Kun Zhang[a]

Jie Tang*[,a,b], Shiqi Lin[a,b], Xiaoliang Yu[a], Shuai Tang[a], Runsheng Gao[a,b], Ta-Wei Chiu[a,b], Luhao Kang[a,b], Wanli Zhang[a,b], Taizo Sasaki[a], Kiyoshi Ozawa[a], Yorishige Matsuba[a], Da-Ming Zhu[c], Lu-Chang Qin[d]

[a] National Institute for Materials Science, 1-2-1 Sengen, Tsukuba, Ibaraki 305-0047, Japan

[b] University of Tsukuba, 1-1-1 Tennodai, Tsukuba, Ibaraki 305-0006, Japan

[c] Department of Physics and Astronomy, University of Missouri-Kansas City, Kansas City, MO 64110, USA

[d] Department of Physics and Astronomy, University of North Carolina at Chapel Hill, Chapel Hill, North Carolina 27599-3255, United States

Tang.Jie@nims.go.jp

Production of Few-Layered Graphene by Enhanced Shear Exfoliation of Graphite in A High Pressure Fluid

Recently, it was reported that graphite could be exfoliated in a liquid under shear.[1-3] It was also demonstrated that a high-speed shear mixing method in liquid phase exfoliation can be a scalable alternative to sonication for the exfoliation of layered materials including graphite.[1, 2] Using this method, exfoliation of graphite into graphene sheets can be achieved in liquid volumes up to hundreds of liters or beyond, as long as the local shear rate in the liquid exceeds 10^4 s^{-1}. The method has been extensively investigated using a simple experimental configuration in which the shear stress was produced by a high speed mixer, of which the rotor/stator combination generates a Couette flow in a graphite dispersed solution. The graphene produced by this method has been found to be largely free of oxidation and basal-plane defects, and is almost indistinguishable from that produced by the sonication and electrochemical method.[4,5] The results were quite astonishing as for exfoliation of graphite to occur, it requires only that the shear rate exceed certain threshold, and high speed shear mixing typically delivers the solution of the exfoliated material a power density which is only a small fraction of that delivered in sonication.[1] However, one problem with this method is that exfoliation of graphite takes place only in the vicinity of the rotor/stator, limiting the production rate. To overcome this problem, attempts have been made to generate high shear rate in all regions of the liquid with approaches such as exfoliation of graphite using a kitchen blender[6,7] with high speed rotating blades and a microfluidizer.[8] In this work, we explore an alternative yet facile method of enhanced shear exfoliation in a high pressure fluid to produce mono-/few-layer graphene sheets. In the exfoliation process, an N-Methyl-2-Pyrrolidone (NMP) solution with dispersed graphite flakes was pushed through the exfoliation tube by a high pressure pump which produces a high shear stress on the graphite flakes, leading to the peeling-off of graphene sheets from the graphite. The produced graphene sheets are stabilized by the interactions between NMP molecule and graphene. Graphite solution can be continuously treated in the circular loop. Under the conditions that we have tested so far, exfoliated graphene was obtained with a yield of about 15±0.3% which corresponds to a concentration of 1.5 ± 0.3 mg/mL in the solution. The morphology and structure of the obtained graphene were characterized by scanning electron microscopy (SEM), atomic force microscopy (AFM), transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS), infrared (IR) and Raman spectroscopy analyses (Figure 1). The results confirmed that the graphene obtained is mono-/few-atomic layer thick without introducing noticeable defects on the basal planes. Furthermore, the electrochemical properties of the exfoliated graphene were also characterized when it is used as the electrode material for supercapacitors.[9]

References

[1] Paton, K. R.; Varrla, E.; Backes, C.; Smith, R. J.; Khan, U.; O'Neill, A.; Boland, C.; Lotya, M.; Istrate, O. M.; King, P.; Higgins, T.; Barwich, S.; May, P.; Puczkarski, P.; Ahmed, I.; Moebius, M.; Pettersson, H.; Long, E.; Coelho, J.; O'Brien, S. E.; et al. *Nat. Mater.* **2014**, *13*, 624−630.

