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Percolation scaling in composites of exfoliated MoS₂ filled with nanotubes and graphene

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Applications of films of exfoliated layered compounds in many areas will be limited by their relatively low electrical conductivity. To address this, we have prepared and characterised composites of a nano-conductor (nanotubes or graphene) embedded in a matrix of exfoliated MoS₂ nanosheets. Solvent exfoliation of MoS₂ nanosheets, followed by blending with dispersions of graphene or nanotubes allowed the formation of such composite films by vacuum filtration. This gave spatially uniform mixtures with fully tuneable nano-conductor content. By addition of the nano-conducting phase, it was possible to vary the electrical conductivity of the composite over nine orders of magnitude. For both filler types the conductivity followed percolation scaling laws both above and below the percolation threshold. In the case of SWNT-filled composites, conductivities as high as ~40 S m⁻¹ were achieved at volume fractions as low as ~4%.

Inorganic layered compounds are an exciting class of materials which have received renewed attention in recent years. These systems consist of 2-dimensional nanosheets which stack, typically by van der Waals interactions, to form three dimensional crystals.¹ These materials are exciting because they are found in a wide range of types with a broad palate of physical properties. After graphite, probably the most well-known layered compounds are the family of transition metal dichalcogenides (TMDs). These materials have the chemical composition MX₂ where M is a transition metal (commonly, but not limited to Ti, Nb, Ta, Mo, W) and X is a chalcogen (*e.g.* S, Se, Te). This family of materials is of interest due to their versatile electronic and electrochemical properties.^{2,3} Another family of layered compounds are the transition metal oxides,⁴ with layered MnO₂ (*i.e.* δ-MnO₂) showing potential for applications in supercapacitor electrodes.⁵ Also well-known are the layered materials; Bi₂Te₃, Sb₂Te₃, Bi₂Se₃ and Sb₂Se₃, which have great potential as thermoelectric materials.⁶

However, these layered materials have a number of significant failings – notably their relatively low electrical conductivity.¹ For example, the low electrical conductivity of MoS₂ has limited their development for use as lithium ion battery electrodes.^{7,8} Alternatively, the promise of layered MnO₂ as a supercapacitor electrode has not been realised, again due to its poor electrical performance.⁹ Finally, Bi₂Te₃ is an exceptional thermoelectric material. However, because the thermoelectric figure of merit scales with the electrical conductivity, there is scope for further improvement if the electrical conductivity could be increased.¹⁰

We believe that recent advances in the processing of layered compounds can be used to produce films of layered materials with dramatically increased electrical conductivity. It has recently been shown that layered compounds such as graphite, boron nitride, TMDs, MnO₂ and Bi₂Te₃ can all be exfoliated to give few-layer nanosheets in large quantities by sonication in certain solvents or aqueous surfactant solutions.^{10–23} Such processes are quick, easy and insensitive to environmental conditions. Once the nanosheets have been exfoliated in a liquid, normal solution processing techniques can be applied, making the formation of films straightforward.^{3,10} More importantly, because almost all of these layered compounds, including graphene,¹⁴ (and carbon nanotubes^{24,25}) can be exfoliated in the same set of solvents, it is possible to produce composite dispersions and so composite films by simple mixing.^{3,10} This is a very straightforward yet powerful technique because it will allow the fabrication of a wide range of composite types through various combinations of components and compositions. Importantly, if nano-conductors such as single walled nanotubes (SWNTs)²⁶ or graphene²⁷ are added to insulators such as MoS₂, the resulting composite will have a conductivity that is potentially tuneable over a wide range.^{3,10} This has the potential to solve the conductivity problem described above.

