A Self-driving Laboratory Optimizes A Scalable Materials Manufacturing Process

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Abstract

Solution-based coating methods offer a low-cost method for depositing coatings at scale. It is difficult, however, to obtain high quality coatings using these methods due to the complex physical phenomena at play. Here, we show how a self-driving laboratory can optimize a scalable spray-coating process applicable to manufacturing diverse clean-energy technologies. We demonstrate this system by optimizing a spray-combustion process for depositing conductive palladium films. This optimization yielded films with conductivities of 4.08 MS/m, doubling the state-of-the art film conductivity possible with this process and rivaling Pd film conductivities obtained using vacuum-based sputtering processes (2 to 6 MS/m). The rich data gathered by the self-driving laboratory also provides mechanistic insights into the coating process. The champion coating conditions were scaled up to an 8× larger area using the same spray-coating apparatus with no further optimization and no reduction in coating quality. This work shows how self-driving laboratories can optimize spray-coating for depositing coatings at scale.

1 Introduction

Large-scale coating methods are essential for manufacturing clean energy technologies such as photovoltaics [1], electrochromics [2] and electrolyzers [3]. Methods for depositing coatings at scale include vacuum-based methods (e.g. sputtering, thermal evaporation) and solution-based methods (e.g. blade coating, inkjet printing, spray-coating). Solution-based coating methods create new opportunities to inexpensively manufacture clean energy technologies because these methods can reduce energy use and costs relative to vacuum-based coating methods. It is often challenging, however, to obtain large, performant and defect-free coatings using solution-based methods [4, 5]. These methods involve a complex interplay between wetting phenomena [6], solvent evaporation [7], solidification processes [8, 9] and, in some cases, chemical reaction kinetics [10]. Moreover, the small-scale processes commonly used to study solution-based coatings in the laboratory (e.g. spin-coating, drop-casting) do not translate to large-scale manufacturing. Large-scale solution-based coating processes are challenging to optimize, however, because they employ more complex apparatus and involve additional variables (e.g. flowrates, temperatures) and objectives [11, 12, 13] (e.g. speed, waste, cost). Self-driving laboratories present an untapped opportunity to accelerate the development of solution-based coating methods suitable for large-scale, low-cost manufacturing of clean energy technologies.

A self-driving laboratory (SDL) consists of an automated experiment controlled by an experiment-planning algorithm. These autonomous laboratories use data from completed experiments to algorithmically plan future experiments. This data-driven approach to experiment planning enables SDLs to optimize material properties and synthesis procedures 10-100× faster than automation alone [14, 15]. While numerous SDLs have implemented lab-scale solution-based coating methods

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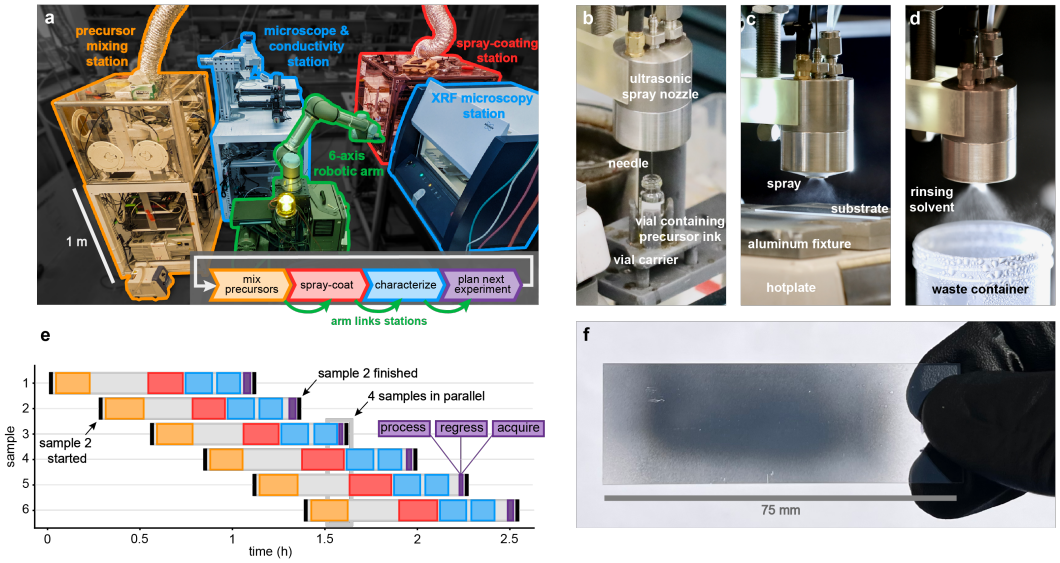

