Mesoscale assembly of chemically modified graphene into complex cellular networks

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The widespread technological introduction of graphene beyond electronics rests on our ability to assemble this two-dimensional building block into three-dimensional structures for practical devices. To achieve this goal we need fabrication approaches that are able to provide an accurate control of chemistry and architecture from nano to macroscopic levels. Here, we describe a versatile technique to build ultralight (density $\leq 1 \text{mg cm}^{-3}$) cellular networks based on the use of soft templates and the controlled segregation of chemically modified graphene to liquid interfaces. These novel structures can be tuned for excellent conductivity; versatile mechanical response (elastic-brittle to elastomeric, reversible deformation, high energy absorption) and organic absorption capabilities (above 600 g per gram of material). The approach can be used to uncover the basic principles that will guide the design of practical devices that by combining unique mechanical and functional performance will generate new technological opportunities.

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A wide range of emergent technologies, from tissue engineering to energy storage or environmental cleaning demand strong, lightweight porous structures able to provide a wide range of functionalities such as support for cells or nanoparticles or high thermal or electrical conductivity. The engineering and scientific challenge is to design and fabricate these structures in practical dimensions while maintaining an accurate control of their chemistry and architecture from the nano-level and up. This is particularly difficult when using a material like carbon. Although its low density and versatility make it extremely appealing in many applications, its reactivity and hydrophobicity creates serious difficulties for most conventional processing techniques. In this respect carbon nanomaterials such as nanotubes or graphene have not only opened new opportunities but also new challenges. For example, graphene is a truly two-dimensional material with unique functional and mechanical properties from tunable electrical and optical response to high intrinsic stiffness and strength, chemical versatility, controllable permeability or extremely high specific surface area (2,630 m² g⁻¹) (refs 1–4). If properly integrated into macroscopic highly porous complex structures, graphene has the potential to form novel platforms for a wide range of functional systems from batteries to supercapacitors, reactive catalytic supports or filters and membranes to name a few5–7. However, to achieve this goal we need to develop ways for the controlled assembly of three-dimensional (3D) structures using a two-dimensional (2D) building block.

As the first reports on graphene 3D structures based on chemical vapour deposition coatings on metallic foams, different approaches based on freeze drying and subcritical drying⁸,⁹, leavening⁷, nucleation boiling¹⁰, hydrothermal processes¹¹,¹², hydrothermal carbonization¹³ or microwave irradiation¹⁴ have been used to fabricate porous 3D graphene and graphene-based networks. However, the challenge still remains on how to effectively tailor their chemistry and architecture for specific applications. Furthermore, structural design has to be based on a fundamental understanding of how architecture determines performance.

These challenges underline the need to develop more flexible and cost effective processing technologies that allow the manipulation of structure. In this respect, wet-processing approaches such as emulsion-based techniques are very appealing. They are well developed for a wide range of organic and inorganic materials and they are very attractive due to their flexibility, scalability and relative low cost¹⁵–¹⁷. Wet-processing with graphene still requires much research as it depends on an accurate control of surface chemistry and particle size to enable the formulation of suspensions with controlled rheological response. Here we show that the use of chemically modified graphene (CMG, namely graphene oxide, GO, and its reduced form rGO) opens many possibilities.

In this paper, we propose a self-assembly strategy for the fabrication of complex CMG cellular networks (CMG-CN)s via a multi-step soft/hard template mechanism that combines emulsion and ice templating. Our approach is based on controlling the segregation of CMG to liquid interfaces to use it both as an emulsifier and as a building block. Two key challenges are maintaining the stability of the structures and manipulating the properties of CMG such that they approach those of pristine graphene. To this purpose, a range of additives and thermal
Results

Assembling 3D CMG-CN wires with controlled architectures. The assembly strategy (Fig. 1e) is based on the preparation of oil-in-water (o/w) GO emulsions (GO-em), by the emulsification of water-based GO suspensions (GO-sus) with a hydrophobic (oil) phase. GO acts as a surface-active amphiphile self-assembling at the interface between the oil droplets and the water phase and stabilizing the GO-em for several months. The oil droplets template the formation of spherical- to polyhedral-shaped cells (Fig. 1a). The cell walls and the volume between cells are formed by an arrangement of CMG flakes (Fig. 1b,c). The challenge is to prepare stable emulsions with high oil content to fabricate highly porous materials while maintaining the stability of the network once the liquid phase is removed.

