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**Awarded to:**
Michigan Technological University

**Project Title:**
Heterojunction of Boron Nitride and Carbon Nanotubes: Synthesis and Characterization

**Principal Investigator:**
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October 26, 2017

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October 31, 2017

**Executive Summary**

The advancement of silicon (Si) technology has led to faster and smaller computers and smart cellphones. Unfortunately, further miniaturization of semiconductor devices will encounter fundamental physics limitations, including short channel effects, high contact resistance, and high heat dissipation, which will deteriorate device energy efficiency. In this project, we have explore into the creation of tunneling field effect transistors (TFETs) and switches without using semiconductors. Since these devices did not involve the use of semiconductors, our approach would have bypassed the above-mentioned limits of Si devices. During the course of this two-year funding period, we have successfully 1) Identify the essential conditions for the synthesis of co-axial hetero-junctions of boron nitride nanotubes (BNNTs) and carbon nanotubes (CNTs), i.e., co-axial BNNTs/CNTs junctions. 2) Investigate the switching behaviors of a series of precursor materials, including a) branching BNNTs/CNTs junctions, b) graphene-BNNTs junctions, and c) quantum-dots functionalized BNNTs (QDs-BNNTs).

## 1. Project Scope

The far-reaching goal of this research project is to reveal the properties of single walled (SW) heterojunctions of boron nitride nanotubes and carbon nanotubes (BNNT/CNT junctions) with specific zigzag, armchair, or chiral structures. According to theory, [1-4]

- Zigzag BNNT/CNT junctions (Figure1a) are insulator/semiconductor junctions. They have flat band structures and tunable direct band gaps (~0.5 to 2.0 eV) at the interface. Thus these BNNTs/CNTs junctions can be used as nanoferromagnetic materials, spintronic and tunable photonic devices etc..
- Armchair BNNT/CNT junctions (Figure 1b) are insulator/semimetal junctions with tunable direct band gap, and applicable for Schottky devices, quantum dots, etc..

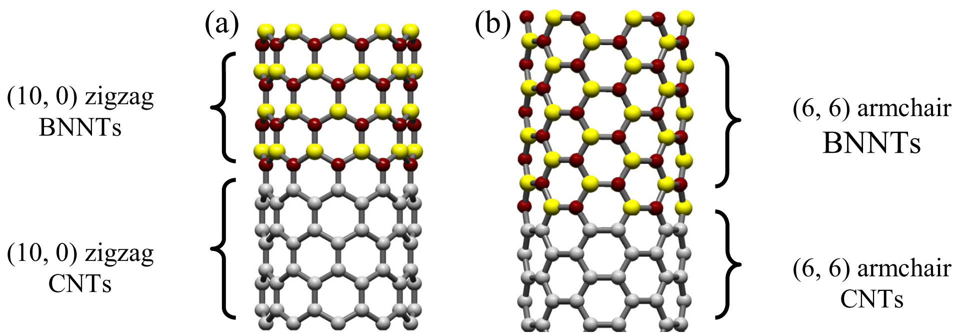


Figure 1. Ball-and-stick representations of (a) a zigzag (10, 0) and (b) an armchair (6,6) BNNT/CNT junctions.

This ultimate goal is currently not realistic because the science and engineering on chirality controls of both BNNTs and CNTs are not well established. In particular, technology to grow SW-BNNTs is still not fully achievable in the field.

Instead, the **major objectives of the current project are** to

1) Understand the science behind the synthesis of co-axial multiwalled (MW) BNNT/CNT junctions through a series of promising procedures that we have identified.

2) Investigate the novel physical properties of BNNT/CNT junctions, and their precursors that we have discovered during the pass funding period, including a) branching BNNT/CNT junctions, b) graphene-BNNT junctions, and c) quantum-dots functionalized BNNTs (QDs-BNNTs).

## 2. Project Activities

### 2.1. BNNT/CNT Heterojunctions

We have continue the study of branching BNNT/CNT heterojunctions. Results suggested that branching BNNT/CNT junctions are insulator-semimetal junctions applicable as Schottky switches with non-linear current-voltage (I-V) behaviors. Unfortunately, we can did not detect gate effect on branching junctions. We believe that this is due to the presence of Fe catalyst particles at the junctions, which causes shielding effect of the applied gate potential. Therefore, we have devoted our efforts into the formation of coaxial BNNT/CNT junctions without using catalyst particles. As shown in Figure 1, co-axial BNNT/CNT junctions are formed. Further optimization is needed to improve the synthesis yield before we proceed for the characterization of their electronic properties.