However, when preparing such composites, it will be critical to keep the nano-conductor content to a minimum. There are a number of reasons for this. Most importantly, conducting fillers take up space and reduce the amount of active material present, a significant problem for battery or supercapacitor electrodes.⁸ Secondly, some nano-conductors such as carbon nanotubes or metallic nanowires can be very expensive, making composites with high loading levels economically unattractive. To date, very little is known about these layered matrix composite systems; for example it is not known if reasonable conductivities can be achieved by adding small quantities

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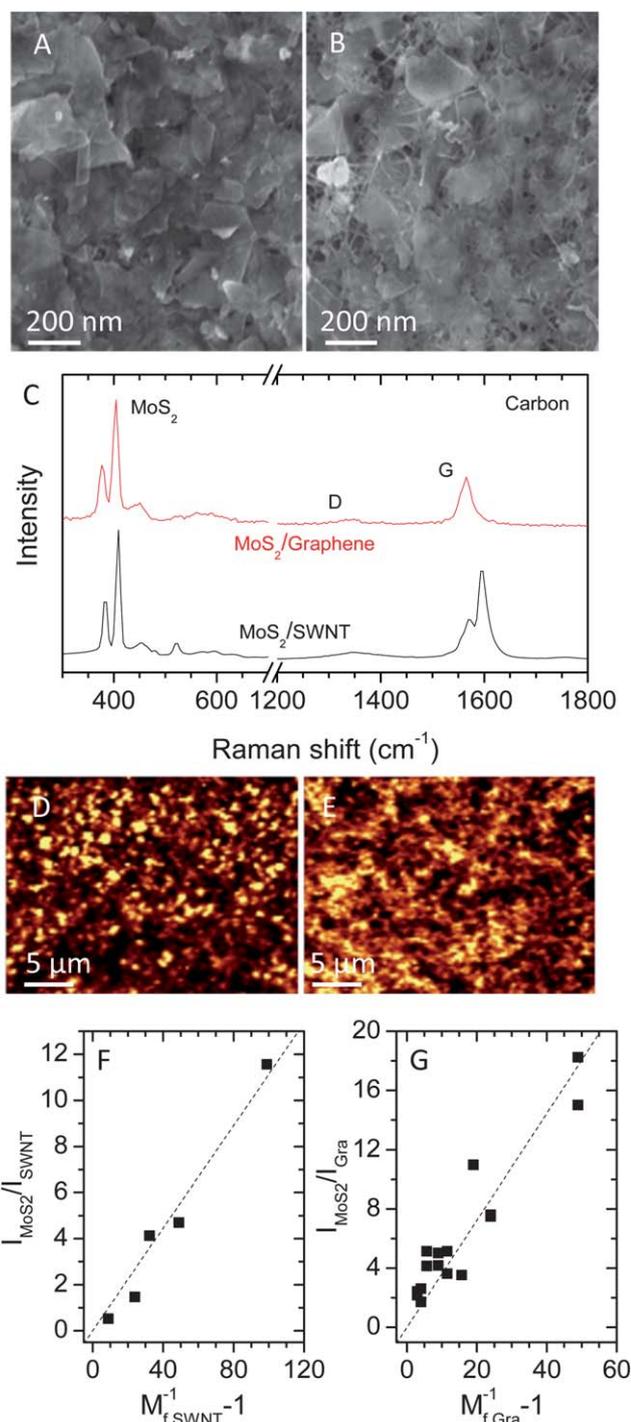


Fig. 1 SEM images of the surface of films of (A) MoS₂-graphene (85 : 15 by weight) and (B) MoS₂-SWNT (90 : 10 by weight) (thickness ~150 nm). (C) Raman spectra for MoS₂-graphene (80 : 20 by weight) and MoS₂-SWNT (95 : 5 by weight) films. In each case, these spectra are averages over 50 spectra taken along a line of 180 μm in length. The D and G bands of the carbon components of the spectra are labelled. (D and E) Raman maps are measured on a grid of 120 × 120 points over an area of 30 μm × 30 μm for MoS₂-graphene (90 : 10 by weight) and MoS₂-SWNT (90 : 10 by weight) films. The intensity is the ratio of intensity of the A_{1g} MoS₂ to carbon G band. (F and G) Plot of the ratio of intensity of MoS₂ to carbon peaks versus $M_{f\text{-carbon}}^{-1} - 1$ where $M_{f\text{-carbon}}^{-1}$ is the carbon mass fraction. This plot is expected to be linear for a uniform

of nano-conductors. In this work, we use MoS₂ as a model compound to investigate how the conductivity of composites of layered materials embedded with both nanotubes and graphene scales with nano-conductor content. We show that these systems follow percolation theory and that conductivity as high as 40 S m⁻¹ can be achieved for nanotube content as low as 4 vol%.

