

# Preparation of nano nickel oxide using a biological template chicken egg endometrium and its electrochemical properties

YUN GAO\*, YING ZHAO, XIAOMIAN WANG, YI YANG

College of Chemical Engineering, Hebei united university, Tangshan 063009, PR China

We used chicken egg endometrium as a template, citric acid as the chelator, and a sol – gel method to prepare nano NiO. The preparation conditions included: temperature of 70 °C, reaction ratio  $[n(\text{Ni}^{2+}): n(\text{citric acid})]$  of 1:1; calcination temperature of 500 °C; and calcination time of 2 h. The resulting powder sample was tested for the size using X-ray diffraction (XRD). SEM and TEM were used to examine the morphology. The nano NiO powder had a specific capacity of 198.1F/g. After 100 cycles, the discharge capacity was reduced to 177F/g, suggesting a electrochemical performance of the nano NiO.

(Received November 8, 2014; accepted January 21, 2015)

**Keywords:** Sol-gel preparation, Chicken egg endometrium, Nano NiO, Electrochemical performance

## 1. Introduction

Nano nickel oxide is an important functional material with particle sizes ranging from 1 – 100 nm. It has important uses in materials science, electronics, and chemical industries and is mainly used for the preparation of catalysts [1], supercapacitors [2], gas sensitive materials [3] and optoelectronic materials [4].

Chicken egg endometrium is rich in proteins. In these peptide chains there are a large number of sites that can bind with metal ions. Thus, chicken egg endometrium is a cheap and practical natural template. Here, we used a sol - gel method to grow nano nickel oxide on the biological template. The  $\text{Ni}^{2+}$  ions were adsorbed on the chicken egg endometrium proteins and reacted with absolute ethanol to produce metal alkoxides. Citric acid, an organic acid containing multiple carboxyl groups, was complexed with the metal alkoxide to form the sol - gel [5]. The meshed chicken egg endometrium controlled the size of the gel. After dehydration and drying, we obtained the precursor to be loaded into the chicken egg endometrium. Nano nickel oxide was obtained after calcination. Chicken egg endometrium has been used as the template for the synthesis of some nano-materials [6], but thus far there has been no report on the preparation of nano NiO using egg endometrium.

## 2. Materials and methods

### 2.1 Reagents and instruments

Reagents included: nickel nitrate hexahydrate ( $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ); citric acid ( $\text{C}_6\text{H}_8\text{O}_7 \cdot \text{H}_2\text{O}$ , CA); and absolute ethanol ( $\text{CH}_3\text{CH}_2\text{OH}$ ). All water was deionized.

Instruments included: SX2-4-10 muffle furnace; DF-101S heat-gathering magnetic stirrer; GZX-9076MBE digital blast oven; D/MAX 2500PC X ray diffractometer (Cu target,  $\text{K}_\alpha$  ray); JEM-2010 transmission electron microscope (TEM); S-4800 field emission scanning electron microscope (SEM); IM6E electrochemical workstation; and CT-2001A LAND battery testing system.

### 2.2 Preparation of nano nickel oxide

Nickel nitrate hexahydrate was weighed and dissolved in absolute ethanol in a conical flask and placed in a water bath at 70 °C. Fresh egg shells were used to peel the endometrium, which was rinsed with deionized water and subjected to natural air drying. The chicken egg endometrium was then soaked in nickel nitrate for 3 h. Finally, citric acid was placed into the conical flask and stirred until the solution turned into a green sol. The soaked chicken egg endometrium was removed, drip-dried, and then dried in an 80 °C oven. The dried chicken egg endometrium was put in a crucible and calcined in a muffle furnace. The products were stored and tested after natural cooling.

