Mixed-Dimensional Heterostructures for Electronic and Energy Technologies

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Layered two-dimensional (2D) materials interact primarily via van der Waals bonding, which has created new opportunities for heterostructures that are not constrained by epitaxial growth. However, it is important to acknowledge that van der Waals interactions are not limited to interplanar interactions in 2D materials. In principle, any passivated, dangling bond-free surface interacts with another via non-covalent forces. Consequently, layered 2D materials can be integrated with a diverse range of other materials, including those of different dimensionality, to form mixed-dimensional van der Waals heterostructures [1]. Furthermore, chemical functionalization provides additional opportunities for tailoring the properties of 2D materials [2] and the degree of coupling across heterointerfaces [3]. In order to efficiently explore the vast phase space for mixed-dimensional heterostructures, our laboratory employs solution-based additive assembly. In particular, constituent nanomaterials (e.g., carbon nanotubes, graphene, transition metal dichalcogenides, black phosphorus, boron nitride, and indium selenide) are isolated in solution, and then deposited into thin films with scalable additive manufacturing methods [4]. By achieving high levels of nanomaterial monodispersity and printing fidelity, a variety of electronic and energy applications can be enhanced including photodetectors, optical emitters, supercapacitors, and batteries [5-8]. Furthermore, by integrating multiple nanomaterials into heterostructures, unprecedented device function can be realized including anti-ambipolar transistors, gate-tunable Gaussian heterojunction transistors, and neuromorphic memtransistors [9-12]. In addition to technological implications for electronic and energy technologies, this talk will explore several fundamental issues including band alignment, doping, trap states, and charge/energy transfer across van der Waals heterointerfaces.

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Carbon Nanotubes: Challenges in the Fundamental Science and Unique Applications

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Almost 30 years since their discovery, carbon nanotubes' growth mechanism(s), especially chirality (helicity) selective growth, remain to be confirmed at least by production of macroscopic amount, while their application fields, including unique ones, are successfully expanding year by year. In this presentation I will review the fundamental understanding of the growth mechanisms for common growth methods, their common bases and where they fall short. In addition, examples of unique applications of the carbon nanotubes will be presented, especially in renewable energy areas.

Single Chirality Nanotubes, Reaching the Holy Grail?

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We will discuss this long-standing challenge in the field, and outline an emerging mathematical-kinetic solution: how a helicity type "ordered at will" can be synthesized in a well-targeted way.

Experiments on Catalyst Activity and SWNT Thin Film Color Tuning During the FCCVD Synthesis

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Floating-catalyst CVD (FCCVD) is a highly promising technique for the scalable synthesis of single-walled carbon nanotubes (SWNTs), especially for the direct deposition SWNT thin films for flexible electronics applications. The number concentration (NC) as well as the activity of the catalyst particles are important process parameters influencing the yield and the purity of the as-produced SWNTs. In the conventional FCCVD methods, catalyst particles are usually synthesized by thermal decomposition of gaseous organometallic precursors like e.g. ferrocene inside the FCCVD reactor. Being in-situ catalyst formation in conventional FCCVD, it is an open question what is the activity of the catalyst particles, i.e. how many SWNTs a single catalyst particle can grow? Herein, we used pre-made catalyst particles made by a spark discharged based FCCVD technique which decouples the formation of catalyst particles and SWNTs synthesis into two subsequent process to investigate effects of catalyst NC on SWNTs synthesis. The NC and number size distributions (NSD) of both catalyst particles and SWNTs in gas-phase were quantitatively determined using an aerosol size spectroscopic method, i.e. the differential mobility analyzer (DMA). The DMA measurements supported with atomic force microscopy and X-rays photoelectron spectroscopy revealed that under carefully chosen reaction conditions in FCCVD (where typical residence time is < 10s), a single catalyst particle can grow more than one SWNTs.

Using ferrocene as the catalyst precursor, CO as the carbon source and CO_2 as the growth promoter, we show that the SWNT (n,m) distribution and the related thin film color can be directly tuned during the FCCVF synthesis by adjusting the CO_2 concentration.

Dynamic Instability of Individual Carbon Nanotube Growth Revealed by In Situ Homodyne Polarization Microscopy

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Understanding the kinetic selectivity of carbon nanotube growth at the scale of individual nanotubes is essential for the development of high chiral selectivity growth methods. Here we report that homodyne polarization microscopy can be used for high-throughput imaging of long individual carbon nanotubes under real growth conditions (at ambient pressure, on a substrate), and with sub-second time resolution [1]. Our in situ observations on hundreds of individual nanotubes reveal that about half of them grow at a constant rate all along their lifetime while the other half exhibits stochastic changes in growth rates, and switches between growth, pause and shrinkage. Statistical analysis shows that the growth rate of a given nanotube essentially varies between two values, with similar average ratio (~1.7) regardless of whether the rate change is accompanied by a change in chirality. These switches support that the nanotube edge or the catalyst nanoparticle fluctuates between different configurations during growth.

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Swinging Interfaces of Growing Carbon Nanotubes

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In classical crystal growth, the interaction of the growing object with its support and the energies of the different facets determine the growth mode and the resulting crystalline structures. The synthesis of carbon nanotubes by chemical vapor deposition poses somewhat similar yet more complex issues. The catalytic particle is both a support and a reactive interface with the growing tube, and many properties are altered because of the nanometric size of the objects.

In this context, we have identified different growth modes driven by the thermodynamic properties of the interface [1, 2] and developed a model of the interface [3], emphasizing the importance of the configurational entropy of the nanotube edge to stabilize chiral tubes and to account for the temperature dependence of tube helicity distributions. This simple model is pushed further to account for more general interface structures and kinetic Monte Carlo (KMC) simulations are developed [4] to study the growth mechanisms and kinetics, and analyze growth rates in relation with the chiral selectivity of the synthesis.

In this presentation we theoretically investigate new in situ measurements of individual CNT growth rates by homodyne polarization microscopy [5] with better temporal and statistical resolution than previous studies [6]. The growth kinetics are surprisingly complex and exhibit instabilities characterized by stochastic alternations of growth, etching, stops and sometimes restarts. These events occur with or without changes in the structure of the single-walled nanotube. We study the latter case, propose a simple modeling and KMC simulations, thus shedding new light on the role of the tube/catalyst interface dynamics for both thermodynamic and kinetic aspects of the growth.

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Graphene in a Flash: Trash to Treasure

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Flash joule heating of inexpensive carbon sources—such as coke from coal, biochar, carbon black, mixed plastic, food waste, pistachio shells and rubber tires—can generate turbostratic graphene in ~100 ms. A capacitor bank passes up to 450 VDC and 1000 amps through gated transistors to provide pulse width modulation and controllably heats the conductive carbon-containing sample to 3100K in about 20 ms. Volatile gases are flashed off and the carbon assembles into graphene sheets. The single-atom thick sheets stack like highly crystalline graphite, except with random angular orientation about the C-axis, as the time is too short to anneal into AB-stacked graphite. This turbostratic graphene -- which previously had only been observed as a bilayer or a few layers – retains its 2D character, as indicated by Raman spectroscopy. The weakened van der Waals interaction between adjacent sheets makes it more readily dispersible, and shows promise for reinforcing concrete, composites, plastic, etc. The process is fully scalable. Feedstock that is of very low value or even negative value can be upcycled with < $100/ton in electricity cost to graphene worth tens of thousands of $$ per ton; and since it is inert, TS graphene can also be a terminal sink for carbon.

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Kinetic Control of Intrinsic Pores in 2D Proton Exchange Membranes

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I will discuss kinetic control of 2D material synthesis via chemical vapor deposition (CVD) for proton selective pores and facile fabrication of large-area atomically thin proton exchange membranes. Using a resistance-based transport model in conjunction with systematic liquid and gas phase transport measurements on the same membrane, we study the influence of such Angstrom scale pores on selective proton transport through centimeter-scale Nafion|Graphene|Nafion sandwich membranes. Additionally, we report on a approach that effectively mitigates transport of un-desired species (small ions and gas crossover) without adversely affecting proton transport. Our insights on kinetic control of 2D material synthesis as well as facile membrane fabrication approaches offer new avenues to enable functional large-area atomically thin proton exchange membranes.

Programming Crystal Structure in 2D TMDs with Defects and Strain: Atomistic and Mesoscale Simulations (Plus a Note on Substrate Corrugation Formation in Graphene CVD)

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The first part of this talk will outline simulation and theory studies of crystal structure transformations in 2D TMDs with an eye toward controlled creation of designed, switchable structural domain patterns with multiple potential functional uses [1,2]. The effects of dislocations and grain boundaries on strain driven transformations are described, and these effects are exploited in defect-based strain / phase programming strategies to yield a variety of patterns and material properties. Creation, annihilation, and accumulation of new lattice defects under rapid cyclic transformations is also characterized. In the last part of the talk, a brief analysis of the mechanisms behind substrate corrugation formation and coarsening in graphene CVD will be presented [3]. We propose that the dominant driving force is interlayer atomic disregistry energy associated with initially atomic-scale steps, and that this energy is reduced by a dynamic interplay between misfit dislocations and corrugations.