Figure 1: A self-driving laboratory designed to optimize scalable spray coating processes. **(a)** The self-driving laboratory consists of synthesis and characterization stations linked together by a central robotic arm. This robotic arm transports spray-coating precursor inks (in 2-mL vials, see panel b and methods) and thin-film samples (on 75 mm × 25 mm glass substrates, see panel f) between stations as required to execute the closed-loop optimization workflow (see inset). **(b-d)** The spray coating station has been custom designed to load precursor inks through a needle at the front of the nozzle b, spray the material on a heated substrate c, and clean itself automatically d. **(e)** The "station" architecture allows Ada to run multiple experiments in parallel. This parallel workflow enables up to one hundred spray-coating experiments per day. **(f)** a characteristic spray-coated palladium sample.

[16, 15, 17, 18, 19], a self-driving laboratory for optimizing large-scale solution coating processes has not yet been reported. Here, we use a self-driving laboratory to optimize a scalable spray-coating process (Fig. 1).

Spray-coating is a versatile coating technique suitable for manufacturing fuel cells [20], electrolyzers [21], Polymer OLEDs [22, 23], CO_2 electrolyzers [24], and perovskite solar cells [25]. Spray-coating is capable of coating small substrates (e.g. for exploratory materials research) and large substrates (e.g. for manufacturing). Spray-coating thus facilitates the scale-up of laboratory results to large-scale manufacturing. Spray-coating processes are challenging to optimize, however, due to the numerous process parameters and the complexity of the coating process [11, 26, 12] (supplementary Fig. S1).

To autonomously optimize spray-coating processes, we leveraged flexible automation to upgrade our existing SDL [16, 15], "Ada", with a purpose-built ultrasonic spray-coater (see Figs. 1a-d, supplementary methods). We designed this spray-coater to enable rapid, automated spray-coating experiments. A retractable needle enables this spray-coater to aspirate precursor inks directly into the nozzle, minimizing the volume of precursor ink required to prime the nozzle. This feature enables small volumes (<1 mL) of precursors to be rapidly loaded and sprayed. When spraying is complete, residual precursor ink is automatically rinsed out of the nozzle. Ada iteratively optimizes the spray-coating process variables and precursor ink composition under the control of a Bayesian optimization algorithm (see inset to Fig. 1a and supplementary methods). Ada uses a parallelized workflow (Fig. 1e) to perform up to 100 spray-coating experiments per day without human intervention. These capabilities make Ada a generic platform suitable for optimizing a wide range of organic and inorganic thin-film materials and coatings. Here, we demonstrate the power of this platform by using it to optimize the conductivity of palladium films depositing using a spray-combustion process (Fig. 1f). Ada identified experimental conditions that double the state-of-the-art Pd film conductivity possible with this process [27, 28, 15].