[2] Liu, L.; Shen, Z.; Yi, M.; Zhang, X.; Ma, S. A Green, *RSC Adv*. **2014**, *4*, 36464-36470.
[3] Chen, X. J.; Dobson, J. F.; Raston, C. L. *Chem. Commun*. **2012**, *48*, 3703-3705.
[4] Blake, P.; Brimicombe, P. D.; Nair, R. R.; Booth, T. J.; Jiang, D.; Schedin, F.; Ponomarenko, L. A.; Morozov, S. V.; Gleeson, H. F.; Hill, E. W.; Geim, A. K.; Novoselov, K. S. *Nano Lett*. **2008**, *8*, 1704-1708.
[5] Zhou, M.; Tang J.; Cheng, Q.; Xu, G.; Cui, P.; Qin, L. *Chemical Physics Letters* **2013**,*572*, 61-65.
[6] Varrla, E.; Paton, K. R.; Backes, C.; Harvey, A.; Smith, R. J.; McCauley J.; Coleman, J. N. Nanoscale 2014, 6, 11810–11819.
[7] Yi, M.; Shen, Z. *Carbon*. **2014**, *78*, 622–626.
[8] Karagiannidis, P. G.; Hodge, S. A.; Lombardi, L.; Tomarchio, F.; Decorde, N.; Milana, S.; Goykhman, I.; Su, Y.; Mesite, S. V.; Johnstone, D. N.; Leary, R. K.; Midgley, P. A.; Pugno, N. M.; Torrisi, F.; Ferrari, A. C. *ACS Nano* **2017**, *11*, 2742−2755.
[9] Zhang, K.; Tang, J.; Yuan, J.; Li, J.; Sun, Y.; Matsuba, Y.; Zhu, D.; Qin L. *ACS Applied Nano Materials* **2018**, 1, 2877-2884.

Figures

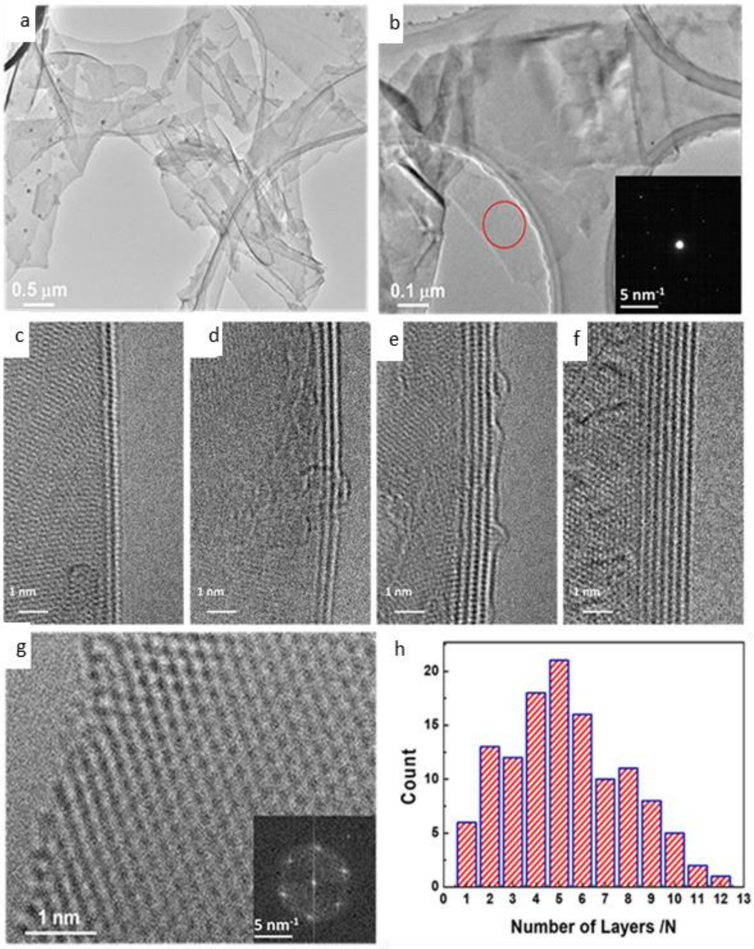

Figure 1: (a) TEM image of a large number of few-layer exfoliated graphene sheets. (b) TEM image of a monolayer graphene sheet. Inset: electron diffraction pattern of graphene sheet taken from a selected region marked by circle. (c-f) HRTEM images of exfoliated graphene sheets with two, three, five and seven atomic layers. (g) HRTEM image of a monolayer graphene sheet. Inset: power spectrum of the image. (h) Statistical analysis of TEM images showing histograms of the number of layers per sheet.