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High Current Transport in CNT Composite Networks and a Summary of BNNT Synthesis at Boronite

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Carbon nanotubes have been made into yarn, and this yarn in turn fabricated into cable, although electrical conductivity has remained low compared to copper and aluminum. Individual nanotubes typically have excellent charge carrier mobility, so we posit that scattering, transmission through junctions, defects, and low charge carrier density are responsible for the degradation of cable performance. We discuss these phenomena and present a theory and a manufacturing method that addresses these problems. We have developed a method for manufacturing metal-CNT composite power cables and present conductivity data from a large prototype cable (SuperWire) fabricated using the Boronite methods. We outline and provide examples of how metalized carbon nanotube-based power cables can be mass-produced in high volume and address the charge carrier mobility problem. We posit that wetting the CNT surfaces with metal (copper alloy or aluminum) is essential and show how this can be done in mass production. We also suggest a mechanism to reduce defects near the interface between metal and the CNT graphene surface. We aim at a specific conductivity exceeding 14,000 Sm^2/kg and engineering conductivity of 20 MS/m. So far, we have achieved about 12,500 Sm^2/kg and 15 MS/m. We present test data measured by an outside company on a large diameter 1.25-meter long SuperWire cable prototype (~0.635 cm). An extraordinary ampacity of over 500 amperes for a 6.5 mm diameter cable was demonstrated for 30 seconds without cable damage or reaching a fusing current.

Assessing the environmental consequences of the technology will require weighing the contamination associated with the synthesis process against the significant benefits resulting from extremely lightweight cables, including power cables for aircraft, satellites, and terrestrial applications, coaxial cables for communication, electric motor winding, and medical wiring. We expect an overall net reduction in carbon dioxide emissions, achieved from weight savings in all applications, especially in moving and rotating machinery over the long lifetimes of these products.

Finally, we review some advances and applications of boron nitride nanotubes synthesized by CVD.

Simulated Nucleation Mechanisms of Low-Dimensional Boron Nitrides during Chemical Vapour Deposition

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Over the last few decades, catalytic chemical vapour deposition (CVD) has matured as a synthetic technique for producing many low-dimensional inorganic nanomaterials, such as carbon nanotubes, graphene and boron nitrides. However, in contrast to carbon nanomaterials, such as graphene and CNTs, little is known regarding the catalytic pathways underpinning CVD synthesis of boron nitride nanomaterials.

I will present the first mechanism explaining the nucleation of boron nitride nanotubes (BNNTs) via CVD of boron oxide [1,2] and ammonia borane [3], based on reactive molecular dynamics simulations. These simulations show that BNNTs nucleate via a 'network fusion' mechanism, by which distinct planar BN fragments first form before 'clicking' together on the nanoparticle surface (Figure 1) [3]. We also reveal key roles played by H_2O and H_2 partial pressures and the presence of solid-phase catalytic nanoparticles on this mechanism [4].

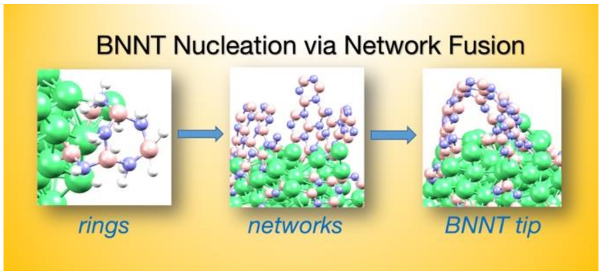

Figure 1. *Reactive non-equilibrium MD simulations reveal the mechanism of BNNTs on Ni nanoparticles via BN network fusion.*

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CVD Synthesis of 1D vdW Heterostructures Based on SWCNTs

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A typical one-dimensional (1D) van der Waals (vdW) heterostructure consists of coaxial single-walled carbon nanotubes (SWCNT), boron nitride nanotube (BNNT), and molybdenum disulfide nanotube (MoS2NT) [1]. The coaxially nested structure based on SWCNTs, which has various electronic properties (metallic or semiconducting), can expand the board application possibilities of 1D vdW heterostructures [2-6]. Semiconductor SWCNT wrapped with BNNT can be regarded as the ideal building blocks of field-effect transistors (FET) [2]. We have demonstrated the radial semiconductor–insulator–semiconductor (S-I-S) tunneling heterojunction diode by using a micrometer long 1D vdW heterostructure SWCNT@BNNT@MoS2NT [7]. By comparing optical properties of films of BNNT@MoS2NT and SWCNT@BNNT@MoS2NT, we found strong photoluminescence (PL) from monolayer MoS2NT and quenching of PL by coupling to SWCNT through thin BNNT [8]. The large population of free charges and inter-tube excitons are demonstrated by ultrafast optical spectroscopy [9]. The inter-tube excitons are similar to inter-layer excitons for 2D heterostructures.

Precise control of each layer's chemical vapor deposition (CVD) process is essential since the mechanical exfoliation and stacking technique for 2D counterpart is not possible for 1D vdW heterostructures. The challenges are both CVD growth of BNNT and nanotubes of transition metal dichalcogenides (TMDC). We have been optimizing BNNT growth on suspended SWCNTs, chirality-sorted SWCNTs [10], film of SWCNTs, and vertically aligned SWCNTs. The surprisingly sharp edge of BNNT grown on SWCNT is the signature of preference of nitrogen terminated zig-zag edge of h-BN common to 2D counterpart [11]. The next challenge is the CVD growth of various TMDC nanotubes on BNNTs. In addition to MoS_2 nanotubes [1], we will discuss the growth control of WS_2 nanotubes and NbS_2 nanotubes. A general strategy we can tune the CVD condition from 2D flake to 1D tube is proposed [12].

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Holmes: A Decision-Making Framework for Real-World Autonomous Experiments

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Closed-loop, sequential decision-making is an essential component of autonomous experimental platforms. Complementary to high-throughput methods that result in large amounts of data, sequential decision-making allows robot scientists to intelligently and adaptively select experiments to get the best data. Many methods treat experiments as a black box: processes that generate some experimental response given some experimental inputs. However, many (if not most) experiments have nuances that deviate from this idealized perspective. Often, not integrating such nuance results in poor decision-making and longer times to research deliverables. However, modeling such nuance is a time-consuming task, requiring expertise in machine learning, statistics, and an appreciation for problem-specific structure. In this talk, we present work on Holmes, a decision-making framework meant to better model problem-specific structure typically found in experiments. We have developed Holmes in close collaboration with several experimentalist groups, and thus the framework reflects experiment structure found among a broad range of autonomous platforms. We present an overview of the Holmes framework and its usage for a few example problems. We then demonstrate an easy-to-use web-based application programming interface that non-experts can use to drive their own closed-loop research campaigns.

Autonomous Research for CNT Synthesis

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The current materials research process is slow and expensive; taking decades from invention to commercialization. The Air Force Research Laboratory pioneered ARES™, the first autonomous research system for materials development. A rapidly growing number of researchers are now exploiting advances in artificial intelligence (AI), autonomy & robotics, along with modeling and simulation to create research robots capable of doing iterative experimentation orders of magnitude faster than today. We will discuss concepts and advances in autonomous experimentation in general, and associated hardware, software and autonomous methods. For Carbon Nanotubes (CNTs), we show progress in autonomous and data science methods to understand and control the fundamental mechanisms that drive CNT synthesis via CVD. We will explore the importance of the oxidizing or reducing nature of the CVD environment on nucleation and growth. In the future, we expect autonomous research to revolutionize the research process, and propose a “Moore’s Law for the Speed of Research,” where the rate of advancement increases exponentially, and the cost of research drops exponentially. We also consider a renaissance in “Citizen Science” where access to online research robots makes science widely available.

