SOCIETY OF PHYSICS STUDENTS
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SPS Chapter Research Award Proposal

Project Proposal Title	Ultrathin PTAA Layer and Phenylhydrazinium Iodide for Defect Passivation and Enhanced Charge Carrier Mobility in Perovskite Solar Cell.
Team Leader	Abdullah Al Maruf
Name of School	South Dakota State University
SPS Chapter Number	6514
Total Amount Requested	$1,999.61

Abstract

In recent years, hybrid perovskite solar cells (HPSCs) are of great interest in the scientific community due to their impressive photovoltaic performance and low-temperature solution processing capability. This project is devoted to developing HPSCs with a novel material, phenylhydrazinium iodide (PHAI), as an additive in FAPbI3 perovskite, as well as introducing an optimally designed ultrathin poly(triarylamine) (PTAA) layer in the stacks of HPSC – to solve two of the crucial problems in HPSCs, low carrier life time and interfacial recombination, affecting the solar cell's power conversion efficiency and stability. South Dakota State University's (SDSU) SPS Chapter will lead this research project, which will potentially help to solve the current limitations of next generation solar cells, as well as train undergraduate students in rigorous experimental and computational physics research.

Proposal Statement

Overview of Proposed Project

In our project, we are developing hybrid perovskite solar cells with high power conversion efficiency, a fill factor (FF), and a short-circuit current density (J_{sc}). Our optimally designed perovskite solar cell will ultimately result a structure which suppress the interfacial recombination and accelerate the hole transfer in the device.

Perovskite solar cells convert light energy into electrical energy through photovoltaic effect. It is known that incident light photons have the energy of $E_{Ph}=h\upsilon$, where h is the plank's constant and υ is the frequency of light. The absorption of light depends on the bandgap (E_g) of the semiconductor material. When photon energy is larger than the bandgap of the semiconductor materials ($E_{Ph}> E_g$), light is absorbed, and electrons receive enough energy to jump to conduction band (CB), while leaving holes in valence band (VB). Thus, the charge carriers are generated as shown in figure 2.1a. This scenario also occurs in organic materials, where electrons (e^-) jump from highest occupied molecular orbital (HOMO) to lowest unoccupied molecular orbital (LUMO). These photogenerated holes and electrons form the bound excitons, namely electron-hole pairs, which are attracted to each other by the coulombic force [1, 2]. In case of perovskite, the exciton binding energy is relatively weak, and can be separated to free charges (electrons and holes) at room temperature.

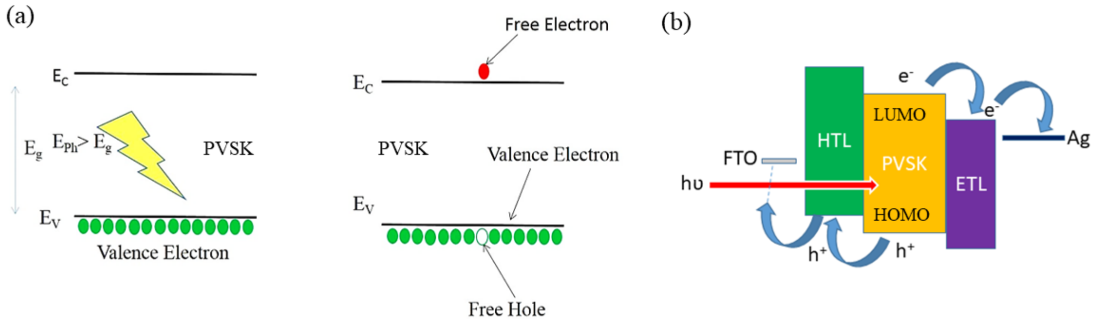

Figure 2.1. a) Generation of charge carriers in perovskite active material by absorbing light energy.
b) Charge separation in band energy diagram of perovskite solar cell.

