System Identification of ZnO Nanostructure Based On Physical Field Analysis and Deep Learning

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Abstract. Zinc oxide nanowire is a widely used one-dimensional nanomaterial. The topological structure of nanowire determines its performance. At present, many researches have made on the growth conditions and structural parameters of zinc oxide nanowires through experimental methods. However, there is a lack of quantitative research on the correlation between macro physical fields and the parameter of structure. In this paper, we propose NPPN (Nanostructure-Parameter Prediction Network) based on deep learning algorithms to explore the correlation between physical fields and nanostructure parameters. The dataset is firstly created by experimental results and CFD simulation. We carry out large batch of preparation experiment of zinc oxide nanowires using the KQS automated machine based on the low-temperature two-step hydrothermal method. Meanwhile, we simulate the real physical field distribution of the reaction chamber through CFD software. The results show that the NPPN model has good predictive performance for the structural parameters of zinc oxide nanowires.

Keywords: Zinc Oxide Nanowire, CFD, Convolutional Neural Network, Deep Learning.

1. Introduction

Environment and energy are two important issues closely related to human life and daily production. Photocatalytic technology is an emerging green technology. In recent years, due to the excellent photocatalytic and piezoelectric properties, one-dimensional nanostructures have received extensive attention. Nanowires, nanorods and nanotubes in nanomaterials show excellent performance in heterogeneous catalysis [1].

Among one-dimensional nanomaterials, zinc oxide (ZnO) nanowires are particularly widely used. Zinc oxide has a wide direct band gap (3.37 eV) and a large binding energy (60 meV) which is much higher than other commonly used wide band gap materials. Thus, zinc oxide has a higher electron mobility and exciton binding energy. Zinc oxide nanowires have the material properties common to nano-scale materials, such as high specific surface area, integration, low power consumption and quantum effects. Meanwhile, ZnO nanowires exhibit physical and chemical properties that are different from other materials, such as piezoelectrics thermoelectric and optical characteristics. Nowadays, ZnO nanowires are widely used in advanced electronic and optical equipment. Fan et al. pointed out that the sensitivity of zinc oxide nanosensors depends on the diameter of the nanowires, and the photovoltaic...
performance of solar cells with zinc oxide nanowires as the main component depends not only on the size, but also on the orientation of the nanowires [2]. The size and orientation of the zinc oxide nanowires are determined by the growth conditions and growth methods used. Therefore, the key issue for the potential technical application of zinc oxide nanostructures is to achieve suitable growth conditions and growth methods.

Many methods for the synthesis of zinc oxide nanowires have been developed in the past few decades. Since Vayssieres et al. first applied the hydrothermal method to the preparation of zinc oxide nanowire arrays in 2001 [3]. The hydrothermal method is available for selection due to its environmental protection, low cost and convenient low-temperature operation. The zinc oxide nanowires prepared by the hydrothermal method are neatly arranged and perpendicular to the substrate. By changing the physical conditions and process formula of the hydrothermal method, zinc oxide nanowires with different spatial orientation and structural characteristics can be oriented and prepared.

In summary, zinc oxide nanowires can be used in a variety of fields and have excellent effects. Zinc oxide nanowires can be prepared by a variety of physical and chemical methods, and their performance depends on the topological structure of the nanowires. In order to meet the needs of different application scenarios, the controlled synthesis of zinc oxide nanowires with determined orientation and morphology is a problem to be solved at present. In the low-temperature hydrothermal method, the hydrothermal temperature field, the reactant concentration field and the flow field are the key to controlling the quality of zinc oxide nanowires. Controlling the physical field through process parameters is very important for the morphology of zinc oxide nanowires. As far as we know, in the current research, the relationship between the physical field of the hydrothermal reaction and the final nanomaterial structure has not been clarified, and there remains a lack of quantitative research on the production conditions and structural parameters of product.

The research direction of this paper is aimed at the correlation between the structural parameters of the zinc oxide nanowires and the production conditions. By changing the various process parameters of the hydrothermal method, large-scale automated experiments are carried out and the parameters of the nanostructure are extracted from the SEM images. We analyzed the physics field of the hydrothermal reaction chamber through the method of coupling the temperature field and the flow field constructed by CFD simulation. Due to the large scale of data, NPPN (Nanostructure-Parameter Prediction Network) deep-learning model is proposed to explore the correlation between physical field and nanostructure parameters.