Conductive palladium coatings have numerous applications in sensing [29, 30] and catalysis [31, 32, 33]. Sputtering is a common technique for making high-conductivity metal films, but requires

expensive vacuum equipment. Spray-coating provides a one-step, atmospheric-pressure process to deposit conductive Pd coatings from solution using a technique known as spray-combustion synthesis [10, 27, 28, 15]. Spray-coated Pd films have been reported with conductivities up to 2.0 MS/m [15]. As the conductivity of sputtered Pd films can reach 6 MS/m [34], here we sought to further optimize the spray-combustion process to maximize the Pd film conductivity. It has been observed that that combustion synthesized palladium films with precursors deposited by drop-casting exhibit a trend of increasing film conductivity with annealing temperature up to 280 °C . Spray-coating the exact same precursors, however, failed to deposit continuous films at 250 °C [15], revealing a major difference between drop-casting and spray-coating. This finding provides an example of how the translation of a laboratory coating technique (drop-casting) to a more scalable manufacturing technique (spray-coating) can create unanticipated difficulties. We performed preliminary experiments showing that addition of a higher-boiling co-solvent (DMSO) could increase the temperature at which continuous films could be deposited by spray-coating (see Fig. S2). This observation showed that the precursor ink composition and spray-coating process variables must be optimized simultaneously. We therefore configured Ada to perform such an optimization.

2 Results & Discussion

We configured Ada to autonomously maximize the Pd film conductivity by manipulating seven experimental variables that control the spray-coating process (Fig. 2). Each manipulated variable was chosen according to a hypothesis. Hotplate temperature was varied because higher synthesis temperatures are known to improve charge transport in combustion synthesized films [10, 15]. Precursor concentration was varied because it influences overall film thickness, which can influence conductivity through percolation and boundary scattering effects [35, 36]. The number of spray-coating passes was varied because it influences the thickness of the reacting precursor layer, which is known to control film porosity in combustion-synthesized films and may thus impact conductivity. Spray nozzle height, precursor ink flowrate, and air flowrate are also known to impact the roughness of spray-coated films [11] and roughness tends to decrease film conductivity [37]. DMSO content was varied because our initial observations (see Fig. S2) and literature data both show that adding a co-solvent with a high boiling point has the ability to increase the temperature at which coatings can be deposited by spraying [38]. The ranges of values over which each variable was manipulated are shown in Fig. 2b.

Ada optimized the Pd film conductivity by autonomously performing 91 cycles of precursor preparation, spray-coating, film characterization and algorithmic experiment planning (see Fig. 1a and supplementary methods). In each cycle, a unique experimental condition was tested in duplicate (except for rare instances where duplicates were missed due to system failures). Ada began each experimental cycle by requesting an experimental condition to test from a single-objective Bayesian optimization algorithm. To initialize the optimizer, the first 15 experimental conditions were chosen from a uniform random distribution over the input space. The precursor mixing station then prepared 0.38 mL of spray-coating precursor ink in a 2-mL vial. The precursor ink vial and a clean 25 mm × 75 mm glass substrate were then transported from the precursor mixing station to the spray-coating station by the central robotic arm. The precursor ink was then sprayed onto a pre-heated glass substrate to form an approximately 10 to 100-nm thick Pd coating. The Pd coating thickness was then measured by X-ray fluorescence microscopy (XRF). The coating conductance was measured via four-point probe. Each film was also imaged using an optical microscope. The Pd coating sample was then returned to a storage rack. The coating conductivity was then calculated by combining conductance and thickness measurements (see supplementary methods). To complete each cycle, the experimental data generated (i.e. the condition tested and the resulting coating conductivity) was passed to the optimizer. The optimizer then selected the next experimental condition to test using all the data available from previously completed samples.

To maximize experimental throughput, Ada was configured so that all hardware stations operated on different samples in parallel. This configuration enabled the system to work on up to four samples at any one time (see Fig. 1e). To support this parallelization scheme and avoid replicating the same experimental condition more than twice, we configured the optimizer with an acquisition function that alternated between four modes. The first three modes used the upper confidence bound acquisition function with $\beta = 0.25$, 25, and 400, respectively. The fourth mode selected a space-filling point (i.e. a point as far as possible from any previously tested point in the input space, see supplementary

methods). This optimizer configuration was intended to balance exploitative optimization of the conductivity response surface with exploration of the parameter space. Further details of the optimizer configuration are provided in the supplementary methods

The results of the optimization are shown in Fig. 2. The experimental condition yielding the highest mean conductivity across duplicates (4.08 MS/m) was identified after 63 cycles of experimentation (Fig. 2a). This champion experiment doubles the best previously reported value of 2.0 MS/m for Pd films deposited by spray-combustion [15]. The relative conductivity difference between the duplicate samples created using the champion experimental conditions was less than 1% (see SI for a discussion of the experimental variability and possible sources thereof).

