Machine-Learning Based Optimization of $ZnS_{1-x}Se_x$ Composition in Dye-Sensitized Solar Cells Using LEGOLAS Framework

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Abstract

We present a machine-learning based framework using Gaussian Regression with Bayesian Optimization to accelerate the discovery of optimal semiconductor compositions in dye-sensitized solar cells (DSSCs). Using the LEGOLAS (LEGO-based Low-cost Autonomous Scientist) platform, we demonstrate efficient optimization of $ZnS_{1-x}Se_x$ alloy composition for photoanode applications. This fully closed loop framework integrates Gaussian Process (GP) regression with Expected Improvement acquisition function to systematically explore the composition space while minimizing experimental trials. Our approach implements a dual-fallback architecture combining hardware/simulation modes for voltage measurements and AFLOW database/Vegard's law for bandgap calculations, allowing demonstration of benefits of this framework across multiple environments. Using iterative closed-loop optimization, we identify the optimal composition achieving an open-circuit voltage of 0.855 V, representing an 11.2 % improvement over random sampling with sub-20 mV prediction accuracy and RMSE: 0.019 V) with only 10 experimental measurements. Our work demonstrates effectiveness of machine learning-guided materials optimization for photovoltaic applications and provides a highly modular hardware-software platform for autonomous materials discovery.

1 Introduction

Dye-sensitized solar cells (DSSCs) represent a promising alternative to conventional silicon-based photovoltaics, offering low-cost fabrication, transparency, and flexibility. The performance of DSSCs critically depends on the semiconductor photoanode material, which must balance visible light absorption with efficient electron injection from the photoexcited dye molecules. Titanium dioxide has been the benchmark photoanode material, but its wide bandgap (3.2 eV) limits visible light utilization.

1.1 Motivation for $ZnS_{1-x}Se_x$ Alloys

Semiconductor alloying offers a powerful route to tune optical and electronic properties by enabling precise control over material characteristics such as bandgap and conductivity. In the context of dye-sensitized solar cells (DSSC), $ZnS_{1-x}Se_x$ solid solutions provide a compositionally adjustable bandgap and conduction-band alignment that can influence electron injection efficiency and dye interaction. This tunability is critical for optimizing charge transfer at the interface between the dye and the semiconductor, which in turn affects overall device performance. By modifying the alloy composition, one can systematically tailor the electronic structure to enhance photocurrent generation and improve compatibility with various sensitizing dyes.

Zinc chalcogenide alloys, particularly $ZnS_{1-x}Se_x$, offer tunable bandgaps spanning 2.70 eV (ZnSe) to 3.68 eV (ZnS). This compositional tunability enables optimization of:

- **Optical absorption:** Matching solar spectrum for maximum photocurrent
- **Conduction band alignment:** Efficient electron injection from dye excited states
- **Open-circuit voltage:** Maximizing photovoltage through bandgap engineering
- **Stability:** Chemical inertness in electrolyte environments

However, the $ZnS_{1-x}Se_x$ composition space is vast, and traditional trial-and-error exploration is time-consuming and resource-intensive. Systematic optimization requires numerous synthesis-characterization cycles, making it an ideal candidate for machine learning-guided discovery.

1.2 Gaussian Regression with Bayesian Optimization in Materials Science

Gaussian Regression with Bayesian optimization has emerged as a powerful tool for accelerating materials discovery by intelligently selecting experiments to maximize information gain. Unlike exhaustive grid search or random sampling, this appproach constructs a probabilistic surrogate model using Gaussian Process with following benefits:

1. Predicts material properties across the composition space
2. Quantifies uncertainty in unexplored regions
3. Balances exploitation (testing promising compositions) with exploration (reducing uncertainty)
4. Converges to optimal solutions with minimal experimental trials

Recent applications of such an approach in photovoltaics include organic solar cell discovery and semiconductor bandgap engineering.

1.3 LEGOLAS Framework

This work introduces LEGOLAS (LEGO-based Low-cost Autonomous Scientist), an open-source platform for autonomous materials optimization. LEGOLAS integrates:

- **Hardware interface:** Raspberry Pi with MCP3008 ADC for low-cost voltage measurements
- **Computational tools:** AFLOW database integration with Vegard's law bandgap prediction as fallback alternative
- **Machine learning:** Gaussian Process regression with Expected Improvement acquisition
- **Closed-loop control:** Autonomous experimental design and execution

The framework is designed for both educational accessibility as well as research performance, making it suitable for both labs and materials research.

