Communicating Research to the General Public

At the March 5, 2010 UW-Madison Chemistry Department Colloquium, Prof. Bassam Z. Shakhashiri, the director of the Wisconsin Initiative for Science Literacy (WISL), encouraged all UW-Madison chemistry Ph.D. candidates to include a chapter in their Ph.D. thesis communicating their research to non-specialists. The goal is to explain the candidate's scholarly research and its significance to a wider audience that includes family members, friends, civic groups, newspaper reporters, program officers at appropriate funding agencies, state legislators, and members of the U.S. Congress.

Over 40 Ph.D. degree recipients have successfully completed their theses and included such a chapter.

WISL encourages the inclusion of such chapters in all Ph.D. theses everywhere through the cooperation of Ph.D. candidates and their mentors. WISL is now offering additional awards of $250 for UW-Madison chemistry Ph.D. candidates.

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Correlating Spatial Heterogeneity with Electronic and Optical Properties of Transition Metal Dichalcogenides

by

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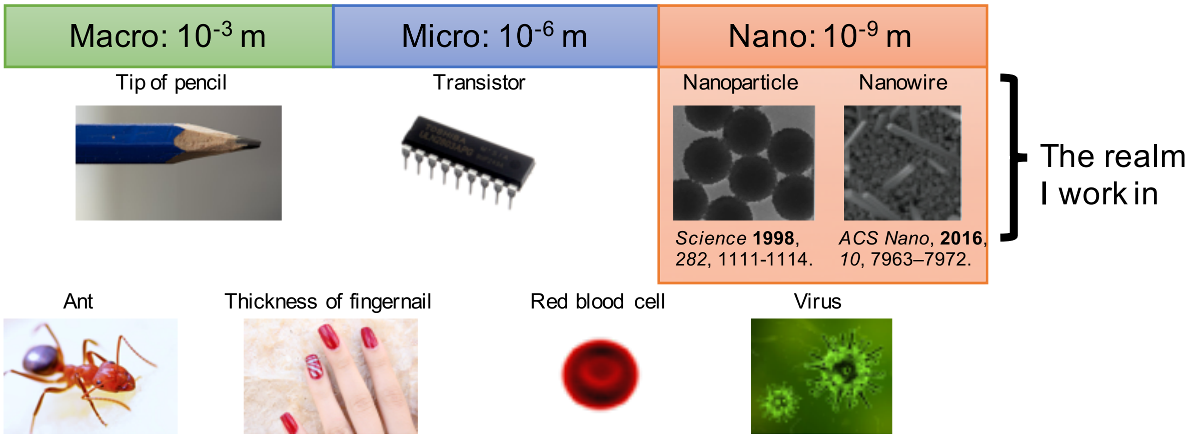
Chapter I

An Introduction for Non-chemists

I.1.1 Properties and applications of nanomaterials

Nanomaterial: a material that has at least one dimension between 1-100 nanometers (nm).

1 nm = 1×10^{-9} meters (m)



Current applications of nanomaterials:

Food

Titanium dioxide (TiO_2)

Sunscreen

Zinc oxide (ZnO)

Displays

Cadmium selenide (CdSe)

Why are nanomaterials so interesting?

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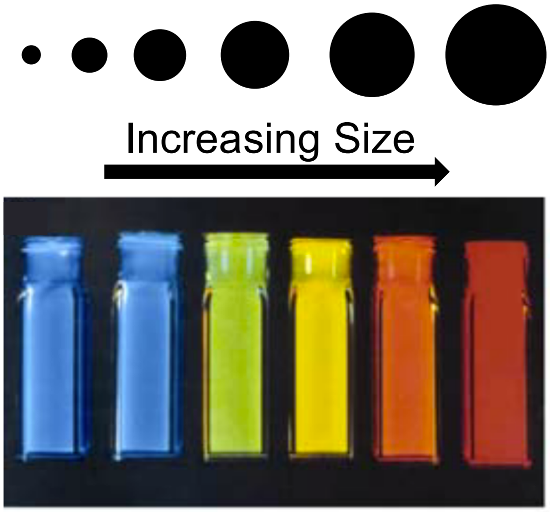
When a material is made into a nanomaterial, interesting properties start to emerge because light interacts differently with the material at this small size. The cup pictured here is known as the Lycurgus cup, and was made by the Romans in the 4th century. Surprisingly, this cup contains gold nanoparticles, and yet glows red when you shine light through it! The Romans didn't know it then, but this phenomenon occurs because gold nanoparticles absorb blue light and reflect red light back to our eye.

