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A SPECTRAL DENSITY FUNCTION APPROACH FOR DESIGN OF ORGANIC PHOTOVOLTAIC CELLS

Umar Farooq Ghumman¹
Mechanical Engineering
Northwestern University
Evanston, IL, USA

Akshay Iyer¹
Mechanical Engineering
Northwestern University
Evanston IL, USA

Rabindra Dulal
Physics and Astronomy
University of Wyoming
Laramie, WY, USA

Aaron Wang
Physics and Astronomy
University of Wyoming
Laramie, WY, USA

Joydeep Munshi
Mechanical Engineering and
Mechanics
Lehigh University
Bethlehem, PA, USA

TeYu Chien
Physics and Astronomy
University of Wyoming
Laramie, WY, USA

Ganesh Balasubramanian
Mechanical Engineering and
Mechanics
Lehigh University
Bethlehem, PA, USA

Wei Chen²
Mechanical Engineering
Northwestern University
Evanston, IL, USA

ABSTRACT

Organic Photovoltaic Cells (OPVCs), having received significant attention over the last decade, are yet to be established as viable alternatives to conventional solar cells due to their low power conversion efficiency (PCE). Complex interactions of several phenomena coupled with the lack of understanding regarding the influence of fabrication conditions and nanostructure morphology have been major barriers to realizing higher PCE. To this end, we propose a computational microstructural design framework addressing the Processing–Structure–Performance (PSP) linkages for designing the active layer of P3HT:PCBM based OPVCs conforming to bulk heterojunction architecture. The framework pivots around the Spectral Density Function (SDF), a frequency space microstructure characterization and reconstruction methodology, for microstructure design representation. Nanostructure images obtained by novel Scanning Tunneling Microscopy are used to validate the applicability of SDF for representing active layer morphology in OPVCs. SDF enables a low dimensional microstructure representation that is crucial in formulating a parametrized microstructure optimization scheme. A level-cut Gaussian Random Field (governed by SDF) technique is used to generate reconstructions that serve as Representative Volume Elements (RVEs) for structure-performance simulations. A novel

structure-performance simulation approach is developed using physics-based performance metric, Incident Photon to Converted Electron (IPCE) ratio, to account for the impact of microstructural features on OPVC performance. Finally, an SDF based computational IPCE optimization study using metamodels created using design of computer experiments over three design variables results in 36.75% increase in IPCE, underlining the efficacy of proposed design framework.

1. INTRODUCTION

Design of nanostructured material systems (NMSs) [1] has recently gained impetus due to its potential for developing high performance metamaterials by cost-effective nanofabrication techniques [2-6]. A convenient way of categorizing NMSs is based on the presence of periodicity in the morphology. Periodic designs involve deterministic arrangement of identical building blocks (a.k.a. unit cells), with optimal performance realized through evolutionary algorithms [3, 7, 8] and topology optimization [4, 9]. However, fabrication of periodic NMSs requires top-down nanomanufacturing techniques which are often expensive and time consuming to ensure precise material deposition at nano- and micro- scales [10]. In contrast to periodic NMSs, a quasi-random nanostructure contains no periodic arrangement of unit cells, but a seemingly random material

¹ Equal Contribution

² Corresponding Author: weichen@northwestern.edu

distribution governed by an underlying spatial correlation. Such structures have been observed in nature [11-14] as well as artificially synthesized materials [15-18] using low cost and bottom-up manufacturing processes [19] (which uses atoms/molecules as the building blocks, self-assembled to create complex nanostructures) such as nanowrinkling [2, 17].

OPVCs [20-23] are one such example of man-made quasi-random nanostructures. Owing to a series of advantages such as flexibility, light weight, low production cost, and lack of heavy metals (environmental friendly), OPVCs have received significant attention as one of the promising materials for next generation solar cells [24, 25]. The short mean free path (2-10 nm) of the excitons [26] in organic molecules requires that the locations of exciton creation should be in the vicinity of the electron donor-acceptor interface for efficient charge separation. It has been shown that the bulk heterojunction (BHJ) architecture of the active layer is key to ensure high efficiency due to its quasi-random nanostructures satisfying the aforementioned short exciton mean free path limitation [26]. As illustrated in Figure 1(a), charge separation at the donor-acceptor interfaces and transport to the electrodes are critical to high performance of the device. Among the various electron donor/acceptor combinations investigated previously, phenyl-C61-Butyric-Acid-Methyl Ester (PCBM) interspersed with poly(3-hexylthiophene-2,5-diyl) (P3HT) has been the “best seller” [27]. To achieve optimal PCEs, several structure and process synthesis parameters, such as electron donor-acceptor composition, thickness of the active layer, annealing temperature, and annealing duration etc., need to be optimized simultaneously. Previous efforts only focus on one or two structure and processing parameters at a time to search for optimal devices. However, the optimal parameters are not independent from each other, indicating that better strategies are needed. Currently, there is no reported methodology to consider the influences of all

fabrication conditions simultaneously on the microstructures or the influences of the microstructures on the device performance.

To produce cost-effective devices with targeted properties, formulating a holistic material design strategy [28-33] is essential. Since the device’s microstructure influences its behavior at different length scales, microstructure mediated design [30, 34] or microstructure sensitive design [35] has assumed prime importance. Deconvolving the Structure–Performance (S-P) relationship has been the focus of many articles, covering a wide range of material systems [36-41]. Due to its high dimensionality, one needs to extract the salient features from a microstructure image before its influences on material behavior can be studied. Microstructure Characterization and Reconstruction (MCR) [42, 43] has enabled a quantitative approach to analyze microstructural images and subsequently construct models for investigating S-P relationship. The essence of MCR is its ability to capture significant microstructural details and subsequently generate statistically equivalent reconstructions. The widely used MCR approaches [42] for non-deterministic systems are based on spatial correlation functions [43-45], descriptor-based methods [40, 46] and machine learning techniques [47-49]. The correlation function approach captures the microstructure from a probabilistic perspective but relies on a pixel (voxel in 3D) swapping strategy for reconstructions and is therefore computationally prohibitive for microstructural design. Descriptor-based approach uses a small set of uncorrelated features which embody significant microstructural detail and has been successfully used for design of nanocomposite polymers [40, 46, 50-52], that contain clusters of filler material dispersed in polymer matrix. However, this approach assumes filler aggregates to be ellipsoidal and descriptors are regular geometrical features (aspect ratio, equivalent radius etc.), thus, falling short in representing arbitrary geometries encountered in