2. Experiment and Simulation

2.1. Preparation of ZnO Nanowires
In this experiment, we used low-temperature two-step hydrothermal method to prepare zinc oxide nanowires. Firstly, the DDS ultrasonic atomization device is used to prepare a layer of ZnO film on the substrate to reduce the mismatch between the nanowires and the substrate. The seed solution is prepared by a methanol solution of sodium hydroxide and zinc acetate. In the second step, a growth solution using water as a solvent is used for the nanowire growth reaction in a sealed reaction chamber at a certain temperature and pressure. The growth solution adopts a quaternary reaction system [4]. Zinc nitrate hexahydrate \((\text{Zn(NO}_3\text{)}_2 \cdot 6\text{H}_2\text{O})\) provides zinc source for ZnO nanowires. Ammonium hydroxide \((\text{NH}_4\text{OH}, 25-28 \text{ wt\% in water})\) can inhibit the homogeneous nucleation in the growth solution and provide a weak alkaline environment for the growth. Hexamethylenetetramine (HTMA) can be used as a non-polar surface chelating agent to inhibit the radial growth of nanowires. Polyethyleneimine (PEI) can also inhibit homogeneous nucleation and promote the axial growth of ZnO nanowires. The following chemical reactions occur:

\[
\text{Zn(NO}_3\text{)}_2 \rightarrow \text{Zn}^{2+} + 2\text{NO}_3^- \tag{1}
\]
\[
(\text{CH}_2\text{)}_6\text{N}_4 + 6\text{H}_2\text{O} \rightarrow 6\text{HCHO} + 4\text{NH}_3 \tag{2}
\]
\[
Zn^{2+} + 4NH_3 \rightarrow Zn(NH_3)_4^{2+} 
\]

(3)

\[
Zn^{2+} + 2OH^- \leftrightarrow Zn(OH)_2 \text{ or } Zn^{2+} + 4OH^- \rightarrow Zn(OH)_4^{2-} 
\]

(4)

\[
Zn(OH)_2 \rightarrow ZnO + H_2O
\]

(5)

Because the change of each process parameter will affect the morphology of zinc oxide nanowire, it is necessary to precisely control the process parameters. Therefore, we used the KQS automated machine developed by the NPMEMS laboratory to synthesize zinc oxide nanowires in batches based on the low-temperature hydrothermal method. The device achieves precise control of the volume of the reaction solution and the reaction temperature through the solenoid valve, peristaltic pump and PTC heater controlled by the Labview program. KQS has 32 reaction chambers so that we can deposit zinc oxide nanowires on 32 substrates in one batch of experiment which further improves the experimental throughput. Using the KQS automated machine, we prepared large quantities of zinc oxide nanowires by adjusting the parameters and inspected their microstructure with SEM.

2.2. Simulation Model

2.2.1. Basic Simulation Model. The temperature recorded by the thermocouple in the reaction chamber is the point temperature. In the case of single measurement point of temperature, there are situations where the stable reaction time point temperature of the two cavities is same but the temperature distribution in other areas is inconsistent. Using CFD simulation method to analyze the physics field is a necessary way to solve the problems. We have established a simulation model of the KQS reaction chamber by using CFD software CFX. The chamber is composed of the Teflon main cavity, the substrate holder, the aluminum heating base, the PTC heater and silicone sleeve as shown in the Figure 1.

Figure 1. KQS reaction chamber (a) Actual experimental conditions (b) CFD simulation model.

By setting the boundary conditions, we obtain the temperature field and flow field distribution of the reaction solution in the steady state. Firstly, we set the physical properties of the reaction chamber material such as density, specific heat capacity and heat transfer coefficient. The reaction fluid is set as incompressible Newtonian fluid with a density of \(998.2 \text{ kg} \cdot \text{m}^{-3}\) and a dynamic viscosity of \(1.003 \times 10^{-3} \text{ kg} \cdot \text{m}^{-1} \cdot \text{s}^{-1}\). Secondly, the standard K-epsilon model is used for the natural convection of the fluid domain. The ambient pressure is 1 atm. Considering the buoyancy caused by the density difference under gravity, the Boussinesq hypothetical model is set up. The solid and fluid domain heat transfer model contains the settings of solid-solid interface, liquid-solid interface, wall surface and symmetry
plane. The thermal conductivity of the interface is set as conservative interface flux and the heat conduction property is set as heat transfer coefficient considering the convection with the environment. The initial temperature of the material and the environment temperature is set to 25°C and the heat transfer coefficient is set to $100 \text{W} \cdot \text{m}^{-2} \cdot \text{K}^{-1}$. The heat source is the PTC heater whose power is a function of time.

In order to reflect the heat transfer and flow characteristics while ensuring accuracy, double precision and the large number are used for the flow and heat transfer equation discrete format in the solver settings. The semi-implicit SIMPLE algorithm is used in the pressure-flow field coupling solution of the Navier-Stokes equations. The algorithm is iterative in the CFX solver. The residual error is used to determine convergence where $RMS_{\text{Energy}} < 10^{-4}$ and $RMS_{\text{Momentum}} < 10^{-4}$. The time step of the solver is an adaptive solution.

