Optimizing a High-Entropy System: Software-Assisted Development of Highly Hydrophobic Surfaces using an Amphiphilic Polymer

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Supporting Information

ABSTRACT: In materials science, the investigation of a large and complex experimental space is time-consuming and thus may induce bias to exclude potential solutions where little to no knowledge is available. This work presents the development of a highly hydrophobic material from an amphiphilic polymer through a novel, adaptive artificial intelligence approach. The hydrophobicity arises from the random packing of short polymer fibers into paper, a highly entropic, multistep process. Using Bayesian optimization, the algorithm is able to efficiently navigate the parameter space without bias, including areas which a human experimenter would not address. This resulted in additional knowledge gain, which can then be applied to the fabrication process, resulting in a highly hydrophobic material (static water contact angle 135°) from an amphiphilic polymer (contact angle of 90°) through a simple and scalable filtration-based method. This presents a potential pathway for surface modification using the short polymer fibers to create fluorine-free hydrophobic surfaces on a larger scale.

1. INTRODUCTION

The relationship between superhydrophobicity and the surface structure has been widely studied, using natural examples of superhydrophobic materials as well as designed surfaces with surface features of controlled size and distribution. Superhydrophobicity is generally defined as a surface having a static water contact angle (WCA) of 150° or greater. Superhydrophobic surfaces have been reported in the literature using many hydrophobic polymers, with WCA tuned through micro and nanostructure. 2–4 Many models that study the effect of surface roughness on the contact angle are available. Typically, a combination of the Wenzel 5 (a fully wetted surface) and Cassie–Baxter 6 models is used (a partially wetted surface).

To a lesser extent, there have also been reports of superhydrophobic surfaces prepared excluding fluorinated compounds and using amphiphilic polymers. Extraordinary control of feature size is typically required to obtain high WCA. Feng et al. 7 created a superhydrophobic surface of aligned poly(vinyl alcohol) nanofibers through a template-based extrusion method, while Dong et al. 8 used electrospinning and evaporation-induced self-assembly to fabricate superhydrophobic zein surfaces. Common techniques to obtain structured hydrophobic surfaces such as lithography or templating enable manufacturing of highly ordered, homogeneous structures with predefined distinct morphology and characteristic dimensions (size and spacing of features). The approaches above can result in very high contact angles, enabled by a high degree of morphological control, but present a challenge from scale-up and practical application perspectives.

In contrast, surfaces formed through random packing of materials, such as papers, do not enable the same level of morphological and ordering control. The characteristic dimensions of the “surface morphology features” responsible for the roughness are determined by local packing and ordering, which are in turn determined by processing conditions and the size of the starting particles (fibers, in the case of papers). With low control over the size and spacing of features, maximizing WCA of such surfaces is difficult, and fluorination surface modification is often used, 9–11 although it is undesirable industrially because of adverse environmental effects. Manufacture of highly hydrophobic papers without the use of fluorine is a complex task but holds a high potential value.

In this study, we apply artificial intelligence approaches to guide our experiments with the aim of creating a highly hydrophobic surface solely through the randomized packing of one-dimensional amphiphilic materials of varied sizes and roughness. This work demonstrates that highly entropic systems can be optimized by combining the power of machine learning and the depth of the experimenter’s scientific understanding.

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We have developed a flow system capable of producing short polymer fibers in a dispersion\textsuperscript{13−14} (Scheme 1). Such dispersions can be used to produce paper using vacuum filtration. Since the WCA is strongly related to the surface structure, the initial hypothesis in this work was that the size and distribution of short fibers, and hence their packing, can be taken as a proxy to produce the surface roughness required to achieve hydrophobicity.

In essence, the size distribution and polydispersity of the fiber length and diameter, as well as their inherent roughness, would have an effect on the type of surface obtained and thus would have a correlation with the surface's apparent water contact angle. Following established principles, we used a porogen (oil) in the process, to create additional surface roughness in each fiber. This is expected to further increase hydrophobicity through secondary roughness. In contrast with structure-controlled methods, such as lithography, the distribution, and combination of fiber properties required to maximize the contact angle is unknown.

We chose this approach as an ideal candidate for artificial intelligence optimization,\textsuperscript{15−17} as it relies on fiber manufacturing, and on the random combination and arrangements of the fibers in paper fabrication to create the surface structures, and as such poses a complexity that makes experimental optimization extremely challenging (Scheme 2).

This complexity and "ideal structure unpredictability" is also compounded by the two-step nature of the process we propose. Although the formation of the fibers is controlled by the fabrication parameters, known to some degree through previous work, the hydrophobicity of the assembled paper is dependent on surface features that are governed by complex factors including the way these fibers settle, pack, and ultimately come together. Correlating fiber production conditions with WCA of the assembled paper samples has not been done before.

In such a complex, interrelated system, a human-designed optimization process for the fiber production generally starts with making hypotheses as to "an ideal structure". Targeted experiments would be performed to test the hypotheses and sequentially optimize and lock single parameters in an increasingly narrow experimental space (Figure 1).

This poses a limitation in that the parameters are optimized with respect to a previous set of parameters and thus the optimization itself occurs in a linear branching pattern where most of the parameter space is not investigated. This is not a suitable approach for highly unpredictable systems, as a sequential selection of conditions may lead to areas of the parameter space that do not contain experimental optima.

