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A machine learning-based nano-photocatalyst module for accelerating the design of Bi₂WO₆/MIL-53(Al) nanocomposites with enhanced photocatalytic activity†

Xiuyun Zhai *^a and Mingtong Chen^b

It is a great challenge to acquire novel Bi₂WO₆/MIL-53(Al) (BWO/MIL) nanocomposites with excellent catalytic activity by the trial-and-error method in the vast untapped synthetic space. The degradation rate of Rhodamine B dye (DR_{RhB}) can be used as the main parameter to evaluate the catalytic activity of BWO/MIL nanocomposites. In this work, a machine learning-based nano-photocatalyst module was developed to speed up the design of BWO/MIL with desirable performance. Firstly, the DR_{RhB} dataset was constructed, and four key features related to the synthetic conditions of BWO/MIL were filtered by the forward feature selection method based on support vector regression (SVR). Secondly, the SVR model with radical basis function for predicting the DR_{RhB} of BWO/MIL was established with the key features and optimal hyperparameters. The correlation coefficients (*R*) between predicted and experimental DR_{RhB} were 0.823 and 0.884 for leave-one-out cross-validation (LOOCV) and the external test, respectively. Thirdly, potential BWO/MIL nanocomposites with higher DR_{RhB} were discovered by inverse projection, the prediction model, and virtual screening from the synthesis space. Meanwhile, an online web service (http://1.14.49.110/online_predict/BWO2) was built to share the model for predicting the DR_{RhB} of BWO/MIL. Moreover, sensitivity analysis was brought into boosting the model's explainability and illustrating how the DR_{RhB} of BWO/MIL changes over the four key features, respectively. The method mentioned here can provide valuable clues to develop new nanocomposites with the desired properties and accelerate the design of nano-photocatalysts.

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1 Introduction

Against the background of the energy crisis and environmental pollution worldwide, photocatalysts have been widely paid attention and developed^{1,2} due to their distinct advantages of energy conservation, high efficiency, green environmental protection, *etc.*^{3–5} They can capture solar energy to completely decompose organic pollutants into CO₂ and H₂O, decompose H₂O into O₂ and H₂, *etc.* The Bi₂WO₆/MIL-53(Al) (BWO/MIL) composites that we studied are a type of nanomaterial^{6–10} as well as a novel kind of visible-light photocatalyst whose morphology and size affect the specific surface area and the number of surface active sites, subsequently impacting the visible-light catalytic activity. Therefore, the key to the preparation of efficient visible-light photocatalysts is to adjust their

morphologies and sizes by selecting different preparation methods and suitable surfactants.

The photocatalytic principle is shown in Fig. 1. The photocatalyst is excited to produce photogenerated electron-hole pairs under irradiation of light (*hν*). The electrons jump from the top of the valence band (VB) to the bottom of the conduction band (CB). During migration to the surface under electric field or through diffusion, some photogenerated carriers recombine and then release absorbed energy in the forms of heat or light.

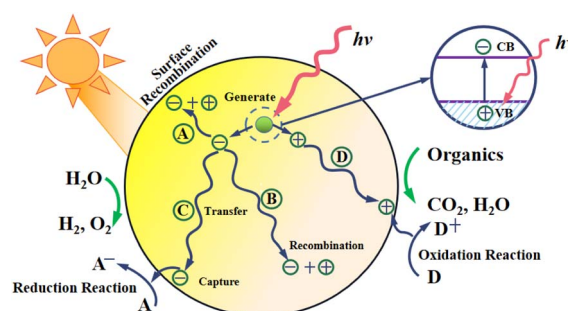


Fig. 1 Diagram of the photocatalytic principle.

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DR_{RhB} of BWO/MIL, which can help to save significant time and cost of synthetic experiments of BWO/MIL. Moreover, all researchers who are interested in BWO/MIL nanocomposites don't need to be familiar with ML technology to access and utilize the service freely.

2 Material and methods

2.1 The formation of MLM-BWO/MIL

A MLM-BWO/MIL for speeding up the design of BWO/MIL nanocomposites with enhanced photocatalytic activity was constructed by the following steps (shown in Fig. 2): construct dataset, establish prediction model, optimize experimental parameters and conduct SA.