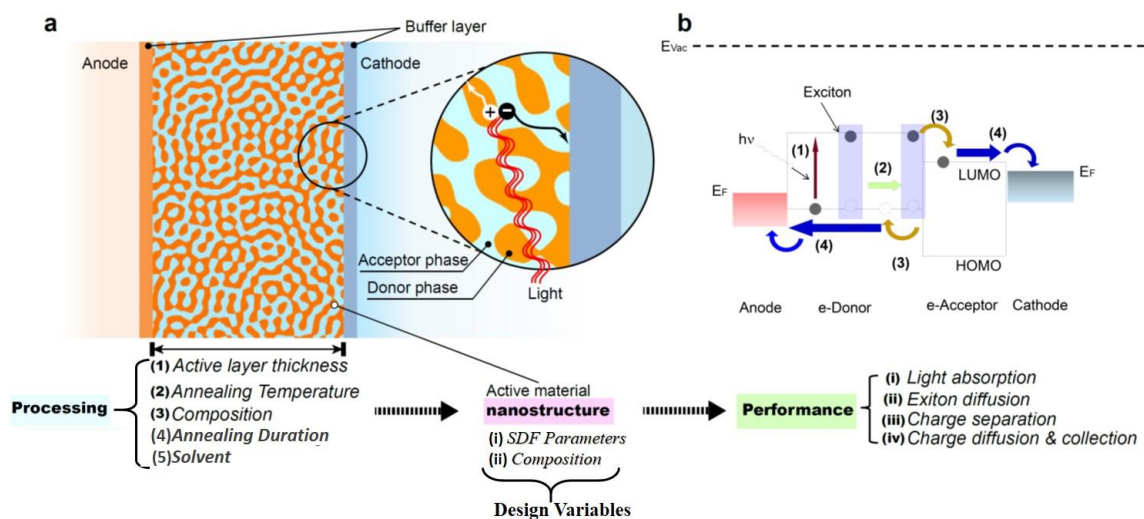


Figure. 1: Variables of interest in Processing-Structure-Performance framework and design scope, (a) A schematic representation of OPVC with Bulk Heterojunction (BHJ) architecture; (b) a four-step energy conversion mechanism.

quasi-random NMSs. While machine learning methods, which are capable of modelling highly nonlinear systems, have been implemented as MCR tools, the lack of physical interpretation of parameters learned from these methods has limited their use in material design.

SDF [2, 5, 6, 53] has emerged as a new method for low-dimensional, physics aware representation of quasi-random NMSs. For isotropic materials, SDF is a one-dimensional function of spatial frequency, calculated as the radial average of the squared magnitude of Fourier spectrum of a quasi-random structure [53] and represents the structural correlation in Fourier space. Analogous to the way correlation functions describe structural correlations in real space, SDF provides this description in reciprocal space. Our previous efforts in design of photonic NMSs with SDF [2, 5, 6] have highlighted its advantages in representing quasi-random microstructures with a small number of required design variables. Yu et.al. [6] presented the first comprehensive MCR study on application of SDF for quasi-random NMSs used as light trapping structure in thin-film solar cells. They showed that low-dimensional microstructure representation enabled by SDF, its direct association with material functionalities and relationship with processing conditions, was instrumental in design optimization and led to a 4.7-fold enhancement of single wavelength light absorption. In another recent article, Lee et.al. [2] integrated a novel wafer scale nanofabrication procedure, wrinkle lithography, with SDF based microstructure representation to bridge the processing-structure and structure-performance relationship for concurrent design of photonic nanostructures. The study showed that parameters in SDFs have physical implications closely associated with the material processing conditions, improving the feasibility of fabricating the optimal nanostructures obtained from computational design methods.

In this paper, we investigate the applicability of SDF for design of the active layer in OPVCs and propose a design framework built on SDF based Structure-Performance (S-P) evaluations (Sec. 2). Active layer samples comprising P3HT:PCBM and conforming to BHJ architecture are fabricated and imaged using novel cross-sectional Scanning Tunneling Microscopy and Spectroscopy (XTM/S) (Sec. 3). Further, this article focuses on establishing S-P relationship by creating protocols for SDF based microstructure representation (Sec. 4) and developing a novel, physics-based performance evaluation strategy (Sec. 5). To demonstrate the usefulness of microstructure representation using SDF and the S-P relationship investigated here, we formulate a performance optimization problem to determine the optimal microstructure (Sec. 6). State-of-the-art computational design methods are employed to improve the efficiency of simulation-based design optimization. Specifically, Optimal Latin Hypercube Sampling [54] is used to create a metamodel based on Kriging metamodeling [55], overcoming the challenges of computational cost and time. Finally, Sobol sensitivity analysis [56] is used to elucidate the effect of each design variable (sec. 7).

2. SPECTRAL DENSITY FUNCTION BASED MICROSTRUCTURE DESIGN FRAMEWORK

Low-dimensional, physics-aware nanostructure representation is critical for computational design of quasi-random NMSs. In this section, we first demonstrate SDF to be a convenient frequency space representation which embodies significant real space features and assumes simple parametric form for isotropic materials. Then, an SDF based microstructure design framework is presented in the context of active layer design for OPVCs.

2.1 Introduction to Spectral Density Function

SDF is one of the tools developed to characterize the structural information of a given material. The backbone of SDF is Fourier Transform (FT). FT decomposes a waveform (e.g. 1D signal or a 3D image) into a sum of sinusoidal waves of different frequencies [57]. When the FT operator is applied to a microstructure image, real space structural features are represented in the spatial frequency space and enable identification of spatial correlations. SDF has demonstrated its ability to characterize intricate heterogeneous microstructures as well as generate statistically equivalent reconstructions [42]. For isotropic materials, the shape of radially averaged SDF curve generally takes a simple parametric form which significantly reduces the design complexity of an otherwise high dimensional material structure.

To characterize a microstructure using SDF, a two-phase image, X , is required. The image must contain high resolution details at the microstructural level. The Fourier Transform $F(k)$ of the image is calculated as:

$$F(k) = F\{X\} = A_k e^{i\phi_k} \quad (1)$$

Here, $F\{\cdot\}$ represents the FT operator, k is a vector which represents frequency, $i = \sqrt{-1}$, and A_k and ϕ_k represent the magnitude and phase angle of the FT, respectively. For isotropic materials, the vector k can be reduced to a scalar by radially averaging in the space domain. Thus, the SDF of the microstructure, $\rho(k)$, is then calculated by radial averaging of the squared magnitude of FT.

$$\rho(k) = \frac{\int_0^{2\pi} |F(k)|^2 d\theta}{2\pi} = \frac{\int_0^{2\pi} A_k^2 d\theta}{2\pi} \quad (2)$$

This gives a 1-D $\rho(k)$ function.

The resulting SDF plots can take various forms. A few examples of 1-D SDF plots and their respective images are shown in Figure 2. The widely used 2-Point Correlation Function (CRF) is equivalent to inverse FT of SDF [58], but compared with 2-point CRF, SDF is more convenient in differentiating spatial correlation features as evidenced in Figure 2. Figure 2a and Figure 2b represent two nanostructures with different structural properties. Figure 2b is an image of an ordered structure and has one distinctly strong correlation at one specific band of spatial frequency (Figure 2d). This feature is also visible in the insets of Figure 2b by a distinct circle in the Fourier spectrum. In contrast, Figure 2a is less ordered and hence its SDF is more dispersed over the entire frequency spectrum (Figure 2c). These

