

Raman Studies in Graphene

Nkemdilim Oghedo
Chemical Engineering, Yale University

NNIN REU Site: Center for Nanotechnology, University of Washington, Seattle, WA

NNIN REU Principal Investigator(s): Mehmet Sarikaya, Genetically Engineered MSE Center, University of Washington

NNIN REU Mentor(s): Dr. Yuhei Hayamizu, Genetically Engineered MSE Center, University of Washington

Contact: nkemdilim.oghedo@yale.edu, sarikaya@u.washington.edu, hayamizu@u.washington.edu

Abstract and Introduction:

Single-layer graphene has emerged as a significant material for post-silicon nano-electronics. Due to its two-dimensional structure, all carbon atoms are exposed to the atmosphere, rendering graphene highly sensitive. Thus, localized surface disturbances can modify its electronic structure and conductivity [1].

Genetically engineered peptides for inorganics are small biomolecules found to selectively bind to inorganic solids such as gold, silica and graphite [2]. This research focused on two forms of graphite binding peptides (GrBP5): the original Wild-Type (WT) peptide (-2 charge) and a mutant peptide (+2 charge). The mutant peptide was designed by replacing two negatively charged amino acids on a WT peptide sequence with two positively charged ones. This project investigated the doping capabilities these peptides have on single-layer graphene with respect to their sequence changes. We also examined the degree of doping as it relates to peptide solution concentrations and incubation times.

Raman spectroscopy unobtrusively provides information on the chemical composition and electronic properties of a sample. Analysis of the characteristic G ($\sim 1580 \text{ cm}^{-1}$) and 2D ($\sim 2690 \text{ cm}^{-1}$) peaks of graphene spectra reveals the number of graphene layers in a sample [3]. One can also use Raman to monitor changes in graphene's electronic structure by observing shifts in the G and 2D bands. These shifts correlate to alterations in charge carrier density and conductivity. Theory predicts that both p- and n- doping on graphene correspond to an increase in G band energy and decrease in G band width [4]. Observation of these changes indicates the occurrence of molecular doping on graphene.

Environmental Procedures:

Graphene was made using the micro-mechanical exfoliation technique and deposited onto a silicon substrate (silicon layer topped by a 300 nm thermally oxidized layer). Raman measurements were performed with a 514 nm laser, $1 \mu\text{m}$ in diameter, for 30 seconds at 40% laser exposure (Renishaw Raman Microscope). These parameters obtained the most information without overheating the sample. 2D and G peaks were analyzed with the "Start Fit" operation on the Wire 2.0

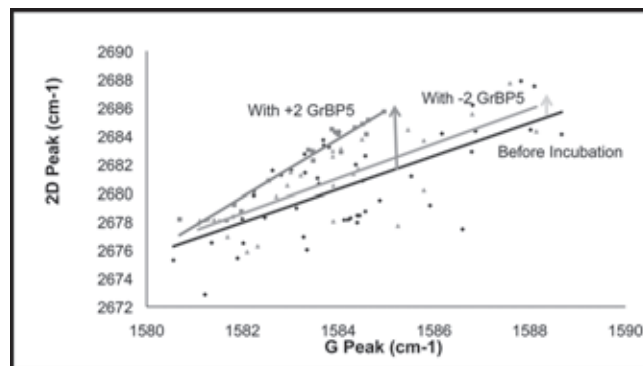


Figure 1: G versus 2D-peak positions before and after peptide incubations ($1 \mu\text{M}$, 24 hours).

software from Renishaw. Peak position, width and height were recorded. Samples were incubated under a humidity controlled hood, and then rinsed twice with deionized water. Previously probed locations were found and probed again under the same laser parameters. Peak information was re-recorded.

Results:

Changes in both the G and 2D bands after incubation were examined. From Figure 1, it is clear that both peptides caused an increase in the G and 2D peak positions, with +2 GrBP5 peak positions increasing more significantly. Figure 2

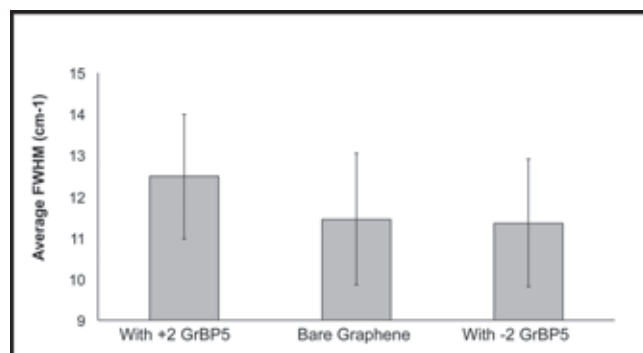


Figure 2: Average full-widths-at-half-maximum (FWHM) of G-peaks before and after peptide incubation ($1 \mu\text{M}$, 24 hours).

shows that +2 GrBP5 causes a widening of the G band while -2 GrBP5 causes a slight narrowing. This inconsistency can be explained by theory, which predicts very minor changes in G band width for ± 50 meV shifts in Fermi Energy [4]. Our peptides caused energy shifts in this range, and therefore did not affect noticeable changes in G band width.

