Formation of one-dimensional nickel wires by chemical reduction of nickel ions under magnetic fields†

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One-dimensional wires of metallic nickel with width fluctuation were prepared in the presence of magnetic fields, and the chemical reduction of $[Ni(N_2H_4)_x]^{2+}$ under magnetic fields was investigated.

Generally, magnetic field is recognized as an important parameter for studying the physical properties of materials.[1–5] In recent years, magnetic field, similar to the conventional reaction conditions such as temperature and pressure, has been introduced as a new tool to control chemical reactions and materials synthesis in several systems, such as electrochemical process,[6,7] solid state reactions,[8,9] hydrothermal synthesis,[10] and chemical vapour deposition,[11] especially in preparing ordered nanoarrays. Up to now, several groups have employed magnetic fields to achieve the assembly of magnetic nanoparticles. For example, our group introduced magnetic fields in a hydrothermal system to synthesize one-dimensional wires of acicular nickel nanocrystallites.[12] Williams *et al.* have reported the millimeter scale alignment of cobalt ferrite nanoparticles ($CoFe_2O_4$) functionalized microtubules with magnetic fields.[13] Similarly, magnetic field directed self-assembly of Fe_3O_4 nanoparticles has proved to be an efficient method for obtaining long range ordering structures.[14] However, most of those researches were focused on the variation of aggregate morphology from the point of view of assembly, little attention has been paid to special features of the chemical reactions occurring under magnetic fields.

It is well known that nickel is an important anisotropic ferromagnetic material. One-dimensional nickel nanostructures have attracted intensive interest owing to their potential applications in magnetic sensors and memory devices.[15–17] Herein, we report the chemical reduction of nickel ions and formation of one-dimensional structures in a solvothermal system under weak magnetic fields, and the chemical reaction involved is taken as an example to study the effect of weak magnetic fields on the nucleation and growth of magnetic metal. Furthermore, a schematic illustration is also given to tentatively explain the reduction process of $[Ni(N_2H_4)_x]^{2+}$ to Ni under a magnetic field.

A facile solvothermal synthesis route was developed to confirm that the nucleation and growth of nickel may occur along the magnetic line of force, instead of in the whole reaction system. Nickel chloride and polyvinylpyrrolidone (PVP, K-30) in a mixed solvent of distilled water and ethanol formed a homogenous solution, which benefited the slow release of nickel ions, and the separation of the growth step from the nucleation step.[18] Then nickel ions were reduced to nickel metal by hydrazine. A detailed report on the effect of the quantities of hydrazine hydrate and PVP used , as well as solvent proportion *etc.* will be reported in a full paper.

Fig. 1 shows XRD patterns of ZF (prepared without a magnetic field), $AF_{0.25T}$ (prepared with a 0.25 T magnetic field) and $AF_{0.40T}$ (prepared with a 0.40 T magnetic field) samples. All the reflection peaks can be well indexed as face-centered cubic Ni (PDF standard cards, JCPDS 01–1260, space group *Fm*3*m*). No impurities such as NiO or $Ni(OH)_2$ were detected in the patterns, which implies phase-pure cubic Ni can be obtained under the current synthetic route. The crystallite size of ZF sample (60 nm) was larger than that of $AF_{0.25T}$ sample (35 nm), calculated by Scherrer's equation from the full width at half-maximum of (111) reflection. The intensity ratio of (111) peak to (200) peak increased with the increase of magnetic field strength, indicating a preferential orientation of some Ni grains in the one-dimensional wires, and became more distinct when the magnetic field was increased. These results suggested that the nucleation and growth of nickel crystallites could be influenced by magnetic fields. The wires were too large to be characterized by high-resolution transmission electron microscopy (HRTEM), and further investigations of the wires are under way.

The Field Emission Scanning Electron Microscopy (FESEM) images of nickel samples are shown in Fig. 2 and Fig. 3. Without a magnetic field applied, only spherical particles with an average diameter of about 350 nm can be observed (Fig. 2a). It is interesting that one-dimensional nickel wires (Fig. 2b and Fig. 3) were obtained as magnetic fields were applied. Fig. 3d clearly shows a one-dimensional nickel wire with width fluctuation which

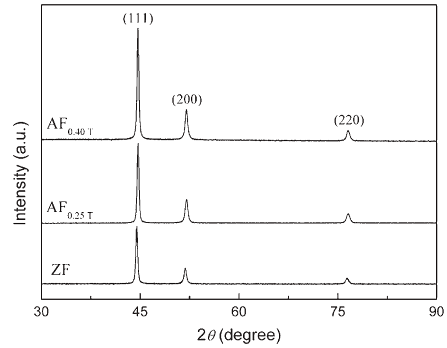

Fig. 1 XRD patterns of ZF, $AF_{0.25T}$ and $AF_{0.40T}$ samples.

