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Magnetic-field-assisted synthesis of Ni nanostructures: Selective control of particle shape

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ABSTRACT

Metallic nickel particles have been selectively synthesized via chemical reduction using a static magnetic field. Our results demonstrated that both reduction temperature and magnetic-field strength were the crucial factors in determining the final particle shapes. Upon subjecting a 0.02 T magnetic field, the particles change from sea urchin-like, through spherical, to one-dimensional (1D) in shape with decreasing the reduction temperature. In the synthesis of 1D structure, sphere-chains with fluctuant diameter are assembled under weaker magnetic field while relatively smooth nanowires are formed under stronger one. Thermal analysis of the particles was also investigated.

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1. Introduction

Ultrafine nanometer-sized nickel particles have been studied extensively over the past two decades due to their potential applications in optical, electronic, catalytic, and magnetic materials [1]. Most physical and chemical properties of these nanoparticles (NPs) depend on their size and shape. The shape control of nanostructures has therefore become a new and interesting research field, and considerable efforts have been devoted to prepare nanoscaled structures with special morphologies [2]. To date, it is still challenging to develop general synthesis strategies that enable us to systematically tailor the morphology and the structure of the Ni NPs to fine-tune their properties. As a well-established approach, wet chemical process has superior capability for controlling composition, size and shape of the NPs and is widely used to synthesize monodisperse nanostructures. Take for example the case of Ni nanostructures, which are usually synthesized via the reduction of Ni²⁺ ions by hydrazine. In aqueous-solution synthesis, however, the as-synthesized particles tend to be oxidized owing to their high surface reactivity. Moreover, the reaction process is rather complex and parameters such as the pH, concentration of metal ions, and reduction temperature need to be carefully controlled. To avoid these drawbacks, polyol has accordingly been used instead of aqueous medium. With these methods, many metallic NPs such as Ag, Fe, Co, Pt, Ni, Pd, Ru, Te, and FePt, have been successfully prepared [3–11]. In these processes, the poly-alcohol is used as both solvent and reducing agent. The polyol itself can also act as protective agent to avoid particle agglomeration and restrain the growth [12]. In

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addition, this method facilitates the decrease in critical radius of nuclei, which is of advantage to grow small sized particles.

Recently, magnetic interaction has attracted increasing attention in the assembly and alignment of ferromagnetic NPs since the superparamagnetism-ferromagnetism transition was observed by Puntes et al. [13]. A magnetic field could be employed to orient 1D ferromagnetic nanostructures [14-16]. More interestingly, magnetic-field-assisted hydrothermal process was proven to be an effective way for directing the growth of several 1D magnetic materials when a parallel magnetic field was applied during the synthesis. Though various 1D structures such as Co, Fe₃O₄ and FeS_x nano-/ microwires have been successfully obtained using this method [17–19], there have been few reported systemically regarding the crucial technological parameters, aside from verifying the feasibility of 1D structure assembly. In this work, Ni particles have been synthesized via a magnetic-field-assisted non-aqueous wet chemical process. The shape evolvement of the particles was studied in view of the reduction temperature and magnetic-field strength, respectively.

2. Experimental

All chemicals were of reagent grade and used without further purification. In the case of Ni NPs synthesis, the reducing ability of polyol, ethylene glycol (EG), is insufficient to reduce the Ni ions. Thus hydrazine monohydrate (N₂H₄·H₂O) is employed as a reducing agent. Two $6 \times 3 \times 1$ cm permanent magnets were fixed face-toface to generate a static magnetic field, its strength being controlled by adjusting the interval between these two magnets. In the central region of the two magnets, where the reduction of Ni²⁺ was carried out, the magnetic field was a nearly parallel field. In a typical





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synthesis, the starting solution was prepared by dissolving 1.25 mmol nickel sulfate hexahydrate (NiSO₄·6H₂O) in 40 ml of EG (98%) in a beaker. 0.02 mol of NaOH was added to control the pH of the solution and the obtained precursor was stirred vigorously for 30 min to form a transparent green solution. Afterward, the beaker was moved into the center of magnetic field: the magnetic-field strengths on the inner surface of the beaker near magnets were fixed at 0.02, 0.01 and 0.005 T, respectively. The solution was heated to the set temperature followed by pouring-in of 3 ml N₂H₄·H₂O (98%). After reduction, the black products was filtered and washed repeatedly with distilled water and methanol. Subsequently, the sample was dried in an oven at 100 °C for 1 h.