Internal strain, induced by the micro-mechanical exfoliation procedure, also contributed to this discrepancy. Peak positions higher and lower than average correspond to regions of compression and tension, respectively. This strain caused a widening of the G band, which opposed the narrowing of the G band caused by peptide doping [5]. This conflict further explains the inconsistent changes of the G band width.

From these results, we concluded that +2 and -2 GrBP5 are able to dope graphene, with mutant +2 GrBP5 doping more significantly.

Discussion:

Samples incubated with a $1 \mu\text{M}$ peptide solution concentration for 24 hours provided the clearest results. Other incubation parameters included $1 \mu\text{M}$ solution for one hour and $0.1 \mu\text{M}$ solution for 24 hours. $0.1 \mu\text{M}$ concentrations were too low to significantly influence doping. Twenty-four hour incubations proved more informative than one hour incubations due to the fact that longer incubation times gave peptides more time to bind, assemble and align on graphene. A more crystalline peptide alignment resulted in more uniform interactions between the peptides and graphene, leading to more consistent and significant doping effects.

Figures 3 and 4 show that compressed graphene regions exhibit opposite peak shifts than regions with little to no strain. This may result from a change in peptide-graphene interactions due to the distorted graphene lattice with significant compression. This suggests an interesting relationship between internal strain and doping capabilities to be studied further.

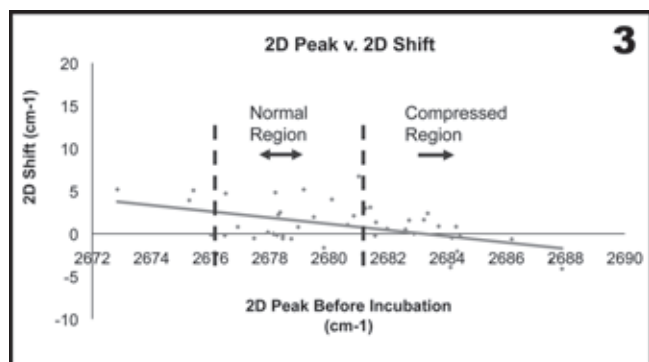


Figure 3: Initial 2D-peak versus 2D-peak shift for both peptides ($1 \mu\text{M}$, 24 hours).

Conclusion:

Results show that -2 GrBP5 and oppositely charged mutant, +2 GrBP5, successfully dope charges onto single-layer graphene. These peptides cause positive shifts in G and 2D Raman peaks and changes in the G Band width, which, in accordance with theory, result from molecular doping. In addition, internal strain may affect molecular doping and/or peptide binding behavior.

Acknowledgements:

I would like to thank the National Science Foundation, National Nanotechnology Infrastructure Network Research Experience for Undergraduates (NNIN REU) Program, the University of Washington Materials Research Science and Engineering Centers (MRSEC) and the Genetically Engineered Materials Science and Engineering Center (GEMSEC). The research was carried out at the NNIN and GEMSEC facilities, a part of the MRSEC-Materials Research Facilities Network. I would like to thank my mentor, Dr. Yuhei Hayamizu, and my faculty supervisor, Prof. Mehmet Sarikaya.

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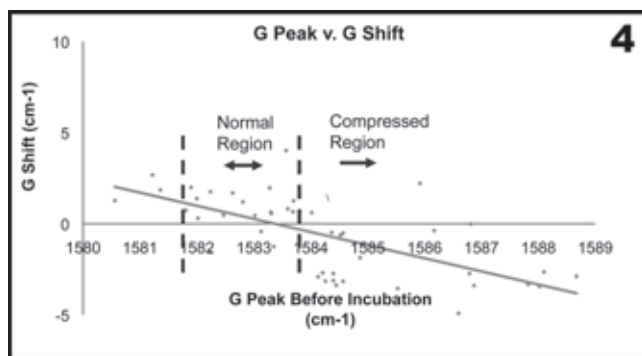


Figure 4: Initial G-peak versus G-peak shift for both peptides ($1 \mu\text{M}$, 24 hours).