Tuning Electrical Properties in GaN Nanowires for Optimization of Artificial Photosynthesis

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1. Background
1.1. Motivation

As part of their 17 sustainability goals, the United Nations addresses that increasing CO_2 levels is significantly contributing to detrimental climate change. Figure 1 shows projected sea level temperatures under different CO_2 level prediction models and suggests that higher concentrations of CO_2 in the atmosphere will result in significantly higher surface temperatures, and from this depiction it becomes obvious that immediate action must be taken, as increasing temperatures contribute to rising sea levels and sporadic weather conditions that are detrimental to the planet. The primary contributor to CO_2 levels is emissions from burning fossil fuels: fossil fuel combustion accounts for approximately 74% of the United States total green house gas emissions. From this we understand that in order to avoid disastrous changes to our planet, we must take urgent action to move away from a fossil fuel-powered society and transition primarily into renewable energies.
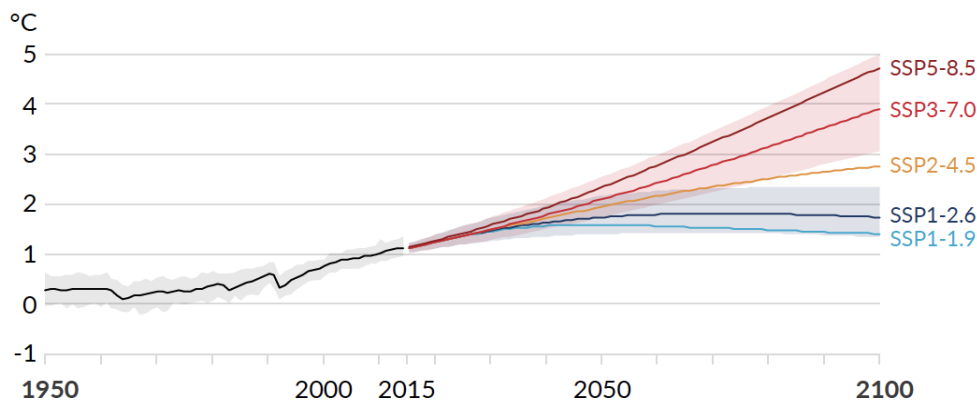

Figure 1: Plotted average sea level temperature over time, including projected temperatures under varying CO_2 level prediction models

In 2020 solar generation and distribution made up 3% of the United States' total energy generation (Office, n.d.) showing great potential for replacing fossil fuels. Another potential solution is found in wind energy, which in 2021 made up for 9.2% of the total United States utility-scale electricity generation. However, there are a variety of issues that prevent solar and wind energy from completely replacing fossil fuels. Current solar cell materials, the most common being silicon, can't balance cost with efficiency. Wind energy can be sporadic and varies with weather conditions. Both renewable energy sources are only viable in very specific environments that meet their needs; this makes it difficult and impractical for places like

Michigan, which don't experience consistent winds or high intensities and durations of sunlight year-round, to implement these energy solutions.

Some locations have conditions that can make up for the rest: if a desert area with dimensions 100 miles by 100 miles were to be covered by solar panels, it would be able to power the entire United States. However, the problem then becomes one of electricity transmissions. Power plants use transformers to significantly increase the voltage of generated power for long distance transmissions, enabling the electricity that almost everyone in the United States uses in their homes. While power loses are minimal due to low resistance wire materials, they quickly add up over long distances, requiring the existence of substations that transform the power into lower voltages that are accessible in higher densities for end users. A transition to solar or wind energy would allow for significantly fewer power plants, requiring more infrastructure in substations which are also points of inefficiency. Without superconducting materials that can operate at ambient earth temperatures, renewable energy sources that rely on transporting generated electricity become unviable without extremely high power and efficiency.

