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# Prediction of powder characteristics of uniform NiO precursor prepared by homogeneous precipitation①

HUANG Kai(黄 凯)[1, 2], GUO Xue-yi(郭学益)[2], ZHANG Duo-mo(张多默)[2],
HE Yue-hui(贺跃辉)[1], HUANG Bai-yun(黄伯云)[1]
(1. State Key Laboratory of Powder Metallurgy, Central South University, Changsha 410083, China;
2. School of Metallurgical Science and Engineering, Central South University, Changsha 410083, China)

**Abstract:** Uniform NiO precursor particles were prepared by homogeneous precipitation in the presence of urea. Optimal discrimination plan, one of the chemical pattern recognition techniques, was applied to analyze the experimental data and the quantitative relationships among the process parameters and powder characteristics of the obtained particles were determined. It proves that the model fits well with the experimental results and it is quite effective to guide the process design. Based on the above results, an improved La Mer model and the reasonable formation mechanism of the particles are proposed.

**Key words:** chemical pattern discrimination; optimization and prediction; NiO precursor particle; homogeneous precipitation

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## 1 INTRODUCTION

One of the unresolved fundamental problems in the precipitation of uniform solids from homogeneous solutions is the inability to predict the powder characteristics such as particle size and morphology. In recent years, a large number of monodispersed particles are prepared, which has provided numerous examples of the effects of the experimental conditions on the size distribution and shape of the product particles[1－6]. Matijevic and his co-workers have made distinguished achievements in this field, and in their study the experimental results are often indicated as the figures, in which the precipitation boundaries are delineated for the powders with different chemical composition and morphology obtained at different process parameters[7, 8]. Just like dish menu, these figures can be used to predict the powder characteristics to some degree and are quite convenient to guide the preparation of monodispersed powders. In these figures, usually only two parameters, i. e. the concentrations of metal ion and urea, are involved, while other parameters such as temperature, time, pH, and dispersant concentration are not illustrated[9]. So in this study, a new method is considered to solve this problem, and chemical pattern recognition technique is applied to establish the discrimination rules that enable us to differentiate the formation conditions of the precipitated powders obtained from the homogeneous solution and further to develop a more effective means which could be available to handle more variables in one figure. In this paper, nickel(Ⅱ) nitrate-urea system is adopted to prepare the monodispersed nickel oxide precursor particles and the experimental data were treated by chemical pattern recognition techniques.

## 2 EXPERIMENTS AND DATA ANALYSES

### 2.1 Experimental procedures

The effects of the concentration of nickel(Ⅱ) nitrate, urea and dispersant solutions, and the reacting time and temperature on the properties of the obtained particles would be investigated in detail.

All solutions were prepared using reagents of analytical purity and distilled water. Before experiments, the solutions were filtered to remove the insoluble impurity.

The reaction solutions contained in capped bottles (150 $cm^3$) were aged in a water bath preheated at the desired temperatures. The initial pH of the aged solutions was adjusted at around 6.0. Once the aging was completed, the obtained suspensions were cooled down in cold water, then centrifuged, and the solid was resuspended in anhydrous alcohol or acetone in an ultrasonic bath and dried at 50 ℃ in a desiccator. The obtained powders were inspected by scanning electron microscopy (SEM) to evaluate the particle

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**Correspondence:** HUANG Kai, PhD; Tel: +86-731-8836207; E-mail: meishan123@163.com

size, size distribution and other powder characteristics.

### 2.2 Principles of optimal discrimination plan(ODP)

The purpose of pattern recognition is to categorize a sample of observed data as a member of the class to which it belongs. Chemical pattern recognition includes principal components analysis, cluster analysis, trend analysis, artificial neural network, genetic algorithm and so on[10-12]. These techniques were widely used to extract and visualize the significant features or attributes of the multivariate data, which made it more convenient and powerful to analyze the complex data. In this study, optimal discrimination plan was applied to analyze the experimental data. A brief introduction is given here, and the details can be referred to Refs. [13-15].

Let $\boldsymbol{X}$ be a standardized training set with $n$ samples and $m$ features, and let $\boldsymbol{T}$ be its projection set (score set) to the corresponding optimal plan on which the features of the data set can be discriminate best effectively. The above-mentioned plan is the ODP, which is constructed by two orthogonalized vectors, one being Fisher vector and the other being Sammon vector[13]. In the ODP framework, we have Eqn. (1), where $\boldsymbol{P}$ is a corresponding $m \times 2$ orthonormal matrix.

$$\boldsymbol{T} = \boldsymbol{XP} \quad (1)$$

Thus, the obtained $T_1$ and $T_2$, as the coordinate axes, can construct a 2-dimension map, in which the different classes of each sample can be visualized. By this approach an empirical relationship is derived from a collection of objects, by which the interesting properties are known. This relationship is then used to predict the obscure properties of unknown objects.

### 2.3 Data analyses

Each homogeneous precipitated sample (case) is considered as an assembly of 5 variables in this study, i.e., concentration of nickel nitrate solution ($X_1$), concentration of urea ($X_2$), reaction time ($X_3$), reaction temperature ($X_4$), and dispersant amount ($X_5$). A data matrix whose rows were the cases or samples and whose columns were the variables was built as indicated in Table 1. Twenty-nine experimental results obtained under different experimental conditions were used as the training samples for chemical pattern recognition.

**Table 1** Data of experimental samples

| Sample No. | $X_1$/ (mol·L$^{-1}$) | $X_2$/ (mol·L$^{-1}$) | $X_3$/ min | $X_4$/ ℃ | $X_5$/ mL | Dispersity① | Average size/ μm | Distribution② |
|---|---|---|---|---|---|---|---|---|
| 1 | 0.01 | 1.0 | 90 | 92 | 0 | NA | 0.94 | U |
| 2 | 0.02 | 1.0 | 60 | 92 | 0 | NA | 1.25 | U |
| 3 | 0.05 | 1.0 | 60 | 92 | 0 | A | 1.81 | B |
| 4 | 0.05 | 1.0 | 90 | 92 | 0 | A | 1.88 | B |
| 5 | 0.05 | 1.0 | 60 | 92 | 2 | NA | 1.50 | B |
| 6 | 0.01 | 1.0 | 90 | 92 | 1 | NA | 0.88 | U |
| 7 | 0.042 | 0.833 | 80 | 92 | 0 | A | 2.18 | B |
| 8 | 0.01 | 1.0 | 85 | 80 | 0 | NA | 0.69 | U |
| 9 | 0.01 | 1.0 | 115 | 80 | 0 | NA | 1.06 | U |
| 10 | 0.01 | 1.0 | 145 | 80 | 0 | NA | 1.12 | U |
| 11 | 0.01 | 1.0 | 175 | 80 | 0 | A | 1.19 | U |
| 12 | 0.01 | 1.0 | 205 | 80 | 0 | A | 1.30 | B |
| 13 | 0.01 | 1.0 | 235 | 80 | 0 | A | 1.39 | B |
| 14 | 0.01 | 0.5 | 90 | 90 | 0.5 | NA | 1.10 | U |
| 15 | 0.02 | 2.0 | 90 | 90 | 1 | NA | 1.51 | B |
| 16 | 0.03 | 2.0 | 90 | 90 | 1 | NA | 1.59 | B |
| 17 | 0.04 | 2.0 | 60 | 90 | 0 | NA | 1.98 | B |
| 18 | 0.06 | 2.0 | 90 | 90 | 1 | NA | 2.29 | B |
| 19 | 0.01 | 4.0 | 90 | 90 | 0.5 | NA | 1.60 | U |
| 20 | 0.10 | 2.0 | 35 | 90 | 2 | NA | 1.82 | B |
| 21 | 0.10 | 2.0 | 60 | 90 | 2 | NA | 2.25 | B |
| 22 | 0.01 | 0.1 | 150 | 92 | 0 | NA | 1.35 | U |
| 23 | 0.01 | 0.2 | 150 | 92 | 0 | NA | 1.41 | U |
| 24 | 0.10 | 2.0 | 90 | 90 | 0.5 | A | 2.52 | B |
| 25 | 0.05 | 1.0 | 60 | 88 | 2.1 | NA | 1.42 | B |
| 26 | 0.06 | 2.0 | 90 | 90 | 0 | A | 2.41 | B |
| 27 | 0.08 | 1.0 | 100 | 100 | 0 | A | 2.86 | B |
| 28 | 0.10 | 2.0 | 120 | 100 | 2 | A | 2.73 | B |
| 29 | 0.04 | 1.0 | 120 | 100 | 0.5 | A | 2.43 | B |

① NA — Non-aggregated, A —Aggregated; ② U —Uniform, B —Broad

ODP belongs to a kind of supervised pattern recognition technique, which assumes a prior knowledge of the number of classes as well as the class membership of each sample in a training set. In this data set, the main criteria of classification for each sample are the following features: dispersity, average size and size distribution of the precipitated powder. Thereafter, the data set can be divided into two classes of samples according to the above properties respectively. Here, we defined the particles with average size below 1.8 μm as the fine particles, and above 1.8 μm as the coarse ones. The program of optimal discrimination plan was developed by ourselves in the computer language of MATLAB.

## 3 RESULTS AND DISCUSSION

The data in Table 1 should be auto-scaled before inputting into the ODP program, and a series of calculation results were shown in the following figures. Figs. 1 – 4 show the classifying diagrams of pattern recognition according to the dispersity, average size, size distribution and monodispersity respectively. In these figures, the different classes of precipitated powder were separated into the different domains.

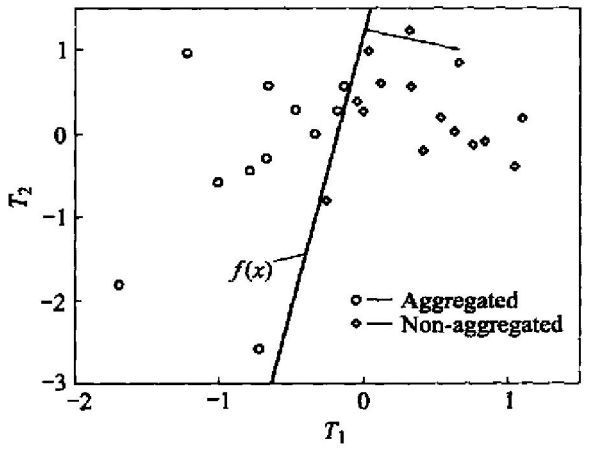


**Fig. 1** Optimal projection map after feature selection by ODP according to dispersity of particles

### 3.1 Pattern recognition by dispersity of particles

Taking dispersity of the precipitated particles as the classification criterion, the data set was treated by ODP and the results are shown in Fig. 1.

In Fig. 1, a line which is illustrated as $f(x)$ can be drawn to divide the samples into two classes distinctly with the dispersity as the criterion. By calculation, the equation of the line was obtained as follows:

