Introducing the Versatile Carboxylate Handle on Graphene by Reductive Carboxylation

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Abstract

The use of graphene has been suggested for as widespread applications as molecular electronics, drug delivery systems, anti-corrosive coatings, polymer reinforcements, and much more.[1] For all of these diverse applications to be viable, chemical tools are needed to handle graphene in its various forms and control its properties in detail. Reduction of aryldiazonium salts, both spontaneously [2] and electrochemically,[3] has been the preferred tool to carry out functionalization so far, although hydrogenation[4], fluorination[5] and plasma[6] modification are possibilities as well. The great advantage of the diazonium procedure is that it allows modification of graphene with a large variety of functional groups. Unfortunately, these reactions are rather uncontrolled, usually resulting in large multilayer structures on top of the graphene sheets.

In this work we introduce a new method to functionalize CVD grown graphene on copper and nickel substrates with the carboxylate group using an electrochemical procedure developed for graphite[7] and glassy carbon[8]. Electrochemical reduction of graphene generates a highly negatively charged polynucleophilic substrate with intercalated positively charged tetrabutylammonium ions, which in a second step may react with added carbon dioxide to form carboxylate groups (Figure 1). For the multilayered graphene samples on nickel the separation of the individual graphene sheets by intercalation permits carboxylation to be carried out between the graphene layers. Excellent control on the functionalization degree is obtained through repetitive use of the outlined stepwise procedure.

The carboxylate groups which are introduced directly into the basal plane of graphene are versatile chemical handles for further chemical functionalization. At the same time the small size of the carboxylate group compared to, e.g., the arylic multilayers derived from diazonium functionalization[9], makes them ideal candidates for developing useful sensors. As a proof of concept, we show that these carboxylate groups can be utilized for further functionalization through attachment of Bovine Serum Albumine proteins using an EDC-NHS coupling reaction. The proteins are attached in a well-dispersed manner across the graphene sheets, as investigated by transmission electron microscopy.

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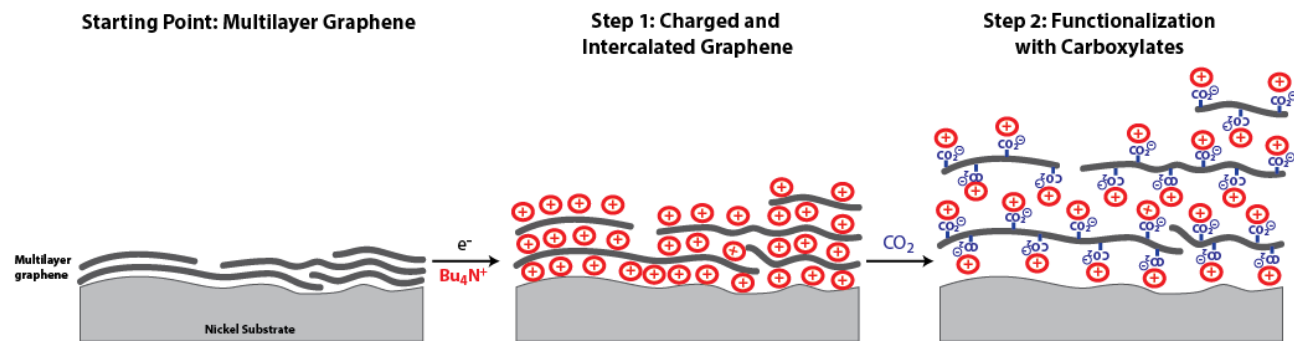
Figures

Figure 1. The two steps involved in the functionalization of multilayer graphene using carbon dioxide: 1) Graphene sheets are reduced to enforce intercalation of positively charged counter ions between and underneath the negatively charged layers and 2) reaction with added carbon dioxide to form graphene-functionalized carboxylates.