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Controllable synthesis of nickel dendritic crystals induced by magnetic field

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Abstract

We demonstrated in this paper a simple and easy method for the preparation of dendritic nickel crystals in an external magnetic field in boiling ethylene glycol (EG) solution. The structural features and morphology of the sample were investigated using powder X-ray diffraction (XRD), scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The values of saturation magnetization (M_s) and coercivity (H_c) of the dendritic crystals characterized by using a vibrating sample magnetometer (VSM) are 170.3 emu g^{-1} and 50.7 Oe, respectively. It was clear that the external magnetic field was the most important factor for controlling the morphology of the product.

Keywords: A. Magnetic materials; A. Nanostructures; B. Chemical synthesis; B. Crystal growth; C. X-ray diffraction

1. Introduction

Developing ways of tailoring the structure of materials on specific morphology has been one of the important goals of material scientists. The shape and size of inorganic materials are well-known to have great effect on their widely varying properties [1]. For example, the carrier motion of 1D magnetic Fe_2O_3 is restricted in two directions so that they are expected essentially to improve photochemical, photophysical, and electron-transport properties [2]. In recent years, much effort has been devoted to the fabrication of different magnetic materials with various shapes, such as nanoparticles, nanorods, nanotubes, microflowers, etc. [3–7]. Among the current shape-controlling techniques, there are many factors affecting the shape of the product, such as the internal structure of the product, external conditions of solvents, temperature, concentration of the reactants, the kinds of templates, etc. [8]. Up to now, to the best of our knowledge, few investigations have been reported about the synthesis of dendritic magnetic materials due to an external magnetic field used for the control of their morphologies.

A general method for the preparation of nano-scaled magnetic particles is through the rapid decomposition of corresponding metal carbonyl compounds in organic solvents, while using amine and oleic acid as surfactants to

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improve size dispersion and nanocrystal stability. This method can give high quality monodisperse magnetic particles [9–13]. Herein, we present a new one-pot reaction route to synthesize a type of magnetic material in boiling ethylene glycol solution. Induced by an external magnetic field, large-scale Ni dendritic crystals could be controllably synthesized in boiling ethylene glycol solution.

2. Experimental procedure

All chemicals used were of analytical grade and used as received without further purification. In a typical synthesis, 1 mmol $Ni(CH_3COOH)_2{\cdot}4H_2O$ was dissolved in 50 mL EG and was heated to 60 °C, then 0.25 mmol poly(vinyl pyrrolidone) (PVP, MM = 30,000) was added to the reaction mixture as a stabilizer. The reaction solution was heated slowly to the boiling point (197 °C). After refluxing about 15 min the color of the solution turned from green to grey black, indicating the formation of Ni crystals. The mixture was refluxed about 1 h in total and cooled to room temperature quickly. In addition, the overall experimental process was performed in an external magnetic field with a value of 280 Oe. The obtained black precipitate was centrifuged and washed with water and ethanol several times, then dried in air.

The as-prepared powder sample was characterized by XRD on an XRO-PERT-PRO (Netherlands) X-ray diffractometer with Cu Kα radiation (λ = 1.5406 Å). The morphology was determined by using a scanning electron microscopy (SEM) (JSM-5600LV) and a transmission electron microscopy (TEM) (JEOL JEM-2010EX). Magnetic properties of the product were investigated by using a vibrating sample magnetometer (Lake shore 7304 VSM).

3. Results and discussion

Fig. 1 shows an XRD pattern of the resulting product. The XRD spectrum of the as-prepared powder exhibits multiple intense peaks, and all the peaks can be perfectly indexed to crystalline Ni, not only in peak position but also in their relative intensity, indicting that the as-prepared powders are crystalline Ni. These peaks at the scattering angles (2θ) of 44.54°, 51.88° and 76.42° correspond to the reflections from the 1 1 1, 2 0 0 and 2 2 0 crystal planes, respectively, of the cubic phase of Ni. The lattice parameter for the unit cell of the Ni sample is calculated as a = 3.524 Å in good agreement with the known lattice parameter for crystalline Ni (a = 3.523 Å, JCPDS No. 87-0712). The crystallite size estimated from each diffraction peak using the Scherrer equation is $D_{1\,1\,1}$ = 26.7 nm, $D_{2\,0\,0}$ = 12.2 nm, $D_{2\,2\,0}$ = 12.9 nm.