In order to produce electricity from solar cells, these photo-generated free electrons and holes need to be extracted before recombination. For this purpose, electron transport layer (ETL) and hole transport layer (HTL) are used as shown in figure 2.1b. HTL and ETL are designed to be p-type and n-type materials, respectively. Energy level alignment plays important role at the interface between charge transport layers and perovskite. The ETL is designed in such a way that it only allows electrons transferring from the active layer to the cathode, and blocking the holes at the same time, which reduces the recombination of the free charge carriers at the interface. To achieve this, the CB of ETL is kept slightly lower than that of perovskite, which helps to accelerate electrons at the interface to migrate from perovskite to the electrode. On the other hand, much lower VB of the ETL than that of perovskite can efficiently block the migration of holes simultaneously.

Whereas, HTL is designed in opposite to ETL so that, it blocks electrons, and allows holes transferring from perovskite to the cathode.

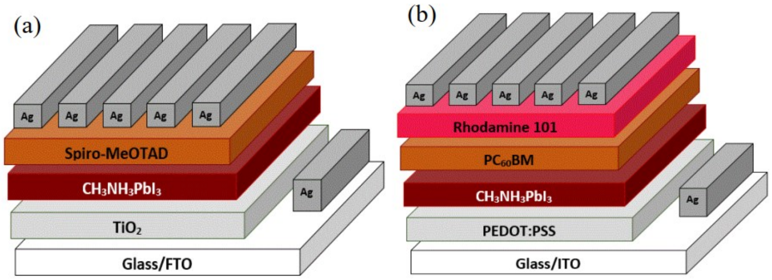

Figure 2.2. Planar device architecture of Perovskite solar cells. a) n-i-p. b) p-i-n.

Figure 2.2 illustrates planar n-i-p and p-i-n device architecture of Perovskite solar cells [3]. In n-i-p structure, perovskite layer is fabricated on top ETL (e.g. TiO2) and then HTL (Spiro-MeOTAD) on top of perovskite.

Objective:

(1) Device Fabrication and Testing:

In our project, we will fabricate an inverted p-i-n structure for HPSC. The device will be fabricated on top of a transparent and conductive metal oxide (TCO) substrate such as FTO or ITO. Light can directly enter through the ITO or FTO glass substrate. Then there is a very thin (30-50 nm) HTL (e.g. PEDOT.PSS) where light absorption is negligible. When the absorber layer FAPbI3 (CH(NH2)2PbI3) Perovskite receives photons, it will generate the excitons. Due to low exciton binding energy in CH(NH2)2PbX3, dissociation of hole and electron are predominant at room temperature near the interfaces [4, 5]. Separated holes will subsequently transfer to Ag electrodes through ETL (e.g. PC60BM) and electrons to TCO through HTL.

Buffer layer (e.g. Rhodamine) will be used between the ETL and metal electrodes for better alignment of relevant energy levels. On the other hand, because of having longer diffusion length and higher extinction coefficient, the thickness of perovskite absorber is very small like 300-600 nm for highly efficient HPSCs according to previous report [6]. Thin absorber layer is advantageous by requiring shorter charge transport paths which reduces the possibility of charge recombination.

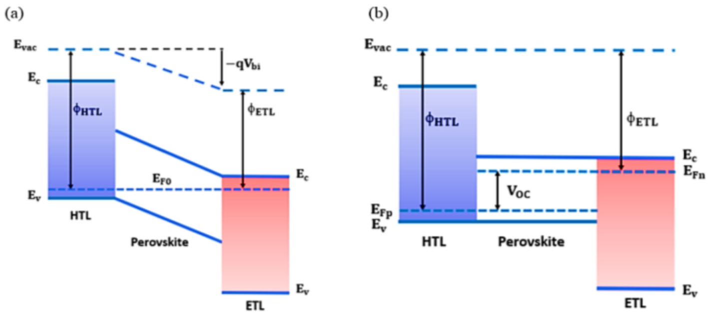

Figure 2.3. Perovskite solar cell's band diagram at a) short circuit and b) open circuit conditions.

