Final report for project DE-FG02-06ER46294

Project Title:
Hetero-junctions of Boron Nitride and Carbon Nanotubes: Synthesis and Characterization

Award Number:
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Summary

Hetero-junctions of boron nitride nanotubes (BNNTs) and carbon nanotubes (CNTs) are expected to have appealing new properties that are not available from pure BNNTs and CNTs. Theoretical studies indicate that BNNT/CNT junctions could be multifunctional and applicable as memory, spintronic, electronic, and photonics devices with tunable band structures. This will lead to energy and material efficient multifunctional devices that will be beneficial to the society. However, experimental realization of BNNT/CNT junctions was hindered by the absent of a common growth technique for BNNTs and CNTs. In fact, the synthesis of BNNTs was very challenging and may involve high temperatures (up to 3000 °C by laser ablation) and explosive chemicals. During the award period, we have successfully developed a simple chemical vapor deposition (CVD) technique to grow BNNTs at 1100-1200 ^{o}C without using dangerous chemicals. A series of common catalyst have then been identified for the synthesis of BNNTs and CNTs. Both of these breakthroughs have led to our preliminary success in growing two types of BNNT/CNT junctions and two additional new nanostructures: 1) branching BNNT/CNT junctions and 2) co-axial BNNT/CNT junctions, 3) quantum dots functionalized BNNTs (QDs-BNNTs), 4) BNNT/graphene junctions. We have started to understand their structural, compositional, and electronic properties. Latest results indicate that the branching BNNT/CNT junctions and QDs-BNNTs are functional as room-temperature tunneling devices. We have submitted the application of a renewal grant to continue the study of these new energy efficient materials. Finally, this project has also strengthened our collaborations with multiple Department of Energy's Nanoscale Science Research Centers (NSRCs), including the Center for Nanophase Materials Sciences (CNMS) at Oak Ridge National Laboratory, and the Center for Integrated Nanotechnologies (CINTs) at Sandia National Laboratories and Los Alamos National Laboratory. Results obtained during the current funding period have led to the publication of twelve peer reviewed articles, three review papers, two book and one encyclopedia chapters, and thirty eight conference/seminar presentation. One US provisional patent and one international patent have also been filed.

1. Accomplishments of the Project

The ***objective*** of this project is to obtain fundamental understanding on the formation of BNNT/CNT junctions and evaluate their unique physical behaviors, including their structural, electronic, photonic/optical, magnetic/spintronic properties. The ***long-term goal*** of the research area is to formulate steps towards the creation of new nanotubular structures with desired sequences of BNNT/CNT junctions. The nature of the proposed work has proven to be ***very challenging but will lead to cutting-edge sciences and technologies.***

During the initial phase of this project, we have evaluated two techniques for the synthesis of BNNT/CNT junctions: plasma-enhanced pulsed-laser deposition (PE-PLD), and chemical vapor deposition (CVD). This phase of work was very challenging especially in identifying the more effective technique that enable the growth of BNNTs (as well as CNTs). Eventually, a simple CVD approach has been developed for the purpose, and the functional catalysts were identified. Based on the CVD approach, co-axial BNNT/CNT junctions was successfully fabricated. However, the yield of these junctions is still low. We have then decided to develop the branching BNNT/CNT junctions, which have enabled us to establish a new class of tunneling switching devices without using semiconductors. During the course of these explorations, we have further developed two new nanostructures: quantum dots functionalized BNNTs (QDs-BNNTs) and BNNT/Graphene junctions.

The details of our accomplishments are described in section 2. Results obtained during the current funding period have led to the publication of 12 peer reviewed articles [1-12], 3 review papers [13-15], two book and one encyclopedia chapters [16-18], and thirty eight conference/seminar presentation (see section 3.3). One US provisional patent and one international patent have also been filed. A few more publications are now in preparation.

2. Project Activities

The theory of BNNT/CNT co-axial junctions will first be summarized in section 2.1. This will be followed by the description of research activities in subsection 2.2 to 2.7.

2.1. Theory of BNNT/CNT co-axial junctions

Theoretical studies indicate that co-axial BNNT/CNT junctions and h-BN/graphite sheets are energetically very stable [19-22]. Calculations have shown that the energy required for a N atom (or B atom) to exchange with a C atom at a BNNT/CNT junction is rather large (2.1 and 2.0 eV, respectively). Such a large "inter-diffusion" energy indicates that abrupt interfaces are energetically preferred for the formation of well-defined BN/C hetero-junctions. Various BNNT/CNT nanotubular junctions have been evaluated and summarized as follows:

1. BNNT/CNT junctions are energetically stable either in the armchair or the zigzag configurations as shown in Figure 1.
2. Zigzag BNNT/CNT junctions (Figure1a) are junctions of insulators/semiconductors. They have flat band structures and tunable direct band gaps (~0.5 to 2.0 eV) at the interface. Thus these BNNT/CNT junctions can be used as nanoferromagnetic materials, spintronic and tunable photonic/optical devices etc..
3. Armchair BNNT/CNT junctions (Figure 1b) are insulator/semimetal junctions with tunable direct band gap, and applicable for Schottky devices, quantum dots, etc..

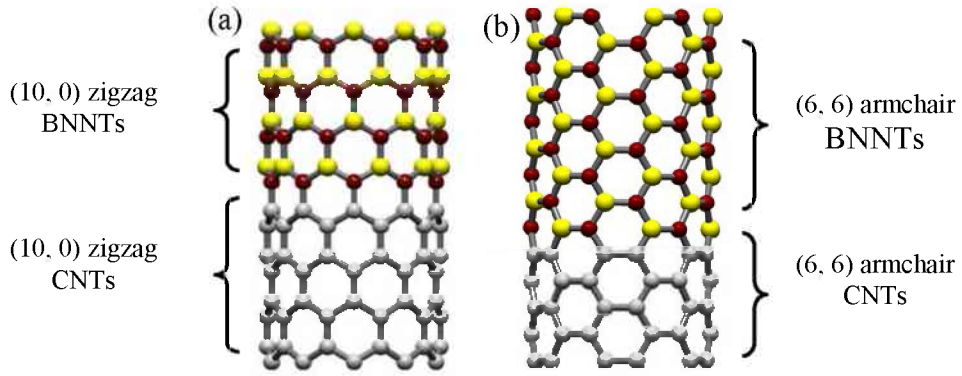


Figure 1. Ball-and-stick representations of (a) Zigzag (10, 0) and (b) armchair (6,6) BNNT/CNT junctions.