It has been previously shown that GO can act as a colloidal emulsifier with its interfacial activity being very dependent on pH due to its structural configuration of more hydrophobic basal plane and more hydrophilic plane edges. However, the use of emulsions to prepare porous materials requires enough GO segregation to the water–oil interface to create stable emulsions with high oil content and controllable droplet sizes in the low micrometre range and, at the same time, to achieve highly concentrated GO suspensions in water such that the structure withstands the capillary forces during solvent elimination. To this end, we have taken advantage of the pH-dependent interfacial activity of GO and have designed a two-step process. First, we prepare stable, highly concentrated GO suspensions in water at neutral pH to assure a high degree of deprotonated –OH and –COOH groups on the surface of GO and to achieve therefore a good dispersion. Just before emulsification, the suspension pH is adjusted between 2 and 3. At such acidic conditions, the oxygen functional groups on GO surface are less deprotonated. This reduces the hydrophilicity of the basal plane and the flakes preferentially segregate to the o/w interfaces (Supplementary Fig. 1). To enable more flexibility in the process, diverse organic additives can be used to enhance dispersion and emulsification ability.

With our approach we are able to homogeneously disperse high concentrations of GO in water (>10 mg mL⁻¹) and subsequently maximize the surface activity of the GO flakes (by means of suspension pH and/or additives) leading to stable emulsions with up to 75 vol% of the oil phase and droplet sizes in the low micrometre scale, one order of magnitude smaller than that previously reported for GO. The viscoelastic properties of the emulsions can be controlled by adjusting the concentration of GO in the continuous phase or the concentration of oil, allowing the fabrication of coatings or the extrusion of long wires that can be down to 200 μm in diameter (Fig. 2). This opens new opportunities for the fabrication of graphene-based complex structures at the macroscale. For example, this technique can be explored for the design of inks with rheological properties tailored for different wet-processing techniques to build structures with porosity determined by droplet size, shape and concentration in the emulsion.

To maintain the stability of the porous structure after removing the liquid phase while effectively manipulating the nano to micro architecture of the network, we use a combination of ice templating and freeze drying. After emulsification, the GO-em is directionally frozen and subsequently the solvents are eliminated by freeze drying (Fig. 1e). As directional freezing progresses, the growing ice crystals control the alignment of CMG in the water phase (and consequently the architecture of the triple junctions between adjacent cells (Fig. 1c)) and encapsulate the liquid oil droplets (as the oil solidification temperature is much lower than that of water). As the droplets are still ‘soft’ in the liquid phase, the roughness of the ice templates the formation of micro to nanorugosity on the CMG-CN cell walls (Fig. 1d).

In contrast to the lamellar structures resulted from the traditional freeze casting of aqueous suspensions here the structural evolution is more complex. The emulsion templates the formation of spherical to polyhedral cells to create a cellular network (Fig. 1a) with ice forming between the oil droplets. In the emulsions used to fabricate cellular networks the high concentration of oil droplets may impede the full formation of lamellar ice (as it has been observed with highly concentrated particle suspensions).