Toward *in situ* Diagnostic-Controlled Automated Laser Synthesis of 2D Materials: Revealing synthesis pathways of Janus monolayers and vdW Heterostructures by PLD

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The nonequilibrium kinetic energies, mixed composition, and digital nature of pulsed laser deposition (PLD) plasmas and secondary laser irradiation are well suited to explore fundamental questions for the bottom-up synthesis and top-down doping or conversion of atomically-thin 2D quantum materials. We will discuss the essential development and application of *in situ* diagnostics bridging multiple length scales. At the macroscale, as shown in **Fig. 1** we used *in situ* plasma diagnostics and reflectivity to measure the kinetic energy range for Se clusters in PLD (3-5 eV/atom) to selectively implant Se within monolayer WS_2 and MoS_2 crystals to form novel Janus WSSe and MoSSe monolayers.[1] At the nanoscale, we employed laser heating *in situ* in the TEM, SAED, and EELS to understand how PLD-deposited amorphous WSe_x

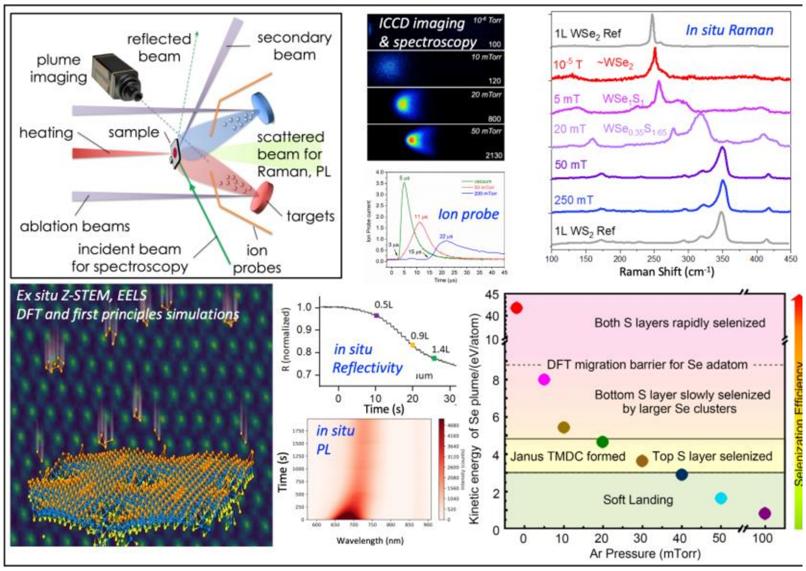

Figure 1. *Schematic shows novel feedback-controlled PLD approach to measure and optimize atomically-thin 2D material properties in situ during processing. ICCD imaging, ion probe, and optical spectroscopy characterize and control the PLD plume kinetic energy and composition. Optical reflectivity monitors film thickness shot-by-shot while in situ Raman and photoluminescence (PL) spectroscopy characterize the structural and compositional evolution of the 2D crystal properties. Representative data (Reprinted with permission from Ref. 1) show the controllable conversion of* WS_2 *crystalline monolayers by PLD hyperthermal implantation of Se clusters in various Ar pressures to form WSSe monolayers pictured at left. Using in situ Raman spectroscopy the plume kinetic energy regimes for soft landing (encapsulation) or conversion into WSSe Janus monolayers, mixed composition alloys, and* WSe_2 *can be determined in conjunction with ex situ atomic-resolution Z-STEM and EELS characterization and DFT and first principles modeling.*

cluster precursors evolve into vdW epitaxial WSe_2 heterostructures on suspended Gr and $MoSe_2$.[2] Here we describe a new automated PLD approach that incorporates not only *in situ* plasma diagnostics of the growth environment but *in situ* Raman, photoluminescence, and reflectance spectroscopies of films as they grow and undergo phase transitions or conversion in PLD, illustrated for Janus monolayer formation in **Fig. 1**. *In situ* secondary laser irradiation of the substrate during/after deposition allows a wide range of laser processing (e.g., thinning, phase conversion, sintering, and annealing) with direct feedback and comparison with *in situ* laser-TEM investigations. Fundamental 2D synthesis questions and the future of autonomous AI/ML-guided PLD and laser processing will be discussed. Synthesis science was supported by the U.S. DOE, Office of Science, Materials Sciences and Engineering Division. This work was performed at the Center for Nanophase Materials Sciences, which is a DOE Office of Science User Facility.

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Epitaxy of 2D Transition Metal Dichalcogenides on Sapphire

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Wafer-scale epitaxial growth of semiconducting transition metal dichalcogenide (TMD) monolayers such as MoS_2, WS_2 and WSe_2 is of significant interest for device applications to circumvent size limitations associated with the use of exfoliated flakes. Epitaxy is required to achieve single crystal films over large areas via coalescence of TMD domains with the same crystallographic direction. In this talk, I will discuss the prospects and challenges associated with the epitaxial growth of TMD monolayers on sapphire substrates for the development of wafer-scale 2D device technologies. Metalorganic chemical vapor deposition is highlighted as a promising approach which enables growth at high temperatures ($> 700^{o}C$) and large chalcogen overpressures which are needed to obtain stoichiometric epitaxial films. The unique aspects of van der Waals epitaxy of TMDs on sapphire will be presented including the role of surface steps and step-edge chemistry in controlling the nucleation site and orientation of TMD domains.

Lateral Epitaxy of 2D Materials and its Practical Applications

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Despite several decades of intense research, the scalable and well-controlled growth of high-quality monocrystalline 2D materials largely remains unachieved. The use of well-developed techniques and methods of classical 3D growth allowed for rapid initial success in low dimensional synthesis relying on structural matching between the substrate and target material. However, over the years, it became clear that the transition from 3D to 2D materials required modification of the methodology that had to start with a deeper understanding of underlying principles. Due to their nature, most 2D materials have minimal plane-to-plane interaction with the underlying substrate making orientation control a difficult task. Luckily, virtually no substrate surface is ever defect-free, presenting new opportunities for growth control. We have demonstrated that interaction between 2D material edge and substrate surface steps and kinks plays a crucial role in the nucleation and orientation of growing material [1]. Furthermore, we formulated geometric complementarity principles that ensure the large-scale defect-free growth of 2D materials.

Unlike many 2D materials, the growth of borophene is plagued by the precisely opposite issue – too strong interaction with the substrate. The metal substrates stabilize the growth of 2D structure due to the strong binding with boron atoms but at the same time prevent subsequent borophene exfoliation hindering its practical applications. On the other hand, the low-interacting substrates typically do not provide sufficient areal interaction resulting in a significant nucleation barrier or formation of 3D clusters. Following principles of lateral epitaxy of 2D material, we propose a dimensionality reduction technique relying on nucleation on naturally present 1D surface defects [2]. On the example of the h-BN substrate, we demonstrate an order of magnitude reduction in the nucleation barrier due to covalent bonding to the exposed substrate steps while maintaining minimal areal adhesion. This approach not only exemplifies the importance of the lateral epitaxy mechanism in the growth of 2D materials but also provides a practical approach to the synthesis of novel nanomaterials.

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Nonequilibrium Synthesis to Tailor Heterogeneity in 2D Materials

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Heterogeneities, such as defect, strain, grain boundary in 2D materials are usually introduced during growth because of the nonequilibrium synthesis environments induced by the variations in chemical potential, temperature, and flux of different species. In this talk I will present how to control such nonequilibrium synthesis variations to tailor the heterogeneity in the growth of 2D transition metal dichalcogenide (TMD) materials by chemical vapor deposition (CVD). I will describe a synergistic approach to reveal the synthetic origins of heterogeneity at multilength scales in 2D TMD materials that involves a combination of in situ diagnostics of growth environment, using primarily optical spectroscopic and electron microscopy techniques, and a correlation between spectroscopic maps of optoelectronic properties and atomistic characterization of heterogeneity, using primarily Z-contrast scanning transmission electron microscopy. Recent progress will be presented in the use of CVD to explore the roles of chemical potential and flux of chalcogen on the formation of antisite defect, and metastable phase in the growth of 2D TMD crystals. I will also present the effect of strain generated during growth on patterned substrates and strain introducing during merging of monolayer crystals on the control of the grain boundaries or twist bilayers of 2D TMDs. Finally, recent progress in demonstrating the role of defects generated by laser and plasma irradiation on mediating the phase transformation in 2D PdSe2 crystals for the formation of new crystalline phases will be discussed.

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van der Waals Effects in van der Waals Materials

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The influence of van der Waals interactions extends well beyond binding energies and encompasses the structural, mechanical, spectroscopic, and even electronic signatures of molecular systems and condensed matter [1]. Here I present and analyze a few remarkable and rarely recognized aspects of vdW interactions:

(1) Their ultra-long range in polarizable molecules and materials [1-3],
(2) Their tunability by applied electric fields,
(3) Their marked influence on observable electronic properties of materials [4],
(4) The possibility to make vdW interactions repulsive for confined molecules [5,9].

The development of efficient many-body methods that explicitly address the non-local collective nature of vdW interactions not only leads to significant improvements in the accuracy of calculations [6-8] but also allows us to discover novel conceptual insights that give us the ability to control these interactions in the design of intricate materials. These facts will be highlighted by presenting a few selected examples from our recent work [1,7-9].

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Controlled creation of defects on monolayer MoS2

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Atomically thin 2D materials provide an opportunity to investigate the atomic-scale details of defects introduced by particle irradiation. Once the atomic configuration of defects and their spatial distribution are revealed, the details of the mesoscopic phenomena can be unveiled. In this work, we created atomically small defects by controlled irradiation of gallium ions with doses ranging from 4.94 10^{12} to 4.00 10^{14} ions/cm^2 on monolayer molybdenum disulfide (MoS2) crystals. The optical signatures of defects, such as the evolution of defect-activated LA-bands and a broadening of the first-order (Eâ€² and Aâ€²1) modes, can be studied by Raman spectroscopy. High-resolution scanning transmission electron microscopy (HR-STEM) analysis revealed that most defects are vacancies of few-molybdenum atoms with surrounding sulfur atoms (VxMo+yS) at a low ion dose. When increasing the ion dose, the atomic vacancies merge and form nanometer-sized holes. A systematic study of fracture mechanics in MoS2 monolayers as a function of the density of atomic vacancies, created by ion irradiation, is reported. Pristine and irradiated materials were studied by atomic force microscopy, high-resolution scanning transmission electron microscopy, and Raman spectroscopy. By inducing ruptures through nanoindentations, we determine the strength and length of the propagated cracks within MoS2 atom-thick membranes as a function of the density and type of the atomic vacancies. We find that a 0.15% atomic vacancy induces a decrease of 40% in strength with respect to that of pristine samples. In contrast, while tear holes in pristine 2D membranes span several microns, they are restricted to a few nanometers in the presence of atomic and nanometer-sized vacancies, thus increasing the materialâ€™s fracture toughness.