In the experiment, 1 cm×1 cm foamed nickel was used as the conductive substrate, and a copper wire was welded to the foamed nickel to serve as the electrode substrate. The NiO, graphite, acetylene black and polyvinylidene difluoride (PVDF) were mixed at 8:1:1:1. After adding a small amount of the N-methylpyrrolidone (NMP) with even grinding, the powder was used to uniformly cover the foamed nickel. This was then dried at 120 °C for 6 h. The powder was then used to cover the foamed nickel, which was dried again to obtain the active electrode. The nano nickel oxide electrode was used as the

study electrode, a platinum electrode was the auxiliary, and an Hg/HgO electrode was the reference. In the resulting three-electrode test system, we used 6 mol/L KOH solution as the electrolyte.

### 2.3 Methods for sample analysis and testing

The resulting powder sample was tested for the size using X-ray diffraction (XRD). Size was determined by positions of the characteristic peaks.

An SEM and a TEM were used to examine the morphology, size of the nanomaterial particles and the particle size distribution.

Cyclic voltammetry (CV) is a commonly used electrochemical testing method. With this method the electrode potential is scanned in triangular waveform at different rates. For each scan of a triangular wave, one oxidation-reduction reaction is completed. This is repeated to plot the current – voltage curve, i.e., the CV plot. By recording the currents at different potentials and the position and magnitude of the current peaks, the reversibility and stability of the electrode is assessed. This determines the electrode's capacitive behavior and operating voltage range.

We used an IM6E electrochemical workstation including a three-electrode system with a NiO working electrode, platinum comparison electrode and an Hg/HgO reference electrode.

Constant current charge-discharge is also a common method for studying the electrochemical properties of raw materials. The method works as follows. The test electrode is put in a charge/discharge state under constant current. Potential changes as a function of time are observed to test the electrode performance and to calculate the specific capacity of the battery. For the constant current charge-discharge test, a two-electrode system was used. The electrode containing NiO was the working electrode, and a Li electrode served as the comparative electrode. The charge-discharge curve of the electrolytic material was determined with the charge-discharge experiment. From the first charge-discharge curve, basic electrochemical properties of the working electrode were determined including specific capacity and cycle performance. The cyclic charge-discharge experiment was performed using a CT-2001A LAND battery test system.

The specific capacity ( $C_m$ ) of the electrode was calculated using the following formula:

$$C_m = \frac{C}{m} = \frac{I\Delta t}{\Delta V m}$$

where:

$C_m$  — the electrochemical capacity of the electrode material, F/g ;

$\Delta V$  — discharge voltage, V;

$\Delta t$  — discharge time, s;

$I$  — charge-discharge current, mA;  
 $m$  — mass of the electrode material, g.

## 3. Results and discussion

The reaction temperature was 70°C. The reaction ratio [n(Ni<sup>2+</sup>): n(citric acid)] was 1:1. Calcination was at 500°C for 2 h. The prepared product was nano nickel oxide.

### 3.1 XRD analysis of the nano nickel oxide product

The XRD spectrum in Fig. 1 has a peak that coincides with the standard spectrum card. This is typical of the face-centered cubic crystal lattice.

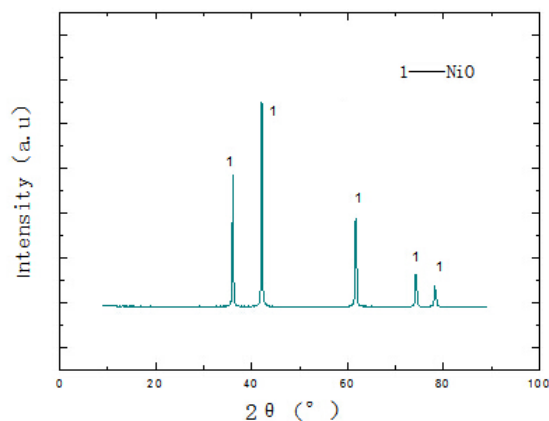


Fig. 1. XRD spectrum of the nano nickel oxide product.

