



DISCUSSIONS

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Synthesis in gas and liquid phase: general discussion

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Varsha Khare opened the discussion of the paper by Pulickel M. Ajayan: The environmental applications of graphene based materials in terms of heavy metal detoxification and particularly the aspect of recyclability, different micro-structures of graphene and doping using solution chemistry leads to better absorption efficiency and recyclability.

Philip Davies said: Could you comment on the present state of knowledge of the interface between carbon nanomaterials and other components.

Pulickel Ajayan responded: This is still a big challenge in my opinion. There has been quite a few single nanotube studies on pull-out from polymer matrices and several of these studies have shown that the interface between nanotubes and polymers can be made strong *via* chemical modification of the nanotube surface (*via* covalent or non-covalent functionalization). Relatively limited number of studies have focused on interfaces between nanotubes and metal matrices or nanotubes and ceramics. The electrical contacts between nanotubes and metals have been studied in detail, some leading to good ohmic contacts. The characterization of such interfaces *via* direct microscopy or spectroscopy has not been very successful.

Thanh Nguyen asked: Could you please comment on the potential biomedical applications of these carbon nanomaterials?

Pulickel Ajayan answered: Carbon nanotubes could be directly used in the form of scaffolds in applications such as tissue engineering or indirectly as sensors or probes in the detection of biomolecules. Several ideas have been conceived like drug delivery, electrodes, membranes *etc.* but one has to be careful

about the long term effects, toxicity, biocompatibility *etc.* before these applications are implemented. I think this area has huge potential and will be one of the important applications of nanomaterials (including nanotubes) in the future.

Pagona Papakonstantinou addressed Pulickel Ajayan, Milo Shaffer and Ian Kinloch: The direct growth of carbon nanotubes on carbon fibers offers new avenues for the reinforcement of laminated polymer composites. What are the current bottlenecks of this technology?

Milo Shaffer answered: The combination of carbon nanotubes with traditional structural fibres to create hierarchical composites, is a very promising and practical approach to improving state of the art materials. In these systems, the objective is to address the critical matrix-dominated failures that normally limit the performance of structural fibre composites (see for example our review by Qian *et al.*¹). There are a range of strategies for introducing the nanotubes. The specific example of direct growth of the CNTs on the carbon fibres offers potential advantages in processing and in the location/orientation of the CNTs. One central challenge is that growing CNTs on carbon fibre tends to damage the underlying carbon fibre; fundamentally, a good catalyst for CNT growth tends to dissolve carbon. Very recently, strategies have begun to emerge to tackle this problem; we ourselves have been able to grow grafted CNTs directly on carbon fibre in a continuous process, to produce carbon fibres that retain their original tensile properties. The resulting CNTs have a relatively small diameter and are short, as desired to obtain a high volume packing fraction of primary fibres in the final composite; it's worth noting that most CNTs grown on fibres are too long from this perspective. We plan to publish our process shortly. Intrinsically it is scalable and compatible with existing carbon fibre technology, and therefore could be practically implemented, in principle.

1 Qian *et al.*, *J. Mater. Chem.*, 2010, **20**, 4751–4762.

Pulickel Ajayan answered: I think the biggest challenge is the interface between the carbon fibers and the grown nanotubes. These are typically weak van der Waals forces and hence delamination of the nanotubes during processing limits the effectiveness of reinforcement. The control of length, density and size of nanotubes and the infiltration of polymers into nanotube forests, all determine the efficacy of this approach.

Philip Davies opened the discussion of the paper by Alan Windle: Could the role of the sulfur be to control the rate of growth of the iron nanoparticles in the early stages of the reactor?

Alan Windle responded: As we have described, it appears that sulphur has a profound influence on the growth of carbon nanotubes from nano-scale iron particles. Furthermore, the key to obtaining single walled nanotubes of good length and with a satisfactory yield, is to enable carbon and sulphur to be available while the iron particles are still very small, ~1 nm. Too much sulphur appears to prevent carbon interacting with the iron, while too much carbon will simply encapsulate the particle. We are suggesting that too much sulphur will initially

prevent CNT formation, but as it 'boils off' in the hotter part of the tube reactor, available carbon will begin to grow nanotubes, but now from iron particles which will have had greater opportunity to grow by collision. The question posed is important. One might expect that a coating of sulphur would make iron less sticky so that collisions would not lead to merging of the particles with such a high probability. However, under conditions where the surface iron and sulphur are highly mobile, I would not expect sulphur to preclude particle growth by collision. However, to put numbers on this statement is a future challenge.

Pulickel Ajayan asked: What is the diameter (or diameter distribution) of the nanotubes you obtain by CVD? Does sulfur make the average diameter larger?

Alan Windle replied: The diameter, and in a related way, the number of walls does seem to depend on the sulphur content. While it is impossible to spin without sulphur (and it is vital that the equipment is completely purged from sulphur to establish this fact) small controlled amounts of sulphur do lead to single walled CNTs in the diameter range 1-1.5 nm. With increasing sulphur there appears to be a jump to collapsed double walled nanotubes some 10 nm in diameter, further sulphur leads to more traditional multiwall tubes of a wide range of diameters. The central point of our paper is that the controlled amounts of sulphur available, along with carbon, as the first nano-sized particles of iron form, appear to be key to the achievement of wholly single-walled nanotubes. Excess sulphur blinds the iron particles, which while continuing to grow by collision, will not become active to grow nanotubes until the sulphur boils off as the reactants heat towards the maximum temperature (~1300 °C) of the continuous flow reactor.

Pulickel Ajayan asked: Are SWNTs the best material for spinning fibers and ensuring mechanical properties of the fiber? People have spun fibers with double walled nanotubes and gotten good results, especially because of the flattening observed for the large double walled tubes, increasing inter-tube adhesion.

Alan Windle responded: Most of our studies so far have concentrated on collapsed double walled CNTs of comparatively large diameter.¹ Indeed, we have pointed out² that the collapsed state would maximise the contact area between the tubes, to the benefit of strength where this was limited by the tubes pulling out from each other under tension. We now find that fibres made wholly from single walled CNTs of diameter of the order of 1 nm show yet better strength. What we do not yet know whether it is because the tubes are single walled or whether they are simply longer, although measuring the length of single walled nanotubes where the axial ratio may be of the order of 106 is a particularly difficult task. Alternatively, there is evidence of a very thin carbonaceous deposit on the outside of the single walled nanotube bundles which is more uniform than in the case of multiwalled tubes. Perhaps this coating has adhesive properties.

1 M. Motta, A. Moisala, I. A. Kinloch and A. H. Windle, *Advanced Materials*, 2007, **48**, 16, 4824–4836.

2 J. J. Vilatela, J. A. Elliott and A. H. Windle, *ACS Nano*, 2011, **5**, 1921–1927.

David Zitoun said: Could you comment on the difference between the CNT fibres produced with your single pot method and those produced with post-CNT-synthesis coagulation spinning?