The morphology of the sample was recorded by SEM and TEM with different magnifications as shown in Fig. 2. Fig. 2a shows a low magnification view of the as-prepared product. Fig. 2b shows that the product prepared in a magnetic field has an evident dendritic morphology, with an average diameter of 300–450 nm and an average length of several micrometers. The TEM image (Fig. 2c) shows a representative pattern of the resulting product, further revealing the dendritic structure. Careful observation finds the dendritic crystal is composed of nanocontacted

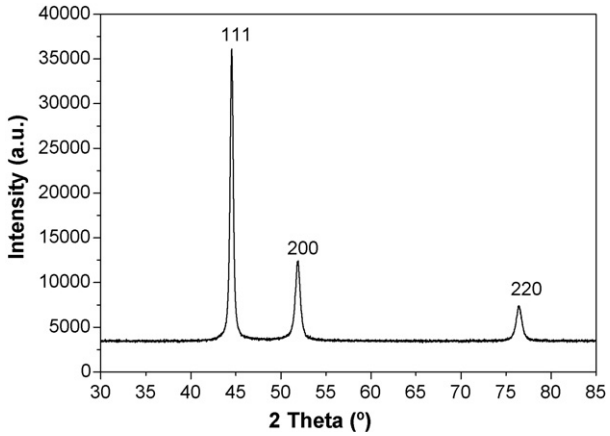

Fig. 1. Powder X-ray diffraction (XRD) pattern of the as-obtained Ni dendritic nanocrystals.

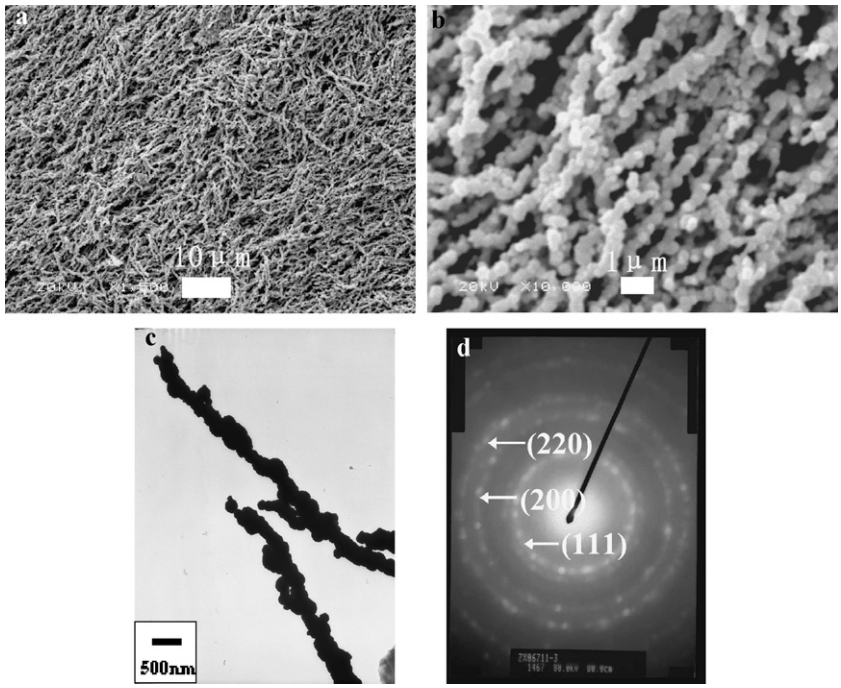

Fig. 2. SEM and TEM images of the sample prepared in an external magnetic field. SEM images of dendritic Ni crystal (a) and (b), TEM image of dendritic Ni (c), and SAED pattern (d).

subunits, which look a bit like pearls on a string. The selected-area electron diffraction pattern (SAED) from a single strand shown in Fig. 2d exhibits multiple intense rings composed of discrete spots, corresponding to the (1 1 1), (2 0 0) and (2 2 0) diffraction planes of cubical phase of Ni, which are consistent with the XRD results above. The multiple intense rings prove that Ni has a poly-crystalline nature.

