Raman Characterization of Liquid-Phase Exfoliated Graphene and Composite Membranes

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Amongst several techniques of graphene production, liquid-phase exfoliation (LPE) shows a great potential as a mass-scalable and low-cost approach for industrial production of graphene. [1, 2, 3] It has been shown that by introducing organic molecules that can behave as stabilizing agents in the dispersion during the LPE process, enhancement of graphene exfoliation and/or improvement of the properties of the final dispersion could be achieved [3,4] Furthermore, graphene dispersions can be used for producing graphene/polymer composites with superior properties [5,6].

However, in order to establish a technology based on LPE graphene, it is essential to be able to characterize the quality of the material, *e.g.*, the yield of single-layers, the amount of defects, the amount of re-stacked material, and so on under different experimental conditions. In this work we show that Raman spectroscopy can be used as a metrology tool to qualitatively track the changes in composition of a dispersion.

We use as example a dispersion composed by mixing n-octylbenzene (NOTBZ) at varying ratio with N-methyl-2-pyrrolidinone (NMP) or ortho-dichlorobenzene, (o-DCB) [8]. LPE process is composed of ultrasonication of graphite flakes in solvents for separation of graphene platelets followed by centrifugation of the dispersion to remove un-exfoliated graphite junks. The above mentioned mixed solvents, i. e. NOTBZ mixed with NMP or o-DCB and PIM-1 dissolved in chloroform, were used for LPE of graphene and the resulting dispersions were characterized.

References

[1] K. S. Novoselov *et al*., Nature 490.7419 (2012) 192-200.
[2] Y. Hernandez *et al*., Nature nanotechnology 3.9 (2008) 563-568.
[3] M. Lotya *et al*., ACS nano 4.6 (2010) 3155-3162.
[4] M. Lotya *et al*., Journal of the American Chemical Society 131 (2009) 3611–3620
[5] T. Kuilla *et al*., Progress in polymer science 35.11 (2010) 1350-1375.
[6] S. Stankovich *et al*. Nature, 442. 7100 (2006) 282-286
[7] N. B. McKeown & P. M. Budd, Chemical Society Reviews 35 (2006) 675–683
[8] S. Haar et al. submitted to Carbon
[9] Y. Shin et al. In preparation.
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Several techniques were employed for characterization of the dispersions and membranes such as UV-Vis and Raman spectroscopy, transmission electron microscopy (TEM) and electron energy loss spectroscopy (EELS). UV-Vis spectroscopy shows that the graphene exfoliation could be enhanced by addition of NOTBZ to NMP/o-DCB. Raman spectroscopy was performed on more than 30 samples and the shape of the 2D peak was analyzed carefully, showing that the amount of single and few-layers increase with the addition of NOTBZ. This result is further confirmed by TEM, showing that Raman can qualitatively predict changes in composition of a dispersion obtained under different experimental conditions.

We then applied our Raman analysis to composites, obtained by mixing graphene with a polymer of intrinsic microporosity, such as PIM-1. [7,9] Samples with different graphene/PIM-1 compositions were made and analyzed by Raman spectroscopy. Despite the strong fluorescence background produced by PIM-1, Raman spectroscopy clearly showed the presence of graphene-based material in the composite membrane. However, the shape of the 2D peak seems to indicate re-stacking and uneven distribution of graphene in the polymer. This could strongly affect the properties of the membranes, so ways to avoid or control re-stacking should be implemented in order to use this composite for applications.

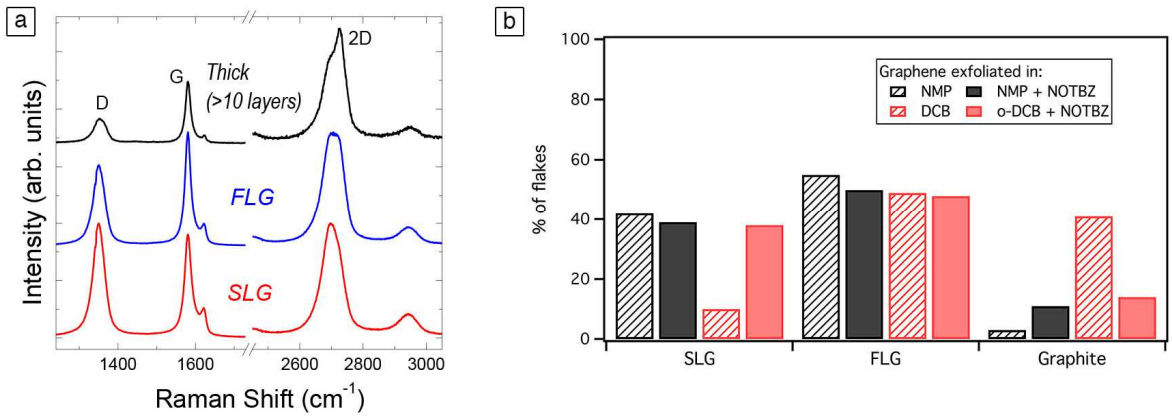

Figure 1: a) Typical Raman spectra observed for LPE graphene dispersions obtained. b) Statistical analysis, based on Raman spectroscopy, on the thickness distribution of the flakes in NMP and DCB before and after addition of NOTBZ.

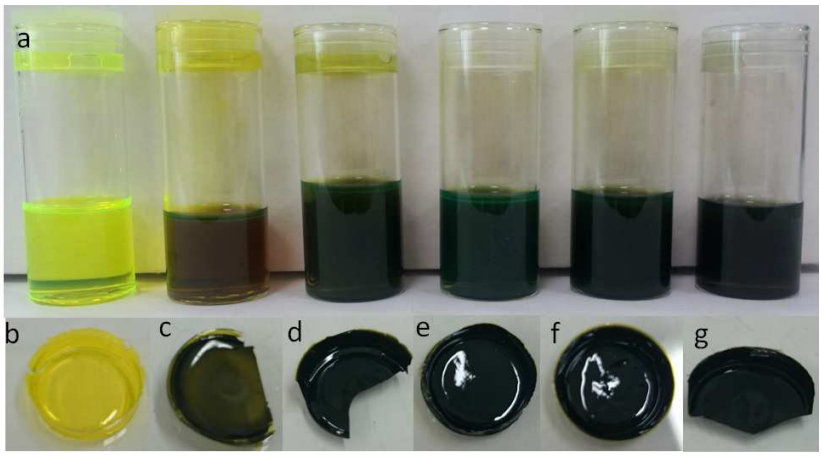

Figure 2: a) Optical picture of PIM-1/graphene composite dispersion solutions with decreasing PIM-1 ratio from left to right and b-g) membranes obtained from the dispersions (the furthest left is pure PIM-1 solution and membrane)