This processing approach can be used to form highly porous GO-CNs with densities ranging from 2 to 20 mg cm⁻³. The cell sizes are in the range 20–65 μm and the walls are formed by a complex arrangement of CMG (Fig. 1a–d). The cell size can be mainly controlled varying the amount and size of GO flakes and emulsification energy, whereas the density can be tuned through the amount of GO in suspension and oil concentration. Different organic additives (such as sucrose or polyvinyl alcohol (PVA)) can be added to further control the architecture and properties although it is possible to fabricate stable structures without the use of any additive. For example, PVA molecules adsorbed on the...
The component at 284.6 eV is due to the sp² carbon, the peak at 286.5 eV is related to the remaining C–O bonding and possible carbon sp³ defects. The full width at half maximum (FWHM) for the C1s core level is 1.253.6 eV, which indicates the presence of oxygen groups on the graphite surface. The Raman spectra (514 nm laser) and C1s XPS of rGO-CNs (prepared without and with organic additives (PVA:sucrose, 1:1 in wt%) are shown in Figure 3. The C1s XPS spectra (hν = 1,253.6 eV) collected on rGO-CN with 5 wt% additives is compared with rGO-CN without additives. The density of the rGO-CN is determined by the weight of the sample divided by its volume. The resulting density is 2.5–3.5 mg cm⁻³, which is higher than the density of amorphous carbon. The density of the rGO-CN with 5 wt% additives is 2.865 mg cm⁻³, which is higher than the density of amorphous carbon. The density of the rGO-CN with 5 wt% additives is 2.865 mg cm⁻³, which is higher than the density of amorphous carbon. The density of the rGO-CN with 5 wt% additives is 2.865 mg cm⁻³, which is higher than the density of amorphous carbon. The density of the rGO-CN with 5 wt% additives is 2.865 mg cm⁻³, which is higher than the density of amorphous carbon.
The Raman spectra of rGO-CNs confirm the formation of predominantly crystalline rGO upon thermal reduction (Figs 3e and 4e). Furthermore, the rGO-CNs produced with organic additives present a more pronounced 2D peak at around 1,700 cm⁻¹, than rGO-CN produced without any additive (Fig. 3e). This indicates that the presence of carbon (due to organic decomposition) during thermal reduction promotes the recrystallization of graphene.

XPS characterization reveals that the oxygen content is about 4% for rGO-CNs prepared initially with 5 wt% additives (in GO-sus) after reduction at 1,000 °C and progressively decreases for higher annealing temperatures. Interestingly, the sp² fraction of rGO-CNs produced with 5 wt% additives is slightly higher (82%) than for additive-free rGO-CNs (80%) as revealed by XPS (Fig. 3f). This further supports the Raman evidence that the presence of the organic additives as a carbon source favours restoration of sp² bonding.

Furthermore, the crystalline quality of CMG can be greatly improved with further treatments at temperatures above 1,000 °C.
Elastic fitting (red line) results in an exponent that is significantly lower (1.3) than those reported for other porous carbon structures (2.3–4.6) and the collapse stress (characteristic for lighter materials) and vacancies, suggesting that the sp² network has been restored comparable to mildly defected graphene with single and double layer CMG films. They open new possibilities for the fabrication of hierarchical 3D structures with a restored sp² network.

Mechanical behaviour and electrical conductivity of rGO-CNs. The mechanical response under compression reflects the range of architectures that can be fabricated using this approach. Their behaviour changes from elastomeric for the lighter materials to elastic-brittle for the denser rGO-CNs. In all cases, during the first compression cycle the structures exhibit first a predominantly linear elastic region that can be associated to cell wall bending and cell face stretching followed by a change in the slope of the strain stress curve akin to ‘yielding’ at strains typically in the range 10–30% (Fig. 6). ‘Yielding’ is typically associated to the collapse of the cells and the mechanisms depend on the density, with stresses that can be up to few MPa for denser materials (Fig. 6d).
As expected, the elastic modulus increases with the density as represented in Fig. 6c with other carbon-based materials\(^8,32-34\). Interestingly, an empirical power law fitting results in an exponent significantly lower than those reported for other materials in the literature and even lower than 2. The deviation from the quadratic dependence and the increased weight of the linear term when using a \(a r^2 + b r\) fitting (Fig. 6c) suggest that the networks behaviour is closer to closed-cell cellular structures where the membrane stresses have a significant contribution to the elastic modulus\(^31\). However, it has to be also noted that the measurement of the Young’s modulus in compression, particularly at very low loads, can be fraught with higher errors as evidenced by the higher deviation in modulus values for low-density materials.