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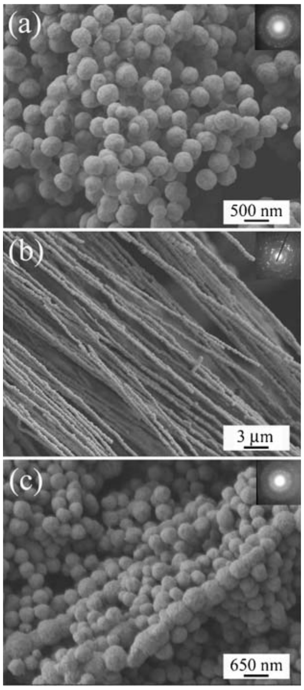

Fig. 2 SEM micrographs of products prepared under different conditions: (a) ZF sample; (b) $AF_{0.25T}$ sample; (c) The ZF sample with a postsynthesis magnetic alignment. The upper right insets display the corresponding SAED pattern.

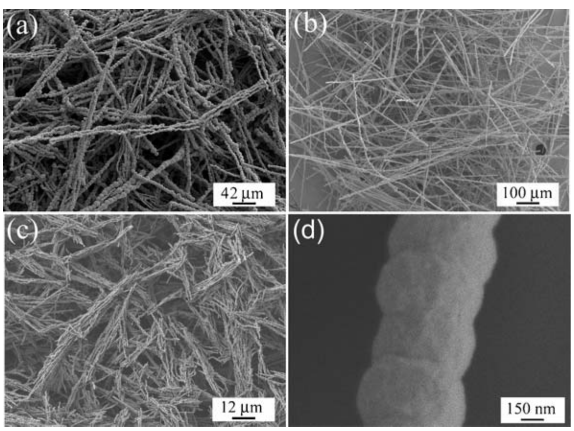

Fig. 3 SEM micrographs of products prepared under different magnetic fields: (a) $AF_{0.10T}$ sample; (b) $AF_{0.25T}$ sample; (c) $AF_{0.40T}$ sample; (d) a higher magnification image of a wire in (b).

is not a simple assemblage of particles. Furthermore, no isolated spherical nickel particles were observed in the AF samples. Compared with the polycrystalline diffraction rings of the ZF samples (Fig. 2a, insert; Fig. 2c, insert), the selected area electron diffraction pattern (SAED) of $AF_{0.25T}$ consists of diffraction rings of low intensity and spots of strong intensity simultaneously, revealing that there would be some large grains or a preferential orientation of some grains in the one-dimensional wires (Fig. 2b, insert). Combined with the results of the XRD analysis, it is deduced that some Ni grains would have a preferential orientation in the one-dimensional wires when magnetic fields were applied in the chemical reduction of nickel ions. Additionally, to better explore the effect of magnetic fields on the nucleation and growth of magnetic particles, a postsynthesis magnetic alignment experiment was carried out on the ZF sample. Compared with the one-dimensional wires in the AF samples, only few short chains can be viewed in the ZF sample with a postsynthesis magnetic alignment experiment (Fig. 2c), which further indicates that magnetic fields applied during the chemical reaction have influenced the nucleation and growth of nickel, instead of inducing a simple assemblage of particles. According to the observed results, we suggest that nickel may easily nucleate and grow along the magnetic lines of force rather than randomly in the reaction vessel, forming wires rather than particles or aggregate spheres. Since paramagnetic metal ions are attracted toward the maximum field,[19] when a magnetic field is applied, the complex $[Ni(N_2H_4)_x]^{2+}$ preferentially migrates to the magnetic line of force due to magnetic attraction and then $[Ni(N_2H_4)_x]^{2+}$ aligns along the magnetic line of force. As a result, the chemical reduction of $[Ni(N_2H_4)_x]^{2+}$ may occur along the magnetic line of force (Fig. 4), leading to the formation of one-dimensional parallel wires. From SEM observation it is found that wires in $AF_{0.10T}$ and $AF_{0.25T}$ samples are obviously longer but fewer than those of the $AF_{0.40T}$ sample, and the length variation can be viewed in Fig. 3. Since the nuclei density could be increased with an increase in the density of the magnetic lines of force, the length of wires would decrease because the amount of Ni remains constant in the reaction systems. This may explain why the length and quantities of these wires change with the variation in magnetic intensity. Fig. 3b shows one-dimensional wires obtained with the $AF_{0.25T}$ sample; the wires are straight and not interconnected. In the $AF_{0.25T}$ sample, only partially ordered wires can be observed (Fig. 2b), since the ultrasonic processing disordered the alignment of the parallel nickel wires. But no broken wires are observed, which indicates a strong force existing in the wires, making the wires stable. Since magnetic particles could be magnetized by magnetic fields, it is reasonable to deduce that one-dimensional wires would also appear in the ZF sample with a postsynthesis magnetic alignment due to magnetic dipole interaction. Actually, after ultrasonic processing, only few short chains were viewed in the ZF sample with a postsynthesis magnetic alignment under a 0.25 T magnetic field for six hours, while stable wires could still be clearly observed in the AF samples after ultrasonic treatment, which further demonstrated that an applied field during the chemical reaction had changed the magnetic structure in one-dimensional wires.

