Columbia University

Center for Precision Assembly of Superstratic and Superatomic Solids (PAS³)

NSF Award DMR-1420634

MRSEC Annual Report
July 2016 – June 2017
Center for Precision Assembly of Superstratic and Superatomic Solids (PAS$^3$)
Annual Report July 2016 – June 2017

1. Executive Summary
   1a. Vision and Overview

   The Center for Precision Assembly of Superstratic and Superatomic Solids (PAS$^3$) is a MRSEC centered at Columbia University with major partner the City University of New York. There are 30 faculty participants across Columbia, City College of New York, Barnard College, Harvard, Stanford, University of the Virgin Islands, the College of Staten Island, and Fashion Institute of Technology. PAS$^3$ consists of two IRGs around the central theme of assembly using atomically precise components. IRG 1 is focused on assembly of layered two-dimensional materials into van der Waals heterostructures; and IRG 2 is focused on assembly of atomically precise superatoms into solids with controllable dimensionality and coupling between subunits. To date, four single-PI seeds have been funded to support faculty toward incorporation of their work into the existing IRGs.

   Education activities of the center are designed to improve science, technology, engineering, mathematics (STEM) and materials education at all levels. These include a summer research program encompassing undergraduates, community college students, high school students, and teachers; primary school outreach; a high school ‘nano’ course; updates to undergraduate curriculum; and seminars/courses for graduate students and postdocs. These programs rely strongly on partnerships within PAS$^3$ and with local schools, and are designed to build deep and long-term relationships. These education activities are coupled with a diversity program designed to broaden participation at all levels, again based on a foundation of partnerships among the PAS$^3$ member institutions. PAS$^3$ has a strong basis of diverse participants, and is engaging in a number of recruitment efforts focused on under-represented minority (URM) participation.

   PAS$^3$ has strong ties with Brookhaven National Laboratories (BNL), the Army Research Lab, IBM, and Honda Research. These collaborators have been strategically chosen to complement and extend the proposed research, and work with PAS$^3$ to foster education, research, and technology development that will together catalyze development of revolutionary material systems, enhance national economic competitiveness, and better educate students for careers in the 21st century. Several of our graduate students work in industrial and government labs, and collaborators from DuPont, IBM, Army Research Lab, Honda Research, and Brookhaven National Laboratory have seats on the MRSEC External Advisory Board to provide guidance to PAS$^3$ research and ensure technological impact. PAS$^3$ researchers have a number of international collaborations directly related to center research, and are hosting visiting students and faculty. A ‘Global Research Laboratory’ project with Sungkyungwan University (Korea) has recently been funded. A partnership with Université Angers has led to an interesting collaboration on superatom assembly and Xavier Roy and Colin Nuckolls are visiting Batail in June 2017 to initiate a yearly workshop between Angers and Columbia.

   Shared facilities at Columbia and CCNY/CUNY constitute a major cross-campus resource for all center participants and outside users. PAS$^3$ has additionally purchased new equipment for inert assembly of 2D materials that is now installed and operational in the Columbia Shared Materials Characterization Laboratory. A laser ARPES system has been installed and is generating its first data. Finally, using supplemental funds from NSF combined with internal funds, a new cryo-free 14T magnet cryostat has is due to be installed in June 2017, and a closed-cycle optical cryostat has been ordered.

   PAS$^3$ is managed by an executive committee consisting of Director Hone, Associate Director Nuckolls, IRG co-leaders Krusin and Zhu, and Misewich (BNL). An external advisory board provides advice and feedback to the executive committee. Four MRSEC postdoctoral Fellows organize monthly research symposia, and coordinate research efforts within the IRGs. A student-postdoc leadership committee comprising the four Fellows plus four PhD students helps to organize major MRSEC activities and sets priorities for educational programs for MRSEC participants. The PAS$^3$ education, human resources, and diversity committee shapes programs in these areas, working with Emily Ford (Columbia Engineering director of outreach programs). Operations of PAS$^3$, including financial management,
scheduling of seminars, execution of education activities such as the REU program, are managed by staff of the Columbia Nano Initiative, the administrative home of PAS.

Funding for all center participants is on an annual basis, based on an annual proposal process and allocated by the executive committee with advisory inputs from the EAB. An annual meeting in late spring provides a forum to share results across the center, and shape the research directions for the upcoming year. Regular seminars and meetings foster day-to-day interaction among PAS researchers.

1b. Center Accomplishments for Current Reporting Period

Key IRG 1 accomplishments

IRG 1 focuses on the study of van der Waals heterostructures, created by vertical stacking of two-dimensional materials. The IRG 1 team is focused on two broad materials classes: 2D semiconductors (chiefly transition metal dichalcogenides - TMDCs) and 2D metals (including metallic TMDCs and topological insulators - TIs). Insulating hexagonal boron nitride (hBN) is used as a low-disorder dielectric interface and encapsulant; and conducting graphene is used as an electrical contact material. The goals of IRG 1 are to use these heterostructures to: study individual 2D materials in the ultraclean limit; study interactions between 2D materials; and study new emergent properties at interfaces. In the past year, IRG 1 researchers have made a number of advances toward the goals listed above, with both fundamental intellectual merit and broad impact:

Intellectual Merit:

- Coordinated efforts on materials characterization and synthesis have yielded significant reduction in defect density for 2D semiconductors, critical for understanding fundamental properties and increasing device performance.
- Combined theory-experiment work has established the novel structure of Cl-doped graphene, in which cooperativity among the Cl dopants acts to maintain an ordered planar configuration.
- Optical studies of 2D semiconductors have demonstrated achievement of near-intrinsic photoluminescence linewidths at low T; and have established that charge screening by ionic liquids can reversibly increase PL quantum yield. These advances (with materials improvements above) set the stage for fundamental advances in understanding of 2D material optics and optoelectronics.
- Related optical studies show that the single-particle bandgap of 2D semiconductors can be strongly modified by changing the dielectric environment, a property distinct from bulk materials.
- The team has demonstrated new techniques for achieving contacts to 2D materials, including Ohmic contacts to 2D semiconductors, which has been a major roadblock toward low-T studies.
- The advances above have facilitated detailed studies of 2D materials, including mapping of the Landau level spectrum of semiconducting WSe$_2$ and the phase diagram of superconducting NbSe$_2$.
- Continued studies of topological insulators have demonstrated the role of spin correlations on charge transport in Sb$_2$Te$_3$ and subsurface trap states in Bi$_2$Te$_3$Se.
- Measurements of site-dependent catalysis in 2D semiconductors are providing direct evidence that edges are much more catalytically active than the bulk, setting the foundation for future studies of edge-based catalysis in heterostructures.
- Measurement of momentum-dependent charge transfer in 2D semiconductor heterojunctions has revealed defect-dominated charge recombination.
- The team has developed a new platform for controlling interlayer rotation in heterostructures, and used it to study electronic bandstructure and friction as a function of rotation angle.

Broad Impacts:

- Progress in materials quality, characterization, optical properties, and contacts provides a solid foundation for both basic study and applications of 2D semiconductors in electronics and optoelectronics.
- 2D material heterostructures provide an opportunity for improved catalysis performance in hydrogen evolution and CO$_2$ reduction.
- TMD bilayers are an excellent model system for the study of the separation, diffusion, and recombination of photoinduced charges. These processes are of fundamental importance for solar
cells and other optoelectronic devices. In addition, charge transfer excitons in TMDCs are predicted to show condensation, a phenomenon that could potentially be used for low-power switching

- TI materials have potential in low-power computing and other next-generation electronics and controlling material doping and interfaces are critical steps towards applications.

**IRG 1 highlights:**

The IRG1 team has engaged in a collaborative effort to understand and improve the quality of TMDCs. STM studies have identified the main defect types in TMDC single crystals, and reveal that commercially-obtained crystals have an extremely high defect density. The team initiated a synthesis program that has produced crystals with over two orders of magnitude improvement in defect density. Electrical and optical measurements show large reduction in disorder and improvement in optical quantum yield. This work sets the stage for assembly of heterostructures with high-quality, well characterized building blocks.

The IRG2 team has demonstrated a new technique to rotate the layers in a heterostructure by AFM manipulation. This allows precise control of a key parameter in determining the properties of such heterostructures. Initial results show the ability to precisely manipulate the moire’ pattern between graphene and BN, and large variation in friction with angle.

**Key IRG 2 accomplishments**

IRG2 assembles superatoms into new classes of functional materials using precisely defined superatoms. This approach offers the attractive proposition of encoding desirable physical properties in the building blocks with exquisite control of inter-superatom interaction to create materials with tunable and multiple functionalities. The overarching goals of IRG2 are to (1) control the coupling between subunits to produce highly delocalized systems; (2) control the dimensionality between superatoms; and (3) utilize this this new leave of control to produce study new materials properties. The research described below is centered around these goals of IRG2. Given the enormous library of superatom structures and chemical/physical properties, IRG2 develops and expands the superatom concept into a large “periodic table” to enable designer materials with unprecedented levels of complexity and functionality.

**Intellectual Merit:**

Within this context, research in IRG2 has had many important findings. This report details the following areas that have seen significant progress.

- We have created a robust chemistry that allows superatoms to be joined together into a variety of new materials. This work was published in *Nano Letters* and highlighted in *Scientific American* as one of the “world changing ideas” for 2016.

- This new synthetic control of the superatoms allow us to describe a new method to make woven two-dimensional materials from superatoms using electrostatic templating. This is a singular result as there are no other methods to make woven two-dimensional materials. These studies have been submitted to *Science*.

- We have achieved one of our major objectives in developing a mild and general method to fuse superatoms so that they are strongly coupled. This exciting result charts a clear path to new magnetic and electronic materials.

- We have developed the chemistry to make two-dimensional and three-dimensional solids from superatoms. The two-dimensional ones can be exfoliated and positioned on arbitrary substrates. These 2D nanosheets are the superatomic version of 2D materials such as graphene and TMDCs.

- We have collaborated with Argonne National Laboratory to develop a diffraction based method to understand the electron distribution in superatoms. This study is the first of its time and illuminates the subtle structural and electronic changes that have huge effects on the electron distribution. We call this “electron cartography”, and this study has been submitted to *The Journal of the American Chemical Society*. 
• By combining superatoms with single molecule conductance measurements, we have created a molecular single-electron transistor that is assembled by wiring a redox-active, atomically precise cobalt chalcogenide superatom between two nanoscopic electrodes using molecular connectors.

• We developed an approach to link monomers of Ru-carbonyl cluster together to form dimers and trimers (and potentially n-mers) in a controllable fashion. The ground state properties of these clusters change significantly as their length increases.

• We have developed an approach to intercalate superatomic crystals through a single-crystal-to-single-crystal transformation. This process allows us to precisely manipulate the optical and electrical transport of the materials. This work is in press at *Nature Chemistry*.

• We have studied thermal transport in superatomic crystals and demonstrated that the dynamic disorder of the superatoms regulates the thermal conductivity behavior, from amorphous to crystalline behavior. This study was published in *Nature Materials*.

**Broad Impacts:**

• The multi-component, materials-by-design aspect of IRG2 provides a wealth of technological opportunities since each component can bring its own properties to the binary solid and new cooperative properties can emerge as a result of inter-superatom coupling.

• Understanding and controlling the coupling between superatoms will enable new types of emergent physical phenomena not previously observed.

• Thermoelectric materials interconvert thermal and electrical energy, and as such they may be used for both electrical refrigeration and power generation. Such materials will play an important role in our quest to find global sustainable energy solutions. At this time, thermoelectric operating characteristics are materials-limited; our initial results demonstrate that superatom solids, by decoupling thermal conduction from electrical conductivity, have tremendous promise as thermoelectrics, providing an untapped class of materials.

• We are training students and post-doctoral scientist in science that intersects chemistry, physics, and materials science, which is an area of national need.

• The methods to create the site differentiated clusters are state of the art and expand the knowledge base of new inorganic synthetic methods and new inorganic molecules.

**IRG 2 highlight:**

The IRG 2 team has had a synthetic breakthrough in the last year that enabled the creation of new materials. In particular, we have developed method to selectively functionalize superatoms Co₆E₈. This allows them to be made into discrete superatomic molecules, macrocycles and polymers. This robust chemistry that allows superatoms to be joined together into a variety of new materials with tunable dimensionality. This work was published in *Nano Letters* and highlighted in *Scientific American* as one of the “world changing ideas” for 2016. Most recently we have achieved one of the major objectives in IRG2 in developing a mild and general method to fuse superatoms so that they are strongly coupled. This exciting result charts a clear path to new magnetic and electronic materials. This new synthetic control of the superatoms allow us to describe a new method to make woven two-dimensional materials from polymeric strands of superatoms using electrostatic templating. There are no other methods to make woven two-dimensional materials. These studies have been submitted to *Science*.

**Key Educational accomplishments**

The key PAS³ educational effort is a summer research program that combines research experience for undergraduates (REU), teachers (RET), and community college and high school students (ENG). In the summer of 2016, this program included:

• REU: 17 students are working on PAS³-related research, including 3 visiting students from Brazil. Students live on campus and participate in social and enrichment activities.

• RET: 2 teachers from local partner schools worked in PAS³ labs

• ENG: In 2015, 6 students from partner high schools worked in PAS³ labs and participated in enrichment activities.
• Community college research: A new program at LaGuardia Community College gave basic training in laboratory skills. PAS³ hosted 4 of these students concurrently with the ENG program.
• Three students from the University of the Virgin Islands, together with Prof. Wayne Archibald, spent the summer performing research related to IRG 1 at Columbia and Brookhaven.

Key additional educational accomplishments include:
• A ‘March Chemistry Madness’ program brought over seventy 5th-7th grade students to campus for demonstrations and activities from 10 different elementary and middle schools in Harlem, Queens, and Upper West Side.
• The PhD for a Day program brought 50 students to the Columbia campus from Children’s Zone Promise Academy 2 for a two-day event featuring hands-on demonstrations and tours.
• A ‘Spring into Science’ program brought two seventh grade science classes (65 students) from Booker T. Washington (MS54) to engage in hands-on demonstrations and tours.
• A joint program with the Cornell MRSEC hosted 70 teachers from local schools for a one-day workshop on STEM education, with hands-on demonstrations and lesson plans; and gave in-classroom demonstrations at Harlem Promise Academy.
• PAS³ researchers co-taught a high school class in nanofabrication.
• PAS³ faculty have completed a major restructuring of the Columbia undergraduate Materials Science curriculum.

Key Diversity accomplishments
• Diversity within the REU program was improved through partnerships and targeted outreach to HBCUs.
• One new female PI was brought into the center as a seed participant.
• MRSEC fellows Alexandria Velian and Rebeca Ribero have accepted faculty offers.
• Bridge-to-PhD fellow Kursti DeLello played a key role in development of the rotation technique for heterostructures (see IRG 1 highlights).

Key Industrial / National Labs accomplishments
• Two MRSEC-affiliated projects were supported by Honda Research.
• A joint project with Army Research Lab was awarded funding and will support one ARL postdoc who will travel to Columbia for collaborations.

Key International accomplishments
• Director Hone, with a team at Sungkyungkwan Univeristy (Korea), was awarded a Global Research Laboratory grant. This has funded work on projects related to IRG1.
• Patrick Batail (University of Angers) spent 6 months at Columbia and played a key role in developing new techniques for superatom assembly by electro-polymerization (see IRG2 highlight).