We have used the processing methods described above^{10,21,23} to prepare mixed dispersions of both MoS₂-SWNT and MoS₂-graphene. Such liquid processing techniques tend to give well exfoliated MoS₂ and graphene flakes with thickness in the range of 1–10 layers and nanotube bundles with diameter of a few nanometers.^{10,14,28} These dispersions were used to prepare composite films with nano-conductor content covering the entire range from 0% to 100% (see Experimental methods). These films were initially characterised using scanning electron microscopy (SEM, Zeiss Ultra Plus). In general, the films appeared uniform when viewed over a large area. Typical images for both types of composites are shown in Fig. 1A and B. Graphene-MoS₂ composite films (Fig. 1A) consist of a disordered array of flakes with graphene and MoS₂ indistinguishable from each other. For the SWNT-MoS₂ films (Fig. 1B), the flakes of MoS₂ are embedded within a SWNT network. Scanning Raman spectroscopy was used to assess the uniformity of the composite films. Characteristic Raman spectra are shown in Fig. 1C for both types of composite films produced. Clearly present are the E_{2g}¹ (~383 cm⁻¹) and A_{1g} (~409 cm⁻¹) modes of MoS₂ (ref. 29) and the characteristic G band (1580 cm⁻¹) of carbon based materials.^{30,31} The D bands are hardly observable due to the quality of both SWNTs and exfoliated graphene. Elemental Raman maps of local areas of the films were obtained by measuring the ratio of the MoS₂ A_{1g} peak intensity to that of the carbon G band. These are shown in Fig. 1D and E for graphene and SWNT based films respectively. Both composite types show relatively good uniformity down to length scales of a few μm *i.e.* close to the size scale expected for exfoliated nanosheets.^{10,14,15,23}

We can assess the uniformity quantitatively by assuming that the Raman intensity for a mode associated with a given material is proportional to the mass that material under the beam. Combining this with the definition of the mass fraction of carbon (*i.e.* SWNT or graphene) – $M_f = M_C / (M_C + M_{\text{MoS}_2})$, we can show the ratio of MoS₂ to carbonaceous Raman intensity is given by

$$\frac{I_{\text{MoS}_2}}{I_C} \propto \frac{1}{M_f} - 1 \quad (1)$$

assuming spatial uniformity. We plot the ratio of MoS₂ to carbonaceous Raman intensity, (averaged over 15 000 measurements taken over a local area of ~0.5 × 0.5 mm) versus $M_f^{-1} - 1$ in Fig. 1F and G for both composite types. Very good linearity is found for the MoS₂-SWNT composite films showing them to be very uniform. However, while still linear, the data for the MoS₂-graphene composite films was relatively scattered suggesting them to be less spatially uniform.

We also measured the electrical properties of these composites. The DC conductivity was measured for all films and plotted as a function of volume fraction of carbonaceous component, ϕ , in Fig. 2A. For each composite type, the conductivity increased from 6×10^{-7} S m⁻¹ for the MoS₂-only film to 103 S m⁻¹ and 670 S m⁻¹ for the graphene-only and SWNT-only films respectively. For each composite type, the

mixture. The data for SWNT and graphene composites are shown in (F) and (G) respectively.