Denser rGO-CNs (typically with densities above 10 mg cm\(^{-3}\)) or those that have been thermally treated at higher temperature reach a plateau after brittle collapse with visible micro-fracture events similar to those observed in the compression of elastic-brittle foams (Fig. 6b)\(^26,35\). However, and despite the micro-fractures, elastic-brittle networks can exhibit recoveries of up to 98% in the first compressive cycle after strains of 50%. This is similar to the behaviour of Ni microlattices that also exhibit damage and recovery during a compressive cycle\(^26\). The exceptions are the structures with densities \(>100\text{ mg cm}^{-3}\), which do not recover after compression that will be consistent with the extensive damage of the cell walls and edges. Lighter materials (densities below \(~10\text{ mg cm}^{-3}\)) recover up to 99% during unloading. After ‘yielding’, their stress/strain curve continues rising although the slope is significantly lower (Fig. 6a). This behaviour resembles more an elastomeric foam where collapse is determined by elastic buckling of the walls\(^31\).

Overall, the rGO-CN s are significantly more resistant than Ni microlattices of similar density and for the lightest networks, the stresses required to reach 50% strains are up to two orders of magnitude higher (Supplementary Fig. 8). The behaviour is very similar for all structures in subsequent cycles. The curves exhibit what can be described as a pseudohardening behaviour, in which the slope of the curve increases very fast with strain corresponding to significant densification with a large degree of recovery during unloading (typically between 99 and 97% for rGO-CN s with densities \(<100\text{ mg cm}^{-3}\)). In general, a gradual degradation in the properties is always observed in the first four cycles, with the biggest drop always between cycles 1 and 2 but then the curves tend to stabilize (Supplementary Fig. 9a) with recoveries that can be up to 95% for the lightest foams after 10 cycles of 50% strain.

The capability of a material to absorb energy is key for several applications, especially in energy conservation systems for space and transportation between others. For these technologies, energy absorption and low density in high performance materials is extremely important for improved cost effectiveness. The energy loss coefficients (the ratio between the energy dissipated within the materials and the work done by compression during the first cycle) can be as high as 0.86 for the lighter materials. The energy absorption capability are among the highest found for foams surpassing the values of foam-like CNT films\(^36\) (\(~0.64\)), 14 mg cm\(^{-3}\) Ni micro lattices\(^26\) (0.77) and just \(>0.82\) obtained for 5.1 mg cm\(^{-3}\) graphene elastomers\(^8\).

Furthermore, a good cycling performance is maintained, stabilizing the coefficient values at \(~0.55\) after the first four compression cycles (Supplementary Fig. 9a).

We can tune the energy absorption capability of the ultra-low density rGO-CN s exhibiting recoverable deformation by controlling their reduction degree. For example, the energy loss coefficient of 0.86 for rGO-CN s with a density of 6.1 mg cm\(^{-3}\) after reduction at 300 °C (Fig. 6a) can go to 0.51 for rGO-CN s of the same composition reduced at 1,000 °C (Supplementary Fig. 10). The higher reducing temperature leads to the formation of higher amounts of C sp\(^2\) bonding\(^24\). The highly crystallized rGO undergoes less damage through cycling and consequently dissipates less energy while maintaining an extremely good dimensional recovery.

The high levels of energy dissipation within the rGO-CN s can be attributed to a combination of mechanisms taking place at different length scales during compression. At the nanoscale, friction and Van der Waals attraction\(^8\) between rGO flakes during loading and unloading are two mechanisms responsible for the high energy loss coefficient during cycling. Specifically, the micro-roughness and organization of rGO flakes in the cell walls increases the contact area, leading to a high degree of friction between flakes while buckling and recovering. In addition to the above-described mechanism, the extra high levels of energy dissipation taking place during the first compression cycles is a result of micro rupturing and wrinkling in the cell walls that remain after the cycle (Supplementary Fig. 9b). These damage mechanisms contribute to the non-recoverable deformation and the decrease in mechanical properties upon cycling (Supplementary Fig. 9a). At the micro-to-macro scale, the materials’ cellular structure contributes to the high degree of recoverable deformation. Each cell wall can deform and recover differently from the stresses. Depending on the cell size, for example, some of them can present more deformation or fracture during buckling/bending than others. However, the predominantly undamaged cells can be recovered from the deformation leading to the macroscopic elastic behaviour of the rGO-CN s.