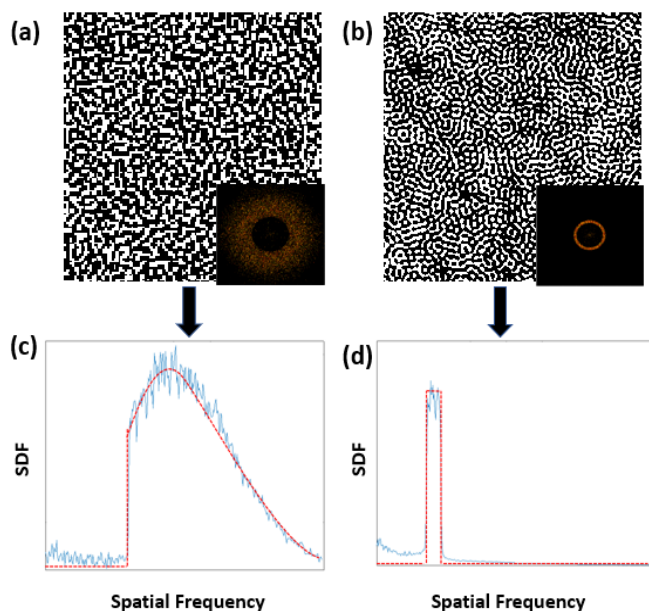


Figure 2: Two sample microstructures (a & b) along with their Fourier spectrum in the insets; (c & d) are the 1-D SDFs of each image. Red dashed line represents the approximated SDF.

differences in SDF based on structural changes corroborate the efficacy of SDF in capturing the structural detail. Furthermore, the SDFs observed in Figures 2c and 2d both assume a simple shape that can be easily parametrized. The parametrized SDFs are represented as red dashed lines in Figure 2c and 2d. For

Figure 2c it is as a truncated Gaussian function, while for Figure 2d it is a step function. Note that all the SDFs presented in this study are normalized for ease of comparison and consistency.

2.2 SDF based Microstructure Design Framework for OPVC Active layer

Under the new paradigm of microstructure-sensitive material design [35, 59], materials are viewed as a complex structural system that can be optimized for achieving superior properties (properties under consideration are subject to targeted application). Using OPVC active layer optimization as an example, we present here a holistic SDF based microstructure design framework (Figure 3) that can be employed for design of quasi-random nano- or microstructural systems based on Structure-Performance (S-P) relations.

The key idea of the proposed framework is to leverage SDF as the representation of OPVC microstructures, enabling direct and inverse S-P mappings. As shown in Figure 3, the framework is initiated by fabricating samples of NMSs of interest (OPVC active layer for this article) using a nanofabrication technique with processing parameters choices based on empirical findings or literature. State-of-the-art imaging techniques are used to visualize the nanostructure in the available samples and the type (form) of SDF is identified. The main advantage of using SDF for quasi-random NMSs is that it can be easily parametrized (Sec. 2.1) and provides a more convenient representation for interpretation and design relative to other design methods [6]. Since SDF corresponds to the magnitude of FT of the microstructure, reconstruction can be cast as a phase recovery

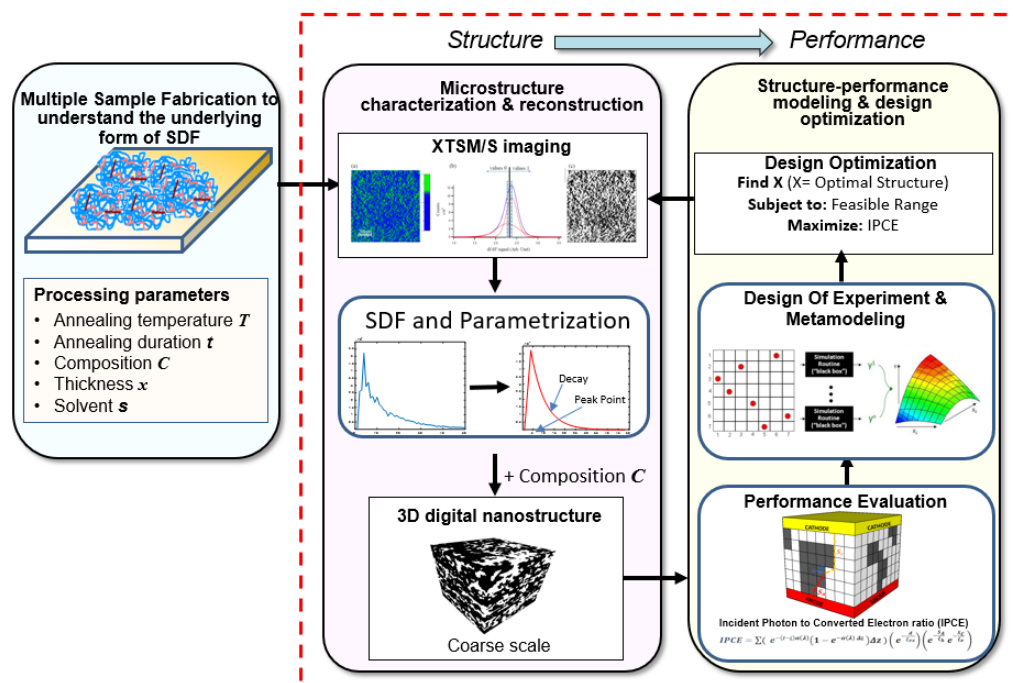


Figure 3: A framework for designing active layer nanostructure in bulk heterojunction OPVC via SDF.

technique [60]. In this article, reconstruction is accomplished by level-cutting a Gaussian Random Field (GRF) governed by the required SDF. Thus, starting from a 2D XSTM/S image, SDF provides a reduced order microstructure representation (only three parameters required in this study) for creating statistically equivalent 3D microstructures which serve as Representative Volume Element (RVE) for performance evaluation.

To evaluate the performance of a RVE, a model is sought that accounts for structural features in addition to device physics and material properties. For OPVCs, the key performance parameter of interest is the IPCE ratio. To evaluate IPCE computationally, a novel strategy based on device physics and nanostructure is developed here. This strategy explicitly states the influence of nanostructure on known physical phenomena and establishes the S-P relationship that forms the basis for performance optimization. However, before the optimization, creating a metamodel to replace the computationally expensive and time-consuming S-P model is highly desirable (see Figure 3). Metamodel, created by careful Design of Experiments (DOE), is essentially a “black-box” that approximates the S-P simulations. Given the set of design variables and their bounds, DOE dictates the S-P simulations that must be performed to determine the corresponding value of objective function (a.k.a. response). A suitable machine learning model is chosen to interpolate between known values of response, forming a metamodel which can be queried at each iteration of the optimization. In this article, we use Optimal Latin Hypercube Sampling (OLHS) to create the metamodel based on the Kriging method, accelerating the search for the optimal design. Design optimization is performed with the pre-determined design variables obtained by parametrizing SDF (Sec. 4) along with the material composition. As mentioned previously, SDF provides a low-dimensional representation in reciprocal space of an otherwise high-dimensional nanostructure image, thereby facilitating a convenient design formulation. In this work, IPCE is chosen as the objective function with an aim of finding its maximum value and the corresponding SDF parameters (i.e. nanostructure). However, it should be noted that the optimum structure is limited to the same type of material system as the tested samples because the form of the SDF function used for optimization is determined based on the fabricated samples. In the following sections, we elaborate the procedure of implementing the proposed framework.

3. SAMPLE FABRICATION AND IMAGING

Fullerene-based acceptors, such as PCBM and PC70BM, have dominated the OPVC field for decades and achieved a decent PCE of 6.82% [61]. Recent developments with non-fullerene-based acceptors further push the PCE of OPVCs to ~13% [62, 63]. Nevertheless, the BHJ quasi-random nanostructure in OPVC is still the dominating design for high PCE devices. Here, we focus on the most studied P3HT:PCBM acceptor/donor combination. The methodology and results presented here can be extended to all kinds of OPVCs with BHJ architecture.

There are five major parameters for fabricating BHJ active layers in OPVC devices: (1) P3HT/PCBM composition; (2) the solvent; (3) annealing temperature; (4) annealing duration; and (5) thickness of the active layer. In this work, the parameter under focus is composition. Annealing temperatures and durations are chosen differently for the two cases (Table 1). Other processing parameters are kept the same.

P3HT (Solaris Chem Inc.) and PCBM (purity >99.5%, Solaris Chem Inc.) are first prepared into separate 1.78 weight % precursor solutions with chlorobenzene (purity ≥99.5%, Sigma-Aldrich). Final solutions with desired P3HT:PCBM weight ratios of 1:1 and 2:1, are made by mixing the precursor solutions with corresponding amounts. The solutions were then spin coated onto the Si(100) substrate at ~1000 rpm for 1 minute. The P3HT:PCBM/Si(100) is annealed at 100 °C for 20 minutes for the 1:1 sample, and at 150 °C for 5 min for the 2:1 sample, respectively. Table 1 summarizes these conditions for the two cases.

Scanning Tunneling Microscopy and Spectroscopy (STM/S) is used to distinguish different organic molecules. More precisely, the OPVC active layers are imaged with cross-sectional STM/S (XSTM/S) [64], which has also been successfully applied to OPVCs [65] and organometallic perovskites [66]. In the XSTM/S imaging, the sample is cut into desired shape and fractured in an ultra-high vacuum (UHV) environment to ensure a contamination-free cross-section surface is exposed for the STM measurement. Figure 4 shows a 100 nm × 100 nm dI/dV mapping of P3HT:PCBM (Case 2) sample. Based on the dI/dV point spectra, the green regions denote the P3HT-rich domains while the blue regions represent the PCBM-rich domains. Note that, here the brightness and contrast are arbitrarily chosen.

To consistently assign regions as P3HT-rich and PCBM-rich, the following procedure is employed. The dI/dV signal from Figure 4a is first plotted into histogram, as illustrated in Figure 4b. This histogram cannot be fit by a single Gaussian function rather two Gaussian peaks suitably represent the distribution, indicating that the data contains two main values, reflecting the two molecules, together with Gaussian noises. By determining the peak positions, one could further determine the mid-point between the two peak values. Then, 1 and 0 are assigned to each pixel respectively based on whether the dI/dV signal in each pixel is larger or smaller than the mid-point value between the two Gaussian peaks. Using this procedure, we can systematically assign the domains for further analyses. The resulting binarized digital images of both cases are presented later in Figure 5 (Section 4.1).

Table 1: Summary of processing conditions of the two cases

	Case 1	Case 2
Weight Ratio (P3HT:PCBM)	1:1	2:1
Annealing temperature & time	100° C for 20 mins	150° C for 5 mins

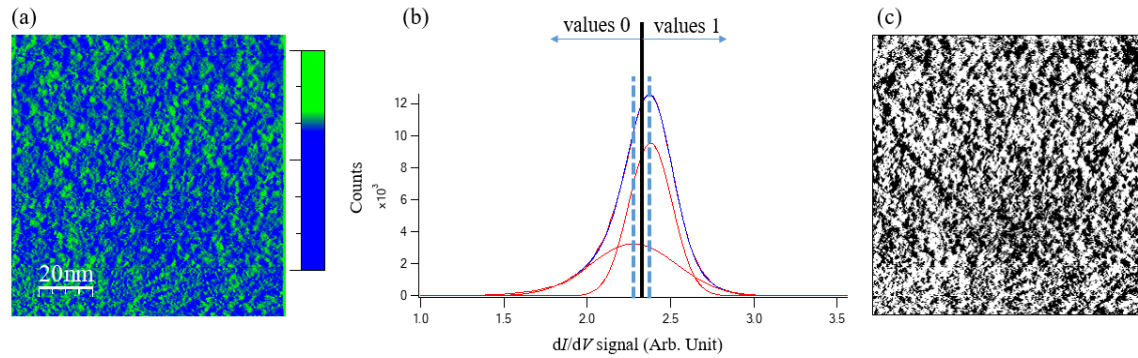


Figure 4: (a) dI/dV mapping of P3HT:PCBM active layer. 100 nm × 100 nm scan size. Brightness and contrast are set arbitrarily. (b) Histogram fitted with two Gaussian functions. Dashed lines indicate the positions of the two Gaussian peaks. Solid line indicates the mid-point between the two Gaussian peak values. (c) Digital values (1 and 0) are assigned based on the dI/dV values in each pixel compared to the solid line in (b).

4. ACTIVE LAYER CHARACTERIZATION AND RECONSTRUCTION USING SPECTRAL DENSITY FUNCTION

This section examines the form of SDF for the two-dimensional STM images of the fabricated active layer samples. Further, an analytical reconstruction method based on level-cutting a Gaussian Random Field is implemented for constructing three-dimensional RVEs, and the associated computational time is discussed.

4.1 Characterization

We attempt to characterize the images of the two Cases, introduced in Section 3, acquired by the STM imaging technique and subsequent post-processing. Figure 5a and 5b show the binarized STM images for Case 1 and Case 2, respectively. The solid lines in Figure 5c and 5d respectively correspond to the SDFs of Case 1 and Case 2. Although the two SDFs have a unique peak point and the decay that follows, the underlying form remains the same. This observation suggests that the triangular type SDF is sufficient for the considered materials and the corresponding fabrication conditions. This form of SDF can be easily approximated by a custom function which is governed by two parameters: peak point and decay factor (which is a multiplication factor in the exponential decay following the peak). For design optimization and exploration purposes, we can vary these variables to obtain different SDFs for reconstruction of the new designs of nanostructures. The dotted lines in Figures 5c and 5d represent the approximated function that concurs very well with the original SDFs.

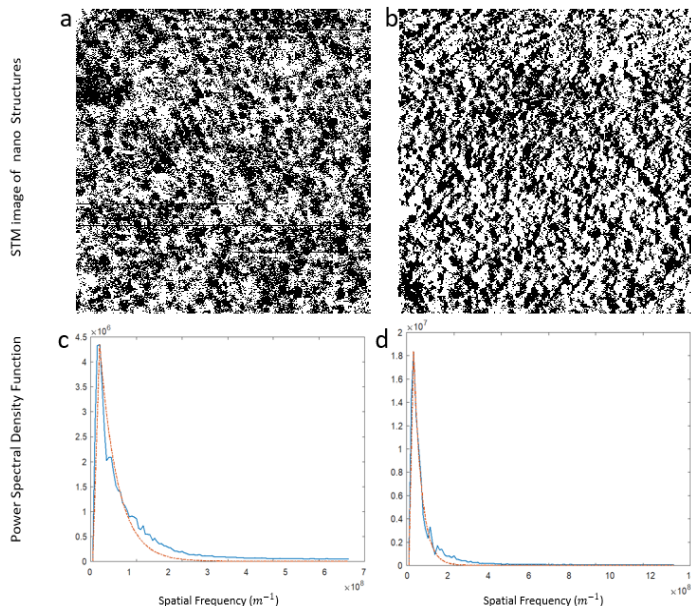


Figure 5: Comparison of SDF of the two cases under study. (a) and (b) are binarized STM images of sizes 120 nm x 120 nm (Case 1) and 100 nm x 100 nm (Case 2) respectively. Both images are 450 x 450 pixels in size; (c) and (d) are the SDFs (solid line) of cases 1 and 2, respectively. In (c) and (d) the dotted line represents the approximations of the SDFs for each case.

4.2 Identifying the size of RVE

To attain accuracy and avoid unwanted computational cost, it is essential that we determine the appropriate RVE size, for the material system of interest. We set 2-Point CRF as our property of interest to find the RVE size. We start with an STM image of 160 nm × 160 nm and observe its 2 Point CRF. Then we reduce our window size so that we only observe 90 % (~144 nm) of the original image, and then calculate the 2-Point CRF. We continue narrowing the window of observation (decreasing 10 % at a time) until the 2-Point CRF deviates significantly from the original image, as shown in Figure 6. The Mean Absolute Percentage Error (MAPE) of the curves exceeds 10 % if the size of the

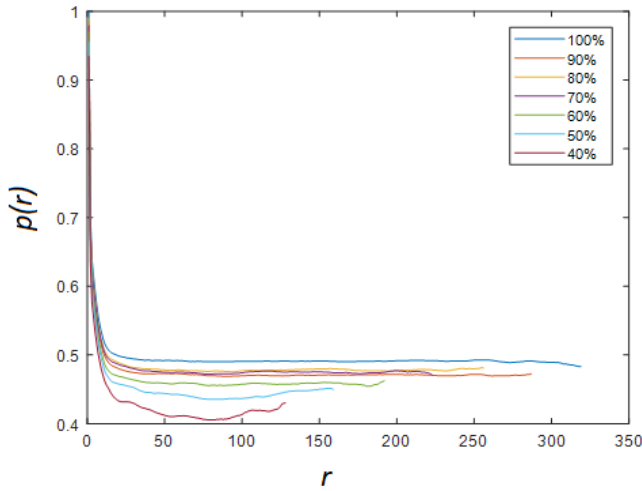


Figure 6: 2 Point correlation function observed at different window sizes. The sizes of the windows vary from 100% (i.e. 160nm) to 40% (i.e. 64nm).

window goes below 60 % (which is equal to 96 nm). Hence, 100 nm is selected as the size of our RVE.

4.3 Microstructure Reconstruction based on SDF

Accurate structure-performance evaluations require digital 3D structures, so it is essential to generate 3D structures from the SDF in the most cost-effective way possible. The efficacy of using SDF for characterization has already been established in section 4.1. In this section, the process of using SDF to create statistically equivalent 3D structures is elaborated.

Realizing the microstructure as a multi-variate sample taken from an underlying Gaussian Random Field (GRF) [42], it can be concluded that the reconstruction of statistically equivalent microstructures can be achieved by finding that GRF. After finding the GRF, microstructures are reconstructed by taking realizations of these GRFs and then level cutting them based on a threshold which is the filler volume fraction of the original image.

For realizing the GRF, the Cahn's scheme [42] is utilized. It is an analytical approach for generating realizations from a GRF that has same SDF as the original microstructure. The governing equation is:

$$Y(\mathbf{r}) = \left(\frac{2}{N}\right)^{\frac{1}{2}} \sum_{i=1}^N \cos(k_i \hat{\mathbf{k}}_i \cdot \mathbf{r} + \phi_i) \quad (3)$$

where $\hat{\mathbf{k}}_i$ and ϕ_i are uniformly distributed on unit circle, and $[0, 2\pi]$, respectively. k_i is a random variable whose probability density function, $P(k)$, is determined by the SDF: $P(k) = \rho(k)k^2$ for a 3D GRF, and $\rho(k)k$ for a 2D GRF. After the generation of GRF, the final structure is extracted by carrying out a level cut based on the desired threshold. The number of samples N plays a critical role in the reconstruction. As we increase N , the statistical accuracy of the final image increases, but so does the computational cost. The result of the accuracy of reconstruction is shown in Figure 7 along with the effects on

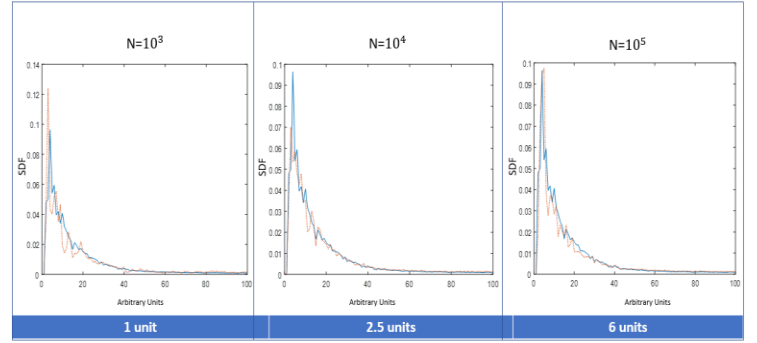


Figure 7: The effect of increasing sampling on accuracy of reconstruction with the time consumed for reconstruction at the bottom. $N = 10^3$ is taken the reference, and the other two reconstruction times are in comparison to the first one.

computation time. The reconstruction using $N = 10^4$ and $N = 5 \times 10^4$ do not match either the height or peak point location on x-axis. The reconstruction using $N = 5 \times 10^5$ captures the feature of the curve more accurately. A sweet spot of $N = 5 \times 10^5$ is identified to be the appropriate and affordable sampling size with a good degree of accuracy.

To check the robustness of the methodology, two realizations are produced of the STM image of Case 1. SDF along with volume fraction is taken as input. Figure 8 quantitatively compares the two reconstructed SDFs with the SDF of the original image. For an enhanced pictorial representation of nanostructure, we reproduce the reconstructed image from one of the two realizations in Figure 9. The reconstructed image qualitatively replicates the main characteristics of the original image.

Extending our tests to 3D, a cube of size $80 \times 80 \times 80$ pixels was created using an arbitrary SDF and volume fraction of 0.3. As seen in Figure 10a, the SDF of the reconstructed image matches well with that of the original. The 3D reconstructed structure is shown in Figure 10b. Resolution of the structure can be improved by increasing the size of reconstruction, the tradeoff

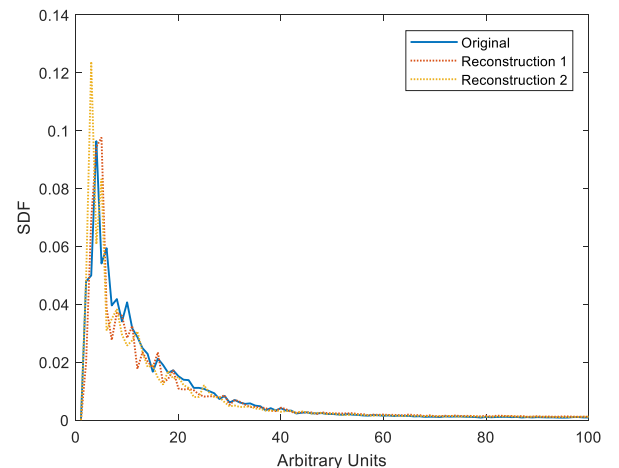


Figure 8: SDF of original image along with two reconstructed

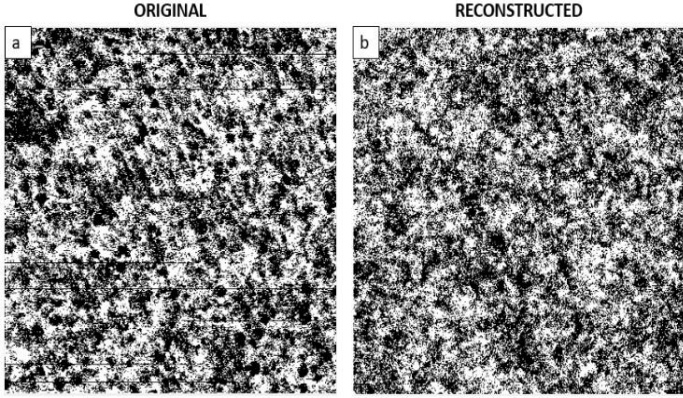


Figure 9: a) STM image b) Reconstructed Image (both images of size 450 x 450 pixels)

being an increase in the computational time. So, this size has been set as standard for optimization.

5. STRUCTURE-PERFORMANCE MODELING USING A NOVEL ANALYTICAL EQUATION

This section provides the details of the novel approach for finding the IPCE of an OPVC structure considering the microstructural features. The first half explains the physics-based theory behind the novel equation, while the second part lists down the assumptions along with presenting three test cases for the pre-validation of our approach.

5.1 Theory of light to electron conversion efficiency of an OPVC

Here, a microscopic equation is developed for the first time to predict the device performance for a given 3D reconstructed microstructure. Under the finite element scheme, the equation for estimating performance from the microstructure can start with counting the number of collected electrons/holes per unit time through a summation of contributions from each volume element (voxel) over the whole active layer as:

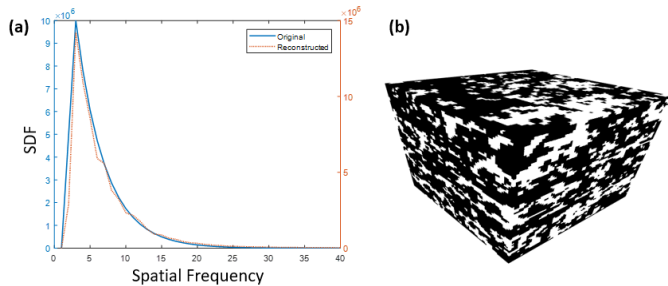


Figure 10: (a) SDF of original image in comparison with the SDF of reconstructed 3-D image/structure. (Note that both y-axes are normalized for each graph); (b) 3-D Realization of the reconstruction.

$$\frac{n(\lambda)}{\Delta t} = \int_v \left(\frac{I(\lambda)}{h \frac{c}{\lambda}} e^{-(t-z)\alpha(\lambda)} dx dy \dots \right. \\ \left. P_{ex}(\lambda) dz \right) \left(e^{-\frac{d}{\xi_{ex}}} \right) (P_{sep}) \left(e^{-\frac{S_A}{\xi_h}} e^{-\frac{S_C}{\xi_e}} P_{col} \right) \quad (4)$$

The four parentheses in Eq. (4) represent the four steps illustrated in Fig. 1: (i) light absorption (exciton creation); (ii) Exciton diffusion; (iii) charge separation; and (iv) charge diffusion & collection. Here t is the thickness of the active layer; $\alpha(\lambda)$ is the absorption coefficient of active layer as function of the light wavelength, λ ; P refers to probability for exciton creation (ex), for charge separation (sep), and for charge collection (col); d is the distance to the nearest interface from the location of the exciton creation; ξ the diffusion lengths of exciton (ex); of hole (h); and of electron (e); S are the lengths of the path to anode (A); and to cathode (C). In this equation, the recombination behaviors of the charges are simply assumed to follow exponential decay over the distance it moves.

From previous study the value of ξ_e (diffusion length for electron) is found to be ~ 340 nm [78]; the value of ξ_h (diffusion length for hole) is found to be ~ 90 nm [67]; the value of ξ_{ex} (diffusion length for exciton) is found to be 5.4 ± 0.7 nm [68] and $\alpha(\lambda)$ (absorption coefficient) is measured and could be found in [69].

Among the variables in Eq. (4), the probability of exciton creation, $P_{ex}(\lambda)$, and the absorption coefficient, $\alpha(\lambda)$, could be related to each other through the following relationship:

$$P_{ex} = 1 - e^{-\alpha(\lambda) \Delta z} \quad (5)$$

This relationship is deduced by assuming:

$$P_{ex}(\lambda) = \left(\frac{\text{no. of photon absorbed}}{\text{no. of Photon incident}} \right) x \dots$$

$$\left(\frac{\text{no. of exciton created}}{\text{no. of photon absorbed}} \right) \quad (6)$$

where the second term is closely related to the internal quantum efficiency, which is very close to 100 % in many cases [70] and assumed to be 1 here. On the other hand, the first term is closely related to the photon absorption coefficient, $I(z) = I_0 e^{-\alpha(\lambda)z}$.

Thus Eq. (4) could be expressed as:

$$\frac{n(\lambda)}{\Delta t} = \int_v \left(\frac{I(\lambda)}{h \frac{c}{\lambda}} e^{-(t-z)\alpha(\lambda)} dx dy \dots \right. \\ \left. (1 - e^{-\alpha(\lambda) \Delta z}) dz \right) \left(e^{-\frac{d}{\xi_{ex}}} \right) (P_{sep}) \left(e^{-\frac{S_A}{\xi_h}} e^{-\frac{S_C}{\xi_e}} P_{col} \right) \quad (7)$$

We compute the IPCE, which is the number of electrons collected per photon incident, as: $IPCE(\lambda) = \frac{n(\lambda)}{\Delta t} \frac{1}{\frac{I(\lambda)}{h \frac{c}{\lambda}} A}$ where

A represents the area of the sample illuminated by light. In this simulation, it is assumed that the whole sample surface is illuminated by light, indicating the sample surface area is A . The

final working equation for evaluating IPCE from nanostructure is expressed as the summation over every voxel:

$$IPCE(\lambda) = \sum \left(e^{-\frac{d}{\xi_{ex}}} \right) (P_{sep}) \left(e^{-\frac{S_A}{\xi_h}} e^{-\frac{S_C}{\xi_e}} P_{col} \right) \quad (8)$$

where, z , d , S_A , and S_C of each voxel are determined from the nanostructure. Eq. 8 is used to evaluate the performance of the OPVCs with the known quasi-random nanostructures in this study.

5.2 3-D Structure Performance Simulation

To evaluate the IPCE for a 3D binary structure, some assumptions are made: (i) no void space exists in the structure – the whole space is filled by either one of the two materials: P3HT and PCBM; (ii) only P3HT is responsible for creating excitons upon light absorption. This condition is based on the fact that in the solar spectrum wavelength range, P3HT has 2-5 times larger absorption coefficient compared to PCBM. For simplification, both P_{sep} and P_{col} are set to 1 which being mere multiplication factors, will not affect the optimization. λ is chosen to be 510 nm, at which P3HT has the highest absorption coefficient ($\alpha(\lambda) = 4.3 \times 10^6 \text{ m}^{-1}$) [69]. Consideration of the whole wavelength range of solar spectrum can be easily implemented in the future.

Under these assumptions, there are four major parameters viz., z , d , S_A and S_C at each voxel, required for optimizing the IPCE. In our 3D binary model, P3HT is assigned with 0s or black regions, while PCBM is assigned as 1s or white regions. Figure 11 illustrates these distances with an exciton created at the shaded cell and corresponding distances. First, excitons are created (step (1) in Section 5.1) at the shaded cell with the light intensity determined by the depth of this cell: $t-z$. After creation, the exciton diffuses to the nearest interface (step (2) in Section 5.1) with a distance d . When the exciton dissociates into electron and hole at the interface, the hole diffuses towards the anode through the shortest path in the black medium (step (4) in Section

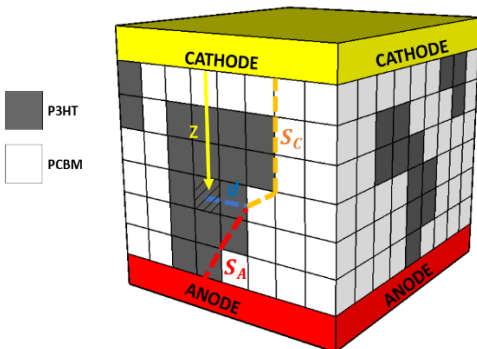


Figure 11: A sample of structure with an excited particle at the center (shaded cell). Yellow arrow represents light's path towards the prospective region; Blue represents exciton's path; Orange represents electron's path; Red represents hole's path

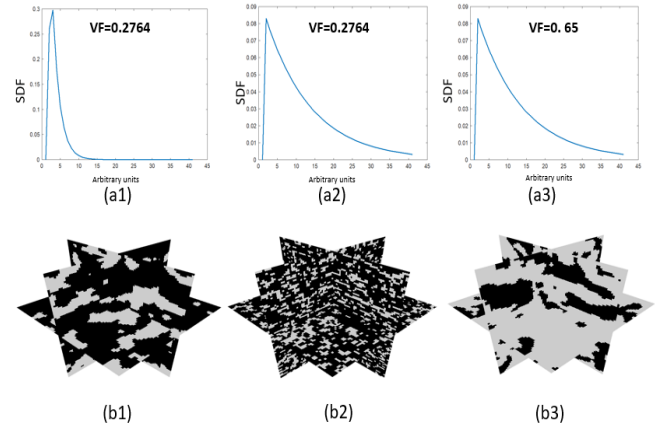


Fig. 12: Testing our performance model. (a1-a3) are input parameters: SDF and volume fraction; (b1-b3) are random cross-sectional slices of the reconstructed structure.

5.1), S_A , while the electron diffuses towards cathode through the shortest path in the white medium (step (4) in the section 5.1), S_C .

To explain the contribution of each of the three factors, Peak Point, Decay and VF, we randomly created three test structures for a basic preliminary verification of our model. The input parameters along with the cross-sectional slices of the resulting structure are shown in Figure 12. The performance results are broken down in Table 2. As seen in the table, test 1 and test 2 both have same VF, but different IPCE. This is because of the difference in the dispersion of the material which is caused by the different SDF inputted. The SDF in the test 1 has faster decay rate, thus, test 1 has larger clusters in real space; while the SDF in the test 2 has slower decay rate, infers to smaller clusters in real space. This results in larger average d and S_C in test 1 than that in test 2. With the same VF, the exciton creation is in the same order in the two test cases, thus the higher IPCE found in test 2 is attributed to the shorter average diffusion lengths, as shown in Eq. 8. On the other hand, comparing test 2 and 3, which have the same SDF but different VF, the difference in VF dominates the IPCE value. With similar microstructure texture due to the same SDF input, the test 2 has higher amount of P3HT molecules (lower VF), hence higher IPCE. It is worth noting that even test 2 and 3 have same SDF input, their average diffusion

Table 2: Average values of d , S_A & S_C are tabulated for the three cases presented in Figure 1w. Exciton generated is the number of elements in the structure that will contribute towards performance.

	Test 1	Test 2	Test 3
Average d	4.3 nm	1.77 nm	2.76 nm
Excitons generated	370483	370483	179200
Average S_A	61.6 nm	60.4 nm	80.5 nm
Average S_C	96.0 nm	82.5 nm	65.2 nm
IPCE	4.97 %	8.41 %	3.04 %

lengths are affected by the VF. Thus, simultaneously optimizing the IPCE with consideration of both SDF and VF is critical and will be discussed in later sections.

6. DESIGN FORMULATION AND METAMODELING

With the S-P relationship established through IPCE (Eq. 8), design formulation can be cast as an optimization problem to find the active layer nanostructure that delivers highest IPCE. Due to the short exciton diffusion length (~ 10 nm), the state-of-the-art OPVC nanostructure follows the BHJ architecture with the electron donor and acceptor domains in ~ 10 nm scale in the active layer. Ideally, to have all four major charge carrier processes optimized, the nanostructures in BHJ should possess the following characteristics: (a) thickness identical to the light absorption depth (typically $\sim$ hundreds of nm to a micron), to best utilize the light flux; (b) the length scale of the nanostructures is of the order of the exciton mean free path (~ 10 nm); (c) maximizing effective interfacial charge separation volumes for efficient charge separation; and (d) minimizing the isolated domains where there is no path to electrodes for charge collection.

We leverage the low-dimensional structure representation enabled by SDF to formulate a design paradigm using a small set of variables. The active layer thickness is determined by the size of RVE, 100 nm (Sec. 4.2), while the SDF parameters—Peak Point and Decay – account for structural characteristics that control the charge separation and transport phenomenon discussed above. Further, the assumption that exciton generation is restricted to P3HT molecules necessitates the inclusion of donor/acceptor composition as an additional design variable. Here, PCBM volume fraction is chosen as the composition design variable. Note that composition also plays a critical role in level cutting the GRF for the reconstruction. Thus, only three variables are required: two from SDF and one as the PCBM volume fraction.

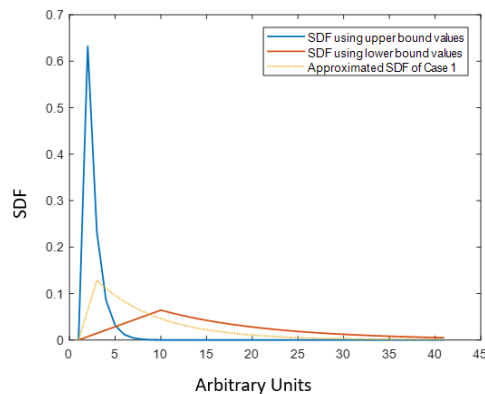


Figure 13: SDF curves are plotted using the upper bounds and lower bounds of design variables of SDF. SDF of Case 1 is also plotted for reference.

The bounds for design variables are selected by analyzing the SDF of the two fabricated samples (Table 1) to estimate the three SDF parameters. Then a broad range for each of the three parameters is selected to ensure diverse SDF curves. Figure 14 plots the SDF obtained by setting parameters to their lower and upper bounds, along with the SDF of Case 1 for comparison. Previous studies, focusing only on active layer composition, have revealed that the ideal PCBM volume fraction (VF) is 0.37 approximately [25, 71]. To explore a wider range of values around the optimum, we allow VF to vary between 0.15 and 0.75. With the objective of maximizing IPCE ratio, the design formulation along with the design variables and their corresponding bounds are summarized in Table 3. The optimization problem can be stated as:

$$\begin{aligned} \max \quad & IPCE = f(p, d, vf) \\ \text{w.r.t} \quad & p, d, vf \\ \text{s.t.} \quad & 2 \leq p \leq 10 \\ & 1 \leq d \leq 12 \\ & 0.15 \leq vf \leq 0.75 \end{aligned} \quad (9)$$

Where p = peak point, d = decay, and vf = volume fraction.

