PETAFLOPS SIMULATION AND DESIGN OF NANOSCALE MATERIALS AND DEVICES

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PI: Jerzy Bernholc[1]
Co-PIs: Emil L. Briggs[1], Miroslav Hodak[1], Carl T. Kelley[1], Wenchang Lu[1]
Collaborators: Rui Dong[1], Yan Li[1], Zhongcan Xiao[1], Bing Zhang[1], Jiayong Zhang[1]

[1]North Carolina State University

EXECUTIVE SUMMARY

This project focuses on high-performance calculations for materials and devices of high current interest and on development of petascale methods for such simulations. This past year, we concentrated on three challenges. First, we investigated two paradigmatic sensor configurations for detection of biologically important molecules through *ab initio* calculations: a noncovalently functionalized nanotube for glucose detection, and a covalently functionalized nanotube for ethylene detection. Second, we analyzed high-performance dielectric materials that store and release energy electrostatically through polarization and depolarization. We showed that blending two disparate strongly polar polymers, e.g., a poly(arylene ether urea) (PEEU, K = 4.7) and an aromatic polythiourea (ArPTU, K = 4.4), the resulting mixture exhibits a very high dielectric constant, K = 7.5, while maintaining low dielectric loss (< 1%.). Third, in the pursuit of atomically precise and bottom-up fabrication of graphene-based electronics, we determined and understood the atomic mechanism responsible for controlled conversion of a polymer to a nanoribbon, stimulated by hole injection through an scanning tunneling microscope (STM) tip.

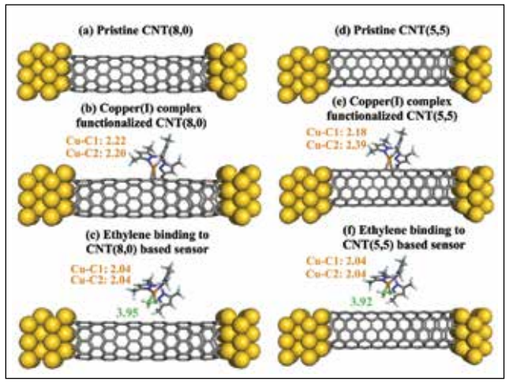

Figure 1: Optimized structures for ethylene detection in semiconducting CNT(8, 0)-based systems (a, b, c) and metallic CNT(5, 5)-based systems (d, e, f). The copper-carbon bond lengths (in Å) are labeled in brown; the closest distances between the ethylene molecule and the nanotube surface (in Å) are labeled in green.

RESEARCH CHALLENGE

Biomolecular detection is a rapidly growing field in biochemical and biomedical sciences. It is widely recognized as one of the key technologies for environmental monitoring and disease diagnosis. Functionalized carbon nanotube (CNT)-based nanosensors have shown great potential for detection, due to their sensitivity and selectivity. We computationally investigated the sensing mechanisms and capabilities of two paradigmatic sensor configurations based on single-walled carbon nanotubes (SWCNT): the covalently functionalized sensor for ethylene detection and the noncovalently functionalized sensor for glucose detection.

Dielectric materials store energy electrostatically through various polarization mechanisms and release it by depolarization. Dielectric capacitors are unparalleled in flexibility, adaptability, and efficiency for electrical energy storage, filtering, and power conditioning. We have discovered a practical and widely applicable mechanism for enhancing the dielectric constant through nanostructure engineering of dipolar polymers.

In the pursuit of atomically precise and bottom-up fabrication of graphene-based electronics, impressive advances have been made with the synthesis of graphene nanoribbons (GNR) by polymerizing monomers on different catalytic metal surfaces. We investigated the formation of GNRs from quasi-freestanding polymers assisted by hole injections from an STM tip. While a catalytic cyclodehydrogenation occurs in a cooperative domino-like conversion process during the thermal annealing, the hole-injection-assisted reaction happens at controlled molecular sites selected by the STM tip.

METHODS & CODES

The quantum transport and large-scale electronic structure calculations used the RMG code that we developed. For polymer simulations, the LAMMPS code was used. For calculations that include van der Waals interactions, the PWSCF code was used.

