Imaging Reactive Sites on Carbon Materials during Electrochemical Reaction

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Abstract:
We aim at chemically imaging the reactive sites on carbon-based materials such as single-walled carbon nanotubes, multi-walled carbon nanotubes and graphene sheets at sub-diffraction resolution. In order to achieve this goal, we use single-molecule fluorescence microscopy of fluorogenic reactions. The carbon materials are further imaged separately through scanning electron microscopy (SEM), and superimposed on the map of reactive sites later on. This project requires us to fabricate arrays of position markers on the substrate, which facilitates the overlapping.

Summary of Research:
Our group has recently developed a single-molecule fluorescence approach to study the electrochemical catalysis on single-walled carbon nanotubes [1,2]. In this approach, we designed a two-stage reduction reaction as the probe. At each individual reactive site, we were able to capture the fluorescent signal of the product molecule one at a time. This approach can remove the ensemble averaging, reveal the heterogeneity between reactive sites, and thus help us to understand the mechanisms and dynamics of nanocatalysts. Moreover, we developed a sub-diffraction imaging method to chemically map out the reactive sites on nanocatalysts. By applying this method, we can push the optical resolution to ~ 20 nm, which enables us to study the distribution of reactivity on carbon materials at much higher precision.

In one of our studies, we measured the electrochemical catalysis on aligned single-walled carbon nanotubes. The samples, prepared by our collaborator in CNF, went through three individual photolithography steps. The fabrication started with etching micron-sized position makers on a piece of quartz wafer, followed by patching arrays of iron catalyst layer for carbon nanotube growth. After growing carbon nanotubes, 50 nm thick gold is deposited through an evaporator on the substrate to cover the iron catalyst layer. The morphology of the final sample is shown in Figure 1. The gold serves as the electrode and has direct contact with each individual single-walled carbon nanotubes, which enables us to measure the electrochemical processes occurred on nanotubes.

Once the chemical imaging step is done, we further image the sample with SEM, and superimpose the reactive sites on carbon nanotubes with the help of etched position markers. Our preliminary results showed that there are localized “hot” spots on single-walled carbon nanotubes, which exhibit much higher reactivity than other areas. The reactivity is different from site to site, and they are tunable upon applied potential.

We are also working on applying a similar strategy to other carbon-based materials, such as multi-walled carbon nanotubes and graphene sheets.

References:
Figure 1: SEM image of aligned SWNTs on ST cut quartz slide.

Figure 2: SEM of gold electrode and etched position markers.