Perovskite solar cells are heterojunction as ETL/perovskite and HTL/perovskite interfaces form two different junctions. In figure 2.3 [7], it depicts that perovskite along with the HTL and ETL share the same Fermi level of EF0 when in dark means short circuit (SC) condition. Highest energy state in a material which is occupied by electrons is known as Fermi level. Besides that, the built in potential (V_{bi}) emerged from the difference of HTL and ETL work functions, contributes to the offset between EV and EC which appears as -qVbi. In the contrary, HTL and ETL Fermi levels are split into E_{Fp} and E_{Fn} at open circuit condition under illumination. The difference between E_{Fp} and E_{Fn} is the open circuit voltage (V_{oc}).

And the power conversion efficiency (η) of a solar cell will be tested, which is the ratio of maximum output power to incident photon power. η is directly proportional to FF, where,

$$\eta = \frac{P_{max}}{P_{in}} = \frac{I_{sc} \times V_{oc} \times FF}{P_{in}} \qquad (1.1)$$

(2) Benefit of the proposed study and the SPS involvement:

Our project will help the local SPS chapter by creating undergraduate research opportunities for SPS students at SDSU and prepare them for graduate school. This will also help our chapter to grow as we do more interdepartmental outreach through Physics colloquiums, besides SPS programs/activities, and get more students excited about the research, potentially recruiting more members for our local and national SPS. Additionally, the SPS research will help facilitating our chapter's public relationship with companies like Daktronics, Raven Industries, 3M, etc. in South Dakota, since our proposed project has direct applications in industries with an interest in sustainable energy. The industry relationship can be also useful in terms of fundraising for our local SPS chapter to organize large meetings in the future, boosting the overall image of our local SPS community in the university and nationally. Our project is also helpful in green energy technology revolution, since highly efficient and long-lasting solar cells are much needed to transition to clean energy technology. Moreover, we will present our work in the annual SPS regional/national meetings. Last year (2019), an officer of SDSU SPS chapter, Abdullah Al Maruf, won the best (research) poster award in the SPS Zone-11 Meeting-2019 at the University of South Dakota. The national SPS will be acknowledged in the final manuscript as we're aiming to publish our work in a reputed scientific journal by the end of the project.

Background for Proposed Project

In the last few years, active research works on hybrid perovskite solar cells (HPSCs) have been going on throughout the world as a part of clean energy revolution. HPSCs have already proved their potentiality as future solar technology through their promising photovoltaic performances and ability for low temperature based solution processing. Nevertheless, still there are remaining challenges of better charge carrier dynamics and defects minimization in HPSCs. Overcoming these challenges are very important to achieve high power conversion efficiency (PCE) practically. Aiming this, a novel organic halide salt called Phenylhydrazinium iodide (PHAI) is proposed as additive with CH(NH2)2PbI3 perovskite precursor solution in this study. Incorporation of a very small amount of PHAI along with introducing ultrathin layer of PTAA will result enhancement of charge carrier dynamics in HPSCs, increasing the device's short circuit current density. In addition, PHAI treatment help will help to reduce perovskite grain boundary defects significantly compared to the pristine CH(NH2)2PbI3 HPSCs. This reduction in defects will contribute to minimize the non-radiative recombination of photogenerated charge carriers. Consequently, overall a large improvement in PCE will be expectedly achieved through PHAI additive treatment providing high efficient CH(NH2)2PbI3 inverted hybrid perovskite solar cells. Besides, PHAI treated HPSCs exhibited superior ambient stability than the pristine devices in unencapsulated condition in our initial experiments.

Expected Results

By conducting this project, we will able to synthesize hybrid perovskite solar cells, in which the interfacial defects will be suppressed. We will also perform the initial validation for defects passivation capability of PHAI. Additioanly we will analyze the perovskite film morphology and crystallinity in effort to achieve a long-lasting / stable cell. Device performance analysis will also be carried out in order to examine the smooth perovskite film, which will ultimately execute low charge transfer resistance, thus increasing efficiency. Finally, we will perform charge recombination and defects analysis to in order to achive the reduced non-radiative recombination, which is related to the observed open circuit volatage (V_{oc}). V_{oc} will increase in the treated devices as V_{oc} depends on voltage loss due to non-radiative recombination given by $V_{oc}=V_{oc}^{max}-V_{oc}^{non\text{-}rad}$.