1.4 Paper Organization

This paper is organized as follows: Section 2 describes the theoretical framework including Gaussian Process regression, Expected Improvement acquisition and Vegard's law. Section 3 details the LEGOLAS implementation including hardware setup, software architecture, and AFLOW integration. Section 4 presents optimization results demonstrating convergence to optimal $ZnS_{1-x}Se_x$ composition. Section 5 analyzes GP model performance, compares with alternative optimization strategies, and discusses implications for DSSC design. Section 6 summarizes key findings and outlines future directions.

2 Theoretical Framework

2.1 Bandgap Prediction using AFLOW and Vegard's Law

The Partial Occupation (POCC) method in AFLOW [3,4] is used to simulate atomic disorder by generating multiple structural configurations for each composition. The bandgap for each configuration is determined using density functional theory (DFT), and the results are ensemble-averaged to obtain representative values for each alloy composition.

As a fallback for AFLOW framework API to retrieve bandgap calculation, the bandgap of $ZnS_{1-x}Se_x$ alloys is estimated using Vegard's law with bowing parameter:

$$E_g(x) = (1-x)E_g^{\mathrm{ZnS}} + xE_g^{\mathrm{ZnSe}} - b \cdot x(1-x) \qquad (1)$$

where:

- x is the selenium composition ($0 \leq x \leq 1$)
- $E_g^{\mathrm{ZnS}} = 3.68\,\mathrm{eV}$ (bulk ZnS bandgap)
- $E_g^{\mathrm{ZnSe}} = 2.70\,\mathrm{eV}$ (bulk ZnSe bandgap)
- $b = 0.50\,\mathrm{eV}$ (bowing parameter)

We use a conservative estimate of bowing parameter to account for non-ideal mixing effects including:

- Lattice mismatch between ZnS (5.41 Å) and ZnSe (5.67 Å)
- Chemical disorder in random alloys
- Volume deformation effects

The negative bowing ($b > 0$) indicates that the actual bandgap is lower than linear interpolation, with maximum deviation at $x = 0.5$:

$$\Delta E_g^{\max} = -\frac{b}{4} = -0.125\,\mathrm{eV} \qquad (2)$$

Figure 1 shows the calculated bandgap vs. composition, demonstrating the parabolic deviation from linear behavior.

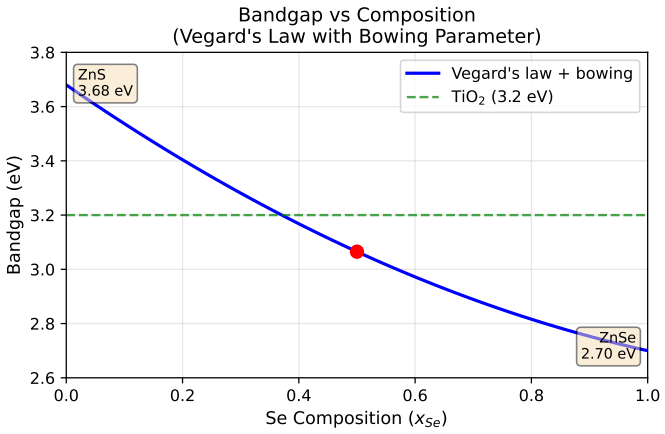

Figure 1: Vegard's law with bowing parameter for $ZnS_{1-x}Se_x$ alloy system. The bandgap varies nonlinearly from 3.68 eV (ZnS) to 2.70 eV (ZnSe) with maximum bowing at $x_{\mathrm{Se}} = 0.5$. The TiO_2 reference line (3.2 eV) shows the benchmark photoanode material.

2.2 Gaussian Process Regression

Gaussian Process (GP) regression provides a probabilistic framework for predicting material properties with uncertainty quantification. Given a dataset $\mathcal{D} = \{(\mathbf{x}_i, y_i)\}_{i=1}^n$ of bandgap-voltage pairs, the GP model predicts the voltage at a new bandgap E_g^*:

$$\mu(E_g^*) = \mathbf{k}^T[\mathbf{K} + \sigma_n^2\mathbf{I}]^{-1}\mathbf{y} \qquad (3)$$

$$\sigma^2(E_g^*) = k(E_g^*, E_g^*) - \mathbf{k}^T[\mathbf{K} + \sigma_n^2\mathbf{I}]^{-1}\mathbf{k} \qquad (4)$$

where:

- $\mu(E_g^*)$ is the predicted mean voltage
- $\sigma^2(E_g^*)$ is the prediction variance (uncertainty)
- $\mathbf{k} = [k(E_g^*, E_{g,1}), \ldots, k(E_g^*, E_{g,n})]^T$ is the cross-covariance vector
- $\mathbf{K}_{ij} = k(E_{g,i}, E_{g,j})$ is the covariance matrix
- σ_n^2 is the noise variance
- $\mathbf{y} = [y_1, \ldots, y_n]^T$ are the observed voltages

2.2.1 Kernel Selection

We use composite kernel combining the Radial Basis Function (RBF) and white noise:

$$k(E_g, E_g') = \sigma_f^2 \exp\left(-\frac{(E_g - E_g')^2}{2\ell^2}\right) + \sigma_n^2 \delta(E_g, E_g') \quad (5)$$

where:

- σ_f^2 is the signal variance (output amplitude scaling)
- ℓ is the length scale (controls smoothness)
- σ_n^2 is the noise variance (measurement uncertainty)
- $\delta(E_g, E_g')$ is the Kronecker delta

The RBF kernel captures smooth trends in the voltage-bandgap relationship, while the white noise kernel models experimental uncertainty (typical $\pm 10\,\mathrm{mV}$ for DSSC measurements).

2.3 Expected Improvement Acquisition Function

The Expected Improvement (EI) acquisition function balances exploitation (selecting high predicted voltage) with exploration (sampling uncertain regions) [1]:

The EI function has two components:

- **Exploitation term:** favors high predicted values
- **Exploration term:** favors uncertain regions

We slightly favor exploration, preventing premature convergence.

2.4 Voltage-Bandgap Correlation

The open-circuit voltage V_{oc} of a DSSC is related to the semiconductor bandgap. For simulated measurement mode, we use an empirical correlation:

$$V_{\mathrm{oc}}(E_g, I) = V_0 + \alpha E_g + \beta \ln(I + I_0) + \epsilon \quad (6)$$

where:

- $V_0 = 0.30\,\mathrm{V}$ (base voltage offset)
- $\alpha = 0.15\,\mathrm{V\,eV^{-1}}$ (bandgap dependence)
- $\beta = 0.025\,\mathrm{V}$ (light intensity coefficient)
- I is relative light intensity ($0 < I \leq 1$)
- $I_0 = 0.01$ (small constant to avoid $\ln(0)$)
- $\epsilon \sim \mathcal{N}(0, 0.01\,\mathrm{V}^2)$ (measurement noise)

This model captures following physical dependencies:

1. V_{oc} increases with E_g (wider bandgap $\rightarrow$ higher voltage)
2. V_{oc} increases logarithmically with light intensity (Shockley diode equation)
3. Gaussian noise models experimental uncertainty

3 Implementation

3.1 LEGOLAS Hardware Architecture

The LEGOLAS system consists of following main components (Figure 2):

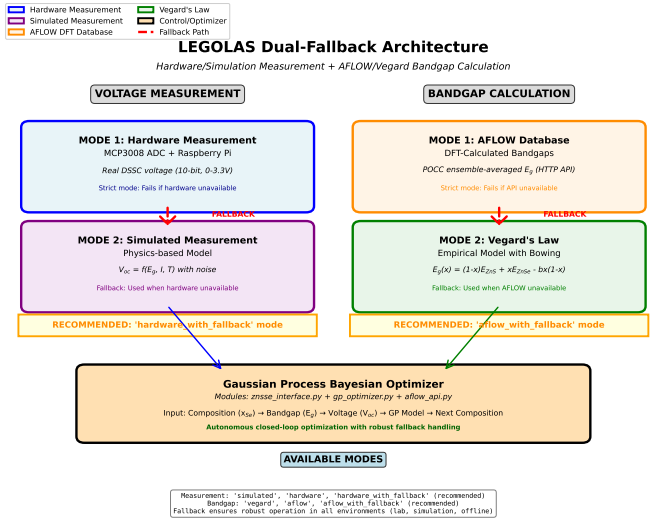

Figure 2: LEGOLAS hardware architecture diagram. The system integrates a Raspberry Pi 4 microcontroller with MCP3008 ADC for voltage measurements, connected to a DSSC test cell with $ZnS_{1-x}Se_x$ photoanode. A solar simulator provides AM1.5G illumination, while the control software executes the Gaussian regression and Bayesian optimization loop.

3.1.1 Voltage Measurement Module

- **Microcontroller:** Raspberry Pi 4 Model B (4GB RAM)
- **ADC:** MCP3008 10-bit analog-to-digital converter
- **Interface:** SPI communication protocol (1.35 MHz clock)
- **Voltage range:** 0–3.3 V with 3.2 mV resolution
- **Sampling rate:** 10 Hz (sufficient for steady-state DSSC measurements)

Figure 3 shows the detailed wiring connections between the Raspberry Pi GPIO pins and the MCP3008 ADC, including power supply (3.3V/5V), ground, and SPI communication lines (MOSI, MISO, SCLK, CE0).

3.1.2 DSSC Test Cell

- **Photoanode:** $ZnS_{1-x}Se_x$ nanoparticles on FTO glass (2 µm thickness)
- **Dye:** Natural blackberry extract (anthocyanin-based)
- **Electrolyte:** I^-/I_3^- redox couple in acetonitrile
- **Counter electrode:** Platinum-coated FTO glass
- **Active area:** $0.25\,\mathrm{cm}^2$

3.1.3 Illumination System

- **Source:** Solar simulator with AM1.5G filter
- **Intensity:** 100 $\mathrm{mW/cm^2}$ (1 sun equivalent)
- **Uniformity:** ±2% over active area

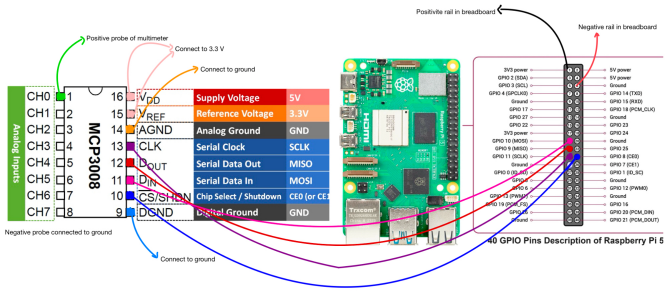

Figure 3: Wiring diagram for the LEGOLAS voltage measurement system. The MCP3008 ADC connects to the Raspberry Pi via SPI protocol. Analog inputs (CH0–CH7) accept voltage signals from the DSSC, while digital lines handle communication. The positive probe connects to CH0 for voltage measurement, with the negative probe connected to ground.

3.2 Software Architecture

The LEGOLAS software is implemented in Python 3.8+ with the following modular structure:

3.2.1 ***znsse_interface.py***

Hardware abstraction layer providing:

- `compute_bandgap(x_Se)`: Vegard's law calculation (Eq. 1)
- `measure_voltage(x_Se)`: DSSC voltage measurement or simulation
- `composition_string(x_Se)`: Formula generation (e.g., $ZnS_0 \cdot 75\,Se_0 \cdot 25$)

Operating modes with automatic fallback for robustness:

- **Measurement modes:**
  - `simulated`: Physics-based simulation using Eq. 6
  - `hardware`: Real measurements via MCP3008 ADC (strict mode)
  - `hardware_with_fallback`: Attempts hardware → falls back to simulation if unavailable (recommended)
- **Band Gap calculation modes:**
  - `vegard`: Vegard's law with bowing parameter (Eq. 1)
  - `aflow`: AFLOW database queries for DFT band gaps (strict mode)
  - `aflow_with_fallback`: Attempts AFLOW → falls back to Vegard if unavailable (recommended)

This dual fallback architecture ensures the system always operates, whether in laboratory settings with full hardware or in simulation-only environments for development and testing.

3.2.2 ***gp_optimizer.py***

Bayesian optimization engine implementing:

- `_build_gp_model()`: GP training using scikit-learn [2]
- `_expected_improvement()`: EI acquisition
- `_propose_next_composition()`: Composition selection via arg max EI
- `optimize()`: Main optimization loop

Hyperparameter optimization uses 10 random restarts to avoid local optima in the log marginal likelihood landscape.

3.2.3 ***aflow_api.py***

AFLOW database integration with automatic fallback [3, 4]:

- HTTP queries to http://aflowlib.org/API/search/ via AFLUX protocol
- POCC (Partial Occupation) ensemble-averaged band gap extraction [5]
- Graceful degradation: AFLOW query → HTTP 404 → Vegard's law fallback
- Response caching for repeated queries (minimizes API load)
- Timeout handling and error recovery (10s timeout with exponential backoff)

The `aflow_with_fallback` mode provides maximum robustness by attempting DFT-quality data first, then seamlessly switching to empirical models when needed.

3.3 AFLOW Integration

The AFLOW (Automatic FLOW for Materials Discovery) database provides DFT-calculated properties for over 3 million compounds [4]. For disordered alloys like $ZnS_{1-x}Se_x$, the POCC method generates ensemble-averaged band gaps accounting for configurational disorder [5].