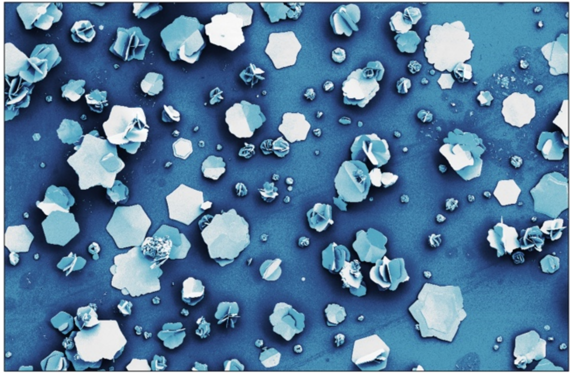
Simply changing the size of an individual nanostructure can drastically alter its material properties. For example, nanoparticles with a cadmium selenide (CdSe) core can emit a rainbow of colors that correspond to the size of the nanoparticle, shown here. This versatility is why CdSe nanoparticles are currently being used in TV displays.



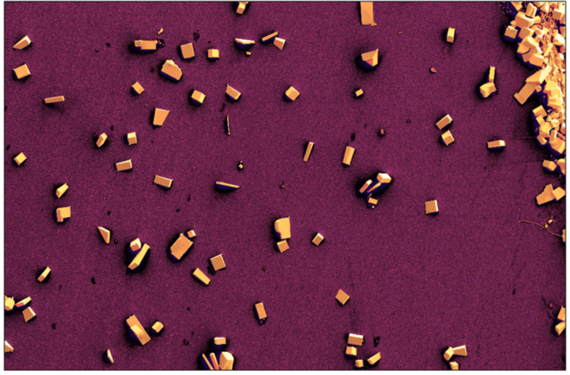
J. Phys. Chem. B **1997,** *101*, 9463–9475.

The properties of nanomaterials vary based on their size, shape, and the composition of the nanomaterial. My research group (along with many others) has focused on making diverse sets of nanomaterials with a variety of shapes, sizes, and material composition. To highlight the structural diversity that we have developed in our lab, I have taken images of a sampling of the nanomaterials we have grown, shown below.

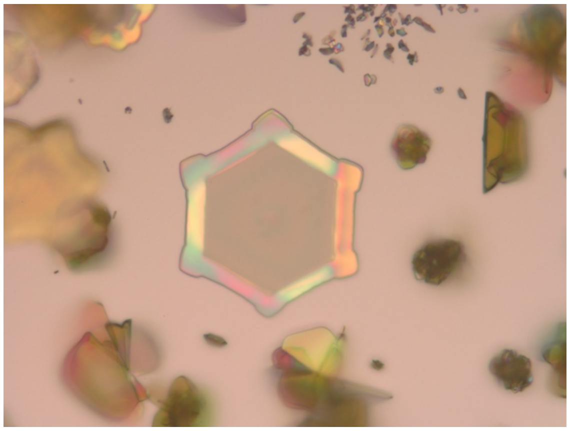
Nano-snowflakes
Tin disulfide (SnS_2)



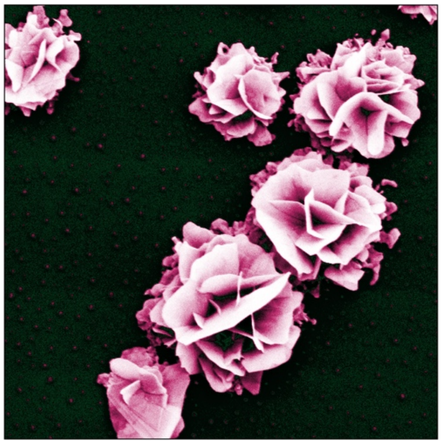
Nanorods and nanocubes
Cesium lead bromide ($CsPbBr_3$)



Nanoplate
SnS_2



Nano-roses
Tungsten diselenide (WSe_2)

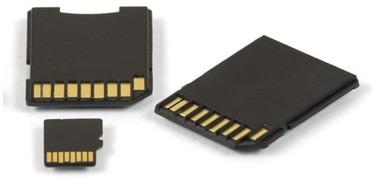


Once we have control over the size and shape of each material, we can tailor their properties for specific applications.

I.1.2 WSe_2 Introduction

Applications our group focuses on:

Information Storage



- Increase memory
- Decrease size

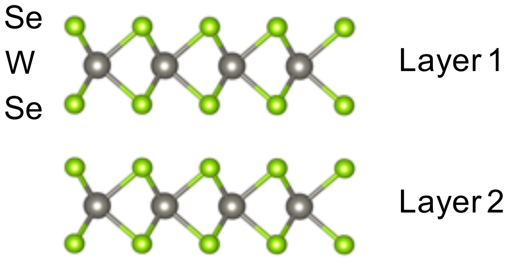
Solar Energy

- Increase efficiency
- Decrease cost

Batteries

- Increase lifetime
- Increase efficiency

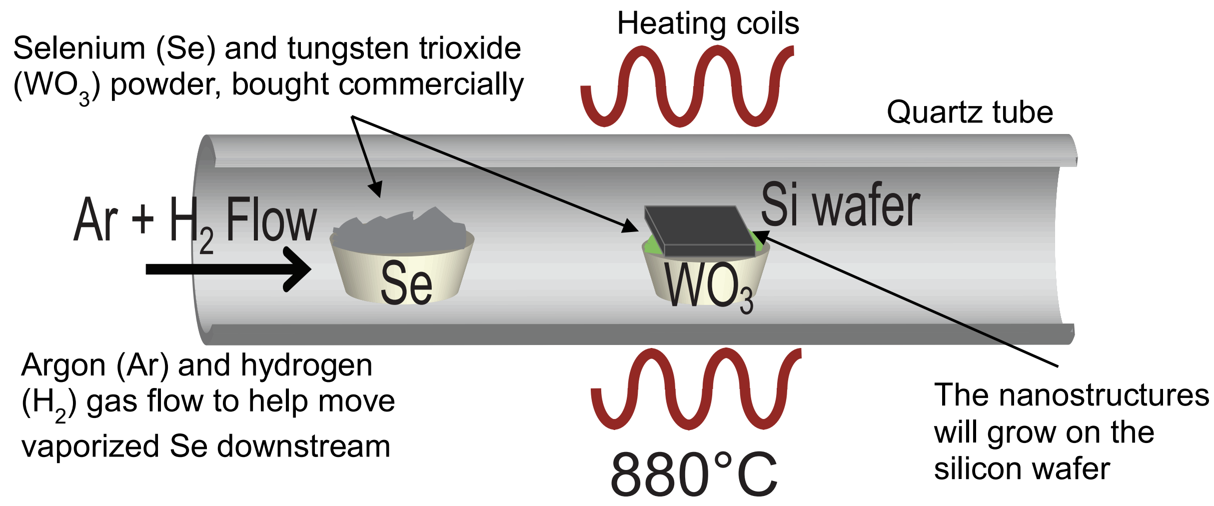
Nanomaterial of choice: Tungsten Diselenide (WSe_2)



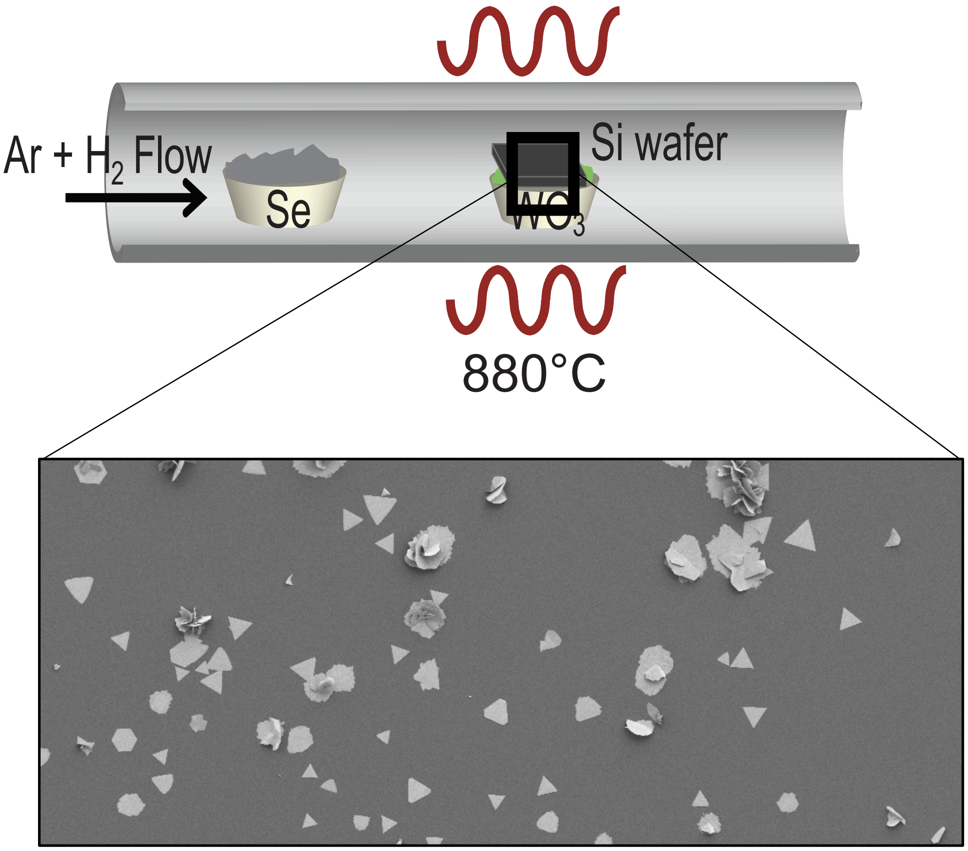
WSe_2 is a layered material, shown on the left, where each layer contains two rows of selenium (Se) atoms (green) that sandwich the tungsten (W) atoms (grey). The way these layers stack is critically important for the properties of this material. WSe_2 is relatively earth-abundant and low cost, and exhibits properties useful for all of the above applications. Therefore, we are actively trying to understand the properties it has in its nano form so we can access all of these applications.