Experimental Procedures

(3.1) Solar Cell Fabrication

First, FTO-coated glass substrates will be etched with Zn powder and 0.1M HCl before cleaning. Then, the etched substrates will be cleaned with detergent water, de-ionized water, acetone and isopropanol sequentially. The substrates will be dried with dry N2 and then cleaned by UV–O3 for 20 min.

Figure 3.1. Ultra-sonication of the substrate.

PEDOT:PSS solution at room temperature will be filtered by 0.45 µm filter, followed by spin coating at 4500 rpm for 45 s and annealing at 145 0C for 10 mins. Substrates with PEDOT:PSS film will then be transferred to a N2 filled glove box. 70 µL of filtered perovskite solution will be spin coated on top of PEDOT:PSS layer at 750 rpm for first 20-30 s, followed by 4000rpm for an additional 60 s. We will then drip 165 µL of toluene as anti-solvent onto the perovskite film during spin coating at 40th s. The FAPbI3 precursor will be prepared from 581 mg of PbI2 and 209 mg of FAI mixture dissolved in a solvent mixture of GBL and DMSO with 7:3 (v/v) ratio, stirred for 12-15 hours at 70 °C

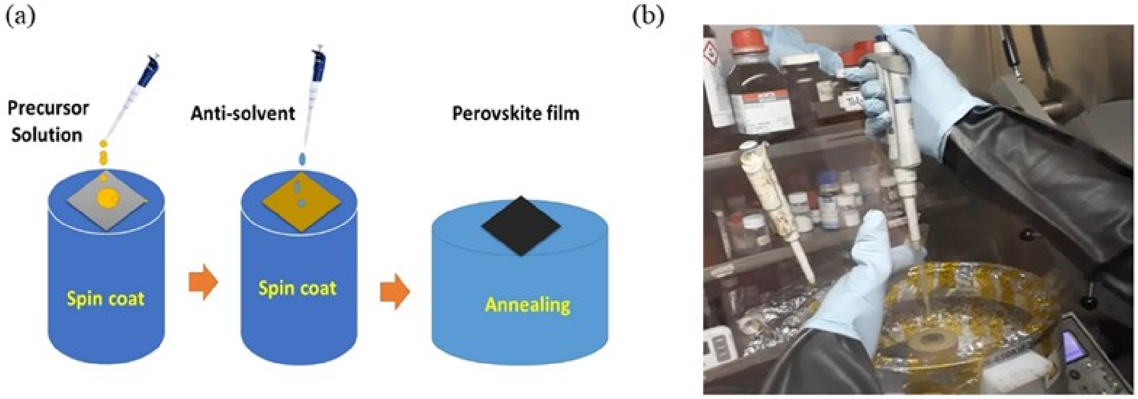

Figure 3.2. a) Schematic of step by step perovskite film fabrication.
b) Anti-solvent dripping while spin coating the perovskite film inside the N2 glove box.

inside the N2 glovebox. PHAI additive will be mixed with the precursor 2-3 hours before of the spin coating. The spin coated perovskite films will be annealed for 10 minutes at 700-800C. After the substrates are completely cooled down, 60 µL of filtered hot solution of PCBM will be spin-coated at 2000 rpm for 40 s and subsequently annealed for 5 minutes at 80 °C. After cooling down, 0.5 mg Rhodamine in per mL dry IPA will be spin-coated at 5000 rpm for 20 s. Finally, 85 nm thick silver electrodes will be deposited by thermal evaporation [8].

