 6F the contact resistance is directly proportional to the inverse of the function used to fit the conductivity data ($R_c = 8.4 \times 10^7/\sigma$). This implies that the contact resistance is somehow directly linked to the film resistivity, probably via the resistance associated with the current spreading from the contacts to flow through the entire thickness of the film.

Key findings and interpretation of results

We demonstrate the general methodology for a liquid-interface deposition method, and the deposition parameters required for using this method to deposit a homogeneous film of electrochemically exfoliated graphite ($c_{\text{ink}} = 0.02$ g/L, mass/area = 21 g/m²). We have shown that stacking of multiple layers of graphene is possible to produce films with high conductivities (1.3×10^5 S/m) at low thicknesses (11 nm). Such conductivities are comparable to the state of the art for graphene films in general¹⁵ and an order of magnitude increase compared to thin printed graphene films without the use of complex post-processing strategies²¹. This can all be of value to improvements in the performance of solution-processed graphene in thin-film device applications. We believe that the deposition method described here will be useful in a range of applications where highly conductive, yet extremely thin films are required. Examples include high-performance electrodes in solution-processed TFTs⁶⁴, flexible transparent conductive electrodes² and strain gauges⁶⁵ for wearable electronics, antennae⁶⁶, and high-frequency electromagnetic interference shields⁶⁷.

More generally, this work shows a reliable route to minimizing the junction resistance observed in 2D material networks, which is promising for applying the method for a broader range of nanomaterials, which have previously been deposited using similar liquid-interface techniques without the optimization demonstrated here^{68–70}. Indeed, we expect this method to be extremely versatile and in principle applicable to a wide range of 2D materials as well as various substrates. Using this technique to overcome the problem of low network mobilities that have been previously observed in TMD-based transistors due to large junction resistances^{27,68} may be particularly promising for the fabrication of heterostructures over large areas.

Methods

Electrochemical exfoliation

Electrochemically exfoliated graphene was prepared according to the following procedure. Two pieces of graphite foil (Alfa Aesar) with dimensions 50 x 30 x 0.25 mm³ were connected as anode and cathode to a DC power supply and immersed in 100 mL of an aqueous electrolyte solution of 0.1 M (NH₄)₂SO₄ with a separation of 2 cm between them. 10 V were applied to the electrodes for 30 min, with a current that increased from ~ 1 A to ~ 1.8 A during the process. The resulting expanded material in the electrolyte solution was filtered and repeatedly washed with DI water (~ 1 L), and then sonicated in 100 mL of DMF for 10 min to complete the exfoliation into a dispersion of graphene nanosheets. The resulting ink was centrifuged at 3000 rpm (940 g) for 20 min to remove incompletely exfoliated particles. The graphene sheets were sedimented at 6000 rpm (3780 g) for 90 min and redispersed in isopropyl alcohol. This final step was repeated once more to

remove residual DMF. The resulting 1 g/L 3780 g graphene ink in IPA was used for the study.

AFM

Atomic force microscopy (Bruker Multimode 8, ScanAsyst mode, non-contact) was used to measure the nanosheet thickness and lateral dimensions in the size-selected graphene ink. Measurements were performed in air under ambient conditions using Al-coated silicon cantilevers (OLTESPA-R3). As detailed in the SI, to convert the apparent thickness to actual thickness, the AFM measured height values are subtracted by 0.5 nm and divided by 0.95 nm, the apparent thickness of a graphene layer. When this value is rounded down, this gives the number of layers in a nanosheet. This value is multiplied by 0.34 nm, the crystallographic thickness of a graphene layer, to yield the actual thickness of the nanosheet⁵⁴.

UV-Vis spectroscopy

Ink characterisation. UV-Vis extinction measurements were carried out using a Cary 50 spectrophotometer, having subtracted off an IPA background with a sampling interval of 0.5 nm and a sample length of 4 mm.

Ink concentration measurements. Using the same apparatus as before, with a sampling interval of 1 nm and a sample length of 1 mm. An extinction coefficient of $2640 \text{ g L}^{-1} \text{ m}^{-1}$ at 660 nm was used to determine the concentration of the measured ink from the acquired spectrum.

Pre-treatment of glass substrates with KOH

Potassium hydroxide was dissolved in ethanol under continuous stirring until saturation was achieved. The resulting orange solution was decanted from the undissolved potassium hydroxide and used for substrate surface treatment as detailed in SI section S1.2.