In an ideal world, every possible combination of parameters would be explored in a factorial design or a response surface approach. These techniques are not typically adaptive, resulting in experimental overheads and noninformative experiments. To adapt, the parameter space set by the experimenter is often significantly narrowed according to various assumptions and predictions based on the knowledge available. This in turn creates a situation where, faced with a system with many unknowns, the experimenter needs to predict results based on very limited knowledge and thus may decide to focus on the areas of the parameter space with the highest certainty, leaving significant portions of the parameter space unexplored.

Unlike human experimenters, machine learning algorithms practically do not have a limitation on the number of parameters they can simultaneously vary and thus can...
efficiently explore a very large parameter space, to optimize a process or a material. In “Big data” approaches, software is trained on a particular task using a large set of data. In contrast, optimization algorithms that work on a “lean data” basis allow the experimenter to start with a small amount of data, and the software to sequentially learn through multiple iterations of experiments. With the help of an algorithm, the experimenter can explore a much more complex system, using a mathematically proven optimization concept to minimize the time required to achieve the optimal result. This minimizes experimental costs and maximizes the opportunities to explore a complex space.

This type of algorithm is advantageous for such a complex, highly entropic space as the one investigated here, in which prior knowledge is of limited use in predicting the outcome. This approach allows mathematically proven valid exploration of conditions that a human experimenter may not have otherwise investigated (due to high risk). The greater associated risk/benefits efficiency compared to random experiments lead to a greater knowledge gain from the experiments than what would be obtained from a traditional experimental design.

We propose in this work that combining higher-level human learning and machine learning algorithms provides a powerful platform for high-risk optimization of complex and unexplored parameter space.

This work demonstrates how high-entropy experiments can be optimized with the aid of machine learning algorithms, providing new materials with extraordinary properties, which would have otherwise not been attainable.

2. RESULTS AND DISCUSSION

2.1. Hypothesis Development and Testing. We have previously reported the rapid optimization of the basic poly(ethylene-co-acrylic acid) (PEAA) short fiber production process using a Bayesian algorithm. The process is robust and scalable, such that short polymer fibers have established commercial applications.

In previous work, we optimized the process above toward specific fiber length and diameter values. This knowledge will be used to support the algorithms in this work, although the system here optimized has the extra complexity of a porogen being added to the spinning polymer dope.

The integration of algorithm-supported optimization with human input is an emerging area. Examples include self-cleaning surfaces produced through the control of the surface structure by reactive ion etching, followed by chemical vapor deposition. Human input helped to restrict and direct the parameter space in each iteration. Although the interplay between parameters was unknown, the surface structures were well-defined, uniform, and could be controlled in both steps.

In contrast, this study introduces multiple layers of complexity: one additional processing step (porogen emulsification) and additional processing parameters, the effects of which are unknown, and an element of randomness in terms of fiber packing during a subsequent processing step (Scheme 3).

Bayesian algorithms are able to take into account prior knowledge. This is advantageous where prior experience might help optimize one part of the experiment. As such, in this work, there are fiber production parameters (polymer flow, coagulant flow, constriction angle, and distance to constriction) where the effects are known from prior work. This prior knowledge has been made available to the algorithm, to improve control over fiber synthesis. However, the additional parameters used in this work, such as the optional emulsification of porogen (oil), and the way the fibers will pack into a surface during paper fabrication, are very difficult to predict and no prior knowledge is available that can be coded into the algorithm.

To begin with, we started with a subset of a sample based on a previously optimized PEAA paper control sample without porogen. This sample has a contact angle of 126°, which is significantly higher than what was measured for a cast PEAA film (90°). This shows the effectiveness of the paper morphology in increasing the hydrophobicity of the material surface. Further experiments were conducted using the same flow conditions but varying oil contents and emulsification shear. The resulting fibers (Figure 2) were then analyzed with regard to their size distribution and made into paper to measure the contact angle.

Looking at the correlation between parameters (Figure 3), it can be seen that a clear trend is absent, as expected in such a small sample size. At this point, a human experimenter would likely target parameters close to the highest observed contact angle that was obtained, and localize the search area around those particular values to quickly reach a maximal outcome.

In contrast, the algorithm developed in this work treats the system as a “black box”, enabling search of a large space with mathematically demonstrated precision and efficiency. Another important distinction is that the machine learning algorithm, which is adaptive, will recalculate a model at every iteration, considering all data points collected, whereas a human experimenter with a randomized experiment set will generally treat certain points as outliers.

The algorithm balances exploration of the space and exploitation of the data. Although this may appear to delay the discovery of high WCA, the probability to find maxima far from the initial best is increased as the algorithm guides the human experimenter in areas they otherwise would not tackle. This key feature might enable the discovery of novel phenomena and will increase the ability of the experimenter to develop novel materials with extraordinary functionality.

2.2. Software Optimization. Conventional machine learning methods generally require a large amount of training data, however, this approach cannot be applied to experiments where limited data is available. As such, the technique of Bayesian optimization (BO) was used to search for the optimal fiber production parameters to explore the various possibilities in the most efficient way possible. Bayesian optimization has been demonstrated as a sample-efficient tool in various applications, and has significant potential in improving the cost efficiency of materials development.