Alan Windle replied: Coagulation spinning, developed by the Bordeaux group of Philip Poulin, was probably the first successful method for the production of continuous carbon nanotube fibre. However, the essential difference in terms of the product is that in the case of coagulation spinning the resultant fibre is a polymer/CNT composite material. In terms of the process, as you point out, it is a two stage process requiring first the synthesis of the nanotubes as a powder, and their suspension in a liquid before the actual spinning. The original polymer used was polyvinyl alcohol, and property improvements have been reported as a result of post spinning treatments. We all await the commercialization of the process. It appears that a company, Canoe, has this in hand as a part of a wider program to spin fibres enabled with nanocomposites, so we must watch this space.

Chris Ewels asked: Is your sulphur model transferable to other growth impurities/heteroatoms, such as oxygen?

Alan Windle responded: I have been attracted to the chemical similarities between oxygen and sulphur, spurred on perhaps by research into cast irons, where the influence of sulphur and oxygen on the growth form of graphite on cooling the metal from the melt, is assessed as a 'sulphur/oxygen equivalent'. Our experience is that if we supply modest oxygen, perhaps by using ethanol as our main source of carbon, we still need sulphur for the synthesis to work, although the actual synthesis process worked very smoothly with alcohol feedstocks in general (except of course methanol, where all the carbon tended to elope with the oxygen). However, it is probably worth pointing to a major difference between sulphur and oxygen in the context of the process. Namely that carbon's affinity for oxygen is very considerable, with carbon monoxide being one of the most stable of molecules, at least in terms of bond strength, whereas carbon disulphide has, in comparative free energy terms, only marginal stability. I am sure we can learn more by ranging more widely across the periodic table, especially with respect to the choice of catalyst metal, although we have to confess we need to keep one eye on the commercial scaleability of the process, and ferrocene is cheap and widely available.

Thurid Gspann addressed Chris Ewels and Alan Windle regarding question 11:

We're talking about oxygen and sulphur analogies and probably also have to consider nitrogen in this context. These analogies are known *e.g.* from metallurgy regarding cast irons. However, in our process regarding floating nano-catalyst particles, there appear to be marked differences in their second role. We have not been able to spin without sulphur, even with oxygen in the process. In the case of sulphur, we typically grow either single walled tubes with small diameters or, if the system is overloaded with sulphur, we grow multi walled CNTs, both uncollapsed.

On the other hand, the double-walled collapsed tubes were mainly observed in alcohol spun CNTs, thus we can assume the oxygen acts as an etchant that leads to the destruction of or prohibition of formation of small diameter tubes, hence

favouring thin walled big diameter CNTs which can collapse under atmospheric pressure.^{1,2}

- 1 M. Motta, A. Moisala, I. A. Kinloch, and A. H. Windle, *Adv. Mater.*, 2007, **19**, 3721–3726.
2 J. A. Elliott, J. K. W. Sandler, A. H. Windle, R. J. Young, and M. S. P. Shaffer, *Phys. Rev. Lett.*, 2004, **92**, 9, 095501-1.

Ayse Turak said: Since the particulates decorate the outside of the CNTs, it was unclear how the wood knot analogy you used to explain that they do not affect the strength would apply. Your analogy would suggest that the defect should be inside the fiber. Could you please clarify?

Alan Windle responded: Your question raises an important matter of detail regarding the continuous spinning process that we have developed at Cambridge. The aligned aerogel as it emerges from the reactor is dilute, with a density approximately 1% of that of the final fibre. Condensation is achieved by spraying the aligned aerogel with atomised acetone, where surface tension effects achieve condensation. However, the process by which it achieves its final density, is not exactly affine, and is a combination of both shrinkage and folding. It is the folding component of this process which takes particles, originally on the outside of the aerogel, into the inner regions of the final fibre.

Thurid Gspann regarding question 13 addressed to Prof. A. Windle: We are reaching the very interesting point, where we possibly have to change our view of what is considered to be the ideal material for macroscopically usable, mechanically strong materials. One reason for the presented study (paper 2) was that impurities were considered to be the main reason that CNT fibres did not reach the high strength values expected. However, with the achievement of pure fibres, yet without changing the fibre comprising CNTs themselves, the expected strength increase did not appear; although the consistency of properties was improved significantly. On the other hand it becomes clearer, that constructing fibres out of pure CNTs with a finite length and pure carbon-carbon contacts means intending to construct a fibre out of a lubricant. Hence, a certain amount of defects increasing the roughness and friction between the CNTs, also counting covalent cross-links which would show in Raman in the so called D(defect)-peak, or as well a certain amount of entanglement without disrupting the bundle alignment too much, can help revealing the CNT properties in macroscopically useful objects.

Milo Shaffer enquired: At several points, you discuss the issue of trapping of particles within the fibres, both when considering the incorporation of catalyst agglomerates and the possibility of length fractionation. Is there any effect of 'sieving' through the growing networked 'sock' of nanotubes, such that material outside the sock is rejected in the exhaust and material inside the sock is collected in the fibre? In your model, the catalyst agglomerates form near the furnace wall and can be rejected, if they do not become sufficiently 'hairy' to entangle with the 'sock'. Shorter nanotubes might grow in the faster flowing central region of the furnace, but the opportunity for fractionation might be more limited. Is it possible to estimate the 'mass balance' of the process, namely what proportions

of the feedstock ends up in the final fibre, in rejected solids/nanoparticles, or gaseous waste?

Alan Windle replied: I cannot answer this question in full, as the developed process which all but eliminates the particles in the fibre is comparatively new and we have not carried out the full mass balance yet. It is perhaps worth making a note about the 'sock' here. The carbon nanotube aerogel, as it moves down the reactor appears to form a cloud, concentric with the reactor which is darker at its edges than in the centre, hence the term 'sock'. However, when running under conditions which lead to minimal particle encapsulation in the eventual fibre after condensation, then we do not see a sock but simply a 'sausage' of aerogel along the reactor axis. At this stage we speculate that the dark periphery of the 'sock' was in fact caused by the additional particulate materials from the slower moving gas stream near the walls which, because they were 'hairy' with badly formed CNTs became attached to the aerogel proper. The mechanical fractionation, ideally, would mean that only CNTs of greater than the entanglement length would appear in the fibre. We, of course, cannot rule out that much shorter nanotubes would still become incorporated in the fibre. But, very detailed examination by high resolution TEM does not show any population of shorter nanotubes either within the bundles or between them, indeed nanotube ends are only seen on very rare occasions. It may be that the process simply does not make shorter tubes within the aerogel itself.