2.2.2. Validation. To verify the reliability of the CFD simulation results, we selected multiple batches of KQS automated zinc oxide nanowire preparation experiments for validation. In CFD simulation, the same physical parameters are set as the experiment. The body power of PTC heater is set as $3.238 \times 10^6 \text{W} \cdot \text{m}^{-3}$. We compared the point temperature of the simulation results with the experimental values recorded by the recorder. The result shows that CFD simulation results and experimental data fit well as Figure 2. In the steady state, the temperature of simulation and the experimental measurement value are stable at 79°C which proves that the CFD simulation can represent the steady-state experimental results within the allowable error range.

![Figure 2. Comparison of experiment and CFD simulation model.](image)

2.3. Datasets

2.3.1. Inputs. The proper approach is taken to convert the CFD results to inputs of deep learning model. Two kinds of reaction chambers and 16 PTC heaters are combined orthogonally. As a result, we created 120 simulation models of the temperature field and flow field in the steady state. The calculation results are pre-processed as Figure 3. First, we use CFX post to obtain the cross-section of the YZ plane of the reaction chamber and extract the contour map of the temperature field and the flow field. Second, in order to ensure the integrity of the temperature field and the flow field characteristics, the three-dimensional data points of the temperature field and the flow field are added with a weight of 1:1 according to the spatial distribution. The parameter matrix of the temperature-velocity coupled physical field is cut with resolution of 56×56 as the input data of the NPPN model.
2.3.2. Targets. We used the KQS automated machine to synthesize zinc oxide nanowires in batches based on the low-temperature hydrothermal method. On this basis, SEM images of zinc oxide nanowires under multiple process conditions are obtained as shown in Figure 4. From the SEM image, we can see that the diameter difference of different samples on the substrate is small, which proves that the KQS system can achieve uniform deposition of zinc oxide nanowires. The zinc oxide nanowires are in the shape of regular single crystal hexagonal prisms. We assume that the end faces of the zinc oxide nanowires are regular hexagons and the circumference of the regular hexagon is \( C \). The diameter of nanowires can be described as \( D = \frac{1}{3} C \).

![Figure 3. Image pre-processing of physical field.](image1)

![Figure 4. SEM image of zinc oxide nanowires.](image2)

The parameter extraction of the average diameter of zinc oxide nanowires was carried out using software annotation, Nano Measurer. After importing the SEM image into Nano Measurer, we use the polygon tool to measure the end surface circumference of zinc oxide nanowires. From calculating the measurement results of circumference we get the statistical average and variance of the diameter of the end face of the zinc oxide nanowire.

2.4. Deep learning model

The NPPN (Nanostructure-Parameter Prediction Network) model is proposed to explore the mapping relationship between the temperature and flow velocity coupled physical field images and the structure parameters of the zinc oxide nanowires. The model contains two parts. The first part is the optimized
VGG16 model to extract physical field image features. The second part uses the extracted feature matrix to perform regression prediction on structural parameters. This section mainly introduces the basic structure and improvement of the NPPN model.

VGG16 is a basic CNN composed of a convolutional layer and a pooling layer which can handle image classification problems [5]. Based on VGG16, this paper further proposes the NPPN model which can solve the regression problem. The structure of NPPN is shown in the Figure 5. The input is the image of the coupled physical field of temperature and flow velocity. The target is the average diameter of the zinc oxide nanowire.

In the module of feature extraction, NPPN retains 3 sets of convolution operations. 3x3 small convolution kernels are used in all convolutional layers. With the deepening of the layer, the amount of channels of the convolutional layer increases in the order of 16, 16, 32, 32, 64, 64. The activation function is ReLU and a 2x2 pooling layer is inserted to gradually reduce the space size of intermediate data. The feature extraction part outputs a feature map with a size of 7x7.

In the module of regression, we insert the fully connected Affine layer which expand the data into one-dimensional feature vector. The length of the feature vector is 256 and the activation function is ReLU. Then we insert a fully connected Affine-dropout layer. The L2 regularization parameter is added in the parameter matrix to avoid over-fitting problems and improve the generalization of the model. Finally, the one-dimensional feature vector is directly connected to a single neuron which generate the predicted floating value of the average diameter of the zinc oxide nanowire.