The XRD peak of the crystal grain becomes wider as the size of the crystal grain increases. There is a quantitative relationship between the particle size and the full width at half maximum (FWHM) of the XRD peak. Hence the particle size can be calculated using the Scherrer equation:

$$D = \frac{k\lambda}{\beta \cos \theta}$$

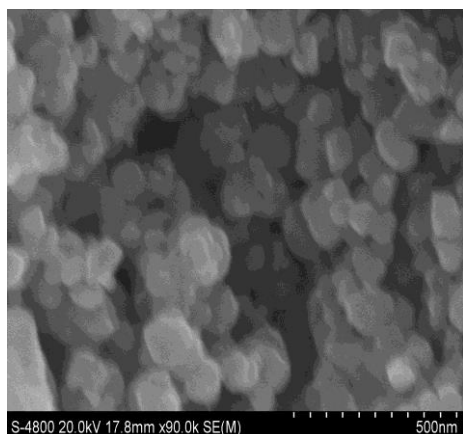
Here,  $D$  is the diameter of the crystal grain;  $k$  is a fixed constant, generally set to be 0.89;  $\lambda$  is the wavelength of the incident ray (because CuK $\alpha$  target was used its value is 0.154 nm);  $\beta$  is the FWHM of the diffraction peak; and  $2\theta$  is the diffraction angle corresponding to the highest diffraction peak. The calculation indicated that the particle size is 7.5 nm.

### 3.2 SEM and TEM analyses of the nano nickel oxide product

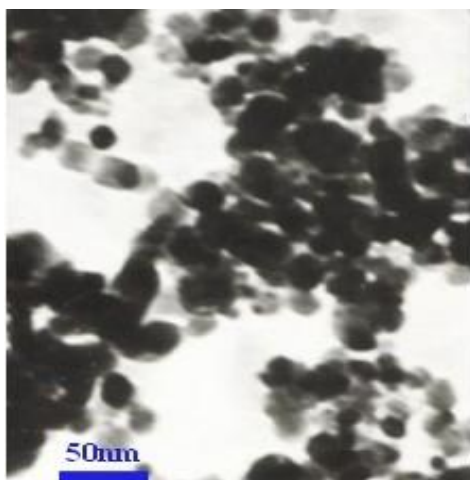
Fig. 2 shows the SEM and TEM images of the nano

nickel oxide product.

As seen in Fig. 2, the prepared NiO crystal grains were spherical, and the grain size distribution is uniform with no notable agglomeration. The particle sizes were 30 nm or below. This is basically the same as the result obtained using the Scherrer equation.



(a)SEM



(b)TEM

Fig. 2. SEM and TEM images of the nano nickel oxide product.

### 3.3 The CV curve of the nano nickel oxide product

The nano NiO was used to make an active electrode material. A three-electrode system with a scanning voltage window from 0-0.4V, and electrolytic KOH was used for the CV experiments (Fig. 3). In the electrolysis process there were obvious oxidation and reduction peaks. These are different from the nearly rectangular cyclic curve of electric double layer capacitor. This suggested that the nano NiO underwent a Faraday reaction showing notable Faraday quasi-capacitance behavior (pseudo-capacitance). The redox peaks indicate reversible oxidation and reduction reactions between  $\text{Ni}^{2+}$  and  $\text{Ni}^{3+}$ .

### 3.4 The electrochemical performance of the nano nickel oxide product

Fig. 4(a) illustrates the first charge-discharge curve of the prepared nano NiO electrode in 6 mol/L KOH solution. The current density was  $5\text{mA}/\text{cm}^2$ . Fig. 4(b) plots the relationship between the discharge capacity of the prepared nano NiO powder electrode and the number of cycles at 0-0.4 V and current density of  $5\text{mA}/\text{cm}^2$ . We completed 100 cycles of charge and discharge.