Zigzag BNNT/CNT Junctions

Okada et. al predicted that both zigzag h-BN/graphene hetero-sheets and BNNT/CNT junctions have interesting band structures [20, 21]. The calculated total energy, spin density, and energy bands reveal that these zigzag BNNT/CNT junctions have direct band gaps and flat-band ferromagnetism (almost no dispersion over the entire Brillouin zone near the Fermi level). Periodic arrangement of doped BNNT/CNT junctions (practically, vacancies or impurities) will form a one-dimensional itinerant ferromagnetic state.

An isolated zigzag junction can be used to create spin polarization. Such a junction is equivalent to one border state embedded between the continuums of CNT and BNNT states. Unpolarized electrons injected from the CNT segment are expected to become spin polarized when passing through the junction [22]. Thus zigzag BNNT/CNT junctions can be used for spintronic devices. Furthermore, the direct band gap of the zigzag BNNT/CNT were found to decrease with the increase of the length of the CNTs segments as shown in Figure 2 [22]. Thus, BNNT/CNT junctions are prospective materials for ***photonic/spintronic/magnetic devices with tunable energy band gaps***.

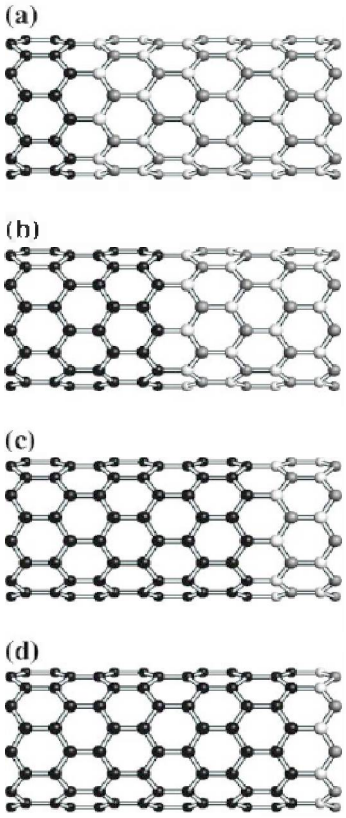


Figure 2. (9, 0) zigzag BNNTs/CNTs junctions with increasing CNTs segment (black circles on the left) from (a) to (d).

Armchair BNNT/CNT Junctions

The armchair BNNT/CNT junctions possess direct band gaps like the zigzag junctions but without the flat band nature [20, 21]. Because of the insulating nature of the BNNTs segments and the semi-metallic character of the CNTs segments, armchair junctions could be used as a Schottky barrier to create isolated islands for charge storage. This is applicable as ***quantum dots, nanocapacitors, and single electron transistors***.

Possible Growth Mechanism

Theory suggests that single walled BNNT/CNT junctions are energetically stable. Multi-walled BNNT/CNT junctions are also stable due to their larger diameters (smaller curvatures) with lower strain energy barriers. Since the synthesis of CNTs are well established with the use of catalysts, ***the synthesis of co-axial BNNT/CNT junctions can be obtained simply by switching the growth species and growth conditions*** as schematically drawn in Figure 3. This is possible if common catalyst for the growth of BNNTs and CNTs are identified. As shown, one could first (a) grow BNNTs segments on the catalyst and then (b) CNTs segments. The switching process can be repeated to form (c) superlattices. A reversed process in (d) to (f) is also possible. Experimentally, we have demonstrated the growth of both multi-walled BNNTs and CNTs by common catalysts (Fe, Ni) and techniques (PE-PLD & CVD). Also, we have evaluated the related growth mechanisms of these CNTs and BNNTs. We confirmed that our CNTs and BNNTs are following the ***base growth mode*** and vapor-liquid-solid (VLS) processes.