Milo Shaffer asked: Do you yet have a full mass balance for the process, to determine the fate of all of the injected carbon feedstock, including both collected fibre and the waste gas stream? For example, it would be interesting to know if shorter CNTs were escaping with the waste gas stream rather than becoming entangled in the 'aerogel', or if other nanoparticles or complex aromatics were forming.

Alan Windle commented: I think this point was partly addressed in my response to your question 15. There is no doubt that the waste gas drawn out through the gas valve contains particulate matter including nanotubes. It is difficult to determine the relative amounts of nanotubes and approximately equiaxial particles present, as the filters will always discriminate in favour of nanotubes, but that is not to say that it shouldn't be attempted.

Nazario Martin asked: Could the methodology developed for the synthesis of the CNTs be applicable for preparing chiral CNTs? What parameters should be changed? Do you think that a new scenario would be needed? I mean, for instance, the use of nanorings, *etc.*

Alan Windle answered: This is an important issue. Viewed from outside the chemistry community, one cannot but wonder that if classical synthetic chemistry can make almost any polymer molecule that can be imagined, then why cannot they create single walled carbon nanotubes, in a process potentially scaleable to industrial levels. Of course it is not as easy as that, but there has been progress using a variety of synthetic schemes, some involving ring assembly. Perhaps the most recent advance was reported in *Nature* last month by Sanchez-Valencia

et al.,¹ where a particular aromatic arrangement laid on a Pt catalyst, was made to spontaneously reassemble into the end cap combined with a very short starting length of an armchair, single walled nanotube. The tube was then lengthened from this seed using catalytically decomposed hydrocarbon gas. I plan to say more about this different route to nanotubes at the end of the meeting (Paper 25).

1 J. R. Sanchez-Valencia *et al.*, *Nature*, 2014, **512**, 61–64.

Pagona Papakonstantinou said: Could graphene platelets be synthesized using the floating catalyst method?

Alan Windle responded: Wow! Thank you for making us think out side the box. One tends to want graphene flat, and covering a decent area, perhaps a few square microns or more. If one could generate graphene in the gas phase not coated onto a catalyst, and one is thinking in terms of single layered material, then I do not see how one could stop it rolling up, or joining up with other sheets perhaps in an unfortunate, disorganised way. If one can coat facets of the catalyst particles with graphene, particles which are small enough to be entrained in a gas flow, yet large enough to produce graphene of an acceptable area, then it might be possible. Perhaps another route would be to use larger particles and form a fluidised bed through which the reactants are passed. Of course the graphene would still have to be subsequently removed from the particles and transferred.

Pedro Costa opened the discussion of the paper by Mark Baxendale: How are the different iron structures (alpha and gamma) arranged structurally along the nanotubes? Is there a preferential presence of one of the phases at the tips?

Mark Baxendale responded: The gamma phase is most frequently observed at the tips but it is also observed along the length but much less frequently.

Pedro Costa asked: Are the arms in the sea-urchin like structures fully filled? What would be their relative filling yield across the sample?

Mark Baxendale replied: It is difficult to give figures in answer to both questions because the sea-urchin 'arms' are not easily accessible with the TEM. The best statement that we can make is that continuous filling on the micrometre scale is frequently observed whereas a surface-grown structure prepared under similar vapour conditions is dominated by 10–100 nm scale encapsulated nanowires with 100–1000 nm gaps between them.

Thurid Gspann asked: You mentioned that substrate grown MWCNTs are inconsistently filled with ferromagnetic material, while the MWCNTs grown on spherical particles grown by boundary layer chemical vapour synthesis are very consistently filled. Do you see any differences in the ferromagnetic properties depending on the consistency of the filling, and is there a minimum size the nanowires have to reach to show any ferromagnetic properties at all?

Mark Baxendale answered: The saturation magnetisation is relatively unaffected by the continuity of the MWCNT-encapsulated ferromagnetic nanowire.

However, owing to the influence of shape anisotropy, the coercive field is enhanced by better continuity. If the nanowire dimensions are less than that of a single ferromagnetic domain, *circa* 10 nm, we would expect to observe a superparamagnetic response.

Pulickel Ajayan remarked: In the Fe filled nanotubes produced by CVD reported before, people have observed the gamma Fe phase and found them to be ferromagnetic due to the presence of carbon impurities and lattice distortion? How do you tell about the ferromagnetic phases in your sample?

Mark Baxendale responded: The evidence for antiferromagnetic components is largely from the observation of exchange bias features, that is, an offset hysteresis loop and pinned moments in the ferromagnetic components at low temperature, as one would expect from antiferromagnetic and ferromagnetic phases in contact. The former is difficult to confirm experimentally since magnetometers have a small remnant field which comes from the components in the measurement system. The latter can be determined by comparing a weighted sum of the saturation magnetisations for each component, calculated using the bulk values and the relative abundances of the phases (antiferromagnetic components have a small or no net magnetisation), with the measured value. Typically, the measured values are a factor of two to three times less than the calculated value, indicating significant pinning. If, within the nanowire, there are significant ferromagnetic gamma-Fe components, the measured value would be greater than the calculated value. Our magnetisation measurements are conducted on powder extracted from the reactor so these comments apply to the net magnetisation, it does not exclude a small ferromagnetic component from gamma-Fe. There are several reports of exchange bias phenomena in iron-filled nanotube systems, the debate is whether the junctions are arranged sequentially along the length of the nanowire or coaxially.

Toshiaki Enoki asked: Magnetic particles are included in the sample. Some are ferromagnetic. I am expecting that the application of external magnetic field will affect the orientation of magnetization and subsequently the orientation of nanoparticles. So the growth progress is modified by applying the magnetic field. My question is what happens in the growth process under the application of the magnetic field?

Mark Baxendale answered: There is always an unintentional magnetic field in a reactor heated by resistive heating elements which carry a large current. For our reactor, we calculate that this field is too weak to orient magnetic domains at the formation temperature of the structures (900 °C) so thermal randomization of the moments will erase any preferred orientation due this magnetic field. We have not tried to intentionally introduce a strong magnetic field to influence the growth process. We anticipate that such an axial field would keep the particles in the vapor for longer and, therefore, increase the length of the radial nanotube 'arms'. But there are other ways to achieve this, for example by introducing trace quantities of sulfur to accelerate the growth and selecting precursor molecules with higher metal-carbon ratios (this ratio in ferrocene is 1 : 10).

Thanh Nguyen said: Could you please comment on the potential of these iron-based nanowires encapsulated by multiwalled carbon nanotubes for treating cancer by magnetic hyperthermia?