Another potential renewable energy source is hydrogen gas due to its wide variety of advantages. Hydrogen gas societies have been proposed due to hydrogen gas being highly energy dense and easy to transport. A hydrogen society means completely replacing fossil-based final energy to hydrogen, including mobility, households, and industry as shown in Figure 2. Enacting this system requires very high hydrogen gas production, as this gas is then transported to all other use cases from cars and buildings to businesses and households. But current technologies to generate hydrogen gas are extremely inefficient and rates of hydrogen production aren't sufficient to meet the needs of the world. The primary means of generating hydrogen gas is through electrolysis, and a transition into a hydrogen society would require improvements in technology, primarily to increase the rate of electrolysis.
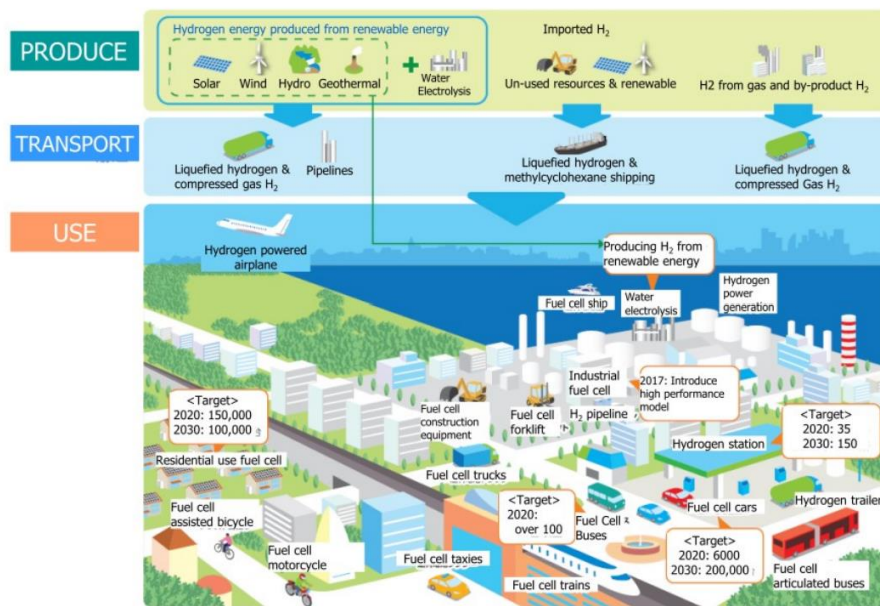

Figure 2: Depiction of a possible hydrogen society, highlighting the three main stages of produce, transport, and use.

1.2. Electrolysis

Electrolysis is a method of driving a chemical reaction that's normally non-spontaneous by using a DC current. This is done physically by using the current to stimulate the flow of ions that are associated with the non-spontaneous chemical reaction and induce it to occur. The process is often used to separate a substance into its original elements or components, and to generate hydrogen gas through electrolysis the substance being separated is water which gives the process the name "water splitting." Electrolysis reactions are also reduction-oxidation (redox) reactions meaning they involve the processes or oxidation where electrons are released and reduction when electrons are obtained. In the case of water, the electrolysis reaction is:

$$2H_2O(l) \rightarrow 2H_2(g) + O_2(g) \tag{1}$$

Redox reactions can be split into two half reactions to better reflect the oxidation and reduction components. Below, equation (2) is the reduction reaction as electrons are being obtained and equation (3) is the oxidation reaction due to electrons being released.

$$2H^+(aq) + 2e^- \rightarrow H_2(g) \tag{2}$$

$$2H_2O(l) \rightarrow O_2(g) + 4H^+(aq) + 4e^- \tag{3}$$
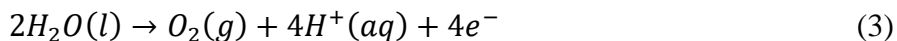
The addition of these half reactions will produce the overall reaction, and the reduction half reaction is what produces the hydrogen gas as shown in equation (2). For water splitting, the hydrogen reduction reaction is the rate-limiting step, and because this step is so slow the overall electrolysis process becomes extremely slow which is the primary reason that hydrogen gas isn't commercially viable as a renewable energy source yet. This step is so slow because it has an extremely high activation energy: if we can find methods or techniques to speed up this half reaction, the overall reaction will be sped up and hydrogen gas will become significantly more viable.

1.3. Artificial Photosynthesis

A proposed method to increase the rate of electrolysis is called artificial photosynthesis. It's termed this because it harnesses the sun to accelerate the rate of the electrolysis reaction. This is done by having two primary components in the system, a semiconducting component and a photocatalyst.