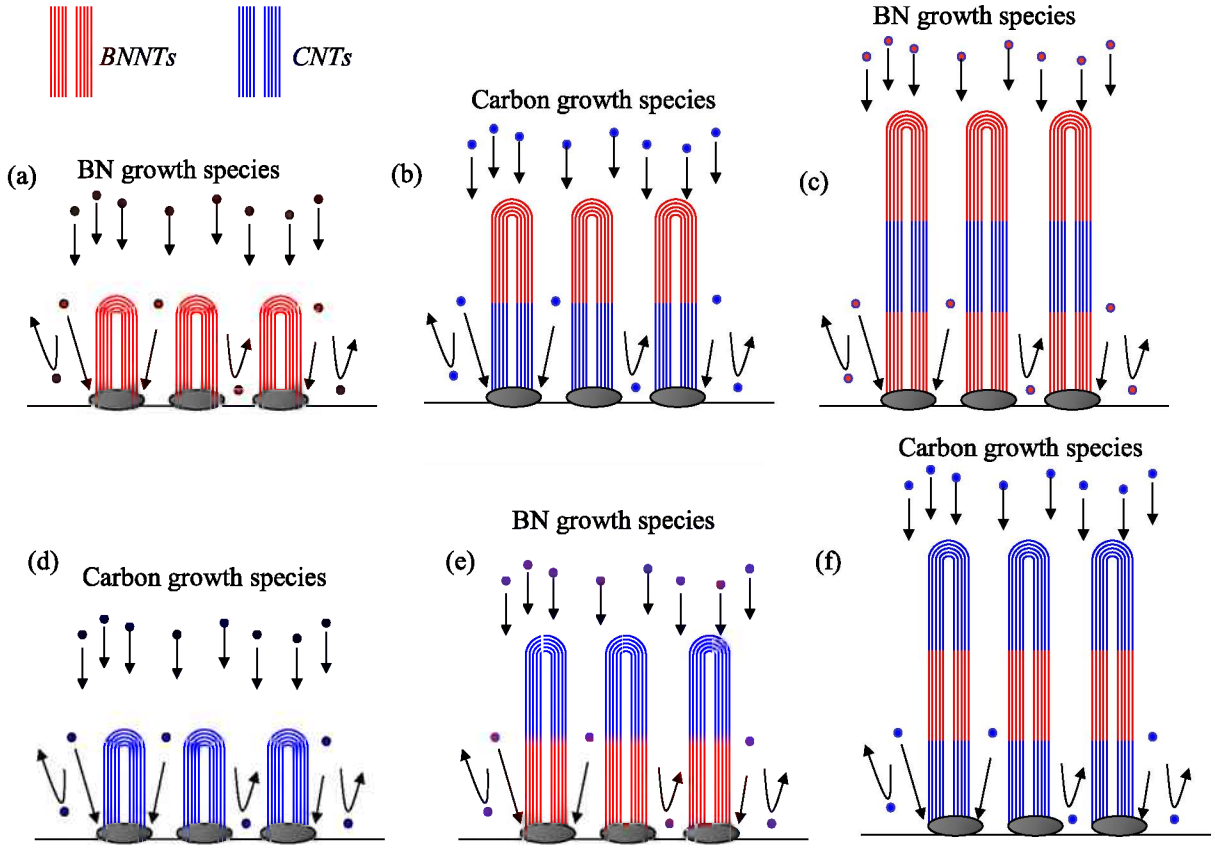


Figure 3. Schematic of growing BNNT/CNT co-axial junctions (a and b or d and e) and superlattices (c and f) in a base growth mode.

The objective of this proposal is not to grow specific types of BNNT/CNT junctions (Zigzag or Armchair). Such a goal is not realistic because controlling of the chirality has not yet beeing demonstrated for both BNNTs and CNTs. Instead, we will scrutinize the basic growth conditions that will enable the growth of single- and multi- walled BNNT/CNT junctions and establishes their unique new physical properties.

2.2. A Simple CVD Technique for the Growth of BNNTs

Prior to our breakthrough achieved in this project, the synthesis of BNNTs required special instrumentation, high temperatures (up to 3000 °C), and/or toxic precursors. At the beginning of this funding period, we have focused on investigating the growth of BNNTs by our PE-PLD and thermal CVD approaches. Although our ***PE-PLD*** technique managed to grow high crystalline BNNTs at 600 °C with high purity [23], we later determined that the approach is not optimum as ***the growth rate and yield of BNNTs are low*** [7]. Concurrently, we have developed a simple ***thermal CVD*** approach for effective growth of BNNTs. Our approach is ***based on the theory of nucleation*** where the nucleation rate of BNNTs is enhanced by using our ***growth vapor trapping (GVT)*** approach, which increase the growth vapor pressures [1]. As shown in Figure 4, the growth vapors generated from the precursors are trapped and confined at the closed end of the test tube to achieve sufficient partial pressures for the nucleation and growth of long BNNTs at 1100-1200 °C. The following chemical processes were proposed:

$$2B\,(s) + MgO\,(s) + FeO\,(s) \rightarrow B_2O_2\,(g) + Mg\,(s) + Fe\,(s)$$

$$B_2O_2\,(g) + Mg\,(s) + Fe\,(s) + 2NH_3\,(g) \rightarrow 2BN\,(BNNTs) + Fe\,(s) + Mg\,(s) + 2H_2O\,(g) + H_2\,(g)$$

The major advantages of our GVT approach are 1) using a regular tube furnace commonly used for the synthesis of CNTs, 2) simple set-up, and 3) not involving corrosive or toxic materials. The success of our GVT technique has led to a series of discovery including 1) the discovery of superhydrophobicity of BNNT films as insulating, transparent (wide band gap) self-cleaning coatings [3, 9], 2) the understanding of unique electrical and mechanical properties of individual BNNTs by *in-situ* scanning probe microscopy inside a transmission electron microscopy system (SPM-TEM) [4, 6, 8, 11], and 3) functionalization and cutting of BNNTs [10].

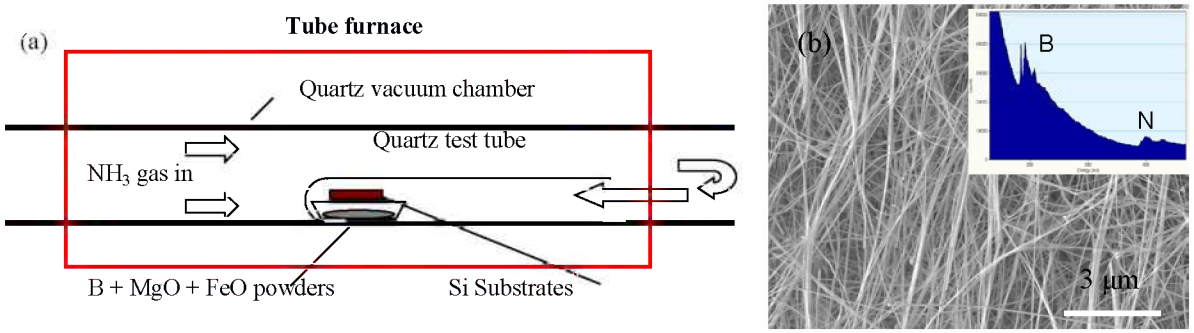


Figure 4. (a) Schematic of "growth vapor trapping" for the growth of BNNTs. (b) SEM images of the as-grown BNNTs and the spectra of electron energy loss spectroscopy (EELS).

2.3. Controlled Growth of BNNTs by Catalytic Chemical Vapor Deposition (CCVD)
Although we have succeeded in growing MW-BNNTs by our ***GVT*** approach, the formation of these BNNTs are based on ***spontaneous nucleation***. This means, ***the catalyst responsible for the growth is not clear*** (MgO, FeO, Mg, Fe, etc.. generated from the precursors?). This will hindered the technique for being used for the growth of BNNT/CNT co-axial junctions.