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Reduction, Dewetting, and Ripening Kinetics: Generalizable Concepts for Nucleation Success Rate

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As the Guadalupe family commemorates two decades of fruitful discussions, it seemed appropriate to revisit some of the lessons learned and embrace the nascence of new CNT research paradigms. I should clarify that the intent of this talk is not to provide an in-depth review of three decades of work but rather to find some common threads from retrospective analyses and our observations. We will first evoke a few key historical findings in the context of nucleation success rate. Then, we will dive into a series of in situ experiments tied by three common threads: catalyst reduction, dewetting, and ripening kinetics. We will touch base on some of the steps associated with the aforementioned, and evaluate how these are influenced by physico-chemical drivers. We will go over concrete examples from AP-XPS (Ambient Pressure X-ray Photoelectron Spectroscopy), ETEM (Environmental Transmission Electron Microscopy), and ARES (Autonomous Research System) work that highlight the role of input parameters (e.g., catalytic compound, synthesis conditions, surface properties etc.) on 'intermediate' processes (e.g., diffusion mechanisms, particle kinematics, carbon solubility, energetics, etc.) and on growth outputs (e.g., nucleation success rate). We will also ponder on common mitigation practices in the context of the three common threads above, and provide a snip of recommendations accordingly. Lastly, we will discuss the use of in line, closed-loop, and autonomous research for increasing nucleation success rate. As a concluding remark, I will share some thoughts on nanotube research and scalability in the context of readiness levels.

Why Do Carbon Nanotubes Grow?

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Carbon nanotubes (CNTs), first synthesized three decades ago, have since been at the forefront of materials science and nanotechnology, with enormous expectations in the future of electronics. Despite intense research efforts dedicated to understanding their growth, the most fundamental question "why do carbon nanotubes grow" remain unanswered because that the catalyst encapsulation by a surrounding graphitic carbon seems energetically more favorable than forming a CNT from every aspect. Here we answer this problem by introducing the interfacial energy between the edge of the CNT and the catalyst, which is significantly larger than the van der Waals interaction between a graphitic wall and the catalyst surface but was overlooked in the past. Our study reveals that the strong CNT edge-catalyst interaction is contact angle dependent. During the lift off of a graphitic cap, the increased contact angle leads to a drastic decrease of the interfacial formation energy, up to 6-9 eV/nm, which overcomes the van der Waals adhesion between the graphitic cap and the catalyst surface and drives the nucleation of a CNT. Validated by molecular dynamic simulations and ab initio calculations, mapping this interplay allows us to understand why CNTs grow for the first time. The deep insights into the mechanism of CNT growth allows us to design catalysts for selective carbon nanotube growth.

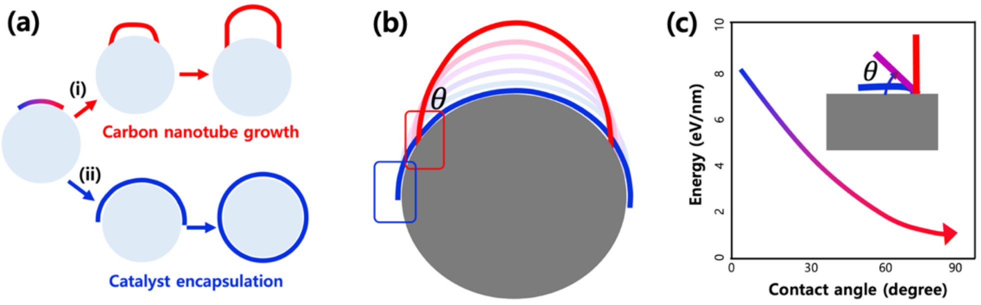

FIG. **(a)** two possible routes for the evolution of a graphitic carbon cap on a surface of a catalyst particle: **(i)** lift of the graphitic carbon into a graphitic cap and subsequent CNT growth; **(ii)** continuous growth of the graphitic carbon to surround the catalyst particle finally resulting in catalyst encapsulation. It is apparent that the final state of route **(ii)** is energetically more favourable because of the adhesion between graphitic carbon and the catalyst surface. **(b)** the lifting of a graphitic cap leads to an increase in the contact angle between the edge of the graphitic carbon and the catalyst surface from zero. **(c)** the increase of the contact angle leads to a significant decrease in the energy and, thus, drives CNT growth.

Single-Walled Carbon Nanotubes and Nucleating Catalysts

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Catalysts play important roles in the controlled growth of single-walled carbon nanotubes (SWCNTs). Insight into the relationship between nanotube and catalyst is of crucial importance for understanding the growth mechanism and achieving selective growth. Relying on the *in-situ* characterization with an aberration-corrected environmental transmission electron microscopy, we unambiguously revealed the effects of the state and atomic structure of the catalysts on the growth modes of SWCNTs.

The growth modes highly depend on the state of the catalysts. SWCNTs grown from molten metal nanoparticles via a vapor-liquid-solid (VLS) process generally present similar diameters to the catalysts, showing a strong size correlation between the nanotubes and the catalysts. But SWCNTs grown from solid state catalysts via a vapor-solid-solid (VSS) process always possess smaller diameters than the catalyst nanoparticles, exhibiting an independent relationship between their sizes. However, the diameter distribution of SWCNTs grown from crystalline Co_7W_6, which have a unique atomic arrangement, is discrete and that for nanotubes obtained from crystalline Co is randomly dispersed. We further studied the behavior of the catalysts during the SWCNT nucleation and growth in VSS processes. The growth of SWCNTs by Co catalysts associates to the partial carbonization of catalysts as well as carbon dissolving and precipitation. However, the Co_7W_6 nanocrystals are stable at the temperature of 1100 °C under carbon feeding condition and no carbon dispersion within the nanocrystal happened. This observation explanans the origination of chirality selectivity of intermetallic Co_7W_6 catalysts. These findings sketch a clear picture of the function of catalysts in the growth of SWCNTs, which will enlighten the rational design of catalysts for chirality-controlled growth of SWCNTs.

Functionalized alkyne precursors for direct placement of heteroatoms in carbon nanotube growth

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Functionalization of carbon nanotubes (CNTs) with heteroatoms enables covalent attachment, opening up a world of potential material structures. However, common functionalization techniques are hazardous and lack precision. Here, we evaluated an in-situ functionalization technique utilizing oxygen-containing alkyne precursors and alkyl-functionalized alkyne precursors coupled with acid vapor treatments. CNTs were successfully derived from propargyl alcohol, propiolic acid, and other heteroatom-containing alkyne species. While there was no substantial increase in the oxygen content of resultant CNT structures (all less than 1% O), Fourier transform infrared spectroscopy (FTIR) revealed subtle incorporations of carboxyl and hydroxyl functionality with propargyl alcohol and propiolic-acid fed growths, including specifying hydroxyl or carboxyl chemistry. These results support the universality of alkyne-promoting chemistries and delineate the limits of stable, heteroatom-bearing alkynes to support point-directed functionalization schemes or reduce the environmental burden of wet chemical synthetic approaches.

Exploring the Best CVD Conditions for Growth of Small-Diameter Single-Wall Carbon Nanotubes Using an Autonomous Research System

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Due to the breadth of parameters that affect CVD growth of single-wall carbon nanotubes (SWCNTs), rapid experimentation is a powerful tool for investigating conditions for selective growth of small-diameter SWCNTs. Here we utilize an Autonomous Research System (ARES)—an automated, high throughput, laser-induced CVD system with in situ Raman spectral feedback—to study the roles of Ru promotion of Co catalyst and type of feedstock in the growth of small-diameter SWCNTs at different temperatures. We demonstrate through over 200 growth experiments in ARES and ex-situ multi-excitation Raman spectroscopic characterization that Ru-promoted Co catalyst nearly doubles the selectivity of small-diameter SWCNTs (diameters below 1nm) between growth temperatures of 650°C and700°C in comparison to pure Co. At elevated temperatures between 800 and 850°C, Ru stabilizes Co catalyst nanoparticles and increases selectivity of small-diameter SWCNTs by almost a factor of three. Results reveal SWCNT diameters are not only dependent on the size of catalyst but also on the precursor chemistry as selectivity towards small-diameter SWCNTs decreases in the following order: ethylene > acetylene (1% in He) > FTS-GP (Fischer-Tropsch synthesis gaseous product mixture). Density functional theory (DFT) simulations using a 13- and 55-atom clusters with similar Ru/Co ratio provide mechanistic insight into the observed phenomenon, revealing increased cohesive energies of Co clusters after the addition of Ru irrespective of the location. Our findings indicate the presence of ~10% Ru in Co increases sintering resistance and stability of small nanoparticles, as well as selectivity towards small-diameter SWCNTs.

