The Investigating of Graphene Chemistry using Scanning Electrochemical Microscopy

CNF Project # 1283-04
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Abstract:
Graphene garnered widespread attention across many scientific disciplines since its discovery in 2004. We are interested in using scanning electrochemical microscopy (SECM) to study the chemistry of graphene. First we discuss the study of the local chemical reactivity of graphene and the passivation of the defect sites using o-phenylenediamine. We then discuss surface diffusion (“sliding”) of an electrochemically active tripodic molecules on graphene.

Summary of Research:
We are using SECM, a quantitative scanning probe technique that allows for the measurement of the (electro)chemical reactivity of electrodes with spatial resolution. SECM can detect the surface diffusion of adsorbed molecules through imaging of their differential reactivity with respect to the bare graphene surface.

“Healing” Graphene Defects. One key problem of chemical vapor deposition (CVD) graphene, yet to be solved, is the defect sites created during fabrication. McCreery and co-workers reported that the edges and defects of highly oriented pyrolytic graphite (HOPG) are more active chemically when compared to the basal plane of HOPG [1]. The difference in the chemical reactivity of defects could hinder our understanding of graphene chemistry and creates a hurdle in the application of...
graphene. We used scanning electrochemical microscopy to examine the local reactivity of graphene and passivated the active edges with o-phenylenediamine. By biasing the tip potential and the substrate potential at reducing and oxidizing potentials, respectively, a redox-active molecule can be reduced and oxidized. Simultaneously, a feedback current can be measured. The variations of the feedback current provide us information about the local reactivity.

The 3-D plot in Figure 1 shows that the feedback current of the edges of graphene is much larger than that of the general area of graphene. The projection of the 3-D plot shows clearly the differences in feedback current between graphene (green), Si/SiO₂ (dark blue), and graphene edges (orange). After deposition of o-phenylenediamine, the feedback current at the graphene edges become comparable to their surroundings shown in Figure 2.

**Molecular Diffusion on Graphene.** In collaboration with Prof. William Dichtel’s group, we have studied the adsorption of electrochemically active tripod molecules with “flat feet” (Figure 3), in which a strong chemisorption is observed due to pi-stacking. This interaction should yield a low displacement barrier for the tripod and we propose to study this “sliding molecule” effect through in situ surface diffusion measurements in an electrochemical environment. The design of mobile electroactive species is of interest for the design and study of electrocatalysts and for reactant delivery platforms. SECM probes can be used to collect substances produced by the tripod, e.g. hydrogen peroxide as a product of oxygen reduction, or can be used with a redox mediator to probe the localized electron transfer kinetics through a feedback current. Diffusion of the strongly adsorbed tripod molecules changes the spatially-resolved probe current upon imaging at different times, as shown in Figure 2.

In this example, the tripod molecule was locally adsorbed on spots of radius ~ 50 µm, and allowed to diffuse freely on the graphene surface around it when in solution, thus changing the intensity of the signal as the diffusing tripod gets radially diluted. Control experiments to show this effect were carried out by: 1) blocking surface diffusion by impeding the mobility of the tripod molecules using adsorbed polymers, 2) verifying the stability of the catalytic activity of graphene and of the graphene/tripod spots, and 3) using microfabrication at CNF to create graphene microelectrodes in which the activity of the tripod was constrained to a known area. These graphene microelectrodes will be also used for the characterization of relevant parameters for the catalytic activity of graphene (e.g. for oxygen reduction) and of its modification by the adsorption of redox active molecules.

**References:**