After a series of investigations, we are able to ***suppress the spontaneous nucleation*** of MW-BNNTs in the growth chamber, yet enable sufficient growth vapors to form high-quality MW-BNNTs on Fe and Ni catalysts (Figure 5a). This catalytic-CVD (CCVD) approach enabled the first success in ***controlled growth of long MW-BNNTs on patterned catalysts*** (Figure 5b) [2]. The as-grown MW-BNNTs are clean with high structural orders (Figure 5c). UV-Vis absorption spectra suggest an optical band gap of ~6eV without any sub-band absorption levels. These BNNTs are higher quality than those grown by our thermal CVD where small defect absorption bands were detectable at ~4.78 eV and 3.7 eV (Figure 5d).

The major impact of this breakthrough has enabled the growth of BNNTs on Fe and Ni catalysts that are commonly used for the synthesis of CNTs. This CCVD approach is the prospective technique for the growth of co-axial BNNT/CNT hetero-junctions.

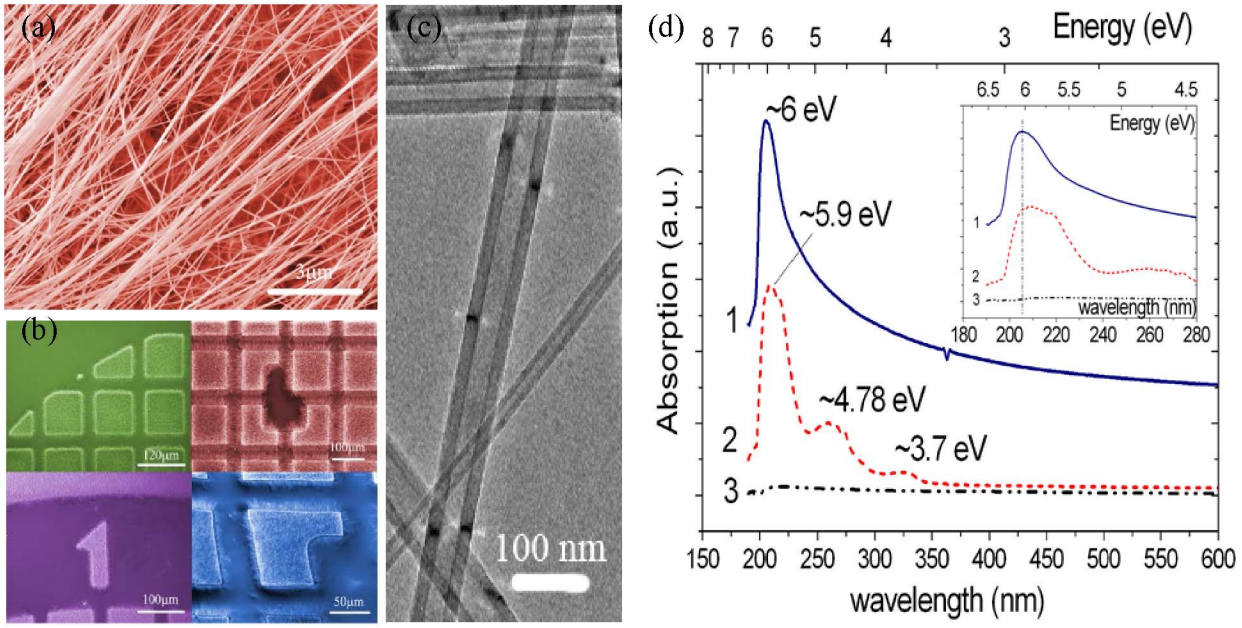


Figure 5. SEM images of (a) long and clean MW-BNNTs grown at (b) desired patterns. (c) TEM images of MW-BNNTs and (d) Absorption spectra showing a band gap of ~6eV without sub-band absorption levels (1: for high-quality MW-BNNTs by CCVD, 2: for MW-BNNTs grown by thermal CVD, 3: ethanol).

2.4. Electronics without Semiconductors: Branching BNNT/CNT Hetero-junctions

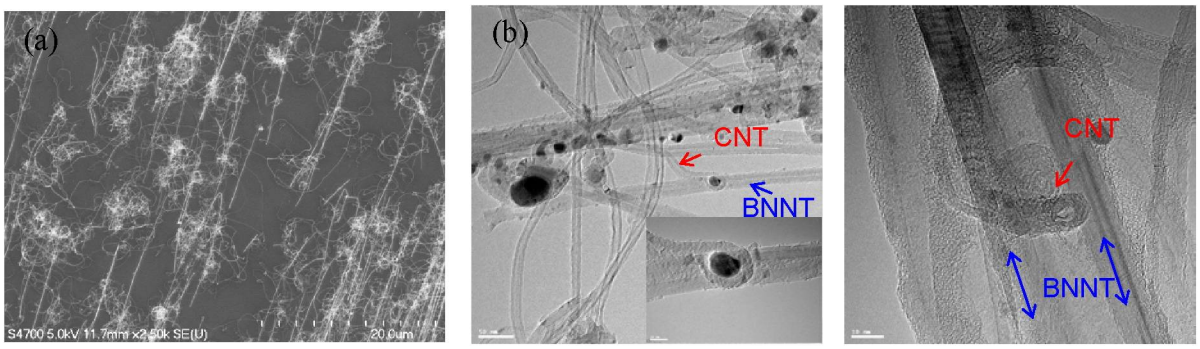


Figure 6. (a) SEM images of branching CNTs from a regular array of BNNTs (scale bar=20 microns). TEM images of branching CNTs with (b) and without (c) residual Fe catalyst on the BNNTs. Scale bars are 50 nm (b), 10nm (inset), and 10 nm (c).

After the success of growing BNNTs by CCVD, we have started to explore the growth of co-axial BNNT/CNT hetero-junctions (results as shown in sections 2.7). Concurrently, we have begun to study the transport properties of branching BNNT/CNT junctions. These branching junctions can be grown by first ***horizontally dispersed*** Fe catalyst-coated BNNTs on oxidized Si substrates followed by the growth of CNTs. This is ***the key advancement during our project in which BNNTs coated with Fe catalysts can be horizontally dispersed on substrates***. This has enabled the study of their transport properties. As shown in Figure 6a, MW-CNTs are branching out from these horizontally dispersed BNNT arrays. Residual Fe catalysts can be found on the side walls of these branching junctions (Figure 6b) but occasionally is not found on the junctions (Figure 6c).