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Insights into Spatial Dependence and Population Dynamics of Catalyst Nanoparticles in Chemical Vapor Deposition of Carbon Nanotubes

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How can we mathematically describe and simulate the coupled physical and chemical processes and interactions involved in catalyst pretreatment, activation and deactivation for carbon nanotube growth? In this work we show that combining in situ environmental transmission electron microscopy (E-TEM) with automated image processing and statistical machine learning uniquely enables formulating interpretable mathematical models as well as creating accurate simulation toots. In particular, there is a need for a better understanding, characterization, and prediction of the proximity effects among dense populations of metal nanocatalysts as they form and evolve over time. Here, we leverage point process theory—a branch of statistical machine learning—to "learn" the spatial dependencies among ensembles of adjacent alumina-supported iron nanoparticles from a time sequence of E-TEM images. We construct a set of point process models to make statistical inferences about the nature of spatial dependencies that govern the rapid formation, or "popping" of nanoparticles during thin film dewetting, concomitant with metal reduction in the presence of acetylene at 750 °C. We show that nanoparticles exhibit strong dispersion behavior, i.e. new nanoparticles pop in dispersed locations at a predictable distance from their existing territorial neighbors. We also show that the Softcore model, a class of Gibbs point processes, adequately describes the pairwise interactions underlying such time-dependent spatial variations. Further, we leverage the probabilistic nature of our statistical models to develop a computational simulation tool capable of producing accurate simulations of the spatio-temporal evolution of formation patterns of nanoparticles at both finer time resolutions and larger spatial domains than experimental observations. This is a much needed capability, wherein the behavior of hard-to-model coupled nanoscale phenomena involving complex chemical and physical processes are accurately captured in machine-learned mathematical formulations; thus overcoming current limitations in computational methods supporting the design and analysis of collective nanocatalyst populations. Combined with insights regarding the effects of rapid thermochemical pretreatment on both catalytic lifetime and activation percentage, this work enables independently engineering the decoupled stage of catalyst preparation including oxide reduction and thin film dewetting from the stage of catalytic activation and nanotube lift off.

Enhanced Mechanical Properties by Engineered Carbon Nanotube Materials

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Synergistically improved specific mechanical properties such as specific-modulus, -strength, and -toughness in lightweight materials is critical for protective applications—from mitigating projectile impacts in space and battlefield to damping undesirable vibrations in aircraft and spacecraft. Macroscale materials derived from carbon nanotubes (CNTs) provide us with an opportunity to tailor the structure of individual CNTs and their organization across multiple lengthscales from micro to macroscales to achieve desirable bulk properties. In this talk, we present two examples of such CNT materials—Vertically aligned carbon nanotube (VACNT) foams with mesoscale architectures and Aramid nanofiber (ANF)-reinforced CNT mats—which exploit the superior intrinsic properties of CNTs and their multiscale structural organization to provide superior mechanical properties at significantly low weight.

Using the Design of Experiment (DoE) approach, we design and fabricate mesoscale cylindrically architected VACNT foams by a floating-catalyst chemical vapor deposition process on photolithographically patterned substrates. By exploiting size-confined synthesis and interactive morphology from the architected mesoscale elements, we show that the specific modulus, -strength and -energy absorption can synergistically be improved. Importantly these architected VACNT foams also can recover more than 80% from large strains up to 50%.

We fabricate the ANF-reinforced CNTs by mixing small concentration (up to 12% wt) of ANFs into a homogeneous solution of functionalized MWCNTs prepared from our VACNT foams, and then fabricate the mats by vacuum assisted filtration. Using a laser-induced microprojectile impact testing (LIPIT) technique, we study the impact response of the target ANF-reinforced CNT mats and pure ANF and CNT mats subjected to microprojectile (9.2 um) impacts at supersonic velocities between 200 m/s to over 1 km/s. We demonstrate that the ANF reinforcement in CNT mats—which enables stronger and dynamic hydrogen bond interactions between ANFs and CNTs—enhance the specific energy dissipation by ~100% compared to pure CNT mats. We also perform experiments at timescales comparable to the hydrogen bond dynamics and demonstrate their dynamic response timescale effects towards enhancing energy absorption.

Synthesis of Hierarchical Nanostructured Materials for Composites with Enhanced Mechanical and Multifunctional Performance

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Bulk nanostructured materials offer tremendous opportunity for re-inventing materials, but also pose many challenges both in terms of characterization, design, processing, and scaling. I will start with an overview our group's work developing nanoengineered hierarchical advanced (aerospace-grade) composites with enhanced mechanical properties, with a focus on imparting multifunctionality. Such hybrid advanced composites employ aligned carbon nanotubes (A-CNTs) in several architectures and volume fractions, building multifunctionalities concurrent with mechanical property improvements that includes thermal and electrical conductivity tailoring for energy storage, ice protection, and self-manufacturing, among others. Within this context this talk will focus on the growth of carbon nanostructure directly over aerospace-grade carbon fibers (or even polymers) by low temperature chemical vapor deposition synthesis using relatively unexplored catalysts such as sodium and copper. While sodium catalysts resulted in tubular carbon nanofibers with the significant advantage of the catalyst being easily removed by heat treatment, copper catalysts can produce amorphous, "bamboo-like" or turbostratic nanofibers useful in energy storage among other applications, as well as a new aerogel-like 3D porous turbostratic nanostructure, depending to the synthesis temperature.

A second part of the talk will focus on multifunctional composites for energy storage. We have developed the concept of a "structural separator" comprised of electrically-insulating aligned alumina nanotubes, which realizes a structural, or mechanically robust, function in addition to allowing charge transfer in a battery or supercapacitor for structural energy storage. More recently we developed the synthesis of aligned boron nitride nanotubes (A-BNNTs) to further improve the structural properties of such separators as well as exploring other forms of energy harvesting (piezoelectricity) and properties (thermal conductivity, neutron absorption, etc.). Our mm-scale A-BNNTs have high quality and low light absorption which will enable the manufacturing of nanocomposites with a broad range of functionalities.

Engineering Carbon Nanotubes for Electronic Applications: A Journey from Lab to Fab

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The unique electronic properties of carbon nanotubes (CNTs) arising due their one-dimensional structure has led several groups around the world to study them for a variety of electronic applications. Materials purity and scalable processes are critical for realizing the commercial potential of CNT electronics. For example, in order to integrate CNTs in production semiconductor foundries (fabs), strict contamination controls and fab compatible wafer scale deposition are a must. This talk will give an overview of how these requirements were achieved by Nantero in order to develop our CNT based non-volatile memory (NRAM®). The talk will highlight engineering controls both at the nano-scale and macro-scale for consistent manufacturing of CNT films on 300 mm wafers. Some key characteristics of the NRAM® memory device will also be discussed. In general, an ultra—high purity CNT material technology platform that is fab-compatible can be used for developing a variety of CNT based electronic devices in a manufacturing setting. Some examples of CNT based electronic applications will be discussed with focus on material requirements. Lastly, need for controlled synthesis of CNTs for certain targeted applications will be a topic for open discussion.

Carbon Nanotube Transistors: Recent Progress Towards Applications in Highly-Scaled and High-Performance CMOS Logic

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More than three decades of fundamental research on Carbon Nanotube (CNT) materials and devices have generated tremendous progress towards useful applications. In this talk, we will first introduce the motivations and review the challenges towards utilizing semiconducting single-walled CNTs as a channel material in highly-scaled and high-performance CMOS transistors. We will summarize recent experimental advances towards CNT transistors by our team and collaborators, ranging from fundamental materials growth & assembly studies to advanced transistor component breakthroughs. We will then share a transistor perspective on the desired qualities for aligned semiconducting CNT arrays to encourage future research directions in the scientific community.

Electrical control of the SWCNTs growth

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Chemical vapor deposition (CVD) is widely used for the efficient growth of single-walled carbon nanotubes (SWCNTs). The growth mechanism comprises the mass and heat transport, gas phase and surface chemical reaction, and the interaction between the SWCNTs and the substrate/catalyst. Correspondingly, the controllable parameter space is conventionally focused on the mass flow of each component, the temperature of the reaction chamber and substrate, and the material and structure of the substrate/catalyst. In this talk, we will introduce a new perspective of electrochemistry and electrostatic energy for the selective growth of semiconducting SWCNTs (s-SWCNTs). Since 2016, we have discovered that the as-grown CNTs are all negatively charged after Fe-catalyzed CVD process. An in-situ measurement verified that the extra electrons come from the charge generation and transfer during the growth of CNTs, which indicates that an electrochemical process happens in the surface reaction step. Furthermore, the impact of the Fermi level in Fe catalysts on the chirality of ultralong CNTs inspired us to use electric field to control the growth. Based on the above observations, we reported an electro-renucleation approach that twists the chirality of the SWCNTs to produce nearly defect-free s-SWCNTs horizontally aligned on the substrate with less than 0.1% residual metallic SWCNT. The remarkable difference of quantum capacitance between m-SWCNT and s-SWCNT separates the electrostatic energy plot of SWCNTs into two branches. With an external electric field applied, the large aspect ratio of CNTs enables a strong local electric field generated by the charge stored at the CNT tip to contribute a prominent electrostatic effect that greatly affects the total free energy change. In principle, this residual percentage can be further reduced to less than 1 ppm simply by tuning the SWCNTs' diameters to around 1.3 nm. With the deep study of electrical control, we realized that there were 3 main challenges need to be addressed for improving the purity of s-SWCNT array. First, there was always a variation of the positions where the chirality transitions happen. It was very sensitive to the implement time of electric field reversal. Second, the s-SWCNTs had chance to be twisted back to metallic ones. Third, the required electric field is too large (200V/mm), which is very close to breakdown the feed gas at high temperature.