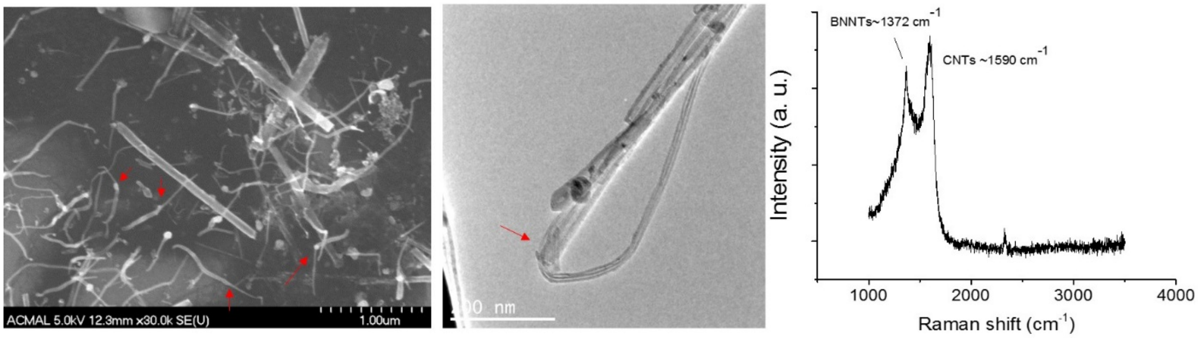


Figure 1. SEM and TEM images of co-axial BNNT/CNT junctions and the Raman spectra.

## 2.2. Electronics without Semiconductor by QDs-BNNTs

During the course of investigating the branching BNNT/CNT junctions, we have discovered a new class of functional materials: quantum-dots functionalized BNNTs (QDs-BNNTs).[5] As shown in Figure 2a, we have managed to deposit these crystalized gold NPs on one side of the BNNTs. These 1D arrays of NPs have diameters ranging from 3-10 nm and spacing of about 1-5 nm in between. At low bias voltages, this QDs-BNNT is insulating like pure a wide band gap BNNT. By applying increasing bias voltages, this QDs-BNNT allowed current to flow along the nanotube (Figure 2b). The turn-on voltage ($V_{on}$) decreases with the shortening of the length between probes and is tunable by gate potential. We explain the detected I-V characteristics (switching behaviors) by quantum tunneling across these NPs as also proven by a kinetic Monte Carlo simulation. Because of their function in facilitate the tunneling and single electron transport processes, we called these NPs as QDs. These tunneling field effect transistors (T-FETs) represent a new class of electronic switches with the use of any semiconducting property.

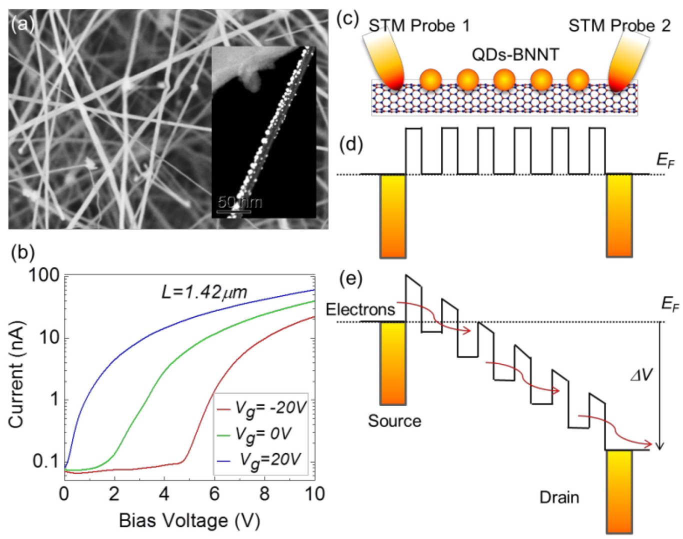


Figure 2. (a) Image of QDs-BNNTs and (b) the I-V characteristic at various gate potential ($V_g$). (c) Schematic of the tunneling channel at (d) off and (e) on states.