The phase structure was identified by X-ray diffraction (XRD, Rigaku Geigerflex) using Cu K α radiation with a graphite monochromator. The particle size and morphology analyses were performed using field emission (FE-) scanning electron microscopy (SEM, Hitachi S-4500, with accelerating voltage of 30 kV). Thermogravimetry/differential thermal analysis (TG/DTA, Bruker AXS TG-DTA2000SA) of the samples were conducted at a heating rate of 5 °C min⁻¹ under dry air.

3. Results and discussion

Table 1 summaries the experimental observations and particle characteristics at different technological parameters. After reduction by hydrazine, the initial green solution turned colorless for all samples and the black Ni particles were drawn to the magnets. In Table 1, the reduction time represents the interval from the addition of hydrazine to the absolute formation of colorless solution.

The reduction of Ni ions was first carried out under a 0.02 T magnetic field to investigate the effects of reduction temperature. At temperatures above 150 °C, the solution intensely boiled with copious evolution of gas bubbles and the reduction of Ni ions was instantly completed. The final particles were sea urchin-like in shape with an average particle size of ca. 0.5 µm, as shown in Fig. 1a. In the solution synthesis, the Ni particle usually grows into sphere due to the smallest specific surface energy. The growth rate of the sphere depends upon its radius which is increasing with time. As the particle grows large, the solidification rate decreases [20]. In the rapid synthesis, the original spherical growth will be interrupted as the growth rate is too slow. To maintain the growth rate, therefore, the solidification of the reduced Ni atoms then follows the dendritic growth mode, which leads to a faster growth than spherical mode does. In our previous work, similar multibranched particles were observed in aqueous solution via a rapid chemical reduction [21]. In comparison, the average size of the particles synthesized in such a polyol medium is rather smaller

Table 1	
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Particle shape and	l size vs.	technological	parameters
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than those (about $2.5 \,\mu$ m) in aqueous solution. By adjusting the pH value of EG solution, uniform urchin-like Ni particles with average size in a range of 250–500 nm could be produced at 150 °C. As observed from the SEM image, the sea urchin-like particles were of fat branches, which was different from the sharp ones grown in aqueous solution. In polyol medium, the diffusion coefficient for reduced Ni is lessened. And the difference of solidification rate between the tip and the side of a branch is not large enough to grow sharp dendrites.

With the decrease in reduction temperature, the reduction proceeded quiescently at 100–120 °C. A representative SEM micrograph of the Ni particles obtained at 110 °C is shown in Fig. 1b. The produced particles are spherical in shape with average size of ~0.3 μ m. From the SEM image, it can be seen that these particles are monodisperse with narrow size distribution and most of them were of rough surfaces.

1D nickel nanowires were obtained when reduced at temperature lower than 90 °C. Fig. 1c shows a typical SEM image of Ni nanowires synthesized at 70 °C. The Ni nanowires show smooth surfaces and good uniformity. The mean diameter of these nanowires was about 150 nm; their length was in the range of $3-10 \mu$ m. No curly nanowire was observed in the SEM image, suggesting that it is a facile method to synthesize straight nanowires. Comparably, only those with spherical shapes were obtained at 70 °C in the absence of magnetic field while keeping other parameters the same (not shown here). This reveals that the magnetic field plays a crucial role in determining the morphologies of the products. The nanowires are likely formed due to the tight aggregation of Ni nanospheres drawn together by magnetic interattraction force. It is important to note that under a 0.02T magnetic field, 1D Ni nanowires can be obtained only at relatively low temperature.

In general, the average size of the final particles decreased with decreasing reduction temperature, except for synthesized at 60 °C. Apparently, an elevated reduction temperature was guite helpful in accelerating the reaction rate. It is believed that no further nucleation will occur once the number of nuclei is large enough to lower the concentration of reduced atoms [22]. At high temperature, the nuclei generated at the nucleation step can efficiently consume the reduced Ni atoms by particle growth. In this regard, a large amount of Ni species reduced at the later period of reaction are directly involved in particle growth rather than form new nuclei. Accordingly, the total number of nuclei generated throughout the reaction decreases with increasing reduction temperature, and large sized particles are formed. Inversely, only a few nuclei are generated at the nucleation step in the rather slow reductions (<60 °C). The amount of solute available for particle growth per growing particle increases with the decrease in reduction temperature. This reaction mechanism also leads to forming large nickel