Recently, we propose the intelligent synthesis of SWCNTs that the position of chirality change can be automatically fine controlled by a closed loop including in-situ monitoring and real-time interventions. A high-temperature-tolerant circuit is fabricated on growth substrate for sensing and responding to the synthesis processes. As a result, either highly pure s-SWCNT arrays or metallic-semiconducting (m-s) junction arrays with different junction positions is simply synthesized by programming the responding signal. The intelligent synthesis shows much higher efficiency and controllability compared with conventional methods. Besides, we herein report an approach to stabilizing the semiconducting-to-metallic chirality change under a weak perturbation (10V/mm-alternating electric field) by contacting growing SWCNTs with low work-function electrodes, such as Hafnium Carbide (HfC) or Titanium Carbide (TiC). When in contact with low work-function electrodes, SWCNTs and their catalysts will be negatively charged (n-doped) due to the electrode work-function, which causes a large free energy gap between m-CNTs and s-SWCNT and a reduction of the twisting barrier from m-SWCNT to s-SWCNT.

We anticipate the growth of large-scale, uniform and high-purity s-SWCNT array will be eventually achieved by all-electrical control.

Nanoscale Carbon for Print-in-Place and Recyclable Electronics

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For decades we've been hearing about the promise of printing electronics directly onto any surface. However, despite significant progress in the development of inks and printing processes, reports on fully, direct-write printed electronics continue to rely on excessive thermal treatments and/or fabrication processes that are external from the printer. In this talk, recent progress towards print-in-place electronics will be discussed; print-in-place involves loading a substrate into a printer, printing all needed layers, then removing the substrate with electronic devices immediately ready to test. A key component of these print-in-place transistors is the use of inks from various nanomaterials, including 1D carbon nanotubes, 2D graphene and hexagonal boron nitride, and quasi-1D silver nanowires. Using an aerosol jet printer, these mixed-dimensional inks are printed into functional 1D-2D thin-film transistors (TFTs) without ever removing the substrate from the printer and using a maximum process temperature of 80 ºC with most processing occurring at room temperature. To achieve this, significant advancements were made to minimize the intermixing of printed layers, drive down sintering temperature, and achieve sufficient thin-film electrical properties. Devices are demonstrated on various substrates, including paper, and evidence of the potential for printing directly onto biological surfaces will be shown. What's more, recent progress towards a completely recyclable printed transistor will be discussed, fabricated entirely using nanoscale carbon-based inks.

High Value Carbon and Hydrogen from Natural Gas

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Environmental pressure is forcing the oil and gas industry to find non-combustion applications for their hydrocarbon assets. Making hydrogen from natural gas is an attractive option, but to compete with SMR and future projections for low cost electrolysis, the hydrogen production must be subsidized with a high value carbon co-product. Nanotubes could be the answer. The challenges include process economics and finding applications for CNT based structural carbon at the megaton scale.

Evolution of NoPo HiPCO® SWCNT from 2011-2021: Progress in Repeatability and Scalability

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NoPo Nanotechnologies began working on HiPCO® in 2011 when interest in the process declined due to difficulties in scaling, consistency and market. Diligent efforts by the team during the last decade have created a highly consistent process referred to as the NoPo HiPCO process. Effect of parameters such as CO_2 and H_2O. Engineering of mixing injectors that could maintain consistency throughout the run time. Novel in-line gas monitors. Development of unit reactors for scaling production to overcome problems in consistency faced in earlier efforts. Some of the applications developed to showcase material capabilities such as in fibers and water filtration will be showcased.

Greener Production of Carbon Nanotubes and Battery Applications

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Extensive research has been made for synthesis of carbon nanotubes (CNTs) of higher quality and performance. To contribute to the sustainable society, greener production and appropriate use are important.

(Sub)millimeter-long CNTs can be synthesized both on 2D substrates and in 3D fluidized bed. Using the lab-scale experimental data, we performed cradle-to-gate life-cycle assessment (LCA) [1]. The CNTs produced on Si substrates in milligram-scale accompanied huge green-house gas (GHG) emission of 29 kg_{CO2e}/g_{CNT} due to the huge electric power for sputtering and chemical vapor deposition (CVD). Fluidized bed reduced the emission to 9.9 kg_{CO2e}/g_{CNT}, in which catalyst deposition onto ceramic beads by sputtering was the bottle neck. Replacement of sputtering with CVD resulted in significant reduction to 2.1 kg_{CO2e}/g_{CNT}, and the replacement of carrier gas from Ar to N2 resulted in further reduction to 0.48 kg_{CO2e}/g_{CNT}. To approach the emission factor of carbon fiber (CF; 0.02 kg_{CO2e}/g_{CF} = 20 kg_{CO2e}/kg_{CF}), not only scale up from $g_{CNT}/cm^3{}_{reactor}$, $kg_{CNT}/L_{reactor}$, to t_{CNT}/m^3reactor, reducing energy loss by 1/10 and 1/100, but also reducing the huge amount of carrier gas (x90 of C_2H_2 to dilute C_2H_2 to 1.1 vol%) are essential.

Elemental technologies for greener production have been developed. The catalyst deposition by CVD accompanies small GHG emission but uses high-cost organometallic vapors. The mist deposition method was developed which feeds aqueous solution of low-cost Fe and Al nitrates to fluidized bed [2]. By replacing the carbon source and etchant at low concentrations (1.1 vol% C_2H_2 and 0.06 vol% H_2O) with less active ones at high concentrations (10–20 vol% C_2H_4 and 1 vol% CO_2), Ar carrier gas at high rate (x90 of C_2H_2) was replaced with N_2 at low rate (x4–x9 of C_2H_4) [3]. We found that the CO_2-assisted CVD can be further enhanced by reducing the Fe/AlOx catalyst under highly reductive condition of H_2 without CO_2 before CVD [4].

One promising application of CNTs for GHG reduction is rechargeable batteries. We have used the self-supporting, sponge-like paper of CNTs as 3D current collector and realized light-weight Li-ion batteries without using polymeric binders and metallic foils. Li-S has a huge theoretical energy density of 2510 Wh/kg_{Li2S} but actual one is much less due to the excess use of metal foils, additives, and electrolyte. We found that Li_2S_x supported on CNT sponge works with small amount of electrolyte and thin Li foil, and realized 400-500 Wh/kg_{cell} based on the total mass of interior cell [5]. Safety gets more important for cells of higher energy. A new cell architecture with excellent thermal stability was developed by using CNT sponge for electrode and boron nitride sponge for separator [6].

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We can use carbon to decarbonize—and get hydrogen for free

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Constraints on CO_2 emissions are confronting society with multiple massive challenges: creating new sources of clean energy beyond solar and wind; electrifying our transportation systems and using lighter weight materials; decarbonizing the industrial sector; and dealing with the economic fallout associated with shrinking the fossil hydrocarbon industry, which accounts for about 7% of the world economy. At first blush, the solutions to these dilemmas appear to be at odds with one another. In this lecture, I will show that there may be a way forward that positively influences all of these aims: Our vision is a zero-emission future, where large scale technology is deployed to co-produce clean hydrogen and carbon materials that house, move, clothe, and feed people. To foster this vision, we have established the Carbon Hub as a non-competitive partnership of industry, academia, government, and non-profit organizations.

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POSTERS

Extreme Dynamic Performance of Nanofiber Mats under Supersonic Impacts Mediated by Interfacial Hydrogen Bonds

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Achieving extreme dynamic performance in nanofibrous materials requires synergistic exploitation of intrinsic nanofiber properties and inter-fiber interactions. Regardless of the superior intrinsic stiffness and strength of carbon nanotubes (CNTs), the weak nature of van der Waals interactions limits the CNT mats from achieving greater performance. We present an efficient approach to augment the inter-fiber interactions by introducing aramid nanofiber (ANF) links between CNTs, which forms stronger and reconfigurable interfacial hydrogen bonds and π–π stacking interactions, leading to synergistic performance improvement with failure retardation. Under supersonic impacts, strengthened interactions in CNT mats enhance their specific energy absorption up to 3.6 MJ/kg, which outperforms widely used bulk Kevlar-fiber-based protective materials. The distinct response time scales of hydrogen bond breaking and reformation at ultrahigh-strain-rate (∼10^7–10^8 s^–1) deformations additionally manifest a strain-rate-dependent dynamic performance enhancement. Our findings show the potential of nanofiber mats augmented with interfacial dynamic bonds─such as the hydrogen bonds─as low-density structural materials with superior specific properties and high-temperature stability for extreme engineering applications.