As inspired by the mechanical flexibility of nanotubes, we have explored the switching behavior of QDs-BNNTs in flexible electronics. As shown in Figure 3a, tunneling current would confine along the path of the linear QD chain. According to our simulation, the I-V behaviors of such QDs-BNNTs would be sensitive to the bending of the nanotubes as shown in Figure 3b. This is due to the change in the distance between QDs upon tensile or compressive stress. This would be different for a QDs-BNNT with randomized QDs. As shown in Figure 3c, the path of tunneling current is nonlinear, follow the path of QDs that has smallest QD gaps (minimum tunneling resistance and tunneling junction width). Statistically, this current path will be equally affected by bending at both the compressed and the stretched surfaces. While the current flow will be enhanced at the compressed surface but will be compensated by the degradation occurred at the stretched surface. This averaging effect led to a I-V behavior that is not sensitive to bending as experimentally proven (Figure 3d).

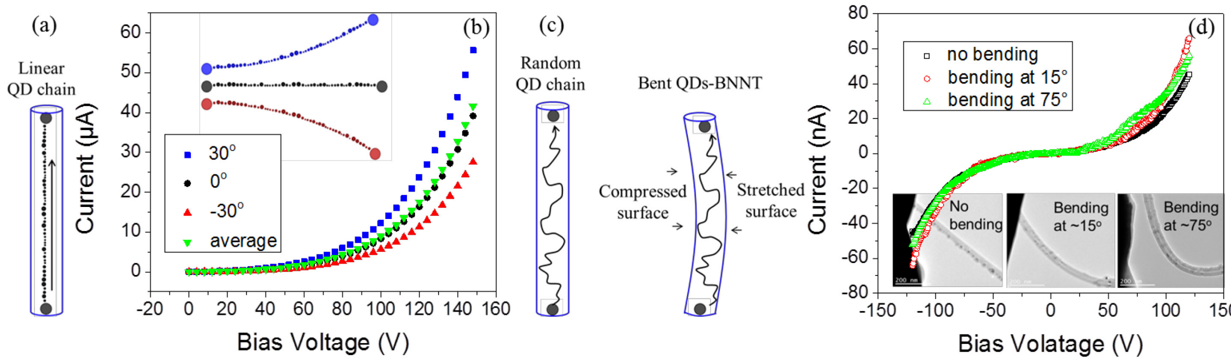


Figure 3. (a) Tunneling current on a QDs-BNNT with linear QD chain, and (b) the simulated I-V characteristic at various bending angle. (c) Tunneling current on a QDs-BNNT with randomized QD chain, and (d) the experimental I-V characteristic at various bending angle.

### 2.3. Electronics without Semiconductor by Graphene-BNNTs

More recently, we have verified our new idea of forming carbon-BN hetero-junctions without using catalysts. Such a self-assembly process was first tested by using graphene sheets as the "substrates" for the growth of BNNTs. As shown in Figure 4a, BNNTs are selectively grown on the surfaces of graphene sheets. The stability of these hetero-junctions was also proven by total energy calculations performed by plane wave pseudopotential approach within the local density approximation (LDA) of density functional theory (DFT). Results indicate that these graphene-BNNT junctions are current rectifiers (Figure 4b and 4c), resembling a novel class of electronics without using semiconductors.

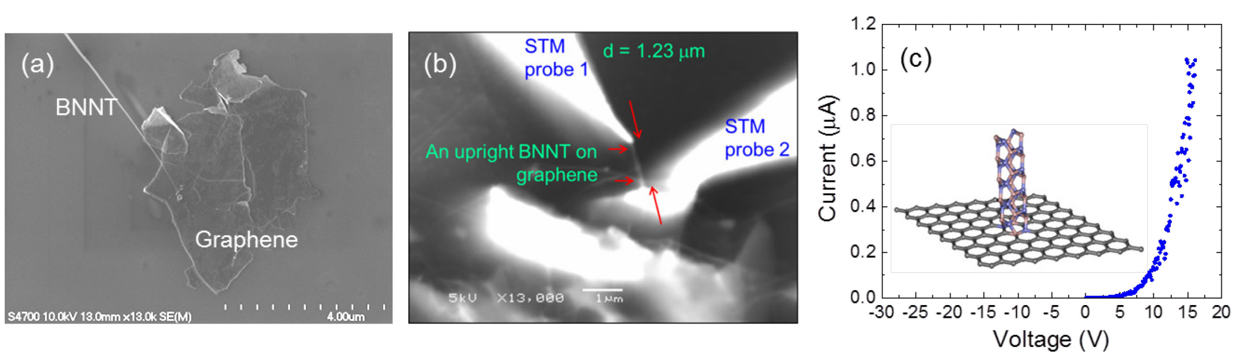


Figure 4. (a) SEM image of a BNNT grown selectively on graphene. (b and c) The formation and switching behaviors of these graphene-BNNT junctions are theoretically and experimentally proven.