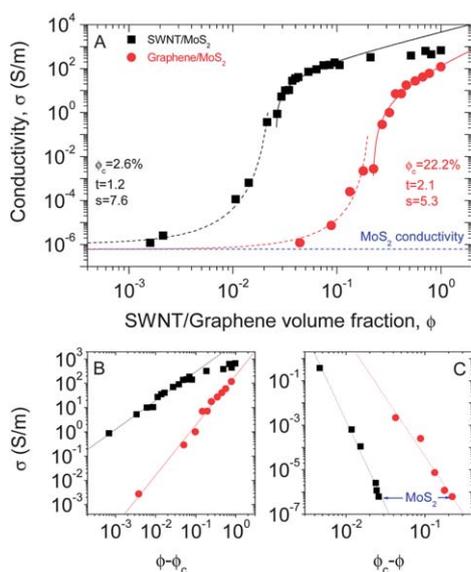


Fig. 2 (A) Graph of conductivity versus carbon (*i.e.* SWNT or graphene) volume fraction for the composites studied in this work. (B and C) Conductivity plotted as percolation graphs for both SWNT–MoS₂ and graphene–MoS₂ composites for volume fractions (ϕ) that are (B) above and (C) below the percolation threshold (ϕ_c). The datasets have been fit to eqn (2) (B) and (3) (C). These fit lines have been reproduced on panel (A) along with the fit parameters. The blue dashed line in (A) shows the measured conductivity of an MoS₂-only film.

conductivity increased dramatically over a narrow range of volume fraction; ~ 1 to 3 vol% and ~ 15 to 30 vol% for MoS₂–SWNT and MoS₂–graphene composites respectively.

Such behaviour is consistent with percolation effects. When an electrically conducting filler is added to an insulating matrix, significant increases in conductivity can only occur once the first conducting path through the sample is formed. The volume fraction of filler where this occurs is known as the percolation threshold, ϕ_c . Above the percolation threshold the conductivity scales as^{32,33}

$$\sigma_{DC} = \sigma_C \left(\frac{\phi - \phi_c}{1 - \phi_c} \right)^t \quad (2)$$

where σ_C is nominally the conductivity of a film of the conducting filler alone and t is the percolation exponent. We note that percolation theory has been applied to mixtures of graphite in a hexagonal boron nitride matrix.³³ However, these composites were prepared by pressing mixtures of unexfoliated graphite and boron nitride powders into discs. The work described in this paper represents the first example of percolation studies of an exfoliated nanosheet filler in a matrix of exfoliated nanosheets.

We have analysed the data for both composite types in terms of eqn (2) as shown in Fig. 2B. While the data for the MoS₂–graphene composites follows eqn (2) extremely well over the entire range, the MoS₂–SWNT composites only follow the percolation scaling law for volume fractions close to the percolation threshold. From the fits, we find the percolation thresholds to be $\phi_c = 2.6$ vol% and $\phi_c = 22.2$ vol% for the MoS₂–SWNT and MoS₂–graphene composites respectively (all fit constants are given in Table 1). For both 1- and 2-dimensional fillers in three dimensional composites, the percolation threshold is generally thought to be close to the ratio of smallest to largest

Table 1 Percolation fit parameters

Composite	ϕ_c	t	s	σ_C (S m ⁻¹)	σ_{MoS_2} (S m ⁻¹)
MoS ₂ –SWNT	2.6%	1.2	7.6	4530	8.8×10^{-7}
MoS ₂ –graphene	22.2%	2.1	5.3	129	6.0×10^{-7}

dimension.^{34,35} Thus, the value of ϕ_c found for the MoS₂–SWNT system is typical of what is generally found³⁶ and is consistent with nanotube bundle diameters of ~ 10 nm coupled with lengths of $\sim \mu\text{m}$.

However, the value of ϕ_c observed for the MoS₂–graphene system is much larger than values previously reported for 3-dimensional composites with graphene as a filler (< 1 vol%).^{37,38} In addition, it is much smaller than the fixed percolation threshold of $\sim 67\%$ expected for 2-dimensional composites with planar fillers (mutually penetrable filler particles).³⁹ However, our result is consistent with recent theoretical predictions that, for composites of *randomly oriented*, mono-disperse conducting discs in an insulating matrix, the percolation threshold is actually independent of disk diameter.⁴⁰ This work suggests ϕ_c to scale only with disk thickness, a , as $\phi_c = 2a/\lambda(5\pi + 6)$, where λ is the hopping distance. The independence of disk diameter is due to the effect of volume exclusion.⁴⁰ This equation should apply in the limit where λ and a are both very much smaller than the width of the disks, as is the case here. Taking $a = 1$ nm and $\phi_c = 22.2$ vol%, this gives a value of $\lambda \approx 0.4$ nm, which seems reasonable. Applying the same theory to perfectly parallel disks (in the limit of very large aspect), which arguably is more realistic for our type of system, gives a similar result: $\phi_c = a/8\lambda$, in which case $\lambda \approx 0.6$ nm.