RESULTS & IMPACT

The sensing mechanism of glucose detection that we established can be generalized to detect other carbohydrate molecules, which are also known as saccharides. Carbohydrates are involved in a wide range of biological and pathological processes, such as cancer metastasis, cell signaling, protein function regulation, and cellular communication. Detection of specific carbohydrates is thus essential for investigating their roles in numerous natural processes, as well as for obtaining insights into the mechanisms involved and diseases provoked. The glucose sensor configuration and mechanism we described could be very useful in the design of other carbohydrate sensors. Moreover, the glucose sensing mechanism and the computational framework we developed can be applied for detection of the prostate cancer biomarker, which is known as osteopontin (OPN). Experimentalists have demonstrated that nanotube devices show detectable sensitivity to OPN when covalently functionalized with a receptor called scFv. One possible explanation is that the charged sites on the scFv's surface are neutralized by opposite charges associated with the bound OPN, leading to a change of electrostatic potential at the nanotube surface. However, the precise mechanism for the observed sensing response remains to be determined. The computational approach established here could provide a quantitative understanding of the sensing mechanism.

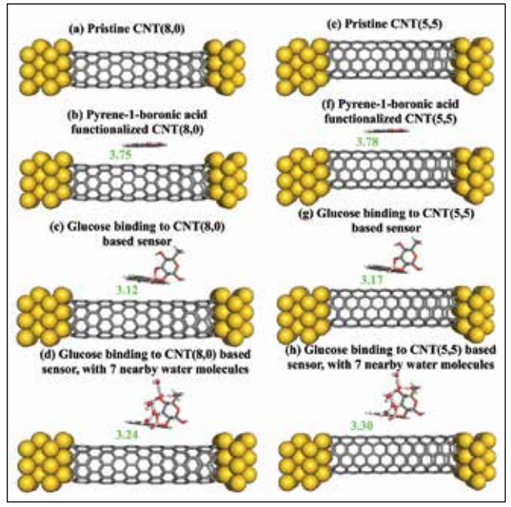

Figure 2: Optimized structures for glucose detection in the semiconducting CNT(8, 0)-based systems (a, b, c, d) and the metallic CNT(5, 5)-based systems (e, f, g, h). The closest distances between the pyrene-1-boronic acid molecule and the nanotube surface (in Å) are labeled in green.

It is a great challenge in dielectric polymers to achieve a high dielectric constant while maintaining low dielectric loss and high operating temperatures. We show that by blending two dipolar polymers in glassy state, i.e., poly(arylene ether urea) (PEEU, K = 4.7) and an aromatic polythiourea (ArPTU, K = 4.4) to form a nanomixture; the resulting blend exhibits a very high dielectric constant, K = 7.5, while maintaining low dielectric loss (< 1%). The experimental and computer simulation results demonstrate that blending these dissimilar dipolar polymers causes a slight increase in the interchain spacing of the blend in its glass state, thus reducing the barriers for reorientation of dipoles in the polymer chains along the applied electric field and generating a much higher dielectric response than the neat polymers.

We have established how the bottom-up synthesis of a graphene nanoribbon can be controlled by charge injections from an STM tip. From our experiments and first-principles calculations, it was found the hole injections from an STM tip can trigger a cooperative domino-like cyclodehydrogenation even when the polymers are quasi-freestanding with suppressed substrate effect. The hole injections greatly reduce the energy barrier in the key step of the carbon-to-carbon bond formation. The hydrogen atoms migrate to the edge and dissociate into the vacuum as H_2 molecules. As the STM tip treatment can be performed at selective molecular sites without involving a traditional catalytic effect from the metal substrate, the results point to a new way for bottom-up and controllable synthesis of freestanding GNRs and heterojunctions, which is critical for practical GNR-based nanodevices.

WHY BLUE WATERS

The applications described above require a very large parallel supercomputer with a high-speed interconnect among the nodes (due to the frequent exchange of substantial amounts of data among nodes). Each project required many runs to explore the various scientific issues, with a substantial amount of analysis between the runs. High availability and quick turnaround are thus also very important for timely progress in our research.

PUBLICATIONS AND DATA SETS

Li, Y., M. Hodak, W. Lu, and J. Bernholc, Selective sensing of ethylene and glucose using carbon-nanotube-based sensors: An *ab initio* investigation. *Nanoscale*, 9 (2017), pp. 1687–1698.

Ma, C., et al., Controllable conversion of quasi-freestanding polymer chains to graphene nanoribbons. *Nature Communications,* 8 (2017), p. 14815.

Thakur, Y., et al., enerating high dielectric constant blends from lower dielectric constant dipolar polymers using nanostructure engineering. *Nano Energy*, 32 (2017), pp. 73–79.

Dolgova, N.V., Binding of Copper and Cisplatin to Atox1 Is Mediated by Glutathione through the Formation of Metal–Sulfur Clusters. *Biochemistry*, 56 (2017), pp. 3129–3141.