Synthesis of Electrochromic Supramolecular Polymers Driven by Data Science

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ABSTRACT

Materials informatics has recently garnered significant attention as a potent tool for the development of a wide array of functional materials. The successful integration of materials informatics into polymer design holds the promise of streamlining the synthesis of polymers with tailored properties, thereby enhancing efficiency and specificity in material engineering. Machine learning is a subset of artificial intelligence (AI), which involves algorithms learning from data to make predictions or decisions. The machine learning, especially Bayesian optimization method is widely used in materials science.

In this paper, we report our recent approach on the search of electrochromic (EC) metallo-supramolecular polymers (MSPs) with the help of materials informatics. Four components were selected among many components of MSPs. Among all the combination of the variations, the selected number of the corresponding MSPs according to an orthogonal table were synthesized. A coloration efficiency (CE) of 1281 cm^2/C was obtained compared to our previous work. We found that this method with statistics was useful to find the polymers with better EC properties quickly.

1 Introduction

Electrochromism, which is defined as the alteration of color (i.e., changes in absorbance or transmittance within the visible spectrum) achieved through the application of an external voltage.[1] The development of electrochromic materials has a long history. In 1969,[2] Deb and co-workers founded the first example of electrochromic materials, which was referred as a trigger of the investigation and development of electrochromic materials. In the past decades, several generations of ECMs were developed, including metal oxides, transition metal complexes, and organic molecules with conducting polymers. The development of these ECMs significantly contributed to the research of the physical and chemical properties of a variety kind of chromic materials. Additionally, many researchers used these materials to develop a variety of instruments that are widely used in daily life, such as smart windows, adaptive camouflages and displays. The newest generation of ECMs are metallo-supramolecular polymers.

With the help of materials informatics. Four components were selected among many components of MSPs. Including the central metal, the ligand structures, the branch unit, and the degree of branching. Among all the combination of the variations, the selected number of the corresponding MSPs according to an orthogonal table were synthesized.

2 Experiment

2.1 Synthesis of MSPs

For Fe-based and Co-based MSPs, were synthesized according to the literature,[3] with the substituted of the metal salt, corresponding linear ligands and branch units. Ru-based MSPs and Os-based polymers were also synthesized according to the literature.[4]

2.2 Preparation of the Polymer Film on the ITO-Glass

First, the polymer was dissolved in methanol (3 mg/mL) and stirred at room temperature for 24 hours. The solution was then filtered to remove any insoluble residues. Clean ITO glass (2.5×2.5 cm) was placed on a 60°C hot plate, and the polymer solution was spray-coated using an automated instrument at 200 rpm with six cycles. For a 3 mg/mL concentration, six cycles produced a film with high contrast during electrochromic changes. For the counter electrode, an aqueous NiHCF solution was spray-coated on ITO glass, dried at 85°C for 1 hour, and then at room temperature for 24 hours. Device fabrication involved mixing $LiClO_4$ (0.3 g) and propylene carbonate (2.0 mL), stirring for 20 minutes, then adding PMMA (2.0 g) and stirring under vacuum for 1 hour. The resulting liquid was applied to NiHCF-coated ITO glass, covered with the polymer-coated ITO glass, and heated at 95°C and 40% humidity for 1 minute to complete the solid device.

2.3 Machine Learning Models

A machine learning algorithm, including Gaussian Naïve Bayes (GNB)[5] was trained for predicting the possible coloration efficiency (CE) of MSPs. The model was directly programmed using Python with the scikit-learn package.[6]

3 Results

3.1 Preparation of dataset

To gain the initial dataset, we introduced the Design of Experiments (DoE), which is a branch of mathematical statistics (Fig 1). First, we select for example 4 kinds of factors for the synthesis of EC polymers. Then, we create initial mathematical models based on the statistical theories. Next, synthesize EC polymers based on the initial models and evaluate the characteristics of the synthesized EC polymers, for example, the coloration efficiency, and feedback to the models. After the optimization of models, feedback to experiments to avoid doing meaningless experiments. Then, judge if the synthesized EC polymers meet our expectation or not, if not, re-select the initial factors and start this process again. By this way, we can obtain the EC polymers with good properties in a short time. According to this way, 18 kinds of combination was selected as the dataset for training the machine learning model.

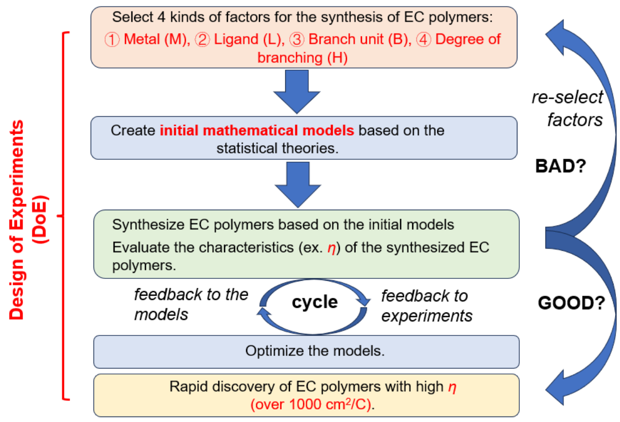

Fig. 1 Technique Route of DoE

3.2 Synthesis and characterization od MSPs based on initial model

Based on the strategy of Design of Experiments, we have successfully made the orthogonal table made by the initial 4 factors. Each factor has several sub-factors represented by the number. By using the orthogonal table, we can largely reduce the number of experiments. Among all the combination of the variations, 18 kinds of the corresponding MSPs according to an orthogonal table were synthesized according to the literature.[2-4]