$$f(x) = T_2 - 6.72T_1 - 1.26 = 0 \quad (2)$$

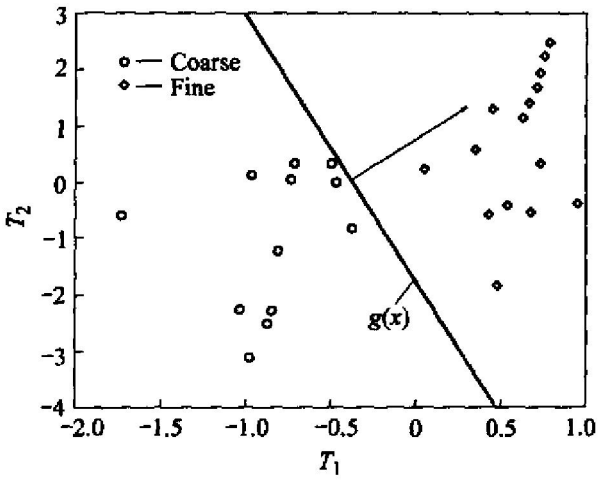


**Fig. 2** Optimal projection map after feature selection by ODP according to average size of particles

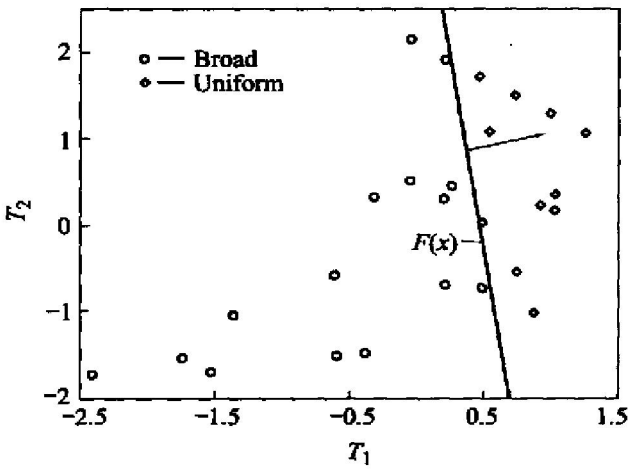


**Fig. 3** Optimal projection map after feature selection by ODP according to size distribution of particles

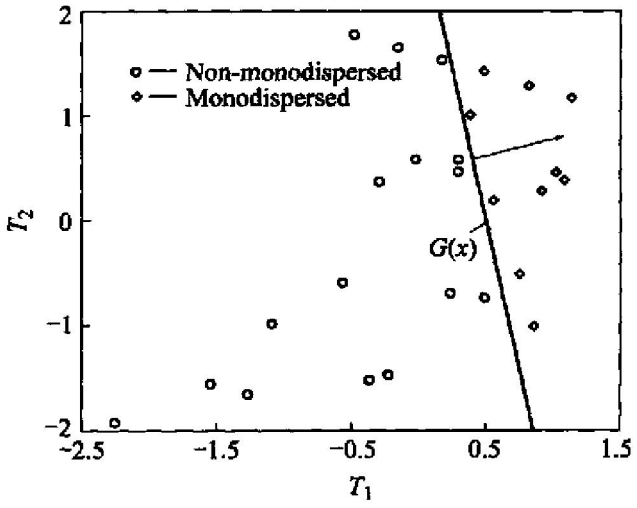


**Fig. 4** Optimal projection map after feature selection by ODP according to monodispersity of particles

The area the arrow points at is the formation area of non-aggregated powders. And the two coordinate axes are established by Eqn. (1) and they can be expressed as follows:

$$T_1 = -0.707X_1 + 0.000\,8X_2 - 0.504X_3 - 0.151X_4 + 0.472X_5 \quad (3)$$

$$T_2 = 0.392X_1 - 0.020X_2 - 0.437X_3 - 0.797X_4 - 0.136X_5 \quad (4)$$

Incorporating Eqns. (3) and (4) into Eqn. (2), then the equation for $f(x)$ is turned into Eqn. (5):

$$f(x) = 5.14X_1 - 0.025X_2 + 2.95X_3 + 0.22X_4 - 3.31X_5 - 1.26 = 0 \quad (5)$$

When $f(x)$ is less than zero, i.e., $f(x) < 0$, it indicates that non-aggregated particles can be obtained; while $f(x) > 0$, aggregated particles can be produced. Eqn. (5) shows the different effect of each parameters on $f(x)$, i.e., the absolute value of each parameter weight indicates the effect degree, and the sign of each parameter indicates the effect direction. So from Eqn. (5), it is known that the effect degree of each parameter is as follows: $X_1 > X_5 > X_3 > X_4 > X_2$, that is, the effect of the concentration of nickel ion on the dispersity of particles is the largest, then the concentration of dispersant, the period of reaction time, reaction temperature and the concentration of urea. Clearly, in order to prepare non-aggregated particles, it should decrease the value of $X_1$, $X_3$, $X_4$ and increase the value of $X_2$, $X_5$ to lead to the less $f(x)$.

### 3.2 Pattern recognition by average size of particles

Taking the average size of the particles as the classification criterion, the data set is treated by ODP and the results are shown in Fig. 2. In Fig. 2, a line which is illustrated as $g(x)$ can be drawn to divide the samples into two classes with the average size as the criterion.

By calculation, the equation of the line was obtained as follows:

$$g(x) = -12.33X_1 + 0.03X_2 + 1.86X_3 - 2.54X_4 + 4.11X_5 + 10.33 = 0 \quad (6)$$

Eqn. (6) indicates that the effect degree of each parameter on the average particle size is as follows: $X_1 > X_5 > X_4 > X_3 > X_2$. In order to make the particles finer, $g(x)$ must be more positive than zero, i.e., $g(x) > 0$. So it is necessary to decrease the value of the concentration of nickel ion solution, reaction temperature and increase the value of the concentration of urea, reaction time and the concentration of dispersant.

### 3.3 Pattern recognition by size distribution of particles

Taking the size distribution of the particles as the classification criterion, the data set was treated by ODP and the results are shown in Fig. 3. In Fig. 3, a line which is illustrated as $F(x)$ can be drawn to divide the samples into two classes with the size distribution as the criterion.

By calculation, the equation of the line was obtained as follows:

$$F(x) = -7.41X_1 - 0.38X_2 - 3.07X_3 - 1.76X_4 - 2.59X_5 - 4.09 = 0 \quad (7)$$

Eqn. (7) indicates that the effect degree of each parameter on the average particle size is as follows: $X_1 > X_3 > X_5 > X_4 > X_2$. In order to make the size distribution of the particles smaller, $F(x)$ must be larger than zero, i.e., $F(x) > 0$. So it is necessary to decrease the value of the parameters based on the average value of the sample data set.