Mark Baxendale responded: Surface-grown equivalent structures are receiving a lot of attention in the literature for this application. The advantage of the MWCNT-encapsulation is that the nanowire is passivated and the surface is relatively straightforwardly functionalised with desirable molecular groupings (antibodies, drugs, *etc.*). For surface-grown structures, the localised heating in an applied r.f. magnetic field comes from the rotation of the structure in response to the field but immobilisation can allow the hysteretic dissipation to be usable. The structures also exhibit MRI contrast agent functionality. The dimensions of the radial structures that we have so far produced are *circa* 10 micrometres; scaling to the 1 micrometre is required for this application. The radial morphology has the advantage of minimising the torque in the r.f. field and having a component of the magnetic easy axis in the direction of the external field for all orientations (structures disperse randomly in a tumour), this means that the hysteretic component of heating is likely to be better than an equivalent rod-like structure.

Milo Shaffer queried: The driving force for nanotube growth has been much discussed, especially in the earlier carbon filament literature (see for example Baker's review in *Carbon* 1989)¹. Whilst both temperature and concentration gradients have been mooted, the insensitivity to the exothermic/endergonic nature of the carbon source decomposition tends to favour concentration arguments. Do you have evidence yet, in your experiments to favour temperature over concentration effects, or indeed steric interactions thought to influence CNT array growth? Have you been able to prove whether tip or base growth dominates?

1 R. T. K. Baker, *Carbon*, 1989, 27, 315-323.

Mark Baxendale answered: The radial structures nucleate and grow in both concentration and thermal gradients in the reactor but only when the flow rate is low (15 cm). The relevance of the low flow rate is that local thermal gradients will not be damped; the nucleation imposes a spherical diffusion gradient as the central particle consumes vapour feedstock and feedstock to the tip growth fronts is directed by spherical diffusion gradients created by the endothermal graphite carbon formation and exothermal hydrocarbon decomposition at the tips. We exclude base growth - by which I mean the growth of the nanotube 'arms' is fed by vapour supply to the central particle - because the outer diameter of the radial structures does not depend on residence time, that is, the duration of exposure to the vapour. This observation is consistent with the tip growth model because the growth is 'switched off' by contact with the isothermal surface, that is, the thermal gradients at the tips are damped by this contact. The degree of order seen in the radial structures, particularly the continuity of the central nanowire, is better than that observed with surface-grown structures in the same reactor conditions, so we can conclude that the absence of steric interactions improves order; in other words, the perturbation of the vapour feedstock flow to tips created by a near neighbour creates the discontinuities in the central nanowire.

Pulickel Ajayan commented: In terms of growing graphene ribbons or corrugated graphitic filaments grown by CVD, perhaps these could be done by vapor phase growth without using metal catalysts; we have previously used non-catalytic methods, such as the arc discharge, to produce platelets and filaments along with tubes. The metal catalysts seem to produce tubular forms in general.

Juan Casado responded: I fully agree with this statement.

Pulickel Ajayan commented: The difficulty in measuring mechanical properties, and the role played by defects such as edges and grain boundaries *etc.*, is that it leads to a scatter in the measured values of the mechanical properties

Pulickel Ajayan commented: The nomenclature issue is a tough one since there is so much variability in structure and this is closely related to physical properties like mechanical strength.

Pulickel Ajayan asked: Since there are so many structural and dimensional variations in the nanotubes grown by various techniques, it may be a difficult task to categorize them (in assigning nomenclature) by structure or dimensions. Wouldn't it be more interesting to categorize them by conductivity or strength, similar to what has been done for carbon fibers?

Varsha Khare asked: What are the possibilities of the formation of metallobenzene after the synthesis or after dissociation of ferrocene *i.e.* after complete synthesis? Was this verified by XPS.

Alan Windle replied: In working to understand the important factors which control our synthesis of CNTs from floating catalysts, it has become very clear that the decomposition of the reactant precursors is complicated. With respect to ferrocene, it is clear from the literature (as referenced in our paper) that autocatalysis is an important feature, with the pre-existence of iron particles or surface deposits totally changing the kinetics of the decompositions. In lay terms one might see that iron present as the metal will steal the iron atom away from a ferrocene molecule, whereas if the molecule is simply left to its own devices, there is evidence that the carbon rings start to decompose with the iron atom *in situ*. The adsorption of benzene on the iron catalyst surface, is an important point as it could play a part in CNT assembly at the surface. I would be eager to see any experimental evidence for this, bearing in mind that modelling is also likely to provide insights in the near future. Overall, the studies reported in our paper underline that the iron particles, once they start to form, are not only catalysts for the growth of nanotubes, but also play a very important role in catalysing not only the further breakdown of ferrocene, but also the breakdown of thiophene and the plain hydrocarbon feedstock too. This fact has been articulated by chemists since the inception of CVD routes to make nanotubes, but it has also been overlooked from time to time.

Varsha Khare commented: I agree with the idea of edge-enhancement by the coexistence of sulfur and oxygen as demonstrated in our work on sulfur doped graphene.

Philip Davies said: Sulfur chemisorption on metal surfaces is very complicated (see for example ref. 1 and 2). The introduction of another adsorbate (carbon in this case) will add a whole new level of complexity (see ref. 3 for example) and so it is not surprising that the chemistry involved in your system is poorly understood.

1 J. Oudar, *Bulletin De La Societe Francaise Mineralogie Et De Cristallographie*, 1971, **94**, 225.

2 A. F. Carley, P. R. Davies, R. V. Jones, *et al.*, *Surface Science*, 2000, **447**, 39-50.

3 A. F. Carley, P. R. Davies, R. V. Jones, *et al.*, *Chemical Communications*, 2000, 185-186.

Alan Windle responded: Thank you for this input. An understanding of the complexities of the role of sulphur as a surface promotor/surfactant will be necessary before we can have full scientific confidence in the floating catalyst synthesis of carbon nanotubes. However, we appear to have a further complicating factor in that, compared with, for example the system described in the questioner's reference 3, especially at small sizes, as the metal particles will not be crystalline, although there could be ordered faceting of their surfaces. Hence, the level of atomic disorder which will have to be faced before any exact explanation can emerge, is much higher.

Malcolm Heggie remarked: You mentioned you had been asked if your aerogel technique could be applied to make graphene. According to our DFT calculations sulfur should be capable of breaking open folded graphene.¹ Thus the wide nanotubes you made in early work - the ones which collapsed like a fireman's hose and have been termed 'dog bone' might be capable of being opened up by exposure to sulfur, forming sulfur terminated graphene ribbons.

1 J.-J. Adjizian, C. D. Latham, S. Öberg, P. R. Briddon, M. I. Heggie, *DFT study of the chemistry of sulfur in graphite, including interactions with defects, edges and folds*, *Carbon*, 2013, **62** 256-262.