In addition, the percolation exponents were observed to be $t = 1.2$ and $t = 2.1$ for the MoS₂–SWNT and MoS₂–graphene composites respectively. The former value is close to the universal exponent of $t = 1.33$,³² expected for 2-dimensional composites and consistent with a number of nanotube containing composites.³⁶ However, the graphene exponent is considerable higher and close to the universal exponent of $t = 2.0$,³² expected for 3-dimensional composites. We note that the SWNT data deviates from the percolation scaling law for $\phi > 0.01$. Above this volume fraction the data fits an empirical scaling law of the type $\sigma \propto \phi^m$ where $m \approx 0.6$. This low apparent exponent is interesting. Such low values have been observed for a number of SWNT networks in transparent conductor applications.⁴⁹ This work suggests that such low apparent exponents are associated with networks which are far from the percolation threshold.

The DC conductivity below the percolation threshold is also described by a scaling law:^{32,41,42}

$$\sigma_{DC} = \sigma_{\text{MoS}_2} \left(\frac{\phi_c - \phi}{\phi_c} \right)^{-s} \quad (3)$$

where σ_{MoS_2} is the conductivity of the matrix and s is a second percolation exponent. We have fit this equation to the data for both composites as shown in Fig. 2C obtaining values of $s = 7.6$ and $s = 5.3$ for the MoS₂–SWNT and MoS₂–graphene composites respectively. These are extremely high values. While there is little experimental data available, previous reports have clustered close to the predicted^{42,43} value of $s \approx 1$.^{32,33,41,44–46} It is unclear why the values found here are so high.

It is worth noting that although the degree of exfoliation currently achievable by the methods used here is very good, it is not perfect. Both MoS₂ and graphene are expected to be present as thin multi-layer flakes rather than monolayers while the nanotubes are present

as bundles rather than individual SWNTs. We would expect future work to lead to improvements in the exfoliation state of all components. For the graphene and SWNTs (*i.e.* the conducting filler), improvements in degree of exfoliation should result in reduction in percolation threshold and so significant increases in conductivity at lower filler content. However, it is less clear as the effect of MoS₂ (*i.e.* the matrix) exfoliation state on the film properties. To the authors knowledge this work represents the first detailed study of such 2D–2D and 1D–2D composites. As such, further work is required to understand the role of the matrix nanostructure in determining the performance of such composites.

In conclusion we have prepared thin film composites of both SWNTs and exfoliated graphene nanosheets (the conducting nanofiller) in a matrix of exfoliated MoS₂ nanosheets. A combination of scanning electron microscopy and Raman spectroscopy showed the mixtures to be uniform to a length-scale of \sim microns. Electrical measurements showed an increase in conductivity of up to \sim 9 orders of magnitude on addition of nano-conductors. In both cases, the conductivity obeyed percolation scaling laws both above and below the percolation threshold. The percolation thresholds were $\phi_c = 2.6$ vol% and $\phi_c = 22.2$ vol% for the MoS₂–SWNT and MoS₂–graphene composites respectively. For the SWNT filled composites, this low percolation threshold means that conductivities as high as ~ 40 S m⁻¹ for volume fractions as low as ~ 4 vol%. We expect similar results to be found for other exfoliated layered compounds filled with nano-conductors. Such materials will be important in a range of applications from thermoelectric devices to electrodes in batteries and supercapacitors.