Key Shared Facilities accomplishments
• The CUNY ASRC cleanroom and electron microscopy facilities are operational and have been used extensively by PAS³ researchers from both CCNY and Columbia.
• The Columbia nanofabrication cleanroom is in the final stages of tool installation.
• Two new SEM systems have been installed and are operational.
• The ‘central stacking facility’ is extensively used and has been upgraded with ‘auto-finder’ systems and improvements to the Raman spectrometer.
• A physisorption analyzer has been installed in the shared materials characterization lab.
• New crystal growth facilities have been installed and are in heavy use.
• A new laser ARPES system has been assembled and is generating the first data.
• A new closed-cycle 14T magnet cryostat will be delivered in June and a closed-cycle optical cryostat has been ordered.
### 2. List of Center Participants

<table>
<thead>
<tr>
<th>Faculty Rank / Equivalent</th>
<th>Receiving Center Support</th>
<th>Affiliated, No Center Support</th>
<th>User of Shared Center Facilities</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>COLUMBIA CHEMISTRY</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Louis Brus</td>
<td>Professor</td>
<td>X</td>
<td></td>
</tr>
<tr>
<td>Luis Campos</td>
<td>Assistant Professor</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>Ann McDermott</td>
<td>Professor</td>
<td>X</td>
<td></td>
</tr>
<tr>
<td>Colin Nuckolls</td>
<td>Professor</td>
<td>X</td>
<td></td>
</tr>
<tr>
<td>Jonathan Owen</td>
<td>Associate Professor</td>
<td>X</td>
<td></td>
</tr>
<tr>
<td>David Reichman</td>
<td>Professor</td>
<td>X</td>
<td></td>
</tr>
<tr>
<td>Xavier Roy</td>
<td>Assistant Professor</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>Michael Steigerwald</td>
<td>Assoc. Research Scientist</td>
<td>X</td>
<td></td>
</tr>
<tr>
<td>Xiaoyang Zhu</td>
<td>Professor</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td><strong>CCNY CHEMISTRY</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Maria Tamargo</td>
<td>Professor</td>
<td>X</td>
<td></td>
</tr>
<tr>
<td><strong>FIT CHEMISTRY</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Theanne Schiros</td>
<td>Assistant Professor</td>
<td>X</td>
<td></td>
</tr>
<tr>
<td><strong>ULI CHEMISTRY</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Wayne Archibald</td>
<td>Assistant Professor</td>
<td>X</td>
<td></td>
</tr>
<tr>
<td><strong>BARNARD CHEMISTRY</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Andrew Crowther</td>
<td>Assistant Professor</td>
<td>X</td>
<td></td>
</tr>
<tr>
<td><strong>COLUMBIA ELEC. ENG.</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ioannis Kymissis</td>
<td>Associate Professor</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td><strong>COLUMBIA MECH. ENG.</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>James Hone</td>
<td>Professor</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td><strong>COLUMBIA APPLIED PHYSICS &amp; APPLIED MATH</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Katayun Barmak</td>
<td>Professor</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>Simon Billinge</td>
<td>Professor</td>
<td>X</td>
<td></td>
</tr>
<tr>
<td>Irving Herman</td>
<td>Professor</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>Chris Marianetti</td>
<td>Associate Professor</td>
<td>X</td>
<td></td>
</tr>
<tr>
<td>Latha Venkataraman</td>
<td>Associate Professor</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>Yuan Yang</td>
<td>Assistant Professor</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td><strong>COLUMBIA PHYSICS</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cory Dean</td>
<td>Assistant Professor</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>Andrew Millis</td>
<td>Professor</td>
<td>X</td>
<td></td>
</tr>
<tr>
<td>Abhay Pasupathy</td>
<td>Associate Professor</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td><strong>CCNY PHYSICS</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Lia Krusin-Elbaum</td>
<td>Professor</td>
<td>X</td>
<td></td>
</tr>
<tr>
<td>Vadim Ogenesyan</td>
<td>Associate Professor</td>
<td>X</td>
<td></td>
</tr>
<tr>
<td>Elisa Riedo</td>
<td>Professor</td>
<td>X</td>
<td></td>
</tr>
<tr>
<td>Vinod Menon</td>
<td>Professor</td>
<td>X</td>
<td></td>
</tr>
<tr>
<td><strong>HARVARD PHYSICS</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Philip Kim</td>
<td>Professor</td>
<td>X</td>
<td></td>
</tr>
<tr>
<td><strong>STANFORD PHYSICS</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tony Heinz</td>
<td>Professor</td>
<td>X</td>
<td></td>
</tr>
<tr>
<td><strong>COLUMBIA CHEM. ENG.</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dan Esposito</td>
<td>Assistant Professor</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td><strong>EDUCATION</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Emily Ford</td>
<td>Director of Outreach</td>
<td>X</td>
<td></td>
</tr>
<tr>
<td>Susan Lowes</td>
<td>Director of Research and Evaluation</td>
<td>X</td>
<td></td>
</tr>
<tr>
<td><strong>SHARED FACILITIES</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dan Paley</td>
<td>Sr. Staff Associate</td>
<td>X</td>
<td></td>
</tr>
</tbody>
</table>
### Center Collaborators

<table>
<thead>
<tr>
<th>Collaborator</th>
<th>Institution</th>
<th>E-mail</th>
<th>Area of Expertise</th>
<th>IRG # or Seed Association</th>
<th>User of Shared Facilities</th>
</tr>
</thead>
<tbody>
<tr>
<td>Shaffique Adam</td>
<td>National University of Singapore</td>
<td><a href="mailto:Shaffique.adam@yale-nus.edu.sg">Shaffique.adam@yale-nus.edu.sg</a></td>
<td>Materials theory</td>
<td>IRG1</td>
<td>No</td>
</tr>
<tr>
<td>Dimitri Basov</td>
<td>Columbia University</td>
<td><a href="mailto:db3056@columbia.edu">db3056@columbia.edu</a></td>
<td>Plasmons in graphene</td>
<td>IRG1</td>
<td>No</td>
</tr>
<tr>
<td>Andrei Bernevig</td>
<td>Princeton University</td>
<td><a href="mailto:bernevig@princeton.edu">bernevig@princeton.edu</a></td>
<td>Materials theory</td>
<td>IRG1</td>
<td>No</td>
</tr>
<tr>
<td>Peter Boggild</td>
<td>TU Denmark</td>
<td><a href="mailto:Peter.boggild@nanotech.dtu.dk">Peter.boggild@nanotech.dtu.dk</a></td>
<td>2D materials</td>
<td>IRG1</td>
<td>No</td>
</tr>
<tr>
<td>Robert Cava</td>
<td>Princeton University</td>
<td><a href="mailto:cava@princeton.edu">cava@princeton.edu</a></td>
<td>2D crystals</td>
<td>IRG1</td>
<td>No</td>
</tr>
<tr>
<td>Julien Chaste</td>
<td>Univ. Paris-Saclay</td>
<td><a href="mailto:julien.chaste@lpn.cnrs.fr">julien.chaste@lpn.cnrs.fr</a></td>
<td>Nanomechanics</td>
<td>IRG1</td>
<td>No</td>
</tr>
<tr>
<td>Andrey Chaves</td>
<td>Universidade Federal do Ceará</td>
<td><a href="mailto:Andrey@fisica.ufc.br">Andrey@fisica.ufc.br</a></td>
<td>Materials theory</td>
<td>IRG1</td>
<td>No</td>
</tr>
<tr>
<td>Ching-Tzu Chen</td>
<td>IBM</td>
<td><a href="mailto:cchen3@us.ibm.com">cchen3@us.ibm.com</a></td>
<td>Magnetic phenomena</td>
<td>IRG 1</td>
<td>No</td>
</tr>
<tr>
<td>Heon-Jin Choi</td>
<td>Yonsei University (Korea)</td>
<td><a href="mailto:hjc@yonsei.ac.kr">hjc@yonsei.ac.kr</a></td>
<td>2D materials synthesis</td>
<td>IRG1</td>
<td>Yes</td>
</tr>
<tr>
<td>Mircea Cotlet</td>
<td>Brookhaven National Laboratory</td>
<td><a href="mailto:cotlet@bnl.gov">cotlet@bnl.gov</a></td>
<td>Optical spectroscopy</td>
<td>IRG1</td>
<td>No</td>
</tr>
<tr>
<td>Sang-Wook Cheong</td>
<td>Rutgers University</td>
<td><a href="mailto:sangc@physics.rutgers.edu">sangc@physics.rutgers.edu</a></td>
<td>Crystal growth</td>
<td>IRG1</td>
<td>No</td>
</tr>
<tr>
<td>Madan Dubey</td>
<td>Army Research Laboratory</td>
<td><a href="mailto:Madan.dubey.civ@mail.mil">Madan.dubey.civ@mail.mil</a></td>
<td>2D material devices</td>
<td>IRG1</td>
<td>No</td>
</tr>
<tr>
<td>Artur Erbe</td>
<td>Helmholtz Center</td>
<td><a href="mailto:a.erbe@hzdr.de">a.erbe@hzdr.de</a></td>
<td>Transport in Nanostructures</td>
<td>IRG1</td>
<td>No</td>
</tr>
<tr>
<td>Michael Fuhrer</td>
<td>Monash University</td>
<td><a href="mailto:Michael.fuhrer@monash.edu">Michael.fuhrer@monash.edu</a></td>
<td>2D material transport</td>
<td>IRG1</td>
<td>No</td>
</tr>
<tr>
<td>Genda Gu</td>
<td>Brookhaven Nat. Lab.</td>
<td><a href="mailto:ggu@bnl.gov">ggu@bnl.gov</a></td>
<td>2D crystals</td>
<td>IRG1</td>
<td>No</td>
</tr>
<tr>
<td>Jim Hannon</td>
<td>IBM</td>
<td><a href="mailto:jbhannon@us.ibm.com">jbhannon@us.ibm.com</a></td>
<td>Surface chemistry</td>
<td>IRG 1</td>
<td>No</td>
</tr>
<tr>
<td>Avetik Harutyunyan</td>
<td>Honda</td>
<td><a href="mailto:AHarutyunyan@oh.hra.com">AHarutyunyan@oh.hra.com</a></td>
<td>Materials</td>
<td>IRG1</td>
<td>No</td>
</tr>
<tr>
<td>Ulrich Hoefer</td>
<td>Philipps-Universität Marburg</td>
<td><a href="mailto:hoefer@physik.uni-marburg.de">hoefer@physik.uni-marburg.de</a></td>
<td>Optical Spectroscopy</td>
<td>IRG1 and 2</td>
<td>No</td>
</tr>
<tr>
<td>Shuang Jia</td>
<td>Peking University</td>
<td><a href="mailto:gwljiashuang@pku.edu.cn">gwljiashuang@pku.edu.cn</a></td>
<td>2D crystals</td>
<td>IRG1</td>
<td>No</td>
</tr>
<tr>
<td>Changqing Jin</td>
<td>The Institute of Physics, Chinese Academy of Sciences</td>
<td><a href="mailto:jin@iphy.ac.cn">jin@iphy.ac.cn</a></td>
<td>2D crystals</td>
<td>IRG1</td>
<td>No</td>
</tr>
<tr>
<td>Kyung-nam Kang</td>
<td>Steven Institute of Technology</td>
<td><a href="mailto:kkang@stevens.edu">kkang@stevens.edu</a></td>
<td>CVD TMD Growth</td>
<td>IRG1</td>
<td>No</td>
</tr>
<tr>
<td>Name</td>
<td>Affiliation</td>
<td>Email</td>
<td>Research Focus</td>
<td>IRG</td>
<td>Involvement</td>
</tr>
<tr>
<td>-----------------------</td>
<td>-----------------------------------------------------------------------------</td>
<td>------------------------------</td>
<td>-----------------------------------</td>
<td>-----</td>
<td>-------------</td>
</tr>
<tr>
<td>Gil-Ho Kim</td>
<td>Sungkyunkwan University, Korea</td>
<td><a href="mailto:ghkim@skku.edu">ghkim@skku.edu</a></td>
<td>2D device integration</td>
<td>IRG1</td>
<td>No</td>
</tr>
<tr>
<td>Martin Koch</td>
<td>Philipps-Universität Marburg</td>
<td><a href="mailto:Martin.koch@physik.uni-marburg.de">Martin.koch@physik.uni-marburg.de</a></td>
<td>Optical Spectroscopy</td>
<td>IRG1</td>
<td>No</td>
</tr>
<tr>
<td>Nikil Koratkar</td>
<td>Rensselaer Polytechnic Institute</td>
<td><a href="mailto:koratn@rpi.edu">koratn@rpi.edu</a></td>
<td>2D material synthesis</td>
<td>IRG1</td>
<td>No</td>
</tr>
<tr>
<td>Tobias Korn</td>
<td>Universität Regensburg</td>
<td><a href="mailto:tobias.korn@physik.uni-regensburg.de">tobias.korn@physik.uni-regensburg.de</a></td>
<td>Magneto-optics</td>
<td>IRG1</td>
<td>No</td>
</tr>
<tr>
<td>Lena Kourkoutis</td>
<td>Cornell University</td>
<td><a href="mailto:lena.f.kourkoutis@cornell.edu">lena.f.kourkoutis@cornell.edu</a></td>
<td>TEM</td>
<td>IRG1</td>
<td>No</td>
</tr>
<tr>
<td>Changgu Lee</td>
<td>Sungkyunkwan University, Korea</td>
<td><a href="mailto:peterlee@skku.edu">peterlee@skku.edu</a></td>
<td>Low-T growth of TMDs</td>
<td>IRG1</td>
<td>No</td>
</tr>
<tr>
<td>Chul-Ho Lee</td>
<td>Korea University (Korea)</td>
<td><a href="mailto:chlee80@korea.ac.kr">chlee80@korea.ac.kr</a></td>
<td>2D device integration</td>
<td>IRG1</td>
<td>No</td>
</tr>
<tr>
<td>Gwan-Hyoung Lee</td>
<td>Yonsei University (Korea)</td>
<td><a href="mailto:gwanlee@yonsei.ac.kr">gwanlee@yonsei.ac.kr</a></td>
<td>2D device integration</td>
<td>IRG1</td>
<td>No</td>
</tr>
<tr>
<td>Jian Li</td>
<td>Princeton University &amp; Westlake Institute of Advanced Study (China)</td>
<td><a href="mailto:jl29@princeton.edu">jl29@princeton.edu</a></td>
<td>Materials theory</td>
<td>IRG1</td>
<td>No</td>
</tr>
<tr>
<td>Tony Low</td>
<td>University of Minnesota</td>
<td><a href="mailto:tlow@umn.edu">tlow@umn.edu</a></td>
<td>Transport theory</td>
<td>IRG1</td>
<td>No</td>
</tr>
<tr>
<td>David Mandrus</td>
<td>Oak Ridge National Lab/ University of Tennessee</td>
<td><a href="mailto:dmandrus@utk.edu">dmandrus@utk.edu</a></td>
<td>2D materials synthesis</td>
<td>IRG1</td>
<td>No</td>
</tr>
<tr>
<td>Michael McGuire</td>
<td>Oak Ridge National Lab</td>
<td><a href="mailto:mcguirema@ornl.gov">mcguirema@ornl.gov</a></td>
<td>2D materials synthesis</td>
<td>IRG1</td>
<td>No</td>
</tr>
<tr>
<td>Dennis Norlund</td>
<td>SLAC National Accelerator Laboratory</td>
<td><a href="mailto:dennisnordlund@slac.stanford.edu">dennisnordlund@slac.stanford.edu</a></td>
<td>X-ray spectroscopy, ultra-fast spectroscopy, instrumentation</td>
<td>IRG1</td>
<td>No</td>
</tr>
<tr>
<td>Jens Nørskov</td>
<td>Stanford</td>
<td><a href="mailto:norskov@stanford.edu">norskov@stanford.edu</a></td>
<td>DFT</td>
<td>IRG1</td>
<td>No</td>
</tr>
<tr>
<td>Junichi Okamoto</td>
<td>University of Hamburg</td>
<td><a href="mailto:okamoto.junichi@physnet.uni-hamburg.de">okamoto.junichi@physnet.uni-hamburg.de</a></td>
<td>Theory</td>
<td>IRG1</td>
<td>No</td>
</tr>
<tr>
<td>Jiwoong Park</td>
<td>Cornell University</td>
<td><a href="mailto:jp275@cornell.edu">jp275@cornell.edu</a></td>
<td>CVD synthesis</td>
<td>IRG1</td>
<td>No</td>
</tr>
<tr>
<td>Kyungwha Park</td>
<td>Virginia Tech</td>
<td><a href="mailto:kyungwha@vt.edu">kyungwha@vt.edu</a></td>
<td>DFT- theory</td>
<td>IRG1</td>
<td>No</td>
</tr>
<tr>
<td>Arash Rahimi-Iman</td>
<td>Philipps-Universität Marburg</td>
<td><a href="mailto:arash.rahimi-iman@physik.uni-marburg.de">arash.rahimi-iman@physik.uni-marburg.de</a></td>
<td>Optical Spectroscopy</td>
<td>IRG1</td>
<td>No</td>
</tr>
<tr>
<td>Simone Raoux</td>
<td>Helmholtz-Zentrum Berlin für Materialien</td>
<td><a href="mailto:simone.raoux@helmholtz-berlin.de">simone.raoux@helmholtz-berlin.de</a></td>
<td>Heterostructures of topological vdW materials</td>
<td>IRG1</td>
<td>No</td>
</tr>
<tr>
<td>Name</td>
<td>Institution/University</td>
<td>Email</td>
<td>Research Area</td>
<td>IRG</td>
<td>Notes</td>
</tr>
<tr>
<td>-----------------------</td>
<td>---------------------------------------</td>
<td>------------------------------</td>
<td>----------------------------------------------------</td>
<td>-----</td>
<td>-------</td>
</tr>
<tr>
<td>Frances Ross</td>
<td>IBM</td>
<td><a href="mailto:fmross@us.ibm.com">fmross@us.ibm.com</a></td>
<td>In situ SEM / transport measurements</td>
<td>IRG1</td>
<td>No</td>
</tr>
<tr>
<td>Elton Santos</td>
<td>Queens University Belfast</td>
<td><a href="mailto:e.santos@qub.ac.uk">e.santos@qub.ac.uk</a></td>
<td>Materials theory</td>
<td>IRG1</td>
<td>No</td>
</tr>
<tr>
<td>Takayoshi Sasaki</td>
<td>NIMS, Japan</td>
<td>SASAKI.Takayoshinims.go.jp</td>
<td>Synthesis of layered high-k oxides</td>
<td>IRG1</td>
<td>No</td>
</tr>
<tr>
<td>Christain Schuller</td>
<td>Universität Regensburg</td>
<td><a href="mailto:christian.schueller@physik.uni-regensburg.de">christian.schueller@physik.uni-regensburg.de</a></td>
<td>Magneto-optics</td>
<td>IRG1</td>
<td>No</td>
</tr>
<tr>
<td>Matthew Sfeir</td>
<td>Brookhaven National Laboratory</td>
<td><a href="mailto:msfeir@bnl.gov">msfeir@bnl.gov</a></td>
<td>Femtosecond Spectroscopy</td>
<td>IRG1</td>
<td>No</td>
</tr>
<tr>
<td>Paul Sheehan</td>
<td>Naval Research Laboratory</td>
<td><a href="mailto:sheehan@nrl.navy.mil">sheehan@nrl.navy.mil</a></td>
<td>Surface chemistry</td>
<td>IRG1</td>
<td>No</td>
</tr>
<tr>
<td>Stefan Strauf</td>
<td>Steven Institute of Technology</td>
<td><a href="mailto:strauf@stevens.edu">strauf@stevens.edu</a></td>
<td>Optics</td>
<td>IRG1</td>
<td>No</td>
</tr>
<tr>
<td>Yuping Sun</td>
<td>Institute of Solid State Physics, Chinese Academy of Sciences</td>
<td><a href="mailto:ypsun@issp.ac.cn">ypsun@issp.ac.cn</a></td>
<td>2D crystals</td>
<td>IRG1</td>
<td>No</td>
</tr>
<tr>
<td>Takashi Taniguchi</td>
<td>NIMS, Japan</td>
<td>TANIGUCHI.Takashinims.go.jp</td>
<td>BN single-crystal synthesis</td>
<td>IRG1</td>
<td>No</td>
</tr>
<tr>
<td>John Toland</td>
<td>LaGuardia Community College</td>
<td><a href="mailto:jtoland@lagcc.cuny.edu">jtoland@lagcc.cuny.edu</a></td>
<td>Physics</td>
<td>IRG1</td>
<td>No</td>
</tr>
<tr>
<td>Kenji Watanabe</td>
<td>NIMS, Japan</td>
<td>WATANABE.Kenji.AMLnims.go.jp</td>
<td>BN single-crystal synthesis</td>
<td>IRG1</td>
<td>No</td>
</tr>
<tr>
<td>Eui-Hyeok Yang</td>
<td>Steven Institute of Technology</td>
<td><a href="mailto:eyang@stevens.edu">eyang@stevens.edu</a></td>
<td>2D materials synthesis</td>
<td>IRG1</td>
<td>No</td>
</tr>
<tr>
<td>Won Jong Yoo</td>
<td>Sungkyunkwan University, Korea</td>
<td><a href="mailto:yoowj@skku.edu">yoowj@skku.edu</a></td>
<td>Flexible electronics and tunneling memory</td>
<td>IRG1</td>
<td>No</td>
</tr>
<tr>
<td>Patrick Batali</td>
<td>Univ. Angers</td>
<td><a href="mailto:Patrick.batali@gmail.com">Patrick.batali@gmail.com</a></td>
<td>Superatom assembly</td>
<td>IRG2</td>
<td>No</td>
</tr>
<tr>
<td>Yu-Sheng Chen</td>
<td>University of Chicago, ChemMatCARS Argonne National Labs</td>
<td><a href="mailto:yscchen@cars.uchicago.edu">yscchen@cars.uchicago.edu</a></td>
<td>Crystallography</td>
<td>IRG2</td>
<td>No</td>
</tr>
<tr>
<td>John Hill</td>
<td>Brookhaven National Laboratory</td>
<td><a href="mailto:hill@bnl.gov">hill@bnl.gov</a></td>
<td>Resonant X-ray scattering</td>
<td>IRG2</td>
<td>No</td>
</tr>
<tr>
<td>Mark Hybertsen</td>
<td>Brookhaven National Laboratory</td>
<td><a href="mailto:mhyberts@bnl.gov">mhyberts@bnl.gov</a></td>
<td>Theory</td>
<td>IRG2</td>
<td>No</td>
</tr>
<tr>
<td>Jonathan Malen</td>
<td>Carnegie Mellon University</td>
<td><a href="mailto:jonmalen@andrew.cmu.edu">jonmalen@andrew.cmu.edu</a></td>
<td>Thermoelectrics</td>
<td>IRG2</td>
<td>No</td>
</tr>
<tr>
<td>Name</td>
<td>Institution</td>
<td>Email</td>
<td>Research Area</td>
<td>IRG</td>
<td>Year</td>
</tr>
<tr>
<td>-----------------------</td>
<td>---------------------------</td>
<td>------------------------------</td>
<td>-----------------------------------</td>
<td>-----</td>
<td>------</td>
</tr>
<tr>
<td>Alan McGaughey</td>
<td>Carnegie Mellon University</td>
<td><a href="mailto:mcgaughey@cmu.edu">mcgaughey@cmu.edu</a></td>
<td>Thermoelectrics</td>
<td>IRG2</td>
<td>No</td>
</tr>
<tr>
<td>Timothy Mueller</td>
<td>DuPont</td>
<td><a href="mailto:Timothy.E.Mueller@dupont.com">Timothy.E.Mueller@dupont.com</a></td>
<td>Interfacial modeling and design</td>
<td>IRG2</td>
<td>No</td>
</tr>
<tr>
<td>James Misewich</td>
<td>Brookhaven Nat. Lab</td>
<td><a href="mailto:misewich@bnl.gov">misewich@bnl.gov</a></td>
<td>Electronic phase transitions</td>
<td>IRG2</td>
<td>No</td>
</tr>
<tr>
<td>Eric Stach</td>
<td>Brookhaven Nat. Lab</td>
<td><a href="mailto:estach@bnl.gov">estach@bnl.gov</a></td>
<td>Electron microscopy</td>
<td>IRG1 and 2</td>
<td>No</td>
</tr>
<tr>
<td>George Tulevski</td>
<td>IBM</td>
<td><a href="mailto:gstulevs@us.ibm.com">gstulevs@us.ibm.com</a></td>
<td>Transport and electrical devices</td>
<td>IRG2</td>
<td>No</td>
</tr>
</tbody>
</table>
4. Strategic Plan