1.3.1. Photocatalyst component

Catalysts are materials that increase the rate of a reaction by easing the process. As shown in Figure 3, this is done by providing a surface that either (1) allows reactants to orient themselves in ways that are more probable for reaction or (2) bonds more strongly with the reactant to accelerate another step of the reaction.
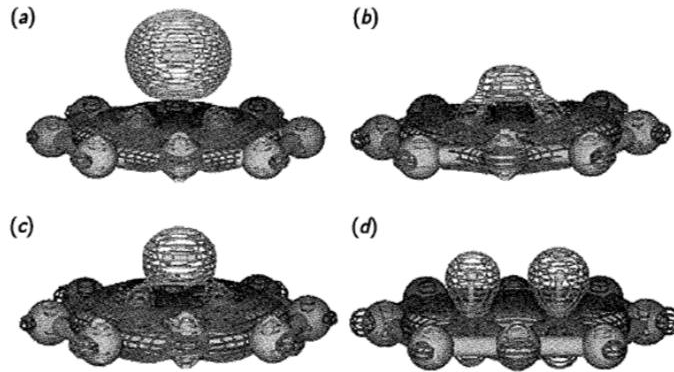
Figure 3: Model of hydrogen gas being split on a platinum surface, where a) the hydrogen gas comes in contact with the surface b) the hydrogen gas interacts with the platinum surface c) the hydrogen gas bonds to the platinum surface d) the hydrogen-platinum is preferred over the hydrogen-hydrogen bond, causing the hydrogen gas to split.

Hydrogen fuel cells are only possible thanks to the usage of catalysts, where the catalyst often enables the oxidation half reaction to react fast enough for the overall reaction to occur at a reasonable rate. Photocatalysts are catalytic materials that are more efficient or even can only function in the presence of sunlight. The photocatalyst is the site where the electrolysis reaction occurs. Submerging our system in water provides the water with a reaction surface to accelerate the electrolysis process.

1.3.2. Semiconductor component

Semiconductor materials are unique in that they have an energetic band gap where electrons can't exist, as shown in Figure 4.
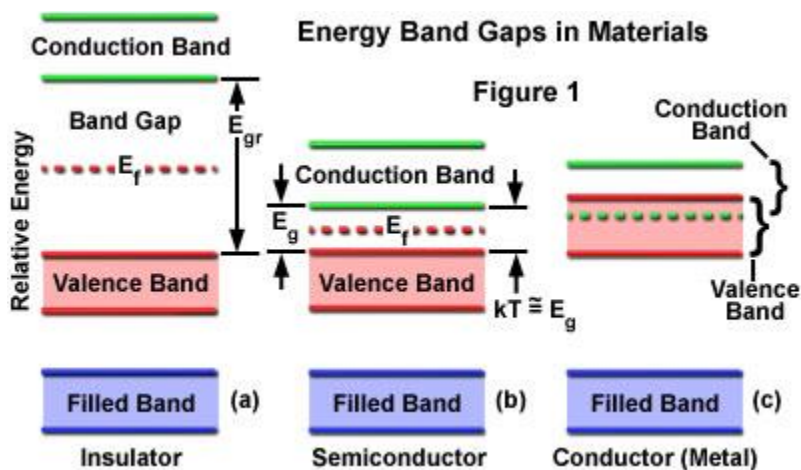

Figure 4: Energy band structure of different material classes. Semiconductor band structure is shown in (b), where there is a smaller band gap between the valence and conduction bands.

The bottom end of the band gap is the valence band below which most electrons exist, and the top end of the band gap is the conduction band above which only electrons with sufficient energy can exist. Because valence electrons are so crowded below the valence band, they don't contribute to electrical current while conduction electrons have both the energy and mobility to be free and generate electricity. When enough energy is provided to a valence electron for it to overcome the energy barrier of the band gap, it can move into the conduction band and become free, in which case you can use it for any applications. In this case the free electrons are transported to the photocatalyst which accelerates the reduction reaction, as increasing the concentration of reactants increases the overall rate of reaction. Electrons in semiconductor materials can be excited by a variety of inputs, the most common being sunlight as seen in solar panels. In the artificial photosynthesis system, as photons from the sun collide with the electrons in the valence band of the semiconductor, those valence band electrons become excited if the photon has enough energy to overcome the energetic band gap. These excited electrons naturally move to the photocatalyst due to the energy landscape of the system and help accelerate the reduction half reaction by increasing the concentration of reactants. It is thought that this step is what significantly increases the efficiency of the water splitting process, as a high density of electrons can be excited in certain semiconductor materials.