![Figure 5. Structure of NPPN model.](image)

2.5. Training

The main purpose of NPPN is to explore the mapping relationship from the input to the label. The label is a one-dimensional vector representing the structural parameters of the nanowire which can be described as $Y_0 = \{y_1, ..., y_i, ..., y_n\}$. The output is the one-dimensional feature vector predicted by the model which can be described as $\hat{Y} = f(X_i; W) = \{\hat{y}_1, ..., \hat{y}_i, ..., \hat{y}_n\}$, where $X_i$ is the input image data matrix and $W$ is the weight parameter matrix that needs to be learned. The model parameter training process minimizes the Euclidean distance between $Y_0$ and $\hat{Y}$.

$$L = ||f(X_i; W) - Y_0||_2$$

Mean Square Error (MSE) can well characterize the Euclidean distance between the label and the predicted value. Therefore, the loss function is defined as:

$$\phi = \frac{1}{K}\sum_{i=1}^{K}\|y_i - f(x_i; W)\|_2^2$$

Where $K$ is the number of samples, and $y_i$ is the label of the $i$-th training sample. The smaller the MSE, the closer the predicted value to the label value.

Model performance can be described using Pearson correlation coefficient.
Where $K$ is the number of samples, $\frac{x_i - \bar{x}}{\sigma_x}$ is the standard score of the $x_i$ sample, $\bar{x}$ is the sample average and $\sigma_x$ is the sample standard deviation. The correlation coefficient can evaluate the degree of correlation between the predicted value and the label value. The closer to one, the two variables tend to be positively correlated. In the training process, the correlation coefficient is used to present the accuracy of model evaluation.

The deep learning models are trained on a workstation equipped with Intel Core i7-8700k CPU, 16GB RAM and NVIDIA GeForce GTX 1080Ti GPU. The open-source deep learning framework TensorFlow is used to implement neural networks through GPU acceleration. In the training process, a stochastic gradient descent (SGD) optimizer is used to reduce the loss. The learning rate is $\alpha=0.01$ and the number of neurons retained in the dropout layer is 0.7. Since a small sample dataset is used, the dataset is randomly divided into training set and test set at a ratio of 5:5 to improve the generalization ability of the trained network. The loss and accuracy of the training process are shown in the Figure 6.

![Figure 6. The loss and accuracy of the training process.](image)

3. Result

Through the NPPN model, we trained 120 sets of coupled physical field images and the corresponding zinc oxide nanowire structural parameters. A well-fitting network model is obtained through multiple parameter optimization. We recorded the predicted value of the average diameter of zinc oxide nanowires and compared the predicted value with the label value. The performance of the result is measured by the correlation coefficient and the mean square error. Table 1 lists the evaluation indicators of the prediction results of the test set in the five model training.

| Number | R  | MSE  |
|--------|----|------|
| 1      | 0.849 | 0.246 |
| 2      | 0.854 | 0.266 |
| 3      | 0.861 | 0.229 |
| 4      | 0.871 | 0.237 |
| 5      | 0.870 | 0.238 |
| 6      | 0.856 | 0.234 |

From the result, we can see that the test set showed the highest correlation coefficient $R=0.871$ in the fourth training result, and the test set showed the lowest mean square error $MSE=0.229$ in the third training result. Totally, the correlation coefficient is close to 1 and the mean square error does not exceed...
0.266 which indicates that the predicted value of the trained model on the test set is well fitted with the average diameter of the real nanowires. At the same time, the results of repeated experiments show that the model has good robustness.

These prediction values and the targets of six experiments performed visual display, as shown in Figure 7. The dotted line represents the linear regression line $y = x$. As can be seen in the data points are uniformly dispersed in both sides of the regression line. The correlation coefficient is close to 1 indicating that there is a high correlation and low error between the prediction result and the target value. This reflects the good predictive performance of the NPPN model.

![Figure 7. The correlation coefficient of prediction values and the targets.](image)

We selected the real value as the comparison standard. The actual measurement value is manually measured by Nano Measurer software. The end surface circumference of each zinc oxide nanowire is measured on the SEM image with 20000 times magnification. The average circumference is 1152.39 nm which corresponding to the average diameter of 384.13 nm. The predicted value of the average diameter from NPPN model is 395.15 nm which shows 2.87% error from the actual measured value.

4. Conclusions
In this paper, we propose a CNN-based NPPN model to solve the regression task from the physical field conditions of zinc oxide nanowire growth to the final structural parameters. Our model can predict the average diameter of zinc oxide by inputting the temperature-velocity coupled physical field image from the CFD simulation. The test set results show that the model has good predictive performance. The predicted value has low error and high correlation with the experimental measurement value. This model has certain application potential in the industrial scene of nanomaterial production which can help predicting the size of nanostructures generated by computer methods to avoid experimental trial and error.

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