Architected Vertically Aligned Carbon Nanotube Foams with High Specific Energy Absorption and High Specific Modulus for Protective Applications

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Protective applications demand lightweight structural materials with high energy absorption, mechanical strength, and elastic modulus. However, these properties typically have a tradeoff, e.g. strength vs. energy absorption, and modulus vs. energy absorption. To mitigate multiple high-velocity impacts additionally requires high strain recovery in protective materials. To address this challenge, we design and synthesize cylindrically-architected vertically aligned carbon nanotube (VACNT) foams that offer synergistic improvement in energy absorption, modulus, and compressive strength along with high strain recovery. We use a floating-catalyst thermal chemical vapor deposition (CVD) process on photolithographically patterned substrates with specific architecture. We test them in quasi-static cyclic compression of up to 50% strain and up to five loading-unloading cycles to investigate their mechanical behavior.

We adopt a Design of Experiment (DoE) statistical approach to evaluate the factors that synergistically enhance SEA and specific modulus of architected VACNT foams and propose a model that allows us to predict the optimal property space that is desirable for a given application. We exploit an unusual combination of size confinement effect and nanoscale lateral interactions that arise because of the hierarchically engineered interactive morphology of VACNT foams. The floating-catalyst CVD synthesized bulk VACNT foams have been shown to exhibit high specific energy absorption (SEA) during compression and can recover from large strains upon unloading because of their interactive hierarchical structure: individual multiwalled CNTs form an entangled forest like morphology on the microscale and grow into vertically aligned bundles in mesoscale to create the macroscale VACNT foams. By introducing mesoscale architectures to VACNT foams, we show that the intrinsic density within each mesoscale cylinder wall as well as the nanotube interactions among neighboring cylinders tailor the progressive collective buckling the VACNT foams undergo, leading to high SEA. The thickness confinement by the cylinder walls simultaneously leads to a higher specific modulus because of the higher microstructural alignment of the CNT bundles resulting from the size-confined CVD synthesis. Architected VACNT foams with optimized design parameters demonstrate more than one order of magnitude higher SEA, specific strength, and specific modulus than the conventional polymeric foams of similar densities. Our findings on the correlation among size-confined growth, resultant structure, and material performance provide an optimized design template of architected materials for protective applications.

Stability of 2D Transistors Designed for Sensor Applications

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Among emerging 2D materials, transition metal dichalcogenides (TMDs) are some of the most promising for applications in future nanoelectronic device technologies. As one of the most abundant TMDs, molybdenum disulfide (MoS2) has been studied for use in many sensor applications as well as future low-power field-effect transistors (FETs). Its atomically thin form-factor and favorable electronic properties make it a promising candidate for nanoscale FET-based electronic sensors. Unfortunately, MoS2 FET devices have been shown to be susceptible to molecular adsorption, which can lead to an unstable threshold voltage when operated continuously in ambient air. Effective protection from oxygen, water, and other molecular adsorbents is needed both to overcome these instabilities and to better understand the mechanisms at work. We studied the effects of bias stress on MoS2 field-effect transistors with a variety of surface passivation (capping) layers, investigating the trends of threshold voltage shifts in the FETs stressed under ambient conditions. The choice of capping layers was made based on propensity to prevent molecular adsorption and thus stabilize the threshold voltage of the devices. Thick SU-8 films and thin conformal atomic-layer-deposited Al2O3 both proved to be effective and far superior to either PMMA or SiNx capping layers. Next, we will study the impact of modifying the substrate interface underneath the MoS2 to determine how it can be best utilized to optimize device stability and sensitivity. And in particular, fabrication of these devices on insulating substrates enables their deployment in a wider variety of applications, including liquid-based sensors such as immunosensors and other biosensors. These results help to shed light on both the feasibility and the challenges of deploying currently available 2D materials in a variety of sensor applications.

Origins of Preconditioning Effect in Hierarchical Nanofibrous Materials

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Many fibrous biological materials and filled rubbers exhibit softening in quasistatic stress-strain response for the first few loading-unloading cycles, a phenomenon known as the preconditioning effect. The preconditioning effect is critical in characterizing material behavior for engineering applications and developing constitutive models. However, there is no consensus across literature on its physical origin. We used synchrotron X-ray scattering and mass attenuation measurement techniques to study the nanoscale origin of the preconditioning effect in vertically aligned carbon nanotube (VACNT) foams—a model system for hierarchical fibrous materials. We observed decay in CNTs vertical alignment across multiple length scales and broadening of (002) X-ray scattering peak as a function of compression cycles. Examination of X-ray scattering results and supporting evidence from electron microscopy and highspeed imaging suggests that the preconditioning in such hierarchical fibrous materials arises not just due to mesoscale rearrangement of nanofibers as believed previously but also due to permanent deformation induced in the nanoscale structure of the CNTs. Our study gives insights into the fundamental mechanisms resulting in preconditioning effects that can guide the material design and fabrication techniques to minimize this effect to achieve superior properties.

Alternative Carbon Nanotube Functionalization Processes for Morphological Integrity and Footprint Reduction

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Carbon nanotubes (CNTs) are commonly modified via the covalent addition of chemical functional groups, allowing them to bind to or disperse in diverse species. However, common functionalization processes require refluxing CNTs with nitric acid, lacking specific control over resulting material properties. Concentrated acid use also exerts safety, cost, and environmental burdens. Here, we examined the opportunity for a vapor-based functionalization technique in place of a liquid-based technique to limit morphological damage to the CNT forest, and evaluated hydrochloric acid as an alternative treatment choice across CNTs grown from alkynes, while comparing carbon footprint and ecotoxicity of treatment modalities.

Feedstock Effect in the Catalyzed Synthesis of Encapsulated Nanocarbons

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Fully understanding of the growth mechanisms of novel carbon nanostructures inside a carbon nanotube is still elusive [1, 2]. In our simulation-based study, we investigate the Ni-catalyzed nucleation and growth of encapsulated carbon nanostructures from different carbon (Cx), hydrocarbon (CxHy) and oxygen-containing hydrocarbon (CxHyOz) precursors using reactive molecular dynamics simulations with a support of first-principles calculations [2-5]. In particular, our results show that the growth of different encapsulated carbon nanostructures, i.e., nanotube, nanoribbon, carbyne, etc., can be determined by the choice of Cx and CxHy feedstocks (Fig.1) [2, 3]. On the other hand, CxHyOz precursors prevent association of carbon networks due to either the poisoning of catalyst particle [4] or the restructuring of host carbon nanotube.

The results also indicate that all obtained carbon nanostructures contain metal (catalyst) atoms in the case of carbon and hydrocarbon case and thus such structures are less stable than their pure counterparts [2]. Consequently, the oxidation-based purification mechanism of these structures is studied (Fig.1) [2]. Moreover, we find that chemical modification of the obtained encapsulated nanocarbons result in structural changes as well as semiconducting to metallic transition [3, 4].

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Demystifying the Interactions of Process Parameters and Carbon Source Structure in Carbon Nanotube Synthesis

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Numerous studies in the carbon nanotube (CNT) synthesis literature report differing results on the role of the molecular structure of the carbon source, ranging from categorically different results to no effect when other parameters are accounted for. These differences have made it difficult to apply knowledge from one reactor system to other systems using different carbon sources. Using the high-throughput floating catalyst autonomous research system (FC-ARES) developed at the Air Force Research Laboratory we carried out a systematic, comparative study of floating catalyst CNT growth with three similar carbon source molecules with related structures: ethanol, 1-propanol, and 2-propanol at a range of temperatures. Using optical and spectroscopic methods we characterized the carbon yield, quality, and radial breathing modes of the produced CNTs over 141 experiments covering 30 unique experimental conditions. Conditions were selected to assess the impact of process parameters such as the elemental flow rates of carbon, oxygen, and catalyst (iron) as well as interatomic ratios such as the carbon/iron and oxygen/iron ratios. Gas flow conditions and reactor geometry were held constant to control for differences in transport phenomena. Along with supporting kinetic simulations of the homogeneous pyrolysis products within the reactor processes, these results establish a link between the two disparate camps in the CNT synthesis literature and facilitate a better understanding of how both the selection of carbon source and process parameters can be exploited to achieve desired synthesis goals.