1.4. Current Mi Lab Initiatives

The Mi Lab has been a pioneer in accelerating artificial photosynthesis technology and efficiency. Their system uses gallium nitride (GaN) nanowires to function both as the photocatalyst and the semiconducting component. By combining the two functions onto a single forest of GaN nanowires, the transport of electrons is significantly simplified, and the system becomes incredibly efficient: the Mi lab has demonstrated that using GaN can double the efficiency and stability of water splitting compared to other hydrogen generation technologies. The Mi lab's current initiatives involve better understanding the physical phenomena involved, including the catalysts mechanisms, carrier dynamics, photoelectrochemical reactions, and the synthesis of the materials, all in order to push the technology towards high production to change the energy landscape of our society.

2. Important Questions

The Mi group's artificial photosynthesis is far from the point of large-scale production, and there are still many questions to address with regards to this technology. Among these are:

- What about GaN structure allows it to function as a photocatalytic material
- What model can describe the trend between electron transport and water splitting efficiency
- **What model can describe the trend between temperature and electron excitation and transport to the photocatalytic material**

The question that this project focused on is bolded above: how temperature effects the efficiency of electron transport and excitation in our system. This question is not very well understood because of the many interactions happening in our system. While electron dependencies with temperature are understood in semiconductor materials and photocatalysts respectively, combining all these interactions into a single system makes everything difficult to track, and there aren't any existing studies that have dived into this question for such a complex system. To address this question, this project utilizes materials simulation software to study to the electronic landscape of GaN and combine this description with theory to try and predict how electrons move throughout the system and determine if this can be correlated to water splitting performance.

3. Methods
3.1. Density Functional Theory

Density functional theory (DFT) is a successful theory to calculate electronic structures of atoms, molecules, and solids. What makes it so powerful is that electronic structure calculations are extremely intensive: normally the solution to Schrödinger's equation is approximated for some number N interacting electrons. The solution to Schrödinger's equation for just two interacting electrons is already nontrivial, and so the computational complexity grows exponentially as N increases. It would be difficult even for some supercomputers to compute electronic structures of relatively simple molecules using this traditional method, but by using DFT, even modern laptops can calculate the electronic structures of relatively simple atoms and molecules.

DFT makes this possible by using a one-body density wave function as the fundamental variable as opposed to the many-body wave function that would be used to describe N interacting electrons. By simplifying the density to one-body describing all of the electrons, the problem is only concerned with three spatial coordinates instead of 3N coordinates due to the three dimensions associated with each electron. DFT exists as a result of the combination of two theorems, the Hohenberg-Kohn theorem and the Kohn-Sham theorem.

Hohenberg-Kohn theorem is the central statement of DFT, describing mathematically how the problem is simplified. DFT is still concerned with studying the interaction of all N electrons, and thus the Hamiltonian is described by:

$$\hat{H} = \hat{T} + \hat{V} + \widehat{V_{ee}} \tag{4}$$

Where $\hat{T}$ is the kinetic energy operator, $\hat{V}$ is the potential energy operator, and $\widehat{V_{ee}}$ is the interacting energy operator describing the energy interactions between the N electrons. From this, there are three statements that encompass the theorem:

1) The ground state electron density of a system of interacting electrons, n(r), determines all physical properties of the system.
   a. This statement is true because n(r) uniquely describes the external potential V(r) in which the electrons are moving.

2) There exists a variational principle involving only density.
   a. This means that the ground-state energy E_0 can be written as a function of density
   b. Additionally, this says that a functional $E_{V0}[n]$ exists.
3) There exists a functional $F[n]$ such that the energy functional can be:

$$E_{V_0}[n] = F[n] + \int d^3 r V_0(r) n(r) \tag{5}$$

The Kohn-Sham theorem provides equations that describe the system of interacting electrons with a fictitious system of non-interacting particles that maintain the same density as if they were interacting. This provides a significant simplification and approximation to describe the system of electrons, and by combining these equations with Hohenberg-Kohn equations and plugging in the potentials of different electron energies as they correspond to different materials, the electronic structures of the material can be determined in terms of its densities of states and band structures.

3.2. Materials Studio

Many programs exist to perform DFT calculations and simulations. Among them is a software called Materials Studio by BIOVIA. Materials Studio can perform a variety of functions and calculations, ranging from calculations of thermodynamic equilibrium to quantifying the kinetics of different reactions and systems. Among these functions is DFT: Materials Studio can perform calculations and provide the electronic properties of a material based on the atomic structure. The Cambridge Serial Total Energy Package (CASTEP) performs DFT using a plane wave basis set and provides a variety of calculation and analysis functions that allow the user to calculate properties like the density of states, band structure, electron densities, IR spectra, Raman spectra, etc. Within CASTEP there are three main steps: structure definition, calculation step, and analysis.

