How the Band Structure of Graphene/Nanomesh Bilayers Depends on its Stacking Symmetry

Veronica Show

Chemistry, Harvey Mudd College

Global Quantum Leap International Research Training Experience (GQL IRTE) Program

GQL IRTE Principal Investigator: Dr. Toshikaze Kariyado, National Institute of Material Science (NIMS), Tsukuba, Ibaraki, Japan

Primary Source(s) of Research Funding: Global Quantum Leap's International Research Training Experience (GQL IRTE) through the NSF AccelNet program under award numbers OISE-2020174 (U. Minnesota) and OISE-2020184 (Cornell University)

Contact: vshow@hmc.edu, Kariyado.Toshikaze@nims.go.jp

Website: https://cnf.cornell.edu/education/reu/2022

Abstract:

Here, we explore a bilayer system which includes graphene and a graphene nanomesh with a potentially tunable bandgap. Using computational methods, we find that the behavior of the system is similar to a superposition of the two monolayers. Additionally, we find that the stacking symmetry of the system affects its band structure; AA graphene/nanomesh bilayers exhibit semiconductor behavior whereas AB graphene/nanomesh bilayers exhibit conductor behavior.

Introduction and Methods:

Graphene has become a material of interest in the past few years due to its unique band structure features. Its Dirac cone band structure (as shown in red in Figure 1 at the Γ point) makes it an effective conductor. Additionally, Du, et al., found that introducing pores into graphene, such as the one shown boxed in blue in Figure 1, causes a direct band gap opening of 3.2 eV [1].

Recent efforts to synthesize these nanomeshes have been successful using bottom-up polymerization methods [2]. Due to its physical and electronic structure, graphene nanomeshes have potential application in many fields including phonon control, hydrogen storage, and water filtration. Additionally, when two of these sheets are stacked with any lattice constant mismatch or angle mismatch, it results in large-scale interference patterns, or moiré lattices. In a moiré lattice, the overall structure is periodic with many local differences.

Two regions of significance can be defined as an AA stacked region, where two layers are aligned so every carbon atom is directly on top of another carbon atom, and an AB stacked region, where two layers are staggered so the top layer is shifted along the diagonal of the nanomesh unit cell by exactly one side length of the hexagon. This difference in structure can result in unique electronic behavior which could indicate that electrons can be localized to certain regions of the moiré lattice.

Calculations were completed using GGA functionals in Quantum Espresso, an open-source program which calculates the electronic properties of nanoscale materials using density functional theory, pseudopotentials and plane waves [3,4]. The crystal structure of the materials was visualized using XCrysDen [5,6].

Results and Discussion:

First, the crystal structure for a graphene monolayer and the graphene nanomesh (shown boxed in blue in Figure 1) monolayer were optimized. The unit cell of graphene was found to have a lattice constant of 2.464 Å (7.3920 Å for the 3×3 supercell), and the unit cell of the graphene nanomesh was found to have a lattice constant of 7.5115 Å. Using these optimized structures, the band structure for both monolayers were calculated. The graphene band structure (using the 3×3 supercell to have symmetry with the nanomesh) contains the distinctive Dirac cone at the Γ point, and the band gap of the nanomesh is found to be 2.4021 eV. This band gap is much less than literature values [1], but this is due to GGA being used, which is known to underestimate band gaps, whereas HSE06 was used in literature calculations, which usually gives more accurate results. The overall shape of the band structures for both the graphene and nanomesh monolayers match literature results [1,7].

Using the optimized monolayer structures, AA and AB bilayers were approximated by stacking one nanomesh monolayer on one graphene monolayer with the nanomesh lattice constant and a bilayer distance equal to bilayer graphene, shown in the inserts of Figure 2 and 3 respectively. Using these unit cells, the band structure for each bilayer was calculated, as shown in Figure 2 and 3 for AA and AB respectively. There are many similarities in the band structures of the bilayers and the superposition of the 3×3 graphene supercell and the graphene nanomesh, especially for AB. Specifically, the band gap at the K point and curve at the Γ point appear in both the AA and AB band structures. Additionally, the Dirac cone of the 3×3 supercell at the Γ point is observed exactly in the AB band structure. In the AA band structure, the feature is similar, but it also has a band gap opening of 0.0557 eV. This is significant because it indicates that while the structures are very similar, the AB bilayer behaves like a conductor whereas the AA bilayer behaves like a semiconductor.

Conclusions and Future Steps:

In conclusion, the band structure of a graphene/nanomesh bilayer depends on its stacking symmetry: the AA bilayer has a direct band gap and the AB bilayer has a Dirac cone. This difference suggests in a moiré lattice, electrons will be confined to the AB, or conductive, regions. Further work is needed to fully model the moiré lattice and determine what relaxation effects may occur when stacking the two layers. Additionally, further research consists of determining the band structure of these bilayers with different types of nanomeshes, including changes in pore size and distance between pores.