We have employed a four-probe scanning tunneling microscopy (4-probe STM) system to characterize the transport properties of these hetero-junctions. This was performed through a ***user project in the center for nanophase materials science (CNMS)*** at Oak Ridge National Laboratory (ORNL). Figure 7a shows the probing of a hetero-junction with probe 1 on the junction (without touching the CNT) and probe 2 in contact with the CNT. As shown in Figure 7b, no current (off state) was detected at low bias voltages (~ ±0.8V, inset). At higher bias voltages, sufficient band bending allows electron tunneling through the junction and causes current to flow (Figure 7c). The on-off ratio is estimated to be 10^3. Further experimental and theoretical works are now in progress.

The major finding of this study is that hetero-junctions of multi-walled BNNT/CNT are Schottky barriers of insulators/semimetals as predicted by theory for armchair nanotubes. While the junction in this study have branching configuration and catalyst particles may presented at the junctions. We are expecting a better on-off ratio from seamless co-axial junctions, in which resistance and electron-phonon scattering are lower at the junctions. We show that branching BNNT/CNT junctions could lead to ***new electronic devices without the use of semiconducting materials***.

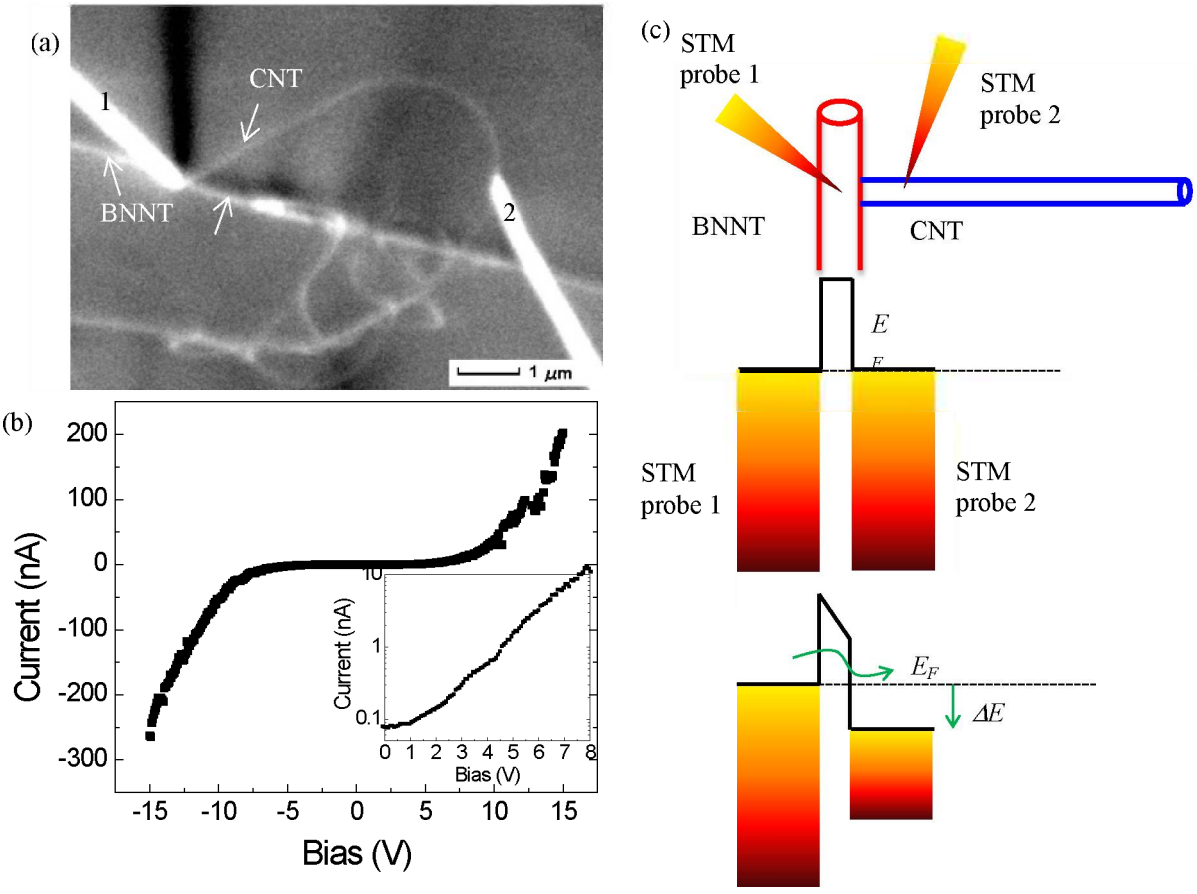


Figure 7. (a) Image of two STM probes on a branching BNNT/CNT hetero-junction. Probe 1 is on the junction (without shorting on CNT) while probe 2 is in contact with the CNT. (b) I-V character across the junction. (c) Schematic of the measurement and the related energy diagram before and after applying a bias voltage on the probes.

2.5. Electronics without Semiconductors: Quantum-Dots Functionalized 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)***. These QDs-BNNTs are BNNTs coated with nanoparticles including Fe that we used for the growth of branching junctions discussed earlier. We have further found that controlled deposition of these nanoparticles leads to a ***pseudo-one dimensional (1D) array of QDs on the side walls of BNNTs*** as shown in Figure 8. As shown, we have managed to deposit these crystalized QDs on one side of the BNNTs. These pseudo-1D arrays of nanoparticles have diameters ranging from 3-10 nm and spacing of about 1-5 nm in between.