I.1.3 Growing WSe_2 Nanostructures: Chemical Vapor Deposition (CVD)

In CVD, we react chemicals in their gas (vapor) phase to form new materials, and deposit the newly-formed materials onto a surface such as a silicon (Si) wafer. Many CVD reactions occur between materials that are solids at room temperature, which requires heating the reactions to very high temperatures; my reaction operates at 880°C, or 1616°F. With help from my undergraduate mentee, I developed a CVD method to grow WSe_2 nanoplates. The details of this synthesis are shown below.



The Se reacts with the tungsten trioxide (WO_3) to form WSe_2 nanostructures and oxygen (O_2) gas. We optimized the temperature, gas flow rate, amount of Se and WO_3, and reaction time in order to produce WSe_2 nanoplates consistently.

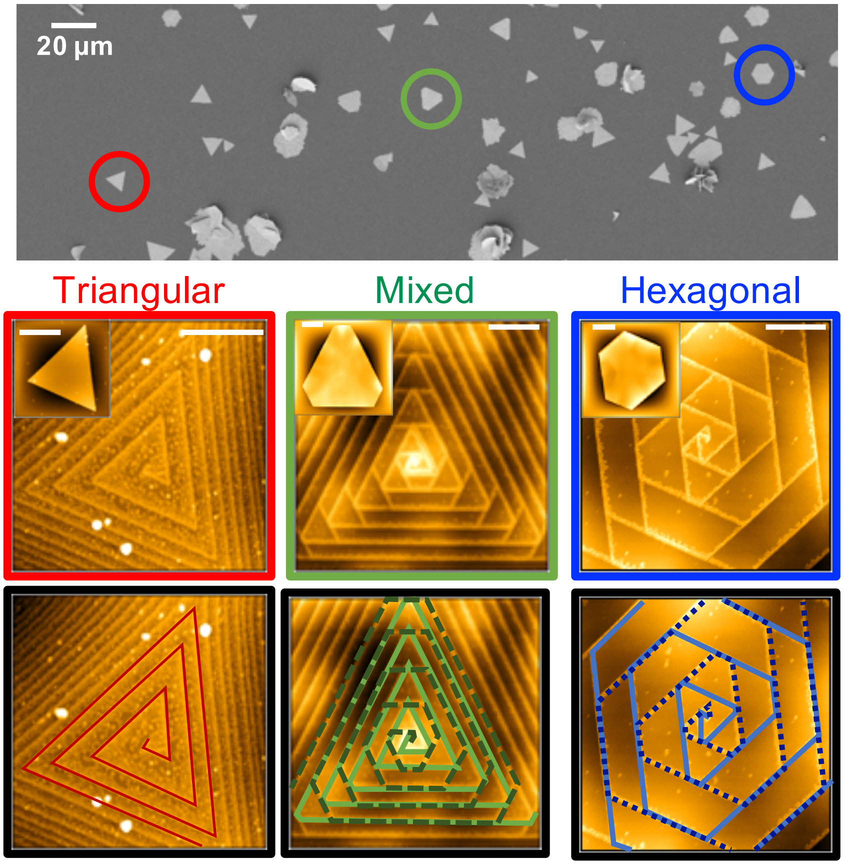


Using this method, we synthesized a variety of different tungsten diselenide (WSe_2) nanoplates of all shapes and sizes. This image was taken using a scanning electron microscope, which can be used to see structures that cannot be seen by the naked eye or with conventional optical microscopes.

I.1.4 Characterization of the WSe_2 Nanoplates

Micrometer (μm) = 10^{-6} meters

Remember that only 1 dimension needs to be nano for a material to be considered a nanomaterial—for these plates, the height is on the nanoscale (around 100 nm).

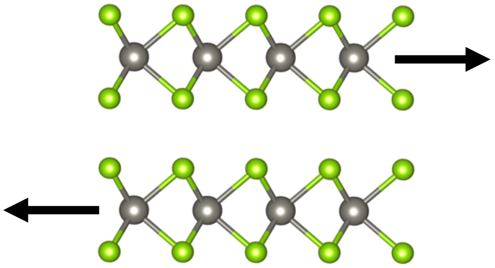


Scale bars: 2 μm (inset) and 500 nm

We noticed that there are different shapes of these flat WSe_2 nanoplates, and when we zoom in on the surface of each plate, we see distinctive spiral features.

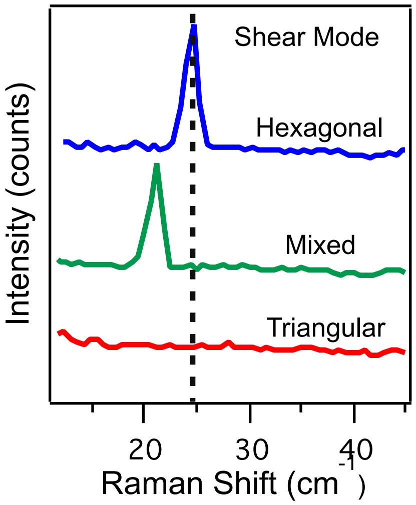
Here, I have traced out the spirals. There are triangular and hexagonal spirals, and some plates have multiple intertwining spirals. This diversity was an unexpected result that intrigued us. Do these different spiral patterns have different properties?