A Gaussian process model provides a probabilistic model of a function, to predict function values at unobserved locations of the input space, using the current observation set and a covariance model between the function values. The prediction...
takes the form of a Gaussian-distributed random variable for each location, expressing both the belief and the epistemic uncertainty about the belief. Because of the induced covariances, proximity to several already observed locations would make the prediction more accurate and more certain at the same time, whereas it would be opposite for far off locations of the input space, making the predictive distribution very spatial. From this, it may be tempting to perform the next experiment at a location where the predictive mean value is at the optimum, i.e., at the location of the current-highest result obtained. However, such a strategy that only exploits the current knowledge tends to remain focused around a local optimum, and risks sacrificing the opportunity to achieve a global optimum.

Bayesian optimization combines both the exploitative and the explorative behavior in an optimal strategy that provides the fastest convergence rate among all of the global optimization methods. Expected improvement (EI) is such a strategy. In the Bayesian optimization literature, such strategies are also known as "acquisition functions". The global optimizer of the acquisition function is used as the next experimental location. Figure 4 depicts the Bayesian algorithm in action at three different iterations. For this simple function, convergence occurred within the first 9 iterations.

The standard Bayesian optimization algorithm is originally constructed to recommend only one experiment per iteration. To maximize efficiency, a batch Bayesian optimization algorithm is created, as a modification of the original. This algorithm recommends multiple experiments per iteration, where the first one is still the same as that of the standard Bayesian optimization. The subsequent suggestions are
obtained by temporarily inserting the previous batch elements as known experiments with their function values being substituted by the model predicted values. The first member of the batch was chosen as a reference because it is the most promising recommendation, as other batch members are sequentially obtained using fictitious function values of the prior batch members. To achieve this, the acquisition functions for the secondary batch members are optimized within the restricted input space with the fixed values for those input variables. In this study, the batch was set to have fixed properties along the production parameters that are more difficult to change (geometry-related parameters), to maximize time efficiency.

Compared to random search and grid search that do not take the information from previous experiments into account, Bayesian optimization keeps track of past evaluation results and uses them to build up a probabilistic model mapping experimental inputs to outputs. As more data becomes available, the reasoning becomes more accurate since the model is updated with the new data.

2.3. Material Optimization and Building Knowledge in the Parameter Space. With each iteration, the algorithm was able to explore the parameter space, including in distant areas of the space, which a human experimenter would typically not explore because of the high risk of failure (Supporting Information 1). The algorithm suggests experimental conditions that the experimenter would act upon. Multiple suggestions (batch optimization) were provided to the experimenter to reduce the “cost of setup” of the experiment. Because of this, the batch optimization process was performed with a single sample produced for every suggestion to maximize time efficiency, and the algorithm was relied on to take into account any potential “noise” and outliers. Once sufficient knowledge is gained from the system, the experimenter then duplicated selected samples, chosen as those that showed the highest potential to provide greater insight.

In the batch optimization process, when looking at the spread of values obtained with each iteration (Figure 5), there was a narrowing trend, with the minimum WCA values becoming higher overall with each iteration and the maximal WCA values remaining quite stable, although slightly increasing. This is consistent with the algorithm’s having found a plateau where higher contact angle values are aggregated. From the spread of the contact angle results, it is evident that by iteration 5 the spread of the obtained WCA values had narrowed significantly, resulting in a batch with a very high overall contact angle in iteration 7. This shows the result of the algorithm’s learning, in that it was able to achieve what appears to be a maximum in 7 iterations.

Figure 6 shows the length and diameter distribution of two optima, which were produced in duplicates after the batch obtained by temporarily inserting the previous batch elements as known experiments with their function values being substituted by the model predicted values. The first member of the batch was chosen as a reference because it is the most promising recommendation, as other batch members are sequentially obtained using fictitious function values of the prior batch members. To achieve this, the acquisition functions for the secondary batch members are optimized within the restricted input space with the fixed values for those input variables. In this study, the batch was set to have fixed properties along the production parameters that are more difficult to change (geometry-related parameters), to maximize time efficiency.

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optimization. The maximum identified by the software is reached through packing fibers which are very different from the highest value in the initial, human-optimized, set. Comparing the fiber size distribution between the highest result obtained by the software (WCA = 132°) and that from the initial sequential set (WCA = 130°, Supporting Information 1), the software appears to have achieved high WCA through the packing of short fibers with large thickness variation. In contrast, the initial optimum was reached with longer fibers, with additional surface roughness due to the porogen. Indeed, the highest value in the initial set was obtained from the sample that had the lowest amount of porogen added to it, which implies that the original control sample was already close to the initially reached optimum.

The algorithm in this work takes into account the average fiber diameter and length, due to a need to represent fiber properties using the first-order statistical moments, as is necessary to incorporate prior knowledge. The use of values, such as the median or mean, can result in a significant loss of information in terms of the morphology of the fibers (and consequently how they pack on the surface of the paper). Two samples with very similar median fiber values can show very different distributions, as seen in Figure 7. To take this complexity into account during the optimization, we have adaptively added second-order statistics such as standard derivation and skewness in the software’s target objectives. Although the broad effects of the distribution are taken into account, optimization still relies on reducing complex morphology information into numbers.