These QDs-BNNTs are then characterized by 4-probe STM at CNMS. An isolated QDs-BNNT can be probed by using two of the STM probes at desired conductance length (L) as shown in Figure 9a. At low bias voltages, this QDs-BNNT is insulating like pure BNNTs. By applying increasing bias voltages, this QDs-BNNT allowed current to flow along the nanotube (Figure 9b). The ***turn-on voltage (V_{on}) of this QDs-BNNT decreases with the shortening of L***. V_{on} can be determined by plotting the current-voltage (I-V) curves into a log scale (inset) as about 35V, 20V,

11V, and 2.0V for L = 2.37 mm, 2.06 mm, 1.73 mm, and 1.29 mm, respectively. The on-off ratio of these channels is 10^3.

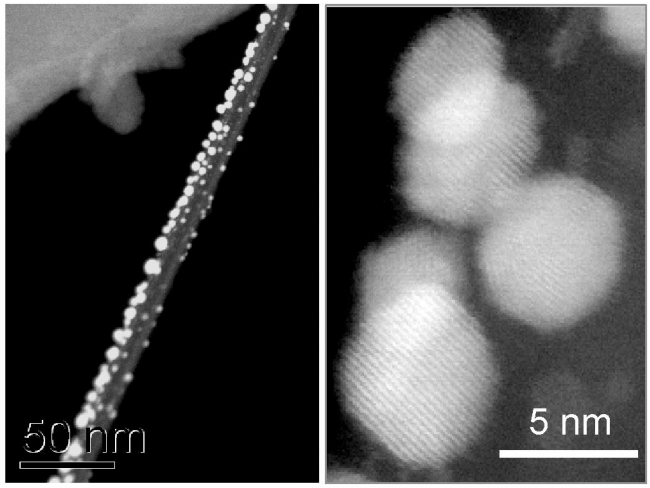


Figure 8. QDs-BNNTs with pseudo-1D array of nanoparticles on BNNTs.

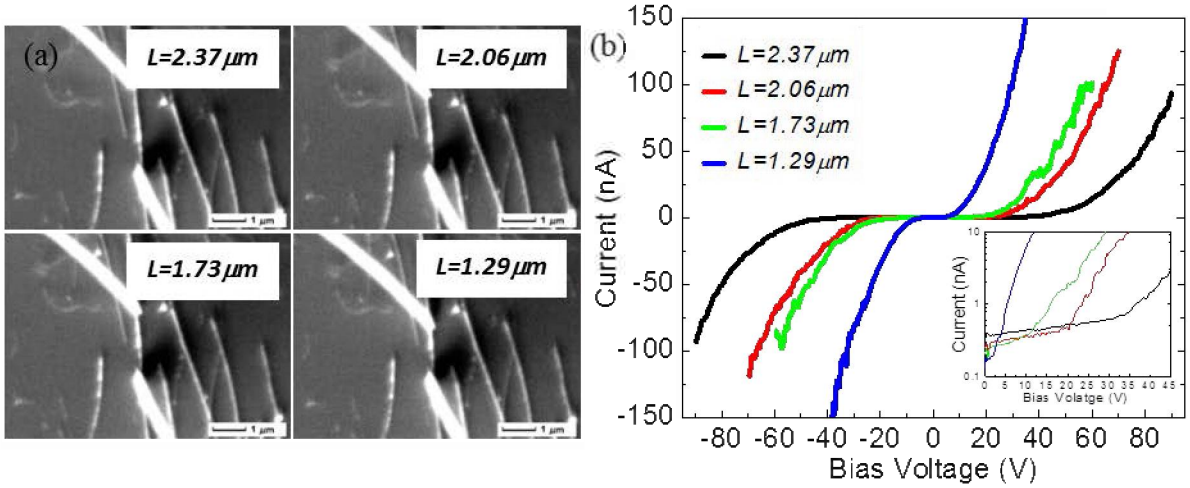


Figure 9. (a) Probing of an isolated QDs-BNNT with two STM probes at various conduction lengths (L). (b) Turn-on voltage (V_{on}) decrease with L.

We explain the detected switching behaviors by quantum tunneling across the QDs as proven by a ***kinetic Monte Carlo simulation*** (Figure 10a). This was conducted in collaboration with Professor John Jaszczak in our department. As shown, theory predicted that V_{on} will decrease with the number of gap (N) between QDs (i.e., conduction length, L), consistent to experimental observation (Figure 9b). This means, short QDs-BNNTs would potentially applicable as room-temperature, zero-dimensional (0D) tunneling switches with low turn-on voltages. The predicted V_{on} is lower than those observed experimentally due to the assumption of uniform gaps. Non-uniform gaps will lead to larger V_{on} as those observed experimentally (not shown here).

Furthermore, these switching behaviors can be modulated by gate potential (not shown here). Details of all these result will be reported in future publications. Further experimental and theoretical works are in progress.

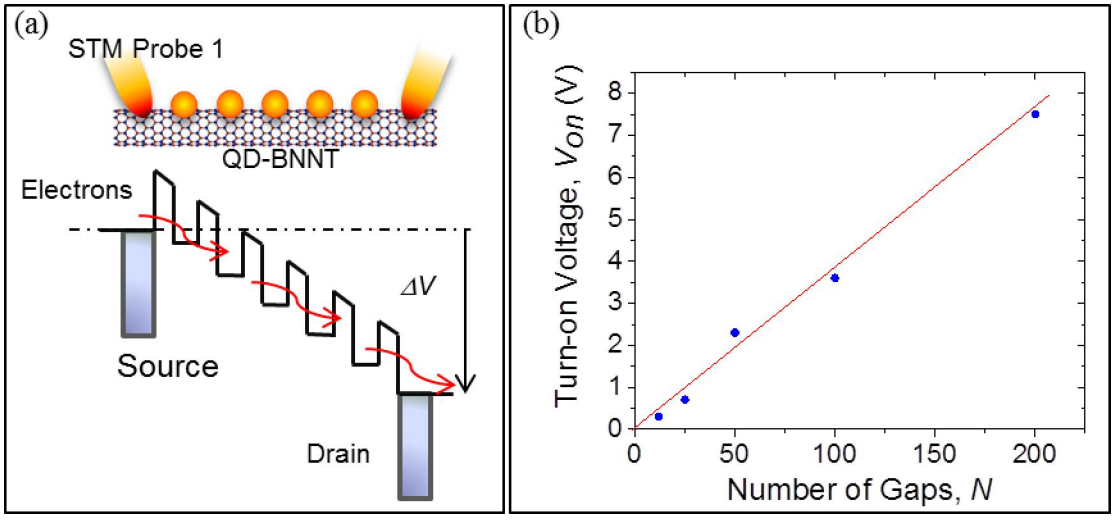


Figure 10. (a) Schematic of kinetic Monte Carlo simulation of a QDs-BNNT. (b) V_{on} is predicted to decrease with the number of gap (N) between QDs as consistent to experimental data (Figure 9).