Sample	Reduction temp. (°C)	Field strength (T)	Reduction time (min)	Particle shape ^a	Particle size (µm) ^b
#1	170	0.02	<0.2	U	0.55
#2	150	0.02	0.2	U	0.50
#3	120	0.02	0.8	U	0.44
				S	0.25
#4	110	0.02	1	S	0.30
#5	100	0.02	3	S	0.30
#6	90	0.02	4	W	0.28
#7	80	0.02	5	W	0.27
#8	70	0.02	10	W	0.15
#9	60	0.02	>180	W	0.40
#10	70	0.01	20	Ν	0.20
#11	70	0.005	20	S	0.25

^a U: sea urchin-like; S: spherical; W: nanowire; N: necklace-like.

^b The particle size reveals the average diameter for nanowires.



Fig. 1. SEM micrographs of the Ni particles synthesized in the presence of a 0.02 T magnetic field at (a) 150 °C (sample #2), (b) 110 °C (sample #4), and (c) 70 °C (sample #8). (d) A magnified image of a nanowire taken from the black square in (c).



Fig. 2. SEM micrographs of Ni particles synthesized at 70 °C under (a) 0.01 T and (b) 0.005 T magnetic field. The inset shows a magnified view.

particles. Taken together, the Ni particles obtained at 70 $^\circ \! C$ are of the smallest average size.

To evaluate the effect of magnetic-field strength, the synthesis was carried out at 70 °C under weaker magnetic fields. As shown in Fig. 2a, necklace-like Ni chains with fluctuant diameters were obtained under a 0.01 T magnetic field. Obviously, 1D chains are formed due to the alignment of Ni spheres. Upon subjecting a 0.005 T magnetic field, only a fraction of Ni spheres showed a tendency towards the formation of 1D array, suggesting that the driving-force induced by the magnetic field is too weak in this case. Wang et al. reported that between the weak-field produced zerodimensional (0D) particles and strong-field conduced 1D nanowires, there was an intergradation for Fe₃O₄ synthesis in which 0D particles and 1D uniform-diametered nanowires coexisted in the products. By contrast, our results denote a different transitions in particle morphology: (i) With decreasing the magnetic-field strength, all the 1D structures change from uniform to fluctuant in diameter (Fig. 2a). (ii) In the 0D and 1D coexistence, the 1D particles are sphere-chains, i.e. their diameter is not uniform. It also suggested that the magnetic field in the solution was relatively homogeneous, which could not result in weak-field products (0D) and strong-field resultants (1D) simultaneously. In addition, it was found that the average diameters of 1D nanostructures decreased a little with increasing the magnetic-field strength, which implied the external magnetic field facilitated the reduction of Ni²⁺ to generate a larger amount of nuclei.

Although magnetic-field-assisted hydrothermal route has been used to construct a variety of magnetic particles, the assembly mechanism of 1D structure has not been well understood. On the basis of our results, the probably formation process for 1D Ni nanostructures is schematically illustrated in Fig. 3, taking the case of uniform-diametered nanowire for example. During the growth of nanowires, magnetic-field strength and reaction temperature remain constant and the particle morphology changes with growth time only. At the beginning of the growth, the total magnetic moment of an individual particle can be considered as zero in spite of subjecting a magnetic field. These small particles grow into dispersed nanospheres, drifting randomly just as in the usual hydrothermal process. After the blocking time $T_{\rm B}$, the magnetic moment of a particle appears to be in the same direction and the magnitude keeps increasing with time (stage II). Influenced by the magnetic field, the moment tends to regulate its direction along that of the external field. The particles with their magnetic moments in other directions will be subject to a torque. As a result, almost all the particles in the solution have a same magnetic moment direction (stage III). In addition, the interaction force between the dipoles becomes prominent. When the diffusing particles are in a close range, they are draw to encounter by the



Fig. 3. Schematic illustration of the formation of Ni nanowires.

magnetic dipole interattraction. And 1D necklace-like chain of particles with their dipoles aligned head-to-tail, parallel to the magnetic field is formed, as shown in stage IV. To decrease the surface energy, the solidification of nickel at the later stage takes place preferentially on the sphere–sphere interface to construct uniform-diameter nanowires.

In the 1D assembly by dipole interaction, it is influenced by several key parameters such as reaction temperature, magnetic field intensity and also particle concentration. At high temperature, the particles are in vigorous movement and the disturbances from the solution may counteract the magnetic dipole interattraction. This is the reason that no 1D structure can be obtained at temperatures >90 °C in this study. The magnetic field intensity is also important since the blocking time will be greatly enhanced by the magnetic field. A stronger magnetic field results in the earlier assembly of 1D chains and the formation of smaller-diameter nanowires, which is demonstrated in Table 1. Also, the stronger field will induce larger magnetic moment, thus increasing the dipole interaction between the neighboring particles. This indicates that the formation temperature of 1D structure can be raised provided a magnetic field with a large enough magnitude is used. With a much strong field (0.25 T), 1D Co microwires were obtained at 110 °C and Fe₃O₄ nanowires at even 130 °C [17,18]. A high particle concentration means a large encounter probability, which likely leads to the growth of long 1D structure.

Due to the same direction moments of the assembled spheres, the final moment of the nanowire is along the diameter. And the moment magnitude is greatly enhanced. Thus a weak magnetic field can cause them preferential orientation. Fig. 4 shows the



Fig. 5. XRD patterns of the Ni particles: (a) sample #2, (b) sample #4, and (c) sample #8.

SEM micrographs of the nanowires after magnetic alignment (H = 0.001 T). These nanowires under the magnetic field exhibit aligned distribution in contrast to the randomly oriented 1D structures in Figs. 1 and 2.

Fig. 5 shows the XRD patterns of the particles synthesized at different reduction temperature. The characteristic peaks located at 44.5° , 51.8° , 76.4° , and 92.9° have been assigned to Ni(1 1 1), (2 0 0), (2 2 0), and (3 1 1) planes, respectively. All the diffraction peaks of these samples match well with the Ni face-centered cubic (fcc) structure. By comparison of the intensities of the XRD peaks, it can be deduced that the size of crystallites in the nanowires (Fig. 5c) are smallest, which is due to the small diameter. As shown in Fig. 1, the urchin-like particles consists of several branches, whose size is smaller than that of the spherical particles. Thus crystallites in such a structure are smaller in comparison with those in Fig. 1b, which is in accord with the XRD results.

The oxidization properties of various shaped Ni nanostructures were characterized with TG/DTA (Fig. 6). For all samples, the weight loss occurred at 255 °C, which was likely attributed to the evaporation of EG adsorbed on the particle surface. In Fig. 6a and b, weight gain of 22.5% started at 275 °C and then stopped at 530 °C, implying that the nickel particles had been oxidized thermally to form NiO powders. The weight gain of nanowires occurred at ca. 295 °C. The Ni nanowires presented better oxidization stability based on the shift in weight gain to high-temperature region. It should be mentioned that the weight gain of nanowires (19.0%) is a little smaller than those of nanospheres and nano-sea urchins. This may be attributed to that the oxide layer formed on the surface of



Fig. 4. SEM image of field aligned Ni nanowires.



Fig. 6. TG curves of the Ni particles: (a) sample #2, (b) sample #4, and (c) sample #8.

nanowires at the initial stage prohibits the penetration of oxygen atoms. Eventually, the nanowires are partially oxidized. The good thermal stability also suggests that the nanowires are tightly integrated structures rather than loose aggregates of nanospheres.

4. Conclusion

We have presented here a facile strategy for preparing Ni nanostructures using a magnetic-field-assisted non-aqueous wet chemical method. SEM observation reveals that under a given magnetic field, Ni nano-sea urchins, nanospheres and nanowires can be selectively synthesized by varying the reduction temperature. Our results demonstrate that the effects of magnetic field can be ignored at high temperature, in which dispersed NPs are produced. On the other hand, 1D Ni nanowires with diameters in the range of 150–400 nm are formed by the magnetic-field directed assembly of nanospheres at low reduction temperature (<90 °C). Moreover, a strong magnetic field leads to growing tight aggregated nanowires instead of necklace-like chains. The Ni NPs obtained have been confirmed to be phase-pure crystalline nickel with fcc structure on the basis of XRD characterization. Thermal analysis indicates that Ni nanowires show superior oxidization stability compared to other shapes.

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