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# Large-scale and shape-controlled synthesis and characterization of nanorod-like nickel powders under microwave radiation

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#### ABSTRACT

The nanorod-like nickel powders were fabricated via hydrothermal liquid phase reduction route under microwave irradiation with hydrazine hydrate as a reducing agent as well as polyvinyl alcohol as a dispersant and/or structure directing agent. The morphology and structure of as-prepared products could be easily tuned by adjusting process parameters such as pH value and microwave irradiation time. The resulting materials were characterized by X-ray diffraction (XRD), scanning electron microscope, transmission electron microscopy and selected-area electron diffraction (SAED). The results demonstrated that pure nickel powders with face-centered cubic (fcc) structure were prepared at relatively mild condition and no characteristic peaks of nickel oxide in the XRD pattern were found. The phenomenon of lattice expansion for Ni powders was explained in details according to the XRD theory. As-prepared Ni sample was of obvious shape anisotropy with length diameter ratio of 5. Magnetic measurements shown that the magnetic properties of nanorod-like (fcc) Ni powders were quite different from those of hexagonal closed-packed (hcp) Ni nanoparticles. Furthermore, it had more strong ferromagnetic properties than that of Ni powders both bulk and nanoparticles.

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## 1. Introduction

Metal nanoparticles with unique nanostructures have recently been subject to extensive research because of their many exotic performances, for instance small size effect, surface effect, quantum size effect, catalytic effect, volume effect, etc. [1–5], which endow them with great application potentials in various fields, such as magnetic recording, electronic devices biological labeling, catalysts, sensors, electrode materials and so on [6-10]. Therefore, research interests on the methodology of nanomaterials have intensified recently due to the fact that the morphology for materials was dependent on the method of preparation in a sense. At present, a host of methods have been used to synthesize nickel nanoparticles with different morphologies, such as needlelike [11] and microspherical [12,13] nickel nanoparticles, respectively. Hollow nickel spheres [14] prepared by means of polymer template method, 3D dandelion-like nickel nanostructures [15] manufactured by template-free method, nanowires [16] synthesized under microwave-hydrothermal reaction was reported previously. With respect to preparation procedure of

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metal nanoparticles, facile, rapid, clean and inexpensive methods were desirable. Microwave-hydrothermal techniques provided a clean, inexpensive, and convenient methodology of heating, so that it usually afforded higher yields and shorter reaction time [16,17]. The combination of microwave and hydrothermal techniques has been used in the last two decades for the rapid synthesis of numerous ceramic oxides [18,19], porous materials [20,21] and metal powders [22,23]. It has been confirmed that microwave-hydrothermal techniques were becoming an increasingly prevalent heating method for nanomaterials synthesis [16,17]. In this regard, nanorod-like Ni powders with fcc structure were successfully prepared via a simple and facile microwave hydrothermal reaction at relatively low temperature in the paper. It was well known that the yield of nanocrystals was lower than that of bulk materials due to the fact that concentrations of precursors for materials synthesis procedure were less than  $0.01 \text{ mol } L^{-1}$  [24–28]. Gram-scale products could be facilely obtained owing to the fact that the concentration of precursor was high  $(0.5 \text{ mol } L^{-1})$  in the paper. The results demonstrated that as-obtained materials were pure phase of nanorod-like Ni powders with fcc structure by means of XRD, TEM and SAED. The nanorod-like Ni powders exhibited significantly enhanced ferromagnetic characteristics in comparison with bulk nickel and nickel nanoparticles.

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#### 2. Experimental

### 2.1. Preparation of nickel powders

Nanorod-like nickel powders were fabricated by a liquid phase reduction with hydrazine hydrate. Nickel acetate tetra-hydrate. polyvinyl alcohol and hydrazine hydrate were used as nickel source, dispersant and/or structure directing agent and reductant. respectively. Typically, 25 ml of solution with certain amount polyvinyl alcohol was heated to 75 °C and pH value was adjusted to 11 by 2 mol L<sup>-1</sup> sodium hydroxide solution. The requisite amount of hydrazine hydrate (N<sub>2</sub>H<sub>4</sub>·H<sub>2</sub>O) was added into the solution mentioned above with stirring. The as-obtained solution was instantaneously mixed with solution of nickel acetate tetrahydrate and vigorously stirred for 2 min. Then the resulting solution was transferred to a 60 ml Teflon autoclave for microwave heating under 85 °C for 20 min. A microwave digestion system (WX-4000) with controllable temperature units made by Shanghai Yi-Yao Instruments (Shanghai) was used for the preparation of nanorod-like nickel powders. The metal powders were obtained after filtered, washed with deionized water three times, dried at 50 °C for 24 h and grinded.

