Preparation and magnetic properties of nickel nanowires by reduction in ethylene glycol medium under the influence of magnetic field

Wanshuo Sun¹, Junsheng Cheng, Lankai Li, Shunzhong Chen, Kun Chang

Institute of Electrical Engineering, Chinese Academy of Science, Beijing 100190, China

E-mail: sunwanshuo@mail.iee.ac.cn

Abstract. Nickel nanowires have successfully been fabricated through a simple liquid reduction in ethylene glycol medium with a 0.3T magnetic field applied. The effect of uniform magnetic field and solvent on the morphology and the crystal structure of magnetic nickel were studied. Scanning electron microscope images and transmission electron scope images show that the effect of the external magnetic field on the morphology of nickel nanowires. X-ray diffraction shows the crystal structure of as-prepared products. And a energy dispersive spectroscopy and a vibrating sample magnetometer are used to analyze the composition and static magnetic properties. The results show that the straight wires with an average diameter of about 100 nm and a length of several microns were obtained and mainly composed by fcc structure in the solvent of ethylene glycol. Magnetic measurements show that the saturation magnetization of the as-obtained products in a 0.3 T external magnetic field is 36 emu/g, less than that of bulk nickel crystal, and the coercivity of them is 186 emu/g, larger than that of bulk crystal with the mole ratio of sodium borohydride to nickel sulfate is 1:1000. This kind of nanowires array has potential applications with the special one-dimensional structures.

1. Introduction

In recent years, nanoscale magnetic metal materials have attracted intensive interest because of their unique physical and chemical characteristics including catalytic properties and magnetic shape anisotropy and electronic properties. Among them because of their one-dimension structures magnetic metal nanowires are a topic of growing interest. Thus they have many promising applications, for example, high density magnetic storage media[1], optoelectronic devices[2], sensors, catalysts and conductive fillers. To date, different techniques have been developed to synthesize one-dimensional nanostructured magnetic metal materials such as electrodeposition into templates[3-6] and reduction in solution without the presence of a template agent[7-9].

This work reports a simple approach for the fabrication of nickel nanowires on a large scale through liquid reduction method at room temperature, assisted by external magnetic field. The method has the merits of simples process, low cost and good performance in which NiSO₄·6H₂O acted as nickel source, NaBH₄ and N₂H₄·H₂O acted as reducing agent, NaOH acted as pH-modifier. We present here the morphology of the product as-prepared and characterize their structure and magnetic properties in our effort to investigate the formation mechanism of nanowires.
2. Experiment

2.1. Preparation of Nickel Nanowires

In a typical experiment, all the reagents are of analytical grade and used as received without further purification.

First, nickel sulphate (Ni concentration of 0.5 M) was dissolved in ethylene glycol under mechanical stirring for 60 min at 40 °C. 6.5 ml 80% hydrazine was mixed with 10 g sodium hydroxide with stirring fast in order to prevent them from agglomeration and the slurry was dissolved to 6.5 ml deionized water. Sodium borohydride was dissolved in 5 ml de-ionized water. In the second step, the reactor containing the nickel sulphate was placed in a magnetic field. Then the sodium borohydride was added to the above solution and some dark grey precipitates appeared immediately. After that, the slurry was quickly added to the reactor. Then a large amount of dark grey precipitates appeared accompanied a large number of bubbles. The precipitates were separated from the solution by placing a magnet under the container and then washed several times with de-ionized water and ethanol to remove any reaction residuals. At last, the as-prepared products were obtained by drying wet precipitates in a vacuum system at 30 °C for 12 h.

2.2. Instruments and measurements

The morphology of the as-synthesized product was recorded by scanning electron microscope (SEM). Transmission electron microscope was used to determine the size of the samples as-prepared. The samples prepared were characterized by X-ray diffraction (XRD) at 50 kV and 30 mA using Cu Kα radiation on Bruker D8X-ray diffractometer. Magnetic hysteresis loops were measured using a Lake Shore 7410 vibrating sample magnetometer (VSM).

3. Results and discussion

In order to examine the influence of the solvent to the reactor, we performed the reaction in deionized water and ethylene glycol when the mole ratio of the sodium borohydride to nickel sulfate is 1:1000 without external magnetic field. Figure 1 shows the transmission electron microscope image of as-prepared products obtained in deionized water and ethylene glycol. It is found that the average particle size of the as-prepared products in ethylene glycol was 86 nm, less than in deionized water (215 nm). In ethylene glycol, its high viscosity compared with deionized water to some extent hindered the spread of nickel ion. At the same time, the ethylene glycol hydroxyl absorbed on the surface of the nickel particles and in a certain extent prevented the growth and conglomeration of the nickel particles.

Figure 1. TEM image of the nickel particles in different solvent (a) deionized water (b) ethylene glycol.