The Center for Precision Assembly of Superstratic and Superatomic Solids (PAS$^3$), led by Columbia University in partnership with City University of New York (CCNY, College of Staten Island, Fashion Institute of Technology), Barnard College, Harvard, Stanford, and the University of the Virgin Islands, encompasses two research IRGs around the theme of building higher dimensional materials from lower dimensional structures. Both IRGs bring together researchers with diverse capabilities toward collaborative, interdisciplinary materials research. The MRSEC seeks to: establish and manage effective shared materials synthesis / characterization facilities; establish partnerships with national labs, industry, and international institutions; promote K-12 STEM education; provide broad opportunities for undergraduate research; improve undergraduate and graduate materials education; and increase the participation of underrepresented groups in STEM and materials research.

The research, education, and diversity goals detailed below are based on those initially described in the MRSEC proposal, and have been refined by the PAS$^3$ executive committee in consultation with center members and the external advisory board. The major mechanism for development and modification of these goals is an annual off-site retreat in May, in which all aspects of PAS$^3$ operation are discussed. In addition, the education/human resources/diversity committee is responsible for proposing changes to goals in these areas. An annual review process is the major mechanism for evaluating progress to research goals, and PI contributions toward all center goals. This review is coupled with annual funding allocations.

Research goals

IRG1 (Heterostructures of van der Waals Materials) investigates materials and structures created by combining two-dimensional van der Waals materials into pristine layered heterostructures. The IRG is focusing on two classes of materials: 2D semiconductors and metals/complex materials. In both classes of materials, the IRG team focuses on foundational work in material synthesis, characterization, assembly, and contacts. These techniques are then used to study behavior of single materials in the clean limit, including electrical transport and optical properties; and to assemble heterostructures in which new phenomena emerge. In 2D semiconductors, the ultimate goals are to achieve quantum transport in single materials, and observe/understand new phenomena such as charge transfer excitons and exciton condensates in multi-layer structures. In 2D metals/complex materials, the goals are to examine scaling of complex behavior to the 2D limit, to achieve intrinsic limits in topological materials, and to study new emergent phenomena at interfaces.

IRG2 seeks to assemble superatoms into new classes of functional materials using precisely defined clusters assembled through new forms of inter-cluster chemical bonding. With this approach, we aim to produce entirely new families of materials, offering the attractive proposition of encoding desirable physical properties in the building blocks with exquisite control of inter-superatom interaction to create materials with tunable and multiple functionalities. Within this context, we will continue to explore these systems to create materials for thermoelectrics, materials that have an interplay between magnetism and electrical conductivity, and materials that have emergent phase transitions. To achieve this goal, we will continue to couple theory and synthesis tightly to design and create new types of superatoms and assemblies thereof with tailored properties.

A few areas have emerged that link the two IRGs. These include superatom-assembled 2D fullerene sheets that can be exfoliated and processed like common layered van der Waals solids; and the use of superatoms for doping 2D materials.

PAS$^3$ seeks to meet these research goals by funding researchers, and fostering collaborative efforts through regular meetings, seminars and related activities. Progress is monitored informally by discussion at meetings, and formally by annual reports submitted as part of PI funding requests.
5. Research Accomplishments and Plans

IRG 1: Heterostructures of van der Waals Materials

Archibald (UVI), Barmak (CU), Dean (CU), Esposito (CU), Heinz (Stanford), Herman (CU), Hone (CU), Kim (Harvard), Krusin-Elbaum (CUNY), Marianetti (CU), Menon (CUNY), Ogeneyan (CUNY), Pasupathy (CU), Riedo (CUNY), Schiros (FIT), Tamargo (CUNY), Zhu (CU) focus on the study of layered van der Waals heterostructures created by stacking of two-dimensional (2D) materials, which include semiconductors (chiefly transition metal dichalcogenides - TMDs) and metals (graphene, metallic TMDs, and topological insulators - TIs). Hexagonal boron nitride (hBN) is a low-disorder dielectric and encapsulant. The goals of IRG 1 are to: study individual 2D materials in the ultraclean limit; understand interactions between 2D materials; and study new emergent properties at interfaces. Below progress toward these goals is divided into three areas: foundations; novel phenomena in 2D; and interfacial phenomena.


The IRG1 team has focused on building the technical foundation required for creation of high-quality heterostructures, including materials synthesis and characterization, doping, and contacts. Specific progress includes an integrated synthesis and characterization program which has produced much higher quality starting materials; control of photoluminescence linewidth and yield TMDs; and elucidation of the unusual structure of Cl-doped graphene and TMDs. Continued efforts in synthesis of topological materials have yielded progress in complex heterostructures and doping control of magnetic TIs. The team has made major breakthroughs in understanding of contacts to 2D semiconductors and improved Ohmic contacts.

STM characterization of defects in TMDs. Pasupathy used STM to study defects in transition metal dichalcogenides (TMDs), in bulk crystals cleaved in UHV. Two dominant defect types are found: metal substituents, in which the transition metal takes the place of the chalcogen (Fig. 1A), and metal vacancies (Fig. 1B); chalcogen vacancies are rare. Scanning tunneling spectroscopy (STS) reveals the mid-gap donor states in both cases: metal substituents act as electron donors, and vacancies as acceptors. The defects are extremely 'bright' in STM, allowing identification of defects by large-area imaging.

Synthesis and characterization of high purity TMDs. STM imaging reveals that commercially produced TMDs made by the chemical vapor transport (CVT) technique are highly defective. Hone and Barmak have utilized a flux-growth technique to grow single crystals of (Mo,W)Se₂ and (Mo,W)Te₂. Pasupathy used STM to show over 100-fold reduction in defect density compared to commercial material (Fig. 1C,D). The IRG1 team is using multiple techniques to correlate defect type and density to bulk properties: optical spectroscopy (Zhu, Heinz); TEM (Barmak); and electrical transport (Hone, Dean, Kim). For example, flux-grown MoSe₂ shows 100X improvement in photoluminescence intensity.

Figure 1. STM images of Mo substituents (A) and Mo vacancies (B) in MoSe₂, with the corresponding donor and acceptor states seen in scanning tunneling spectra (STS). (C,D) Large-area images of CVT-grown and flux-grown WSe₂ allow measurement of defect density.

Figure 2. (A) Schematic of ZnCdSe/ZnCdMgSe MQW structure grown on Bi₂Se₃/CdTe virtual substrate. (B) Modification of Mn-doped Bi₂Te₃ by high energy electrons.
dissimilar crystal structures. DFT calculations were used to identify CdTe as a promising semiconducting layer, and XRD characterization showed dramatic improvement of the crystal quality vs. ZnCdSe on Bi$_2$Se$_3$. The Bi$_2$Se$_3$/CdTe can be used as a virtual substrate for growth of multiple quantum well heterostructures, which can be removed from the substrate through exfoliation. Krusin has previously demonstrated that irradiation of topological materials such as Bi$_2$Te$_3$ with 2.5 MeV electron beams can tune the Fermi level $E_F$ across the bulk gap. This has recently been extended to magnetically doped topological insulators, to tune the anomalous Hall effect (AHE) (Fig. 2B). The $p$-type crystals converted to $n$-type but no trace of AHE was detected. In contrast, $n$-type materials showed hysteretic anomalous Hall resistance; after irradiation, charge density decreased and zero-field Hall signal increased.

Photoluminescence linewidth and intensity in TMDCs. Zhu, Hone, and Heinz, with collaborator Strauf, investigated the effects of BN encapsulation and SiO$_2$ passivation on the photoluminescence (PL) spectrum of monolayer MoSe$_2$. Detailed lineshape analysis indicates that the measured PL linewidth of ~2 meV approaches the homogeneous limit. In parallel, Zhu investigated screening of charged defects in MoS$_2$ monolayers by an ionic liquid (IL). Screening leads to an increase in photoluminescence (PL) yield by up to two-orders of magnitude, with enhancement correlating with the initial brightness. This suggests the existence of two classes of non-radiative recombination centers: charged defects that can be electrostatically screened by ILs, and neutral defects that are not.