Investigating the properties of individual nanostructures is quite challenging, as you might imagine. To study each plate, I ventured to Oak Ridge National Lab in Tennessee where I used a technique called Low Frequency Raman Spectroscopy.



Raman Spectroscopy: When you shine light on the sample, atoms will absorb some of that light and start vibrating in particular ways. One of these collective vibrations is shown here, where each layer moves in the opposite direction of the other; this is called the *shear mode*. This vibrational mode is very sensitive to changes in the way the layers are stacked.

Because these atoms absorb some energy from light when they vibrate, they reflect light at a different wavelength than the original excitation beam; this is called the *Raman shift*. Changes in the layer stacking give rise to different Raman shifts. Therefore, we can use Raman to see if there are changes in the layer stacking between different nanostructures.

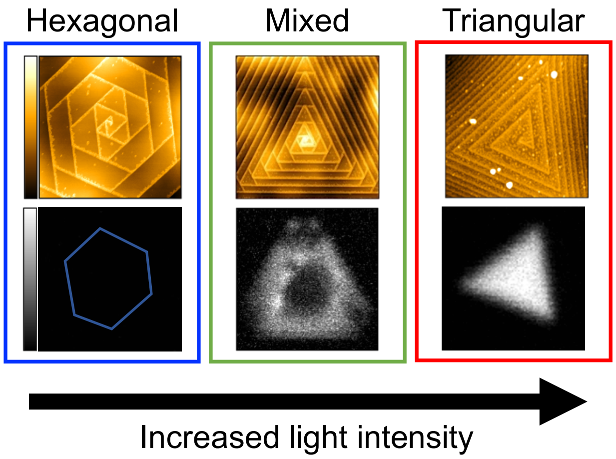


This data shows one strong peak where atoms vibrating in this shear mode reflect light. This looks like simple data, but it actually requires very specialized equipment to measure, as the shift in wavelength from the initial laser beam is so small it is hard to distinguish from the original beam. The unit for the Raman Shift is the wavenumber, or inverse centimeter (cm^{-1}), which is a convenient way to measure the energy of the light relative to that of the original light beam.

The change in the peak intensity as well as the shift of the peak tells me that the interactions between the layers are different for each of the three types of nanoplates. Therefore, the layers are stacked differently in each.

Do these different nanoplates then have different properties?

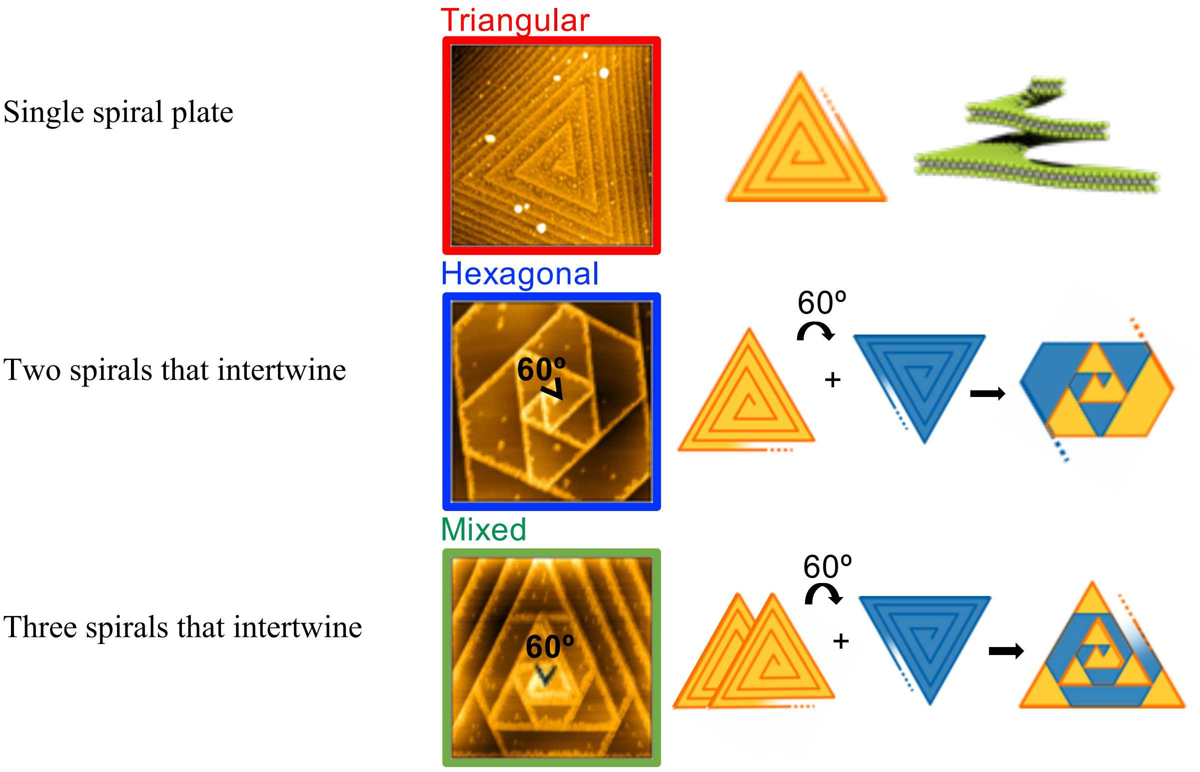
We wanted to know if these different layer stackings lead to unique properties, such as how each plate emits light.