To further reveal the crystal structure of the products shown in Figure 1, X-ray diffraction analysis was carried out. Figure 2 shows the X-ray diffraction pattern of the as-prepared products obtained in deionized water and ethylene glycol at room temperature. It demonstrates that the crystal structure the as-prepared products in deionized water is the mixture of hcp structure and fcc structure. Compared with the peak positions of standard Ni (JCPDS, 04-0850) the diffraction peaks located at 2θ= 44.507°, 51.846°, 76.370° correspond to the (111), (200), (220) planes of fcc-Ni, respectively. Besides, hcp-NiOH (001), (100), (101), (102), (110), (111) have also been indicated. On the other hand, when the solvent is ethylene glycol the typical result for the as-obtained nickel array has been indicated in
Figure 2b. all the reflection peaks can be well indexed with fcc-Ni (space group Fm-3m(225); JCPDS card :04-0850), without impurity peaks.

Figure 2. The XRD pattern of the nickel particles in different solvents (a) deionized water (b) ethylene glycol.

Figure 3 shows the transmission electron microscope images of the as-obtained products in the absence of an external magnetic field when the mole ratio of the sodium borohydride to nickel sulfate is 1:10, 1:100, 1:500 and 1:1000, respectively. It is clearly seen that the average particle size of the nickel particles increased from 47 nm to 86 nm with the mole ratio of the sodium borohydride to nickel sulfate changed from 1:10 to 1:1000.

Nickel irons acted with a strong reducing agent sodium borohydride immediately. And nickel irons were reduced by sodium borohydride into Ni-B nano-particles that catalyzed the following reaction between nickel irons and hydrazine. When the mole ratio of sodium borohydride to sulfate nickel is 1:10, the larger amount of nickel irons were reduced by sodium borohydride. The as-obtained nano-particles acted as catalytic cores to catalyze the remaining smaller amount of nickel irons reduced by hydrazine. Thus the growth of the nickel particles in the last reaction was not sufficient and the size of nickel particles was smaller.

In order to further study if the morphology of the product as-prepared is related to the presence of the magnetic field, a sample has been prepared under similar conditions but in the absence of an external magnetic field. Figure 4 shows the morphology of the as-obtained products with and without an external magnetic field applied. It is clearly seen that the as-prepared products were spherical nickel particles and the nanowires were no longer observed in the absence of an external magnetic field while the nickel nanowires were obtained assisted by external magnetic field of 0.3 T. The nanowires were made up of spherical particles with averaging 100 nm in diameter. The length of the as-prepared nanowires is mostly in microscale. Thus it can be concluded that the external magnetic field is the key factor which control the morphology of products prepared. Figure 5 show the elemental composition of nickel nanowires was carried out on EDS. The EDS spectra show the presence of nickel without other impurities, indicating that the as-prepared products were pure.

Figure 4. The morphology of the products obtained in the presence of a magnetic field of (a) 0 T (b) 0.3 T.

Figure 5. The EDS spectra of the nickel nanowires.
Figure 6 and Figure 7 show the scanning electron microscope image and the transmission electron microscope image of the nanowires prepared by reduction in ethylene glycol in the presence of a magnetic field of 0.3T when the mole ratio of sodium borohydride to nickel sulfate is 1:10, 1:100, 1:500 and 1:1000, respectively. It is clearly seen that the morphology of the products were straight wires. As shown in Figure 3 and Figure 7, the average diameter of the nickel particles changed from 47 nm to 86 nm after by adding an external magnetic field of 0.3 T with the mole ratio of sodium borohydride to nickel sulfate of 1:10. In contrast the average diameter of as-obtained nickel nanowires with different mole ratio of sodium borohydride to nickel sulfate remained about the same.

Figure 6. SEM image of nickel nanowires when an external magnetic field of 0.3 T is applied with the mole ratio of sodium borohydride to nickel sulfate of (a)1:10 (b)1:100 (c)1:500 (d)1:1000.

Figure 7. TEM image of nickel nanowires when an external magnetic field of 0.3 T is applied with the mole ratio of sodium borohydride to nickel sulfate of (a)1:10 (b)1:100 (c)1:500 (d)1:1000.

Magnetization makes nickel particles aggregate along the magnetic line of force by magnetic field-induction whilst the nickel particles distributed in whole reaction system without an external magnetic field. Their self-assembly behavior along the magnetic line forms the final morphology of nanowires.

Figure 8 shows the X-ray diffraction pattern of the nickel nanowires at room temperature. The XRD pattern of as-prepared products with different mole ratio of sodium borohydride to nickel sulfate are similar. It demonstrates that the crystal structure of the nickel nanowires is fcc structure. As shown in Figure 8, the diffraction peaks locate at $2\theta= 44.507^\circ$, $51.846^\circ$, $76.370^\circ$, correspond to the (111),
(200), (220) planes of fcc-Ni, respectively (space group Fm-3m(225); JCPDS card 04-0850). It can be seen that the three main diffraction peaks of the crystal faces of (111), (200), (220) are strong and acute.

**Figure 8.** The XRD pattern of the nickel nanowires with the mole ratio of sodium borohydride to nickel sulfate of (a) 1:10 (b) 1:100 (c) 1:500 (d) 1:1000.