### 2.4. Better understanding on T-FETs based on QDs-BNNTs

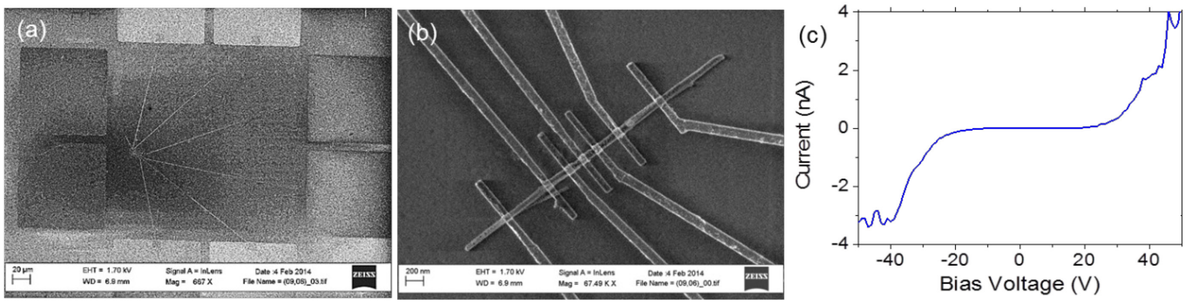


Figure 5. SEM images of the T-FET device and the typical I-V characteristic.

We have attempted to fabricate T-FETs with thinner gate oxide (150nm of $HfO_2$). As shown in Figure 5a, a QDs-BNNT is connected with a series of seven electrode leads to the surrounding microelectrode pads. The distance between two leads is ~100nm to 500nm (Figure 5b). Unfortunately, these switches shown low tunneling current (a few nA) and high threshold potential (~25V, Figure 4c). Further evaluation indicates that some of the distances between QDs are larger than 10nm and are not uniform. This is due to the fact that we used scanning electron microscopy (SEM) to judge the gaps of QDs when we optimize the synthesis of QDs-BNNTs. The resolution of SEM did not allow us to identify the better synthesis condition for QDs with smaller gap (negative fault signal). Therefore, we have switch our study to optimize the synthesis of QDs-BNNTs based on size evaluation of transmission electron microscopy (TEM)

### 2.5. Coulomb Staircase Detection

As suggested by our simulation, T-FETs fabricated by QDs-BNNTs are single electron transistors. To verify this, 4-probe scanning tunneling microscopy (STM) was used to perform *I-V* measurement on QDs-BNNTs at liquid He temperatures. As shown in Figure 6, the evidence of Coulomb staircase is detected near the threshold potential at T=8.8K. Again, the threshold potential is large for this series of tested samples.

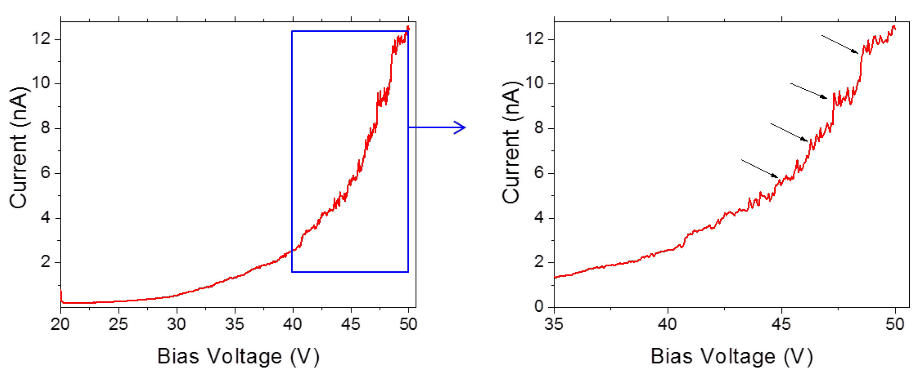


Figure 6. I-V characteristic of QDs-BNNTs detected at T=8.8K.