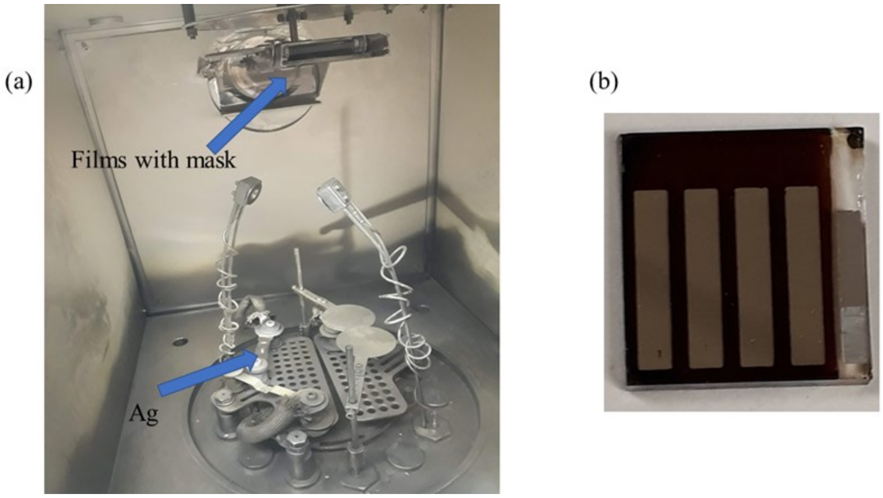

Figure 3.3. a) Preparation for Ag evaporation inside the evaporator chamber.
b) Complete solar cell after evaporation of Ag electrodes.

(3.2) Characterization of materials and Solar Cells

Raman spectroscopy will be carried out using Horiba LabRam HR 800 Raman spectrometer having a green laser beam of 532 nm wavelength. FTIR will be done by Nicolet 6700 FTIR with Smart Orbit ATR Unit. SEM will be carried out by Hitachi-S4700N SEM. And XRD will be measured on Rigaku SmartLab diffractometer with Cu Kα radiation (λ = 1.54178 Å).

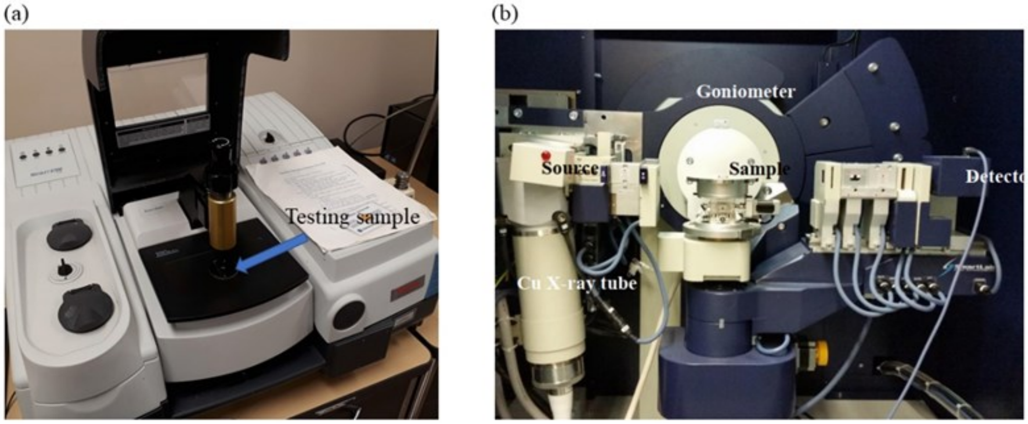

Figure 3.4. a) Nicolet 6700 FTIR. b) Rigaku SmartLab XRD

Agilent 5500 scanning probe microscopy will be utilized for AFM topography and KPFM in tapping mode whereas CS-AFM in contact mode with 1V applied bias. EIS measurement will be performed by Ametek VERSASTAT3-200 potentiostat from 1 Hz-1 MHz frequency at 0.8 V. TPC and TPV will be measured using an oscilloscope and OBB's OL-4300 nitrogen laser coupled with dye laser producing <1 ns pulse at 532 nm wavelength. 50 Ω input oscilloscope impedance will be considered for short circuit conditions. During TPV, 1 sun illumination will be applied to the PSCs and considered 1 MΩ input oscilloscope impedance for open circuit conditions. To obtain photo-CELIV curves, ns pulse width laser will be used by varying delay time between ramp and the laser. Agilent 8453 UV–visible Spectroscopy System will be used for absorption measurement of the films. I-V data will be obtained from Agilent 4155C semiconductor parameter analyzer including a Xenon arc lamp (Newport 67005).