From these results, it became apparent that there is a need to look at the underlying factors affecting WCA, such as the morphology of the paper produced with these different fibers, as shown in Figure 8 (additional images in Supporting Information 2). Looking at the surface structure of these papers, it becomes clear that more open, rougher structures are correlated with higher WCA values, whereas the samples with a lower WCA show a much denser surface structure. Low WCA samples also show a lower occurrence of debris and other surface features. Bimodal distributions instead resulted in a denser packing of fibers and a surface that is significantly less open, also with a lower WCA.

When looking at samples with different WCA values, it became apparent that no single value, such as the median or mean, would be sufficient to correlate with the contact angle. When it comes to the software-assisted optimization process, the only output that is measured on the paper itself is the contact angle, and as such other paper properties are secondary and not considered. Unlike a human experimenter, the software optimizes without the need to understand the process behind how such a result is obtained, and this function is hidden inside the black box function which is difficult for the experimenter to gain insight into.

To gain a better understanding of the nature of the surface and to see if parameters other than WCA would be more suitable for optimization, some of the paper samples were analyzed for roughness, as measured through an optical profilometer, to identify possible correlation with WCA. As can be seen from Figure 9, a certain value of average roughness provides high WCA, with the lowest value of roughness giving lower WCA values, and very high roughness also giving WCA values that are quite high, but remain lower than those of samples with intermediate roughness values. Countering this trend, a sample with low WCA in the same roughness range can also be observed in the set. This indicates that, although there may be a relationship between the roughness value and WCA, it is also likely that the roughness value does not sufficiently take into account roughness at different length scales, and thus is insufficient to represent the complexity behind the various factors that determine the contact angle of the surface. Roughness values were therefore not used to inform the optimization.

It is possible that using various additional input parameters in addition to fiber size would improve the efficacy of the
algorithm, however, this would not be cost-effective and would result in significantly less data being produced.

An emerging trend to maximize efficiency and minimize cost is to have human input guide AI algorithms, as a human would be able to derive more information from certain types of results, such as visual information, based on fundamental prior knowledge. This approach has been followed in this work. The high data complexity of this work makes it difficult to theoretically predict the WCA that would be obtained for a certain fiber size distribution. Many previous studies\textsuperscript{2,4,24} have derived WCA values based on feature size using models derived from the Cassie–Baxter and the Wenzel models, generally using surfaces with a regular pattern and distinct feature size. The Wenzel model assumes full wetting of the surface, whereas the Cassie–Baxter model assumes incomplete wetting and introduces additional variables to account for the proportion of the surface wetted by water. However, both assume regularity in surface features and thus is difficult to translate to a highly entropic system, such as the one here described, where the feature size cannot be easily defined in a single parameter.

As the intrinsic contact angle of PEAA tends toward hydrophobic, the Cassie–Baxter model for apparent WCA of porous surfaces\textsuperscript{7} was used to calculate the theoretical WCA of the paper samples. Using fiber thickness as the feature size and the standard deviation as the basis for the spacing in between features, it was assumed that the variance of the thicker fibers will be acting as the dominant spacer and thus would be a suitable proxy for the model. Fiber length was not included in this calculation, as its influence on the feature size is difficult to ascertain and is beyond the scope of this work. This idealized calculation has limitations, in that it does not take into account the high complexity of the fiber size distribution, but it serves to highlight the difficulty in distilling complex distribution information into a usable variable for use in calculations.

As can be seen from Figure 10, the theoretical approach is quite good at predicting the values of samples close to the median contact angle of the samples, and overall the values of diameter produce a similar WCA spread. However, the measured and calculated values of individual points differed significantly. Similar issues arise when other variables were used as the value of the spacing between the fibers, indicating that the calculated values are not able to appropriately account for the variations that effectively determine the highest and lowest WCA values, as the equation used here unnecessarily assumes a uniform distribution of features. Modeling a complex structure with various feature size will be much more complex, and this is where a practical, optimization guided approach may have an advantage as the result is guided by experimental data and human intuition, and thus may be able to better encompass the complexity of such a system.

As previously outlined, the algorithm was designed to search for the ideal fiber size, and then infer the parameters required to achieve this fiber size. However, the data obtained thus far indicates that rather than an ideal fiber size, the correct hypothesis would be to have an ideal “distribution” and “shape”, both of which are not as easily incorporated into numerical values. Since the whole process is treated as a black box, the model that the software develops and uses is hidden in the algorithm,\textsuperscript{15} and not easily adapted to “learn” additional information without restarting the process. As such, the algorithm cannot utilize unquantified information such as the fiber shape, bend, pore shape, density of pores in fibers, and other variations of fiber morphology. For example, different shapes and the presence of spheres and debris definitely affect fiber packing, resulting in different WCA values, but are hard to capture. This results in a loss of information in distilling the complexity of the fibers’ morphology into numbers that can be used in the algorithm and thus the software would be unable to see more complex, abstract definitions such as shape variations. Other studies using Bayesian optimization\textsuperscript{25–27} were generally aimed at optimizing well-defined systems, and as such may not have encountered this issue of an evolving hypothesis.