Since optimization is an iterative process, it requires several S-P simulations (constructing RVE for current value of design variables and evaluating the IPCE ratio). For an $80 \times 80 \times 80$ voxels RVE, reconstruction requires several minutes, implying that one iteration will need the same time. To overcome this computational burden and accelerate optimization, a metamodel is used.

A metamodel is created by sampling design space efficiently using DOE, followed by an appropriate machine learning method to interpolate and form a continuous input-output mapping in design space. One of the main hurdles in choosing sampling points is to ensure that the design space is thoroughly explored with the minimum number of samples. For the selection of these sampling points, we use OLHS. The main advantages of OLHS include minimization of Integrated Mean Square Error, maximization of minimum distances between samples, and maximizing entropy [72]. Since there are three design variables, 56 space filling samples are obtained from OLHS and corresponding S-P simulations were performed. The machine learning technique used to create the metamodel is Gaussian Process (GP), which is a special case of Kriging method. The main advantage of using Kriging method is that it provides the most accurate results for highly nonlinear models with small number of variables compared to Polynomial Regression, Radial basis Function or multivariate Adaptive Regression Splines [73]. 45 randomly-selected samples are used in creating the metamodel while 11 are used for cross-validation.

7. DESIGN OPTIMIZATION AND SENSITIVITY ANALYSIS

This section discusses the use of the two DOE models for understanding the effect of design variables on the design performance i.e., IPCE. In the this model all design variables -

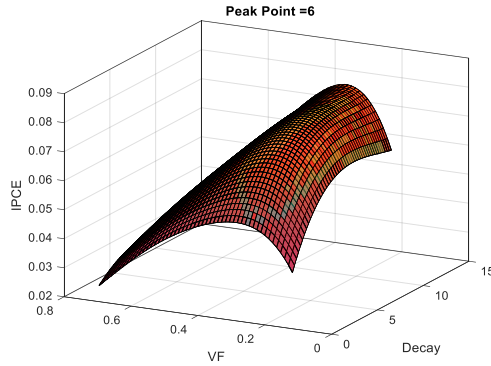


Figure 14: The effect of VF and decay on performance with Peak Point fixed

peak point, decay and volume fraction (VF) are included. Global sensitivity analysis using this model reveals the effects of all the variables on performance.

As mentioned in Section 6, 45 randomly-selected samples from OLHS design were used for creating the Kriging metamodel with all four design variables while 11 were used for cross-validation. The R-Squared value based on validation points is 0.9792, which indicates a fair fit. Because of the highly nonlinear response of the metamodel, Genetic Algorithm(GA) is applied to obtain the global maximum IPCE. To test accuracy, multiple starting designs were selected. For all starting points considered in this study, the optimization routine converges to the same optimal point (Peak Point = 2, Decay = 12, VF = 0.2764 and IPCE = 8.41%). This result relates to a 36.75% increase in IPCE ratio compared to Case 1 which has an IPCE ratio of 6.15%. A RVE is reconstructed using the optimal microstructure design variables and its IPCE ratio is computed. Compared to 8.41% from the metamodel, the reconstructed RVE results in an IPCE ratio of 8.19%, reinforcing the fact that the metamodel used here is sufficiently accurate.

Next, we analyze the effect of each variable in the performance model using the variance-based sensitivity analysis (a.k.a. Sobol analysis [56]). This analysis consists of two indices for each variable i : First order sensitivity (S_i), and Total order sensitivity (S_{Ti}). S_i essentially incorporates the effect of variable x_i alone on the response while S_{Ti} incorporates the total effect of variable x_i , including the interaction effect with other variables

Table 3: Sobol indices for all design variables

	Peak Point	Decay	VF
S_i (MAIN effect)	0.0033	0.1426	0.8253
S_{Ti} (TOTAL effect)	0.0116	0.1710	0.8479

[56]. The Sobol indices for all four design variables are listed in Table 3. We note that VF is the most influential design variable as it has the greatest first order and total effect. Similar conclusions can also be deduced by plotting the variation of

IPCE ratio w.r.t. Decay and VF (see Figure 14). It further confirms the optimal value of VF (0.2764), which translates to a composition of P3HT:PCBM = 1.92:1 (using densities of P3HT and PCBM as 1.1 g/cm³ and 1.5 g/cm³, respectively [74]).

8. CONCLUSION AND FUTURE WORK

This article introduced an SDF based microstructure design framework to accelerate the development of quasi-random NMSs. Instead of following the conventional trial-and-error approach to materials design, the proposed framework enables physics-based, cost-effective design strategy by leveraging physics-aware SDF, an MCR technique capable of representing arbitrary geometries whose distribution is governed by an underlying spatial correlation. The focus of this paper is on implementing the proposed framework for the active layer design in OPVC. Active layer samples conforming to BHJ architecture are fabricated using spin-coating technique, followed by annealing and their microstructure is captured by novel XSTM/S technique. By using SDF to represent these microstructural images, we confirm that the nanostructure in the OPVC active layer can be parametrized using the SDF with only two variables – Peak Point & Decay, providing a low-dimensional representation of an otherwise infinite-dimensional microstructural image. Accurate 3D RVEs are obtained by level-cutting GRFs and the associated computational cost for different sample sizes is discussed. A novel S-P simulation model is developed using the IPCE ratio as the metric to evaluate OPVC performance computationally. In addition to accounting for the physical processes and material properties influencing energy conversion as already established in literature, our proposed IPCE evaluation takes the impact of active layer morphology explicitly into account and delineates its effects on each physical process. The distance to nearest donor/acceptor interface (d), shortest path to anode (S_A) and cathode (S_C) are the three morphological variables influencing IPCE. Procedure to evaluate these variables is discussed, followed by IPCE computation to establish S-P linkage. Our results also demonstrate the effectiveness of using SDF for design representation and the use of computationally guided methods to expedite microstructural design optimization involving expensive S-P simulations. A metamodel created using OLHS and Kriging method is used to accelerate the iterative optimization problem, which is formulated with the objective of maximizing IPCE using only three design variables – two from SDF plus the PCBM volume fraction. The optimal microstructure has an IPCE of 8.41%, a 36.75% increase compared to fabricated sample (Case 1). Global sensitivity analysis using Sobol indices shows that PCBM volume fraction is the most influential design variable followed by Decay (which controls the dispersion of PCBM).

Future work will involve establishing P-S linkage, which necessitates Coarse-Grained Molecular Dynamics (CGMD) simulations for microscopic examination of morphology and construction of atomic-resolution structural realizations of

interfaces and molecular alignment. A wider range of fabrication techniques and processing conditions will be explored and the corresponding forms of SDF will be identified. With the help of CGMD for studying processing-structure relations, the full processing-structure-property (PSP) linkages will be established, and a goal-oriented design methodology will enable optimizing OPVC performance with due consideration of the necessary processing conditions, thus ensuring manufacturing feasibility of the optimized nanostructures. Finally, the obtained optimal nanostructure will be fabricated using a suitable bottom-up nanofabrication technique and its performance will be validated experimentally.

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