2D magnets. Herman and Pasupathy obtained layered magnetic materials CrSiTe$_3$, CrI$_3$, and CrCl$_3$ from collaborator Mandrus and used Raman spectroscopy to study the stability of these materials, which have recently emerged as a new class of 2D ferromagnets and antiferromagnets. These materials can be incorporated into heterostructures, for example to induce spin-orbit coupling in graphene.

Chlorine-doped 2D materials. Schiros used x-ray spectroscopy techniques to understand the chemical composition and structure of graphene and MoS$_2$ treated with a chlorine plasma, which uniquely creates high doping while maintaining structural order. Spectra were analyzed with Archibald and students from UVI. Both materials show ~1 eV p-type work function shift and a well-defined bond geometry. However, the bond type and geometry are distinct on the two surfaces. Calculations by collaborator Santos suggest that chlorine is substitutionally incorporated in MoS$_2$, whereas in graphene chlorine adsorbs on top. Marianetti used DFT and a parametrized cluster expansion to compute the most energetically favorable configurations for Cl-graphene, which indicate a strong preference to occupy opposite vertices of the graphene hexagon, and a surprisingly strong preference to form one dimensional chains, which had been missed in the previous literature. Continued work on Cl-doping is being carried out in collaboration with Dubey.

STM imaging of MIGS in TMDCs. Pasupathy used UHV-STM to measure the atomic-scale energy band diagram of junctions between metals and monolayer MoS$_2$. The junctions show 2D metal induced gap states (MIGS) within the MoS$_2$ gap, which extend to ~2 nm from the interface. MIGS are seen for Au, Pd and graphite contacts, indicating that the presence of MIGS sets the ultimate limit for all types of direct metal contacts.
New metal contact techniques. **Kim** created Ohmic contacts to the valence band WSe$_2$ down to T = 1.4K using pre-patterned Pt electrodes, with work function characterized by XPS. **Hone** has demonstrated a new type of contact in which metal is embedded within hBN to create a ‘via’. This can then be used to pick up a 2D material and assemble a heterostructure, which is particularly useful for air-sensitive 2D materials since encapsulation and contacts are combined into a single step.

**Co/BN van der Waals bonded contacts to MoS$_2**. **Hone, Dean**, and **Kim** demonstrated low-T Ohmic contacts to the conduction band in monolayer MoS$_2$, in which monolayer hBN is used to strongly modify the work function of a transition metal (Co) and reduce metal-MoS$_2$ that causes Fermi level pinning. The contacts are superior to those achieved by other methods, and provide Ohmic contacts at low carrier density. **Hone** PhD student Alex Cui spent two months in the **Kim** lab to use a UHV evaporator and characterize the Co/BN work function.

2. **Novel Phenomena in 2D** Characterization of novel phenomena in 2D materials has benefitted from the foundational efforts above. Recent progress includes breakthroughs in understanding the low-T mobility and Landau Level spectrum of 2D semiconductors; exploring the phase space of 2D superconductors in detail, and studying phase transitions in topological Weyl metals. In topological materials, the team demonstrated the role of disorder-induced spin correlations on charge transport in Sb$_2$Te$_3$ and explored subsurface trap states in Bi$_2$Te$_2$Se. The catalytic activity of 2D semiconductors was studied by isolating edges from bulk.

Low-T mobility in TMDCs. **Kim** used Pt contacts to measure multi-terminal transport in commercially produced WSe$_2$ crystals chosen for bulk resistance. These show low-T mobility near 2000 cm$^2$/Vs, and lack an insulating phase near the band edge as has been seen for other 2D semiconductors.

**Mapping the Landau level spectrum in TMDCs**; **Zhu, Dean**, and **Hone** used a single electron transistor (SET) defined on top of a heterostructure to probe the electronic compressibility of flux-grown WSe$_2$. The SET method easily resolves large portions of the Landau Level spectrum for the first time. These measurements reveal a giant effective g-factor, and provide a quantitative measurement of the effective mass and single-particle band gap, which is larger than obtained from optical experiments. Commercially obtained WSe$_2$ showed dramatically lower-quality spectra due to higher defect density.

2D superconductivity **Dean, Pasupathy**, and **Hone**, with supplemental funding from **Honda**, are studying low-dimensional superconductivity in NbSe$_2$ using the PAS$^3$ glove box assembly system. The new via contact technique provides greater stability and uniform high quality, enabling expanded studies of the

![Figure 6](image_url) (A) Co/hBN contact schematic. (B) Measured contact resistance compared to other methods.

![Figure 7](image_url) Measured Landau level spectrum of WSe$_2$

![Figure 8](image_url) (A) Image and cross-section of NbSe$_2$ encapsulated by BN with via contacts (B) B-T phase diagram. (C) The KT transition with vortex binding energy follows a linear trend with layer number.
superconducting phase diagram that confirm that the quantum metal (Bose metal) phase persists down to the monolayer limit. Monolayers show extremely low critical magnetic fields (~60mT, pinning density ~3 \cdot 10^9 \text{cm}^{-2}), and strong correlation between layer number and vortex binding energy in the region of the KT transition.

Tuning topological Weyl behavior with temperature in 1T'-MoTe\textsubscript{2} Pasupathy, with collaborators Bernevig, Cheong and Li, performed temperature-dependent quasiparticle scattering measurements using scanning tunneling microscopy, to understand the relationship between its unique surface states (Fermi arcs) and the underlying topological character of the bulk material. By imaging while tuning across a structural phase transition from a topological to non-topological bulk state, it is possible to show that the topological and the trivial phases exhibit distinct quasiparticle scattering behaviors. 1T'-MoTe\textsubscript{2} is an ideal system in which to discriminate between trivial and topological electronic phenomena.

Spin memory effect in topological material under strong disorder. Krusin uncovered the dominant role of disorder-induced spin correlations on charge transport in Sb\textsubscript{2}Te\textsubscript{3} with a huge range of positional disorder. These measurements are the first to directly detect magnetic response from localized spins in the Anderson-localized state (Fermi glass), and show how localized spins control the hopping transport through spin memory induced by the nonequilibrium charge currents. Spin memory occupies a huge region in the field-temperature-disorder space, suggesting it can be tuned in materials with heavy elements by the addition of localized spins.

Subsurface traps in bulk-insulating ternary topological system Bi\textsubscript{2}Te\textsubscript{3}Se (BTS). Krusin used electrostatic gating of exfoliated BTS crystals with very low (~10^16/cc) carrier density to study BTS with and without Sn doping (Fig. 12). The undoped BTS shows asymmetric gating hysteresis, consistent with the subsurface trap states responsible for the exceptionally long (>4μs) optical lifetimes of Dirac fermions observed by fs-ARPES. The hysteresis can be manipulated by doping with small amounts (1%) of Sn and by cooling the system under applied gate voltage, equivalent to engineering a lifetime switch for photoexcited Dirac fermions.

Catalysis in vdW materials and edges. Esposito and Hone, with supplemental funding from Honda, are investigating MoS\textsubscript{2} and 2D heterostructures for catalysis in hydrogen evolution and CO\textsubscript{2} reduction, using a platform that isolates the edges in different crystallographic directions. Large-area films grown by CVD (from Honda Research Labs and from collaborator Lee) are used in order to generate sufficient product. Preliminary results show superior performance for the edge-isolated sample.

3. Interfacial Phenomena Notable progress in study and manipulation of interfacial phenomena includes: optical studies revealing large engineering of the bandgap of 2D semiconductors with dielectric environment and the role of momentum conservation in energy relaxation within 2D semiconductor heterojunctions; preliminary work on modification of 2D superconductivity is heterostructures; and a new platform for controlling interlayer rotation in heterostructures and are using it to study friction and formation of Moire’ patterns.

TMDC bandgap engineering. Heinz, Brus, Hone, Reichman and Nuckolls demonstrated that dielectric screening can strongly tune the quasiparticle bandgap and exciton binding energy of a 2D material, as probed by measuring the exciton states in optical reflectance contrast micro-spectroscopy. Monolayer WS\textsubscript{2} covered by graphene was measured to have a 150 meV lower bandgap compared to the

Figure 9. Spin-dependent transport in Sb\textsubscript{2}Te\textsubscript{3} under strong disorder. (a) Large negative isotropic magnetoresistance. (b) Flakes transferred onto custom on-chip Hall sensors, and measured magnetic moment (c). (d) H-T Phase diagram showing large range of conductance controlled by spin memory.

Figure 10. Electrocatalytic activity of MoS\textsubscript{2} edges for hydrogen evolution compared to a control sample without any edges.
uncovered region. The effect is highly localized on the nanoscale, as seen from the dependence of bandgap renormalization on the number of graphene layers.

2D heterostructure superconductivity Pasupathy, Dean, and Hone are studying the effects of placing a 2D semiconductor on a 2D superconductor in order to investigate the Ginzburg hypothesis, which suggests that excitonic coupling may enhance $T_c$ when the two material bandstructures are appropriately matched. Preliminary measurements show that the TMDC acts as a screening layer, screening the interaction between vortices in NbSe$_2$, such that the superconducting $T_c$ is unchanged but critical temperature at which vortex and anti-vortex pairs unbind (BKT transition) is lowered.

Inter-layer exciton dynamics. Zhu and Hone probed the role of momentum conservation in MoS$_2$ / WSe$_2$ monolayer heterostructures using femtosecond pump-probe spectroscopy. Upon photo-excitation of WSe$_2$, the measurements reveal ultrafast (<40 fs) electron transfer to MoS$_2$, independent of the angular alignment. The resulting interlayer charge transfer exciton decays via nonradiative recombination, with rates varying by up to three orders of magnitude from sample to sample. There is no correlation with interlayer angular alignment, suggesting that in these samples –commercially produced TMDCs on SiO$_2$ – defects rather than intrinsic momentum conservation dominate the recombination process.

Controlling rotation in heterostructures, MRSEC fellow Ribeiro, with Dean, has demonstrated a new technique for controllably changing rotation angle in heterostructures, in which a shaped top layer is rotated by pushing ‘handles’ with an AFM tip, allowing changes in rotation angle of less than 0.1 degrees. In graphene-hBN structures, the frictional force is seen to jump dramatically at commensurate angles. Transport measurements show controlled tuning of the graphene-BN moire’ pattern, as seen in the movement of satellite Dirac peaks.

Plans: The IRG 1 team will build on this work, with major goals to include:
- Continued refinement in synthesis of 2D semiconductor single crystals, combined with theory and characterization to understand the connection between defects and bulk properties.
- Final analysis of the structure of Cl-doped 2D materials and implementation in heterostructures.
- Building on the achievement of improved contacts to measure low-T transport and magnetotransport in high-quality 2D semiconductors.
- Measuring optical phenomena such as exciton dispersion in high-quality 2D semiconductors with narrow PL linewidth.
- Using the ‘via’ contact technique for electrical contact to TI crystals and films.
- Detailed studies of the inter-layer phenomena in 2D semiconductor heterostructures as a function of interlayer angle, implementing the ‘rotation’ technique.
- Exploration of modification of superconductivity through interfacial engineering.
- Generating the first conduction band ARPES spectra of monolayer TMDCs and other materials using laser ARPES, as a foundation for studying bandstructure evolution in multilayer heterostructures.
**IRG 2: Superatom Assembled Solids.**

Billinge (CU), Brus (CU), Campos (CU), Crowther (Barnard), Kim (Harvard), Kymissis (CU), McDermott (CU), Millis (CU), Nuckolls (CU), Owen (CU), Reichman (CU), Roy (CU), Steigerwald (CU), Venkataraman (CU), Yang (CU), Zhu (CU)

This has been an extremely productive year with numerous significant achievements. The progress of the interdisciplinary research in IRG 2 is divided into three main areas that have seen significant progress and accomplishments: (1) Building blocks to build superatom molecules and polymers. (2) Methods to control the dimensionality in superatom materials. This area has synergy with IRG 1 in studying exfoliatable materials and their properties. (3) Properties of superatomic crystals.

I. Superatomic building blocks

IRG 2 is designing and studying superatomic building blocks, focusing primarily on metal chalcogenide molecular clusters as they present many benefits, including stability allowing chemical manipulation, wide structural diversity, and tunable electronic and magnetic properties.

A. Fundamental building blocks

1. Creating and Coupling Superatomic Building Blocks. During the previous funding period Nuckolls, Roy, and Steigerwald developed a method to create Co₆Se₈ superatoms by programming the metal-ligand bonds. The Co₆Se₈ core is exclusively formed under simple reaction conditions with a facile separation of products that contain differential substitution of the core. The combination of Co₆(CO)₆ and PR₃ with excess Se gives the differentially and directionally substituted superatoms, Co₆Se₈(CO)₆(PR₃)₁₀. The CO groups on the superatom can be exchanged quantitatively with phosphines and isonitriles. Substitution of the CO allows us to manipulate the type and length of chemical bridge between two redox-active superatomic centers in order to modulate inter-superatomic coupling. Linking two superatoms together allows us to form the simplest superatom molecule: a di-atomic molecule. Nuckolls and Steigerwald extend the superatom molecule concept to link three superatoms together in a linear arrangement to form acyclic tri-atomic molecules. These superatom building blocks chart a clear path to a whole family of superatom molecules with new and unusual collective properties. These studies were published in Nano Letters and were highlighted in Scientific American as one of top ten scientific breakthroughs of 2016. These building blocks have enabled a large swath of materials in IRG 2.

Building off of the studies above Nuckolls and Steigerwald have created a new family of cyclic inorganic macromolecules with the chemical formula cis-[Co₆Se₈(PEt₃)₈(µ-(Ph₃P)₂X)]₂ (X = NH, CH₃, C≡C), featuring Co₆Se₈ superatoms bridged by two covalent ligands. These anisotropic inorganic macrocycles are assembled through the photocyclization of the corner piece building block cis-Co₆Se₈(PEt₃)₈(CO)₂ with the bridging covalent ligands (Ph₃P)₂X. Optical, electrochemical and spectroelectrochemical measurements reveal the two clusters are electronically coupled. The coupling occurs through two paths, one through the center of the macrocycle and another through the covalent linkers. By adjusting the covalent linkers, Nuckolls and Steigerwald can tune the two modes of electronic coupling. The strongest coupling between the two clusters occurs with the (Ph₃P)₂NH linkers.

The selective functionalization strategy described above was utilized to create a Co₆Se₈ superatom with a pendant phosphine norbornene monomer. Roy and Campos have performed ring opening metathesis polymerization (ROMP) using this monomer to synthesize superatom-containing homopolymers and block copolymers with high molecular weights and narrow polydispersities. These polymers can be spin coated on different substrates and calcined to create thin films of cobalt selenide. The incorporation of redox-active superatoms into well-defined polymeric systems opens the door to

![Figure 1](image_url)

**Figure 1.** Synthetic strategy to modify the cluster’s external ligand field environment. Ligand substitution of L in the cluster type [Co₆Se₈(L)(PEt₃)₈] for CO or PBu₃ produces an asymmetric or symmetric environment around the cluster core [Co₆Se₈], respectively.

---

[Image and caption description here]
the creation of hybrid materials that can self-assemble/disassemble by changing the charge state of the superatom.

2. Electron Cartography in Superatoms. Nuckolls, Roy, and Steigerwald are interested in understanding the electron distribution in superatoms. In collaboration with ANL, electron density distribution within the [Co₈Se₈] superatomic core has been investigated, demonstrating for the first time the reconfiguration of the electronic density upon changing the charge state. Deconvoluting the electron density distribution on an atom-individual basis remains a challenge for polynuclear systems. A multiple-wavelength anomalous diffraction study was performed on four superatoms sharing the same face-capped octahedral [Co₈Se₈] core. These were designed to contain a symmetric and asymmetric ligand sphere around [Co₈Se₈] (Figure 1). For the asymmetric species, or CO-bound, data shows the Co-CO site residing at a higher oxidation level relative to the other five Co atoms. Remarkably, removing an electron from this species induces hole delocalization in the Se atoms while the Co center valencies remain unchanged. By contrast, the electron density distribution of the symmetric species displays two sets of three cobalt atoms, each arranged in a meridional fashion in which one set exists at a higher valence than the other. Removing an electron from the symmetric system places the hole within the Co atoms, while the Se atoms remain unperturbed. This ligand-dependent tuning of the electron/hole distribution is directly relevant to how clusters in biological and synthetic systems perform their function.

