Bi and tri layer graphene solution from stage-3 KCl intercalated graphitic compound

Akshaya Kumar Swain [1], Dan Li [2], Dhirendra Bahadur [3]

1 IITB Monash Research Academy, Department of Metallurgical Engineering and Materials Science, IIT Bombay, Mumbai, India 400076
2 Department of Materials Engineering, Monash University, VIC 3800, Australia
3 Department of Metallurgical Engineering and Materials Science, IIT Bombay, Mumbai, India 400076
Contact: dhirenb@iitb.ac.in

Abstract

Certain electronic and optical properties which are absent in single layer graphene (SLG) could be realized through bi (BLG) or tri-layer graphene (TLG) [1]. These novel properties can also be tuned by varying certain parameters such as interlayer spacing, type of stacking, twinning and twisting angle in BLG and TLG for potential electronic applications [2-3]. However, mass production of these materials remains a challenge. Especially depositing BLG and TLG on a arbitrary substrate is a herculean task. The advantage of having graphene in solution form makes it convenient to transfer to a desired substrate or to produce composites of it at ease with fewer parameters involved to manipulate the process. Here we report two important results. First, formation of KCl intercalated graphite at 3rd stage is achieved hydrothermally and reported for the first time. Second, The resulting graphite intercalated compound (GIC) is used as a precursor to produce BLG and TLG solutions. We also have used these GIC precursor as a starting material to synthesize composites which will be reported elsewhere.

Natural graphite powder and KI were taken in proportions in 1,2-dichlorobenzene (DCB) and hydrothermally treated at 300 °C for 12 h in a pressurized vessel. The resultant solution was washed alternatively with ethanol and de-ionized water to remove the un-reacted materials. This was then sonicated in DCB and washed repeatedly to remove un-reacted materials. KCl intercalated graphite was obtained after centrifuging the washed material. The resultant black powder was exfoliated in ethanol by sonication thereby removing intercalated KCl from graphite. The heavy particles settled down were separated to keep the solution which retained the bi and tri layers of graphene in it.

Comparisons of XRD patterns shown in figure 1 clearly indicates that KCl is intercalated into graphite to form stage-3 graphite intercalated compound (GIC). Stage-3 GIC is also being confirmed by virtue of its approximate repeat distance value (Ic = 13.82 Å) obtained from q v/s l plot which lies in the range corresponding to Ic values of stage-3 GIC [4]. A change in color is also seen in stage-3 GIC (black) in comparison to that of graphite (shiny grey). On removing the intercalated material (KCl) from graphite, the original intercalant (graphite) peaks reappear with reduced intensities and peak broadenings [4]. The resulting material after removal of KCl from graphite is called as exfoliated graphite (EG) which is treated as a precursor to produce BLG and TLG solutions. Thus, on the basis of XRD data, for the first time, we report intercalation of KCl into graphite.

Raman spectra (figure 2) was obtained at various incident laser powers from a thin film made by drop casting the solution which was sonicated for 1-2 h. The 2D band was found to contain 3 Lorentzian components which signifies a BLG [5]. It should be noted that 2D band in BLG usually allows 4 peaks to be fitted [6], however due to the presence of two degenerate transition processes, one can have three peaks fitted. Also, deconvolution of G band suggests the formation of defects due to non-zero phonon density of states. By optimizing the sonication time of the EG, one can produce BLG or TLG in a desired solvent. When the sonication time is increased, the TLG starts to deform to form BLG which is verified by high resolution TEM images. BLG produced by liquid phase exfoliation of graphite also shows similar Raman spectra [7].

Figure 3a shows the TEM image of graphene (BLG and TLG) sheets. It can be seen that TLG starts to deform to give rise to BLG eventually depending upon the sonication time. However from the selected area electron diffraction (SAED) and intensity plots therein indicates the presence of two SLG sheets twisted at an angle [7-8]. BLG with such a misoriented angle has interesting electronic properties depending on its twist angle [9].

In conclusion, we intercalated KCl into graphite layers to produce stage-3 GIC and report it for the first time thereby adding another GIC material in its family. The GIC becomes a promising material to make BLG and TLG solutions on a large scale which may further be used for various applications.

We propose that GICs may also be used to form various composites selectively with BLG or TLG which will be reported in future.

References

[1] L Brown, R Hovden, P Huang, M Wojcik, D A Muller and J Park, Nano Lett, 12 (2012) 1609–15.

[2] E Stumpp, Physica, 105B (1981), 9-16.

[3] E Suárez Morell, M Pacheco, L Chico and L Brey, arXiv:1301.3052 [cond-mat.mes-hall].