#### 2.2. Characterization

X-ray diffraction (XRD) measurement was carried out at room temperature using a DX-2000 X-ray powder diffractometer with Cu Ka radiation source ( $\lambda = 0.15418$  nm) and a scanning speed of 3°/min. The accelerating voltage and emission current were 40 kV and 30 mA, respectively. Transmission electron microscope (TEM) images and the selected area electron diffraction (SAED) patterns were recorded on a Philips TECNA120 electron microscope at an accelerating voltage of 200 kV. The scanning electron microscope (SEM) images were obtained using a KYKY-2800B microscope. A small amount of the solid sample was dispersed onto the conductive resin adhered to the metal substrate holder in the air for SEM measurements. Magnetic measurements were carried out at 300 K using a vibrating sample magnetometer (VSM, LS307-9309, USA) with a maximum magnetic field of 20 kOe.

#### 3. Results and discussion

The two XRD patterns of the nickel nano-rods were shown in Fig. 1. Three characteristic peaks at  $2\theta$  (44.73, 52.0, and 76.52) could be indexed to face centered cubic (fcc) nickel (JCPDS 01-1260).



**Fig. 1.** XRD patterns of two typical samples. Addition of 10 ml 0.5 M nickel acetate and 1.0 g PVA at 85 °C in absence of additional  $N_2$  (a) and in presence of additional  $N_2$  (b) under microwave radiation.

The corresponding Miller indices were marked for each diffraction peak with Miller indices  $(1 \ 1 \ 1)$ ,  $(2 \ 0 \ 0)$ ,  $(2 \ 2 \ 2)$  and  $(4 \ 2 \ 0)$  observed in the  $2\theta$  range from  $35^{\circ}$  to  $80^{\circ}$  in Fig. 1a, revealing that the sample was pure fcc nickel. Also, under nitrogen protective atmosphere, similar results reappear in Fig. 1b. Only position of the three peaks slightly shifted to low angle due to the difference of lattice constant for Ni powders. And the three peaks broaden due to smaller grain size. No peaks of the hydroxides, the oxides of nickel and any others were detected in Fig. 1a and b. The results were probably ascribed to the observed phenomenon that N<sub>2</sub> gas was created and bubbled up continuously during the reaction. It could be suggested that the N<sub>2</sub> gas produced during the reaction might autocreate an inert atmosphere, and therefore introduction of additional N<sub>2</sub> was unnecessary for the preparation of nickel nanorod-like in accordance with previous literature [11].

Although the lattice constant  $a_0$  was hardly changed, the occurrence of the lattice expansion or contraction (so-called lattice distortion) for metal nanoparticles based on size and shape effect has been reported previously. Apai et al. [29] reported that lattice parameter for Ni nanoparticles was of contraction. Experiment result by Lu et al. [30] showed that lattice parameter has the character of lattice expansion for Ni nanoparticles. The phenomenon for lattice expansion of Ni nanoparticles was also confirmed by Wei et al. [31]. In theory, the simulation experiment with molecular dynamics method indicated that lattice distortion of contraction or expansion mainly came from size effect and originated from between shape effect and the interfacial structure secondly [32–36]. This phenomenon could be explained according to the thermodynamic theory [31].

As for slight shift to lower angle for diffraction peaks in XRD, the result was the signature of increase in interplanar spacing of (*khl*) planes, implied that lattice distortion (lattice expansion) existed in nanorod-like Ni powders [37].

The calculation result by XRD theory indicated that the lattice parameter *a* (0.3532 nm) of the nanorod-like Ni powders for (1 1 1) planes was larger than the equilibrium value of the perfect single crystal Ni lattice parameter ( $a_0 = 0.3524$  nm). The value of lattice distortion  $\Delta a/a_0$  was equal to 0.0023, where  $\Delta a = |a - a_0|$ . The expansion of crystal cell volume  $\Delta V/V_0$  was ca. 0.68%, where  $\Delta V = |V - V_0|, V = a^3, V_0 = a^3_0$ , respectively. The surface energy and surface tension were responsible for crystal cell volume expansion. Observed lattice expansion for nanorod-like Ni powders could be explained qualitatively, on the basis of a theoretical model of linear elasticity [31,37,38]. The lattice distortion was derived from interfacial energy and mutual surface tension of the nanorod-like Ni powders. The accessional pressure  $\Delta p$  due to the curved surface could be expressed with the following formula

$$\Delta p = \frac{2\sigma}{d} \tag{1}$$

where  $\sigma$  was the surface tension, and d the isodiametric radius of the nanorod-like Ni powders. The compression ratio  $\kappa$  at a given temperature could be formulized by

$$c = -\frac{V^{-1}\Delta V}{\Delta p} \tag{2}$$

k

With respect to the fcc structure, the cell volume *V* was equal to  $a^3$  and the cell volume change ( $\Delta V$ ) might be calculated by

$$\Delta V = 3a^2 \Delta a \tag{3}$$

Combined with Eqs. (3)-(5), the variation of the lattice parameter could be expressed as

$$\Delta a = -\frac{2a\kappa\sigma}{2d} \tag{4}$$

As for formula (4), the expansion of lattice parameter was in direct proportion to the surface tension and the reciprocal of the grain size, ignoring the small change of the compression ratio.