Alan Windle answered: Thank you for drawing attention to this study. Modelling carried out by James Elliott some time back on 'dog-bone' collapsed nanotubes, indicated that the bonds, where the bending was sharpest had distinct sp³ character. So one might expect these to be the most vulnerable to chemical opening and stabilisation, along the lines you predict. However, the fact remains that when we spin carbon nanotube fibres in the presence of sulphur, the nanotubes we make are not unzipped, even in the case of 'dog bone' nanotubes.

Pulickel Ajayan said: Has anyone looked into how sulfur dopes substitutionally into the graphene lattice?

Lyndsey Mooring opened the discussion of the paper by L. S. Hui: A question to the carbon nanomaterials research community was raised. Discussions are covering the next generation of carbon nanomaterials and preparation, along with mixed views on what are desirable attributes. Is there a sense among the community of when this new generation of materials will be available? Whether that be chirally pure or defect controlled materials, for example.

Milo Shaffer answered: It seems to be quite typical that new materials often take 20-30 years to develop from initial observation to practical products. The

majority of the commercial nanotube production currently available in bulk in some way draws on earlier work on carbon filaments in the 1970s and 80s. We should therefore be entering an interesting time for the commercialisation of newer nanocarbons and associated applications, drawing on the explosion of scientific interest from 1991. For example, the price of single walled carbon nanotubes, clearly identified only in 1993, has fallen by around 2–3 orders of magnitude just this year. The continuing development of separated metallic and especially semiconducting SWNTs is also encouraging, especially since semiconducting SWNTs so dramatically outperform other conjugated polymers, particularly in terms of mobility. In an analogous fashion, many current commercialised 'graphene' materials draw on graphite oxide or other exfoliated graphite approaches that pre-date the wave of interest that has emerged since 2004. Practical materials exploiting the understanding of more perfect single layers, established in the last decade, may still take some time to emerge.

Pulickel Ajayan commented: Small start-ups are making specialty products using nanotubes or graphene and these products could become widely available in the next 5–10 years.

Mark Baxendale said: Convincing manufacturers that a synthesis can be scaled to large volume production is one thing but answering the question of why should the manufacturer do so if there is no immediate market for the product is another. We need an application, often called the 'killer application', for which there is an existing large market and the nanocarbon-based technology performs at least one order of magnitude better than the alternative technologies. Considerable benefits will follow from large volume production, such as quality control and economies of scale, which will open up possibilities for nanocarbon technologies that are unrelated to the 'killer'.

Pulickel Ajayan opened the discussion of the paper by A. Turak: When a graphene/copper system is annealed, do you observe any evidence for carbon diffusion into the copper substrate?

Ayse Turak responded: We have not done a systematic study of carbon diffusion into the copper substrate. However, a recent study by Leong *et al.*,¹ has shown that significant C diffusion can be seen for moderate temperature annealing (300°C) of Ni-graphene contacts. In their case, they saw significant growth of the D band with annealing. In our tracking of the impact of low temperature annealing, we did not see such an effect in the Raman spectra. Additionally, they did not see the shift in the 2D band that we observed for neither Ni-graphene (where there was determined to be C diffusion) nor Au-graphene (where there was no C diffusion). We believe that though C diffusion may be a potential explanation for the increased resistance to etching with annealing, it is likely not occurring in the case of Cu. We are planning to perform a follow-up experiment using Ni-graphene to further clarify this mechanism.

1 Leong *et al.*, *Nano Letters*, 2014, **14**, 3840–3847.

Milo Shaffer remarked: Both mechanisms which you propose imply a very high degree of copper mobility; are the diffusion rates reasonable at the temperatures you have studied? Is etching at the flake boundaries a possibility?

Ayse Turak responded: Though we have not measured the diffusion directly, Cu is known to be highly mobile at room temperature, especially in the presence of carbon based molecules (see for example ref. 1) or with oxygen (see for example ref. 2). STM measurements especially have shown the high mobility of Cu atoms at room temperature.² We are confident that the diffusion rates of Cu would be reasonable under the moderate annealing that we performed to allow either of the two proposed mechanisms. The strain relief mechanism in particular does not require much movement of Cu atoms. The observed shift in the 2D band of the Raman spectrum corresponds to only about 0.167% strain relief ($\sim +10\text{cm}^{-1}$), using the values reported for $\delta\omega_{2D}/\delta\varepsilon$ of $\sim -66\text{cm}^{-1}/\%$ strain for deposition induced tensile strain³ and $\sim -64\text{cm}^{-1}/\%$ for applied tensile strain.⁴ Additionally, strain is known to enhance diffusion (see for example Spjut *et al.*)⁵, so a strained Cu surface from high temperature CVD growth would have more mobile surface atoms than the equilibrium surfaces measured with STM. These suggest that the strain relief mechanism might be the correct one for the enhanced coupling with low temperature annealing. With regards to the etching at flake boundaries, we would also expect that etching would begin at the edges of the graphene flakes. However, our visual observations do not support that, as we do not see the graphene flakes getting smaller with etching time. Further study is necessary to understand the impact of the plasma on the graphene itself.

1 Rosei *et al.*, *Science*, 2002, **296**, 328–331.

2 Frerichs and Liberman, *Phys. Rev.*, 1961, **121**, 991; Chapter 17 *Scanning Probe Microscopy and Spectroscopy in Characterization of Solid Materials and Heterogeneous Catalysts*, Wiley, 2012.

3 Yu *et al.*, *Phys. Rev. B*, 2011, **84**, 205407.

4 Mohiuddin *et al.*, *Phys Rev B*, 2009, **79**, 205433.

5 H. Spjut and D. A. Faux, *Surf. Sci.*, 1994, **306**, 233–239.

Alexander Zöpfl communicated: Full etching was confirmed *via* optical microscopy. In the case of oxygen- or air-etching, we could also confirm this with Raman spectroscopy or mapping, since the resulting CuO has specific peaks around 500cm^{-1} . Would it be possible to monitor the etching process itself by comparing the intensity ratios of graphene and CuO peaks?

Lok Shu Hui communicated in reply: Thank you for your question, it is an excellent suggestion. In our Raman measurements, however, we did not observe significant signal peaks around 520 , 640 or 280cm^{-1} , which have all been attributed to Cu oxides.¹ This is true even for scans near the graphene edge or on smaller flakes where a signal is expected both from the graphene and the unprotected Cu surface. One possible explanation could be the formation of metastable cuprous oxide, as suggested by Lengelet *et al.*,² which has a peak between 150 and 250cm^{-1} , below our detection range. Though we have not been successful in tracking the Cu oxidation using the Raman so far, it might be possible to lengthen the scan time and region to collect more of the copper oxide

scattering to enhance the signal. Further studies with XPS are also planned to examine the evolution of Cu oxides.