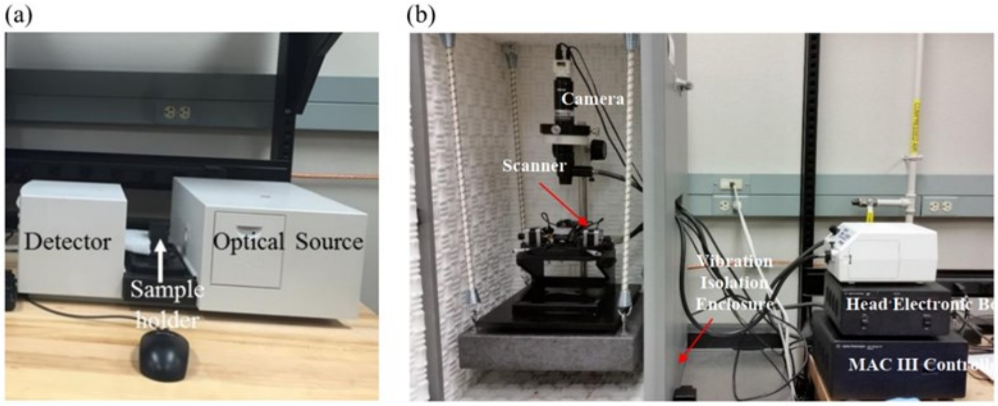

Figure 3.5. a) Agilent 8453 UV–visible Spectroscopy System. b) Agilent 5500 Scanning probe microscopy.

NREL S1133-14 silicon reference solar cell will be used for calibration. The PSCs having an active area of 0.13 cm-2 were swept from 0 to 1.2 V with a scan speed of 1 Vs−1 in forward and reverse direction. For IPCE measurement, Newport 74125 monochromator will be used. Mott–Schottky measurement will be done using the same instrument as used in EIS but at a fixed frequency of 1 KHz for 0-1 V. Edinburgh FLS 920 fluorescence spectrophotometer will be used for steady-state PL. Contact angle will be measured by using the instrument of VCA 2000 video contact angle system [8].

