Final Technical Report

Graphene Charge Transfer, Spectroscopy, and Photochemical Reactions

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This project focused on the special electronic and optical properties of graphene and adsorbed molecular species. Graphene makes an excellent substrate for current collection in nanostructured photovoltaic designs. Graphene is almost transparent, and can be used as a solar cell window. It also has no surface states, and thus current is efficiently transported over long distances. Progress in graphene synthesis indicates that there will soon be practical methods for making large pieces of graphene for devices. We now need to understand exactly what happens to both ground state and electronically excited molecules and Qdots near graphene, if we are going to use them to absorb light in a nano-structured photovoltaic device using graphene to collect photocurrent. We also need to understand how to shift the graphene Fermi level, to optimize the kinetics of electron transfer to graphene. And we need to learn how to convert local graphene areas to semiconductor structure, to make useful spatially patterned graphenes. In this final report, we describe how we addressed these goals.

We explored the question of possible Surface Enhanced Raman spectroscopy from molecular Charge Transfer onto Graphene substrates. We observed strong hole doping of graphene by adsorbed halogens as indicated by the shift of the graphene G Raman band. In the case of iodine adsorption, we also observed the anionic species made by hole doping. At low frequency in the Raman spectrum, we saw quite intense lines from I_3^- and I_5^- , suggesting possible SERS. We reported on Fresnel calculations on this thin film system, which did not show any net electromagnetic field enhancement.

In order to carefully investigate the question of possible chemical SERS, we studied Rhodamine 6G dye (R6G) on graphene, as R6G is the standard, well characterized molecule for high Raman cross section SERS with Ag particles. By comparing the optical contrast visible spectrum, and the Raman spectrum, we were able to determine the absolute Raman cross section for R6G on the graphene surface. We found that the R6G section is perhaps a factor of 3 less on the graphene surface, apparently because the R6G absorption is red-shifted away from the laser line. In this system there is no evidence for field enhancement or chemical SERS. Nevertheless, the R6G Raman shows high signal to noise, as interfering dye luminescence, present for example in solution, is strongly quenched by the metallic graphene. In addition, luminescence from the graphene itself is negligible despite 2% optical absorption of the laser. As a net result, graphene makes an excellent substrate for Raman scattering by adsorbed molecular species.

We also used resonance Raman and optical reflection contrast methods to study charge transfer In 1-10 layer (1L – 10L) thick graphene samples on which strongly electronegative NO2 has been adsorbed. Electrons transfer from the graphene to NO2, leaving the graphene layers doped with mobile delocalized holes. Doping follows a Langmuir-type isotherm as a function of NO2 pressure. Raman and optical contrast spectra provide independent, self-consistent measures of the hole density and distribution as a function of the number of layers (N). As the doping induced Fermi level shift E_F reaches half the laser photon energy, an intensity resonance in the graphene G mode Raman intensity is observed. We observe a decrease of graphene optical band-to-band absorption in the near-IR that is due to hole doping. Highly doped samples are more transparent, and they are expected to have high metallic conductivity. In thicker samples holes are effectively confined near the surface as shown below; the interior graphene

layers show an essentially pristine Raman signal. In these multilayer samples, recent theory suggests that a small band gap opens near the surface due to asymmetric doping.

In addition we completed a detailed study of gaseous Br_2 adsorption and charge transfer on graphene, combining *in situ* Raman spectroscopy and density functional theory (DFT). When graphene is encapsulated by hexagonal boron nitride (h-BN) layers on both sides, in an h-BN/graphene/h-BN sandwich structure, it is protected from doping by strongly oxidizing Br_2. Graphene supported on only one side by h-BN shows strong hole doping by adsorbed Br_2. Using Raman spectroscopy, we determine the graphene charge density as a function of pressure. DFT calculations reveal the variation in charge transfer per adsorbed molecule as a function of coverage. The molecular adsorption isotherm (coverage versus pressure) is obtained by combining Raman spectra with DFT calculations. The Fowler-Guggenheim isotherm fits better than the Langmuir isotherm. The fitting yields the adsorption equilibrium constant (~0.31 $torr^{-1}$) and repulsive lateral interaction (~20 meV) between adsorbed Br_2 molecules. The Br_2 molecule binding energy is ~0.35 eV. We estimate that at monolayer coverage each Br_2 molecule accepts 0.09 e^- from single-layer graphene. If graphene is supported on SiO_2 instead of h-BN, a threshold pressure is observed for diffusion of Br_2 along the (somewhat rough) SiO_2/graphene interface. At high pressure graphene supported on SiO_2 is doped by adsorbed Br_2 on both sides.

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