The electrical conductivity of rGO-CN s is shown together with literature values for other 3D carbon nanomaterials\(^5,8,9,12,33,37\) (Fig. 7). We can tune the electrical conductivities of the rGO-CN s to very high levels; surpassing other 3D materials produced from GO\(^8\) or CNT aerogels\(^37\) with similar densities. The high crystallinity resulting from thermal reduction of CMG at temperatures above 1,000 °C (Fig. 4e) together with their high degree of interconnection in the cellular network leads to a highly conductive path. Although the conductivities are still below those
of graphene chemical vapour deposition foams\(^5\), the electrical conductivity of an ultralight rGO-CN of only 1.5 mg cm\(^{-3}\) (reduced at 1,500\(^\circ\)C), reaches 0.4 S cm\(^{-1}\) which is one order of magnitude higher than that of a graphene elastomer with similar density.

**Absorption of organics.** The rGO-CNs exhibit the perfect characteristics of an organics (organic solvents and oils) absorbent: ultra-low density, extremely high porosity, super-hydrophobicity (Fig. 8a), very good wetting for organics (Fig. 8b), strength and good dimensional recovery. While the rGO cellular network floats when immersed in a vial with water, it efficiently absorbs the organic solvents.

We tested the absorbing capability of the rGO-CN with 99.8% porosity (4.3 mg cm\(^{-3}\) density) with oils and organic solvents (Fig. 8e) and compared with different materials from the literature, including polymeric foams\(^3\), organic fibres\(^39\), rGO-foam films\(^5\), nanowire membranes\(^40\), CNT sponges\(^41\), graphene-based aerogels\(^12\) and ultra-flyweight aerogels\(^2\). The rGO-CNs are among the best absorbers with organics intake reaching 113 to 276 times their own weight. The absorption capability will also strongly depend on the absorber density. In this way, a lighter rGO-CN of 1.5 mg cm\(^{-3}\) can increase its absorption capability for motor oil from 276 g g\(^{-1}\) to values as high as 605 g g\(^{-1}\).

Due to its mechanical and chemical stability, the rGO-CNs maintain the cellular network integrity after exposure to the organics for several weeks. The oil phase can be ‘squeezed out’ of the rGO cellular absorber by compressing it flat above 95% of its initial height (Fig. 8c) and the compressed structure can be directly re-utilized by immersing it in the oil phase again (even before it recovers the shape). The absorber immediately expands to its original shape by the absorption of the oil phase within its structure (Fig. 8d). This process can be repeated over several cycles (at least six were tested for each structure) while maintaining the adsorption capability to levels >95% (Supplementary Movie). This recycling approach is very straightforward, simple and uses the rGO cellular networks as a compressible/expandable absorber making them promising candidates as organics absorbers, filters and membranes for environmental applications.

**Discussion**

In summary, we have developed a mesoscale self-assembly strategy for the highly efficient fabrication of CMG cellular networks. This approach allows the manipulation of the structure at multiple levels from the densities (over two orders of magnitude from 1 to 200 mg cm\(^{-3}\), cell shape (polyhedral to spherical) and sizes (\(\sim 7\) to over 60 \(\mu\)m) at the micro-level to the cell walls topography, porosity and chemistry at the micro-to-nano-level. As a result it is possible to tune properties like surface area, elasticity, specific strength, energy loss coefficient and conductivity. Further, due to the intrinsic flexibility of emulsions, it is possible to extrude CMG wires with cellular architectures showing promise for the fabrication of complex structures at the

