Morphological Characterisation of Printed Nanostructured Networks using High-resolution 3D FIB-SEM Nanotomography

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Abstract

Networks of solution-processed nanomaterials are becoming increasingly important across applications in electronics, sensing and energy storage/generation. Although the physical properties of these devices are often completely dominated by network morphology, the network structure itself remains difficult to interrogate. Here, we utilise FIB-SEM nanotomography to quantitatively characterise the morphology of nanostructured networks and their devices using nanometre-resolution 3D images. The influence of nanosheet/nanowire size on network structure in printed films of graphene, WS$_2$ and silver nanosheets, as well as networks of silver nanowires, is investigated. We present a comprehensive toolkit to extract morphological characteristics including network porosity, tortuosity, specific surface area, pore dimensions and nanosheet orientation, which we link to network resistivity. By extending this technique to interrogate the structure and interfaces within vertical printed heterostacks, we demonstrate the potential of this technique for device characterisation and optimisation.

Introduction

Liquid-deposited networks of 0D nanoparticles, 1D nanowires or nanotubes and 2D nanosheets have shown great promise across emerging applications in printed electronics$^{1-3}$, sensing$^4$, catalysis$^5$ and energy storage$^6$. In particular, devices based on networks of 2D materials have been the subject of intensive research due to the electronic diversity of such materials$^7$, as well as recent advances in both scalable nanosheet production and deposition techniques$^8$. An array of devices based on printed nanosheet networks have been demonstrated including transistors$^9$, capacitors$^{10}$, photodetectors$^{11}$, sensors$^{12}$ and supercapacitors$^{13}$. However, it has become clear that the performance of such devices is almost always limited by network morphology$^{14}$.

Printed 2D networks tend to consist of porous, disordered arrays of nanosheets with variable degrees of connectivity, alignment, and inter-sheet coupling. These morphological factors have been shown to heavily influence carrier mobility in nanosheet devices, where printed networks of poorly-aligned MoS$_2$ nanosheets$^{15}$ demonstrate values of $\sim 0.1 \text{ cm}^2.\text{V}^{-1}.\text{s}^{-1}$, but spin-coated networks of conformally tiled nanosheets$^{16}$ exhibit mobilities of $\sim 10 \text{ cm}^2.\text{V}^{-1}.\text{s}^{-1}$. In printed 2D capacitors and transistors the morphological tailoring of dielectric layers is crucial to ensure spatial continuity and prevent interlayer electrical shorting$^{17}$. Alternatively, network porosity and pore tortuosity determine the degree of accessible nanosheet surface area for sensing or catalysis$^{18,19}$, as well as electrolyte infiltration and ion kinetics in battery and supercapacitor electrodes$^{20}$. Despite the fundamental role morphology plays in maximising the physical properties of such solution-processed devices, optimising their performance remains limited by the lack of morphological characterisation.

While standard techniques such as mercury intrusion porosimetry (MIP) and N$_2$ BET analysis have been used to determine the pore-size-distribution and specific surface area in thick nanosheet networks$^{21}$, such methods require prohibitively large sample volumes (i.e. thick films), and considerable sample
preparation\textsuperscript{22}. Alternatively, AFM and SEM only provide surface information, although SEM can also analyse cross-sections. While 3D-imaging would be optimal, X-ray computed tomography (X-ray CT) is resolution-limited by voxel sizes of 30–500 nm\textsuperscript{23,24}, which are not sufficient to quantify the structure of nanomaterial networks\textsuperscript{25,26}. Crucially, no single technique allows a complete, direct, and simultaneous characterisation of both nanosheets and pores at present.

Here, we present FIB-SEM nanotomography (FIB-SEM-NT)\textsuperscript{27} as a viable means to interrogate the morphology of nanostructured networks with unprecedented resolution. We report 3D-imaging with a voxel size of 5 nm \(\cdot\) 5 nm \(\cdot\) 15 nm and demonstrate a suite of techniques to extract quantitative morphological information from these images. We apply FIB-SEM-NT to characterise network structure in printed graphene, WS\textsubscript{2} and silver nanosheet films, as well as silver nanowire networks, finding the morphological properties to scale with nanosheet or nanowire dimension. We extend this analysis to compare printed networks of graphene nanosheets produced using electrochemical and liquid phase exfoliation, and to quantitatively analyse interfaces within printed vertical heterostacks. Finally, we demonstrate a machine-learning protocol to further enhance resolution in FIB-SEM-NT produced 3D volumes by generating intermediate network images and cubic voxels.

**Results And Discussion**

**3D-imaging using FIB-SEM Nanotomography**

Liquid phase exfoliation (LPE) yields suspensions of nanosheets in various solvents (Fig. 1A) which can then be printed into networks\textsuperscript{28,29}. Conventional surface and cross-sectional SEM imaging of a spray-cast graphene nanosheet network (nanosheet length, \(l_{NS} = 695\) nm, Fig. 1B) allows qualitative observations of network porosity or nanosheet alignment. However, it is difficult to extract quantitative information. Here, we use FIB-SEM-NT to produce a high-resolution 3D reconstruction of portions of the network, which we refer to as 3D-imaging. To achieve this (Fig. 1C), \(\sim 800\) network cross-sections were sequentially milled using the FIB and imaged using the SEM (see Supplementary Information, SI). Each network slice has an in-plane pixel size of 5 nm and average thickness of \(\sim 15\) nm, giving a voxel size of \(\sim 375\) nm\textsuperscript{3}, 10–1000 times smaller than conventional X-ray CT scanners\textsuperscript{30,31}.