3.2.1. Structure Definition

The structure definition gives a way to define the material. The electron landscape of a material is dictated by the layout of atoms, and so the crystal structure of the material can be used to determine what the electron densities and distributions will look like, which in turn allows us to perform the DFT calculations on their interactions. The structure that our project is interested in is GaN, which has a wurtzite crystal structure and thus can be described by two lattice constants of a = 3.186 Å, c = 5.186 Å. These parameters can be specified in Materials Studio to create the corresponding unit cell.

3.2.2. Calculation

The CASTEP package provides a variety of calculation functions, including:

- Energy: Allows calculation of total energy of the 3D system, as well as its physical properties

- Geometry Optimization: Refines geometry of 3D system into stable structure
- Dynamics: Allows simulation of atoms moving under the influence of computed forces

Depending on what is happening physically, different calculations can represent the phenomenon more accurately. For this project, a dynamics simulation is most accurate because we want to observe how atoms and their electrons will be influenced by the effects of temperature which can be thought of as an external force moving the system towards a new equilibrium.

Within the dynamics package, there are different thermodynamic ensembles and parameters that the user can use to further define what is happening physically.

- NVE: Newtonian equations of motion, where total energy is conserved in a fixed unit cell while temperature can vary.
- NVT: A thermostat maintains constant temperature while dynamics are modified to allow the system to exchange heat with the environment.
- NPH: Enthalpy and pressure is a constant of the motion while the size of the unit cell varies.
- NPT: Constant pressure and temperature is maintained while the size of the unit cell can vary.

For this application, the NVE calculation makes the most sense because our device won't be changing in size and the energy should be constant between the energy absorbed by incoming photons and energy used in the water splitting. By using these simulation conditions, successful DFT simulations were run to predict the electronic properties of GaN nanowires.

4. Results

DFT simulations were run using dynamics simulation and an NVE thermodynamic ensemble. For optimal simulation conditions, the GGA electric field functional and PBE exchange-correlation functional were used. While these functionals are related to the solving of Hohenberg-Kohn equations, these parameters are the most appropriate for these experimental conditions. Simulations were performed at different temperature conditions ranging from 0°C-100°C. These are the likely operating temperatures that we can expect the device to function at: below 0°C weather conditions are too poor for proper device operation, and above 100°C the water will boil away before it can be split at the photocatalyst. Performing the CASTEP functions and observing the density of states for GaN, the following data shown in Figure 5 is obtained.
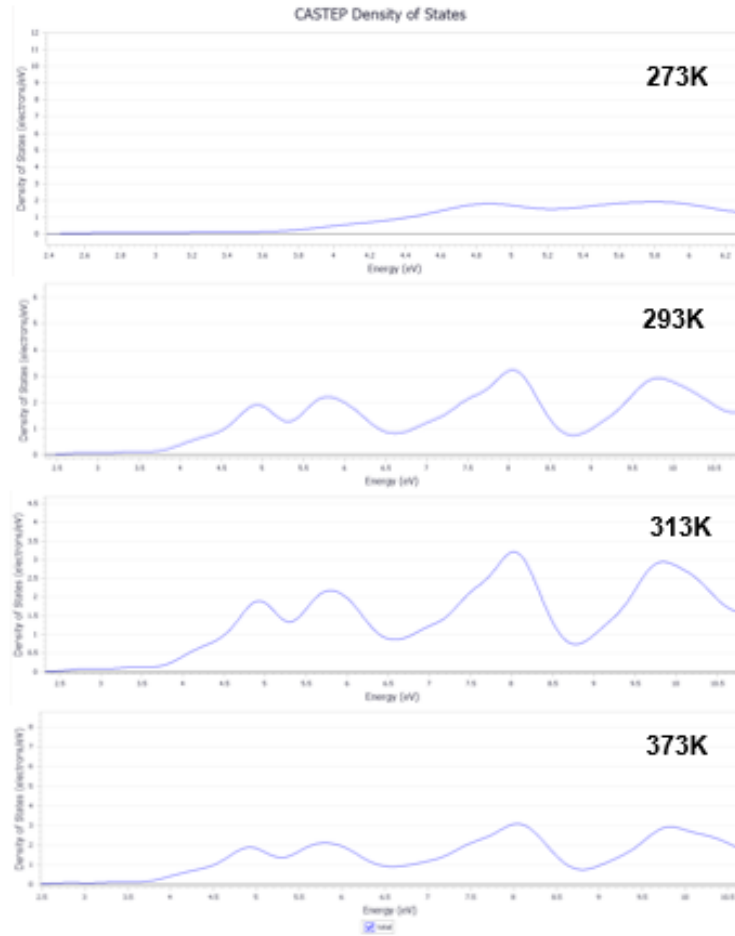
Figure 5: Density of states of GaN under various temperature conditions.
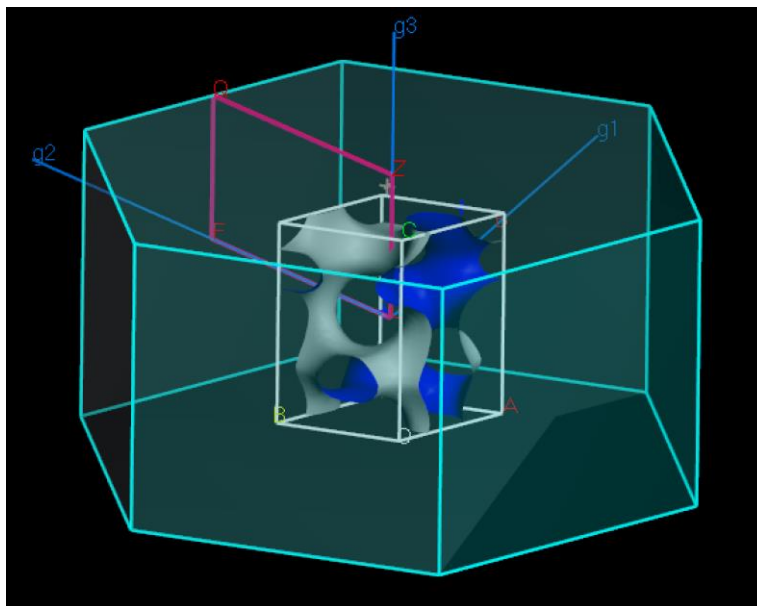