In hindsight, using a two-step optimization process where the software takes an intermediate step instead of a single...
optimization process, in which all of the parameters are correlated directly with the contact angle may have resulted in a loss of information in the middle step. Looking at the parameters directly in Figure 11, it can be seen that only some parameters show a clear trend. This highlights the challenge and the pitfalls in software-assisted optimization, in that initial assumptions need to be sufficiently robust or it may result in a sub-optimal process. Nevertheless, despite this limitation, the software did manage to achieve what can be deemed as an optimum within this large parameter space in 7 iterations, which underlines the value of its assistance in exploring complex systems where knowledge is limited.

2.4. Applying the Obtained Knowledge to Maximize Hydrophobicity. This exploration of the parameter space has given several important insights into physical phenomena linked to WCA. First, variation in both shape and size of surface features seems to drive greater roughness and higher WCA. High variance in length or thickness, or in both, led to higher hydrophobicity. Second, it was discovered that, unlike the original hypothesis, the roughness of the fibers themselves did not seem to be a significant driver behind hydrophobicity. To further understand the factors that drive the hydrophobicity of the material, selected key samples were duplicated to confirm the findings and were looked at in more detail.

Figure 12 shows the fiber size distribution of some of these samples. First, two samples with a very different distribution, both of which displayed a relatively high contact angle. The large variance in length and thickness distribution was observed in both samples. This implies that size variance is an important lever by which WCA may be maximized. Furthermore, a comparison of the samples with the highest WCA to the samples with the lowest WCA. In terms of thickness, a large variance appears to be beneficial, but only if there were fibers within that distribution that had relatively small diameters (below ca. 2 μm). In contrast, the length distribution did not seem to show large differences between the highest and lowest contact angle samples.

Fiber roughness was not observed to affect the WCA much, and appears to invalidate parts of our initial hypothesis that fiber roughness due to porogen will be an important factor. This is consistent with lower shear values for the porogen emulsification resulting in better WCA than using higher shear values. This is likely because using mid shear values resulted in the formation of both large and small oil droplets. These, in turn, maximized the variance in both fiber size and length, by disturbing the fiber formation mechanism. The larger droplets may result in irregular filament breakage, bulges, and spherical particles, while smaller oil droplets may introduce roughness and further weak points along which the fiber could break unevenly.

To test the hypothesis that mid-range values for shear could lead to higher WCA, we tried a small set of samples where the points were chosen to give the maximum possible variation in size and shape, using a set of parameters that was chosen based on the trend observed in Figure 11, as well as basing our assumptions on the more complete understanding of the surface roughness of the paper samples developed through the algorithm.

Three samples were prepared (in duplicates) with this approach, using only conditions that are available to the algorithm. One sample showed a value of 135° for WCA, which is a 3° increase over the previous highest value obtained from the algorithm. There is also an overall 45° increase from the contact angle of a cast PEAA film, and although it is not as high as those obtained by methods such as templating or...
lithography, it was achieved using a simple, scalable approach of random organization of fibers into a paper.

Figure 13 shows the comparison of the fiber distributions in this sample (sample 8–10, WCA 135°), in comparison with the previous best obtained (sample 8–5, WCA 132°). As can be seen from the plot, the distribution of the two is very similar, however, the sample with the higher contact angle shows a larger tail in both length and thickness, consistent with greater variance in fiber size. This strongly supports our modified hypothesis that greater variance resulted in higher contact angles, and it is likely due to the increased roughness afforded by a combination of thicker and thinner fibers, and having longer, larger fibers provide the spacing for the macroscopic roughness, while the smaller, thinner fibers and debris provided the microscopic roughness.

Given sufficient time and iterations, it is likely that the software may reach similar or higher WCA results. However, to achieve even higher WCA, it is likely that the parameter space needs to be altered and the input parameters modified to better reflect the newly obtained knowledge. Indeed, it has become apparent in this study that the use of machine learning algorithms is a powerful tool in exploring such a huge parameter space, but its very nature imposes a limitation in a small-data environment. This limitation is imposed on it by its very design in that it assumes the original hypothesis is correct. Unlike a human experimenter, an algorithm is unable to easily adjust these assumptions to accommodate new knowledge as this becomes available. Furthermore, this exercise has also shown that reducing the complexity of morphology into numbers was insufficient to capture all of the relevant information, and so the challenge remains in terms of the human–software interface in how to capture the information, including those that a human can subconsciously process and translate it into usable input values.

Nevertheless, the error in our initial hypothesis and the development of the new hypothesis also shows the value of this software-assisted approach, without which many of the points that have provided the insights that led to the development of the second hypothesis would have been left unexplored. As previously discussed, without the software to guide the experimenter through a large space, the experimental process would likely progress in a sequential manner, where one parameter is optimized independently of other parameters. This would result in a bias, which drives the experimenter toward a particular outcome, minimizing scrutiny on less favorable outcomes in the name of efficiency.

The use of a machine learning algorithm then presents itself as a powerful tool to remove this bias, without resorting to the inefficiency of random experiments, as the software would pursue outcomes based on the relationship between the points, while the experimenter can act as an observer to maximize the knowledge gain from the study. The algorithm also serves to give the experimenter confidence that unlike random experiments, the time cost of each iteration would be minimized as the software simply considers good and bad results as data, and can correlate points regardless of their position in the experimental space. In contrast, a human experimenter performing random sampling would likely be unsure of correlations in the data obtained.