To enable quantitative analysis, each image in the stack was classified into its pore and nanosheet components using trainable WEKA segmentation\textsuperscript{32} (see SI). As shown in Fig. 1D, regions of each slice were first manually assigned as either nanosheet or pore, providing training data for the classifier. Each slice was then segmented into these components on a pixel-by-pixel basis and converted to a binary image containing only nanosheets or pores. These segmented image stacks were then aligned and interpolated in Dragonfly (see SI) to form a 3D network reconstruction (Fig. 1E). A typical network volume of 20 \(\mu m \cdot 15\) \(\mu m \cdot 2\) \(\mu m\) contains \(\sim 1.6 \cdot 10^{9}\) voxels. This allows the morphological properties of the network to be analysed on a voxel-by-voxel basis at a resolution that preserves the discrete nanosheet and pore components, as shown in for the printed LPE graphene network (\(l_{NS} = 695\) nm) in Fig. 1E.
Analysing 3D-images of nanosheet networks

A printed graphene network ($l_{NS} = 238$ nm) that has been split into its pore and nanosheet volumes is shown in Fig. 2A. The network porosity, $P$, was measured both across the entire volume and on a slice-by-slice basis (Fig. 2B and SI)$^{33,34}$. While the global porosity was calculated to be $41 \pm 1\%$, the scatter in the slice-by-slice data highlights the local inhomogeneity of the network.

Pore connectivity is a key parameter that determines the accessible surface area in sensing or electrochemical applications$^{35,36}$. The pore volume in Fig. 2A was found to be highly contiguous, consistent with MIP/BET data for filtered graphene networks$^{21}$, with $>99\%$ of the total pore volume contained in a single macropore spanning the network. Measurements across different regions of the 3D volume revealed a connectivity length-scale of $\sim 251$ nm, which represents the required depth in the imaging ($z$) direction for discrete pores to coalesce into a highly-connected pore volume (see SI)$^{34}$. To quantitatively assess the pore and nanosheet connectivity we calculated the tortuosity factor$^{37}$, $\kappa$, by determining the reduction of diffusive flux through each network in the in-plane (IP, $x$, $z$) and out-of-plane (OOP, $y$) directions using TauFactor$^{33}$ (Fig. 2C). A tortuosity factor of $\kappa = 1$ represents an unobstructed path through the pore/nanosheet volume in a given direction, while values $>1$ arise from a convolution of the network structure. Bottlenecks in the diffusive flux through the pore volume are shown visually in Fig. 2C. The comparatively smaller nanosheet $\kappa$-values are reflective of a well-connected nanosheet network while $\kappa_{OOP}/\kappa_{IP} > 1$ suggests that the nanosheets are primarily aligned in-plane. This is consistent with directional anisotropies in conductivity and mass transport through solution-processed 2D networks$^{38}$.

Because the pore volume is highly connected, we analyse the cross-sectional area and shape of 2D pore sections in each slice (see SI). The pore circularity, $C$, is plotted as a function of pore cross-sectional area, $A$, for each pore in the network in Fig. 2D, where $C = 4\pi A / \text{(perimeter)}^2$. Here, a value of $C = 1$ represents a circular pore cross-section while smaller values correspond to more irregular and elongated pores. The area-weighted heat map suggests that the pore volume is dominated by pore chambers with cross-sectional areas $>10^4$ nm$^2$, and that larger pores have elongated geometries, consistent with published BET measurements$^{21}$.

It is well-reported that solution-processed nanosheets tend to restack during deposition$^{39}$. We determined the degree and nature of this restacking by measuring the nanosheet length and thickness in the ink ($l_{NS}, t_{NS}$) using AFM, as well as the aggregated nanosheet dimensions ($l_{Net}, t_{Net}$) in the network post-deposition. The restacked nanosheet length and thickness were measured from network cross-sections using the Ridge Detection plugin in FIJI$^{34,40}$ (Fig. 2E, Inset and SI). We define the aggregation factors in nanosheet length, $\chi_l$, and thickness, $\chi_t$, as $\chi_l = l_{Net}/l_{NS}$ and $\chi_t = t_{Net}/t_{NS}$ respectively. Interestingly, we find values of $\chi_l \sim 1.5$ and $\chi_t \sim 6.9$ for the printed LPE graphene network in Fig. 2E. This is in
agreement with a value of $\chi_t \sim 5$ reported for vacuum filtered WS$_2$ networks$^{41}$, and suggests that nanosheets primarily aggregate through vertical restacking with maximised basal plane overlap.