2.1.1 Construct dataset. A series of BWO/MIL nanocomposites in the dataset were fabricated by hydrothermal method. Their photocatalytic activity was evaluated by the degradation of RhB in aqueous solution under visible-light irradiation. The typical preparation procedure of BWO/MIL is described in detail as follows. The meaning of each parameter is listed in Table 1.

(a) First, 2 mmol $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ in 25 mL HNO_3 was dissolved at the molar concentration of C_{HIN} M, and then stirred continuously at room temperature to fully dissolve $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$, yielding the $\text{Bi}(\text{NO}_3)_3$ solution.

(b) 1 mmol $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ and D_{sur} g S_{ur} were dissolved in 20 mL S_{ol} solution to obtain Na_2WO_4 solution.

(c) $1/R_m$ mmol of the MIL-53(Al) was uniformly mixed with Na_2WO_4 solution, then ultrasonically dispersed for 30 min, and added with $\text{Bi}(\text{NO}_3)_3$ solution drop by drop under stirring.

(d) The pH of the mixed solution was adjusted to V_{pH} with R_{pH} solution, then magnetically stirred for T_{stir} hours.

(e) The obtained mixture was transferred into a 100 mL autoclave with PTFE lining, placed into an oven at T_{hyd} °C, and reacted for T_{hy} hours.

(f) After being cooled to room temperature by C_M , the reaction product was centrifuged, washed twice with secondary distilled water, washed once with absolute ethanol, placed in an oven at T_{dry} °C and dried for 10 h by D_M .

Table 1 The meaning of the thirteen features in the dataset

No.	Meanings	Features
1	Reagent for pH adjustment	R_{pH}
2	Cooling method	C_M
3	Drying method	D_M
4	Concentration of HNO_3 (mol L^{-1})	C_{HIN}
5	Surfactant	S_{ur}
6	Surfactant dosage (g)	D_{sur}
7	pH	V_{pH}
8	Stirring time (h)	T_{stir}
9	Hydrothermal temperature (°C)	T_{hyd}
10	Hydrothermal time (h)	T_{hy}
11	Solvent of $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$	S_{ol}
12	Drying temperature (°C)	T_{dry}
13	Mole ratio of Bi_2WO_6 to MIL-53(Al)	R_m

The growth of BWO/MIL is a typical Ostwald aging⁵¹ and self-assembly process. Based on the analysis of the preparation process and characterization results of BWO/MIL, its phase formation mechanism (shown in Fig. 3) is described as follows. Two kinds of tiny crystal nuclei (WO_6 and $\text{Bi}_2\text{O}_2^{2+}$) are formed in the precursor fluid, grown in parallel on the surface of MIL-53(Al), and gradually matured to form two-dimensional Bi_2WO_6 nanosheets with hydrothermal temperature and pressure increasing and with the assistance of the surfactants. The heterojunction generated at the contact interface between Bi_2WO_6 and MIL-53(Al) can effectively inhibit the recombination of photogenerated electron-hole pairs of the BWO/MIL photocatalyst, and then improve the catalytic activity.

The dataset was established by collecting the experimental data of BWO/MIL synthesis from ref. 52, which is a graduate student's dissertation. The mechanism of photocatalytic degradation of BWO/MIL is also provided in ref. 52. The degradation rate of RhB dye (DR_{RhB}) (listed in Table S1 of ESI†) is as the target variable of the dataset. Thirteen features (shown in Table 1), including the twelve experimental parameters and one composition ratio of BWO/MIL (R_m), served as the candidate inputs of the prediction model. The meanings of values for the five features (R_{pH} , C_M , D_M , S_{ur} and S_{ol}) are explained in Table S2.† Before modeling, two samples (No. 5 and 27) were basically without photocatalytic activity due to their very low DR_{RhB} and were deleted from the dataset. Then, the dataset with 53 samples was divided into two parts: the training set, which included 45 samples for modeling, and the testing set,



Fig. 2 Diagram of MLM-BWO/MIL constructed by four steps.



Fig. 3 The formation mechanism of BWO/MIL.



comprised by the remaining samples for validation and marked by asterisks in Table S1.†

2.1.2 Establish prediction model. Removing the redundant features from the candidate feature pool is a critical step to constructing a successful model. The optimal feature subset obtained by feature selection involves essential and sufficient information with very little redundancy. Apparently, feature selection can reduce the training time and the risk of overfitting, and further improve the prediction ability and generalization performance of the model. In this work, FFS-SVR was introduced to find the key features related to the target variable.