Liquid interface deposition—optimization

Various dilutions of the resulting dispersion were prepared (1:2, 1:4, 1:5, 1:8, 1:20, 1:50) and their concentrations were measured using UV-Vis spectroscopy as detailed above. The target substrate was immersed in particle filtered, $18 \text{ M}\Omega \text{ cm}^{-1}$ deionized water. ~5 mL of distilled hexane was pipetted onto the water interface, and then a specific volume of graphene ink of known concentration was pipetted onto the water-hexane interface. The interfacial film was then transferred by vacuuming out the water from below. The resulting films were left to dry under a cover inside a fume hood for approximately 4 h, and then annealed in inert conditions at 120°C for approximately 1 h. Multiple volumes of each of the dilutions were deposited by this method onto KOH-treated glass substrates.

Film transmission scans

The graphene films were scanned using an EPSON Perfection 750 scanner, and resulting images were processed to extract the film extinction distributions and film perimeter (see Fig. 3 and Supplementary Fig. 5).

Conductivity measurements

Arrays of Au electrodes were deposited onto films/substrates with the mask depicted in Supplemental Fig. 2B using a Temescal FC-2000 Bell Jar Deposition System. Electrical resistance between combinations of electrodes along each row were measured by 2-point probe measurements across the film using a Karl SUSS PM probe station, as depicted in Supplementary Fig. 7A.

SEM measurements

SEM was performed with a Carl Zeiss Ultra SEM operating at 2 kV with a $30 \mu\text{m}$ aperture at a working distance of 5 mm. Images are acquired using the secondary electron inlens detector.

Raman

A WITec Raman spectrometer using a 532 nm wavelength laser is used to acquire spectra. The spectra for each network is averaged over 3

accumulations with a $100\times$ objective. An incident power of ~1 mW was used to minimise possible thermal damage.

Liquid interface deposition—layer by layer

The stock 1 g/L graphene dispersion was centrifuged at 200 g for 30 min in 5 sequential steps, taking the supernatant discarding the sediment each time, to yield a monolayer enriched ink, which was diluted to a concentration of 0.02 g/L using IPA. This ink was injected to a water-air interface and transferred onto treated glass substrates deposited with Au electrode arrays, using a refined setup that rotated the interface as a set quantity of ink was injected at a steady rate ($100 \mu\text{L}/\text{min}$) using an auto-injector. Following the deposition, the films were placed on a hot plate at 80°C and covered to dry for 1 h. The resulting films were then annealed at 120°C in ambient conditions for 1 h, and then briefly dipped in acetone to prepare for the deposition of a subsequent layer. This procedure is further detailed in Supplementary Section 1.7. Following this, we fabricated 16 samples of different deposition numbers (1 to 16), each of which were then annealed under vacuum at 500°C for 1 h. The same methods of scanning and electrical measurements as before were then performed on the films.

Data availability

The authors declare that the data supporting the findings are available within the paper and its supplementary information. The corresponding authors can also provide data upon reasonable request.

Received: 1 July 2024; Accepted: 27 December 2024;

Published online: 08 January 2025

References

- Geim, A. K. & Novoselov, K. S. The rise of graphene. *Nat. Mater.* **6**, 183–191 (2007).
- Miao, J. & Fan, T. Flexible and stretchable transparent conductive graphene-based electrodes for emerging wearable electronics. *Carbon* **202**, 495–527 (2023).
- Liu, Z. et al. Water-dispersed high-quality graphene: a green solution for efficient energy storage applications. *ACS Nano* **13**, 9431–9441 (2019).
- Jeong, H. Y. et al. Graphene oxide thin films for flexible nonvolatile memory applications. *Nano Lett.* **10**, 4381–4386 (2010).
- van Hazendonk, L. S. et al. Printed stretchable graphene conductors for wearable technology. *Chem. Mater.* **34**, 8031–8042 (2022).
- Seekaew, Y. et al. Low-cost and flexible printed graphene-PEDOT:PSS gas sensor for ammonia detection. *Org. Electron.* **15**, 2971–2981 (2014).
- Caffrey, E. et al. Quantifying the piezoresistive mechanism in high-performance printed graphene strain sensors. *ACS Appl. Mater. Interfaces* **14**, 7141–7151 (2022).
- Large, M. J. et al. Large-scale surfactant exfoliation of graphene and conductivity-optimized graphite enabling wireless connectivity. *Adv. Mater. Technol.* **5**, 2000284 (2020).
- Zhou, X. et al. A sustainable approach towards printed graphene ink for wireless RFID sensing applications. *Carbon* **218**, 118693 (2024).
- Pan, K. et al. Sustainable production of highly conductive multilayer graphene ink for wireless connectivity and IoT applications. *Nat. Commun.* **9**, 5197 (2018).
- He, P. et al. Screen-printing of a Highly Conductive Graphene Ink for Flexible Printed Electronics. *ACS Appl. Mater. Interfaces* **11**, 32225–32234 (2019).
- He, P. et al. An energy-saving structural optimization strategy for high-performance multifunctional graphene films. *Carbon* **222**, 118932 (2024).
- Gang, Z. et al. High thermal conductivity and increased thickness graphene nanosheet films prepared through metal ion-free route. *Ceram. Int.* **48**, 3711–3719 (2022).