Here, I have looked at the same three WSe_2 nanoplates. The top row shows a zoomed-in image of each plate, and the bottom row shows light that the entire plate emits after illumination with a laser. The hexagonal plates emit no light, while the triangular plates emit quite strongly, and the mixed plates fall in-between.

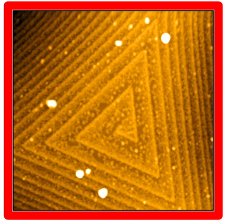
Clearly, the different plates have different properties. We developed a model to explain how the spiral shapes change the layer stacking and create these different properties, shown below.

I.1.5 Tying it all together



Using this model, we classified the layer stacking of many different types of nanoplates, revealing layer stackings of WSe_2 that had never been observed before. Each different layer stacking can be tied to a different potential application, examples of which are shown below. This spiral growth method, then, gives rise to a diversity of layer stackings and properties of this material.

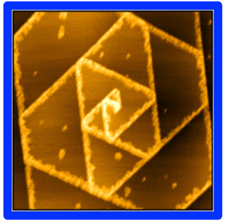
Triangular



Batteries

-Ions can move into layers
-Improved conductivity

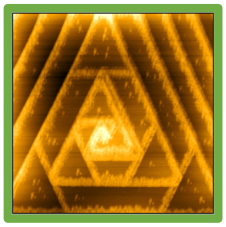
Hexagonal



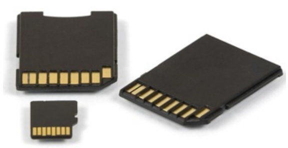
Solar Energy

-Absorbs visible light well
-Stable

Mixed



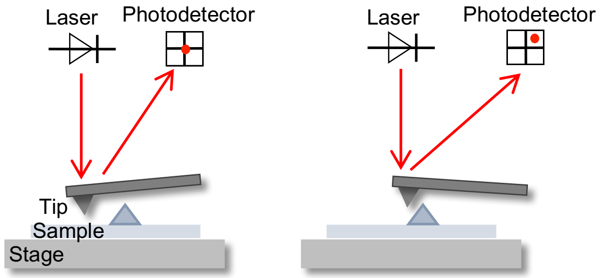
Information Storage



-Can control electrons in a unique way to decrease size

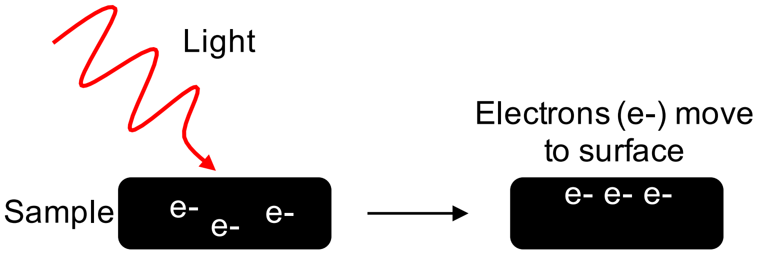
I.2.1 Measuring properties of nanomaterials

As I mentioned earlier, it is quite difficult to study the properties of individual nanostructures. In recent years, however, new tools have been developed to help with this problem. Many of these tools I used for the WSe_2 nanoplate project described above. For example, I showed many gold colored images—these are from an Atomic Force Microscope (AFM). The basic schematic of AFM operation is shown below.



In AFM, a very small, sharp tip with a diameter of about 10 nm hovers over the surface of the sample. This sharp tip will move over the surface of the sample, and when it encounters a feature, such as a protrusion that is taller than the rest of the sample, it will be bent or deflected by that feature. This deflection is measured using a laser that reflects off the back of the tip. A photodetector can measure where the laser is being reflected relative to the normal position, and a computer can map this reflection as a change in the height of the sample.

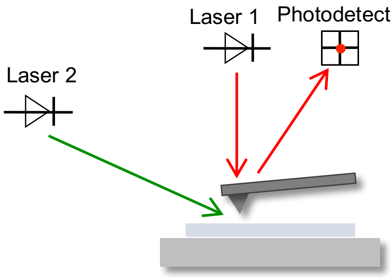
I wanted to develop a method in our lab that could allow us to learn more about individual nanostructures than just changes in the height—to also measure the movement of negatively-charged electrons (e^-), when nanostructures are exposed to light.