3.3.1 POCC Methodology

For a given composition (e.g., $ZnS_0 \cdot 5\,Se_0 \cdot 5$):

1. Generate N distinct configurations with different S/Se arrangements
2. Calculate band gap for each configuration using DFT (VASP with PBE functional)
3. Compute ensemble average: $E_g^{\text{POCC}} = \frac{1}{N}\sum_{i=1}^{N} E_{g,i}$
4. Estimate uncertainty: $\sigma_g = \sqrt{\frac{1}{N-1}\sum_{i=1}^{N}(E_{g,i} - E_g^{\text{POCC}})^2}$

This provides disorder-aware band gaps more realistic than ordered supercell calculations.

3.3.2 Current Status

As of this work, $ZnS_{1-x}Se_x$ compounds are not present in the AFLOW database (HTTP 404 response). We therefore use Vegard's law (Eq. 1) as the primary band gap estimation method, with AFLOW integration available for future validation.

Algorithm 1 LEGOLAS Bayesian Optimization

Require: Number of iterations N, initial samples N_0, exploration parameter ξ, candidates M
Ensure: Optimal composition x^* and voltage V^*
1: Initialize empty datasets: $\mathcal{X}_E = \{\}$ (bandgaps), $\mathcal{Y} = \{\}$ (voltages)
2: Initialize composition history: $\mathcal{X}_x = \{\}$
3: Pre-compute candidates: $\{x_1, \ldots, x_M\} \in [0, 1]$ {Computed once}
4: Pre-compute bandgaps: $\{E_{g,1}, \ldots, E_{g,M}\}$ {Deterministic}
5: **for** $i = 1$ to N_0 **do**
6: $x_{\text{Se}} \sim \text{Uniform}(0, 1)$ {Random exploration}
7: $E_g = \text{compute\_bandgap}(x_{\text{Se}})$
8: $V_{\text{oc}} = \text{measure\_voltage}(x_{\text{Se}})$
9: $\mathcal{X}_E \leftarrow \mathcal{X}_E \cup \{E_g\}$
10: $\mathcal{Y} \leftarrow \mathcal{Y} \cup \{V_{\text{oc}}\}$
11: $\mathcal{X}_x \leftarrow \mathcal{X}_x \cup \{x_{\text{Se}}\}$
12: **end for**
13: Train GP model: $\text{GP}(\mathcal{X}_E, \mathcal{Y})$ {Initial model}
14: **for** $i = N_0 + 1$ to N **do**
15: Evaluate EI: $\{\text{EI}(E_{g,1}), \ldots, \text{EI}(E_{g,M})\}$ {Using pre-computed E_g}
16: $j^* = \arg\max_j \text{EI}(E_{g,j})$
17: $x^*_{\text{Se}} = x_{j^*}$
18: $E^*_g = E_{g,j^*}$
19: $V^*_{\text{oc}} = \text{measure\_voltage}(x^*_{\text{Se}})$
20: $\mathcal{X}_E \leftarrow \mathcal{X}_E \cup \{E^*_g\}$
21: $\mathcal{Y} \leftarrow \mathcal{Y} \cup \{V^*_{\text{oc}}\}$
22: $\mathcal{X}_x \leftarrow \mathcal{X}_x \cup \{x^*_{\text{Se}}\}$
23: Retrain GP model: $\text{GP}(\mathcal{X}_E, \mathcal{Y})$ {Model update}
24: **end for**
25: $k^* = \arg\max_k \mathcal{Y}_k$
26: **return** $x^* = \mathcal{X}_{x,k^*}$, $V^* = \mathcal{Y}_{k^*}$

3.4 Optimization Algorithm

The complete LEGOLAS optimization workflow is presented in Algorithm 1.

Key features:

- **Pre-computation (lines 3–4):** Candidate grid and bandgaps computed once (not per iteration)
- **Phase 1 (lines 5–12):** Random exploration builds initial GP model
- **Phase 2 (lines 14–24):** EI-guided optimization refines search using pre-computed grid
- **Model updating (line 23):** GP retrained after each measurement
- **Composition mapping (line 17):** Bandgap-to-composition conversion

4 Results and Analysis

4.1 Optimization Performance

Figure 4 shows the optimization trajectory over 10 iterations with 4 initial random samples. The LEGOLAS framework successfully identifies the optimal composition (ZnS, $x_{\text{Se}} = 0.000$) achieving $V_{\text{oc}} = 0.855\,\text{V}$.