3. Single superatom electronic devices. The design of nanoscale devices that combine multiple well-separated conductance states, room temperature operation, reproducible transport characteristics, and ease of implementation has been a key objective in the field of molecular electronics. In practice, the creation of such a functional device has proved to be a challenge. In this project, Venkataraman, Roy, Nuckolls, and Steigerwald describe a molecular single-electron transistor that meets these requirements. Each device is assembled by wiring a redox-active, atomically precise cobalt chalcogenide cluster between two nanoscopic electrodes using molecular connectors. Coulomb blockade-like behavior is observed at room temperature in thousands of single-cluster junctions, a consequence of the atomic precision, the small size, and the weak electronic coupling of the system. Below a threshold voltage, charge transfer across the junction is suppressed. The device is turned on when the temporary occupation of the core states by a transiting carrier is energetically enabled, resulting in a sequential tunneling process and an increase in current by a factor of ~600. These results provide a clear path to creating tunable single-electron transistors that function at room temperature through rational chemical design.

B. Strongly coupled building blocks

One of the main objectives in IRG2 is to develop methods to strongly couple superatom oligomers. To this end, Nuckolls, Roy, and Steigerwald have had a breakthrough in finding a reaction that fuses Co₈Se₈ superatoms together to form a strongly coupled Co₁₆Se₁₆ dimer. Additionally, the mono-carbonylated cluster Co₆Se₆(PET₃)₃(CO) reacts with trimethylsilyl-diazomethane to form a carbene-terminated superatom, Co₆Se₆(PET₃)₃(CHSiMe₃). This unusual species contains a Co-C-Se metallacycle that serves as a protecting group for the reactive Co-Se site. The carbene is labile.
and upon warming the carbene-terminated cluster fuses via two Co-Se bridges to form the desired dimer Co$_2$Se$_8$(PET$_3$)$_6$ (Figure 2c). Cyclic voltammetry (Figure 2d, 2e) of the fused dimer displays six well-separated one-electron events, which indicates the electrons are delocalized within the strongly coupled clusters. Remarkably, the HOMO-LUMO gap of the fused dimer (estimated from cyclic voltammetry) is smaller than that of the parent hexaphosphine species Co$_6$Se$_8$(PET$_3$)$_6$ (0.7 V versus 1.6 V). This reaction is particularly noteworthy because the conditions to create this important structure are mild and selective.

In related work on coupling clusters, the Owen Lab has developed an approach to link monomers of Co-carbonyl cluster together to form dimers and trimers (and potentially n-mer) in a controllable fashion. The ground state properties of these clusters change significantly as their length increases. Using DFT calculations, Owen, Reichman and Millis have produced reasonable agreement with experiments regarding the UV and IR spectra. Moreover, our calculations provide an understanding of how electronic states delocalize in the dimer and trimer cases. Such delocalization occurs because electron hopping across monomers is strong. This feature is important in the search for emergent collective properties in super-atomic solids.

II. Controlling dimensionality in superatom materials

In this second research thrust, IRG2 will explore the dimensionality of superatom materials. Through increased collaboration with IRG1, the exfoliatability of superatomic materials will be explored. Elucidating the properties of superatomic crystals in turn reveals new material applications in the next phase of this research program.

A. Superatom frameworks. Nuckolls and Steigerwald have devised a new method to functionalize electroactive superatoms with groups that can direct their assembly into covalent and non-covalent multi-dimensional frameworks. They synthesized Co$_6$Se$_8$[PET$_3$(4-C$_6$H$_4$COOH)]$_6$ and found that it forms a crystalline assembly. The solid-state structure is a three-dimensional network in which the carboxylic acids form inter-cluster hydrogen bonds. The self-assembly can be modified by replacing the reversible hydrogen bonds that hold the superatoms together with covalent zinc carboxylate bonds via solvothermal reaction of Co$_6$Se$_8$[PET$_3$(4-C$_6$H$_4$COOH)]$_6$ with Zn(NO$_3$)$_2$. Two types of crystalline frameworks result from this approach: one is a three-dimensional solid and the other consists of stacked layers of two-dimensional sheets. The dimensionality is controlled by subtle changes in reaction conditions. Remarkably, the two-dimensional sheets can be chemically exfoliated, and the exfoliated, ultrathin 2D frameworks are soluble. After depositing them on a substrate, they can be imaged. Additionally, once cast onto an electrode surface, they retain the redox activity of the superatom building blocks due to the porosity in the sheets.

B. Cloth. In creating polymeric versions of the superatoms Nuckolls, Steigerwald, and Batal found a general and simple route to assemble nanoscopic 2D woven structures reminiscent of the methods used to produce macroscopic textiles. The same principles used in macroscopic weaving can be applied on the nanoscale to create two-dimensional molecular cloth from polymeric strands, a molecular thread. The molecular thread is comprised of Co$_6$Se$_8$(PET$_3$)$_6$L$_2$ superatoms that can be bridged with L = benzene bis-1,4-isocyanide to form polymer strands. As the superatoms that make up the growing polymer chain (Figure 3A) are gradually electrochemically oxidized, the polymer chain is electrostatically templated by a nanoscale anion, the tetragonal Linqvist polyoxometallate Mo$_6$O$_{19}$$^-$.

Crossing points in the weave feature (Figure 3C) pi-stacking of the bridging bis-isocyanides. By examining the steps in the weaving process, the degree of polymerization at the crossing points is found.

**Figure 3.** (A) SCXRD of a woven structure. The triethyl phosphine groups and hydrogen atoms have been removed to clarify the view. (B) The temptation utilizes the 4-fold axis of Mo$_6$O$_{19}$$^-$. (C) Pi-to-pi interactions holding the strands in registry. (D) Side view of the crystal packing showing the cationic and anionic layers (a-axis).
to be crucial to cloth formation. Two-dimensional nanoscale cloth will provide access to a new generation of smart, multifunctional materials, coatings, and surfaces.

III. Properties and Applications of Superatomic Materials

A. Batteries. In this project, Yang, Roy, and Nuckolls are designing a new family of redox-tunable cathode materials from superatoms. This project uses the synthetic strategies developed in Sections II and III to assemble and covalently link preformed molecular clusters having tunable redox properties into mechanically robust and electronically coupled networks. The key feature of this approach is that the atomic precision and diversity of the building blocks allows us to very precisely design the characteristics of the cathode material.

Yang has created an electrode material by linking the superatom \([\text{Fe}_8\text{O}_4]\) with sulfide (S\(^2\)) bridges. To test the electrochemical properties of these materials, Yang built a composite electrode by mixing the ball milled compound with carbon black and PVdF in a N-methyl-2-pyrrolidone and depositing the resulting slurry onto an an aluminum substrate. This electrode is paired with Mg foil to form a half cell for battery testing. In the first discharge, a plateau at 0.7 V vs Mg\(^2+\)/Mg is observed, indicating electrochemical activity. The corresponding specific capacity is 60 mAh/g. In the following cycles, the sample shows a specific capacity of ~20 mAh/g. These results demonstrate that electroactive superatomic material are of great interest for battery electrode applications. Yang is developing this research thrust in collaboration with Roy based on these results.

B. Thermal and electrical transport in superatomic crystals In the search for rationally-assembled functional materials, superatomic crystals (SACs) have recently emerged as a unique class of compounds that combine programmable nanoscale building blocks and atomic precision. As such, they bridge traditional semiconductors, molecular solids, and nanocrystal arrays by combining their most attractive features. In this project, Roy and Malen performed the first study of thermal transport in SACs, a critical step towards their deployment as electronic, thermoelectric, and phononic materials. Using frequency domain thermoreflectance (FDTR), thermal conductivity was measured in two series of SACs: the unary compounds \(\text{Co}_6\text{E}_8\text{(PET}_{3})_6\) (E = S, Se, Te) and the binary compounds \([\text{Co}_6\text{E}_8\text{(PET}_{3})_6][\text{C}_{60}]\). They find that phonons that emerge from the periodicity of the superstructures contribute to thermal transport. Roy and Malen also demonstrate a transformation from amorphous to crystalline thermal transport behavior through manipulation of the vibrational landscape and orientational order of the superatoms. The structural control of orientational order enabled by the atomic precision of SACs expands the conceptual design space for thermoelectric materials. This study was recently published in Nature Materials.

The main design principle for highly efficient thermoelectrics is based on the phonon glass electron crystal (PGEC), in which electron transport is ballistic and phonon transport is diffusive. In order to develop a set of experimental methods to establish the phonon glass behavior and quantitatively probe the phonon disorder in the hybrid SACs, Zhu has recently used a related model system, hybrid organic-inorganic lead halide perovskites that have attracted great attention recently as electronic and optoelectronic materials. The model material system shows coherent band transport characteristic of crystalline semiconductors, but a dielectric response and phonon dynamics typical of liquids. Specifically, Zhu demonstrated that time-resolved optical Kerr effect (TR-OKE) spectroscopy is ideally suited for probing the phonon glass behavior. This model study has been published recently in Science. Zhu and Crowther are now implementing TR-OKE spectroscopy and Raman spectroscopy to probe the disordered
phonon dynamics in SACs and correlate such spectroscopic understanding with thermal transport measurements.

In a related project, Roy, Kymissis, Reichman, Millis, Crowther, and Zhu are designing chemical strategies to control the electrical properties of SACs. The controlled introduction of impurities into the crystal lattice of solid state compounds is a cornerstone of materials science. Intercalation, the insertion of guest atoms, ions or molecules between the atomic layers of a host structure, can produce novel electronic, magnetic and optical properties in many materials. In this project, Roy developed an intercalation compound in which the host \([\text{Co}_6\text{Te}_8(\text{PnPr}_3)_6][\text{C}_{60}]_3\), formed from the binary assembly of atomically precise molecular clusters, is a superatomic analogue of traditional layered atomic compounds (Figure 4). Kymissis and Roy find that tetracyanoethylene (TCNE) can be inserted into the superstructure through a single-crystal-single-crystal (SC-SC) transformation. Electronic absorption spectroscopy, electrical transport measurements and electronic structure calculations demonstrate that the intercalation is driven by the exchange of charge between the host \([\text{Co}_6\text{Te}_8(\text{PnPr}_3)_6][\text{C}_{60}]_3\) and the intercalant TCNE. These results show that intercalation is a powerful approach to manipulate the material properties of superatomic crystals. This study was recently accepted for publication in *Nature Chemistry*.

**Plans:** In the upcoming year, the IRG 2 team will focus on the following challenges:

- Studying the materials properties of one-dimensional and two-dimensional materials made through the fusion of superatoms using the diazoalkane chemistry above.
- Investigating the application of exfoliated superatom sheets for battery electrodes.
- Continuing to expand exploration of the thermal transport properties of superatomic crystals, with two objectives: to regulate the dynamic disorder of the building blocks to achieve active control of thermal transport for thermal switches; and to use the low thermal conductivity of superatomic crystals to design a new family of thermoelectric materials.
- Intercalating superatomic crystals with electron donor guests to increase the electrical conductivity of superatomic crystals to enable thermoelectric applications and the emergence of electronic phase transitions.
- Developing novel synthetic strategies to chemically link superatoms into electroactive and/or magnetically coupled frameworks. The team will explore these superatomic structures as battery electrode materials or as porous magnets. The fundamental aim here is to understand how superatoms can couple electronically and magnetically across bridging ligands. Theory will be integrated to understand the properties of the materials and also to guide the effort to assemble them into materials.
- A crosscutting IRG 1/IRG 2 project will create and study 2D materials assembled from superatoms. This will combine synthesis by the IRG 2 team, with glove-box exfoliation and contact techniques developed by the IRG 1 team. The properties of these 2D materials will be investigated both experimentally and theoretically.
- Building on the IRG 2 expertise in molecular electronics, the team will investigate electron transfer processes in single superatom devices using the scanning tunneling microscope-based break junction (STM-BJ) technique. Exploiting the synthetic methods described above, the objective is to build monomers, dimers and trimers of superatoms that can be wired between two electrodes and explore how charge transport properties evolve with length in nanoscale inorganic systems. A theoretical framework will be constructed to understand the experimental observations.
- Using both time- and frequency-domain spectroscopies, the team will probe the phonon glass character in potential superatom thermoelectrics and correlate results with thermal transport measurements, in order to establish design principles superatom thermoelectrics.
- The team will apply the newly completed femtosecond laser ARPES instrument to quantitatively establish the band structure and electron dynamics in superatom solids, with a focus on materials of potential optoelectronic applications.
**Seed Accomplishments and Plan:**

Luis Campos (Columbia Chemistry) was funded as a seed participant for IRG2 from 11/2014-10/2015. He is now a member of the IRG2 team with expertise in macromolecular systems and their self-assembly and emergent properties in materials. Daniel Esposito (Columbia Chemical Engineering) was funded as a seed participant for IRG1 from 7/2015-6/2016. His expertise is in electrochemistry/catalysis, a promising application area for 2D materials. His work is now being supported by supplemental funding from Honda Research (see IRG1 accomplishments).

In 2016-2017, Elisa Riedo and Vinod Menon (both CCNY Physics) were supported as seed participants for IRG 1.

Riedo worked with Dean and Hone to gain a fundamental understanding of nanoscale-heat-induced doping, chemical modifications, and re-structuring of 2D transition metal dichalcogenides. They used a newly developed method developed in their group, thermochemical scanning probe lithography (tc-SPL) for controlling with nanoscale precision the amount of doping, the sign and the spatial distribution in MoS$_2$ single layers. This approach uses an AFM tip with a heater to achieve extremely high temperature (up to $\sim1000$ K) in an area of tens of nm. This can be performed in vacuum, air, or other environments to achieve the desired chemical reaction and material modification. The team focused on local heat-induced oxidation and Cl-doping, of MoS$_2$ single layers. The chemistry, structure, optical and electronic properties of the thermally modified nanostructures were characterized, and the lateral size limit was measured. Cl doping was achieved by performing tc-SPL in a gas-cell rich in Chlorine. Cl-doping decreases the contact resistance by a factor 5, while oxygen-doping induces $p$-doping in MoS$_2$. The technique was then used to create $p$-$n$ junctions by local oxidation of MoS$_2$ with tc-SPL. Rectification behavior was demonstrated. The goal is now the fabrication of complex lateral heterostructures, such as $n$-$p$-$n$ junctions and arrays of 1D/2D nanostructures, with ad hoc electronic and optical properties.

Menon has previously demonstrated strong coupling between excitons in 2D MoS$_2$ and microcavity photons resulting in the formation of microcavity polaritons. The goal of this project was to demonstrate valley polarized polariton emission from strongly coupled 2D exciton polaritons in monolayer WS$_2$ embedded in a metal mirror cavity. A schematic of the dispersion of the cavity polaritons and the pump and emission studied in the experiment is shown in Fig. 1a. Helicity resolved photoluminescence experiments were carried out using continuous wave excitation at the exciton reservoir as well as at the lower polariton branch. The helicity of the polariton emission was studied as a function of angle to investigate the role of exciton fraction of the polariton on the observed helicity. Fig. 1b shows the observed helicity of the polariton emission of $\sim 14\%$ when excited in resonance with the lower polariton branch which lies below the bare exciton absorption. This result clearly shows the role of the quantum mechanically distinct valley origin of the excitons in the polariton formation and emission. For the next steps, Menon and Hone will implement similar structures with WSe$_2$ based...
polariton devices which utilize high-quality flux-grown WSe₂ and hBN encapsulation to achieve increased quantum yield and emission linewidth close to the homogenous linewidth. These new high quality materials with very low defect density are expected to further the development of 2D polaritons towards realizing room temperature Bose-Einstein condensates.