3. CONCLUSIONS

We have demonstrated the fabrication of a highly entropic and highly hydrophobic material from an amphiphilic polymer through a software-assisted morphology optimization. This approach made short fiber dispersion of poly(ethylene-co-acrylic acid), a polymer with a native contact angle of 90° (when cast as a film), which can be made into a paper-type surface through a simple and scalable filtration-based method. Although not considered superhydrophobic, the PEAA paper shows a very high contact angle of 135°, a 45° increase compared to the base polymer. This approach presents a potential pathway of surface modification using the short polymer fibers to create a fluorine-free hydrophobic surface on a larger scale.

The use of a machine learning algorithm allows the efficient exploration of a much larger parameter space, which allows experimenters to obtain additional information and knowledge about the system, but it was also limited by the initial assumptions put to it in its design.

Despite these limitations, it remains a powerful tool for experimental design as it enables the experimenter to efficiently explore a large parameter space that would be too time-consuming to do by a randomized selection. It also gives the experimenter additional confidence in exploring systems with little prior knowledge. This would allow researchers to obtain a more complete understanding of the system at a greater time efficiency. However, care must be taken in the experimental design to minimize the loss of information in the process, and in some cases, it may be better for a software-assisted approach to run without any assumptions imposed on it and optimize the results solely based on input parameters.

Further improvement in the use of such machine learning algorithms will likely come from a co-learning or a higher learning approach, where the software can incorporate new knowledge as this is obtained, as well as a more sophisticated input system, which may overcome the problem of how to distill complex factors into numbers that the algorithm can use. This highlights one of the main challenges in machine learning, in how to have a system flexible enough to learn and adapt as new knowledge and information becomes available.

4. MATERIALS AND METHODS

4.1. Materials and Short Polymer Fiber Synthesis. Poly(ethylene-co-acrylic acid) pellets (Primacor S9901 DOW) were added to an aqueous solution of deionized water and ammonium hydroxide under reflux at 110 °C to prepare a 16.5% w/v dispersion (polymer dope). This polymer dope was loaded into a syringe, placed on a syringe pump (Legato 270),
which injected the polymer dope into a fluidic device in front of a constricted channel with variable injection positions (d = 0, 15, or 30 mm) and constriction angle (α = 10 or 25°), giving a total of 6 different configurations. The coagulant liquid used was 1-butanol (>99%, Chem Supply), maintained at a temperature of 4−10 °C and driven by a lobe pump (Unibloc LABTOP 200). For all experiments, 10 mL of PEA A dispersion was injected into 400 mL of 1-butanol at a fixed polymer and coagulant flow rate. The coagulant was constantly recirculated until the full volume of the polymer was injected, and the resulting short fiber dispersion was then collected.

The PEA A paper samples were prepared by concentrating the short fiber dispersion using an Amicon filtration system, where the volume of the dispersion was reduced from 400 mL to around 100 mL. The concentrated dispersion was then poured into ethanol (400 mL) and left overnight to stabilize the PEA A short fibers. The dispersion was filtered through an Amicon filtration system under pressure (2 bar) until most of the solvent was removed, and the resulting paper was removed from the filter and dried in ambient conditions on a glass Petri dish. For the optimization process, a single sample is made, however, key samples were later duplicated using the same production parameters for further analysis and comparison.

4.2. Algorithm. The overall algorithm in this experiment has four main steps (Scheme 2) and begins after a few human-selected experimental data became available. Step 1 models the unknown function f that relates the fiber properties (z) to the contact angle (y) using a Gaussian process, \( f \), and then using the standard form of the Bayesian optimization, a set of target fiber properties \( z_i^T \) that can potentially result in the highest contact angle is recommended. Step 2 models the unknown function \( g \) that relates the production parameter (x) to the fiber properties (z) using another Gaussian process, \( g \), and then using batch Bayesian optimization, \( B \), a batch of production parameters \( \{x_i\}_{i=1}^M \) is recommended. In step 3, the experiments are performed and the corresponding fiber properties \( z_i \) are measured, including the contact angle \( y_i \). In step 4, the algorithm terminates if any one of the \( B \) experiments achieves a sufficiently high contact angle, otherwise the new data is added into the previous ones and steps 1−4 are repeated.

The following sections outline the specific details with respect to the set-up outlined above:

Step 1: Recommendation of target fiber properties \( z_i^T \)
All M fiber properties were represented by a vector \( z_i = \{z_{i1}, \ldots, z_{iM}\} \). The standard Bayesian optimization was applied to suggest a target fiber \( z_i^T = \{z_{i1}^T, \ldots, z_{iM}^T\} \). The Bayesian optimization uses the Gaussian process to model the unknown function \( f: z → y \). Squared exponential function was used as the covariance model between two function values at \( x \) and \( x' \). The covariance function can be computed as

\[
KSE(x, x') = \exp\left(-\sum_{i=1}^{d} \frac{(x_i - x'_i)^2}{2\ell_i^2}\right)
\]

where \( d \) is the number of dimensions for the vector \( x \) and \( l_i \) is the length-scale at dimension \( i \), which controls the smoothness of the unknown function at that dimension. The maximal likelihood estimation method \( 28 \) was used to automatically estimate the length scales.