Ada tested a large number of diverse experimental conditions over the course of the optimization campaign (Fig. 2b). This rich data provides insights about the Pd spray-combustion process beyond the simple identification of conditions that maximize the film conductivity. Most strikingly, the data reveal that the film conductivity was strongly correlated with thickness (see Fig. S3). We attribute this observation to the gradual percolation of conductive Pd islands as the film thickness increases, as has been observed, for example with nanogranular gold films [35] (we note that our Pd films show nano-granularity in SEM images, see Fig. S4). Given the strong observed correlation between Pd film conductivity and thickness, we were able to identify explanations for the optimal spray-coating conditions that are supported by data from the optimization campaign, follow-up experiments and the literature.

Ada identified a high precursor concentration (20 mg/mL) as optimal. High precursor concentration increases film thickness (and thus conductivity) by simply adding more Pd to the film (see Fig. S5).

Ada found that nozzle height closer to the substrate (10 mm) was optimal. Low nozzle height increases film thickness (and thus conductivity) by reducing overspray and thus depositing a larger fraction of the precursor onto the substrate (see Fig. S4).

The optimal values for the remaining input parameters appear to arise due to a complex interplay between the Leidenfrost effect, the film thickness, the precursor composition, the spray-coating conditions and the local substrate temperature. The Leidenfrost effect occurs when a droplet of a liquid impinging on a hot surface becomes suspended on a cushion of its own vapour. This effect is known to slow or prevent film deposition of spray-coated materials at high temperatures by repelling precursor droplets from the heated substrate [38].

Ada identified an intermediate temperature (259 °C) as optimal. This optimum appears to avoid the detrimental Leidenfrost effect that would occur at higher temperatures while providing sufficient thermal energy to drive the combustion of the precursor [15, 28].

Ada found that adding large amounts of DMSO (30% v/v) into the precursor ink maximized the conductivity. The beneficial effect of DMSO appears to arise from the suppression of the Leidenfrost effect. DMSO (T_{vap} = 189 °C) is a higher boiling solvent than the other solvent used in our precursor inks (acetonitrile, T_{vap} = 82 °C) (Fig. S6). To support this conclusion, we used Ada to perform a series of follow-up experiments that show that inks containing DMSO result in thicker Pd films at higher temperatures (Fig. S7).

Ada found that a high flow rate of air from the nozzle (control valve opened to 98% of the maximum) was optimal. We attribute this to suppression of the Leidenfrost effect caused by transient cooling of the substrate by this impinging airflow. Transient cooling enables the precursor to efficiently coat the substrate by avoiding the Leidenfrost effect, while subsequent reheating promotes the complete transformation of the precursor into metallic Pd. Thermography and thermocouple data show that the nozzle causes rapid transient cooling and reheating of the substrates in our system, with temperature swings as large as 30 °C (see Fig. S8). Stronger transient cooling of the substrate may also be an additional benefit of low nozzle height.

Ada found that low flow rate of ink from the nozzle (2.8 uL/s) was optimal. Since the ink volume sprayed was fixed, lower ink flow rates lead to slower nozzle speeds. This caused the nozzle to remain over the substrate for longer, providing more time for the air from the nozzle to locally cool the surface and further suppress the Leidenfrost effect (see Figs. S8, S9).

The number of spray-coating passes appeared to be the least important manipulated variable; high conductivity films were obtained across all settings for this variable.