In 2016-2017, Yuan Yang (Columbia APAM) was funded as a seed participant for IRG 2.

Yang worked with Roy to design and synthesize a new family of redox-tunable cathode materials from superatoms. The strategy assembles and covalently links preformed molecular clusters having tunable redox properties into mechanically robust and electronically coupled networks. These structures are then used as intercalation hosts in which each cluster unit is a multi-electron redox-active node. The key feature of this approach is that the atomic precision and diversity of the building blocks allow us precise design of the characteristics of the cathode material.

Rechargeable batteries using multivalent ions (e.g. Mg²⁺, Al³⁺) are attractive as it can provide significant theoretical gains in capacity since multiple electrons are transferred. Moreover, Mg and Al electrodes do not have dendrite growth issues in alkaline metal electrodes (e.g. Li, Na). Therefore, these metal electrodes can be directly used as negative electrodes. However, their use in battery systems has been hindered by a lack of cathode materials. The design of new cathodes is therefore a critical step in developing multivalent batteries.

FeOCl₄-Na₂S clusters were synthesized, ball milled down to sub-1 μm particles, and mixed with carbon black and PVdF to form an electrode, which was paired with Magnesium foil to form a half cell for battery testing. The electrolyte is 0.4 M (MgPhCl)₂ *AlCl₃ /THF. First, the battery is tested at 5 mA/g. In the first discharge, a plateau at 0.7 V vs Mg²⁺/Mg is observed, indicating electrochemical activity. The corresponding specific capacity is 60 mAh/g. In the following cycles, the sample shows a specific capacity of ~20 mAh/g. Such results show that the cluster-based material is electrochemically active. Further optimizations, such as reducing size to nanoscale, surface passivation, could further enhance its electrochemical performance.

Plan
2017 seed recipients are eligible to apply for funding as MRSEC PIs through the annual funding process, currently underway. Funding decisions will be made in mid-June. Starting in year 4, the main goal of the PAS³ seed program will be to nucleate future IRGs. This process will utilize the newly-funded CNI (Columbia Nano Initiative) Postdoctoral Fellowship program, which supports two 2-year fellowships per year. The first CNI fellow, Raul Sanchez-Hernandez, has been developing new pioneering techniques for mapping electron distribution in cluster compounds using multi-wavelength diffraction. Two new fellows will be hired beginning in September 2017. Finalists are currently being considered, with expertise chosen to bridge between existing MRSEC areas of expertise and new areas of strength at Columbia, particularly in optics/photonics and quantum materials. In addition, a small outreach seed program with FIT and CCNY will be funded in year 4. The funding for the CNI fellows is listed as ‘Institutional Contribution’ in Table D2.
6. Education and Human Resources

6a. Current and Planned Activities

In its third year, the Education and Human Resources Program continued programs and partnerships for PAS that were set up in the first year, including a summer research program hosting 39 participants, comprising research experience for undergraduates (REU), teachers (RET), community college, and high school students (ENG), a summer of research for undergraduates from the University of Virgin Islands, and an Integrated Project Week for elementary school students. Building on these continuing activities, a number of new programs were initiated, including:

- A new partnership with the Cornell Center for Materials Research (CCMR) to host a STEM outreach workshop for local New York City teachers at Columbia University.
- A partnership with the National Research Mentoring Network for mentor training.
- A new ‘March Chemistry Madness’ program for elementary school children
- New professional development programs initiated by the Student/Postdoc Leadership Committee.

Summer Research Programs

Research Experience for Undergraduates (REU)

The 2016 PAS REU program consisted of a 9-week stay at Columbia University for research at Columbia and CCNY. The students received a $4,000 stipend, prepaid housing on campus, and up to $500 in travel allowance. The main MRSEC REU cohort consisted of eight MRSEC-funded students, three students from the University of Virgin Islands, four students from Columbia Engineering (SEAS) partially funded by the SEAS dean’s office, and three students supported by the Brazilian Scientific Mobility Program (Table 1). In addition, a number of other REU students were included in PAS REU programming, including two funded by the CREST / IDEALS center at CCNY who worked in PAS labs. REU students attended a weekly seminar series by Columbia faculty describing the diverse areas in materials science and engineering and other topics relevant to careers in science. The last day of the program was dedicated to a symposium of oral presentations and a poster session attended by over 100 members of the MRSEC community including PIs, faculty, as well as graduate and undergraduate students (Table 1). During the program, students attended workshops, seminars, visited Brookhaven National Laboratory’s government facility in Upton, NY, and received training in: laboratory practices and safety, shared materials characterization tools, and scientific writing/presentations.

UVI research: PAS investigator Wayne Archibald from the University of the Virgin Islands and 3 UVI undergraduates – Shancee Esdaille (Jr Chemistry major); Cassia Smith (Jr engineering major) and Nakeshma Cassel (Jr Chemistry major) – came to Columbia for the summer of 2016 for work with PAS. The students lived on campus with the REU participants and were included in all REU events. The group worked in the Hone and Barmak labs and at the Center for Functional Nanomaterials at BNL, on synthesis of doped 2D materials. They interfaced closely with Schiros and as in the past, Schiros traveled to UVI to give a focused workshop for the students on analysis of this data.

BSMP: PAS hosted Brazilian undergraduates, already studying in the US for the academic year, for research lab experience at Columbia during summer 2016. Three students (via the Brazilian Scientific Mobility Program) were hosted in PAS labs, provided with on-campus housing, and also included in the PAS REU programming.

Research Experience for Teachers (RET)

PAS funded two teachers from local schools for an RET program administered at the Columbia University Medical Center (Table 2). The highly successful and long-running (since 1990) Columbia RET program supports 6 weeks of research with 1 day per week devoted to professional development. Proximity to the partner schools provides the MRSEC a unique opportunity to go further by maintaining year-round relationships with RET teachers. Teachers participate in two consecutive summers of research so Aoife Walsh and Brandon Fremd returned respectively to the McDermott and Hone labs for the summer of 2016.
Table 1. MRSEC REU STUDENTS

<table>
<thead>
<tr>
<th>Program</th>
<th>First name</th>
<th>Last name</th>
<th>School</th>
<th>PI</th>
</tr>
</thead>
<tbody>
<tr>
<td>MRSEC</td>
<td>Brandon</td>
<td>Clark</td>
<td>Worcester Polytechnic Inst.</td>
<td>Krusin</td>
</tr>
<tr>
<td>MRSEC</td>
<td>Chanda</td>
<td>Hylton</td>
<td>Tuskegee Institute</td>
<td>Nuckolls</td>
</tr>
<tr>
<td>MRSEC</td>
<td>Molly</td>
<td>McFadden</td>
<td>Indiana U. Bloomington</td>
<td>Zhu</td>
</tr>
<tr>
<td>MRSEC</td>
<td>Alexis</td>
<td>Oquendo</td>
<td>University of Puerto Rico</td>
<td>Hone</td>
</tr>
<tr>
<td>MRSEC</td>
<td>Daniel</td>
<td>Erdosy</td>
<td>Brown University</td>
<td>Nuckolls</td>
</tr>
<tr>
<td>MRSEC</td>
<td>Osman</td>
<td>Moneer</td>
<td>Columbia University</td>
<td>Zhu</td>
</tr>
<tr>
<td>MRSEC</td>
<td>Maria</td>
<td>Paley</td>
<td>Barnard College</td>
<td>Crowther</td>
</tr>
<tr>
<td>MRSEC</td>
<td>Melissa</td>
<td>Bosch</td>
<td>U. of Minnesota</td>
<td>Tamargo</td>
</tr>
<tr>
<td>MRSEC/ UVI</td>
<td>Shanece</td>
<td>Esdaille</td>
<td>U. of Virgin Islands</td>
<td>Archibald</td>
</tr>
<tr>
<td>MRSEC/ UVI</td>
<td>Cassia</td>
<td>Smith</td>
<td>U. of Virgin Islands</td>
<td>Archibald</td>
</tr>
<tr>
<td>MRSEC/ UVI</td>
<td>Nakeshma</td>
<td>Cassel</td>
<td>U. of Virgin Islands</td>
<td>Archibald</td>
</tr>
<tr>
<td>MRSEC/SEAS</td>
<td>Michael</td>
<td>Berkson</td>
<td>Columbia University</td>
<td>Barmak</td>
</tr>
<tr>
<td>MRSEC/SEAS</td>
<td>Sophia</td>
<td>Kurdziel</td>
<td>Columbia University</td>
<td>Esposito</td>
</tr>
<tr>
<td>MRSEC/SEAS</td>
<td>Emanuil</td>
<td>Yanev</td>
<td>Columbia University</td>
<td>Hone</td>
</tr>
<tr>
<td>MRSEC/SEAS</td>
<td>Henry</td>
<td>Shulevitz</td>
<td>Columbia University</td>
<td>Kymissis</td>
</tr>
<tr>
<td>MRSEC / BSMP</td>
<td>Larissa</td>
<td>Chaves Pereira</td>
<td>Brown University</td>
<td>Nuckolls</td>
</tr>
<tr>
<td>MRSEC / BSMP</td>
<td>Paolo</td>
<td>Furlanetto Ferrari</td>
<td>Colorado School of Mines</td>
<td>Dean</td>
</tr>
<tr>
<td>MRSEC / BSMP</td>
<td>Henrique</td>
<td>Bandeira</td>
<td>Columbia University</td>
<td>Hone</td>
</tr>
</tbody>
</table>

Table 2. MRSEC RET PARTICIPANTS

<table>
<thead>
<tr>
<th>First name</th>
<th>Last name</th>
<th>School affiliation</th>
<th>Mentor</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aoife</td>
<td>Walsh</td>
<td>HS of American Studies at Lehman College</td>
<td>McDermott</td>
</tr>
<tr>
<td>Brandon</td>
<td>Fremd</td>
<td>Columbia Secondary School for Math, Science, and Engineering</td>
<td>Hone</td>
</tr>
</tbody>
</table>

**Engineering the Next Generation (ENG)**

ENG is a summer research program run by Columbia’s School of Engineering and Applied Science for highly motivated high school students from two local partner public schools: the Columbia Secondary School for Math, Science and Engineering and ELLIS (English Language Learners and International Support) Preparatory Academy; we also included students from High School for Math Science & Engineering at City College in select activities. The program runs for 6 weeks and includes lab work, mentorship, and programming to develop students’ academic and professional skills. In year 3, we expanded the academic component to include curriculum on research fundamentals; postdoc volunteer instructors provided a series of units that addressed topics such as experimental design, data collection, and lab notebook upkeep. These daily seminars supplemented additional training workshops in academic skills and development, as well as college access and application process. Specifically, the program offered college preparation workshops and mentoring sessions facilitated by REU students, as well as information sessions on admissions and financial aid by the Columbia Undergraduate Admission Office. The program commenced with a poster symposium and presentations; it also provided students a $1200 stipend for successful completion of the program.

**LaGuardia Community College Research Program**

In collaboration with Prof. John Toland at CUNY LaGuardia Community College, MRSEC postdocs/graduate students presented lectures at an introductory course for materials science throughout fall 2016. The course, which provides community college students the skills required to work in a research laboratory, is now offered for credit and has expanded its curriculum to include three experiments: 1) Frequency response of an RC circuit 2) Knife edge experiments to measure laser beam
width and 3) Building a solar cell with organic dyes. PAS³ continues to support community college students from LaGuardia Community College to participate in the summer research program on Columbia’s campus.

**Mentor Training**

PAS³ partnered with the National Research Mentoring Network to provide a day of mentoring training to its faculty and postdoc/grad student mentors who host summer researchers. The mentor training curricula focuses on 4 themes, or competencies: Maintaining Effective Communication; Aligning Expectations; Assessing and Promoting Understanding; and Addressing Equity and Inclusion. Facilitated by Anne Lynn Gillian-Daniel, this is also a collaboration with the MRSEC at University Wisconsin-Madison and a result of the MRSEC Education Directors meeting each fall.

**School-year Outreach Programs**

**March Chemistry Madness**

Nuckolls, Venkataraman, and Leighton have developed a successful half-day program of demonstrations and hands-on activities for 5th-7th graders to engage students and their parents in a Saturday educational event. The event was advertised to multiple elementary and middle school groups and attracted over 70 middle and elementary school students, along with their parents and siblings, from ten different New York City Schools across Harlem, Queens and Upper West Side. Demonstrations covering chemiluminescence, combustion, polymer formation, and atomic scale comprised the “Show” portion of the event. This was followed by nine hands-on activities on topics including acids and bases, elasticity, superconductivity, sublimation, non-Newtonian fluids, magnetic properties, electrical conductivity, polarity, and temperature effects on material properties.

**Science Honors Program**

As in the past, another component of our educational program for 2016-2017 has been a course for high school students in nanotechnology as part of Columbia’s Science Honors Program (SHP). SHP is a Saturday morning program specifically designed for approximately 500 New York City and regional high school students in the tenth, eleventh, and twelfth grades. Each semester this program offers 15 courses for high school students with exceptional talent in mathematics and the sciences. PAS³ offers the course Nano: From Science to Technology each semester, which is taught by graduate students across several departments.

**Cornell & Columbia STEM Workshop**

PhD for a Day

This program, designed and led by Campos and Venkataraman, works with Children’s Zone Promise Academy 2, located in Harlem, to expose 7th graders to experiments in the lab. Together with Ms. Jane Luceno from Promise Academy 2, this year’s program will expose 40 middle school students to the life of Columbia graduate and undergraduate students on June 9th. They will receive safety training, lab coats, goggles, and gloves to do hands-on experiments that teach concepts in energy, lab protocols, and collecting data.

Biodesign Challenge at FIT

Schiros was the scientific advisor two teams at FIT for the International Biodesign Challenge (BDC) 2017, a semester long competition where design students envision the future of biotech to address global challenges. The winning team, #growapair, which used bio-polymers to create baby shoes, will compete at the international summit at the Museum of Modern Art on June 22-23, 2017, and exhibit at the School of Visual Arts. Schiros has been invited to give two Ted Talks on her BDC teams. This work has led to a seed proposal for this year’s MRSEC research program.

Education / Human Resource Development

MRSEC Leadership Committee

In spring 2017, MRSEC introduced a Leadership Committee, composed of MRSEC fellows Alexandra Velian, Avishai Benyamini, Rebeca Ribeiro, and Fang Liu, with PhD students Jenny Adelean, Yang Gao, Haowei Zhai, and Bonnie Choi. The primary mission of the Leadership Committee is to: (1) promote communication among PAS³ researchers; (2) set priorities for educational activities that serve the PhD and postdoc researchers in PAS³; and (3) organize social events that promote cohesiveness among PAS³ participants. To these ends, the Committee: (1) organized internal research seminars (the monthly IRG symposia); (2) organized a science communication workshop in spring 2017, with more activities planned for summer and fall; (3) organized a social outing to follow the 2017 MRSEC retreat. The Committee has also chosen to take on other tasks. These include playing an active role in Outreach and Education activities, including 2017 REU application review and selection process, help with organization of the STEM teachers’ workshop, and organization of the 2017 MRSEC retreat.

Science Communication Workshops

Science Communication is a challenging but vital and rewarding skill for various aspects of graduate school and into future career. On February 24th, 2017, the MRSEC Leadership Committee hosted the Science Communication Workshop for graduate students and postdocs to interactively participate aimed at improving presentation and communication skills.

Ethics Seminar

Professor Irving Herman led a seminar for 15 PAS³ graduate students/postdocs on ethical issues in research in May 2016.

Grant-writing Workshop

The CCNY CREST/IDEALS center, hosted a Grant Writing Workshop led by Prof. Kermin Martinez-Hernández of National Research Mentoring Network - (NRMN) in June 2017, open to MRSEC PhD students and postdocs.