### 3.4 Pattern recognition by monodispersity of particles

Taking the monodispersity of the particles as the classification criterion, the data set was treated by ODP and the results are shown in Fig. 4. In Fig. 4, a line which is illustrated as $G(x)$ can be drawn to divide the samples into two classes with the monodispersity as the criterion.

By calculation, the equation of the line was obtained as follows:

$$G(x) = -5.83X_1 - 0.32X_2 - 2.34X_3 - 0.84X_4 - 1.76X_5 - 2.60 = 0 \quad (8)$$

Eqn. (8) indicates that the effect degree of each parameter on the average particle size is as follows: $X_1 > X_3 > X_4 > X_5 > X_2$. In order to make the particles more monodispersed, $G(x)$ must be larger than zero, i.e., $G(x) > 0$. So it is necessary to decrease the value of all the parameters by the average value of the sample data set.

### 3.5 Preparation of monodispersed particles with guide of ODP results

In Fig. 4, at the right direction of $G(x)$ line, a point of ($T_1 = 1$, $T_2 = -1$) belongs to monodispersed particles and at the left direction of $G(x)$ line, a point of ($T_1 = -0.2$, $T_2 = -1.5$) belongs to non-monodispersed particles. By back-mapping calculation[6, 7], the original parameter values for the above two points can be defined as (0.01 mol/L, 1.0 mol/L, 105 min, 82 ℃, 0.3 mL) and (0.09 mol/L, 2.0 mol/L, 65 min, 85 ℃, 1.5 mL) respectively. Prepare the particles under the conditions as shown above, and SEM micrographs of the particles are shown in Fig. 5. In Fig. 5, it can be found that the particles obtained under the two sets of conditions are quite consistent with the predicted results by ODP. So it proves experimentally that the optimal discrimination plan is an effective pattern recognition method to analyze the experimental data and to predict the relation of particle characteristics with the prepared conditions. Compared with the traditional method used in Matijević's

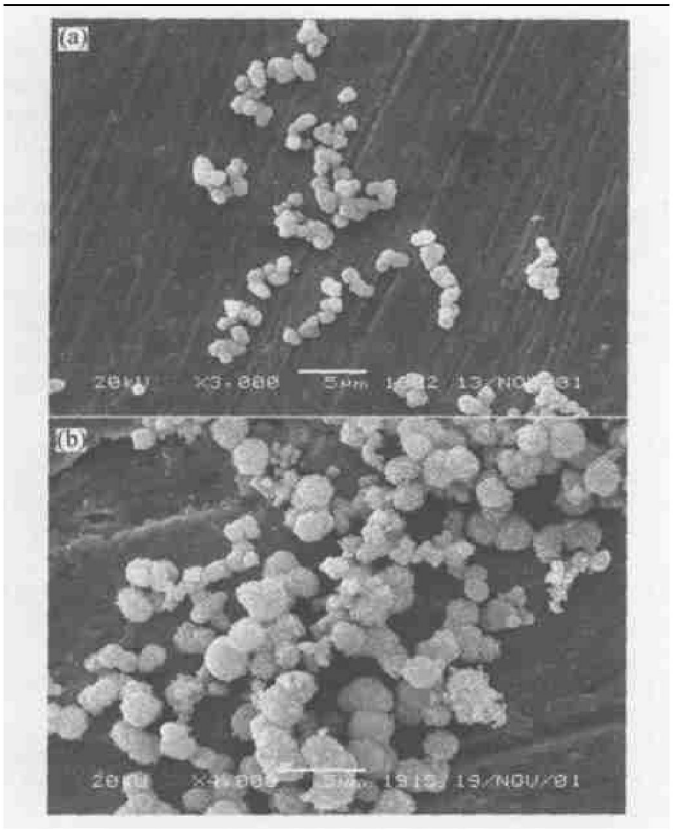


**Fig. 5** SEM images of particles prepared under different conditions
a) —Aging at 80 ℃ for 105 min in 0.01 mol/L $Ni(NO_3)_2$+ 1.0 mol/L urea+ 0.3 mL dispersant;
(b) —Aging at 85 ℃ for 65 min in 0.09 mol/L $Ni(NO_3)_2$+ 2.0 mol/L urea+ 1.5 mL dispersant

study[7, 8], chemical pattern recognition can treat the data with more complex data structure and so it is quite useful to guide the practical process.

