NMR detection of graphene nanoribbons

Yale University School of Medicine

Ashish Aphale [1], Daniel Coman[2,3], Prabir Patra[4,5] , Fahmeed Hyder[2,3,6]

[1]Department of Computer Science and Engineering, University of Bridgeport, CT, USA
[2]Quantitative Neuroscience with Magnetic Resonance (QNMR), Yale University, CT, USA
[3]Department of Diagnostic Radiology, Yale University, CT, USA
[4]Department of Biomedical Engineering, University of Bridgeport, CT, USA
[5]Department of Mechanical Engineering, University of Bridgeport, CT, USA
[6]Department of Biomedical Engineering, Yale University, CT, USA

Abstract

Nobel prize winning material as "the thinnest material in our universe"[1], graphene, a single atom thick sheet of sp^2 carbon atoms, promises a diverse range of applications from composite materials to quantum dots [2-7], and even in several bioengineering applications [8]. For graphene, that availability is encumbered by having to surmount the high cohesive van der Waals energy (5.9 kJ mol^{-1} carbon)[9] adhering graphitic sheets to one another. Moreover, graphene being extremely hydrophobic, it has low solubility in water. Here we demonstrate the feasibility of developing biological graphene dispersions using wet chemistry and ultra sonication. ^{13}C NMR spectra of graphene dispersions indicate the presence of graphene carbon signature in solution. Our future work is to use this graphene dispersion in a cellular assay to explore graphene-protein binding and also to study the graphene nanoribbon structures as contrast agents and drug delivery.

Introduction

Graphene sheets—one-atom-thick two-dimensional layers of sp2-bonded carbon are shown in Fig. 1 & 2. Their thermal conductivity and mechanical stiffness may rival the remarkable in-plane values for graphite (~3,000$Wm^{-1}K^{-1}$ and 1,060 GPa, respectively); their fracture strength should be comparable to that of carbon nanotubes for similar types of defects. Recent studies have shown that individual graphene sheets have extraordinary electronic transport properties [10]. Graphene being extremely hydrophobic, it has low solubility in water. E.T. Samulski et al. have demonstrated the production of the water soluble graphene, by reducing the Graphene Oxide (GO) by wet chemistry at high temperature. Here we demonstrate a way to disperse the graphene nanoribbons at room temperature using the standard cellular assay buffer solutions, such as Tris-EDTA, EDTA and Tris and Trypsin-EDTA solution using ultra sonication for prolong time. We used ^{13}C NMR to show the presence of graphene in solution (Fig.3).

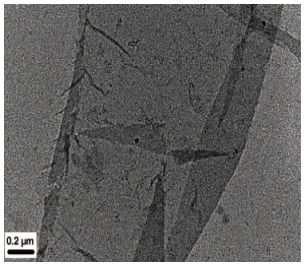

Fig.1 TEM image of partially folded water soluble graphene sheet. Yongchao Si et al. Nano Letters, 2008

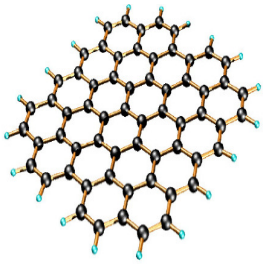

Fig 2. Idealized structure of a single graphene sheet

Experimental Details

Graphene nano platelets (Cheaptubes Inc.) are highly hydrophobic in nature it is almost impossible to disperse in water. We prepare the graphene dispersion using four different solution viz. EDTA (Promega Inc. 0.5M, pH 8.0), Tris (TEKnova, 1M, pH 7.5), Tris-EDTA (TE)buffer 1X solution (0.01M Tris & 0.001 M EDTA, pH 7.4) and Trypsin-EDTA (0.25%). We used 0.01 gm of Graphene in 10ml of each solutions and then was kept for sonication for atleast 1 hr till we see the graphene power is well dispersed in the solution with no agglomeration.

Results and Discussion

Amine and carboxylic functionalities of buffer solutions are enabling reasonably good graphene dispersions. As shown above we are able to observe the graphene carbon signature from the dispersions

Conclusions

We have been able to observe graphene signature from the dipsersion. The observed graphene signature will help us understand graphene-protein bindings, thus enabling graphene-biomolecule assembly (graphene-DNA, graphene-protein, etc) and their devices in biomedical applications.

Future work

After establishing the NMR signature of the graphene we plan to explore the variation of graphene NMR signatures as a function of pH, temperature, ionic strength of dispersions and nature of proteins. We will also characterize the graphene dispersion solution with TEM and SEM to observe the surface morphology and their implications in graphene-protein assembly.

References

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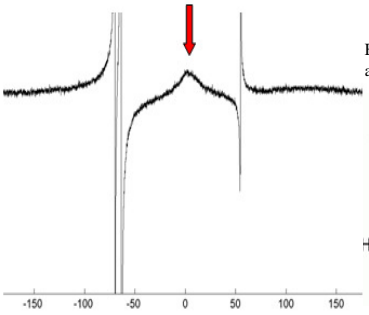
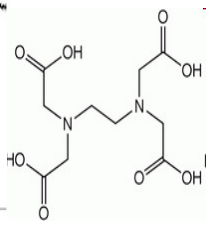
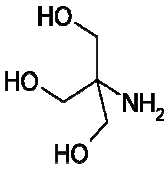
1) 0.01 gm Graphene dispersion in EDTA 500mM solution.



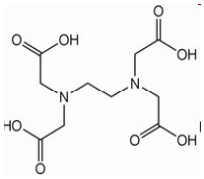
Ethylenediaminetetraacetic acid (EDTA)



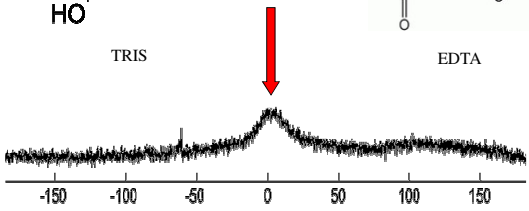
2) 0.01 gm Graphene dispersion in TE buffer = 10 mM TRIS (pH 8.0) and 1 mM EDTA.



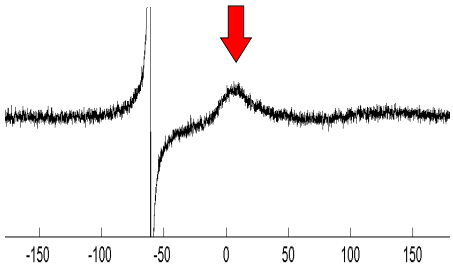
TRIS

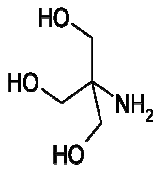


EDTA



3) 0.01 gm Graphene dispersion in Tris = 10 mM.





TRIS

4) 0.01 gm Graphene dispersion in Trypsin-EDTA

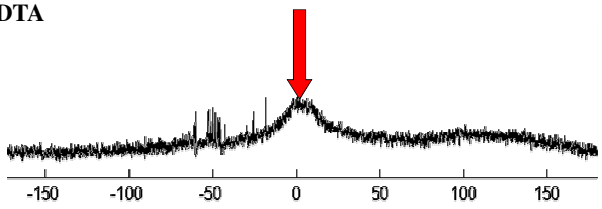


Fig 3. ^{13}C NMR spectrum of graphene in various solvents (whose structures are also indicated) showing the presence of graphene dispersions in solution