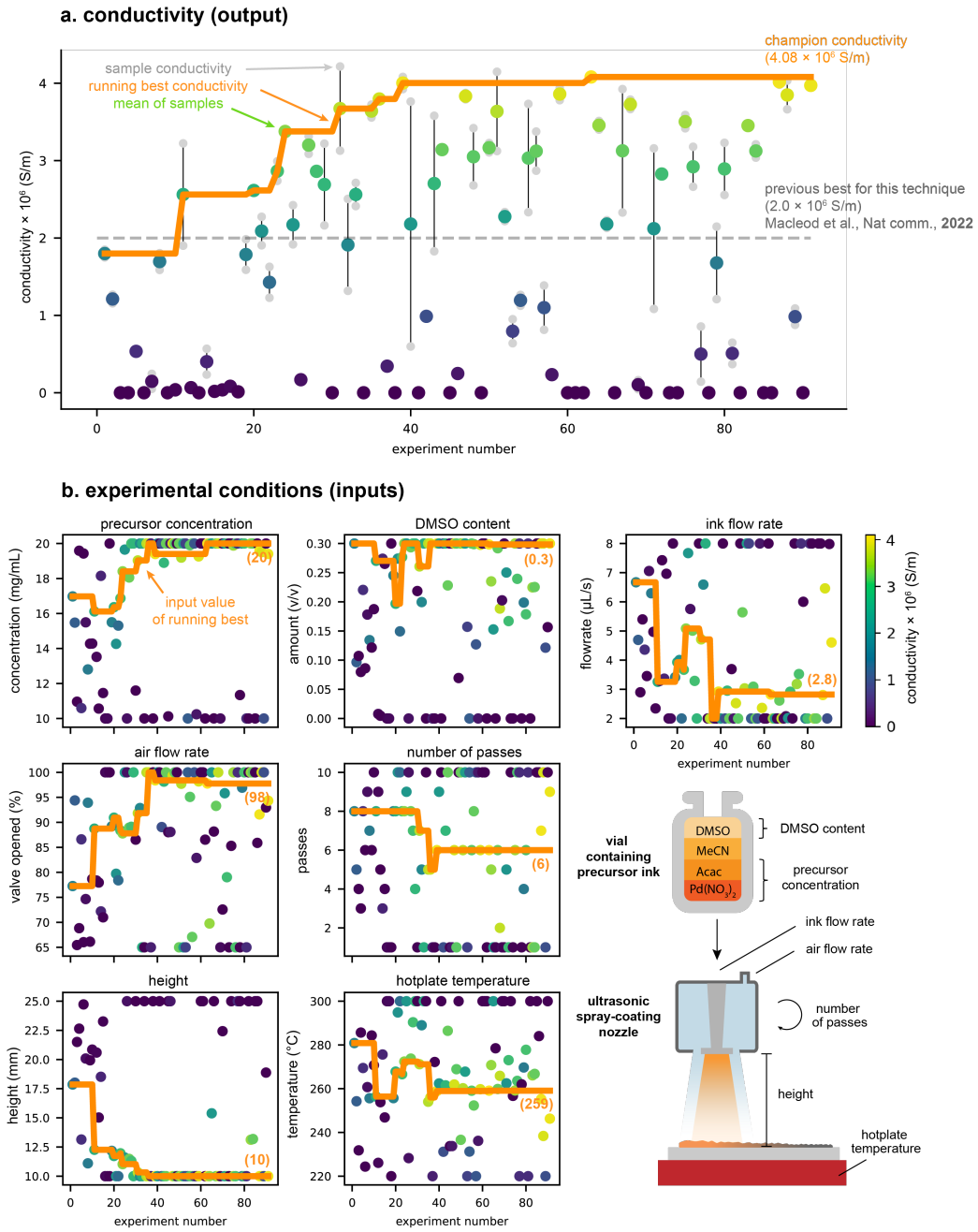

Figure 2: Autonomous optimization of the conductivity of a spray-coated palladium film. **(a)** The conductivity of the samples increased throughout the optimization campaign. Each experiment was performed in duplicate and a maximum mean conductivity achieved was 4.08MS/m, more than double the previous state-of-the-art for this technique. The orange line represents the running best conductivity over time. **(b)** Seven input variables were manipulated: two ink composition variables (DMSO content and solute concentration) and five spray-coating variables (ink flowrate, air flowrate, number of passes, height, and hotplate temperature). The experimental conditions requested for each experiment are shown in each plot. The orange line represents the input values associated with the running best conductivity. The input value yielding the champion recipe is shown at the end of each orange line.