The magnetic properties of materials are believed to be highly dependent on the sample morphology, crystallinity, magnetization direction, *etc.*[18] Thus, a remarkably enhanced ferromagnetic property of the as-prepared one-dimensional nickel wires, compared to that of Ni microspheres, should be supposed. Fig. 5 shows *M–H* hysteresis loops of the products measured at room

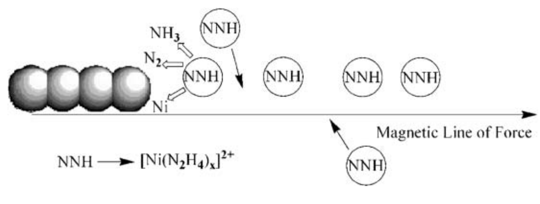

Fig. 4 Schematic illustration showing the reduction process of $[Ni(N_2H_4)_x]^{2+}$ to Ni in the presence of an applied magnetic field.

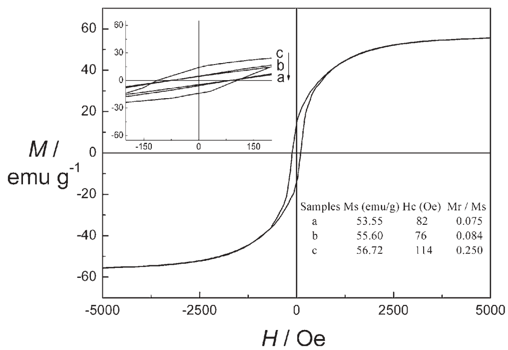

Fig. 5 The hysteresis loops measured at 305 K for the $AF_{0.40T}$ sample. The upper left inset shows the hysteresis loops of (a) ZF sample; (b) ZF sample with a postsynthesis magnetic alignment; (c) $AF_{0.40T}$ sample. Magnetic properties of the three samples are summarized in the lower right inset.

temperature (305 K). There are few differences between the magnetic properties of the ZF sample and the ZF sample with a postsynthesis magnetic alignment. Compared to the H_c value of the ZF sample (82 Oe) and to that of the ZF sample with a postsynthesis magnetic alignment (76 Oe), the $AF_{0.40T}$ sample exhibits significantly enhanced coercivity (114 Oe). Consistently, the value of reduced remanence (M_r/M_s) of the $AF_{0.40T}$ sample (0.250) is larger than that of the ZF sample (0.075) and that of the ZF sample with a postsynthesis magnetic alignment (0.084). Accordingly, it is reasonable to conclude that a postsynthesis magnetic alignment can not affect magnetic structure or then magnetic properties as applied magnetic fields do in chemical reactions. The improved magnetic properties of the $AF_{0.40T}$ sample may be due to the magnetic structure variation in one-dimensional nickel wires. As discussed above, the nucleation and growth of nickel along the magnetic line of force determined the one dimensional wires formation. Therefore, it is expected that a weak magnetic field could be developed as an important tool to control the structure and properties of materials, especially magnetic materials. Although, the applied field in our study was too weak to change electron spin, and then alter reaction mechanism, it is clear that it can change growth behavior and magnetic properties of magnetic materials.

In summary, the formation of one-dimensional nickel wires by chemical reduction of $[Ni(N_2H_4)_x]^{2+}$ under magnetic fields was investigated. One-dimensional wires of metallic nickel with lengths up to several hundreds of microns and an average diameter of about 350 nm were prepared in the presence of magnetic fields, while without an applied magnetic field metallic nickel microspheres were obtained. Based on our experimental results, it is concluded that a magnetic field applied during the chemical reaction can synchronously influence both the nucleation and the parallel growth of nickel. Furthermore, the possible growth model that the chemical reduction of $[Ni(N_2H_4)_x]^{2+}$ may easily occur along the magnetic lines of force instead of in the whole reaction system was proposed. It is suggested that weak magnetic fields could be developed as promising approaches to control the nucleation and growth of materials in chemical reactions, leading to the enhancement of magnetic properties.

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