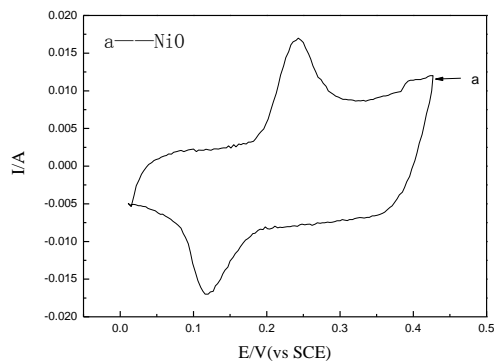
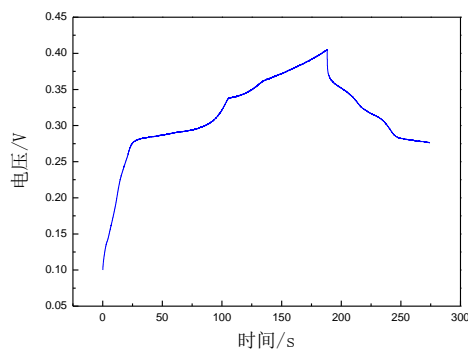
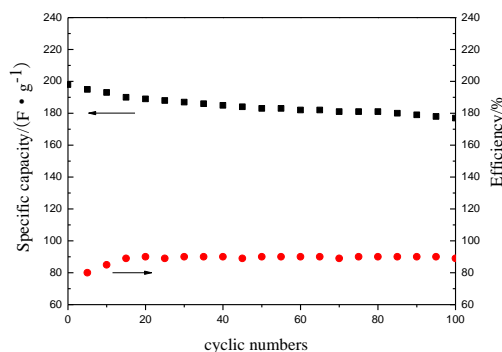


Fig. 3. The cyclic voltammetry performance curve of the nano nickel oxide product.



(a)



(b)

(a) The first charge and discharge performance curve of nano NiO; (b) The cyclic performance of the nano NiO electrode.

Fig. 4. Electrochemical properties of the nano nickel oxide.

As shown in Fig. 4(a), the capacitance per unit mass of the NiO powder was  $198.1\text{F}/\text{g}$ . Fig. 4(b) presents the

stable discharge capacity and discharge efficiency of the electrode. The initial discharge capacity of the electrode was 198.1F/g. After 100 cycles, the discharge capacity decreased to 177 F/g—90% of the first charge discharge capacity. This shows that these nano NiO powder has a satisfactory cycle life.

#### 4. Conclusions

In this study, we combined a sol – gel method with a biological template. The resulting sol – gel transition occurred in the template pores. After calcination, nano NiO was prepared. The ideal conditions used a molar ratio of Ni<sup>2+</sup> to citric acid of 1: 1 and reaction at 70 °C. The product was calcined for 2 h at 500 °C. The nano NiO showed crystal grains with structural integrity, small particle size, and a pure single component nature. The maximum specific capacity of the prepared nano NiO powder was 198.1F/g. After 100 cycles, the discharge capacity decreased to 177 F/g, suggesting that the nano NiO powder exhibited good cyclic charge-discharge performance.

#### Acknowledgments

The work was financially supported by the Natural Science Foundation of Hebei Province of China (No. E2012209033) and Hebei Province Foundation for Returness.

#### References

- [1] Bandara A, Kubota J, Onda k, et al. *J. phys. Chem. B*, **102**, 5951 (1998).
- [2] Kong Deshusi, Wang jianming, Shao Haibo, et al. *Journal of Alloys and Compounds*, **509**, 561 (2011).
- [3] Liu Xiaoming, Zhang Xiaogang, Fu Shaoyun, et al. *Materical Research Bulletin*, **41**, 620 (2006).
- [4] Miura N, Wang J, Nakatou M, et al. *Sensors and Actuators B: Chemical*, **114**, 903 (2006).
- [5] Qian J C, Cheng F, Qian Q, et al. *Chemical Journal of Chinese Universities*, **31**, 2116 (2010).
- [6] Liu J K, Wu Q S, Ding Y P. *Cryst Growth Des*, **5**, 445 (2005).

---

\*Corresponding author: gaoyunhuagong@126.com