The major impact of this study is the discovery of tunneling switching behaviors on QDs-BNNTs. We show that creative use of metallic QDs and 1D insulators (BNNTs) could lead to ***novel electronics without the use of semiconducting materials***.

2.6. Self-assembly of Graphene-BNNT Hetero-junctions

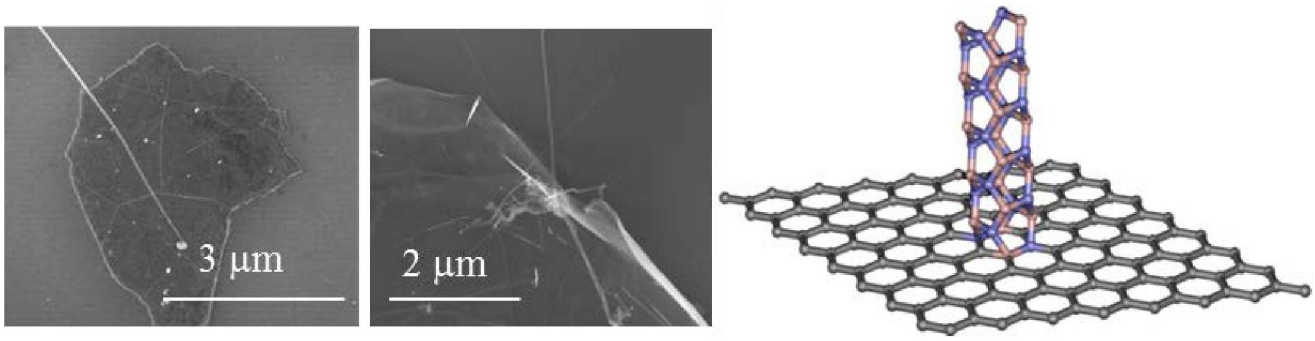


Figure 11. SEM images of BNNTs grown selectively on graphene (right). The formation of these novel graphene-BNNT junctions is also proven by theoretical calculation (left).

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 11, BNNTs are selectively grown on the surfaces of graphene sheets. BNNTs are not grown on the oxidized Si substrates under our

controlled growth condition without catalyst. 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)***. This was conducted in collaboration with Professor Ravi Pandey in our department. Band structure calculation predicted ***flat band features*** at the junctions suggesting that the novel materials may be used for magnetic/spintronic devices. Further investigations are now in progress.

The major finding of this study is the discovery of novel graphene-BNNTs hetero-junctions, which may have interesting properties for future electronic, spintronic, and magnetic devices.

2.7. Catalytic Growth of Co-axial BNNT/CNT Hetero-junctions

We have attempted to grow co-axial BNNT/CNT hetero-junctions by CCVD using Fe and Ni common catalysts. Although these common catalysts have been identified, the growth conditions for CNTs and BNNTs are very different. In our case, optimum growth of CNTs can be carried out at 650-750 ^{o}C by using C_2H_2 gas in H_2 ambient. On the other hand, BNNTs are grown at 1100-1200 ^{o}C in NH_3 ambient in the presence of powder precursors (B + MgO + FeO). Apparently, the growth of co-axial BNNT/CNT heterojuctions requires *in-situ* switching of the growth temperatures and the growth ambient, while keeping the B + MgO + FeO precursor powders in the chamber.

Many experiments have been performed by 1) first growing the BNNT segments, switching the growth conditions, and following with the growth of CNT segments (as in Figure 3a and 3b), or 2) the reverse (as in Figure 3d and 3e). Both routes required *in-situ* switching of the growth conditions without exposing the sample to air. We have also attempted the growth of hetero-junctions by using newly grown CNTs or BNNTs as the "substrates" for the growth of subsequent BNNT or CNT segments. In this case, switching of the growth condition is not needed but the starting CNTs (or BNNTs) are exposed to air prior to the second step. Samples obtained by these experiments were first screened by Raman spectroscopy for the signals of both CNTs and BNNTs. Prospective samples were then examined by Fourier-transform IR spectroscopy (FTIR), SEM, TEM, and EELS as needed. Unfortunately, ***no consistent or conclusive results*** were obtained. The major issue here is the ***low yield of the hetero-junctions (even if they are formed) and usually embedded in the forest of pure CNTs or BNNTs***.

Recently, ***we have changed the strategy*** to use patterned catalysts (Figure 12a) for our exploration. This has prevented the exhaustive search of hetero-junctions from the dense forest of nanotubes. For example, we can examine the as-grown nanotubes at the edges of the growth region (Figure 12b) and identify suspicious hetero-junctions as judged by their morphologies (Figure 12c and 12d). This is based on the fact that our ***CNTs are smaller in diameters (~10-30nm) versus the thicker BNNTs (20-80nm)***. In these cases, BNNTs were first grown at 1200 ^{o}C, followed by the growth of CNT segments after reducing the temperature to 650 ^{o}C and switching the NH_3 gas to H_2+C_2H_2 gases. Some of these samples were examined under TEM (Figure 13). After examine numerous samples under TEM, we have identified some tubular structures with necking features, which is not usually present on our pure CNT and BNNT samples. Again, higher yield of these hetero-junctions is needed for further characterization of the elementary and electronic properties. Experiments are now in progress towards these goals.