The Effect of Iron Flow Rate and Sulfur/Iron Molar Ratio on CNT Synthesis by Floating Catalyst Chemical Vapor Deposition (FCCVD)

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Since the early 1990s, CNTs have triggered a significant number of research studies due to their exceptional optical, thermal, mechanical and electrical properties. Although CNTs have been investigated as promising nanomaterials for various applications, they haven’t been commercially produced at a large scale while achieving high quality. Floating catalyst chemical vapor deposition (FCCVD) is a widely used method to produce CNTs; however, after more than two decades of studies, many challenges still remain with FCCVD technology, mainly due to the complexity of the reaction process and insufficient understanding of the reaction mechanism. Furthermore, FCCVD literature has few quantitative reports on key inputs correlated to CNT quality and properties, which are important to understand and advance CNT reaction engineering. In this presentation, I will share recent data on the relationship of catalyst precursor and growth promoter (ferrocene and thiophene respectively) to CNTs grown including controlling high quality CNT synthetic selectivity, a key metric to develop a commercially viable process. Through our recent experimental results, I will provide new insights into the effect of Fe flow rate and S/Fe molar ratio on CNT and undesired carbon species production rates. We found high Fe flow rates contributed to increasing carbon impurity production rates when key parameters were not co-optimized (e.g. S/Fe molar ratio, reaction species spatial-temporal coupling), making scaling of high quality CNT productivity more challenging. We employed numerous analytical techniques to quantitatively characterize the FCCVD CNT reaction process and products. In addition, to further verify and elucidate Fe nanoparticle catalyst effects, several methodologies including thermogravimetric analysis (TGA), transmission electron microscopy (TEM), time of flight secondary ion mass spectroscopy (ToF-SIMS) and elemental analysis by combustion were used.

Direct Growth of Sub-10nm MoS_2 Nanoribbons and their Width Dependent Quantum Properties

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Many of the electronic and optical behaviors of atomically thin transition metal dichalcogenides are strongly dependent on their number of layers and width. Therefore, it is of central importance to develop facile methods for their controllable synthesis. We report the growth of bilayer MoS_2 nanoribbons enabled by nickel nanoparticles, which promotes both heterogenous nucleation of the first layer of MoS_2 and simultaneously catalyzes homoepitaxial tip-growth of a second layer via vapor-liquid-solid (VLS) mechanism, resulting in bilayer nanoribbons with width controlled by the nanoparticle diameter. Theoretical simulations also confirm the VLS growth mechanism towards nanoribbons and its orders of magnitude higher growth speed compared to the conventional non-catalytic growth of flakes. Coulomb blockade oscillations are observed in the transfer characteristics of the nanoribbons at low temperatures. Such an oscillation behavior is width-dependent, only showing in nanoribbons with width < 20 nm, and observable at temperatures up to 80 K. The phenomenon evidences the value of this proposed synthesis strategy for future nanoelectronics and quantum applications.

Interaction of Gases with Monolayer WS_2: An *in situ* Spectroscopy Study

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The optical and electronic properties of (2D) materials can be tuned through physical and chemical adsorption of gases. They are also ideal sensor platforms, where charge transfer from the adsorbate can induce a measurable change in the electrical resistance within a device configuration. While 2D materials-based gas sensors exhibit high sensitivity, questions exist regarding the direction of charge transfer and the role of lattice defects during sensing. Here we measured the dynamics of adsorption of NO_2 and NH_3 on monolayer WS_2 using in situ photoluminescence (PL) and resonance Raman spectroscopy. Experiments were conducted across a temperature range of 25-250 °C and gas concentrations between 5-650 ppm. The PL emission energies blue- and red-shifted when exposed to NO_2 and NH_3, respectively, and the magnitude of the shift depended on the gas concentration as well as the temperature down to the lowest concentration of 5 ppm. Analysis of the adsorption kinetics revealed an exponential increase in the intensities of the trion peaks with temperature, with apparent activation energies similar to barriers for migration of sulfur vacancies in the WS_2 lattice. The corresponding Resonance Raman spectra allowed the simultaneous measurement of the defect-induced LA mode. A positive correlation between the defect densities and the shifts in the PL emission energies establish lattice defects such as sulfur vacancies as the preferential sites for gas adsorption. Moreover, an increase in defect densities with temperature in the presence of NO_2 and NH_3 suggests that these gases may also play a role in the creation of lattice defects. Our study provides key mechanistic insights into gas adsorption on monolayer WS_2, and highlights the potential for future development of spectroscopy-based gas sensors based on 2D materials.

FC-CVD Utilizing a Novel Microplasma Reactor for Ex Situ Catalyst Generation

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The floating catalyst chemical vapor deposition (FC-CVD) method for synthesizing carbon nanotubes (CNTs) utilizes an aerosol of catalytic metal nanoparticles in the reactor. Typically, a catalyst precursor (such as ferrocene for iron) is introduced to the reactor where it decomposes to form a supersaturated metal vapor which condenses particles. Fortunately, over a range of carbon feedstocks, furnace dimensions, and flow rates, particle formation occurs such that the particles are available in the appropriate location to nucleate and grow CNTs. However, this coupling prevents independent control of catalyst formation and CNT growth, and may not permit each process to occur optimally. Further, the thermal decomposition method is not well suited for the generation of high concentration aerosols at high yield, requiring significant excess iron input. These disadvantages ultimately limit the quality of the CNT product, the controllability of the process, and the scale up of reactor designs.

Here we present the in-progress development and investigation of a FC-CVD system which utilizes a novel microplasma reactor for the ex-situ generation of catalyst particles. The custom-built atmospheric pressure DC microplasma reactor is capable of generating iron aerosols at high number concentration (>10^9 #/cm^3) with narrow size distribution (geometric standard deviation < 1.3) from a ferrocene vapor precursor. We demonstrate precise diameter control down to 1.1 nm and maximum yield near unity. We invoke a charge-mediated formation mechanism to show that the role of the ~10 microsecond plasma residence time is primarily to dissociate the precursor and ionize the resulting supersaturated iron vapor, with particle growth occurring downstream of the plasma domain through aggregation of neutral and ionized vapor and clusters. While this method provides additional degrees of control, the processes are still coupled by the evolution of the catalyst aerosol as it flows into the furnace. Current experimental efforts, including preliminary CNT synthesis, focus on understanding this evolution and deterministically integrating the two reactors.

Kinetics of Wafer-Scale Epitaxial Growth of MoS_2 on Sapphire

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Monolayers of transition metal dichalcogenides (TMDs) such as MoS_2 could potentially revolutionize a range of electronic and optoelectronic applications; however, there is a lack of understanding regarding the basis fundamentals of their growth. Metal organic chemical vapor deposition (MOCVD) with its gaseous precursors allows for tight control and modulation of parameters such as gas phase composition and growth time. MoS_2 ¬films grown on sapphire substrates are epitaxial with minimal strain.

In this work, we discuss the wafer-scale growth of MoS_2 monolayers on sapphire via MOCVD. The films were grown on 2” c-plane sapphire wafers in a horizontal cold-wall reactor at 900-1000 °C using H_2S and $Mo(CO)_6$ as precursors with a nominal chalcogen to metal ratio of 20,000 with H_2 as the carrier gas. Atomic force microscopy and scanning electron microscopy were used to measure the surface coverage and domain density. Additionally, the coverage dependence of Raman, photoluminescence, and absorption spectra along with the in-plane X-ray diffraction patterns will be shown and discussed.

We were able to obtain fully coalesced epitaxial MoS_2 films within only 12 minutes of growth. Within 30 s, the film fully nucleates on the substrate, achieving domain densities of 1-2*10^3 µm-^{2}, which remains relatively constant for the rest of the growth. Then, the domains laterally grow out linearly at a rate of about 150 nm^2/min until they being to merge. After 3 minutes of growth, 65% of the sapphire is covered. However, the growth rate subsequently decreases due to reduced adsorption on the MoS_2. After the film fully coalesces, bi- and multilayer structures begin to grow that eventually evolve into pyramids and spirals at sufficiently long growth times.

To adjust the domain density of the sample, we grew MoS_2 films at different temperatures. Reducing the growth temperature increased the domain density, while for longer growths, bi- and multilayer coverage was minimized when grown at 950 °C. Additionally, pre-annealing the sapphire under a H_2 and H_2S mixture limits nucleation to along the step edges in the substrate and is likely due to sulfur passivation of the sapphire.

Our results help probe the effects of surface chemistry and growth conditions on the MOCVD growth of MoS_2, thereby enabling a deeper understanding of the fundamental kinetics of the system. This knowledge will be applicable to other TMDs as well as other deposition techniques.

Bottom-up Peak Fitting to Determine Chiral Breakdown of Radial Breathing Mode Region of SWCNT Raman Spectra

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The RBM region of single-walled carbon nanotubes Raman spectra encodes information about the diameter and chirality of the tubes, parameters that require careful control to enable widespread adoption of carbon nanotubes as an electrically and mechanically workable material. Determining diameter and chirality from Raman spectra is done by fitting peaks to the region and comparing the peak positions to known vibrational modes on a Kataura plot. This top-down approach of fitting a small number of peaks to a spectrum that may contain tens of convoluted peaks provides limited insight, due to the averaging effects of fitting many peaks with only a few. Borrowing from the machine learning community, a bottom-up approach that reconstructs the Raman response as a linear combination of known RBMs is produced using the model selection operator LASSO (least absolute shrinkage and selection operator). This method allows for automated analysis of the relative abundances of chiralities present in a nanotube spectrum, and creates a powerful feedback tool to further develop diameter and chirality control in any method of carbon nanotube synthesis.