**Figure 8 | rGO-CNs capability for organics absorption, wetting behaviour and recycling approach.** (a) The rGO-CN floats when in contact with water due to its superhydrophobic properties. Water droplet forms a contact angle of 114\(^\circ\) with the rGO-CN surface (insert). (b) rGO-CN rapidly absorbs gasoline filling the highly porous structure with the solvent resulting on its immersion in the gasoline vial. In the insert, gasoline trace left after infiltration in the rGO-CN. (c,d) Recycling approach for rGO-CNs absorbers. After each absorption cycle, the oil phase can be ‘squeezed out’ of the rGO cellular absorber by compressing it (c) and the compressed structure can be directly re-utilized by immersing it in the oil phase again. The absorber immediately expands to its original shape by the absorption of the oil phase within its structure (d) (details in Supplementary Movie). (e) Organics absorption (g g\(^{-1}\)) of rGO-CNs in comparison with several absorbers reported in literature for different organic solvents and oils. The rGO cellular absorbers tested (4–4.5 mg cm\(^{-3}\)) were produced with 1.2 wt% additives in GO-sus (0.65 wt% GO) and thermally treated at 1,000\(^\circ\)C in Ar/H\(_2\) atmosphere.
Characterization of CMG-CNPs. The microstructural architecture of CMG-CNPs was analyzed via scanning electron microscopy (LEO Gemini 1525, operated at 5 kV) and STEM (FEI Titan 80–300 S/TEM, operated at 300 kV). STEM high-angle annular dark field imaging were acquired at 500 kV and 20 mm in diameter and angular detection semi-angles greater than 101 mrad. Cell sizes were measured from scanning electron microscopy images using the linear intercept method (Linear Intercept, TU Darmstadt). The average cell size (d50) was obtained from cumulative size distribution curves. Electron energy loss spectroscopy acquisitions were performed in STEM mode with an acceleration voltage of 200 kV and collection angle β = 7 mrad. The spatial and energy resolutions of the microscope under the experimental conditions were approximately 0.5 nm and ~0.7 eV (defined as the full width at half maximum of the zero-loss peak), respectively. Raman measurements were carried out with a spectrometer (Renishaw Invia Reflex, Oxford, UK) using a 514 nm laser excitation, laser power of 0.5 mW and 10 s accumulation time. Raman measurements were performed on >5 mg of CMG-CNPs, which were placed inside plastic caps with closed filter paper. Using closed caps ensured an accurate weighing of the samples and avoided the extremely light foams from getting suctioned during vacuum. The reliability was confirmed with measurements with different weights. CMG-CNPs were degassed in the Autosorb degasser (Quanta Chemistry) under 0.01 mbar for at least 24 h before the nitrogen adsorption. The nitrogen adsorption isotherm measurements were performed at relative pressures (P/P0) between 0.01 and 1 at a bath temperature of 77 K with 40 points for adsorption and 39 points for the desorption. Cylindrical samples (~20 mm in diameter and 10 mm in height) were used for the isotherm and mechanical testing. Mechanical testing and electrical conductivity measurements. The densities of the CMG-CNPs samples ρ were determined by measuring their dimensions with a standard caliper and their mass with a 0.01 mg accuracy balance. The porosity P was estimated considering the density of the rGO-CN cell walls ρw = 2.2 ± 0.1 g cm−3 (ref. 43) with the following equation: P = 1 − ρ/ρw = 1 − (4/3)πr2h/4πr2h − 4ρw. The rGO-CN cylindrical samples were submitted to 10 compressive cycles of 50% maximum strain, using a 2 kN load cell, in position controlled mode at loading and unloading speed of 0.01 mm s−1. The electrical conductivity of rGO-CN was measured using the four-point method.

Organics absorption test on rGO-CNPs. The adsorption capability of rGO-CNPs was evaluated by immersing the absorbent samples on a selection of organic solvents and oils and measuring the weight uptake with the following equation: Organics absorption (% wt) = (wtf − wto)/(wt − wto) × 100, where wt and wto correspond to the initial dried weight of the rGO-CN absorbent and wt, to the weight of the sample infiltrated with the organics.