Experimental methods

We purchased powdered MoS₂, graphite and P3 singlewalled carbon nanotubes (SWNTs) from Fluka Analytics, Sigma Aldrich and Carbon Solutions Inc. respectively and used all as supplied. Typical MoS₂ and graphene dispersions were made as described previously.^{10,15} In both cases 100 mg of powder was added to 10 ml of *N*-Methyl Pyrrolidone (NMP) in a glass vial. These were sonicated in a Branson 1510E-MT sonic bath (20 kHz) for three hours followed by probe sonication (Vibracell, GEX750, 35% \times 650 W) for a further three hours. After standing overnight, the dispersions were centrifuged in a HettichMikro 22R at 1500 RPM (226g) for 90 minutes. The top 6 ml of each dispersion were then removed for further use. The SWNT dispersion was prepared by adding 20 mg of starting powder to 10 ml of NMP in a glass vial. This sample was then bath sonicated for one hour, followed by 30 minutes probe sonication at 20% amplitude, followed by bath sonicated for one more hour. This sample was centrifuged at 5500 RPM for 90 minutes and the top 6 ml retained. In each case the dispersed concentration was measured by filtration and weighing.

Because all dispersions were made in the same solvent it was possible to blend these dispersions to make composite dispersions of any desired mass ratio. A series of MoS₂–graphene and MoS₂–SWNT blended dispersions were made with MoS₂ content spanning the entire range from 0% to 100%. These composite dispersions were diluted in isopropanol (IPA) and filtered through nitrocellulose membranes (25 nm pores, Millipore) to give films of diameter 36 mm. The film thickness was close to 150 nm in all cases as verified by atomic force microscopy. This thickness is large enough to ensure the

electrical conductivity is bulk-like and not controlled by thickness effects.⁴⁷

Ti–Au electrodes (5–50 nm thick, spacing 60–70 μ m, channel width 1.3 cm) were deposited on SiO₂ (MoS₂–graphene) or glass (MoS₂–SWNT) substrates. Films were transferred onto electrodes by adhering the film to the substrate with IPA and exposing it to acetone vapour followed by washing in acetone baths to dissolve the remaining membrane.⁴⁸ Electrical measurements were carried out using a Karl Suss probe station and a Keithley 2400 source meter controlled by a LabView program.

In order to convert mass fraction to volume fraction, we assumed the densities of graphene and SWNT to be 2200 and 1800 kg m⁻³ respectively. The density of an MoS₂–only film was measured to be 1925 kg m⁻³ by preparing a number of thick films by filtration and carefully measuring their mass and dimensions. This value is considerably lower than that appropriate for an MoS₂ crystal, due to the free volume found in disordered networks of nanostructures. We consider the composites to consist of the nanocarbons embedded in a porous MoS₂ matrix (density 1925 kg m⁻³). In this scenario, the matrix volume is the sum of free volume and the MoS₂ volume.