1 Schennach and Gupper, *Copper oxidation studied by in situ Raman spectroscopy*, *MRS Proc.*, 2003, **766**, E3.2.

2 M. Lenglet, K. Kartouni, J. Machefert, J. M. Claude, P. Steinmetz, E. Beauprez, J. Heinrich and N. Celati, *Mater. Res. Bull.*, 1995, **30**, 393–403.

Thurid Gspann asked: Regarding the post-annealing CET (Fig. 4), assuming the proposed model that by annealing a CuO layer is built up around the graphene edges (Fig. 9), and further assuming that oxygen etches preferentially from the graphene edges or might creep under the graphene, should then the annealing not very effectively protect the graphene etching by oxygen and air? While the CET of N₂ on the other hand, N₂ sputtering being a high kinetic energy process anyway and not necessarily preferential to edges, would not be expected to show such a massive increase by annealing?

Ayse Turak replied: You raise an excellent point with regards to the effectiveness of annealing in oxygen and air if the plasma attacks from the graphene edges. Though we too would expect that the highly reactive edges would interact with the plasma first, our visual observation with air sputtering, where pits were seen at many locations on the graphene flake, suggests that the plasma attacks the whole graphene flake equally. We don't really see a creeping removal of graphene from the edges with any plasma exposure (*i.e.* the graphene flakes do not get smaller and smaller with etching). Rather the whole flake seems to become progressively less visible. More work needs to be done to fully understand the impact that the plasma is having on the graphene, especially with regards to the plasma intensity. We speculate that increasing the plasma dose should shift the CET, though the general trend might remain. N₂ also is a special case, and one where the visual observation of the CET is very misleading. It appears in the case of N₂ what the CET is really tracking is the removal of different copper oxides. This gives us some clues regarding the possible mechanism for the improvement of the mechanical coupling - potentially non-equilibrium forms of copper oxide are being formed during the low temperature annealing, as suggested by Lenglet *et al.*¹ These could be protective of the graphene edges and lead to improved coupling.

1 M. Lenglet, K. Kartouni, J. Machefert, J. M. Claude, P. Steinmetz, E. Beauprez, J. Heinrich and N. Celati, *Mater. Res. Bull.*, 1995, **30**, 393–403.

Philip Davies remarked: Even at room temperature, I would expect a lot of movement from the copper atoms at the surface in the presence of oxygen. Is the bonding of the graphene to the surface strong enough to protect it from oxidation?

Ayse Turak replied: The graphene-Cu bond is expected to be very weak. Yet, graphene is widely reported as a passivation layer,^{1–4} which is also supported by the visual observation in our work of contrast in regions protected by graphene *versus* those unprotected. However, Zhou *et al.*⁵ did show that over the long term,

graphene seems to enhance the oxidation of Cu, so it may be that the mobility of Cu atoms is a factor in such behaviour.

- 1 S. Chen, L. Brown, M. Levendorf, W. Cai, S.-Y. Ju, J. Edgeworth, X. Li, C. W. Magnuson, A. Velamakanni, R. D. Piner, J. Kang, J. Park and R. S. Ruoff, *ACS Nano*, 2011, 5, 1321–1327.
- 2 E. Sutter, P. Albrecht, F. E. Camino and P. Sutter, *Carbon*, 2010, 48, 4414–4420.
- 3 J. Iijima, J.-W. Lim, S.-H. Hong, S. Suzuki, K. Mimura and M. Isshiki, *Appl. Surf. Sci.*, 2006, 253, 2825–2829.
- 4 A. Ferrari and J. Robertson, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2000, 61, 14095–14107.
- 5 Zhou *et al.*, *ACS Nano*, 2013, 7, 6939.

Toshiaki Enoki said: The interaction between graphene and Cu substrate is weak, while other substrates such as Ni and Pd have stronger interactions with graphene. My question is if the results you obtained for the Cu substrate are modified when we employ Ni or Pd as the substrate?

Ayse Turak replied: Our interest in the mechanical coupling was due to the controversy that exists on the strength of the coupling between Cu and graphene. However, other metal systems have also shown a change in properties with low temperature annealing. The metal-graphene contacts most commonly annealed at temperatures similar to ours are usually made from exfoliated graphene, with the improvement in properties often attributed to the removal of resists needed to facilitate the transfer of graphene onto metal contacts. A recent study by Leong *et al.*,¹ has suggested that annealing with Ni leads to significant C diffusion, which could be a potential mechanism for improvement of the mechanical coupling. Though we did not see the increase in the D band with annealing that they observed, a follow-up experiment with Ni is planned to further clarify the potential mechanisms. One caveat of using Ni or Pd is that we can no longer apply our visual observation method to confirm the etching of graphene. Cu conveniently oxidizes with a change in the refractive index at low temperatures and under the plasma. Neither Ni nor Pd has a similar behaviour. However, tracking the graphene removal with Raman spectroscopy should be relatively easy in those cases.

- 1 Leong *et al.*, *Nano Letters*, 2014, 14, 3840–3847.

Andreas Hirsch opened the discussion of the paper by Matthew Rosseinsky: How do you get rid of the metallocene?

Matthew Rosseinsky responded: It is removed in the final antisolvent precipitation step as it is soluble in the hexane used.

Irena Kratochvilova queried: How do you control/understand the electronic structure of a superconducting material? Please, describe in more detail the superconductivity process in this particular case.

Matthew Rosseinsky replied: This is a very broad question, as the mechanism of superconductivity is well-understood in only a very few materials. In our case, the proximity of magnetically ordered states to the superconductors makes it likely that the electronic correlations are important in the superconducting

pairing, although this does not mean that conventional electron-phonon coupling is not also involved. There are recent reviews (e.g. from Tossatti, Capone and colleagues in Trieste)¹ on this interesting and controversial topic.

1 M. Capone, M. Fabrizio, C. Castellani and E. Tosatti, *Reviews of Modern Physics*, 2009, **81**, 943–958.

Chris Ewels remarked: If a Jahn–Teller distortion is splitting the triplet, to reduce this effect would it be possible to "rigidify" the fullerene somehow, for example by using endofullerenes?

Matthew Rosseinsky remarked: This is a very interesting idea, and the recent advances by the Shinohara¹ group in making larger quantities of endohedral fullerenes will enable investigating it, as the challenge to this point has been having enough endohedral material available to systematically identify the chemistry.

1 K. Akiyama, T. Hamano, Y. Nakanishi, E. Takeuchi, S. Noda, Z. Wang, S. Kubuk and H. Shinohara, *J. Am. Chem. Soc.*, 2012, **134**, 9762–9767.

Malcolm Heggie said: The HOMO of C₆₀ is fivefold degenerate and therefore gives a higher density of states at the Fermi level, with possibly higher T_c - why is there no emphasis on hole (super-)conductivity?