### 2.6. Improve Uniformity of QDs-BNNTs

By using TEM imaging, we have further improved the uniformity of QDs on BNNTs as shown in Figure 7. As shown, QDs with diameter <10nm, spacing between QDs ~2-4nm can be deposited at one side of the BNNTs at a length scale of >1 μm. We are now preparing a series of these "optimized" QDs-BNNTs such that devices can be fabricated. Unfortunately, we are still struggling to make more devices due to the failure of electron beam deposition and lift-off issues during the lithography processes.

## Future Plans

We have successfully synthesized co-axial BNNT/CNT junctions. However, there is still a mismatch between the diameters of BNNTs (~20-50nm) and CNTs (~8-15nm). Therefore, this will need to be addressed before we can achieve high-yield synthesis and characterization of their electronic properties. By using the refined approach, we are now able to synthesized QDs-BNNTs with more uniform QD sizes and gaps. We are now attempting to fabricate more devices base on QDs-BNNTs, in collaboration with the Center for Nanophase Materials Sciences (CNMS) in Oak Ridge National Laboratory. These devices will then be investigated for their plasmonic effects.

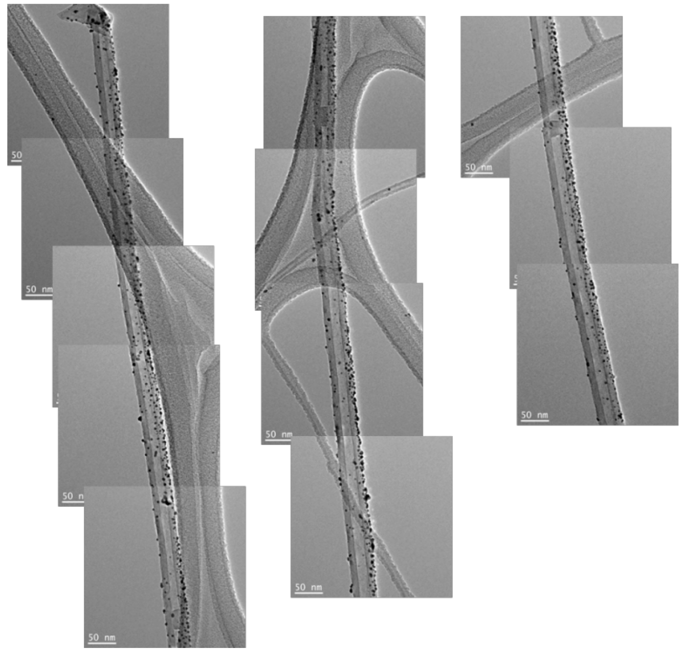

Figure 7. TEM images of uniform QDs deposited on BNNTs.

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**List of Products for this two-year project:**

1. Vyom Parashar, Corentin P. Durand, Boyi Hao, Rodrigo G. Amorim, Ravindra Pandey, Bishnu Tiwari, Dongyan Zhang, Yang Liu, An-Ping Li and Yoke Khin Yap, "Switching Behaviors of Graphene-Boron Nitride Nanotube Heterojunctions," *Scientific Reports* **5**, Article number: 12238 (2015) doi:10.1038/srep12238.
2. Boyi Hao, Anjana Asthana, Paniz Khanmohammadi Hazaveh, Paul L. Bergstrom, Douglas Banyai, Madhusudan A. Savaikar, John A. Jaszczak, and Yoke Khin Yap, "New Flexible Channels for Room Temperature Tunneling Field Effect Transistors," *Scientific Reports* **6**, 20293; doi: 10.1038/srep20293 (2016).
3. (Invited) Yoke Khin Yap, "Transistors without Semiconductors by Functionalized Boron Nitride Nanotubes," Symposium H01 Low Dimensional Nanoscale Electronic and Photonic Devices 8 in the 228th Electrochemical Society (ECS) Meeting (October 11-15, 2015) Phoenix, AZ.
4. (Invited) Yoke Khin Yap, "Transistors without Semiconductors by Functionalized Boron Nitride Nanotubes," Symposium G Multifunctional Inorganic One-dimensional Nanostructures: Status and Potential. 5th Int. Conf. of Smart and Multifunctional Materials, Structures, and Systems, June 5-9, 2016, Perugia, Italy.
5. (Invited) Yoke Khin Yap, "Transistors without Semiconductors by Functionalized Boron Nitride Nanotubes," Symposium NM3: Nanotubes and Related Nanostructures. 2016 Materials Research Society Fall Meeting, Nov 27-Dec 2, 2016, Boston, MA.