A New Industrially Relevant Solvent Exfoliation Route to Graphene

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Abstract
Due to its ultra-thin, 2-dimensional nature and its unprecedented combination of physical properties, graphene has become the most studied of all nano-materials. In the next decade graphene is likely to find commercial applications in many areas from high-frequency electronics to smart coatings. Some important classes of applications, such as printed electronics, conductive coatings and composite fillers, will require industrial-scale production of defect-free graphene in a processable form. For example, graphene is likely to be used as a low cost electrode material in applications such as solar cells, batteries and sensors. Such electrodes will almost certainly be produced by solution-coating and so will require large quantities of graphene in the form of liquid suspensions, inks or dispersions. Thus, liquid exfoliation of graphene will become a critically important technology in the near future[1]. However, no scalable method exists to give large quantities of graphene that is *also* defect free. For example, while oxidative exfoliation of graphite can potentially give large quantities of graphene-like nanosheets, such graphene oxide is typically defective. Alternatively, sonication of graphite[2], or indeed other layered compounds[3], in certain stabilising solvents gives defect-free nanosheets. However, the scalability of the latter process is limited by the use of sonication as an energy source.

Thus, solution-processing methods tend to display either high production rates or low defect contents, but not both. A detailed literature survey shows that no papers describe production rates above 0.4 g/h coupled with Raman D:G intensity ratios (a measure of defect content) below 0.65. In fact 80% of the papers surveyed had production rates below 0.04 g/h, far too low for commercial production. One possible solution would be to find a scalable method of exfoliation which, coupled with the use of stabilising solvents, could lead to large scale graphene production. In collaboration with CRANN (Centre for Research on Adaptive Nanostructures and Nanodevices) at Trinity College Dublin we have developed a new method for exfoliating graphite in liquids to give large-volume dispersions of graphene flakes. We will describe the production of 300 L of graphene dispersion at concentration of ~0.1 mg/ml and production rates of ~5g/hr. We have developed a simple model for the exfoliation mechanism and fully characterized the scaling behaviour of the graphene production rate with processing parameters such as batch volume and processing time. TEM, XPS and Raman spectroscopy show the exfoliated flakes to be thin, unoxidised and defect-free. This method produces pristine, high conductivity graphene nanoplatelets and can also be used to exfoliate BN, MoS_2 and a range of other layered crystals.

References

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2. Hernandez, Y. *et al.* Liquid phase production of graphene by exfoliation of graphite in surfactant/water solutions. *J. Am. Chem. Soc.* **131,** 3611–20 (2009).
3. Coleman, J. N. *et al.* Two-dimensional nanosheets produced by liquid exfoliation of layered materials. *Science* **331,** 568–71 (2011).

Figures

Figure 1: Photo showing large volumes of defect-free graphene dispersions able to be produced.

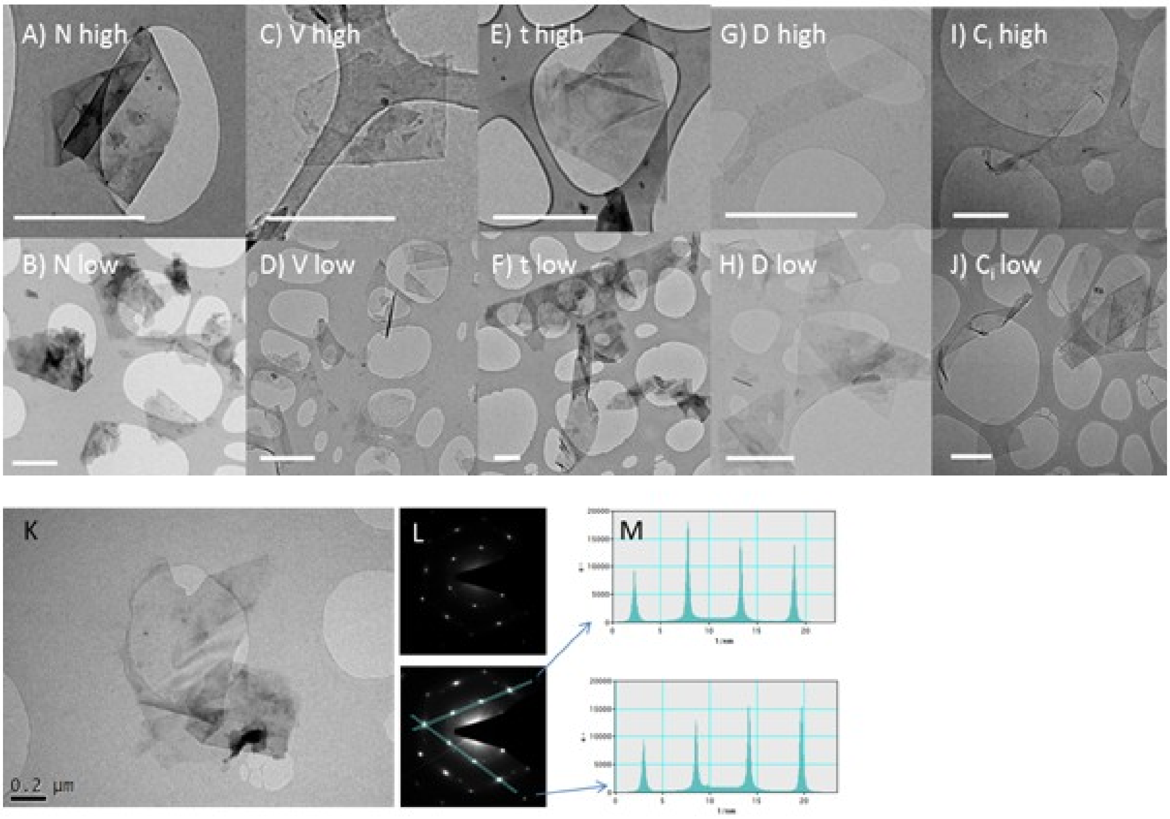

Figure 2: A selection of TEM images (collected from samples prepared with a range of processing parameters) of representative graphene flakes. In all cases, the scalebar is 500 nm. K-M) Evidence for monolayer production. Some of the flakes observed in the survey are clearly monolayers. The flakes observed in K had a diffraction pattern (L) which had more intense inner spots (M). This is a clear fingerprint of a graphene monolayer.