Matthew Rosseinsky replied: It is chemically challenging to make cationic compounds of C₆₀, and the anions that are chemically compatible with these highly oxidising cations tend to be large, and place the cations too far apart, producing insulating behaviour.

Malcolm Heggie asked: For hole conductivity, you say the problem is the large anions - surely these push molecules further apart, reducing the band width. This increases the density of states at the Fermi level and hence T_c, surely?

Matthew Rosseinsky commented : If the material remains metallic and the superconducting pairing is BCS, that is true. The problem is that if the overlap becomes less than the interelectron repulsion, the electrons become localised in the Mott–Hubbard insulating state and the metallic behaviour, and thus the superconductivity is lost. If we could control the spacing between the cations better, we might access the exciting regime just beyond the Mott–Hubbard transition. We are currently limited by the chemistry.

Thurid Gspann asked: Do you think there could be another solvent that would give you better material properties?

Matthew Rosseinsky responded: It's entirely possible, the investigation would need the commitment of a lot of resources though.

Milo Shaffer asked: In your synthesis, you used the specific 3 : 1 stoichiometry as well as controlling the redox potential of your reagent. Can you say whether either of these measures is necessary or sufficient?

Matthew Rosseinsky replied: This is a very interesting point for future investigation – as your question implies, if we are redox-limited then an excess of the metallocene anion would not matter.

Chris Ewels enquired: A question was raised concerning potential standardisation of carbon nanoform/allotrope nomenclature. We recently tried to address this issue through a categorisation of various carbon nanoobjects based on topological transformations of graphene required to produce them. These are ‘thought experiment’ transformations such as introducing wedge disclinations or dislocations, cutting, rolling, *etc.* Qualifiers could then be added to these base-form definitions to describe local/periodic structural variation (such as waviness).¹ The same paper also proposes a chemical structure nomenclature for functionalisation, following literature standard practise for endohedral filling of species B with species A described as A@B, adding species B with species A covalently attached to its surface as A/B. This convention has been developed further by M. Monthieux in his book “Carbon Meta-Nanotubes” to include X:CNTs to indicate carbon nanotubes (CNTs) doped by species X, X-CNTs to indicate CNTs functionalised by species X, X/CNTs to indicate CNTs decorated/coated by X, X@CNTs to indicated CNTs filled with X, and X*CNTs, X*BNNTs to indicate heterogenous nanotubes. Other (more experimental) nomenclature attempts include those by Inagaki and notably Gogotski who focused on growth-based naming.² IUPAC proposed in 1991 a list of 110 individual definitions for carbon materials, but with no attempt to coherently link these into a structured nomenclature. There are now ISO and IUPAC committees looking at this issue.

Taxonomy chart of primary carbon nanoforms

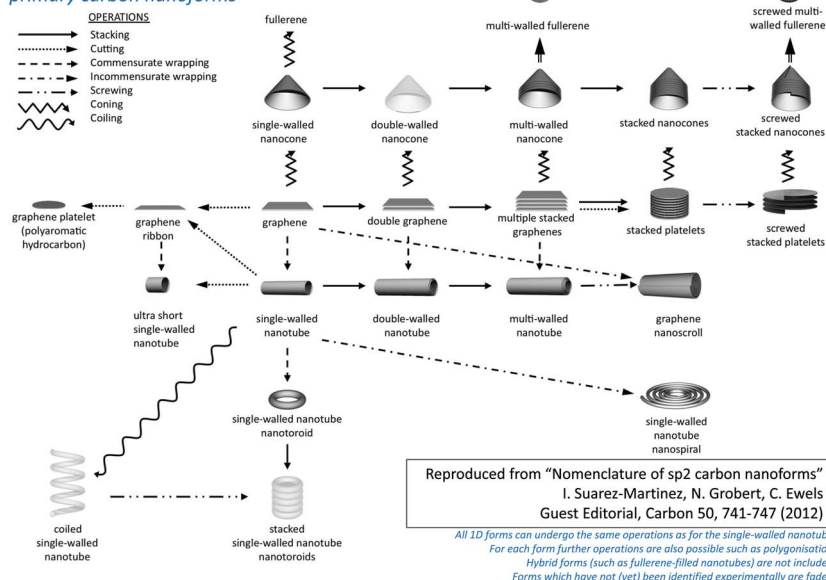


Fig. 1 Classification of the different "primary carbon nanoforms".

- 1 C. Ewels *et al.*, *Carbon*, 2012, **50**, 741.
2 Gogotski *et al.*, *Mat. Res. Innov.*, 2003, **7**, 192.

Vladimir Falko responded: Standardisation is an important issue for graphene applications. To mention, the European Graphene Flagship has a work package dedicated specifically to standardisation of graphene for various applications, including development of characterisation protocols suitable for industry and mass production.

Juan Casado commented: Fully in agreement with the needed uniformization of the nomenclature.

Milo Shaffer replied: There was some discussion about the relevance of topology to carbon materials classification. Whilst not applied to nanomaterials, it may be interesting to note that graph theory has been applied to the determination and classification of all possible periodic carbon allotropes within certain bonding criteria (see for example Strong *et al.*).¹

- 1 Strong *et al.*, *Phys. Rev. B*, 2004, **70**, 045101.

Pedro Costa addressed Pulickel Ajayan and Chris Ewels: Are we any closer to having a taxonomy chart for carbon nanostructures? This is a recurrent point in the field with journal editorials and considerable discussion going on. Before even establishing metrology standards we should have a consensus of what we are standardising (and how we name it). With the advent of industrial applications of nanotubes and graphene, may a forum to establish a roadmap like the ITRS be considered?

Chris Ewels replied: In case it's useful, here is the diagram (Fig. 1) showing the classification of the different "primary carbon nanoforms", reproduced from ref. 1 in the paper but at a higher resolution.

- 1 C. Ewels *et al.*, *Carbon*, 2012, **50**, 741.

Pulickel Ajayan replied: As I have repeatedly mentioned during discussions, it may be better to create an Ashby like chart where the different types of nanotubes are plotted in a stiffness-electrical conductivity (or other properties) map. Rather than separating in terms of structure/dimension/morphology, this type of property based classification (as used for carbon fibers for example) might be more interesting and useful. Of course the roadmap for nanotube based technologies is still premature in my opinion.

Pulickel Ajayan commented: Regarding nomenclature again, is it possible to consider factors other than topology for classification of nanotubes?

Chris Ewels replied: Please see my earlier response.

Malcolm Heggie remarked: I think this is a brave attempt. Where is the theory of topology that applies here, combining different operations? Has this been worked out or does this presage such topological understanding?