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References

- 1 J. A. Wilson and A. D. Yoffe, *Adv. Phys.*, 1969, **18**, 193–335.
- 2 K. Chang and W. X. Chen, *Chem. Commun.*, 2011, **47**, 4252–4254.
- 3 R. J. Smith, P. J. King, M. Lotya, C. Wirtz, U. Khan, S. De, A. O'Neill, G. S. Duesberg, J. C. Grunlan, G. Moriarty, J. Chen, J. Z. Wang, A. I. Minett, V. Nicolosi and J. N. Coleman, *Adv. Mater.*, 2011, **23**, 3944–3948.
- 4 M. Osada and T. Sasaki, *J. Mater. Chem.*, 2009, **19**, 2503–2511.
- 5 G. Zhu, H. J. Li, L. J. Deng and Z. H. Liu, *Mater. Lett.*, 2010, **64**, 1763–1765.
- 6 B. Poudel, Q. Hao, Y. Ma, Y. C. Lan, A. Minnich, B. Yu, X. A. Yan, D. Z. Wang, A. Muto, D. Vashaee, X. Y. Chen, J. M. Liu, M. S. Dresselhaus, G. Chen and Z. F. Ren, *Science*, 2008, **320**, 634–638.
- 7 R. R. Haering, J. A. R. Stiles and K. Brandt, Lithium molybdenum disulphide battery cathode, 1980, US Patent 4224390.
- 8 M. S. Whittingham, *Chem. Rev.*, 2004, **104**, 4271–4301.
- 9 M. Toupin, T. Brousse and D. Belanger, *Chem. Mater.*, 2004, **16**, 3184–3190.
- 10 J. N. Coleman, M. Lotya, A. O'Neill, S. D. Bergin, P. J. King, U. Khan, K. Young, A. Gaucher, S. De, R. J. Smith, I. V. Shvets, S. K. Arora, G. Stanton, H. Y. Kim, K. Lee, G. T. Kim, G. S. Duesberg, T. Hallam, J. J. Boland, J. J. Wang, J. F. Donegan, J. C. Grunlan, G. Moriarty, A. Shmeliov, R. J. Nicholls, J. M. Perkins, E. M. Grieveeson, K. Theuwissen, D. W. McComb, P. D. Nellist and V. Nicolosi, *Science*, 2011, **331**, 568–571.
- 11 P. Blake, P. D. Brimicombe, R. R. Nair, T. J. Booth, D. Jiang, F. Schedin, L. A. Ponomarenko, S. V. Morozov, H. F. Gleeson, E. W. Hill, A. K. Geim and K. S. Novoselov, *Nano Lett.*, 2008, **8**, 1704–1708.
- 12 A. B. Bourlino, V. Georgakilas, R. Zboril, T. A. Steriotis and A. K. Stubos, *Small*, 2009, **5**, 1841–1845.
- 13 Y. Hernandez, M. Lotya, D. Rickard, S. D. Bergin and J. N. Coleman, *Langmuir*, 2010, **26**, 3208–3213.
- 14 Y. Hernandez, V. Nicolosi, M. Lotya, F. M. Blighe, Z. Y. Sun, S. De, I. T. McGovern, B. Holland, M. Byrne, Y. K. Gun'ko, J. J. Boland,