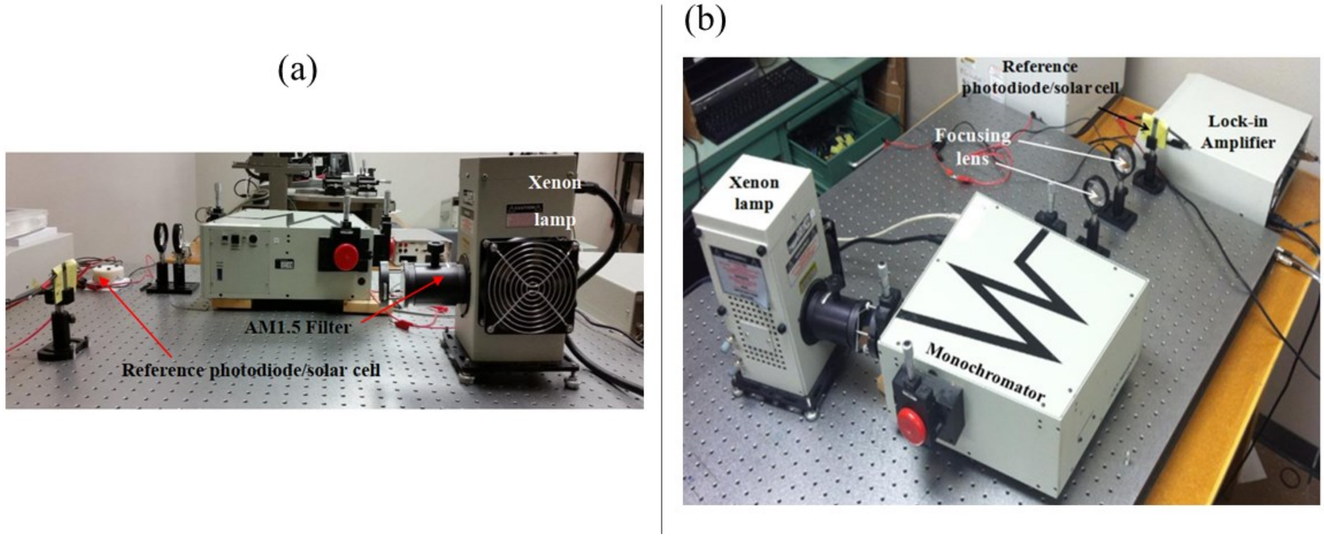

Figure 3.6. a) Arrangement of I-V measurement. b) Setup for IPCE measurement.

Plan for Carrying Out Proposed Project

This research will be performed with a collaboration between South Dakota State University's (SDSU) SPS Chapter in the Physics Department and the Electrical Engineering Department. SDSU's University Center for Commercialization of Sustainable Energies and Precision Agriculture Sensors Technologies has clean room facilities where all the necessary equipment are stationed, and the Physics Department is also located in the same building.

Only local and national SPS student members in the university will be directly involved in the research, which will also count as their Undergraduate Research Experience during the academic year. Majority of the SPS members have previous experience in Physics research during summer, and have sufficient knowledge on designing, fabrication, characterization, and analysis to perform the project successfully. **Dr. Yue Zhou** at the EE department will be our research advisor for the project. The SPS team members, **Abdullah Al Maruf, Nabin Ghimir, Ashiqur Rahman Laskar, Khan Mamun Reza, Mominul Islam, Ke Chen, Zachary Mehlberg** will conduct research. The SDSU SPS advisor and Zone-11 councilor, **Dr. Robert McTaggart**, will oversee the project, and help the SPS research team with guidance during the project.

Project Timeline

1. Assemble all previous work on this project including, but not limited to, previous research reports, ideas, prototypes, and compile useful materials and begin research on instruments. – **Finish by end Jan 2021.**
2. Synthesize FAPbI3, PDOT:PSS, PTAA, PHAI, etc. in order to fabricate and test the HPSCs. **– Finish by mid-March 2021.**
3. Start characterizing all the perovskite solar cells and related structures using Scanning Electron Microscope (SEM), X-ray Photoelectron Spectroscope (XPS), and Transmission Electron Microscope (TEM) and– **Finish by end April 2021**.
4. Fabricate perovskite solar cells in the second stage, based on pervious characterizations and testing. **Finish by end June 2020.**
5. Finish characterizing all the perovskite solar cells and related structures using previous methods and Atomic Force Microscopy (AFM). **Finish by Aug 2021**
6. Collect all the analyzed data of materials' characterization and testing, and prepare a report – **Finish by mid-Sept 2021.**
7. Complete the analysis of all the obtained data on Origin Software **– Finish by end Oct 2020**.
8. Summarize all the data and complete writing a manuscript to publish in a scientific journal – **Finish by mid-Dec 2021**.

Budget Justification

To conduct the SPS research project, we request $1,999.61 to cover the software subscription, materials, and supplies required for the experiments. The cost associated with this project comes largely from Small silver Pellets, Formamidinium iodide, Methylammonium iodide, and Phenylhydrazine, and Lead(II) iodide for synthesizing the perovskite solar cells. The lab equipment (i.e. XRD, SEM, glovebox, glassware and tubes, etc.) will be provided by the university. Another cost that contributes to the budget is paying for the TEM and XPS facilities (two hours each) in Daktronics Inc. Additional funding support will be provided by the SD BoR R&D Grant Program at South Dakota State University.

Bibliography

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Facilities

Some of the SDSU research facilities are shown in the following: