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# Synthesis and characteristics of NiO nanoparticles by thermal decomposition of nickel dimethylglyoximate rods

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#### Abstract

Arrays of NiO nanoparticles have been synthesized via thermal decomposition of nickel dimethylglyoximate precursor. The structure, morphology and properties of the products were characterized by XRD, TEM, SAED and UV–vis spectrophotometry. TEM reveals that onedimensional arrays consist of NiO nanoparticles. XRD and SAED indicate that these NiO nanoparticles crystallize with a polycrystalline structure. The optical absorption band gap of NiO nanoparticles is 3.51 eV.

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### 1. Introduction

Nanomaterials with the size of 1–100 nm have attracted considerable interest due to the difference of properties from bulk phases arising from quantum size effect. In recent years, one-dimensional (1D) nanostructures, such as nanorods, nanowires and nanotubes, have received intensively attention because of both their fundamental importance and the wide range of their potential applications in many areas [1,2]. Various methods have been developed to fabricate 1D structured materials such as laser ablation method, CVD method, hydrothermal method, structure-directing soft or hard templates, and the self-assembly of spherical nanoparticles by oriented attachment [3–5].

NiO, as one of the relatively few metal oxides that tend to be p-type, is a stable wide band gap material and can be used as a transparent p-type semiconducting layer [6]. As a kind of functional material, NiO has received much attention recently due to its attractive application in catalysts, battery cathodes, gas sensors, electrochromic films, magnetic materials, active optical fibers and fuel cell electrodes [7–13]. Therefore, many

\* Corresponding author. *E-mail address:* xueliangli2005@163.com (X. Li). methods have been attempted to synthesize nanostructure nickel oxide, such as thermal decomposition [14], sputtering [15], electrodeposition [16], AAM template synthesis [17] and sol–gel techniques [18]. Zhang et al. [19] have synthesized NiO fibres in the presence of surfactant PVP. Xu et al. [20] have synthesized NiO nanorods by using precursor thermal decomposition in the presence of surfactant nonyl phenyl ether (NP-9/5) and NaCl flux at 1173 K. However, few attempts have been made to prepare one-dimensional arrays of NiO nanoparticles. Furthermore, 1D arrays of nanoparticles, which possess both the advantages of nanoparticles such as high surface areas and quantum size effects and the function of arrays, would hold excellent properties and potential application. Hence, it is of importance and significance to synthesize 1D arrays of NiO nanoparticles with a facile pathway.

In this article, we develop a simple and facile method for the fabrication of arrays of NiO nanoparticles by the thermal treatment of the rodlike nickel dimethylglyoximate precursor, and discuss the crystal structure, morphology and optical properties of 1D arrays of NiO nanoparticles. This method requires neither complex apparatus, nor any catalysts or any surfactants as usually needed in other methods.

# 2. Experimental details

All the analytical chemicals were purchased from the commercial market and used without further purification. In a

typical synthesis, 6 mmol of dimethylglyoxime was dissolved into 25 mL of ethanol to give a homogenous solution. Then this solution was added dropwise into 25 mL of aqueous solution containing 3 mmol NiSO<sub>4</sub> under magnetic stirring for 1 h. Red flocculates of nickel dimethylglyoximate were filtered, washed with distilled water and absolute ethanol several times to remove the impurities, and then dried in an oven at 80 °C for 4 h. Finally, the obtained nickel dimethylgloximate precursor was heated to 400 °C at a heating rate of 5 °C min<sup>-1</sup> and calcining at 400 °C for 2 h.

The crystalline phases of the samples were identified by X-ray diffraction (XRD) using a rotating-target Japan Rigaku D/Max-rB X-ray diffractometer equipped with graphite monochromatized Cu K $\alpha$  radiation ( $\lambda = 1.5406$  Å). The operation voltage and current were 40 kV and 80 mA, respectively. The morphologies of the samples were examined by transition electron microscopy (TEM, Hitachi, Model H-800) with an accelerating voltage of 200 kV. TEM samples were prepared by dropping the ethanol dispersion on a carbon-coated copper grid. Thermal gravimetric analysis (TGA) of the as-synthesized sample was carried out on a Shimadzu TA-50H thermal analyser at a heating rate of 10 °C min<sup>-1</sup> from room temperature to 800 °C in air. Optical absorption spectrum was recorded on a Shimadzu UV-2401PC UV-vis recording spectrophotometer in ethanol with the wavelength rang of 200-800 nm at room temperature.

# 3. Results and discussion

The rod-like nickel dimethylglyoximate precursor was obtained by the reaction between  $NiSO_4 \cdot 6H_2O$  and dimethylglyoxime in ethanol and aqueous solution. Then 1D arrays of NiO nanoparticles were obtained by calcining the precursor. To study the influence of temperature on morphologies of NiO, some experiments were investigated by calcining the precursor at different conditions.