References
1. Geim, A. K. & Novoselov, K. S. The rise of graphene. Nat. Mater. 6, 183–191 (2007).
2. Stoller, M. D., Park, S., Zhu, Y., An, J. & Ruoff, R. S. Graphene-based supercapacitors. Nano Lett. 8, 3498–3502 (2008).
3. Ghosh, S. et al. Extremely high thermal conductivity of graphene: Prospects for thermal management applications in nanoelectronic circuits. Appl. Phys. Lett. 92, 151911 (2008).
4. Gonzalez-Navarro, C. et al. Electronic transport properties of individual chemically reduced graphene oxide sheets. Nano Lett. 7, 3499–3503 (2007).
5. Chen, Z. P. et al. Three-dimensional flexible and conductive interconnected graphene networks grown by chemical vapour deposition. Nat. Mater. 10, 424–428 (2011).
6. Zhu, Y. et al. Carbon-based supercapacitors produced by activation of graphene. Science 332, 1537–1541 (2011).
7. Niu, Z., Chen, J., Hng, H. H., Ma, J. & Chen, X. A. Leavening strategy to prepare reduced graphene oxide foams. Adv. Mater. 24, 4144–4150 (2012).
8. Qiu, L., Liu, J. Z., Chang, S. L. Y., Wu, Y. & Li, D. Biomimetic superelastic graphene-based cellular monoliths. Nat. Commun. 3, 1241 (2012).
9. Zhang, X. et al. Mechanically strong and highly conductive graphene aerogel and its use as electrodes for electrochemical power sources. J. Mater. Chem. 21, 6494–6497 (2011).
10. Ahn, H. et al. Self-assembled foam-like graphene networks formed through nucleation boiling. Sci. Rep. 3, 1396 (2013).
11. Xu, Y., Sheng, K., Li, C. & Shi, G. Self-assembled graphene hydrogel via a one-step hydrothermal process. ACS Nano 4, 4324–4330 (2010).
12. Qian, Y., Ismail, I. M. & Stein, E. M. Vapor condensation from particle-stabilized emulsions. Adv. Mater. 20, 4718–4718 (2008).
13. Deville, S., Saiz, E., Nalla, R. K. & Tomsia, A. P. Freezing as a path to build complex composites. Science 311, 515–518 (2006).
14. Hu, H., Zhao, Z., Wan, W., Gogotsi, Y. & Qiu, J. Ultralight and highly compressible graphene aerogels. Adv. Mater. 25, 2219–2223 (2013).
15. Barg, S., Soltmann, C., Andrade, M., Koch, D. & Grathwohl, G. Ceramic foams by direct foaming of emissive ceramic powder suspensions. J. Am. Ceram. Soc. 91, 2823–2829 (2008).
16. Akartuna, I., Studart, A. R., Tervoort, E. & Gauckler, L. J. Macroporous ceramics from particle-stabilized emulsions. Adv. Mater. 20, 4718–4718 (2008).
17. Deville, S., Saiz, E., Nalla, R. K. & Tomsia, A. P. Freezing as a path to build complex composites. Science 311, 515–518 (2006).
18. Kim, J. et al. Graphene oxide sheets at interfaces. J. Am. Chem. Soc. 132, 8180–8186 (2010).
19. Li, D., Muller, M. B., Galie, S., Kaner, R. B. & Wallace, G. G. Processable aqueous dispersions of graphene nanosheets. Nat. Nanotechnol. 3, 101–105 (2008).
20. Deville, S., Saiz, E. & Tomsia, A. P. Ice-templated porous alumina structures. Acta Materialia 55, 1965–1974 (2007).
21. Liang, J. et al. Molecular-level dispersion of graphene into poly(vinyl alcohol) and effective reinforcement of their nanocomposites. Adv. Funct. Mater. 19, 2997–2002 (2009).
22. Li, Y.-Q., Yu, T., Yang, T.-Y., Zheng, L.-X. & Liao, K. Bio-inspired nacre-like composite films based on graphene with superior mechanical, electrical, and biocompatible properties. Adv. Mater. 24, 3426–3431 (2012).
23. Munch, E., Saiz, E., Tomsia, A. P. & Deville, S. Architectural control of freeze-cast ceramics through additives and templating. J. Am. Ceram. Soc. 92, 1534–1539 (2009).
24. Mattevi, C. et al. Evolution of electrical, chemical, and structural properties of transparent and conducting chemically derived graphene thin films. Adv. Funct. Mater. 19, 2577–2583 (2009).
25. Tillotson, T. M. & Hubsh, L. W. Transparent ultralow-density silica aerogels prepared by a two-step sol-gel process. J. Non-Cryst. Solids 145, 44–50 (1992).
26. Mader, T. A. et al. Ultralight metallic microlattices. Science 334, 962–965 (2011).
27. Graff, S. D., McKenzie, D. R. & Martin, T. P. EELS analysis of vacuum arc-deposited diamond-like films. Philos. Mag. Lett. 57, 285–290 (1988).
28. Cançado, L. G. et al. Quantifying defects in graphene via raman spectroscopy at different excitation energies. Nano Lett. 11, 3190–3196 (2011).
29. Pooncharal, P., Ayani, A., Malliaras, G. & Xu, Z. et al. Effect of rGO/CNT hybrid density on the local electrical conductivity of freestanding bilayer graphene. Phys. Rev. B 78, 113407 (2008).
30. Zhang, Y. et al. High quality graphene sheets from graphene oxide by hot-pressing. Carbon 54, 143–148 (2013).
31. Gibson, L. J. Biomechanics of cellular solids. J. Biomech. 28, 377–399 (2005).
32. Sun, H., Xu, Z. & Gao, C. Multifunctional, ultra-flyingweight, synergistically assembled carbon aerogels. Adv. Mater. 25, 2534–2550 (2013).
33. Worsley, M. A., Kucheyev, S. O., Satcher, J. H., Hamza, A. V. & Raumann, T. F. Mechanically robust and electrically conductive carbon nanotube foams. Appl. Phys. Lett. 94, 073115 (2009).