It was well known that the energy state was improved for the whole system owing to the existence of grain boundary in noncrystalline material. The change of free energy  $\Delta G(T, d) = \gamma A$ , where  $\gamma$  was grain boundary energy, A grain boundary area, d the grain size and T thermodynamics temperature, respectively. It was supposed that the nanorod-like Ni powders were treated by the isodiametric spherical grains, and then the change free energy  $\Delta G(T, d)$  could be expressed as

$$\Delta G(T,d) = 4\Omega \frac{\gamma}{d} \tag{5}$$

where d was grain size (isodiametric spherical),  $\Omega$  atomic volume.

The increase of free energy state would inevitably lead to changes in the lattice structure, which were mainly enhancement of the solubility of vacancies in a solution. The incremental value could be calculated by the Gibbs–Thomson equation [39]

$$\Delta C(T,d) = \frac{4\Omega\gamma C_0}{kTd} \tag{6}$$

where k was the Boltzmann constant,  $C_0$  the equilibrium concentration of vacancies in a coarse grain. Due to the fact that the vacancies were substitutionally situated in the Ni phase, the increase of the concentration for vacancies with rough surface (porosity effect) and granularity reduce would give rise to an increase of lattice spacing [31,34]. Combining Eqs. (4)–(6), it was reasonable to conclude that the vacancy concentration in the lattice would increase owing to the decrease of grain size and the increase of surface roughness (surface pore effect). On the one hand, due to high solidification rate under microwave irradiation process, a number of vacancies were formed easily in crystal growth process. On the other hand, a mass of vacancies was not dissolved out duly in the solid metals. As a result, high vacancy concentration occurred in the nanorod-like Ni powders. In other words, the enhancement of vacancy concentration on the lattice positions was responsible for the lattice expansion and the increase of the lattice constant in the interstitial solid solution nanorod-like Ni powders prepared by microwave radiation method.

Fig. 2 showed typical SEM image of nanorod-like Ni powders obtained by microwave–hydrothermal reaction. The low-magnification image in Fig. 2 showed that the resulting materials consist entirely of nanorod-like Ni powders. The high-magnification image in Fig. 2 (inset) showed the morphology with single nanorod-like

Ni in many directions. They revealed that clear and well-defined nanorod-like structures with loose texture for Ni powders were dispersed well. The loose texture on the surface for nanorod-like Ni powders was confirmed by both the HRTEM and N<sub>2</sub> Nitrogen adsorption/desorption isotherms as well. The length of the nanorod-like nickel powders was  $0.5-2 \mu$ m and the average cross dimension was ca. 5. In order to understand the atomic composition of nanorod-like Ni powders and to confirm the oxide form of obtained nickel nanorod-like powders, SEM-EDS analysis was carried out. The corresponding spectra of different areas for nanorod-like Ni powders were presented as Fig. 2 (left). This clearly supported the XRD results (see Fig. 1) and simultaneously affirmed formation of pure nickel metals.

The Ni ion concentration could be used for tuning the size and shape of the Ni nanoparticles. The Ni<sup>2+</sup> concentration controlled the degree of nucleation of Ni powders in solutions and modified crystal growth by influencing the transport of species. The size and shape for the different precursor concentration conditions were shown in Fig. 3. Visual examination revealed that the Ni powders were 400 nm in diameter with spherical shapes for Fig. 3A and B. However, partial aggregation of Ni nanoparticles was obviously seen. As the Ni ion concentration increased to 1.0 mol  $L^{-1}$ , Ni bulk with peanut-like shape were formed owing to the piecemeal ruin of Ni nanorod-like powders and the mean size of Ni powders was ca. 5 µm (Fig. 3C). Moreover, the aggregation phenomenon of Ni nanoparticles was observed, as compared with Fig. 3A and B. From the above analysis it was concluded that a low concentration of Ni ions was necessary for the formation of aggregation-free Ni nanoparticles under the microwave-hydrothermal synthesis. while the appropriate concentration of precursor was responsible for the formation of nanorod-like Ni powders due to orientation growth via nanoparticle heavy agglomeration.