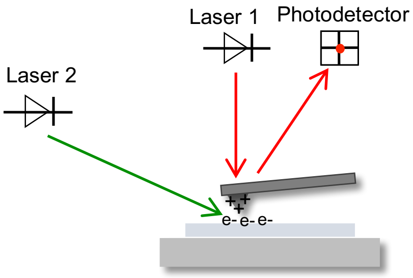


When a material is exposed to light at a certain wavelength, it can absorb that light and give some of its electrons extra energy to move around. These electrons with excess energy are *excited*, and often move to the surface of that material. The movement of electrons under illumination is the fundamental basis of a solar cell, and measuring this movement is critically important for understanding how well a material will function for this application. Although it is relatively straightforward to measure this on a large sample like a wafer or a thin film, distinguishing the movement of electrons within individual nanostructures is difficult.

I.2.2 Implementing the technique

I implemented a modified version of AFM in the lab that allows us to look at the movement of electrons in nanostructures after a sample has been exposed to light. This method involves aligning a new laser so that it illuminates the surface of the sample underneath the tip.



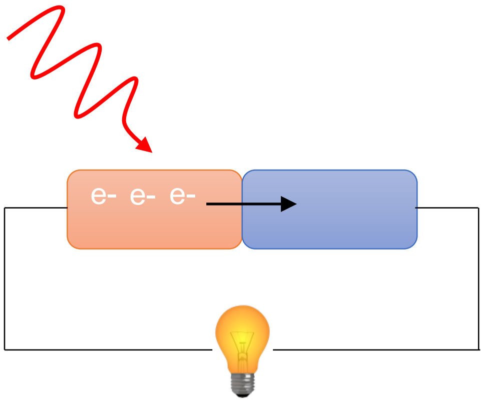


When electrons in the sample are excited by the laser, they may move to the surface of the material and repel electrons in the tip, creating a positive charge on the tip. The amount of positive charge on the tip can be measured and correlated to the number of electrons in the material, and we can then plot the presence or absence of electrons on the surface of the material we are interested in.

I.2.3 Using a model system to demonstrate the technique

Model system: a well-studied sample that demonstrates the viability of a new technique

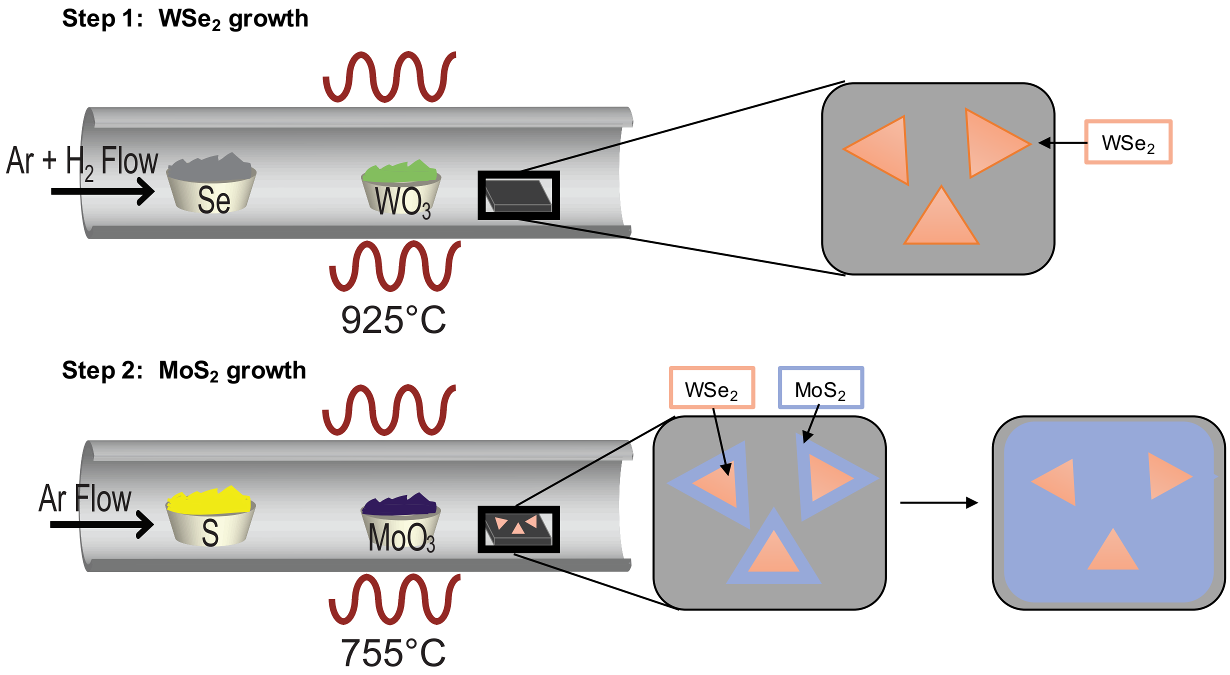
- A good model system for my technique is a heterostructure, which is a nanostructure that contains more than one material.