Then, we measured the electrochromic properties of these MSPs. We synthesized a total of 18 different MSPs, among which one Fe-based MSP can change from blue to transparent at a voltage of 1.2V vs $Ag^{0/+}$. An oxidation peak appeared at around 0.8V vs $Ag^{0/+}$, while a reduction peak appeared at around 0.6V vs $Ag^{0/+}$, indicates that redox reactions occurred, which demonstrating significant electrochemical activity of Fe-based MSP (Fig. 2a). According to Figure 2b, it can be observed that the Fe-based MSP has a strong absorption peak around 600 nm in the absence of external voltage, indicating that the material absorbed yellow light and appears its complementary color, blue. When a voltage of 1.2V $Ag^{0/+}$ is applied, the material becomes transparent. It can be calculated that the transmittance of the material is about 70%. We also measured the response time of the Fe-based MSP for color change between 0V and 1.2V. As shown in Figure 3c, the material takes about 10 s to achieve the color change, indicating a relatively fast response speed. This material showed a shorter switching time but with a higher transmittance change of about 70%, and coloration efficiency was calculated as 1281 cm^2/C compared to our previous work (Fig.2c-2d).

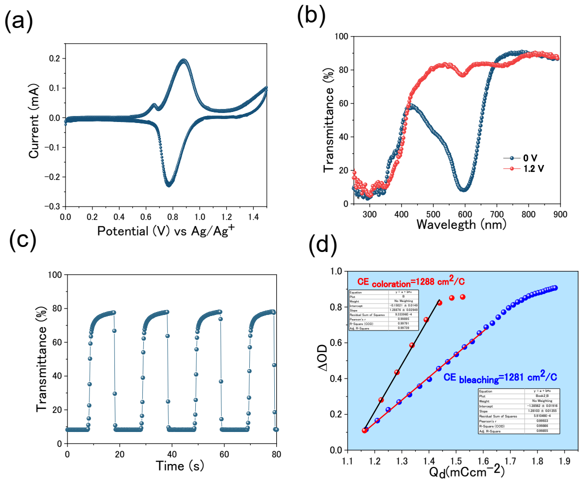

Fig. 2 Electrochromic properties of polyFeL0$_{90\%}$B1$_{10\%}$.

3.3 Feedback

With the encourage of these results, we used the results, which have already measured as a dataset to retrain this machine learning model, in order to obtain more combinations that may have high coloration efficiency. Gaussian processes (GPs) are well-suited for Bayesian optimization methods.[7] Bayesian optimization continuously updates the belief about the objective function (i.e., the Gaussian process model) to iteratively select the optimal set of parameters. This approach is particularly beneficial in scenarios where experiments or computations are costly. Gaussian processes are non-parametric, meaning they do not require a predefined functional form to fit the data.[8] This flexibility allows them to excel in handling complex and non-linear problems.

Moreover, Gaussian processes not only provide the mean of the predictions but also offer the uncertainty (variance) of those predictions.[9] This feature is crucial as it helps to identify regions that might contain better solutions. Additionally, GPs perform effectively even with limited data, which is a significant advantage in many practical applications.[10] The ability to work well with small datasets is vital in scenarios where obtaining data is expensive or time-consuming. These characteristics make Gaussian processes a powerful tool in Bayesian optimization, enabling efficient and effective optimization in a wide range of challenging and resource-intensive problems. In this work, we employ a Python library called 'physbo' for Bayesian optimization. 'numpy' is utilized for numerical computations, 'pandas' is used for data manipulation, 'matplotlib' along with 'plotnine' are used for visualization.

As a result, another 8 kinds of metallo-supramolercular polymers were selected with relatively high expect coloration efficiency up to 739 cm^2/C (Fig. 3).

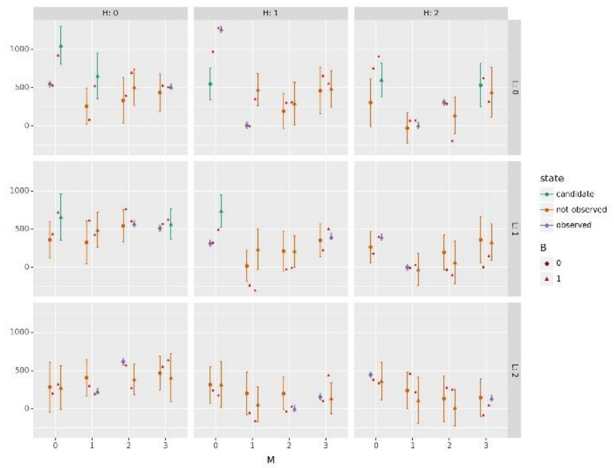

Fig. 3 Results of Gaussian Process and acquisition function.

4 Conclusions

In conclusion, we successfully introduce data science methods to predict the possible coloration efficiency of MSPs, which can save the experimental cost. According to this new method, we achieved the highest coloration efficiency up to 1281 cm^2/C at a lower applied potential of 1.2 V vs $Ag^{0/+}$. In the future, we will train additional machine learning models to ensure the accuracy of the results. Additionally, we will expand the dataset by introducing other central metal atoms and ligands, thereby broadening the application scope of these models.

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