Reaction temperature was considered as an important factor influencing the size and shape of Ni powders. As observed in Fig. 4 for the evolution of the size and shape of the Ni powders as a function of temperature, the Ni powders of size and shape were dependent on the temperature. At low temperature, e.g., 75 °C, regular nanoparticles with size less than 1  $\mu$ m could be synthesized as shown in Fig. 4A. The nanocrystals were almost spherical and seemed to consist of smaller grains. The inset for high magnification in Fig. 4A clearly confirmed that the nanoparticles of Ni powders consisted of smaller aggregates which were less than 200 nm. The irregular bulk particles could be obtained, along with the improvement of crystallinity at 95 °C and 105 °C, as shown in Fig. 4B and C. As for Fig. 4B, a small amount of nanorod-like Ni powders could be still observed, while a lot of Ni block powders



Fig. 2. Low magnification, high magnification (inset) SEM images and corresponding SEM-EDS of nanorod-like nickel powders.



**Fig. 3.** SEM micrographs of the size and shape for Ni powders prepared by different precursor concentration. The Ni<sup>2+</sup> ion concentrations in (A)–(C) were 0.1 mol L<sup>-1</sup>, 0.2 mol L<sup>-1</sup> and 1.0 mol L<sup>-1</sup>, respectively.

could be visualized at 105 °C for Fig. 4C. In the case of the reaction temperature, improving it, Ni powders tended to grow into larger irregular morphologies at designated reaction temperature.

TEM micrograph and SAED pattern of as-prepared nanorod-like Ni presented in Fig. 5. As-obtained sample exhibited a rod-shaped morphology and loose texture based on TEM. The SAED pattern showed diffraction rings agreed well with fcc Ni in the inset of Fig. 5, indicating reflection of a face centered cubic (fcc) structure; this result was also confirmed by means of X-ray diffraction. Tropism of the nanorod-like Ni powders and its size effect caused the widening of the diffraction rings. The rings were composed of many diffraction spots, which indicated that the nanorod-like Ni powders were polycrystalline.



**Fig. 4.** The SEM images of Ni powders with different microwave radiation temperature. The reaction temperatures in (A)–(C) were 75 °C, 95 °C and 105 °C, respectively. Scale bar of the inset in (A) was 1  $\mu$ m.

Nitrogen adsorption/desorption isotherms for nanorod-like nickel powders were depicted in Fig. 6. The curve was found to be of type V in nature as per the IUPAC classification and presented a H3 hysteresis loop, which was related to the type III isotherm in that the adsorbent–adsorbate interaction was weak, but was obtained with certain porous adsorbents. The Type H3 loop, which did not exhibit any limiting adsorption at high  $p/p^0$ , was observed with aggregates of plate-like particles giving rise to slit-shaped pores [38]. That was to say, those pores were actually rough surface pits. The results were consistent with TEM and SEM observation as well as lattice expansion for nanorod-like Ni powders. The results were also confirmed by pore size distribution (PSD) curve in Fig. 4 (inset). As for PSD, no dominant peak was found from 10 to 100 nm,



Fig. 5. TEM photograph and SAED pattern (inset) of nanorod-like nickel powders.



Fig. 7. Hysteresis loop of nanorod-like nickel powders.

indicating that nanorod-like Ni powders were of rough surface. In other word, there were some shallow pits on the surface of nanorod-like Ni powders, rather than through pores for porous materials.

The M-H loops of a typical sample were measured at 300 K and the result was presented in Fig. 7. The up-left inset of Fig. 7 was the magnified hysteresis loop at low applied field. The sample showed hysteresis behavior, revealing that the nanorod-like Ni powders were of ferromagnetism. The saturation magnetization  $(M_s)$ , remanent magnetization  $(M_r)$  and coercivity  $(H_c)$  for the sample were 44.2 emu/g, 19.4 emu/g and 240 Oe, respectively. The saturation magnetization  $(M_s)$  of the sample was very close to that of bulk nickel (55 emu/g) [40], indicating that those nanostructures possessed the metallic characteristic. Generally, the  $M_{\rm s}$  for nanoscale magnetic materials was lower than that of bulk material because the spin disorder on the surface and surface oxidation would significantly reduce the total magnetic moment [41]. Consequently, it was reasonable to explain the decrease of  $M_s$ for the nanorod-like Ni powders. Ultrafine ferromagnetic particles often exhibited greatly enhanced magnetic coercivity compared with the corresponding bulk material. Compared to the H<sub>c</sub> value of bulk Ni (ca. 100 Oe) [42] and that of hollow Ni nanometer spheres (ca. 102 Oe) at room temperature [43], as-obtained nanorod-like



Fig. 6. N<sub>2</sub> adsorption-desorption isotherm of nanorod-like nickel powders at 77 K.

Ni powders represented a much enhanced coercivity (ca. 240 Oe), which may be attributed to their special nanostructure with the reduced size and high shape anisotropy.

#### 4. Conclusions

In summary, nanorod-like Ni powders with fcc structure were successfully and easily prepared by microwave-hydrothermal reaction at considerably low temperature. The nanorod-like Ni powders exhibited significantly enhanced ferromagnetic characteristics than bulk nickel and nickel nanoparticles. This would be vital to their promising applications in engineering.

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