

Novel dendrimer intercalated graphene-based materials

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Graphene, a two dimensional material consisting of a single atomic sheet of conjugated sp² carbon atoms has revolutionized the field of carbon-nanostructured materials.^{1,2} Graphene is currently considered not only the thinnest but also the strongest material. But this unique carbon nanostructure, also exhibits a variety of additional very attractive properties including high electrical conductivity, very low optical absorption, thermal stability, high surface area and low manufacturing cost. Graphene oxide (denoted hereafter as GO) is a widely used graphene chemical derivative exhibiting a basal graphitic plane decorated mainly by -OH (hydroxyl groups), C-O-C (epoxy groups) and -COOH (carboxylic groups).³ For use of graphene in large scale applications, chemical conversion to graphene oxide is currently the most obvious and desirable route towards large quantities of graphene-based materials holding great promises for potential applications in diverse fields such as nanosensors and nanomedicine.

On the other hand, dendrimers are nanoscale, highly branched and monodispersed macromolecules with symmetrical architecture. Their structure is well defined in terms of chemical composition and three-dimensional configuration. They consist of a central core, branching units and terminal functional groups. The core and the internal units determine the nanocavity environment and consequently the dendrimer solubilizing or encapsulating properties, whereas, the external groups influence their solubility and chemical behavior.^{4,5} Therefore, dendrimers display very attractive properties including well-defined chemical structure, large number of reactive end groups per molecule, unique viscosity and accessible, symmetrical cavities. Dendrimers' overall, chemical properties allow controlled molecular weight building (monodispersity) and branching (topology), as well as versatility in design and modification of the terminal end groups, towards multifunctional nano-structures. Since graphene has taken the physics and chemistry communities by storm, very recently much interest is focused on the synthesis of graphene based-dendrimer hybrids.^{6,7,8,9,10} Nevertheless, this field is not yet fully explored. Most importantly, all relative studies report that dendronized graphenes lose their parallel configuration resulting to exfoliated structures consisting of single, dendrimer functionalized graphene sheets.

Instead, we succeed in synthesizing for the first time (to the best of our knowledge), dendrimer intercalated structures by employing low molecular

weight dendrimers. In detail we used diaminobutane poly(propylene imine) dendrimers of 1st, 2nd and 3rd generation (denoted hereafter as DAB). DAB dendrimers of lower molecular weight correspond to smaller sizes of dendritic structures. In turn, the smaller size of DAB dendrimers allows the accommodation of the polymer within the interlayer space of GO, preserving the parallel arrangement of the GO sheets. This feature is critical for the morphology and the properties of the resulting graphene-dendrimer hybrids, since it leads to the formation of graphene porous structures. The interlayer galleries are formed in between the singles layers of graphene as a result of the DAB dendrimer intercalation. In that way the previously (before intercalation) unavailable interlayer surface area of the graphene sheets, becomes accessible for solvents, chemical species and/or gas molecules through the “swelling” occurred due to intercalated DAB dendrimer.

We studied the synthesized novel graphene-dendrimer nanostructures with a combination of experimental techniques. X-Ray diffraction measurements were used to investigate structural order and basal spacing of layered structures, while electron microscopies (SEM and TEM) revealed details regarding their morphology. Using Raman and FT-IR spectroscopies we evaluated the structure and defect density of the starting and the final graphene-based hybrids. X-Ray photoelectron spectroscopy was employed to identify the chemical state and content of the various species both in starting materials and in final hybrids.

The mechanism of bulk DAB intercalation within GO involved the reaction of DAB primary amino groups with the oxygen functionalities of the GO framework. The final hybrids were formed mainly through the covalent immobilization of DAB tails at GO. We found that the interlayer distance of graphene sheets can be easily tuned simply by selecting different molecular weight and/or loading of polymeric intercalant (DAB). Very interestingly, we also found that a large portion of the intercalated DAB reactive end-groups still remain available for further treatment within the created interlayer galleries. Furthermore, our results strongly suggest that the intercalation of DAB is followed by a partial reduction of the starting GO. The observed decrement of the oxygen content in the resulting graphene-based hybrids, will greatly enhance their electron conductive behavior. The latter in conjunction with the increased capacity of the final hybrids to adsorb metal and/or chemical species (such as enzymes) render the synthesized graphene-dendrimer intercalated structures very attractive for the development of electrochemical biosensors.

Acknowledgments

The EU funded project entitled “CarbonComp” (Grant Agreement No. 286413) is acknowledged for partial financial support of current work.

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