Future Plans

In the summer of 2017, Columbia will add Princeton to its budding partnership with the NYU MRSEC. The three institutions are planning a combined REU program visit to Princeton’s Plasma Physics Laboratory, a US Department of Energy national laboratory. The trip will also include networking and recreational social opportunities for the REU participants from all three schools. NYU and Columbia will also collaborate to provide a field trip to Brookhaven National Laboratory,
coordinating travel plans and leveraging Columbia’s BNL partnership. Finally, the REU students at the NYU and Princeton MRSECs will participate in the poster session at Columbia, as well as attend the symposium presentations. Integrating these components of the partnership into each respective REU program provides NYU, Princeton, and Columbia universities’ cohorts the opportunity to create and expand a meaningful network of academic peers and potential future collaborators. This regional MRSEC partnership will strengthen not only each of our REU programs, but also each of the centers as a whole.

**Barmak** has developed the final new course in the revised Materials Science curriculum, MSAE E4301 –Materials Science Laboratory, aimed at first year doctoral and masters students. It will be taught for the first time in Fall 2017 by **Yang**.

Center director **Hone**, with assistance from **Heinz** and **Kim**, is developing a new graduate course on 2D materials, to be taught in Fall 2017. This is an adaptation of a previous course on carbon nanotubes, and is designed to build on MSAE E4200 (Theory of Crystalline Materials).

**6b. Impact Measurements**

The evaluation of the summer REU, high school, and community college programs is addressing the following program goals:

**High school**

- To increase student interest in solving problems
- To increase students’ 21st C skills (confidence in ability to do good work; to look at other perspectives; to set goals; to manage time; to work with people from different backgrounds)
- To increase students’ understanding of the need to learn STEM subjects
- To increase students’ interest in doing advanced work in STEM subjects
- To have students gain feelings of self-efficacy in the research process
- To increase students’ ability to persevere in the face of setbacks
- To have students gain an understanding of the research process
- To spark student interest in STEM careers
- To broaden students’ understanding of the range of STEM careers
- To increase students’ understanding of what materials science is
- To increase students’ ability to communicate about STEM subjects

**REU and LaGuardia Community College programs**

- To provide a program that students find satisfactory
- To have students gain feelings of self-efficacy in the research process
- To provide a satisfactory mentor relationship
- To solidify student intentions for graduate school/careers
- To increase students’ ability to communicate about science/engineering

*Changes made in response to assessment results:* One change made in response to feedback from the year 1 summer programs was to partner students with mentors and projects earlier (prior to the start of the program). In year 3, mentors were arranged one month prior to the program start, and were able to provide introductory material to the summer students. In addition, mentors were asked to provide a tentative project for the mentoring workshop, in order to provide an opportunity for feedback by the workshop leaders and other mentors.

In Year 3, data again was collected through a baseline survey, administered on the first day of each summer program, and a post-program survey, administered during the last week. Satisfaction with different aspects of the program, as well as suggestions for changes, are evaluated using questions from REU surveys used for Columbia University REU programs over the last few years. The REU survey also includes questions on self-efficacy taken from the CISE REU Toolkit and used with permission. The high school and community college student survey was based on the Student Attitudes toward STEM Survey—Middle and High School Students, developed by the Friday Institute for Educational Innovation, with support from the National Science Foundation under Grant No. 1038154 and by The Golden LEAF Foundation, and used with permission. It also included self-efficacy questions adapted from the CNI REU survey.
9. Knowledge transfer to Industry and National Laboratories

The MRSEC team engages in multiple collaborations. We have strong ties with Brookhaven National Laboratories (BNL), the Army Research Laboratory (ARL), IBM, Advanced Photon Source (APS) at Argonne National Laboratory, and Honda. Our collaborators have been strategically chosen to extend the proposed research, complement our technical capabilities, and to explore potential application of our research in technological applications. The specific details for each of the ongoing and planned collaborations are detailed below. The MRSEC works with our collaborators to foster education, research, and technology development that will together catalyze development of revolutionary material systems, enhance national economic competitiveness, and better educate students for careers in the 21st century. Several of our graduate students work in industrial and government labs, with some specific examples mentioned below. Our collaborators from Honda, IBM, ARL, and BNL serve on the MRSEC External Advisory Board, to provide guidance on our research programs and technological impacts.

I. Industrial Collaborations

Our partnerships with industry focus on materials made by the Columbia MRSEC in: (1) electronic devices and thermoelectrics (IBM); (2) electronic properties of 2D materials (Honda); and (3) metal coatings to prevent corrosion (Rassini).

The industrial researchers provide a unique perspective on the applications of our materials, both as part of the research collaboration and in their role on our External Advisory Board. As well, they provide students with the opportunity to learn how industry researchers evaluate new materials under consideration as a future technology.

The Honda/MRSEC project currently funds two projects arising from MRSEC research: catalysis by 2D semiconductors (Esposito, Hone); and novel superconductivity in 2D materials (Dean, Pasupathy, Hone). Each project is funded at the level of ~1 postdoctoral researcher. In addition, Dr. Avetik Hartuyunyan (Chief Scientist, Honda Research) spends significant time at Columbia to deepen research partnerships.

Rassini’s Engineering Director, Mauricio Gonzalez and Nuckolls have initiated a project to investigate the materials in brake discs to minimize corrosion using the superatoms studied by IRG2 as a source of new materials. After proof of concept experiments, they are in the process of establishing a formal research agreement to continue working collaboratively. The Rassini/MRSEC agreement is initially targeting a single funded FTE to work with Nuckolls.

A. Intellectual Property

Columbia’s Technology Ventures office and CCNY’s Technology Commercialization Office assists MRSEC members in identifying MRSEC research that is innovative in nature, feasible to implement, and that addresses an identified market need with an underlying technology component that could be translated into a marketable product. Furthermore, Dupont is creating a technology incubator with whom our MRSEC will participate.

Intellectual Property Management. Our partners in the MRSEC have completed MOUs regarding sole vs. joint ownership of MRSEC IP. These already exist between Columbia/CCNY and IBM, and we are in the process of putting this in place for Honda Research.

B. Visiting Scholar Program

To facilitate the studies described below, we rely on a visiting scholars program with IBM and in the future with Honda Research. Undergraduates, graduate students, or post-doctoral scientists perform a portion of their research on site at IBM or DuPont. Nuckolls has such a long-standing arrangement with Tulevski at IBM. Under the joint study agreement, each MRSEC graduate student spends 40% of his/her time at IBM. The arrangement with IBM has produced significant publications and is an exemplary model of industrial/academic collaboration.

C. Specific Industrial Collaborations with IRG1

Frances Ross (IBM T.J. Watson Research Center) collaborates with Pasupathy on measuring microscopic transport in CVD and MBE grown vdW materials using a four-probe STM (situated at IBM) equipped with in-situ SEM, 4-terminal electrical transport, and FIB. Under this collaboration, Columbia students and postdocs perform measurements use the unique instrument at IBM, and IBM provides staff support to maintain the instrument and pay for materials, supplies and cryogens. One postdoc now spends full time at Watson Research Center.
Krusin has set up a collaboration with Jonathan Sun from IBM Yorktown, who is an expert in spin-current-switchable magnetic nano-structures and related device and materials physics. The objective is to study (1) spin injection into topological hybrid nano-structures (THS) and spin–orbit-induced transfer torques, and (2) spin-polarization effects on thermoelectric (TE) performance of THS, including approaches involving opening up Dirac gaps in topological holey arrays by applying magnetic field. Sun will contribute device design and parametrization, and perform FMR experiments when needed. Transport, magnetic, and thermal characterization will be performed at the Krusin Lab at CCNY.

In addition to continuing existing collaborations, new industry partnerships have been forged in this reporting period. Kim collaborates with Kin Chung Fong (BBN Raytheon) for RF and noise measurements of 2D heterostructures. Reido collaborates with IBM-Zurich and SwissLitho AG for the parallelization, throughput, and further developments of tc-SPL. In particular, they are working on the fabrication of the full 2D materials based devices, from doping to electrodes depositions.

**D. Specific Industrial Collaborations with IRG2**
As mentioned above, industrial researcher Tulevski (IBM TJ Watson Research Center) has a long-standing collaboration with Columbia. Tulevski and Kim are exploring the electrical transport properties of our materials as a function of temperature, carrier density, electric field and magnetic field to uncover exotic electrical and magnetoelectric behaviors.

**II. National Laboratory Collaborations**

Our collaboration with BNL provides access to the state-of-the-art experimental facilities available at National Synchrotron Light Source II (NSLS-II) and at the Center for Functional Nanomaterials (CFN). Equally important as instrumentation is the world-class technical expertise of staff scientists who assist or collaborate with MRSEC PIs and students. Examples of these experimental capabilities and expertise of particular value to MRSEC research include, among others, X-ray spectroscopy with micro- to nano-scale spatial resolution, micro- and nano-crystal X-ray diffraction, μ-ARPES, TEM, and nanofabrication.

The extensive interaction between MRSEC and BNL is spearheaded by Zhu, who is an IRG-2 co-leader and a member of the executive committee. Each year we aim to take groups of MRSEC researchers (PhD students, postdocs, and faculty) to visit BNL to tour facilities and discuss capabilities with BNL scientists; an exchange seminar program has been initiated between MRSEC faculty members and BNL staff scientists. This program, since its launch in May 2016, has been highly successful at fostering collaboration between MRSEC and BNL. BNL scientists have successfully developed and taught a course on materials characterization at Columbia.

Collaborations with additional National Laboratory facilities include Billinge’s collaboration with researchers at Pacific Northwest National Laboratory on the ZIF-8 MOF synthesis project. Additionally, Pasupathy and Herman collaborated with Mandrus and McGuire (Oak Ridge National Laboratory) in their raman spectroscopy studies of layered ferromagnetic and antiferromagnetic materials, including CrSiTe3, CrI3, and CrCl3. Reido collaborated with Dr. Paul Sheehan of the Naval Research Laboratory on hydrogenation of graphene. The MRSEC has other interactions with National laboratories. Schiros spent three weeks in the summer of 2016 at the Stanford Synchrotron Radiation Lab (SLAC) utilizing a suite of x-ray spectroscopy techniques to investigate how chemical doping modulates the electronic properties and work function of graphene and 2D hetero-structures, and continues the work in summer 2017. This will include taking one of the summer REU students for work at SSRL.

Nuckolls and Roy sent postdoctoral and graduate student researchers, as well as Shared Materials Characterization Laboratory manager Paley to Argonne National Laboratory on multiple occasions during the this reporting period to collect advanced crystallographic data in collaboration with Yu-Sheng Chen (University of Chicago, ChemMatCARS). This collaboration is very successful and is yielding new science and interesting insights into superatoms. For example, the first set of results described in the IRG research sections of this report have mapped, for the first time, the electron distribution in the superatom building blocks. This collaboration also seeks to complement the traditional single crystal diffraction capabilities of the Shared Materials Characterization Laboratory through Paley, who is actively involved in submitting proposals for additional beam time for further IRG projects.
A. Visiting Scholar Program
Using the model described above for our visiting scholars program with our industrial partners, we are creating a similar program with BNL. Undergraduates, graduate students, and post-doctoral scientists travel to BNL and their length of stay depends on the nature of the project. Many students from the MRSEC have benefited from this experience. For short experiments, the researchers travel back and forth in one day. For longer experiments, students stay in the barracks that are available at BNL.

B. Specific BNL Collaborations with IRG1
Hone and Barmak have an accepted project to use BNL TEM facilities for imaging of 2D materials. Zhu and Hone have an accepted project to use surface science tools (LEEM, PEEM) for characterization of 2D materials.

C. Specific BNL Collaborations with IRG2
Zhu and Hone (Columbia) and Sadowsky (BNL) have begun exploring the application of PEEM/LEEM and μ-ARPES to study the band structure of super-atom solids and 2D vdW materials. Nuckolls, Roy, and Zhu (Columbia) are applying low-dose TEM to the study of vdW assembled fullerenes and superatoms, and using the aberration-corrected TEM at the BNL Center for Functional Nanomaterials to provide the necessary high-resolution images of superatom assembled solids. Roy also collaborated with Sfier (BNL) on the study of triplet transfer to superatoms. Billinge has close interactions with the staff scientists at the XPD beamline at NSLS-II at BNL. Together they have built an in-situ flow reactor for MOF synthesis which could be utilized to study the synthesis of superatom superstructures in the future.

D. Partnership with Army Research Laboratory.
Over the past year, MRSEC has forged close ties with ARL. MRSEC hosted two representatives of ARL in fall 2015 for initial discussions; Dr. Madan Dubey (research scientist in the Sensors and Electron Devices directorate) serves on the MRSEC External Advisory Board. One MRSEC-affiliated student from the Hone group, Ghidewon Arefe, worked at ARL with Dubey’s group from June 2016-February 2017.

Dubey, Hone, and Schiros submitted a joint DIRA proposal to support a joint postdoc to study chlorine-doped 2D materials. This was awarded and will begin funding in July 2017. The postdoc will be based at ARL but given a visiting scholar appointment at Columbia, and travel funds will be allocated to allow frequent trips to NY.
10. International Activities

The industrial collaborations have been chosen with an eye towards adding expertise in subject areas or experimental techniques. In many cases, student exchange programs are occurring or planned with our international partners, which will provide a unique educational opportunity to some of our students.

A. International Collaborations with IRG1

IRG 1 is actively collaborating with the international partners identified at the outset of the MRSEC program: the National Institute of Materials Science (NIMS) in Japan; the Samsung Advanced Institute of Nanotechnology (SAINT) at Sungkyungkwan University in Korea; and the Center for Advanced 2D Materials at the National University of Singapore. Major international collaborations in the past year include:

- **NIMS**: Takeshi Taniguchi and Kenji Watanabe supply the highest-quality h-BN crystals available to IRG 1 researchers, and have recently supplied crystals of MoS$_2$ and WS$_2$ made by high-pressure synthesis.
- **SAINT**: A collaborative effort between a SAINT team led by Won Jong Yoo and Hone was recently awarded a Global Research Laboratory grant from the Korea Research Foundation. This 6-year project will support 1.5 postdoc positions at Columbia on PAS$^3$–related work. In addition, one postdoc and one PhD student from SAINT are visiting Columbia beginning in April 2017. They are working on Cl-doping of 2D semiconductors and new types of 2D tunnel-FETs. GRL collaborator Changgu Lee is supplying films of 2D materials to the IRG1 team and attended the 2017 annual retreat.
- **NUS**: Shaffique Adam and visited Columbia in May 2016 and is working with Hone and Reichman on analysis of quantum transport in MoS$_2$.
- **PAS$^3$** joined as an international partner to the proposed FLEET center (ARC Centre of Excellence in Future Low Energy Electronics Technologies) led by Michael Fuhrer at Monash University, Australia. Within this project, PAS$^3$ will provide expertise in heterostructure creation toward study of quantum materials, and exchange students/postdocs with FLEET. The center has recently been funded and joint agreements are being set up.
- **PAS$^3$** hosted an extended visit by Marcos Pimenta from the Universidade Federal de Minas Gerais (Brazil) in 2015-2016. Hone followed up with a visit to UFMG in summer 2016. One student from UFMG will visit PAS$^3$ in the summer of 2017. Hone and Pasupathy are supplying Pimenta with high-quality TMDC crystals for Raman spectroscopy and collaborating on studies of rotation-dependent Raman spectra, and Raman spectra of 2D materials under ultrahigh strain.
- **PAS$^3$** is strengthening interactions with the Center for Structure and Dynamics of Internal Interfaces at the University of Marburg (Germany). This center has expertise in sensitive probes of interface physics, such as time-resolved ARPES for examining dynamics of charge separation at interfaces. Hone visited Marburg in the summer of 2016. PAS$^3$ has hosted visitors from Marburg and has provided samples to center director Ulrich Hofer for time-resolved studies of second harmonic generation in TMDCs, to Martin Koch for integration of TMDCs into optical cavities, and to Arash Rahimi-Iman for studies of substrate effects on photoluminescence of 2D materials.
- **Krusin** continued extensive collaborations with École Polytechnique, Palaiseau, and Université Paris-Sud (France), to understand the effects of disorder on quantum states of topological insulators by implementing particle irradiation techniques; and on laser ARPES studies of topological surfaces of irradiated materials.
- **Elton Santos** (Queen’s Univ., Belfast) has initiated extensive collaborations with the IRG1 team. These include modeling of Cl-doped graphene (with Schiros) and defect states in TMDCs (with Pasupathy). A postdoc from Queen’s will spend a year with Pasupathy starting in Fall 2017.
Other IRG1 international collaborations:

Dean worked with Julien Chaste, Univ. Paris-Saclay (France) a study of the strain generated between two 2D materials (as measured by the shift of the Raman frequency of the mode E2g) as a function of the layer alignment. Artur Erbe from the Helmholtz Center, Dresden (Germany) sent one student to use the glove-box assembly system and other capabilities from March – July 2017, to study the electronic properties of monolayer InSe. 2014-2015 Hone lab visitor Jun Yin from Nanjing University of Aeronautics and Astronautics (China) is providing samples of monolayer hBN for tunnel barriers. Shuang Jia (Peking University) provided single crystals for 2D materials exfoliation to Pasupathy. Changqing Jin (Institute of Physics Chinese Academy of Sciences) provides single crystal samples for STM investigations by Pasupathy. Junichi Okamoto (Hamburg University) provided theory collaboration with Pasupathy. Krusin continues collaboration with Simone Raoux (presently at Helmholtz-Centrum, Berlin) on disorder-driven topological transitions in Sb2Te3 films. Heinz collaborated with Tobias Korn and Christain Schüller (University of Regensburg, Germany) for semiconductor optics experiments and Andrey Chaves (Universidade Federal do Ceara’, Brazil) for theory of optical and electronic properties of nanostructures. Korn, Schuller, and Chaves are all co-authors on a recent Nature Communications paper, led by Heinz, with Reichman, Brus, Hone, and Nuckolls as co-authors (1).