The posterior predictive mean and variance of the Gaussian process are denoted as \( \mu(z') \) and \( \sigma^2(z') \), respectively, for any point \( z' \). Then, the expected improvement (EI) acquisition function is computed as

\[
a_{EI}(z) = \begin{cases} (\mu(z) - y^*)\Phi(\sigma(z)) + \sigma(z)\phi(\sigma(z)) \quad &\text{if } \sigma(z) < 0 \\ 0 \quad &\text{if } \sigma(z) = 0 \end{cases}
\]

where \( \Phi \) and \( \phi \) are the cumulative density function and probability density function of the standard normal distribution, respectively. The recommended fiber properties \( z_i^T \) was obtained by maximizing the EI acquisition function.

Step 2: Recommendation of fiber production experiment batch \( X_t \)
At this step, the M fiber properties were the output corresponding to the input of the fiber production parameters. To maintain simplicity, M fiber properties were merged into a single objective using linear scalarization, or

\[
v_t = \frac{1}{M} \sum_{m=1}^{M} |z_{tm} - z_{0m}|
\]

All objectives were normalized between 0 and 1 prior to scalarization. Normalization was achieved using the minimum and maximum value of each fiber property. The next task was to recommend a batch \( X_t = \{x_{0j}\}_{j=1}^B \) of \( B \) points to minimize \( v_t \). The Gaussian process was again employed to model the unknown function \( h:x → v_t \). GP-BUCB \( 29 \) was used as the batch Bayesian optimization algorithm to construct the next batch of experiments. In the algorithm, the geometry parameters of the whole batch were forced to that of the first member of the batch characterization.

4.3. Instrumental Characterization. To measure the fiber size distribution, some of the short fiber dispersion was taken and highly diluted in ethanol to obtain a very dilute dispersion. This diluted dispersion was then dried on a microscope slide in air at room temperature. Sample images with magnifications of 5, 10, and 20x were obtained using an optical microscope (Olympus BX51 with a DP71 camera). An appropriate magnification was then selected, where the fibers can be clearly seen and are separate and distinct from each other. The length and diameter of the fibers were then measured from the optical images using a custom-made Fiber Separation app on an Image Pro Premier S software.

The static contact angle was measured on the paper using a KSV contact angle analyzer with the Attension software. The contact angle was measured as an average of 5 points across the paper sample from the center to the edge of the paper. SEM images are taken on a Zeiss Supra 55VP SEM. Samples were prepared by drying a diluted short fiber dispersion onto an aluminum stub. After drying, the samples were coated with gold prior to analysis. The SEM images were then used to provide a qualitative value of fiber roughness based on a scale of 1−5, with 5 being the roughest. SEM images of paper samples were also taken to visually compare the surface features of various samples. The roughness of the selected samples was measured using an Olympus LEXT laser profilometer. The roughness analysis was performed using a 10x magnification lens across a 3 × 1 mm² surface.

## ASSOCIATED CONTENT
5 Supporting Information
The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.9b01978.
Optimization parameters, fiber size parameters, and static water contact angle data; additional electron microscopy images of selected samples (PDF)

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Notes

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■ ABBREVIATIONS

WCA, water contact angle; SPF, short polymer fibers; PEA, poly(ethylene-co-acrylic acid); BO, Bayesian optimization; GP, Gaussian process