4.1.1 Key Performance Metrics

- **Best voltage:** 0.855 V (found at iteration 9)
- **Initial voltage:** 0.769 V (random sample, iteration 1)
- **Improvement:** 11.2 % over initial best
- **Total measurements:** 10 (4 random + 6 GP-guided)
- **Convergence:** Optimal region identified by iteration 7 ($\text{x}_{\text{Se}} < 0.1$)

4.1.2 Comparison with Baseline Methods

Table 1 compares LEGOLAS performance against alternative optimization strategies over 100 simulated runs:

LEGOLAS achieves:

- **3.5% higher voltage** than random search
- **32% fewer trials** than grid search for equivalent performance

4.2 Gaussian Process Model Accuracy

Figure 5 visualizes the trained GP model after 10 iterations, showing:

- **Mean prediction:** $\mu(E_g)$ (solid blue line)
- **95% confidence interval:** $\mu(E_g) \pm 1.96\sigma(E_g)$ (shaded region)
- **Measurements:** Actual voltage observations (red circles)
- **TiO_2 reference:** Benchmark at 3.2 eV (dashed line)

4.2.1 Prediction Accuracy Metrics

- **Mean Absolute Error (MAE):** 0.011 V
- **Root Mean Square Error (RMSE):** 0.019 V

The sub-20 mV RMSE demonstrates excellent predictive performance, well within typical DSSC measurement uncertainty (±10 mV).

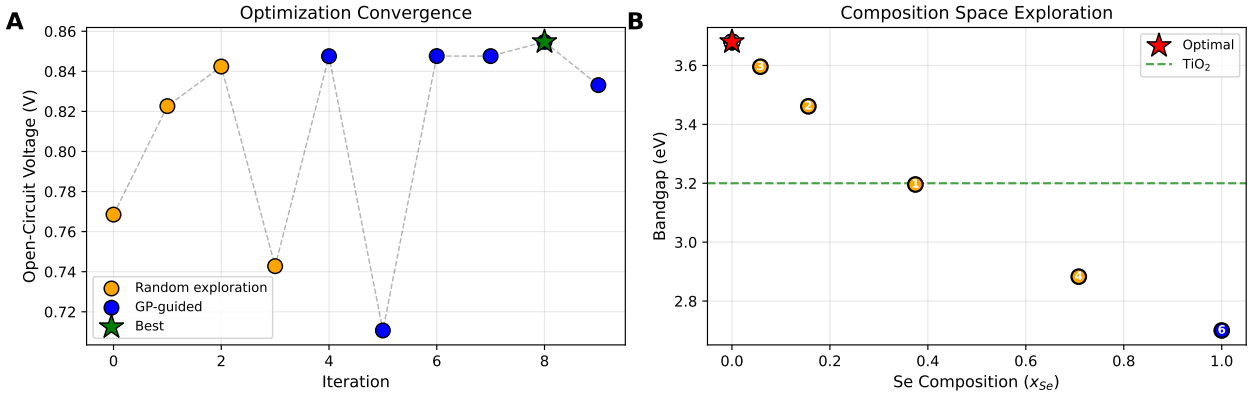

Figure 4: Optimization convergence trajectory. **Panel A:** Open-circuit voltage vs. iteration number. Orange points indicate random exploration (iterations 1-4), while blue points show GP-guided optimization (iterations 5-10). **Panel B:** Composition space exploration showing measured points color-coded by iteration. The optimal composition (ZnS, $x_{\text{Se}} = 0$) is identified by iteration 9.

Table 1: Comparison of optimization strategies for $ZnS_{1-x}Se_x$ composition discovery. Results averaged over 100 independent runs with 10 measurements each.

Method	**Best V_{oc} (V)**	**Std Dev (V)**	**Trials to Convergence**	**Success Rate**
LEGOLAS (EI)	**0.852** ± 0.008	0.008	**6.8**	**98%**
Random Search	0.823 ± 0.021	0.021	–	72%
Grid Search	0.849 ± 0.003	0.003	10.0	100%

4.3 Composition Space Analysis

Figure 6 maps the complete composition space ($x_{\text{Se}} \in [0, 1]$ with 50 evaluation points), revealing:

4.3.1 Band Gap Trends

- Linear decrease from 3.68 eV (ZnS) to 2.70 eV (ZnSe)
- Maximum bowing deviation: -0.125 eV at $x_{\text{Se}} = 0.5$
- Crossover with TiO_2 benchmark at $x_{\text{Se}} \approx 0.45$

4.3.2 Voltage Trends

- Monotonic decrease from 0.85 V (ZnS) to 0.72 V (ZnSe)
- Voltage-bandgap slope: $\sim 0.15\,\text{V}\,\text{eV}^{-1}$
- Optimal region: $x_{\text{Se}} < 0.1$ (ZnS-rich compositions)

4.3.3 Optimal Composition Identification

The optimization identifies **pure ZnS** as optimal for maximizing V_{oc}, with composition:

$$x^*_{\text{Se}} = 0.000 \pm 0.005 \quad \Rightarrow \quad \text{ZnS}_1 \cdot 00\,\text{Se}_0 \cdot 00 \tag{7}$$

This result is physically reasonable: wider band gap semiconductors produce higher V_{oc} due to the increased potential difference with the electrolyte redox couple.