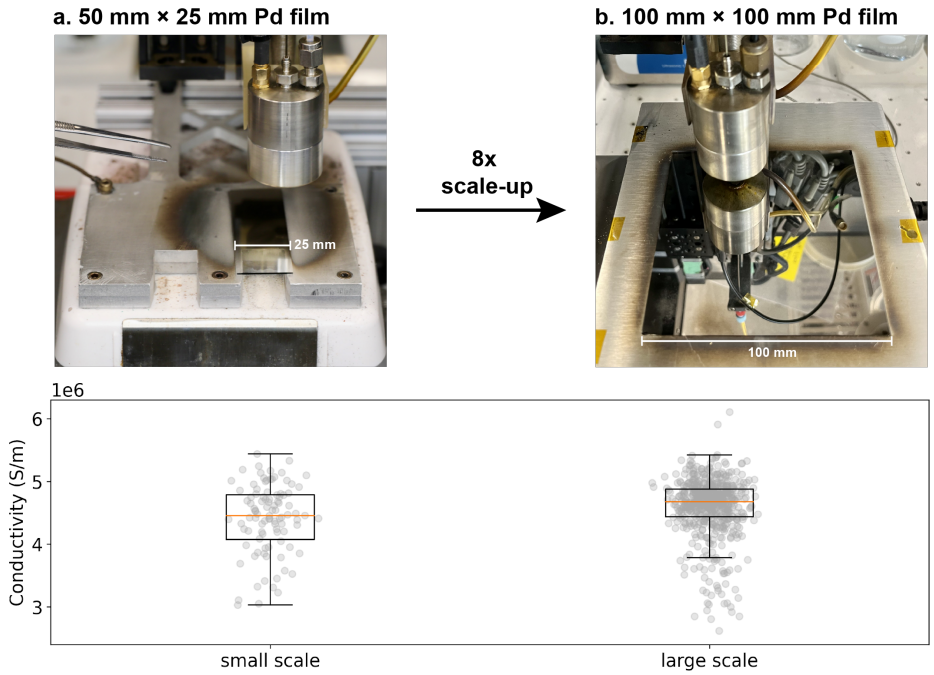

Figure 3: The identified champion coating conditions were scaled-up to an 8× larger area with no further optimization and with no loss in coating conductivity. The champion conditions identified by the optimization campaign were successfully scaled-up 8×, from **(a)** 50 mm × 25 mm to **(b)** 100 mm × 100 mm, with no modification to the identified experimental conditions (other than the requisite increase in the size of the nozzle trajectory and ink volume - see supplementary figure S10) . Conductivity measurements performed on both samples showed comparable conductivities for both the small-scale and the large-scale samples.

The optimal experimental conditions identified by Ada balance the complex, inter-related effects described above to form highly conductive palladium films.

Following the optimization campaign, the conditions yielding the champion Pd film were scaled-up to an 8× larger area with no further optimization and no reduction in coating quality (Fig. 3). Specifically, we used these champion conditions and the same spray-coater used for the optimization campaign to deposit a Pd film on a 100 mm × 100 mm glass substrate (see supplementary methods: "scale-up experiment"). The scaled-up process yielded a highly reflective large-area Pd film that had a slightly higher and more uniform conductivity (4.59 ± 0.49 MS/m) than the small-scale samples autonomously optimized by Ada (4.31 ± 0.86 MS/m). Our success in scaling-up the champion recipe with no further optimization highlights the value of directly optimizing a scalable coating process such as spray-coating using a self-driving laboratory.