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34. Pekala, R. W., Alviso, C. T. & Lemay, J. D. Organic aerogels-microstructural
dependence of mechanical properties in compression. J. Non-Crystal. Solids 125, 67–75 (1990).
35. Gibson, L. J. & Ashby, M. F. Cellular Solids: Structure & Properties (Cambridge
University Press, 1997).
36. Cao, A. Y., Dickrell, P. L., Sawyer, W. G., Ghasemi Nejhad, M. N. & Ajayan, P. M. Super-compressible foamlike carbon nanotube films. Science 310, 1307–1310 (2005).
37. Zou, J. H. et al. Ultralight multiwalled carbon nanotube aerogel. ACS Nano 4, 7293–7302 (2010).
38. Li, H., Liu, L. & Yang, F. Hydrophobic modification of polyurethane foam for
oil spill cleanup. Mar. Pollut. Bull. 64, 1648–1653 (2012).
39. Lin, J. et al. Nanoporous polystyrene fibers for oil spill cleanup. Mar. Pollut. Bull. 64, 347–352 (2012).
40. Yuan, J. K. et al. Superwetting nanowire membranes for selective absorption.
Nat. Nanotechnol. 3, 332–336 (2008).
41. Gui, X. et al. Carbon nanotube sponges. Adv. Mater. 22, 617–621 (2010).
42. Hirata, M., Gotou, T., Horiiuchi, S., Fujitwara, M. & Ohba, M. Thin-film particles
of graphite oxide 1: High-yield synthesis and flexibility of the particles. Carbon 42, 2929–2937 (2004).
43. Stankovich, S. et al. Graphene-based composite materials. Nature 442, 282–286 (2006).

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Author contributions
S.B. designed the processing approach, directed the experiments and wrote the
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mentored the work and revised the manuscript. F.M.P. and P.d.V.P. prepared and
characterized the samples. F.M.P. and S.B. analysed mechanical and electrical perfor-
mance and F.M.P. performed organsics absorption tests. S.B., F.M.P. and P.d.V.P.
performed SEM. N.N. performed STEM and electron energy loss spectroscopy (EELS)
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