- P. Niraj, G. Duesberg, S. Krishnamurthy, R. Goodhue, J. Hutchison, V. Scardaci, A. C. Ferrari and J. N. Coleman, *Nat. Nanotechnol.*, 2008, **3**, 563–568.
- 15 U. Khan, A. O'Neill, M. Lotya, S. De and J. N. Coleman, *Small*, 2010, **6**, 864–871.
- 16 W. Q. Han, L. J. Wu, Y. M. Zhu, K. Watanabe and T. Taniguchi, *Appl. Phys. Lett.*, 2008, **93**, 223103.
- 17 Y. Lin, T. V. Williams and J. W. Connell, *J. Phys. Chem. Lett.*, 2010, **1**, 277–283.
- 18 Y. Lin, T. V. Williams, T. B. Xu, W. Cao, H. E. Elsayed-Ali and J. W. Connell, *J. Phys. Chem. C*, 2011, **115**, 2679–2685.
- 19 J. H. Warner, M. H. Rummeli, A. Bachmatiuk and B. Buchner, *ACS Nano*, 2010, **4**, 1299–1304.
- 20 C. Y. Zhi, Y. Bando, C. C. Tang, H. Kuwahara and D. Golberg, *Adv. Mater.*, 2009, **21**, 2889.
- 21 A. O'Neill, U. Khan and J. N. Coleman, *Chem. Mater.*, 2012, **24**, 2414–2421.
- 22 K. G. Zhou, N. N. Mao, H. X. Wang, Y. Peng and H. L. Zhang, *Angew. Chem., Int. Ed.*, 2011, **50**, 10839–10842.
- 23 G. Cunningham, M. Lotya, C. S. Cucinotta, S. Sanvito, S. D. Bergin, R. Menzel, M. S. P. Shaffer and J. N. Coleman, *ACS Nano*, 2012, **6**, 3468–3480.
- 24 S. D. Bergin, V. Nicolosi, P. V. Streich, S. Giordani, Z. Y. Sun, A. H. Windle, P. Ryan, N. P. P. Niraj, Z. T. T. Wang, L. Carpenter, W. J. Blau, J. J. Boland, J. P. Hamilton and J. N. Coleman, *Adv. Mater.*, 2008, **20**, 1876.
- 25 S. D. Bergin, Z. Y. Sun, D. Rickard, P. V. Streich, J. P. Hamilton and J. N. Coleman, *ACS Nano*, 2009, **3**, 2340–2350.
- 26 R. H. Baughman, A. A. Zakhidov and W. A. de Heer, *Science*, 2002, **297**, 787–792.
- 27 A. K. Geim, *Science*, 2009, **324**, 1530–1534.
- 28 S. D. Bergin, Z. Y. Sun, P. Streich, J. Hamilton and J. N. Coleman, *J. Phys. Chem. C*, 2010, **114**, 231–237.
- 29 C. Lee, H. Yan, L. E. Brus, T. F. Heinz, J. Hone and S. Ryu, *ACS Nano*, 2010, **4**, 2695–2700.
- 30 A. C. Ferrari, J. C. Meyer, V. Scardaci, C. Casiraghi, M. Lazzeri, F. Mauri, S. Piscanec, D. Jiang, K. S. Novoselov, S. Roth and A. K. Geim, *Phys. Rev. Lett.*, 2006, **97**, 187401.
- 31 G. S. Duesberg, I. Loa, M. Burghard, K. Syassen and S. Roth, *Phys. Rev. Lett.*, 2000, **85**, 5436–5439.
- 32 D. Stauffer and A. Aharony, *Introduction to Percolation Theory*, Taylor & Francis, London, 1985.
- 33 J. J. Wu and D. S. McLachlan, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 1997, **56**, 1236–1248.
- 34 A. Celzard, E. McRae, C. Deleuze, M. Dufort, G. Furdin and J. F. Mareche, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 1996, **53**, 6209–6214.
- 35 J. Li and J. K. Kim, *Compos. Sci. Technol.*, 2007, **67**, 2114–2120.
- 36 W. Bauhofer and J. Z. Kovacs, *Compos. Sci. Technol.*, 2009, **69**, 1486–1498.
- 37 H. Pang, T. Chen, G. M. Zhang, B. Q. Zeng and Z. M. Li, *Mater. Lett.*, 2010, **64**, 2226–2229.
- 38 S. Stankovich, D. A. Dikin, G. H. B. Dommett, K. M. Kohlhaas, E. J. Zimney, E. A. Stach, R. D. Piner, S. T. Nguyen and R. S. Ruoff, *Nature*, 2006, **442**, 282–286.
- 39 J. A. Quintanilla and R. M. Ziff, *Phys. Rev. E: Stat., Nonlinear, Soft Matter Phys.*, 2007, **76**, 051115.
- 40 R. H. J. Otten and P. van der Schoot, *J. Chem. Phys.*, 2011, **134**, 094902.
- 41 C. Chiteme, D. S. McLachlan and G. Sauti, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2007, **75**, 094202.
- 42 J. P. Clerc, G. Giraud, J. M. Laugier and J. M. Luck, *Adv. Phys.*, 1990, **39**, 191–308.
- 43 A. L. Efros and B. I. Shklovskii, *Phys. Status Solidi B*, 1976, **76**, 475–485.
- 44 D. S. McLachlan, C. Chiteme, C. Park, K. E. Wise, S. E. Lowther, P. T. Lillehei, E. J. Siochi and J. S. Harrison, *J. Polym. Sci., Part B: Polym. Phys.*, 2005, **43**, 3273–3287.
- 45 G. Sauti and D. S. McLachlan, *J. Mater. Sci.*, 2007, **42**, 6477–6488.
- 46 D. S. McLachlan, C. Chiteme, W. D. Heiss and J. J. Wu, *Phys. B*, 2003, **338**, 261–265.
- 47 S. De, P. J. King, P. E. Lyons, U. Khan and J. N. Coleman, *ACS Nano*, 2010, **4**(12), 7064–7072.
- 48 E. M. Doherty, S. De, P. E. Lyons, A. Shmeliov, P. N. Nirmalraj, V. Scardaci, J. Joimel, W. J. Blau, J. J. Boland and J. N. Coleman, *Carbon*, 2009, **47**, 2466–2473.
- 49 S. De and J. N. Coleman, *MRS Bull.*, 2011, **36**, 774–781.