Reactivity of Monolayer CVD Graphene Imperfections Studied Using Scanning Electrochemical Microscopy

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Abstract:

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. Then we show fabrication of a 500 nm SECM probe electrode to improve the resolution of SECM imaging.

Summary of Research:

We are using scanning electrochemical microscopy (SECM), a quantitative scanning probe technique that allows for the measurement of the (electro)chemical reactivity of substrates with spatial resolution. One key problem of chemical vapor deposited (CVD) graphene, yet to be solved, is the defective regions created during fabrication and processing. McCreery and co-workers reported that the edges and defects of highly oriented pyrolytic graphite (HOPG) are chemically more active 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 have used scanning electrochemical microscopy to examine the local reactivity of graphene.

By biasing the probe electrode potential and the substrate electrode potential at reducing and oxidizing potentials, respectively, a redox-active molecule can be reduced and oxidized, generating a feedback current. The variations of the feedback current provide us information about the local reactivity. The SECM image in Figure 1 shows the spatially resolved reactivity of a mechanically induced defect. The feedback current of the edges of graphene is much higher than that of the general area of graphene. The projection of the SECM shows clearly the differences in feedback current between graphene (green), Si/SiO₂ (dark blue), and graphene edges (red). The chemically induced defect was created by oxidizing the graphene with a solution of NaOCl. The edges have higher feedback current than the general area of graphene as observed in the mechanically induced defect (Figure 2). The optical images show no obvious morphological features at the edges of the two kinds of defects.

The spatially resolved SECM images provide a direct way to understand the chemical reactivity of graphene, however, the resolution of the images is approximately 7 µm. The resolution of the SECM images is determined by the radius of the SECM probe electrode. In this case, we used a 7.5 µm radius Pt electrode.

In order to improve the resolution of the SECM images, a smaller probe electrode has to be fabricated. The thickness of the insulating glass has to be less than ten times the radius of the Pt in order to allow the diffusion of the redox mediator. Figure 3 shows an SEM image of the Pt probe electrode of a radius of 500 nm.

References:

Figure 1: Optical (left) and SECM (right) images of a mechanical defect. No obvious morphological feature was seen at the edge of the graphene in the optical image. The reactivity at the edge of graphene is higher (red) compared to the general area of graphene (green). The exposed Si/SiO$_2$ substrate is in blue. (See full color version on inside front cover.)

Figure 2: Optical (left) and SECM (right) images of a chemical defect. The reactivity at the edge of graphene is higher (red) compared to the general area of graphene (yellow). The exposed Si/SiO$_2$ substrate is in green. (See full color version on inside front cover.)

Figure 3: SEM image of a Pt probe electrode. The radius of the SECM probe electrode is approximately 500 nm.