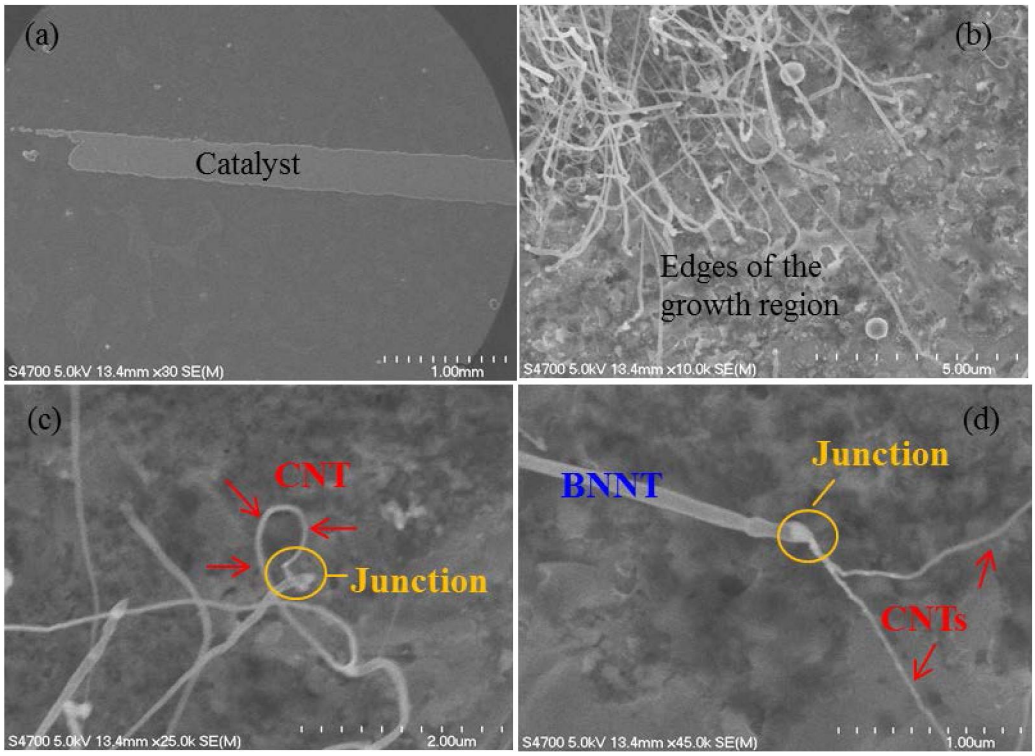


Figure 12. (a) A patterned Fe catalyst strip on oxidized Si substrates (0.3 mm x 2cm) prepared by shadow masks. (b) As-grown nanotubes as observed from the edges of the growth region. (c, d) potential hetero-junctions as-judged by their morphologies.

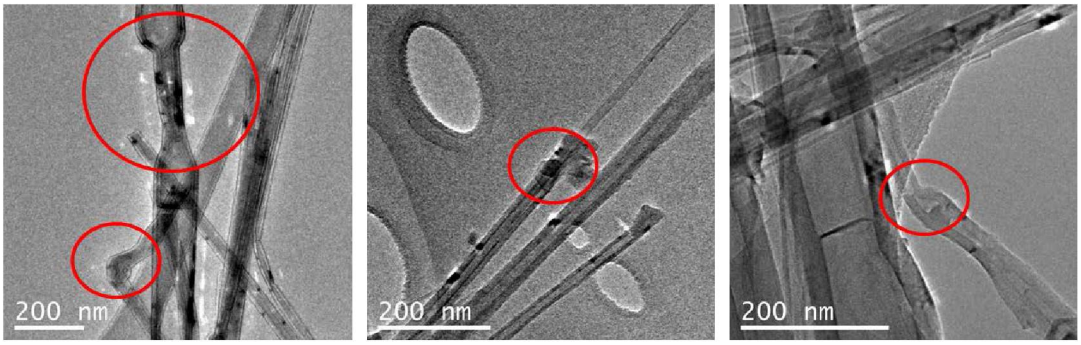


Figure 13. Potential co-axial BNNT/CNT hetero-junctions.

The major finding of this study is the identification of patterned catalysts for the growth of BNNT/CNT junctions. This study also suggested that we need to reduce the diameters of BNNTs to match those of CNTs.

3. Products Developed under the Award

3.1. Peer-Review Articles

1. C.H. Lee, D.Y. Zhang, Y.K. Yap, Functionalization, Dispersion, and Cutting of Boron Nitride Nanotubes in Water, *J Phys Chem* **C**, 116 (2012) 1798-1804.
2. H.M. Ghassemi, C.H. Lee, Y.K. Yap, R.S. Yassar, Field emission and strain engineering of electronic properties in boron nitride nanotubes, *Nanotechnology*, **23** (2012) 105702.
3. L.B. Boinovich, A.M. Emelyanenko, A.S. Pashinin, C.H. Lee, J. Drelich, Y.K. Yap, Origins of Thermodynamically Stable Superhydrophobicity of Boron Nitride Nanotubes Coatings, *Langmuir*, **28** (2012) 1206-1216.
4. H.M. Ghassemi, C.H. Lee, Y.K. Yap, R.S. Yassar, In situ observation of reversible rippling in multi-walled boron nitride nanotubes, *Nanotechnology*, **22** (2011) 145602.
5. M.X. C. H. Lee, J. S. Wang, R. E. Cook, Y. K. Yap, Patterned Growth of Long and Clean Boron Nitride Nanotubes on Substrates, in Nanotubes and Related Nanostructures — 2009, *Mater. Res. Soc. Symp. Proc.*, **1204** (2011) 133-138.
6. (Review) J.S. Wang, C.H. Lee, Y.K. Yap, Recent advancements in boron nitride nanotubes, *Nanoscale*, **2** (2010) 2028-2034.
7. C.H. Lee, M. Xie, V. Kayastha, J.S. Wang, Y.K. Yap, Patterned Growth of Boron Nitride Nanotubes by Catalytic Chemical Vapor Deposition, *Chem Mater*, **22** (2010) 1782-1787.
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3.3. Presentations with the Acknowledgement of DOE Supports

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