Carbene Functionalization of Exfoliated Graphene: Towards Scalable Dispersion and Integration of Chemically Modified Graphene.

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Abstract

In recent years, graphene in both its pristine and chemically functionalized forms have been demonstrated to have significant economic and societal potential in the areas of electronics, sensing and diagnostics, composites, energy storage and catalysis due to the diverse physical and electronic attributes.[1-4]

Graphene in its pristine form has received a great deal of research attention in terms of the fabrication of devices for logic and sensing operation as well as in the area of metrology standards and the demonstration of fundamental physical phenomena.[1-3] While the fabrication of electronic devices and sensor technology based on graphene components may be relatively discreet in terms of total surface area, the emerging utilization of graphene in bulk composites, electronic ink, energy storage and catalytic applications will certainly be dependent on the ability to fabricate, process and integrate graphene on the gram to kilogram scale. To interface graphene with solvent systems, resin matrices, and integrate it with nanoscale components, contacts and substrates there remains tremendous scope for further research directed towards manipulation of the surface chemistry of graphene whilst retaining its fundamentally attractive intrinsic properties.[4] Towards this goal, the development of chemical processing techniques for graphene which are low cost, scalable, and non-destructive are highly attractive.[5-8]

Here we report the development of solution-phase radical based functionalization strategies in order chemically modify graphene in a controlled and scalable manner. This work yields exfoliated graphene nanosheets which retain their wide area whilst integrating additional chemical functionality by the grafting of functional groups to the sp^2 hybridized carbon lattice. Specifically, carbene radical species are generated in the presence of solution exfoliated graphene. Reactive radicals covalently graft to the carbon lattice. Characterization of the covalent functionalization of graphene has been conducted in a systematic manner. Evaluation of specific chemical bonding, quantification of adduct chemistry and the modification of key intrinsic properties of the graphene has been performed as follows.

The presence of the covalent functionalization was characterized using microscopy including HR-TEM, AFM, and SEM. Spectroscopic techniques; FTIR, Raman and X-ray photoelectron spectroscopy (XPS) were employed to fully elucidate the nature of the covalent bonding. Additional characterization techniques; X-ray diffraction (XRD), Time-of-flight Mass Spectroscopy (ToF SIMS), electron energy loss spectroscopy (EELS), thermo gravimetric analysis (TGA) and energy dispersive x-ray spectroscopy (EDAX) were employed to identify and quantify the fraction of the grafted chemical functionality relative to the bulk graphene. Characterization in the UV-Vis and Terahertz frequencies was employed to investigate modification of the optical band-gap and conductivity as a function of the chemical functionalization.

Implications of carbene modified graphene are investigated by its application within a polymer matrix. Graphene-Epoxy nanocomposites are formed and their mechanical properties evaluated. As a result of the chemical modification of the graphene, significant enhancement of mechanical properties are noted relative to pristine unmodified epoxy.

In summary, in this work we present scalable strategies for the non-destructive radical based functionalization of graphene using chemically versatile functional groups. These groups form functional adduct groups at the surface of graphene sheets which may be further derivitized in order to disperse and integrate graphene with solvent and polymer systems. A full characterization strategy forms the basis of a model by which alternative functionalization strategies may be evaluated and applied towards technologically relevant modification of graphene.

References

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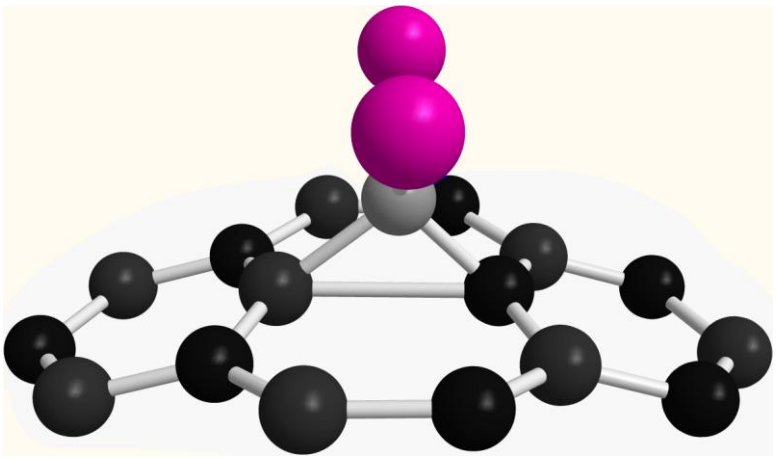
Figures



Dihalocarbene functionalized graphene.