When two materials are placed in close proximity to one another, electrons can sometimes move from one material to the other instead of moving to the surface. These mobile electrons can then be used to do work, such as supply a current to light a lightbulb. This idea, that two materials together can help move electrons under illumination, is how we can construct a working solar cell.

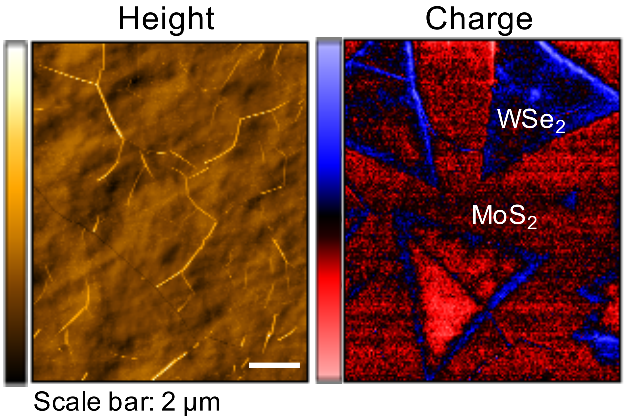
Our specific model system: WSe_2-MoS_2 heterostructure (Tungsten diselenide with molybdenum disulfide)

I.2.4 Synthesis: Chemical Vapor Deposition (CVD) in two steps



Our collaborators at King Abdullah University of Science and Technology in Saudi Arabia developed this heterostructure synthesis and sent us the samples to study using our technique. Typically, these samples are vacuum-packed so that they are protected from any harsh conditions they might encounter. The reaction is similar to my CVD reaction from earlier, with slightly different conditions and involving two separate steps. The first step produces the WSe$_2$ nanoplates from WO$_3$ and Se. After step 1 is completed, our collaborator places the resulting sample into another tube for the second reaction, to grow the MoS$_2$ from the edges of the WSe$_2$ nanoplates. During this second step, eventually the MoS$_2$ completely fills in the gaps between the individual WSe$_2$ plates.

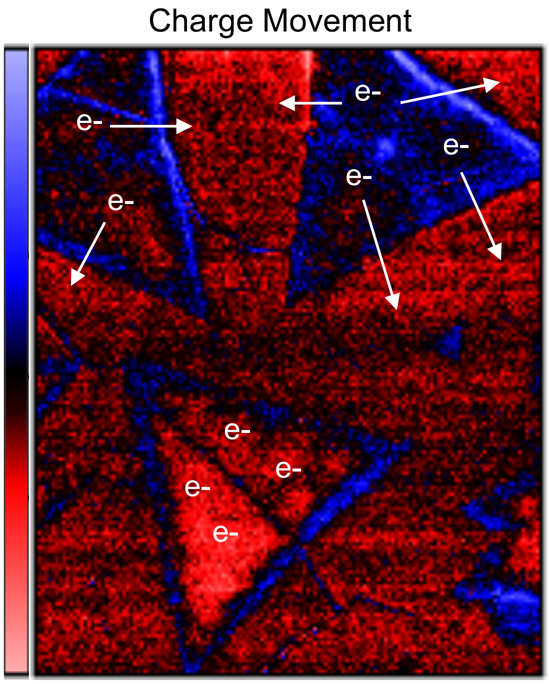
I.2.5 Understanding charge movement in the WSe_2-MoS_2 heterostructures



Scale bar: 2 μm

We measured the charge, namely the excited electrons, of the heterostructure under illumination. The height image on the left shows very few features, because the two materials are very similar in height. The charge image, on the other hand, reveals three WSe_2 triangular flakes that are surrounded by MoS_2. In this image, red indicates areas with a negative charge from an excess of electrons, while the blue indicates areas with a positive charge, where there are fewer electrons present.

If we take a closer look at this charge map, we can begin to understand how the electrons are moving. The two WSe_2 flakes at the top most likely transferred their electrons to the surrounding MoS_2, hence why the MoS_2 is red and the flakes are blue/black. The bottom triangle, however, is bright red, which could indicate that electrons were not able to move from the WSe_2 to the surrounding MoS_2.



This means that not all of these heterostructures work the way we would expect them too—perhaps due to imperfections in the boundary between the two materials. If we wanted to use these heterostructures in an actual solar cell or electronic device, we would need to ensure that each one will act exactly as expected. This technique could be applied to a wide variety of other types of nano and heterostructures to help understand charge movement.

I.3 Conclusion

In this thesis, I worked on understanding how nanomaterial properties are affected by changes in layer stacking and material composition. Only by understanding how we can tune these properties can the next generation of nanomaterials be used for their various applications.