The thermal behavior of the obtained nickel dimethylglyoximate precursor was investigated with thermal gravimetric analysis (see Fig. 1). The TG curve shows that nickel dimethylglyoximate precursor starts to decompose at about 255 °C. The major weight loss happens rapidly between  $\sim 300$ 

100 90 80 Neight loss / % 70 60 50 40 30 20 0 100 200 300 400 500 600 700 800 Temperature (°C)

Fig. 1. TGA curve of the obtained nickel dimethylglyoximate precursor.

and ~385 °C. The first weight loss is mainly attributed to the decomposition of the nickel dimethylglyoximate, whereas the second one may be ascribed to two factors. One is the decomposition of the nickel dimethylglyoximate and the other is due to the air oxidation of Ni above 300 °C. Experiment results show the decomposition mixture contains Ni, NiO and nickel precursor at 300 °C. The total weight loss is about 25.51%, which is close to the theoretical value. The reaction is completed by 385 °C. Therefore we choose 400 °C as the calcining temperature.

Fig. 2 shows the XRD patterns of the as-calcining 1D arrays of NiO nanoparticles at different conditions. The diffraction angle and intensity of the characteristic peaks of the samples are well consistent with those of the standard JCPDS card no. 47-1049. All diffraction peaks can be perfectly indexed to the cubic structure crystalline NiO and readily indexed as (111), (200) and (220) crystal planes. No characteristic peaks of impurities or other precursor compounds were observed. XRD peaks are markedly broadened at relatively lower temperature and in shorter time, which suggests that the particle size of ascalcining NiO increases with increasing the calcining time and temperature. Evaluated from the Debye–Scherrer formula, the average sizes of the obtained NiO particles at different calcining temperature and time are 17.6, 45.2, 35.3, 70 nm, respectively.

The TEM images of the precursor and the oxide are shown in Fig. 3. Fig. 3(a) is a TEM image of the as-synthesized precursor at room temperature. It can be seen that the nickel dimethylglyoximate precursor displays rodlike morphology with an average diameter of 400 nm and length of several micrometers. Fig. 3(b) and (c) shows the morphology of NiO obtained at 400 °C for 2 h, and NiO nanoparticles connected along the original directions of the rodlike precursor are observed. The observed average particle size is about 18 nm, which is consistent with the XRD result. The arrays of NiO nanoparticles could be ascribed to the shape confinement of the precursor. The inset of Fig. 3(c) is the corresponding selected area diffraction (SAED) pattern of the sample. ED patterns



Fig. 2. XRD patterns of NiO samples calcining at different conditions. (a) 400 °C, 2 h; (b) 400 °C, 4 h; (c) 500 °C, 2 h; (d) 700 °C, 2 h.



Fig. 3. TEM images and SAED pattern of samples: (a) the precursor of nickel dimethylglyoximate; (b and c) NiO obtained at 400 °C for 2 h, inset was the corresponding SAED pattern; (d) NiO obtained at 400 °C 4 h; (e) NiO obtained at 500 °C for 2 h, inset was the image with large magnification; (f) NiO obtained at 700 °C for 2 h.

recorded on different particles were essentially the same and the diffraction rings match the XRD peaks very well, which indicates that the nanoparticles are polycrystalline. To study the thermal stability of one-dimensional NiO arrays, we calcined nickel dimethylglyoximate precursor at different time and temperature. From the Fig. 3(d)–(f), we can see that the size of the NiO nanoparticles increases as the increase of calcining time and temperature. When the calcining temperature reaches 700 °C, the image indicates that NiO nanoparticles present apparent aggregation due to sintering (see Fig. 3(f)). The calcining temperature and time have less effect on the morphology of the NiO arrays and the particle sizes of different samples are consistent with the XRD results, respectively.

Fig. 4 shows the optical absorption spectrum of the NiO nanoparticles calcined at 400  $^\circ$ C for 2 h. The strong absorption



Fig. 4. Optical absorption spectrum and  $(Ah\nu)^2 - h\nu$  curve (inset) for NiO nanoparticles.

in the UV region is attributed to band gap absorption in NiO [21]. It is well known that optical band gap  $(E_g)$  can be calculated on the basis of the optical absorption spectrum by the following equation

$$(Ah\nu)^n = B(h\nu - E_g)$$

where  $h\nu$  is the photo energy, A is absorbance, B is a constant relative to the material and n is either two for direct transition or 1/2 for an indirect transition [22]. Hence, the optical band gap for the absorption peak can be obtained by extrapolating the linear portion of the  $(Ah\nu)^n - h\nu$  curve to zero. The inset of Fig. 4 shows the  $(Ah\nu)^2$  versus  $h\nu$  curve for the sample. The band gap of the NiO particles is about 3.51 eV, which is similar to the value (3.55 eV) reported by Boschloo [23]. No linear relation was found for n = 1/2, suggesting that the as-prepared NiO nanoparticles are semiconducting with direct transition at this energy. In the long-wavelength side, the long tail of the absorption is probably due to the scattered radiation of nickel oxide clusters of nanoparticles.

# 4. Conclusions

In summary, a simple and facile method to synthesize arrays of NiO nanoparticles by the thermal treatment of the rodlike nickel dimethylglyoximate precursor is developed. The calcining time and temperature have less effect on the morphology of NiO arrays. With increasing the calcining time and temperature, the size of particles became larger. The optical absorption band gap of the NiO nanoparticles was 3.51 eV. We expect that this method of precursor thermal decomposition can be extended to synthesize 1D arrays of other kinds of metal oxides using corresponding precursors.

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