By isolating discrete nanoplatelets and noting their orientation (Fig. 2F, Inset and SI)$^{42}$, the distribution of angles, $\varphi$, between each nanoplatelet’s normal vector and the out-of-plane ($y$) direction was calculated. The data in Fig. 2F was fit with a Cauchy-Lorentz distribution centred on $\varphi_C \sim -0.6^\circ$, which suggests the nanosheets are primarily aligned in the plane of the film. The full width at half maximum (FWHM) of the distribution provides an estimate of the degree of alignment about $\varphi_c$ in the network$^{43}$. The FWHM of 29 ± 1° for the spray cast network in Fig. 2F is comparable to a value of 21° for an inkjet printed graphene film measured using AFM$^{28}$. In addition, we measured the Hermans orientation factor$^{44}$, $S = \left(3 \left(\cos^2 \varphi \right) - 1 \right) / 2$, to be 0.61 ± 0.07 for the network, which is consistent with partial in-plane alignment. A value of $S = 1$ would imply the nanosheets are perfectly aligned in the plane of the film, while $S = 0$ for randomly oriented nanosheets. This is in broad agreement with a value of $S = 0.79$ for a vacuum filtered Ti$_3$C$_2$T$_x$ nanosheet network measured using wide angle X-ray scattering (WAXS)$^{23}$.

**Characterising size-dependent morphology**

The physical properties of 2D networks are known to scale with nanosheet size$^{45,46}$. Here, we use FIB-SEM-NT to systematically study the morphology of LPE graphene networks for various nanosheet lengths, $l_{NS}$. Size-selected inks were produced using liquid cascade centrifugation$^{47}$, characterised by AFM (Fig. 3A) and sprayed into networks. Reconstructed 3D volumes for networks of two different nanosheet sizes (Fig. 3B) show noticeable changes in network morphology as $l_{NS}$ is decreased from 1087 to 298 nm. Analysis reveals a clear decrease in network porosity from 51 to 39% with decreasing $l_{NS}$ (Fig. 3C), with a corresponding reduction in the characteristic pore size, $\zeta = \sqrt{A}$, in Fig. 3D. The pore circularity data similarly exhibits a dependence on $l_{NS}$ (Fig. 3E), where networks of smaller nanosheets have more circular and compact pore cross-sections. This implies that printed networks comprised of smaller nanosheets are more densely packed, which has been linked to improved charge transfer in graphene films$^{48}$. Alternatively, networks of larger nanosheets are more open and porous, facilitating enhanced electrolyte infiltration and mass transport. Taken together, the data in Fig. 3C-E suggests that changing the nanosheet size offers a simple means to tailor the network porosity for a target application.

The dependence of network morphology on $l_{NS}$ is further reflected in the specific surface area (SSA) of the networks (Fig. 4A), which decreased from 23 to 15 m$^2$.g$^{-1}$ as $l_{NS}$ increased from 80 to 1087 nm. This is consistent with expectations that SSA scales inversely with nanosheet thickness$^{49}$, $t_{NS}$, given $t_{NS}$ and $l_{NS}$ are intrinsically coupled for LPE$^{50}$, and agrees with a value of 25 m$^2$.g$^{-1}$ for V$_2$O$_5$ nanosheet films measured using BET$^{51}$. Such low values of SSA (cf. 2600 m$^2$.g$^{-1}$ for graphene monolayers$^{52}$) are often attributed to restacking during deposition$^{53}$. By comparing the dimensions of the aggregated nanosheets in each network ($t_{Net}$, $l_{Net}$) to the dimensions measured by AFM in the inks ($l_{NS}$, $t_{NS}$), we quantified the degree of aggregation in length, $\chi_l$, and thickness, $\chi_t$, as a function of $l_{NS}$ (Fig. 4B). In each network $\chi_t$ was
considerably larger than $\chi_l$. This suggests the dominant aggregation mechanism during processing is vertical restacking of the nanosheets, with an increase in aggregation observed for smaller nanosheets in Fig. 4B.

The tortuosity factor, $\kappa$, of both the pore and nanosheet volumes is plotted as a function of $l_{NS}$ in Fig. 4C. Both the nanosheet and pore tortuosities are significantly larger in the out-of-plane ($y$) direction due to nanosheet in-plane alignment. Interestingly, while the pore volume was found to become less tortuous with increasing $l_{NS}$, the nanosheet network exhibited the opposite trend, implying improved network connectivity for smaller nanosheets. This is because the tortuosity of a given network is known to scale with the fractional volume occupied by that network$^{54}$. This leads to a well-defined relationship between tortuosity and network volume fraction ($V_f$) for both pore ($V_{f,p}$=$P$) and nanosheet ($V_{f,NS}$=$1-P$) networks in Fig. 4D. The data follow an adjusted Bruggeman relation$^{55}$, $\kappa = \alpha V_f^{1-\beta}$. The extracted exponents for pores ($\beta_{IP} = 3.3$ and $\beta_{OOP} = 5.6$) and nanosheets ($\beta_{IP} = 1.9$ and $\beta_{OOP} = 2.5$) are considerably larger than values of 1.5 predicted by basic models$^{54}$. However, experimentally measured exponents$^{56}$ are usually > 1.5, with values of $\beta = 2–5$ predicted for high-aspect ratio particles$^{57}$.