Acknowledgments:

This work was funded by Global Quantum Leap's International Research Training Experience (IRTE) through the NSF AccelNet program under award numbers OISE-2020174 (U. Minnesota) and OISE-2020184 (Cornell University). Special thanks to Toshikaze Kariyado, Xiao Hu, Dr. Zizwe Chase, and Dr. Lynn Rathbun for their support and guidance.

References:

[1] Du, A., et al., JACS Comm., 2010, 132, 2876-2877, 10.1021/ja100156d.

[2] Bieri, M., et al., RCS Chem. Comm., 2009, 45, 6919-6921.

[3] Giannozzi, P., et al., J.Phys.:Condens.Matter, 2009, 21, 395502.

[4] Giannozzi, P., et al., J.Phys.:Condens.Matter, 2017, 9, 465901.

[5] Kokalj, A., Comp. Mater. Sci., 2003, 28, 155-168.

[6] Kokalj, A., J. Mol. Graphics Modelling, 1999, 17, 176-179.

[7] Newson, Ryan. 2010. Dynamics of Carriers and Photoinjected Currents in Carbon Nanotubes and Graphene.

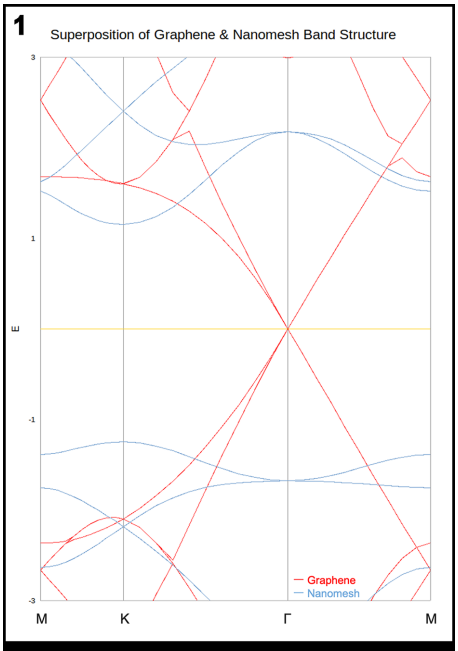

Figure 1, top: Superposition of a graphene monolayer and a nanomesh monolayer. Many of the prevalent features — such as the Dirac cone of graphene at the Γ point and the band gap in the nanomesh at the K point — are observed in both bilayer band structures, especially for AB stacking.

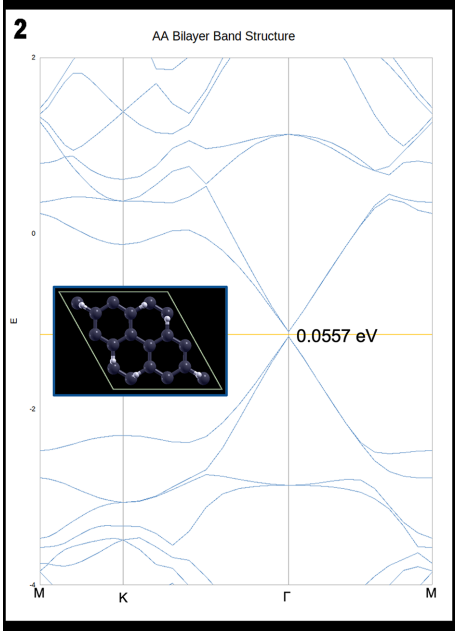

Figure 2, middle: Calculated band structure for the AA stacked graphene/nanomesh bilayer. It exhibits a band gap of 0.0557 eV at the Γ point.

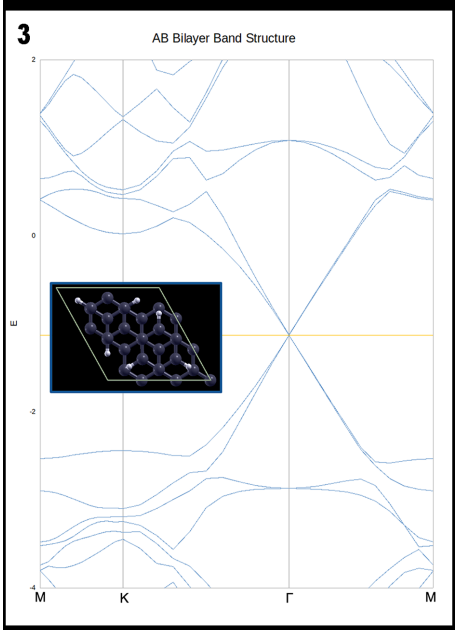

Figure 3, bottom: Calculated band structure for the AB stacked graphene/nanomesh bilayer. It exhibits a Dirac cone at the Γ point. Its features are very similar to the superposition of the graphene and nanomesh monolayers, especially the Dirac cone of the graphene at the Γ point and the band gap of the nanomesh at the K point.