The RBF parameters of SVR were optimized by cross-validation and grid search techniques before building the model. Cross-validation was conducted to avoid the overfitting problem. The SVR-RBF model⁵³ was established for predicting the DR_{RhB} of BWO/MILs with the optimal feature subset. The independent testing set was used to validate the generality of the SVR-RBF model.

2.1.3 Optimize experimental parameters. Inverse projection of pattern recognition was exploited to search some BWO/MILs with possibly higher DR_{RhB} . The SVR-RBF model established was utilized to predict the DR_{RhB} of the BWO/MILs. Virtual screening and web service based on inverse projection and the SVR model were used to find the synthesis parameters of the BWO/MILs with a higher DR_{RhB} than the highest value in the existing dataset.

2.1.4 Sensitivity analysis. To further explain the prediction model and guide the later synthesis experiment, SA based on the model was conducted. SA refers to an uncertainty analysis technique to study the influence of certain changes of key features on one or a group of indicators from the perspective of quantitative analysis. Its essence is to interpret the rule that the DR_{RhB} of BWO/MIL is affected by changing the value of one key feature.

2.2 Inverse projection of pattern recognition

Inverse projection (IP) of pattern recognition refers to mapping of the designed sample points from the two-dimensional space back to the multi-dimensional space, where the experimental condition for material synthesis can be found. A discriminant function related to the known samples and their categories needs to be set up to complete IP. Fisher discriminant analysis^{54,55} was used to determine the weight vector and threshold value in the projection direction by using the given training data, before constructing the discriminant function. Fisher method is a popular method to measure the separation degree between two categories.⁵⁶ Although it was proposed earlier, it is still being used widely and plays an important part in pattern recognition.^{57,58} Certain constraints must be introduced to make the result of IP unique. The constraint for linear IP is to take the fixed values (such as mean value or optimal value) as the coordinate values of the design points on other projection vectors, while the constraint for nonlinear IP is found by minimizing the error function of the inverse projection.

2.3 Software availability

The ML calculations of our work were performed using the HyperMiner software package^{59,60} and the Online Computational Platform of Material Data Mining (OCPMDM),^{61,62} which we developed. HyperMiner can be freely downloaded on the website: <http://materials-data-mining.com/home>. OCPMDM can be freely used on the website of the Laboratory of Materials Data Mining at Shanghai University: <http://materials-data-mining.com/ocpmdm/>.

3 Results and discussion

In order to seek out the most suitable algorithm for modeling, the results of 10-fold cross-validation of several algorithms, including SVR-RBF, SVR based on linear kernel function (SVR-LKF), SVR based on polynomial kernel function (SVR-PKF), and multiple linear regression (MLR), were compared. The results reflected that SVR-RBF algorithm was more suitable for modeling than the others. Therefore, SVR-RBF was identified as the method to establish the model for predicting DR_{RhB} of BWO/MIL nanocomposites.

3.1 Feature selection

Feature selection is the process of selecting an optimal subset from the original features, which falls into three categories according to formation mode: exhaustive method, heuristic method and random method. The forward feature selection method (FFS)^{63,64} used in this work is a heuristic method which starts from an empty set and incrementally adds a feature to the target feature subset from the candidate features. The search process of FFS doesn't end until a feature subset close to the optimal solution is obtained. A SVR model is constructed with the features on each pass of the FFS search. Root mean square error (RMSE) of the 10-fold cross-validation is used as the evaluation indicator of the SVR model. The above feature selection approach is termed the FFS-SVR method. Fig. 4 reveals how FFS-SVR and cross-validation were used to search for the optimal feature set. The result illustrated that RMSE showed concave parabola variation with the increase of feature number, and the minimal and maximal RMSEs occur when the feature numbers are 4 and 12, respectively. It was obvious that the

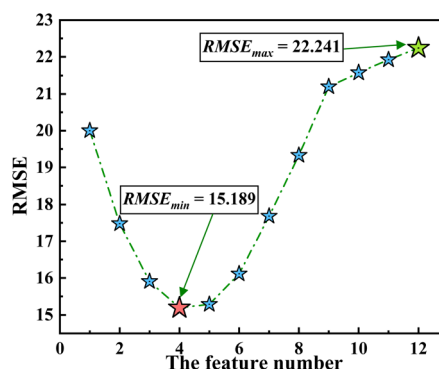


Fig. 4 The process of feature selection in FFS-SVR.



feature set including C_{HN} , S_{ur} , T_{hyd} and R_{m} (highlighted in bold in Table S1†) is best when the RMSE of the model is minimal.