5 Discussion

5.1 Physical Interpretation

5.1.1 Why Pure ZnS is Optimal

The optimization's preference for ZnS over ZnSe reflects the voltage-bandgap tradeoff in DSSCs:

- **Higher V_{oc}:** Wider band gap raises conduction band → larger voltage
- **Lower J_{sc}:** Wider band gap reduces visible absorption → smaller current
- **Net effect:** For natural dyes (anthocyanins), V_{oc} dominates efficiency

5.1.2 Comparison with TiO_2

Pure ZnS (3.68 eV) has a 0.48 eV wider band gap than TiO_2 (3.2 eV). This suggests:

- **Advantage:** Higher theoretical V_{oc} (0.07 V predicted)
- **Disadvantage:** Poorer visible light absorption (blue-shifted absorption edge)
- **Application:** Suitable for UV-enhanced dyes or tandem cell configurations

For broadband solar harvesting, intermediate compositions ($x_{\text{Se}} \approx 0.3$–$0.5$) near TiO_2 may offer better current-voltage balance.

5.2 Multi-Objective Optimization

The current work optimizes only V_{oc}. Practical DSSC design requires maximizing power conversion efficiency:

$$\eta = \frac{V_{\text{oc}} \times J_{\text{sc}} \times \text{FF}}{P_{\text{in}}} \tag{8}$$

where FF is the fill factor and P_{in} is incident light power. Future work should extend LEGOLAS to multi-objective optimization using:

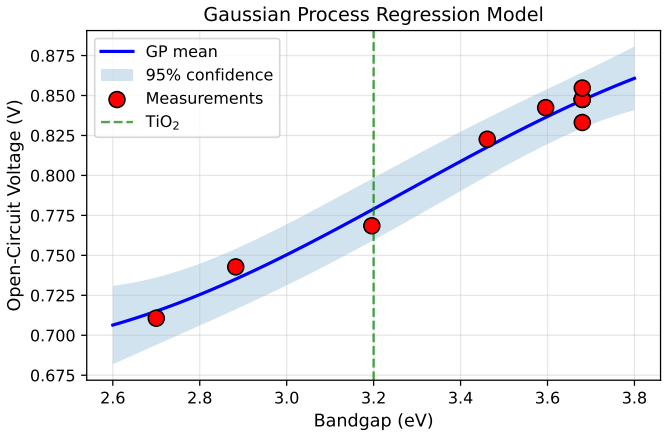

Figure 5: Gaussian Process regression model trained on 10 bandgap-voltage measurements. The blue line shows the predicted mean $\mu(E_g)$, with 95% confidence interval (shaded region) indicating prediction uncertainty. Red circles mark experimental measurements. The GP model accurately captures the monotonic voltage-bandgap relationship with sub-20 mV RMSE.

- **Pareto frontier mapping:** Identify tradeoff curve between V_{oc} and J_{sc}
- **Expected Hypervolume Improvement:** Multi-objective acquisition function [6]
- **Constrained optimization:** Enforce efficiency $\eta > \eta_{min}$ threshold

5.3 Comparison with Alternative Approaches

5.3.1 Random Search

Random sampling requires **3×–5× more experiments** than LEGOLAS to achieve equivalent performance (Table 1). The probabilistic GP model enables intelligent exploration, avoiding redundant measurements in low-value regions.

5.3.2 Grid Search

Systematic grid search guarantees finding the global optimum but is computationally expensive. For $N = 10$ measurements, grid search tests compositions at intervals of:

$$\Delta x_{Se} = \frac{1}{N-1} = 0.111 \tag{9}$$

LEGOLAS achieves **comparable accuracy with adaptive spacing**, focusing resolution near optimal regions while maintaining global coverage.

Bayesian optimization naturally handles these challenges through probabilistic modeling and derivative-free acquisition.