In this experiment, EG itself acts not only as a solvent in the whole process but also as a reductant. At the boiling point, nickel acetate was slowly reduced into nickel nuclei. Since the freshly formed nuclei in the solution are unstable, they have a tendency to grow and were larger as the reaction time increased. In an external magnetic field, freshly formed nuclei grow along the direction of the applied magnetic field due to the dipolar interactions, leading to a dendritic structure. Remarkably, it is believed that the dendritic growth is kinetically controlled [14]. We have carried out a similar experiment without using an external magnetic field, and the spherical structures of pure Ni crystals are

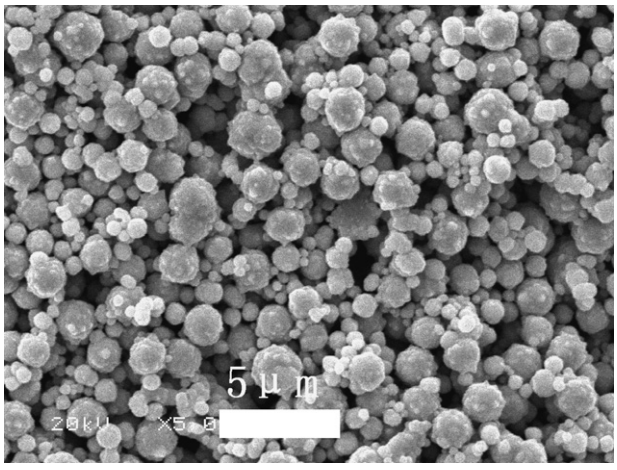

Fig. 3. SEM image of the sample prepared without using an external magnetic field.

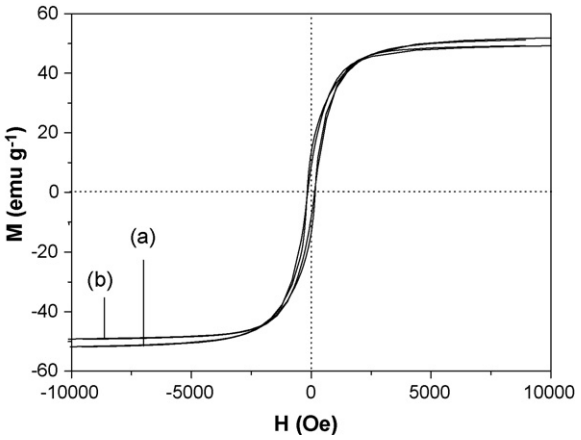

Fig. 4. Magnetic hysteresis loop of the resultant nickel measure at room temperature: (a) dendritic nickel and (b) spherical nickel.

obtained, as shown in Fig. 3. These results prove that the external magnetic field is a critical factor which influences the morphology of Ni crystals. In addition, it is noted that the concentration of the reactants do not have much effect on the size of final product, we suppose that the size of product is somewhat dependent on the different type surfactant [15], and detailed investigations are still being performed in our group.

Nickel is widely used as magnetic material, and its magnetic properties are greatly affected by the size, shape, crystallinity, etc. Fig. 4a shows the magnetic hysteresis loop of the resultant dendritic nickel measured at room temperature in an applied field of 10,000 Oe, showing a coercive force (H_c), saturation magnetism (M_s) and remnant magnetism (M_r) of ca. 170.3 Oe, 50.7 emu g^{-1}, 13.3 emu g^{-1}, respectively. The magnetic behavior of the dendritic structure is strongly dependent on the orientation between the applied magnetic field and a single strand (not known here). Comparing that with spherical nickel (Fig. 4b) (146.1 Oe, 48.8 emu g^{-1}, 8.9 emu g^{-1}), a better enhanced coercive force and remnant magnetism are seen for the dendritic nickel. While, relative to that of the bulk nickel (100 Oe, 55 emu g^{-1}, 2.7 emu g^{-1}), the reduced value of M_s for both samples prepared in and not in a magnetic field could be due to the inclusion of some non-magnetic residues from the production process as well as due to the increased interactions between the nanocontacted subunits, which reduce the total magnetic moment [16].

4. Conclusion

In summary, we have described a shape-controlled synthesis of dendritic nickel crystal in boiling ethylene glycol solution. Induced by an external magnetic field, the morphology of the product could be perfectly controlled and the results are highly reproducible in our experiment. It is expected that other nano-sized magnetic materials can also be prepared by this simple and versatile method.

Acknowledgments

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