14. Qian, W. et al. Scalable assembly of high-quality graphene films via electrostatic-repulsion aligning. *Adv. Mater.* **34**, 2206101 (2022).
15. Clifford, K. et al. Emergent high conductivity in size-selected graphene networks. *Carbon* **218**, 118642 (2024).
16. Mirkhani, S. A. et al. Reduction of electrochemically exfoliated graphene films for high-performance electromagnetic interference shielding. *ACS Appl. Mater. Interfaces* **13**, 15827–15836 (2021).
17. De, S., King, P. J., Lyons, P. E., Khan, U. & Coleman, J. N. Size effects and the problem with percolation in nanostructured transparent conductors. *Acs Nano* **4**, 7064–7072 (2010).
18. Gao, Y., Shi, W., Wang, W., Leng, Y. & Zhao, Y. Inkjet printing patterns of highly conductive pristine graphene on flexible substrates. *Ind. Eng. Chem. Res.* **53**, 16777–16784 (2014).
19. Parvez, K., Worsley, R., Alieva, A., Felten, A. & Casiraghi, C. Water-based and inkjet printable inks made by electrochemically exfoliated graphene. *Carbon* **149**, 213–221 (2019).
20. Marković, Z. M. et al. Semi-transparent, conductive thin films of electrochemical exfoliated graphene. *RSC Adv.* **6**, 39275–39283 (2016).
21. Parvez, K. et al. Electrochemically exfoliated graphene as solution-processable, highly conductive electrodes for organic electronics. *ACS Nano* **7**, 3598–3606 (2013).
22. Suriani, A. B. et al. Synthesis, transfer and application of graphene as a transparent conductive film: a review. *Bull. Mater. Sci.* **43**, 310 (2020).
23. Wu, W. et al. Control of thickness uniformity and grain size in graphene films for transparent conductive electrodes. *Nanotechnology* **23**, 035603 (2012).
24. Bae, S. et al. Roll-to-roll production of 30-inch graphene films for transparent electrodes. *Nat. Nanotechnol.* **5**, 574–578 (2010).
25. Wang, S. et al. High mobility, printable, and solution-processed graphene electronics. *Nano Lett.* **10**, 92–98 (2010).
26. Nakamura, S., Miyafuji, D., Fujii, T., Matsui, T. & Fukuyama, H. Low temperature transport properties of pyrolytic graphite sheet. *Cryogenics* **86**, 118–122 (2017).
27. Kelly, A. C., O'Suilleabhain, D., Gabbett, C. & Coleman, J. N. The electrical conductivity of solution-processed nanosheet networks. *Nat. Rev. Mater.* **7**, 217–234 (2022).
28. Gabbett, C. et al. Understanding how junction resistances impact the conduction mechanism in nano-networks. *Nat. Commun.* **15**, 4517 (2023).
29. Kymakis, E., Stratakis, E., Stylianakis, M. M., Koudoumas, E. & Fotakis, C. Spin coated graphene films as the transparent electrode in organic photovoltaic devices. *Thin Solid Films* **520**, 1238–1241 (2011).
30. Zheng, Q.-B., Shi, L.-F. & Yang, J.-H. Langmuir-Blodgett assembly of ultra-large graphene oxide films for transparent electrodes. *Trans. Nonferrous Met. Soc. China* **22**, 2504–2511 (2012).
31. Beceril, H. A. et al. Evaluation of solution-processed reduced graphene oxide films as transparent conductors. *ACS Nano* **2**, 463–470 (2008).
32. Wang, S. J., Geng, Y., Zheng, Q. & Kim, J.-K. Fabrication of highly conducting and transparent graphene films. *Carbon* **48**, 1815–1823 (2010).
33. Xu, Y. et al. Polymer photovoltaic devices with transparent graphene electrodes produced by spin-casting. *Carbon* **48**, 3308–3311 (2010).
34. Wöbkenberg, P. H. et al. Reduced graphene oxide electrodes for large area organic electronics. *Adv. Mater.* **23**, 1558–1562 (2011).
35. Eda, G., Fanchini, G. & Chhowalla, M. Large-area ultrathin films of reduced graphene oxide as a transparent and flexible electronic material. *Nat. Nanotechnol.* **3**, 270–274 (2008).
36. Katiyar, A. K. et al. 2D materials in flexible electronics: recent advances and future perspectives. *Chem. Rev.* **124**, 318–419 (2024).
37. Schranghamer, T. F., Sharma, M., Singh, R. & Das, S. Review and comparison of layer transfer methods for two-dimensional materials for emerging applications. *Chem. Soc. Rev.* **50**, 11032–11054 (2021).
38. Torres-Huerta, A. M. et al. Morphological and mechanical properties dependence of PLA amount in PET matrix processed by single-screw extrusion. *Polym. Plast. Technol. Eng.* **55**, 672–683 (2016).
39. Gilles, D. G. & Loehr, R. C. Waste generation and minimization in semiconductor industry. *J. Environ. Eng.* **120**, 72–86 (1994).
40. Shin, C.-H. et al. Recovery of nitric acid from waste etching solution using solvent extraction. *J. Hazard. Mater.* **163**, 729–734 (2009).
41. Shen, C. W., Tran, P. P., Ly, P. T. M. Chemical waste management in the U.S. Semiconductor industry. *Sustainability* **10**, 1545 (2018).
42. Gabbett, C. et al. Quantitative analysis of printed nanostructured networks using high-resolution 3D FIB-SEM nanotomography. *Nat. Commun.* **15**, 278 (2024).
43. Neilson, J., Avery, M. P. & Derby, B. Tiled monolayer films of 2D molybdenum disulfide nanoflakes assembled at liquid/liquid interfaces. *ACS Appl. Mater. Interfaces* **12**, 25125–25134 (2020).
44. Vičentić, T., Andrić, S., Rajić, V. & Spasenović, M. Reliable fabrication of transparent conducting films by cascade centrifugation and Langmuir–Blodgett deposition of electrochemically exfoliated graphene. *Beilstein J. Nanotechnol.* **13**, 666–674 (2022).
45. Backes, C. et al. Equipartition of energy defines the size-thickness relationship in liquid-exfoliated nanosheets. *Acs Nano* **13**, 7050–7061 (2019).
46. Yang, Y. et al. Electrochemical exfoliation of graphene-like two-dimensional nanomaterials. *Nanoscale* **11**, 16–33 (2019).
47. Le, T.-H., Oh, Y., Kim, H. & Yoon, H. Exfoliation of 2D materials for energy and environmental applications. *Chem. A. Eur. J.* **26**, 6360–6401 (2020).
48. Abdelkader, A. M., Cooper, A. J., Dryfe, R. A. W. & Kinloch, I. A. How to get between the sheets: a review of recent works on the electrochemical exfoliation of graphene materials from bulk graphite. *Nanoscale* **7**, 6944–6956 (2015).
49. Backes, C. et al. Spectroscopic metrics allow in situ measurement of mean size and thickness of liquid-exfoliated few-layer graphene nanosheets. *Nanoscale* **8**, 4311–4323 (2016).
50. Synnatschke, K. et al. Sonication-assisted liquid phase exfoliation of two-dimensional CrTe₃ under inert conditions. *Ultrason. Sonochem.* **98**, 106528 (2023).
51. Synnatschke, K. et al. Sonication-assisted liquid exfoliation and size-dependent properties of magnetic two-dimensional α -RuCl₃. *J. Phys. D: Appl. Phys.* **56**, 274001 (2023).
52. Synnatschke, K. et al. Liquid exfoliation of Ni₂P₂S₆: structural characterization, size-dependent properties, and degradation. *Chem. Mater.* **31**, 9127–9139 (2019).
53. Gosch, J., Synnatschke, K., Stock, N. & Backes, C. Comparative study of sonication-assisted liquid phase exfoliation of six layered coordination polymers. *Chem. Commun.* **59**, 55–58 (2023).
54. Paton, K. R. et al. Scalable production of large quantities of defect-free few-layer graphene by shear exfoliation in liquids. *Nat. Mater.* **13**, 624–630 (2014).
55. Mei, J. et al. Insights into the conductive network of electrochemical exfoliation with graphite powder as starting raw material for graphene production. *Langmuir* **39**, 4413–4426 (2023).
56. Achee, T. C. et al. High-yield scalable graphene nanosheet production from compressed graphite using electrochemical exfoliation. *Sci. Rep.* **8**, 14525 (2018).
57. Finn, D. J., Lotya, M. & Coleman, J. N. Inkjet printing of silver nanowire networks. *Acs Appl. Mater. Interfaces* **7**, 9254–9261 (2015).
58. Ferrari, A. C. et al. Raman spectrum of graphene and graphene layers. *Phys. Rev. Lett.* **97**, 187401 (2006).
59. Buglione, L., Chng, E. L. K., Ambrosi, A., Sofer, Z. & Pumera, M. Graphene materials preparation methods have dramatic influence upon their capacitance. *Electrochem. Commun.* **14**, 5–8 (2012).
60. Fuchs, K. The conductivity of thin metallic films according to the electron theory of metals. *Math. Proc. Camb. Philos. Soc.* **34**, 100–108 (1938).

61. Namba, Y. Resistivity and temperature coefficient of thin metal films with rough surface. *Jpn. J. Appl. Phys.* **9**, 1326–8 (1970).
62. Zhou, T. J., Zheng, P. Y., Pandey, S. C., Sundararaman, R. & Gall, D. The electrical resistivity of rough thin films: a model based on electron reflection at discrete step edges. *J. Appl. Phys.* **123**, 155107 (2018).
63. Gabbett C. et al. Understanding how junction resistances impact the conduction mechanism in nano-networks. *Nat. Commun.* **15**, 4517 (2024)
64. Kim, J. et al. All-solution-processed van der Waals heterostructures for wafer-scale electronics. *Adv. Mater.* **34**, e2106110 (2022).
65. Neilson, J., Cataldi, P. & Derby, B. Graphene-based transparent flexible strain gauges with tunable sensitivity and strain range. *ACS Appl. Nano Mater.* **6**, 21763–21774 (2023).
66. Tripathi, S. K., Kumar, M. & Kumar, A. Graphene based tunable and wideband terahertz antenna for wireless network communication. *Wirel. Netw.* **25**, 4371–4381 (2019).
67. Wei, Q. et al. Superhigh electromagnetic interference shielding of ultrathin aligned pristine graphene nanosheets film. *Adv. Mater.* **32**, e1907411 (2020).
68. Carey, T. et al. High-mobility flexible transistors with low-temperature solution-processed tungsten dichalcogenides. *ACS Nano* **17**, 2912–2922 (2023).
69. Lee, K. et al. Highly conductive and long-term stable films from liquid-phase exfoliated platinum diselenide. *J. Mater. Chem. C.* **11**, 593–599 (2023).
70. Shcherbakov, A. et al. Solution-processed NiPS₃ thin films from liquid exfoliated inks with long-lived spin-entangled excitons. *ACS Nano* **17**, 10423–10430 (2023).

Acknowledgements

We acknowledge the European Commission through the HORIZON-CL4-2023-DIGITAL-EMERGING-01-CNECT project 2D-PRINTABLE (GA-101135196). We have also received support from the Science Foundation Ireland (SFI) funded centre AMBER (SFI/12/RC/2278_P2) and availed of the facilities of the SFI-funded AML and ARL labs. K.S. acknowledges financial support by the Deutsche Forschungsgemeinschaft (DFG) through SY 217/2-1 and CRC-1415 - 417590517 and Professor Xinliang Feng for granting access to his laboratory and instrumentation.

Author contributions

J.M. and T.C. performed electrochemical exfoliation and Raman measurements, K.S. designed and refined the setup and performed centrifugation-based size selection and did AFM analysis. O.C. and K.S.

performed deposition experiments, did transmission scans, performed extinction measurements, analysed the data, and wrote the initial draft of the manuscript. O.C. programmed python routines. C.G., L.D., O.C., and K.S. performed SEM measurements, performed and evaluated electrical measurements. C.G., L.D., O.C., E.C., and K.S. evaluated and discussed transmission scans. K.S. and J.N.C. conceived the idea, led, oversaw the project, and finalized the manuscript.

Competing interests

The authors declare no competing interests.

Additional information

Supplementary information The online version contains supplementary material available at <https://doi.org/10.1038/s41699-025-00525-9>.

Correspondence and requests for materials should be addressed to Jonathan N. Coleman.

Reprints and permissions information is available at <http://www.nature.com/reprints>

Publisher's note Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.

Open Access This article is licensed under a Creative Commons Attribution-NonCommercial-NoDerivatives 4.0 International License, which permits any non-commercial use, sharing, distribution and reproduction in any medium or format, as long as you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons licence, and indicate if you modified the licensed material. You do not have permission under this licence to share adapted material derived from this article or parts of it. The images or other third party material in this article are included in the article's Creative Commons licence, unless indicated otherwise in a credit line to the material. If material is not included in the article's Creative Commons licence and your intended use is not permitted by statutory regulation or exceeds the permitted use, you will need to obtain permission directly from the copyright holder. To view a copy of this licence, visit <http://creativecommons.org/licenses/by-nc-nd/4.0/>.

© The Author(s) 2025