Figure 6: Electron density distribution for GaN under room temperature conditions.

The density of states describes the available state for electrons to occupy and consequently the energy levels that electrons will have as they fill in these energetic states. Thus, the density of states can be used to describe how much energy electrons in the system have which can be correlated to the likelihood and rate of electron transport to the photocatalyst site. From Figure 5, increasing the temperature of the system increases the number of states available for electrons just above the band gap which is the most likely location for excited electrons to occupy. We can conclude from this that because increasing temperature also increases the energy of electrons and makes it easier to excite them, that increasing the temperature of our system will induce more mobile electrons and provide them with more kinetic energy to in turn move to the photocatalytic site and aid in water splitting. However, it is also observed that at some point, around 75°C, that the density of states begins decreasing. While this initially seems surprising, this matches theory on photoexcitation: among different recombination mechanisms, Shockley Reed-Hall recombination generally scales with temperature, meaning higher temperatures correspond with increasing rates of exciton recombination and in turn a decrease in electron concentrations. Theory predicts that this mechanism isn't as prevalent at lower temperatures where slower mechanisms like radiative and auger recombination are more prevalent and the excitation of electrons is more likely due to the abundance of electronic states, but eventually as temperatures continue to increase it is expected that Shockley Reed-Hall recombination will dominate and cause a decrease in electron availability.

5. Conclusions

The primary question that this project focused on answering is quantifying the temperature dependence of electronic properties in GaN nanowires. To do this, materials simulations were performed to observe how properties like density of states, band structure, and electron densities would vary under different temperature conditions. By observing these properties, we predict that the ideal operating conditions for GaN nanowires is around 75°C by observing how the density of states and electron densities are maximized under these conditions. The overall trends of these results also matches photoexcitation and semiconductor theory, but more detailed quantifications must be done to determine how accurately they match.

While this is one prediction from simulation, we believe that this simulation still isn't accurate enough to resemble the physical system. This simulation only considers bulk GaN crystal and uses electronic properties of the bulk to infer how they will relate to the photocatalyst. Particle transport and catalytic behavior is significantly more complex than these simplifications can accommodate, and Materials Studio is an extremely powerful software that can perform very complex simulations. Future work includes using different ensembles and simulation conditions to expand on the bulk GaN framework and convert it to encompass both nanowire properties and simulate photocatalytic behavior. These results will then be compared to the experimental results from a functioning prototype to observe the accuracy of simulations and determine whether we can properly describe new physical phenomena with our new found results.