Chris Ewels replied: A better term might be morphology; we were using topology somewhat loosely to indicate underlying geometrical forms structurally distinct from one another, to which other structural variations, such as irregular local deformation, waviness, *etc.*, could then be applied. I'm sure higher level topological theory could be usefully applied to these pictures, but with my grounding in materials science I would suggest that the key driver should always be the utility of the classification system for practical materials identification and classification.

Pulickel Ajayan asked: Providing specific history of synthesis or manufacturing is as important as nomenclature - labs need to know what they are buying from vendors. Are there any MSDS (information) sheets for nanotubes, similar to what is available for chemical products?

Nazario Martin enquired: Do you think that the many shown carbon nanoforms should be considered as different carbon allotropes or do they belong to the allotropes of fullerenes? This should be clarified by the IUPAC.

Chris Ewels responded: There is a paper, "The Origin of the Term Allotrope",¹ which traces the origins of the concept of allotropism and its changing meaning over time. This states that Berzelius first used the term allotrope in 1841 to describe the difference between two forms of the same element. Later, in 1877, Otto Lehmann, suggested generalisation to describe any variation of a given substance (element or compound), "traceable to variations in the substance's intermolecular organisation". IUPAC have not followed that and stay with the definition, "Allotropes are different structural modifications of an element". It seems then that allotrope is appropriate if there are distinct structural differences, and if the materials in question are elemental (following IUPAC). So topologically "ideal" forms, such as single- or multi-walled nanotubes, fullerenes, or nanocones could be (should be?) described as different carbon allotropes. I'm not so sure it remains within this definition if these are real materials with *e.g.* varying impurity content, and structural variation within a given form (such as length, diameter, degree of crystallinity and purity in SWNTs). There is sometimes discussion of the difference between nano-*objects** and nano-*materials**, with the focus of the second on the collective properties of multiple similar nano-objects. In a similar vein, and following the spirit of Otto Lehmann's suggestion, one solution might be to stick with "nanoobject" when the individual object structure and behaviour are under study without reference to it necessarily as a representative of a family of alike nanoobjects - in which case allotrope could be used. (Just to muddy the waters still further, Jensen observes that the meaning of allotrope is closer to "other behaviour" while allomorph means "other form". So maybe nanoobjects and carbon nanoscale allotropes should all actually be allomorphs! Following your question, taking allotrope to indicate 'other behaviour' other nanoobjects would not be allotropes of fullerenes once their behaviour was different.)

1 W. B. Jensen, *J. Chem. Educ.*, 2006, **83**(6), 838.

Andreas Hirsch asked: Some carbon nanoforms are not real allotropes of carbon since they contain heteroelements at the boundary.

Nazario Martin commented: I basically agree with the comment. However, in some way, it is the same occurring issue as with other well-known allotropes such as diamond and graphite.

Pulickel Ajayan said: Once again, regarding classification of nanotubes, it might be interesting to put together an Ashby plot (say, conductivity *vs.* stiffness/strength) where different types of nanotubes (based on properties) can be plotted in a two-dimensional map.

Philip Davies opened the discussion of the paper by Alexander Sinitskii† by communicating: Do you have any evidence for the functionalisation of the graphene ribbon edges; does the IR show any OH stretches in the 3300–3600 cm⁻¹ region for example or does the XPS show any oxygen containing species in the 531–534 eV region?

Alexander Sinitskii communicated in reply: There is no evidence for OH functionalization, as there are no peaks in the 3300–3600 cm⁻¹ region in the IR spectra. We do not see any signs of C=O bonds either. In the XPS spectra we do see a tiny O1s peak in the 531–534 eV region, but based on the shape of the C1s peak it is unlikely that this oxygen represents C–O or C=O bonds. Based on FTIR and XPS data this tiny oxygen peak likely corresponds to molecular oxygen that was trapped in a porous GNR powder.

Oana Andreea Bârsan communicated: Based on your I/V curve presented in Fig. 3c, did you calculate a sheet/bulk resistance value for your sample or a conductivity value based on the dimensions of the sample? How do these compare to similarly prepared graphene or graphene nanoribbons samples in the literature?

Alexander Sinitskii communicated in reply: Estimates that are based on the data provided in the paper result in a very high resistance of a GNR pellet (~50 kOhm m), which is higher than in many other graphene materials. Considering the nanoscopic size of GNRs and their intrinsic semiconductor properties, as well as the assembly problems that we discuss in the manuscript, such high resistance is not surprising.

Oana Andreea Bârsan communicated: On page 6, line 45 you mention that “the electrical conductivities of CNTs fibers and composites are much lower than those of individual CNTs by at least one order of magnitude.” While composite materials require the addition of another component (often a polymer) to the carbon nanomaterial which indeed affects their conductivity, many studies have shown that CNTs fibers, bucky paper, and graphene films have a lower resistance with increased thickness of the films,^{1–3} values that are further lowered when applying

† The author was not available to present at the meeting, but questions relating to this paper were submitted afterwards.

even moderate pressures on the films. Could you elaborate on why you would expect your 0.1 mm thick, compressed pellets of pure graphene nanoribbons to have a higher resistance than a single layer?

- 1 F. Bonaccorso, Z. Sun, T. Hasan and A. C. Ferrari, *Graphene photonics and optoelectronics*, *Nature Photonics*, 2011, **4**, 611–622.
- 2 J. Liu, M. Notarianni, G. W. Vincent, T. Tiong, H. Wang and N. Motta, *Electrochemically Exfoliated Graphene for Electrode Films: Effect of Graphene Flake Thickness on the Sheet Resistance and Capacitive Properties*, *Langmuir*, 2013, **29**, 13307–13314.
- 3 B. Marinho, M. Ghislandi, E. Tkalya, C. E. Koning, G. de With, *Electrical conductivity of compacts of graphene, multi-wall carbon nanotubes, carbon black, and graphite powder*, *Powder Technology*, 2012, **221**, 351–358.

Alexander Sinitskii communicated in reply: You probably confuse conductivity/resistivity (intrinsic properties of a material) with conductance/resistance (that do depend on thickness, etc.).

Alexander Zöpfl communicated: After heating to 200 °C you see an improvement of conductivity of your GNR pellet. Do you expect any change in the structure or is this maybe due to impurities which are evaporated during this step? Since you are only measuring the bulk conductivity, the intrinsic properties of a single nanoribbon would be interesting. How do you perform/plan such an experiment in terms of fixing and contacting a single nanoribbon?

Alexander Sinitskii communicated in reply: As demonstrated in the papers on the surface-assisted bottom-up synthesis of GNRs, these ribbons are stable at 200 °C, so there should be no change in their structure upon annealing. It is more likely that the conductivity of a pellet improves because of the removal of residual solvent molecules. We are highly interested in performing electrical measurements on a single nanoribbon, but such experiments would be very challenging due to the small size of a GNR.