3.2 Model establishment

3.2.1 Optimizing hyperparameters. Moderate parameter adjustment for the great majority of modeling techniques is required to achieve optimal performance. Three hyperparameters of SVR-RBF are the regularization parameter C , insensitive parameter ε and gamma value γ . Their optimization ranges are [1, 100], [0.01, 0.09] and [0.5, 1.5], and the step sizes are 2, 0.02 and 0.1, respectively. Parameter C determines the tradeoff between the complexity and precision of the model. The larger C is, the worse the generalization ability of the model is. The smaller C is, the more insensitive ε is, and the larger the training error. Parameter ε controls the sparsity of support vector in SVR and affects the precision of the regression model. Gamma controls the influence distance of a single training point. A model with very large gamma value can easily cause overfitting.

Grid research method and 10-fold cross-validation were employed to optimize the three hyperparameters, and RMSE was used as the evaluation index of the SVR model. The optimization process is shown in Fig. 5, from which the minimum RMSE is 13.724 when C , ε and γ are 29, 0.05 and 1.3, respectively.

3.2.2 SVR-RBF model. The SVR-RBF algorithm with the optimal hyperparameters and four key features was used to

establish the model for predicting the DR_{RhB} of BWO/MILs. The correlation coefficient (R) and RMSE were used as evaluation indices of model performance. The SVR-RBF model is expressed as follows.

$$DR_{\text{RhB}} = \sum_{i=1}^n \beta_i \exp\left(-0.5 \times \|X - X_i\|^2\right) + 0.438 \quad (1)$$

where X and X_i are the unknown and the support vector, respectively. β_i and n are the Lagrange multiplier of the support vector and corresponding number, respectively.

Fig. 6(a) and (b) show the experimental *versus* the predictive DR_{RhB} of BWO/MILs for the training and testing samples, and the LOOCV and 10-fold cross-validation of the training set, respectively. The subscripts “TR”, “TS”, “LCV” and “CRS” in the figure denote “training”, “testing”, “LOOCV” and “10-fold cross-validation”, respectively. It can be seen from Fig. 6(a) that the sample points, whether in the training set or in the testing set, scatter around the diagonal, illustrating that the model has preferable prediction performance and practicability. The results of the model evaluated by LOOCV and 10-fold cross-validation are shown in Fig. 6(b). The R_{LCV} and R_{CRS} of the training set were 0.823 and 0.826, respectively. There are some deviations between the predictive and the experimental values of some samples. That may be due to some errors in experiments and requiring more data for building a predictive model in the vast synthesis space of BWO/MILs. If more experimental data can be gathered in future work, the deviations will be reduced.



Fig. 5 The optimization process of three hyperparameters of SVR-RBF: (a) RMSE *versus* ε and C ; (b) RMSE *versus* C and γ .

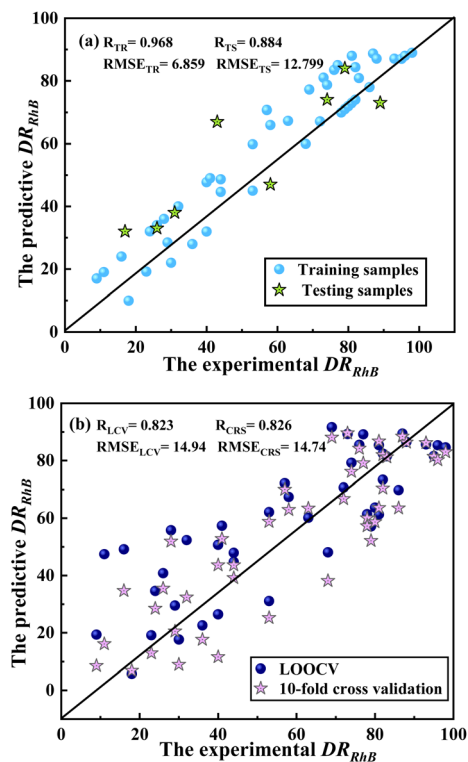


Fig. 6 Experimental *versus* predictive DR_{RhB} of BWO/MILs for (a) the training and testing samples. (b) LOOCV and 10-fold cross-validation of the training set.



3.2.3 Optimization of experimental parameters. The basic principle of pattern recognition is that similar samples approach each other in the pattern space and form a “group”, that is, “birds of a feather flock together”. A given pattern is classified into C classes according to the eigenvector measured by the pattern, and then the classification is discriminated according to the distance between the patterns. The goal of IP based on pattern recognition is to find the synthetic conditions of superior samples in the original multidimensional space. In this work, samples are divided into two categories: superior class with better performance and inferior class with worse performance. The distribution region of superior samples is sought for and built in the pattern recognition diagram. Then, unsynthesized sample points with likely higher performance are designed in the optimal area, whose features in the original space can be derived by IP. Finally, the parameters of the samples with high performance are recognized as the inputs of the SVR-RBF model. The points whose prediction values of the model meet the requirements are the samples we are looking for.

The values of DR_{RhB} in the dataset range from 9 to 98. The maximum of DR_{RhB} can reach 100. The value (55) is close to the median between 9 and 100. Considering unbiased classification, the DR_{RhB} value dividing superior and inferior samples is 55. Samples with greater DR_{RhB} than this value are superior; otherwise, they are inferior. Fig. 7 plots the pattern recognition projection using Fisher method according to the distribution of superior and inferior samples in the training set and the testing set. It can be seen from Fig. 7 that the two classes of samples are clearly distinguished by a purple dotted line apart from four misclassified points. The line is expressed as a linear combination of the key features, which is shown as follows:

$$\text{Fisher}(1) = 0.295C_{\text{HN}} - 0.8559S_{\text{ur}} - 0.02086T_{\text{hyd}} + 0.3427R_{\text{m}} + 2.704 = -0.037 \quad (2)$$

The superior samples are gathered on the right side of the dotted line in Fig. 7, forming the optimal region in which the newly designed samples with high DR_{RhB} should be distributed. It can be seen from Fig. 7 and eqn (2) that the restraint condition of the discriminant function of new promising samples is $\text{Fisher}(1) \geq -0.037$. The features and DR_{RhB} of the designed

BWO/MILs can be derived by IP and predicted by the constructed SVR-RBF model. Obviously, IP can not only supply a suitable projection for classification to prevent the calculation and experiment with inferior samples, but also help us quickly seek the candidates with high DR_{RhB} in the optimal region.

Moreover, massive amounts of virtual samples were generated to improve the probability of BWO/MIL discovery and the quality of new BWO/MILs. Based on the bound of each feature in the existing dataset, the following restrictions were obeyed when generating the new samples.

- ① Concentration of HNO_3 (C_{HN}) changes from 0.5 mol L^{-1} to 4.0 mol L^{-1} in steps of 0.1 mol L^{-1} .
- ② The value of surfactant (S_{ur}) is 0, 1 or 2.
- ③ Hydrothermal temperature (T_{hyd}) ranges from $120 \text{ }^\circ\text{C}$ to $200 \text{ }^\circ\text{C}$ with steps of $5 \text{ }^\circ\text{C}$.
- ④ Mole ratio of Bi_2WO_6 to MIL-53(Al) (R_{m}) ranges from 0.5 to 2 with steps of 0.01.

The IP of pattern recognition and the SVR-RBF model were employed to predict the class and DR_{RhB} of each virtual sample by using the four key features. According to the results of virtual screening, the key features and the Fisher (1) values of the five samples with the top performance are shown in Table S3.† The experimental DR_{RhB} values could likely reach 100 (the maximum value of DR_{RhB}) because the predictive DR_{RhB} values of the samples were already above the highest values (98) in the existing dataset. The two samples with the top DR_{RhB} values among them are shown in Fig. 7 and marked by a purple half-empty circle. Therefore, the above is helpful for experimental researchers to explore the new BWO/MILs with enhanced photocatalytic activity.

3.2.4 Web service. Web services make it very easy to implement the prediction tasks of the clients. A web service based on the SVR-RBF model we constructed was used to predict the DR_{RhB} of BWO/MILs, and a screenshot of the web page is shown in Fig. 8. The researchers who are interested in BWO/MIL synthesis don't need to master the principle of the ML model and can use this service on the clients to know whether the new sample of BWO/MIL has high DR_{RhB} . When using the service, the four key features (C_{HN} , S_{ur} , T_{hyd} and R_{m}) need to be input to the corresponding boxes, and clicking the “Predict” button generates the predictive value of DR_{RhB} . This tool can help researchers accelerate the design of BWO/MILs



Fig. 7 Pattern recognition projection of Fisher method.



Fig. 8 The web service based on the SVR-RBF model for predicting DR_{RhB} of BWO/MIL.





Fig. 9 SA of the four features based on the SVR-RBF model (a) C_{HN} , (b) S_{ur} , (c) T_{hyd} and (d) R_{m} .

with enhanced DR_{RhB} . The web service is available freely on the website: http://1.14.49.110/online_predict/BWO2.

4 Sensitivity analyses

The essence of SA is to explain how the key indicator is affected by changing the values of the relevant variables one by one. Generally, the main parameters are selected for analyses of the sensitivity factors. In this work, the change of DR_{RhB} with one of the key features was observed when the other features were set as their mean values. Fig. 9 shows the SA for the four features (C_{HN} , S_{ur} , T_{hyd} and R_{m}) based on the SVR-RBF model. Fig. 9(a) illustrates that DR_{RhB} increases with C_{HN} when S_{ur} , T_{hyd} and R_{m} are 0.622, 149.777 and 1.189, respectively. In Fig. 9(b) and (c), DR_{RhB} decreased with S_{ur} and T_{hyd} increase, respectively. The convex parabolic relationship between DR_{RhB} and R_{m} is shown in Fig. 9(d). As a whole, S_{ur} and T_{hyd} are more sensitive factors than C_{HN} and R_{m} because a small change in the two prior parameters could lead to a large change in DR_{RhB} . From the trends of the four graphs in Fig. 9, the larger C_{HN} , the smaller S_{ur} and T_{hyd} , and the appropriate R_{m} could result in a larger target value (DR_{RhB}). In other words, it is beneficial to obtain a BWO/MIL with high DR_{RhB} in the above adjustment direction of the experimental parameters. Apparently, SA can interpret the relationships between DR_{RhB} and the features, instruct the adjustment direction of experimental parameters, and assist in revealing the mechanism of BWO/MIL synthesis.

5 Conclusions

A ML-based photocatalyst module for advancing the design of BWO/MIL nano-photocatalysts with the desired photocatalytic performance was established in four steps, including dataset establishment, constructing the prediction model, optimization of experimental parameters and sensitivity analysis. By using FFS-SVR method, four key features (C_{HN} , S_{ur} , T_{hyd} and R_{m}) were selected as the inputs of the model for predicting the DR_{RhB} of

BWO/MIL. The SVR-RBF model constructed with the key features and the optimal hyperparameters has better predictive performance and robustness, and can meet the requirements of rapid BWO/MIL design. The inverse projection based on Fisher method, SVR-RBF model and virtual screening were used to optimize the synthesis parameters of BWO/MIL and find BWO/MILs with higher DR_{RhB} than the highest value in the existing dataset. A web service (http://1.14.49.110/online_predict/BWO2) based on the SVR-RBF model was constructed to predict the DR_{RhB} of BWO/MILs, and it can be freely shared by all researchers interested in BWO/MILs. Furthermore, sensitivity analysis was introduced to analyze the relationship between DR_{RhB} and the four key features. The MLM-BWO/MIL we constructed could be employed to accelerate the design of BWO/MILs with ideal performance and further promote research on ML-assisted material design. This research paradigm is suitable for accelerating the synthesis and development of new materials, including but not limited to photocatalysts. An online prediction service like those mentioned in the paper can be established when enough historical data for the materials are collected.

Author contributions

X. Z. contributed to the writing of the original draft, review and editing, and assisted with the methodology. M. C. contributed to the writing of the original draft and assisted with the formal analysis, visualization, project administration, and investigation.

Conflicts of interest

The authors state that there are no conflicts to declare.

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