Biomimetic exfoliation of natural graphite by proteins
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ABSTRACT
The emergence of graphene, a one atom thick 2D allotrope of carbon has revolutionized material science like never. Advanced materials are designed to mimic the more flexible sequence-structure-property relationships of biopolymers and this is what is intended in this study. Two different structurally different proteins Collagen and Bovine Serum Albumin have been used to exfoliate and disperse few layer graphene (FLG) nanosheets in water. The results shown are part of the ongoing research activities of our group.

Objective: Protein functionalized graphene nanosheets synthesized at ambient conditions as a next generation of bioinspired materials with potential biomedical applications.

INTRODUCTION

“Biomimetics” --- inspired by nature
Why Biomimetics ????
- No heat
- No pressure
- No harsh chemicals
- No mechanical force
- No sonication

Fig 1 (a) Collagen triple helix - a sheet like protein (b) BSA - a globular protein.

Protein solutions having surface energy closely matching with graphene can effectively disrupt the σ-stacking to produce defectless FLG sheets

Fig. 2 A schematic representation of protein assisted exfoliation. The protein molecules intercalate within the stacked graphitic layers weakening the van der Waals interaction, exfoliating them in the process.

METHODOLOGY

Conventional methods of production
i) Micro-mechanical cleavage
ii) CVD
iii) Epitaxial growth
iv) Chemical synthesis

Drawbacks of chemical synthesis
i) Lengthy process (Graphite → Graphite Oxide (GO) → Graphene)
ii) High risk of explosion-use of strong oxidizing agents
iii) Presence of structural defects
iv) Hydrophobic and toxic - Graphene

Recent developments
i) Exfoliation in polar solvents e.g. NMP.
ii) Exfoliation in ionic surfactants e.g. SDS
iii) Exfoliation in protein matrix

Direct exfoliation of graphite (without going through the GO route) with proteins like collagen and BSA initiated by our group has not been reported before.

Currently we are working with multidentate systems where a mixture of proteins and polymers are being used to stabilize graphene dispersions in aqueous medium.

RESULTS

Fig. 3 Surface Enhanced Raman Spectra (SERS) of FLG sheets clearly showing graphite - protein interaction. The spectra was taken for two different graphite concentrations (a) 0.1 mg/ml and (b) 0.01 mg/ml. The presence of D (~1350 cm⁻¹), G (~1590 cm⁻¹) and 2D (~2700 cm⁻¹) peaks in both samples signify few-layered morphology. The disappearance of 2D peak in (b) prove that collagen molecules are the best exfoliant of graphite. (c) UV-Vis spectra of the samples show absorption peaks at 225 nm and 270 nm, characteristic graphene signatures.

Fig. 4 Confocal images (ZEISS LSM 700) of graphene dispersions dried over glass substrate. All the images were recorded in the Bright Field Mode using the laser lines 405nm and 488nm at a magnification of 20X. The images show a uniform global distribution (a) G-BSA, (b) G-Collagen & (c) G- BSA & COLL.

FURTHER RESEARCH QUESTIONS
Our efforts are focused on addressing the following research questions:
i) Development of water dispersible iron - oxide graphene nanocomposites - graphene ferrofluid (6-FF).
ii) To see whether the material is able to enhance T2 relaxivity for MRI.
iii) Is able to easily permeate across the Blood Brain Barrier (BBB).
iv) Possess high Specific Absorption Rate (SAR) for hyperthermia treatment of cancer.

CONCLUSIONS
Natural graphite and the hydrophilic patches of the proteins seem to undergo a dynamic self-organization whereby the graphitic layers overcome the stacking attractive forces (as seen in the greyish-black colloidal dispersion of the graphite-proteins). The absence of the 2D peak suggests the formation of defect free graphene. Two different ratio of graphite and protein (1:10 & 1:50) were tried to understand the effect. We are at a very preliminary stage and working hard on gaining insight.