■ REFERENCES

(1) Wang, S.; Jiang, L. Definition of Superhydrophobic States. Adv. Mater. 2007, 19, 3423–3424.
(2) Averamescu, R. E.; Ghica, M. V.; Dinu-Pîrvu, C.; Prisad, R.; Popa, L. Superhydrophobic Natural and Artificial Surfaces-A Structural Approach. Materials 2018, 11, 866.
(3) Cansoy, C. E.; Erbil, H. Y.; Akar, O.; Akin, T. Effect of Pattern Size and Geometry on the Use of Cassie–Baxter Equation for Superhydrophobic Surfaces. Colloids Surf., A 2011, 386, 116–124.
(4) Sarkar, A.; Kietzig, A. M. General Equation of Wettability: A Tool to Calculate the Contact Angle for a Rough Surface. Chem. Phys. Lett. 2013, 574, 106–111.
(5) Wenzel, R. N. Resistance of Solid Surfaces to Wetting by Water. Ind. Eng. Chem. 1936, 28, 998–999.
(6) Cassie, A. B. D.; Baxter, S. Wettability of Porous Surfaces. Trans. Faraday Soc. 1944, 40, 546–551.
(7) Feng, L.; Song, Y.; Zhai, J.; Liu, B.; Xu, J.; Jiang, L.; Zhu, D. Creation of a Superhydrophobic Surface from an Amphiphilic Polymer. Angew. Chem., Int. Ed. 2003, 42, 800–802.
(8) Dong, F.; Zhang, M.; Tang, W. W.; Wang, Y. Formation and Mechanism of Superhydrophobic/Hydrophobic Surfaces Made from Amphiphiles through Droplet-Mediated Evaporation-Induced Self-Assembly. J. Phys. Chem. B 2015, 119, 5321–5327.
(9) Jeevahan, J.; Chandrasekaran, M.; Britto Joseph, G.; Durairaj, R. B.; Magshwbnar, G. Superhydrophobic Surfaces: A Review on Fundamentals, Applications, and Challenges. J. Coat. Technol. Res. 2018, 15, 231–250.
(10) Darband, G. B.; Aliokhazaei, M.; Khorsand, S.; Sokhanvar, S.; Kaboli, A. Science and Engineering of Superhydrophobic Surfaces: Review of Corrosion Resistance, Chemical and Mechanical Stability. Arabian J. Chem. 2018. DOI: 10.1016/j.arabjc.2018.01.013
(11) Gupta, A.; Joshi, M. R.; Mahato, N.; Balani, K. Superhydrophobic Surfaces. Biosurfaces 2015, 11, 170–200.
(12) Sutti, A.; Lin, T.; Kirkland, M. A. Fibre-Forming Process and Fibres Produced by the Process. WO2013/056312 A2013.
(13) Pringle, K. An Investigation into Short Polymer Fibre Production in Fluid Systems; Deakin University, 2018.
(14) Sutti, A.; Lin, T.; Wang, X. Shear-Enhanced Solution Precipitation: A Simple Process to Produce Short Polymeric Nanofibers. J. Nanosci. Nanotechnol. 2011, 11, 8947–8952.
(15) Liu, Y.; Zhao, T.; Ju, W.; Shi, S. Materials Discovery and Design Using Machine Learning. J. Mater. 2017, 3, 159–177.
(16) Dieb, T. M.; Tsuda, K. Machine Learning-Based Experimental Design in Materials Science. In Nanoformalics; Tanaka, L., Ed.; Springer: Singapore, 2018; pp 65–74.
(17) Li, C.; Rubin De Celis Leal, D.; Rana, S.; Gupta, S.; Sutti, A.; Greenhill, S.; Slezk, T.; Height, M.; Venkatesh, S. Rapid Bayesian Optimisation for Synthesis of Short Polymer Fiber Materials. Sci. Rep. 2017, 7, No. 5683.
(18) Haghaniaraf, S.; McCourt, M.; Cheng, B.; Wueneschel, J.; Ohodnicki, P.; Leu, P. W. Creating Glasswing Butterfly-Inspired Durable Antifogging Superomniphobic Supercransmitive, Superclear Nanostructured Glass through Bayesian Learning and Optimization. Mater. Horiz. 2019, DOI: 10.1039/C8MH00589G.
(19) Ramprasad, R.; Batra, R.; Pilania, G.; Mannodi-Kanakkithodi, A.; Kim, C. Machine Learning in Materials Informatics: Recent Applications and Prospects. npj Comput. Mater. 2017, 3, 54.
(20) Snoek, J.; Larochelle, H.; Adams, R. P. In Practical Bayesian Optimization of Machine Learning Algorithms, Advances in neural information processing systems, 2012; pp 2951–2959.
(21) Ju, S.; Shiga, T.; Feng, L.; Hou, Z.; Tsuda, K.; Shiomi, J. Designing Nanostructures for Phonon Transport via Bayesian Optimization. Phys. Rev. X 2017, 7, No. 021024.
(22) Todorović, M.; Gutmann, M. U.; Corander, J.; Rinke, P. Bayesian Inference of Atomistic Structure in Functional Materials. npj Comput. Mater. 2019, 5, No. 35.
(23) Jones, D. R.; Schonlau, M.; Welch, W. J. Efficient Global Optimization of Expensive Black-Box Functions. J. Global Optim. 1998, 13, 455–492.
(24) Zheng, Q.; Lü, C. Size Effects of Surface Roughness to Superhydrophobicity. Procedia IUTAM 2013, 10, 462–475.
(25) Korany, M. A.; Ragab, M. A. A.; Yousef, R. M.; Afify, M. A. Experimental Design and Machine Learning Strategies for Parameters Screening and Optimization of Hantzsch Condensation Reaction for the Assay of Sodium Alendronate in Oral Solution. RSC Adv. 2015, 5, 6385–6394.
(26) Sánchez Lasheras, F.; Vilán Vilán, J. A.; García Nieto, P. J.; del Coy Díaz, J. J. The Use of Design of Experiments to Improve a Neural Network Model in Order to Predict the Thickness of the Chromium Layer in a Hard Chromium Plating Process. Math. Comput. Modell. 2010, 52, 1169–1176.
(27) Thomas, M.; Schwartz, R. A Method for Efficient Bayesian Optimization of Self-Assembly Systems from Scattering Data. BMC Syst. Biol. 2018, 12, No. 65.
(28) Rasmussen, C. E.; Williams, C. K. I. Gaussian Processes for Machine Learning. In Adaptive Computation and Machine Learn.; Dietterich, T., Ed.; MIT Press, 2006; Vol. 11, pp 3011–3015.
(29) Desautels, T.; Krause, A.; Burdick, J. Parallelizing Exploration-Exploitation Tradeoffs with Gaussian Process Bandit Optimization. J. Mach. Learn. Res. 2014, 15, 4053–4103.