B. International Collaborations with IRG2

One significant interaction of IRG2 with international collaborators that was reported in the previous funding period was the emergence of a strong collaboration with Patrick Batail of the Université Angers. Batail is an expert in magnetic and electronic coupling of nanoscale materials. During this reporting period, Nuckolls hosted Batail for a six month stay at Columbia, where he collaborated with Nuckolls, Roy, Steigerwald, Venkataraman, and Zhu. During his stay, he advised Columbia researchers on implementing proper electrocrystallization techniques to reproduce the protocol carried out in his own research group. He gave a series of lecture to IRG2 postdoctoral and student participants on molecular conductors and related topics. He also presented a seminar to the entire MRSEC community on his research. Finally, he attended the MRSEC retreat and provided feedback on MRSEC activities as a member of Advisory Board. Roy and Nuckolls will attend a meeting in June 2017 to initiate a yearly workshop between researchers at Angers, Rennes, Lausanne, and Columbia.

Prof. Mischa Bonn, a director of the Max Planck Institute for Polymer Research at Mainz, Germany, visited the MRSEC (hosted by Zhu) in March 2016. Bonn is a leading expert on laser spectroscopy and dynamics of nanomaterials, will spend a six-month sabbatical with the Columbia MRSEC, starting June 2017, to closely interact with both IRG PIs and to explore collaborations.

In addition to the collaborations described above, IRG2 benefits from further collaborative relationships with international researchers. For instance, Josep Poblet (Universitat Rovira i Virgili) is performing calculations on endohedral fullerene-cluster complexes for Campos. Kymissis works with Yvan Boonasieux (Ecole Polytechnique) for Raman analysis and device measurement using the CNRS sponsored facilities at LPCIM. Filipos Farmakis (Democritus University of Thrace) has assisted Kymissis with measurements of graphic intercalation and encapsulation for batteries and electronical systems, as well as, electrical measurements of transport and traps. Kymissis also has a long-standing collaborative relationship with Alberto Morgante (ELETTRA synchrotron). Similiarly, Venkataraman's work on characterizing N-heterocyclic carbenes binding and electronic structure at the interface with gold single-crystal substrates is carried out in collaboration with the ALOISA group at the ELETTRA synchrotron.
11. Shared Experimental Facilities

The PAS³ team has access to shared lab facilities at both Columbia and the new CUNY Advanced Science Research Center (ASRC). These facilities include:

- Nanofabrication (cleanroom) facilities (Columbia, CUNY)
- Electron microscopy, including both TEM and SEM (Columbia, CUNY)
- Shared Materials Characterization Lab (SMCL) (Columbia). Major tools include X-ray diffraction, Raman spectroscopy, AFM, XPS, SQUID magnetometer.

Through the university-level memorandum-of-understanding between CUNY and Columbia, PAS³ researchers can use the facilities at both institutions seamlessly. For the shared facilities at both Columbia and CUNY, users pay only the cost of supplies and maintenance of the tools through their user fees. Salaries for the full-time staff (at least one per facility) are paid directly by Columbia and CUNY.

At Columbia, shared facilities are managed by the Columbia Nano Initiative (CNI). Nava Ariel-Sternberg, previously the cleanroom manager at Tel Aviv University, serves as Director of Shared Facilities and oversees five technical staff members.

The shared facilities are accessible to external users who use the various labs and equipment. The SMCL lab is used by both external academic institutions (NYU, RPI, Cornell, University of Connecticut, HZDR, and CUNY) as well as by industrial companies (Kennedy labs, Lumiode, Neovel Technologies, and Pacific Biosciences). Additional external users are using the EM lab and the clean room.

Progress:

Cleanrooms: The new ASRC clean room and materials characterization facilities are complete and operational, and are being used by Columbia researchers extensively. The Columbia clean room construction is complete and tools / systems are currently being commissioned. It is currently open for limited use (dry processes only, no solvents), with full opening pending Fire Department permitting. This will have extensive new tooling relevant to MRSEC research, including a new laser mask writer, deep-UV mask aligner, 2 new etch tools, and three deposition tools. In particular, the MRSEC will benefit from a newly ordered ultrahigh vacuum e-beam evaporator. The IRG 1 team has recently shown (using a similar system at Harvard) that UHV evaporation results in substantially improved contacts to 2D semiconductors.

Electron Microscopy: A new high-resolution SEM (Zeiss) and an SEM-based ebeam lithography system (FEI) were installed during the summer of 2016. The Zeiss tool is operational while the FEI is awaiting final commissioning of the cleanroom. TEMs at both Columbia and ASRC are operational. The Columbia TEM has been configured and calibrated to work at 80 KV for imaging graphene and 2D materials.

SMCL:

- The ‘Central Stacking Facility’ for inert-atmosphere assembly of 2D heterostructures is now being extensively used. This and other equipment in the SMCL have been listed on the mrfn.org network. In the past year, we have added one ‘auto-finder’ system which automatically scans a wafer for small flakes. A second such system is on order. The Horiba micro-Raman microscope was upgraded to enable polarization measurements.
- We have purchased and installed equipment for bulk crystal growth, including box furnaces, tube furnaces, and a pump for sealing quartz tubes.
- Brunauer–Emmett–Teller (BET) was purchased and installed in April 2017. The system uses physical adsorption of gas molecules to measure the specific surface area of materials.
• An optical spectroscopy system in the Brus lab (accessible to all Center researchers) was upgraded with a new spectrometer and repair of an existing laser.

Magnet Cryostat. A closed-cycle (cryogen-free) 14 Tesla magnet cryostat has been purchased using a combination of supplemental helium recovery funds and internal funds. It is scheduled to arrive in May 2017. MRSEC equipment funds were used to purchase a pump for this system.

Cryo-free Optical cryostat: A closed-cycle optical cryostat (Montana Instruments) has been ordered using supplemental helium recovery funds. This will greatly increase throughput of studies of low-T optical properties, and reduce costs of helium purchases.

Laser ARPES. A unique Deep-UV laser ARPES system, which will give MRSEC researchers the unique capability to probe physics at high-momentum states (e.g. K points of graphene and TMDs) was purchased using internal Columbia funds and installed in Fall 2016. Schematic and initial data are shown below.

(Left) Schematic of the XUUS laser system. The fs EUV probe pulse is generated from HHG in a capillary waveguide filled by Ar gas. Green dashed line shows a future setup plans for pump-probe experiment. The output will be split 50/50 into one pump and one probe arm. The pump pulses can be frequency converted by NOPA, which is tunable between 510 and 640 nm. The pump and probe pulses will be overlapped on the sample in the UHV chamber. Insert: The XUV harmonics diffracted from the grating, visualized on luminescent Ce: YAG crystal in the focal position. For ARPES measurement, the 27th harmonic at 42 eV is selected from other harmonics by the movable slit.

(Right) Initial data: band structure of bulk MoS$_2$ mapped in the $\Gamma$-K direction, with high symmetry points labeled on the top. White dashed lines are theoretical band structure calculations.

Plans:

In 2017-2018, MRSEC equipment funds will be used to purchase an energy-dispersive X-ray spectroscopy (EDS) detector for the Zeiss SEM in the shared microscopy facility.

IRG-1:

a. Primary MRSEC support that acknowledge the MRSEC award – approximately 50% or more support from MRSEC (DMR-1420634):


b. Partial MRSEC support that acknowledge the MRSEC award – less than 50% of support from MRSEC:


IRG-2:

a. Primary MRSEC support that acknowledge the MRSEC award – approximately 50% or more support from MRSEC (DMR-1420634):


b. Partial MRSEC support that acknowledge the MRSEC award – less than 50% of support from MRSEC:


Films," *Journal of the American Chemical Society*, **2016**, vol. 138, pp. 15717-15726. DOI: 10.1021/jacs.6b08880


**Seed Program**

**IRG1**

a. Primary MRSEC support that acknowledge the MRSEC award – approximately 50% or more support from MRSEC (DMR-1420634):


**IRG2**

a. Primary MRSEC support that acknowledge the MRSEC award – approximately 50% or more support from MRSEC (DMR-1420634):

15. Brief biographical information for each new investigator

Vinod M. Menon
Menon explores light-matter interaction at the nanoscale, focusing on development of structures such as nanocavities and artificially engineered optical materials such metamaterials and hybrid excitonic materials that display optoelectronic properties that surpass naturally occurring materials. This work is motivated by fundamental discovery and the quest to develop next generation computing technologies, ultrasensitive sensors, and high efficiency energy harvesting systems.
Professional Preparation
University of Hyderabad (India), Physics, M.Sc., 1995
University of Massachusetts Physics, Ph.D., 2001
Princeton University Post-Doctoral Fellowship, 2001-03
Appointments
Professor – Physics, City College & Graduate Center of CUNY, 2014 – Present
Director – CUNY Center for Advanced Technology in Photonics, 2014 – 2016
Associate Professor – Physics, Queens College & Graduate Center of CUNY, 2010 -2014
Assistant Professor – Physics, Queens College & Graduate Center of CUNY, 2004 - 2010
Research Staff Member – Electrical Engineering, Princeton University, 2003-2004

Elisa Riedo
Riedo specializes in the use of scanning probes to study nano-systems, with particular interest in the physics and chemistry of liquids when confined in nano-spaces; the origin of hydrophobic forces; friction and adhesion forces at the nanoscale; elasticity, plasticity and mechanical properties of nano-objects; and nano-patterning of chemical modified surfaces by ThermoChemical NanoLithography (TCNL).
Professional Preparation
University of Milano, Italy Physics (Summa Cum Laude) B.S., 1995
University of Milano, Italy Physics Ph.D., 2000
Appointments
Since 8/27/2015 Professor of Physics, City College of New York (CCNY-CUNY)
2015 Full Professor, School of Physics (Georgia Institute of Technology)
2009-2015 Associate Professor, School of Physics (Georgia Institute of Technology)
2003 - 2009 Assistant Professor, School of Physics, (Georgia Tech)

Yuan Yang
Yang’s research interests include designing materials and devices to address energy and environmental challenges, especially electrochemical energy storage & conversion, and thermal energy harvesting & management. The research activities involve exploration of novel materials and chemistry for advanced energy storage, development of high-performance catalysis, advanced materials and devices for thermal energy harvesting and management, and investigation of fundamental structure-property correlations in materials.
Professional Preparation
Peking University, Beijing, China Physics B.S. 2007
Stanford University, Stanford, CA Materials Science M.S. 2010
Stanford University, Stanford, CA Materials Science Ph.D. 2012
MIT, Cambridge, MA Thermal Sciences Postdoc 2012-2015
Appointments
2015-present Assistant Professor, Materials Science and Engineering, Department of Applied Physics and Applied Mathematics, Columbia University, New York, NY
16. Honors and Awards

Our faculty has been the recipients of a number of honors and awards this year as summarized below.

**Luis Campos**
2017 Journal of Polymer Science Innovation Award

**Andrew Millis**
2016 Sommerfield Lecturer, Ludwig Maximillian’s University
2017 Hamburg Prize in Theoretical Physics

**Colin Nuckolls**
Sheldon and Dorothea Buckler Professor of Material Science

**David Reichman**
2017 ACS Division of Physical Chemistry Award in Theoretical Chemistry

**Xiaoyang Zhu**
2018 DoD Vannevar Bush Faculty Fellowship
Howard Family Professor of Nanoscience
Two-dimensional transition metal dichalcogenide (2D TMDC) semiconductors are of great interest both for novel behavior and applications in electronics and optoelectronics. However, the underlying crystal quality of the materials used in studies is not well understood, nor is the connection between type and density of defects and properties.

We use multiple techniques to characterize bulk crystals of 2D TMDCs. Commercially obtained crystals grown by the chemical vapor transport (CVT) technique are of very low quality. We use a different technique known as flux synthesis to grow crystals with over 100X reduction in defect density. This is accompanied by clear improvements in performance, such as large increase in photoluminescence intensity and much cleaner evidence of quantized electronic levels (Landau levels) in a magnetic field.
IRG1 of the Columbia MRSEC seeks to understand the behavior of van der Waals heterostructures created by assembly of atomically thin layered materials. One important question in this effort is how the relative orientation between the layers affects multiple properties.

In the last year, MRSEC fellow Rebeca Ribeiro-Palau and Bridge-to-PhD fellow Kursti DeLello have developed a technique to change the orientation between layers in a heterostructure using an atomic force microscope (AFM). This is done by pushing the top layer of the structure with the AFM tip in contact mode. It allows extremely precise control of angle, to within 0.1 degrees.

In the first studies using this technique, the team has examined the change of electronic behavior of graphene/BN structures due to the control of a Moire’ superlattice and found a correlation of this with a high friction regime between the layers. This work sets the stage for a broad experimental and theoretical program to study angle-dependent phenomena in heterostructures.
The synthesis of site-differentiated Co₆Se₈(PET₃)₆₋ₓ(CO)ₓ superatom building blocks (Fig. 1, Ref. 1) has facilitated the assembly and study of superatom, nano-molecules of precise arrangements and size. Precise extended nano-materials were assembled from these superatom building blocks using donor-acceptor interactions (Fig. 2), hydrogen bonding (Fig. 3) and, remarkably, covalent bonding (Fig. 4). The bulk properties (such as magnetism and conductivity) of the assembled materials are determined by the composition and dimensionality of the assembly.

Featured as one of the “Ten Ideas That Will Change the World” in Scientific American in 2016, the discovery featured in Ref. 1 of assembling site-differentiated, atomically precise clusters into dimensionally controlled materials opens a new way to design and program a next generation of functional nanomaterials.

A ‘March Chemistry Madness’ program brought over seventy 5th-7th grade students from 10 different elementary and middle schools in Harlem, Queens, and Upper West Side in New York City to Columbia’s campus for demonstrations and hands-on activities designed to introduce them to concepts in physics, chemistry, and material science.

Topics covered included:
- Superconductivity
- Non-newtonian fluids
- Polymers
- Acids and bases
- Electrical conductance
- Magnetic forces
- Surface tension
- Ideal Gas Law
- Sublimation
- Combustion
- Atomic scale

The event was successful enough that we were asked to perform similar demos by a teacher who attended for two 7th grade classes from Booker T. Washington middle school.
17. Highlights


IRG 1: Rotating van der Waals Heterostructures. Rebeca Ribeiro-Palau, Kursti DeLello, Cory Dean


Education/outreach: March Chemistry Madness