Figure 9 shows the M-H hysteresis loops of the as-synthesized products. It can be seen that the saturation and magnetization value $M_s$ of the nickel nanowires formed with the mole ratio of sodium borohydride to nickel sulfate of 1:10 and 1:1000 is 39 and 36 emu/g, respectively. And the coercivity value $H_c$ for the nickel nanowires is 184 and 186 Oe, respectively. The saturation value of bulk nickel is 55 emu/g. The saturation magnetization of the nickel nanowires at room temperature is decreased compared to bulk nickel. The decrease in $M_s$ for the nickel nanowires is usually ascribed to the formation of oxides on the particle’s surface and a decrease in crystallinity[10]. In addition, it also might be partly due to a very small quantity of impurities on the products. The coercivity increased greatly, compared to the value of bulk nickel (100 Oe)[11]. Some literatures have reported that the coercivity of the nanowires depends on the magnetization reversal mechanism that is related to many factors such as the diameter, the presence of the crystalline defects and dipolar interaction[9].

According to the chains of spheres of model, the coercivity $H_c$ under the fanning mechanism [12] is

$$ H_{c,a} = \frac{\mu}{R^3} (6K_n - 4L_n) $$

(1)

Where $\mu$ and $R$ are the dipole moment and diameter of the spherical particles, respectively, and $K_n$ and $L_n$ are the constant interaction between magnetic particles. It is clearly seen that the coercivity $H_c$ varies approximately as the reciprocal of the third power of the diameter, which means the coercivity $H_c$ decreases with the diameter of the nickel particles decreasing.

**Figure 9.** Hysteresis loops of the cobalt particles for different dosage of sodium borohydride.
4. Conclusion
Nickel nanowires have successfully been fabricated through a simple liquid reduction in ethylene glycol medium with a 0.3T magnetic field applied. The average size of the nickel nanowires prepared is about 100 nm in diameter and several microns in length. They crystallize with fcc structure in ethylene glycol medium. A less saturation magnetization and a larger coercivity for the nickel nanowires are achieved compared to the bulk nickel crystal with the mole ratio of sodium borohydride to nickel sulfate is 1:1000 by magnetic induction. It is suggested that this method could be a promising approach to obtain magnetic metal materials with one-dimensional structure and excellent magnetic properties.

Reference
[1] Wu M, Xiong Y, Jia Y, Niu H, Qi H, Ye J and Chen Q 2005 Magnetic Field-assisted Hydrothermal Growth of Chain-like Nanostructure of Magnetite Chemical Physics Letters 401 374-379
[2] Shi J B, Chen Y C, Lee C W, Lin Y T, Wu C and Chen C J 2008 Optical and Magnetic Properties of 30 and 60nm Ni Nanowires Materials Letters 62 15-18
[3] Pirota K R, Navas D, Hernández-Vélez M, Nielsch K and Vázquez M 2004 Novel Magnetic Materials Prepared by Electrodeposition Techniques: Arrays of Nanowires and Multi-layered Microwires Journal of Alloys and Compounds 369 18-26
[4] Imran M M A 2008 Structural and Magnetic Properties of Electrodeposited Ni Nanowires Journal of Alloys and Compounds 455 17-20
[5] Xu C L, Li H, Zhao G Y and Li H L 2006 Electrodeposition of Ferromagnetic Nanowire Arrays on AAO/Ti/Si Substrate for Ultrahigh-density Magnetic Storage Devices Materials Letters 60 2335-2338
[6] Nielsch K, Wehrspohn R B, Barthel J, Kirschner J, Fischer S F, Kronmüller H, Schweinböck T, Weiss D and Gösele U 2002 High Density Hexagonal Nickel NanowireArray Journal of Magnetism and Magnetic Materials 249 234-240
[7] Athanassiou E K, Grossmann P, Grass R N and Stark W J 2007 Template Free, Large Scale Synthesis of Cobalt Nanowires Using Magnetic Fields for Alignment Nanotechnology 18 695-700
[8] Niu H, Chen Q, Ning M, Jia Y and Wang X 2004 Synthesis and One-dimensional Self-assembly of Acicular Nickel Nanocrystallites under Magnetic Fields Journal of Physical Chemistry B 108 3996-3999
[9] Soumare Y, Dakhlaoui-Omran A, Schoenstein F, Mercone S, Viana G and Jouini N 2011 Nickel Nanofibers and Nanowires: Elaboration by Reduction in Polyol Medium Assisted by External Magnetic Field Solid State Communications 151 284-288
[10] Li X G, Murai T, Saito T and Takahashi S 1998 Thermal Stability, Oxidation Behavior and Magnetic Properties of Fe–co Ultrafine Particles Prepared by Hydrogen Plasma–metal Reaction Journal of magnetism and magnetic materials 190 277-288
[11] Hwang J H, Dravid V P, Teng M H, Host J J, Elliott B R and Johnson D L 1997 Magnetic Properties of Graphitically Encapsulated Nickel Nanocrystals Journal of materials research 12 1076-1082
[12] Zhou W, Zheng K, He L, Wang R, Guo L, Chen C, Han X and Zhang Z 2008 Ni/Ni3C Core–shell Nanochains and Its Magnetic Properties: One-step Synthesis at Low Temperature Nano letters 8 1147-1152