[4] C J Shih, A Vijayaraghavan, R Krishnan, R Sharma, J H Han, M H Ham, Z J,S Lin, G L C Paulus, N F Reuel, Q H Wang, D Blankschtein and M S Strano, Nat Nanotechnol, 6 (2011), 439–45.

[5] A C Ferrari, Solid State Commun, 143 (2007), 47-57.

[6] J S Park, A Reina, R Saito, J Kong, G Dresselhaus and M S Dresselhaus, Carbon, 47 (2009),1303 - 10.

[7] Y Hernandez, V Nicolosi, M Lotya, F M Blighe, Z 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, Nature Nanotechnol, 3 (2008), 563 - 568.

[8] K Yan, H Peng, Y Zhou, H Li and Z Liu, Nano Lett, 11 (2011), 1106–10.

[9] K Kim, S Coh, L Z Tan, W Regan, J M Yuk, E Chatterjee, M F Crommie, M L Cohen, S G Louie and A Zettl, PRL 108 (2012), 246103(1-6).

Figures

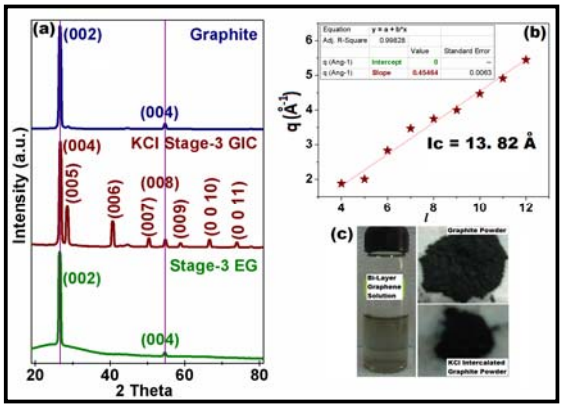

Figure 3. XRD patterns of graphite, KCl intercalated graphite and EG are compared in (a). The repeat distance is computed from q vs l plot in (b). Photographs of graphite powder, GIC and bi & tri layer of graphene solution is given in (c).

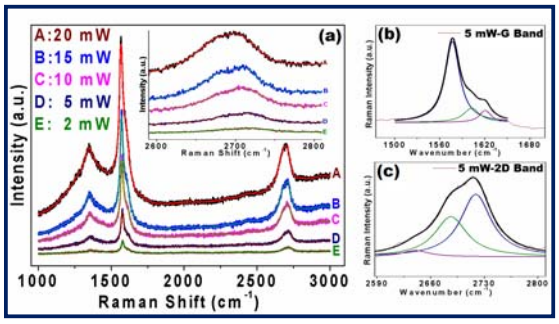

Figure 3. Raman spectra of bi layer graphene at various laser powers obtained by sonication of EG in ethanol is presented in (a). The inset shows the zoom of corresponding 2D bands. Deconvolution of G-band (b) and 2D-band (c) of the Raman spectrum obtained for incidented laser power of 5 mW is presented. 2D band deconvolution confirms the presence of BLG.

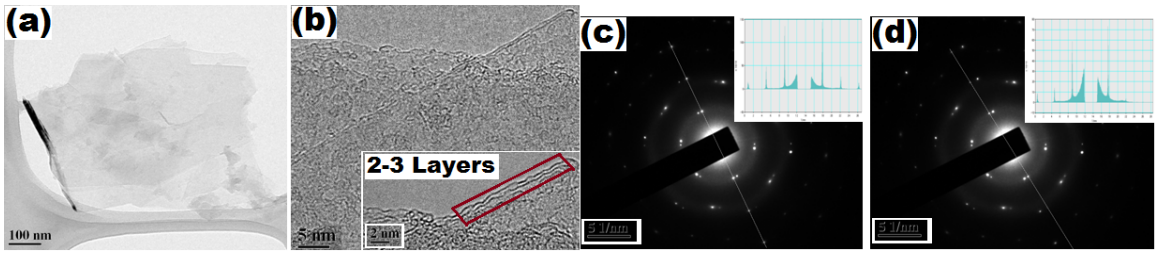

Figure 3. TEM image of graphene and few layer graphene is shown in (a). A part of it is zoomed in (b) to determine the number of layers. The inset in (b) confirms the presence of BLG and TLG. The SAED patterns in (c) and (d) further indicates that the graphene obtained from this technique are twisted by certain angle, while the insets in (c) and (d) showing the intensity profile suggests that the individual layers in the image are indeed monolayers of graphene. This is due to higher intensity of the inner hexagon compared to the outer hexagon which is a signature of SLG.