3 Limitations and potential societal impacts

The resources and expertise currently required to deploy and operate self-driving laboratories currently limit both their potential positive and negative societal impacts. We believe a valuable direction for future work is to develop self-driving laboratories that require fewer resources and less expertise to deploy and operate. A deeper consideration of the potential negative societal impacts of these systems will become necessary as this technology becomes more widely available.

4 Conclusion

Solution-based coating processes offer promise as a lower cost alternative to vacuum-based coating processes. Large-area deposition of solution-based coatings is a challenge, however, due to the complex physical phenomena involved. The differences between lab-scale coating processes (e.g. drop-casting, spin-coating) and large-scale coating processes (e.g. blade coating, spray-coating) limit knowledge transfer from one setting to the other. To address these challenges, we have developed a self-driving laboratory for optimizing scaleable spray-coating processes relevant to the manufacturing of diverse clean energy technologies. We demonstrated the power of this self-driving laboratory by using it to optimize a complex spray-combustion process for depositing conductive palladium coatings. This optimization campaign discovered conditions for preparing highly conductive Pd coatings (4.08 MS/m). This conductivity level is comparable to the conductivities reported for sputtered Pd films (2 - 6 MS/m) and more than doubles the previous best Pd coating conductivity achieved with spray-combustion (2 MS/m) [15]. The optimal coating conditions identified by the self-driving laboratory scaled-up 8× to yield a large area film with conductivity of 4.6 MS/m. Moreover, the rich data generated by the self-driving laboratory yielded fundamental insights into the complex processes at play during the spray-combustion synthesis of Pd coatings. This work shows how self-driving laboratories can be used to address the challenges associated with scale-up of solution-based coating methods.

Data availability

The raw and processed data generated by the self-driving laboratory in this study is available at `https://github.com/berlinguette/ada`. All other data related to this paper is available from the corresponding author upon request. All code used in this study was based on open-source Python packages listed in the supplementary information.

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Checklist

1. For all authors...
   (a) Do the main claims made in the abstract and introduction accurately reflect the paper's contributions and scope? [Yes]
   (b) Did you describe the limitations of your work? [Yes] See Section 3.
   (c) Did you discuss any potential negative societal impacts of your work? [Yes] See Section 3.
   (d) Have you read the ethics review guidelines and ensured that your paper conforms to them? [Yes]
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   (a) Did you state the full set of assumptions of all theoretical results? [N/A]
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3. If you ran experiments...
   (a) Did you include the code, data, and instructions needed to reproduce the main experimental results (either in the supplemental material or as a URL)? [Yes] See supplementary information.
   (b) Did you specify all the training details (e.g., data splits, hyperparameters, how they were chosen)? [Yes] See supplementary information.
   (c) Did you report error bars (e.g., with respect to the random seed after running experiments multiple times)? [Yes] See figure 2.
   (d) Did you include the total amount of compute and the type of resources used (e.g., type of GPUs, internal cluster, or cloud provider)? [N/A]
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   (a) If your work uses existing assets, did you cite the creators? [Yes] See supplementary information acknowledgements.
   (b) Did you mention the license of the assets? [Yes] See supplementary information acknowledgements.
   (c) Did you include any new assets either in the supplemental material or as a URL? [Yes] See data availability section 4.
   (d) Did you discuss whether and how consent was obtained from people whose data you're using/curating? [N/A]
   (e) Did you discuss whether the data you are using/curating contains personally identifiable information or offensive content? [N/A]
5. If you used crowdsourcing or conducted research with human subjects...
   (a) Did you include the full text of instructions given to participants and screenshots, if applicable? [N/A]
   (b) Did you describe any potential participant risks, with links to Institutional Review Board (IRB) approvals, if applicable? [N/A]
   (c) Did you include the estimated hourly wage paid to participants and the total amount spent on participant compensation? [N/A]