## 4 FORMATION MECHANISM OF MONODISPERSED PARTICLES

For the formation of the monodispersed particles, the most typical mechanism is La Mer model. It implies that monodisersed particles are formed, when the process in a homogeneous solution is conducted in a kinetically controlled manner, so that the concentration of constituent species reaches critical supersaturation, resulting in a short single burst of nuclei[5, 8]. The latter allows to grow uniformly by diffusion of solutes to the uniform particles. While in many practical experiments, it is found that the particles are not formed by diffusion instead of aggregation of the smaller particles, i.e., sub-units. So the traditional La Mer model of "single burst of nuclei $\rightarrow$ grow by diffusion of solutes" is modified as "single burst of nuclei $\rightarrow$ aggregation by subunits" in Matijevic's study[7, 8]. In this study, based on the experimental results, we propose an improved model of "single burst of nuclei $\rightarrow$ aggregation by subunits $\rightarrow$ grow by diffusion of solutes", and we will explain it in details from the point of view of the total interface energy of the homogeneous precipitation system. The above-mentioned model can be shown in Fig. 6.

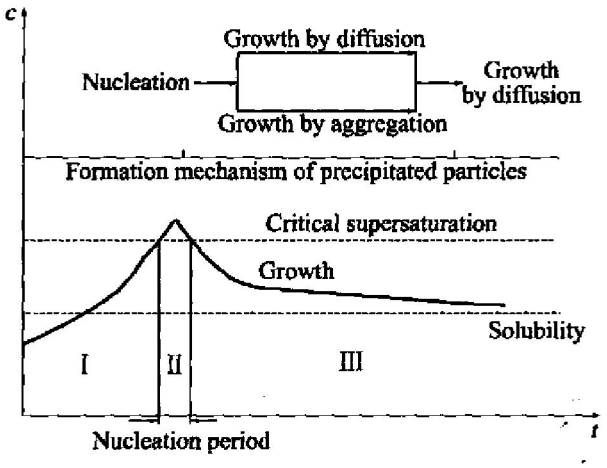


**Fig. 6** Improved La Mer model for formation of precipitated particles

In the homogeneous precipitation system, once the nuclei are produced, the interface energy of the whole system will increase rapidly. At this time, the system has a trend of decreasing the interface energy. The possible ways are growth by diffusion of solute or by aggregation. Obviously, the way which can decrease the interface energy more effective will be the dominant growth means at the early stage of precipitation. So based on this view, it can be known that aggregation will the dominant growth way of the nuclei because it has more efficiency of decreasing the total interface energy for the whole precipitation system than that of diffusion of solutes at the early stage of the precipitation. It is known that after a certain period of precipitation, the nuclei growth by aggregation will tend to reach its thermodynamic equilibrium with aggregation velocity being quite small, then the growth by diffusion of solutes will become more dominant. So the above-proposed model contains a competitive growth process of aggregation and diffusion. In the experimental result, it is found in the high-resolution electron micrographs of the precipitated particles, the particles all aggregate in one with a number of sub-units.

Because aggregation is the dominant growth way of the produced particles, it can be combined with the calculation results from chemical pattern recognition to explain the experimental phenomena in detail. From the point of view of colloid science, it is known that if the ion strength of the solution is larger, the colloidal particles are easier to aggregate[16]. Thus, decreasing the concentration of the nickel ion solution, the more dispersed particles will be obtained. When a certain amount of dispersant is added into the solution, it can prevent the colloidal particles from aggregation effectively, leading to the formation of dispersed and fine particles; while the addition of the

dispersant is too much, because of the inter-twisting effect of the polymers at its high concentration, the particles are easier to aggregate into larger particles with broader size distribution. When reaction time and temperature increase, the probability of over-aggregation becomes larger and consequently the produced particles with bigger size and broader size distribution are formed. The effect of the concentration of urea is less than other parameters, which can be ascribed to its fairly low hydrolysis rate in the solution at the temperature below 100 ℃. The proposed model can explain the formation of monodispersed nickel oxide particles more suitable.

So chemical pattern recognition method is a quite useful tool to analyze the information of the experimental data and often helps to explain the further mechanisms of the process, and in this study it is also successfully applied to predict the characteristics of the precipitated particles and can be used to design the new experimental scheme for the desired particles with better quality.

## 5 CONCLUSIONS

Optimal discrimination plan method is successfully applied to analyze the experimental information of the homogeneous precipitation system which is used to prepare NiO precursor particles. A series of semi-experienced mathematic models are drawn from the experimental sample data by ODP, which can predict the characteristics of the precipitated particles to some extent. Based on the experiments and ODP results, an improved La Mer model is proposed as follows: single burst of nuclei $\rightarrow$ aggregation by subunits $\rightarrow$ grow by diffusion of solute.

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