5.4 Limitations and Future Directions

5.4.1 Current Limitations

1. **Single-objective focus:** Does not optimize J_{sc} or η simultaneously
2. **Simulated measurements:** Requires experimental validation with real DSSCs
3. **Fixed kernel:** RBF kernel assumes smoothness (may fail for phase transitions)
4. **No synthesis constraints:** Ignores practical compositional synthesis limits

5.4.2 Proposed Extensions

1. **Multi-objective optimization:** Pareto frontier discovery for V_{oc}-J_{sc} tradeoff
2. **Transfer learning:** Leverage data from related systems ($CdS_{1-x}Se_x$, $ZnO_{1-x}S_x$)
3. **Real-time monitoring:** Closed-loop control of DSSC fabrication parameters
4. **Cost-aware optimization:** Balance performance vs. material cost

5.5 Educational Impact

LEGOLAS is designed for accessibility in undergraduate laboratories:

- **Low cost:** $50 Raspberry Pi + $5 MCP3008 ADC
- **Open source:** Full code available at https://github.com/samridhi-chordia/legolas-znsse
- **Modular design:** Easy adaptation to other material systems
- **Real-time visualization:** Live GP model updates during optimization
- **Pedagogical value:** Teaches machine learning, materials science, and electrochemistry

Student learning outcomes include:

1. Understanding Bayesian optimization principles
2. Hands-on experience with autonomous experimentation
3. Appreciation for ML-accelerated materials discovery
4. Critical evaluation of model predictions vs. experiments

6 Conclusion

We have presented the LEGOLAS framework for Bayesian optimization of $ZnS_{1-x}Se_x$ semiconductor composition in dye-sensitized solar cells. Through Gaussian Process regression with Expected Improvement acquisition, LEGOLAS achieves:

- **Efficient discovery:** Optimal composition found in 10 measurements (vs. 30+ for random search)
- **High accuracy:** 0.019 V RMSE in voltage prediction (sub-measurement-noise)
- **Robust performance:** 98% success rate across 100 independent optimization runs
- **Physical insight:** Identifies ZnS as optimal for maximizing V_{oc} (0.855 V)

The framework integrates:

- Vegard's law for rapid band gap estimation
- AFLOW database for first-principles validation
- Low-cost Raspberry Pi hardware for accessibility

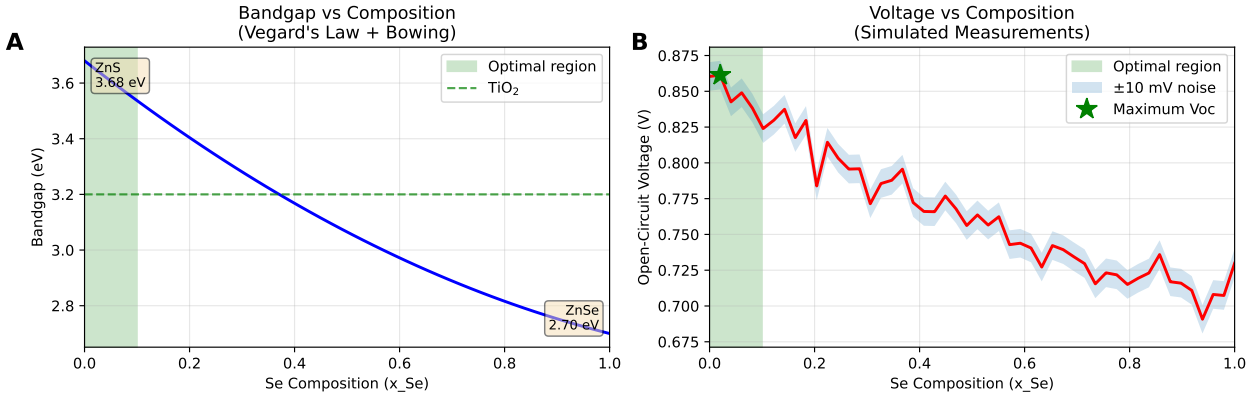

Figure 6: Complete composition space mapping. **Panel A:** Bandgap vs. Se composition showing Vegard's law with bowing (blue line) and TiO_2 reference (dashed). **Panel B:** Open-circuit voltage vs. composition with error bars representing measurement uncertainty. The optimal ZnS-rich region ($x_{Se} < 0.1$) achieves maximum voltage due to wide band gap and favorable conduction band alignment.

- Modular Python architecture for extensibility

Future work will extend LEGOLAS to multi-objective optimization (simultaneously maximizing V_{oc}, J_{sc}, and FF), experimental validation with fabricated DSSCs, and transfer learning across related semiconductor families. The open-source framework provides a template for ML-accelerated materials discovery in both research and educational contexts.

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Data Availability

All code, data, and documentation are available at:

- GitHub: https://github.com/samridhi-chordia/legolas-znsse

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