To characterise the nanosheet orientation with changing nanosheet size, we calculated the Hermans orientation factor, $S$, finding values of 0.54 to 0.7 (Fig. 4E), again implying in-plane nanosheet alignment. This is in agreement with values of $S = 0.67–0.87$ reported for vacuum filtered graphene oxide (GO) networks measured using small-angle X-ray scattering (SAXS)$^{58}$. Interestingly, the orientation factor appears to increase with increasing nanosheet length, $l_{NS}$ (Fig. 4E). This contrasts with solution-processed GO networks, where increased aspect ratios are known to drive improved alignment$^{43,45}$. However, LPE nanosheets are comparatively smaller with roughly constant aspect ratios driven by nanosheet mechanics$^{50}$. Thus, we propose that smaller, thinner nanosheets conform to each other more easily$^{59}$, leading to a reduction in network porosity while increasing the angular dispersion.

The network morphology should strongly impact electrical properties. As shown in the SI, the in-plane resistivity of a nanosheet network, $\rho_{IP}$, is dependent on $P$, $l_{NS}$ and $\kappa_{IP}$, as well as the junction resistance, $R_J$, nanosheet resistivity, $\rho_{NS}$, and aspect ratio, $k_{NS}$:

$$\rho_{IP} \approx \frac{\rho_{NS} + (R_J l_{NS}/k_{NS})}{(1-P)/\kappa_{IP}}$$  

Eq. 1

We measured the network resistivity as a function of $l_{NS}$, with the data plotted in a linearized form in Fig. 4F. We find a very good straight line fit and reasonable values$^{14}$ of $R_J \sim 3 \, k\Omega$ and $\rho_{NS} \sim 31 \, \mu\Omega \cdot m$, highlighting the dependence of network resistivity on morphological factors. This demonstrates that the structure and effective mobility of a network can be tuned by changing the size of its constituent nanosheets. Furthermore, we show in the SI that the specific contact resistivity of the printed networks decreases as $l_{NS}$ is reduced and the nanosheet volume fraction increases. Crucially, these morphological
changes can be quantitatively measured using FIB-SEM-NT, opening a rich parameter space for device characterisation and optimisation.

**Versatility of 3D-imaging**

FIB-SEM nanotomography is a general method to analyse nanoscale networks. To show this, we 3D-imaged printed networks of WS$_2$ nanosheets, silver nanosheets (AgNS) and silver nanowires (AgNWs) (Fig. 5A-C). These images yield unprecedented insights into the structure of these networks. While there are distinct morphological differences between these systems, there are also similarities. Increasing the nanosheet/nanowire length caused the network porosity and pore tortuosity to increase and decrease respectively (Fig. 5D-F), similar to the printed graphene networks. However, the magnitude of the porosity change was somewhat smaller for AgNS than in WS$_2$ (or graphene) networks. These differences in porosity scaling with $l_{NS}$ (see SI) suggest that there are material-dependent factors contributing to the network morphology. Indeed, while the ratio of $(\kappa_{OOP}/\kappa_{IP})$ for nanosheets in the AgNS and WS$_2$ networks was found to be $\sim 1.5$ and $\sim 2.5$ respectively, inferring considerable in-plane alignment, they are each different from the value of $\sim 2.9$ found for graphene networks (see SI). Interestingly, the aligned restacking previously discussed for graphene can clearly be seen in AgNS networks, where vertical stacks of 3–7 AgNS are visible (Fig. 5B, Inset). A similar effect can be inferred for the WS$_2$ nanosheets (see SI).

The 3D-image of the AgNW network (Fig. 5C) allows AgNWs to be resolved both as isolated 1D objects and within small bundles. This highlights the resolution advantage of FIB-SEM-NT, as the AgNW diameter of $\sim 55$ nm is smaller than the pixel size for many X-ray CT techniques. As with the nanosheet data, the porosity of an AgNW network is seen to increase with increasing AgNW length in a manner consistent with a modified version of a reported model (Fig. 5F). The nanowire $(\kappa_{OOP}/\kappa_{IP})$ ratio of $\sim 12$ in the AgNW networks is driven by the considerably higher porosities of $P = 82–91\%$.

**Characterising electrical and device properties**

It has been reported that networks of electrochemically exfoliated (EE) nanosheets display much higher mobility than their LPE counterparts for reasons of morphology. Here, we utilise FIB-SEM-NT to investigate the morphological differences between EE ($t_{NS} = 4$ nm) and LPE graphene nanosheet ($t_{NS} = 20$ nm) networks deposited under identical conditions. 3D-imaging reveals significant differences in the network porosity, $P$, and in-plane tortuosity factor of the nanosheets, $\kappa_{IP}$, while electrical measurements show the EE network to be $\sim 6$ times more conductive (Fig. 6A). Combining the values in Fig. 6A with Eq. 1 (using $t_{NS} = l_{NS}/\kappa_{NS}$) and approximating these networks as purely junction limited ($R_J >> R_{NS} = \rho_{NS}/t_{NS}$), implies $R_J$ in these EE and LPE networks to be very similar. This means that against expectations, the conductivity disparity in this case is predominately due to the nanosheet thickness difference rather than morphological factors ($P$, $\kappa_{IP}$ and $R_J$). By reconstructing the surface topography of both networks (Fig. 6A and SI) we measured the root mean square roughness, $R_{RMS}$, of the EE and LPE networks to be $\sim 122$ nm and $\sim 182$ nm respectively. The reduced surface roughness in such printed EE networks will improve the interface quality in vertically stacked devices.
To highlight the importance of network morphology in vertically stacked devices, LPE graphene networks of two different nanosheet lengths ($l_{NS} = 630$ nm and $215$ nm) were coated with silver nanoparticles (AgNP, diameter ~ 50 nm), mimicking top electrode deposition. 3D-imaging (Fig. 6B) could resolve individual nanoparticles, and by removing the nanosheet layer the incorporation of AgNPs into each network was assessed. Isolated silver nanoparticles were found to have penetrated ~ 1.3 µm into the network of larger nanosheets ($l_{NS} = 630$ nm), with connectivity analysis revealing a percolating AgNP path that reached ~ 725 nm into the layer. However, virtually no AgNP penetration was found in the network of smaller nanosheets ($l_{NS} = 215$ nm). This aligns with the data in Fig. 3C-D and Fig. 4D, which shows networks of smaller nanosheets to be more densely packed with more tortuous pore volumes. To interrogate the AgNP/graphene interface, we measured their respective volume fractions as a function of depth in the out-of-plane ($y$) direction from the top surface of each heterostack (Fig. 6B and SI). By using smaller nanosheets in printed LPE networks, the degree of interlayer penetration can be dramatically reduced, avoiding electrical shorting and leading to improved performance in printed transistors and capacitors$^{63,64}$.

Moreover, this technique can be used to 3D-image complex devices, differentiating various components. Shown in Fig. 6C is a 3D-image of an ITO/Glass/WS$_2$/evaporated-Au vertical heterostack. Four-way segmentation allowed this device to be separated into its discrete layers to enable analysis of the internal nanostructure. By removing the WS$_2$ nanosheets and pores, we could visualise the relationship between substrate and gold, identifying electrical shorts between top and bottom electrodes. Also, discrete device layers like the Au top electrode can be isolated and analysed individually (Fig. 6C). Here, the roughness of the underlying WS$_2$ network has caused holes to form leading to a poor-quality gold film, as reflected by $\kappa_{IP} = 1.8$, implying electrode resistances roughly double what might be expected.

In this work, experimental constraints limit us to non-cubic (5 nm $\cdot$ 5 nm $\cdot$ 15 nm) voxels, which limits resolution and hinders analysis. Although one can produce cubic voxels by linear interpolation between adjacent frames$^{65}$, this yields image elements with blurred edges. Faced with similar problems, the computer-vision community utilise neural networks, such as DAIN$^{66}$. These algorithms, usually trained on the Vimeo90K dataset$^{67}$, generate additional frames between consecutive images, increasing the resolution along the time direction. Here, this strategy can improve the resolution along the cutting direction of FIB-SEM-NT data by introducing intermediate slices between imaged cross-sections. To test this approach, frames were removed from one image stack and replaced by images generated by DAIN. These can then be compared to the removed ground-truth frames, as displayed in Fig. 7A-C. We find extremely good agreement, showing that neural-network based approaches can be used to further enhance resolution in FIB-SEM-NT generated 3D images.

**Discussion**

In summary, 3D-imaging using FIB-SEM-NT allows the morphology of nanostructured networks to be quantitatively characterised with nanometre-resolution. This approach is versatile and can be applied to
both conducting and semiconducting networks of 1D and 2D nanomaterials. We demonstrate the
eXtraction of important morphological parameters from these 3D-images and have applied this to
systematically study the influence of nanosheet/nanowire dimensions on network structure. In addition,
multi-phase segmentation allows FIB-SEM-NT to be extended to heterostacks and devices, where discrete
layers and their interfaces have been analysed. We believe this technique will be an important tool to
investigate and optimise a range of nano-enabled devices for emerging applications.

Methods

Ink Preparation

Nanosheet inks were prepared using liquid phase exfoliation (LPE). Graphite powder (Asbury, Grade
3763) was first sonicated in 80 ml of deionised (DI) water (18.2 MΩ.cm) at a concentration of 35 mg.ml⁻¹
for 1 hour. A horn probe sonic tip (Sonics Vibra-cell VCX-750 ultrasonic processor) at 55% amplitude,
with a pulse rate of 6 s on 2 s off was used. The resulting dispersion was centrifuged for 1 hour at 4900
rpm (Hettich Mikro 220R) to remove potential contaminants from the starting powder. The supernantant
was decanted and the sediment redispersed in 80 ml of DI and sodium cholate (SC, Sigma Aldrich, > 99%)
at a concentration of 2 mg.ml⁻¹. This was sonicated for 8 hours at an amplitude of 55% with a 4s on 4s
off pulse rate. The resulting polydispersion was separated into inks of different nanosheet sizes using
liquid cascade centrifugation. An initial centrifugation step at 500 rpm for 2 hours was used to isolate
unexfoliated material in the sediment. The supernatant was then subjected to additional centrifugation
steps at 1000, 1500, 2000, 2500 and 4000 rpm, retaining the sediment at each interval to isolate
nanosheet fractions of different sizes. In each case the sediment was redispersed in a 2 mg.ml⁻¹ DI:SC
solution. The redispersed 1000 rpm ink was subjected to a further centrifugation step at 500 rpm for 1
hour to separate it into two size fractions. Each ink was then transferred to isopropanol (IPA, Sigma
Aldrich, HPLC grade) for spray coating. To remove the sodium cholate, each dispersion was centrifuged
for 2 hours at 6000 rpm. The supernatant was discarded, and the sediment redispersed in IPA. This step
was repeated twice. WS₂ inks were produced in a similar manner, however, the sonication of bulk powder
(Alfa Aesar, 10–20 µm, 99.8%) was carried out in IPA. The size-selected inks were produced by
centrifugation steps at 1000, 1500, 2000 and 6000 rpm.

To facilitate the LPE vs. electrochemical exfoliation (EE) comparison, graphite powder was solvent
exfoliated in N-Methyl-2-pyrrolidone (NMP, Sigma Aldrich, HPLC grade) with a cleaning step as described
above. The sediment was then redispersed in fresh NMP and exfoliated for 9 hours at an amplitude of
55% with a 4s on 4s off pulse rate. The produced dispersion was centrifuged at 2000 rpm for 2 hours to
remove unexfoliated material and the supernatant was centrifuged at 4000 rpm for a further 2 hours. The
resulting sediment was transferred to IPA as described above to produce the LPE ink. To prepare the ink
of electrochemically exfoliated graphene nanosheets, two pieces of graphite foil (Alfa Aesar, 254 µm
thick, 99.8% metals basis) with dimensions 50 × 30 × 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 (Alfa
Aesar, > 98%) with a separation of 2 cm. A potential of 10 V was applied to the electrodes for 30 minutes, with a current that increased from ~1 to ~1.8 A during the process. The resulting expanded material in electrolyte solution was filtered and repeatedly washed with DI water (~1 L). This was then bath sonicated (Thermo Fisher Scientific, FB11201, 37 kHz) in 100 ml of dimethylformamide (DMF, Sigma Aldrich, HPLC grade) for 10 minutes to complete the exfoliation into a dispersion of graphene nanosheets. The resulting ink was centrifuged at 3000 rpm for 20 minutes to remove incompletely exfoliated particles. The EE graphene sheets were then transferred to IPA for deposition.

Size-selected silver nanosheet (AgNS) inks were produced by diluting the purchased dispersion (Tokusen Nano, N300, lNS ∼ 300–500 nm) in DI water to a concentration of 100 mg.ml⁻¹. This stock dispersion was then centrifuged at 500, 1000, 2000 and 6000 rpm in 5 minute steps. The sediment of the 1000, 2000 and 6000 rpm steps was collected and redispersed in fresh DI water. The purchased silver nanowires (AgNW, Novarials, A60, ∼ 60 nm diameter) were diluted in IPA to a concentration of 0.5 mg.ml⁻¹. The AgNW length was controlled by sonication induced scission of the wires using a sonic bath (Thermo Fisher Scientific, FB11201, 37 kHz). Size-selected inks were produced by sonication of the diluted dispersion for 0, 1 and 2 hours respectively.

**Ink & Nanosheet Characterisation**

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, WS₂ and AgNS inks. Measurements were performed in air under ambient conditions using aluminium coated silicon cantilevers (OLTESPA-R3). The inks were diluted to optical densities < 0.1 at 300 nm in IPA and a drop of dispersion (15 µl) was flash evaporated on pre-heated (175°C) Si/SiO₂ wafers. After deposition, the wafers were rinsed with ~15 ml of DI water and ~15 ml of IPA and dried with compressed nitrogen. Typical image sizes ranged from 10 × 10 µm² for larger nanosheets to 3 × 3 µm² for small nanosheets at scan rates of 0.5–0.8 Hz with 1024 lines per image. Previously published length corrections were used to correct lateral dimensions from cantilever broadening. Bright-field transmission electron microscopy (TEM) was performed using a JEOL 2100 LaB6 system operating at 200 kV. Samples were diluted to a suitable optical density in IPA and drop cast onto holey carbon grids (Agar Scientific) on filter membranes to absorb excess solvent. The grids were left to dry in air and then placed overnight in a vacuum oven at 70°C before measuring. UV-Vis optical spectroscopy (Perkin Elmer 1050 spectrophotometer) was performed to determine the graphene and WS₂ ink concentrations post-transfer using previously developed metrics. Inks were diluted to a suitable optical density and extinction spectra were recorded in 1 nm increments using a 4 mm quartz cuvette. The concentration of the size-selected AgNS inks was found by vacuum filtration of a known volume of ink onto an alumina membrane (Whatman Anodisc, 0.02 µm pore size) and weighing. AgNW lengths were determined by drop casting 300 µl of ink, diluted to a concentration of 0.01 mg.ml⁻¹, onto Au-coated Si/SiO₂ heated to 150°C and measured from SEM images.

**Network Deposition**
Nanomaterial inks were spray coated using a Harder and Steenbeck Infinity Airbrush attached to a Janome JR2300N mobile gantry. A N₂ back pressure of 45 psi, nozzle diameter of 0.4 mm and stand-off distance of 100 mm between the nozzle and substrate were used. All traces were patterned using stainless-steel masks while the substrate was heated to 80°C using a hotplate. The size-selected LPE graphene inks were sprayed at a concentration of 0.2 mg.ml⁻¹ onto ultrasonically cleaned glass slides with prepatterned gold electrodes (Temescal FC2000 metal evaporation system) to facilitate electrical measurements. Each trace was annealed overnight under vacuum at 80°C to remove residual solvent. Electrochemically exfoliated graphene inks were deposited using identical parameters but were annealed for 2 hours at 500°C in a glovebox. WS₂ inks were spray coated at a concentration of 0.5 mg.ml⁻¹. For the ITO:glass/WS₂/Au heterostack, a WS₂ ink was spray coated onto a purchased ITO:glass substrate (Ossila, 100 nm thick ITO, 20 Ω.□⁻¹) and a 100 nm gold top electrode was deposited using a Temescal FC2000 system. The AgNS inks were deposited at a concentration of 10 mg.ml⁻¹ onto Al₂O₃-coated PET (Mitsubishi Paper Mills) with the hotplate heated to 100°C. AgNW inks were spray coated onto Si/SiO₂ substrates (MicroChemicals) at a concentration of 0.5 mg.ml⁻¹. The purchased silver nanoparticle dispersion (Sigma Aldrich, < 50 nm diameter, 30–35 wt % in methyltriglycol) was diluted to a concentration of 20 mg.ml⁻¹ and patterned using an aerosol jet printer (Optomec AJP300).

**Network Characterisation**

Electrical measurements were performed in ambient conditions using a Keithley 2612A source meter connected to a probe station. Two terminal measurements were used to measure the resistivity of the printed LPE graphene networks in the transmission line configuration. Four terminal measurements were used to measure the current-voltage characteristics of the printed graphene networks for the EE vs. LPE comparison. The thickness of the printed films was measured using a Bruker Dektak stylus profilometer (10 µm probe, 19.6 µN force). Scanning electron microscopy (SEM) of the network surfaces was performed using a Carl ZEISS Ultra Plus SEM at an accelerating voltage of 2 kV (5 mm working distance, 30 µm aperture, Inlens and SE2 detectors). FIB-SEM microscopy of network cross-sections was carried out using a dual beam Carl ZEISS Auriga system. All images were captured at a working distance of 5 mm with a 2 kV accelerating voltage and aperture size of 30 µm. FIB-SEM nanotomography was performed using ZEISS ATLAS 5 software (Version 5.3.3.31). All milling of network cross-sections was carried out using a 30 kV:600pA gallium ion beam.

**Image Processing and Analysis**

The generated image stacks for each network were aligned and reconstructed in 3D using Dragonfly (Version 2022.1.0.1231, Object Research Systems). Greyscale network cross-sections were segmented into their nanosheet and pore components using the Trainable WEKA Segmentation plugin in FIJI. Measurements of the network tortuosity, specific surface area and porosity were performed using Taufactor. Network porosity was also measured on a slice-by-slice basis using FIJI, which was again utilised to determine the pore size and circularity in each 2D cross-section. Isolated nanoplatelets in the reconstructed volumes were identified using a 3D Distance Transform Watershed and converted into
equivalent ellipsoids using the *MorphoLibJ plugin*\(^{42}\) in *FIJI*. Pore connectivity analysis was performed using the *Find Connected Regions* plugin in *FIJI*. The nanosheet thickness and length in each network cross-section was measured using the *Ridge Detection*\(^{40}\) plugin in *FIJI*.

**Declarations**

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References


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**Figures**
Figure 1

FIB-SEM Nanotomography of a Printed LPE Graphene Network

(A) Photo of a graphene dispersion and typical TEM image of a liquid-exfoliated nanosheet. (B) Representative surface and cross-sectional SEM images of a printed multilayer graphene nanosheet network (nanosheet length, $l_{NS} = 695$ nm). (C) Schematic of the slice-and-scan process. Network cross-sections are sequentially milled and imaged to produce a stack of 15 nm thick slices. (D) Image segmentation pipeline to classify a greyscale network cross-section into its nanosheet and pore components. (E) 3D reconstruction of a printed LPE graphene network generated using FIB-SEM-NT. Inset: Magnified region showing nanosheets and pores.
Figure 2

Quantitative Analysis of a Reconstructed LPE Graphene Network

(A) Portion of a 3D reconstruction of a printed graphene network ($l_{NS} = 238$ nm) separated into its pore and nanosheet contributions. (B) Porosity measurements for each slice in the network. The red line is the average porosity across the 3D volume. Inset: Histogram of slice porosity values. (C) Tortuosity factor measurements in the out-of-plane ($y$) and in-plane ($x,z$) directions for the nanosheet and pore volumes. Inset: Heat map of diffusive flux in the imaging ($z$) direction through the network. (D) Pore circularity, $C$, plotted as a function of cross-sectional area, $A$, for each pore chamber in the network. The contours denote the percentage of the total pore area contained within each band. (E) Nanosheet aggregation factor in both length, $\chi_l$, and thickness, $\chi_t$, during network deposition, where ($l_{NS}, t_{NS}$) are the nanosheet dimensions in the ink and ($l_{Net}, t_{Net}$) are the restacked nanosheet length and thickness in the network. Inset: Nanosheet dimensions measured from network cross-sections. Individual nanosheets are denoted by red contours, inter-sheet junctions by hollow circles, and the nanosheet thickness by green lines. (F) Distribution of angles ($\phi$) between the nanosheet normal vectors and the out-of-plane ($y$) direction in the network. The solid line is a fit to a Cauchy-Lorentz distribution centred on $\phi = -0.6^\circ$. Inset: Discrete 2D objects in the network isolated using a 3D distance transform watershed.
Fig. 3 Porosity in Printed Graphene Networks as a Function of Nanosheet Size
(A) Relationship between the mean nanosheet length, $l_{NS}$, and thickness, $t_{NS}$, for each size-selected 2D ink. (B) Reconstructed 3D volumes for printed networks comprised of large ($l_{NS} = 1087$ nm) and small ($l_{NS} = 298$ nm) LPE graphene nanosheets. (C) Plot of network porosity, $P$, as a function of $l_{NS}$. (D) Scaling of the mean pore size, $\zeta = \sqrt{A}$, in each network with $l_{NS}$, where $A$ is the average pore cross-sectional area. Inset: Pore identification and labelling in FJII. (E) Plot of the mean pore circularity, $C$, for each network as a function of $l_{NS}$.

Figure 3

See image above for figure legend.
Fig. 4 Morphology of Printed Graphene Networks as a Function of Nanosheet Size

(A) Network specific surface area plotted against $l_{NS}$ in $(\mu$m$^2$, $\mu$m$^{-3})$ and (m$^2$.g$^{-1}$) units. (B) Nanosheet aggregation factors in thickness, $\chi_t$, and length, $\chi_l$, post-deposition plotted as a function of nanosheet length. (C) Plot of the pore and nanosheet tortuosity factors in the out-of-plane ($\gamma$) and in-plane ($\kappa$, $\zeta$) directions against $l_{NS}$. (D) Plot of the pore and nanosheet tortuosity factors in each direction as a function of the volume fraction of pores (P) and nanosheets (1-P) respectively. The solid lines are fits to an adjusted Bruggeman relation described by $\kappa = \alpha P^{1-\beta}$ for the pore data and $\kappa = \alpha (1-P)^{1-\beta}$ for the nanosheets, where $\alpha$ is a prefactor and $\beta$ is the fitted Bruggeman exponent. (E) Hermans orientation factor, S, plotted as a function of nanosheet length for each network. (F) Plot of the morphologically scaled network resistivity $(\rho_{IP}(1-P)) / \kappa_{IP}$ against $l_{NS}$, where $\rho_{IP}$ is the in-plane electrical resistivity and $\kappa_{IP}$ is the in-plane tortuosity factor of the nanosheets. The straight line is a fit to Eqn. 1.

Figure 4

See image above for figure legend.
Figure 5

Morphological Characterisation of Materials Beyond Graphene

Reconstructed network volumes of printed (A) WS$_2$ nanosheets, (B) Silver nanosheets (AgNS) and (C) Silver nanowires (AgNWs). Inset: Representative FIB-SEM cross-sections for each material. (D-F) Plots of the network porosity and pore tortuosity factor as a function of nanosheet/nanowire length for the (D) WS$_2$, (E) AgNS and (F) AgNW networks. The solid line in (F) is the predicted porosity scaling with AgNW length$^{60}$, which we find to describe our data well when scaled by a prefactor of 0.94 (dashed line).
Figure 6

Characterisation of Electrochemically Exfoliated (EE) Graphene Networks, Vertical Heterostacks and Nanostructured Devices

(A) 3D reconstructions and surface topography of printed LPE and EE graphene networks to compare the network morphologies. (B) Printed graphene/silver nanoparticle stacks for two different nanosheet sizes ($l_{NS} = 215$ and $630$ nm) to characterise the degree of interlayer penetration with changing $l_{NS}$. The volume fraction of each phase is plotted as a function of depth in the out-of-plane ($y$) direction from the top surface of each heterostack. (C) A reconstructed Glass/ITO – WS$_2$ – Evaporated Au device segmented into its discrete layers. Removal of the WS$_2$ mid-layer allows vertical shorts through the WS$_2$ network to be identified. The Au electrode has been isolated to show the presence of holes in the layer.
**Figure 7**

**Computer Generated Intermediate Images**

(A) One of the ground-truth images removed from the original stack of FIB-SEM data for a printed LPE graphene network. (B) The correspondent image generated by the video frame interpolation algorithm DAIN\textsuperscript{66}. The scalebars represent the normalised pixel intensity in each image. (C) The intensity difference between the ground truth and DAIN generated images, where identical pixels have a value of zero (white). A positive (red) value indicates that pixels in the ground truth frame were brighter, while a negative (blue) value means the ground truth pixel was darker.

**Supplementary Files**

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