



Morphology-controlled fabrication and magnetic properties of nickel assemblies



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HIGHLIGHTS

- Nickel assemblies with various morphologies have been controlled fabricated.
- The structures include nanospheres, microspheres, pinecone and necklace structures.
- A possible growth mechanism for the formation of different structures is proposed.
- The magnetic properties of nickel assemblies are morphology-dependent.

ARTICLE INFO

Article history:

Received 29 August 2013

Received in revised form

30 April 2014

Accepted 2 May 2014

Available online 5 July 2014

Keywords:

Chemical synthesis

Magnetic material

Magnetic property

Microstructure

Nanostructure

ABSTRACT

In this study, nickel assemblies with various morphologies, including nanospheres, pinecone structures, microspheres, and necklace chains, were synthesized in ethylene glycol solution by adjusting the experimental conditions. We propose a possible growth mechanism for the formation of different structures, which involves the rapid nucleation of primary particles followed by slow aggregation and Ostwald ripening crystallization of the primary particles. The saturation magnetization (M_s) of the nickel assemblies decreased as the particle size declined. We found that the coercivity (H_c) of the necklace chains appeared to be higher than that of other structures due to their shape anisotropy. The results of our study indicated that the magnetic properties of the nickel assemblies were morphology-dependent. The coercivities of the nickel samples with different structures prepared in this study were two orders of magnitude higher than that of bulk nickel (0.7 Oe).

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1. Introduction

Magnetic particles have received considerable attention because of their crucial applications in high-density magnetic storage devices, magnetic fluids, sensors, contrast enhancement in magnetic resonance imaging, magnetic carriers for drug targeting, and catalysis [1–8]. It is clear that the fabrication of nickel (Ni) with different structures is of great scientific and technological importance in practical applications that require materials with magnetic anisotropy. This area has attracted much attention and has been the focus of intense research [9–12]. Ni nanoparticles with various structures have been synthesized successfully by thermal decomposition of organometallic precursors [13], chemical reduction [14],

spark plasma sintering using nanoparticles prepared by the modified polyol process [15], microemulsion [16], ultrasonication [17], and electrochemical reduction [18]. For example, Li et al. [19] reported the controlled synthesis of urchin-like Ni particles and one-dimensional chain-like nanowires using an external magnetic field-assisted method in a solution-phase. Another study achieved the controlled synthesis of Ni nanowires and flower structures using a non-aqueous sol–gel method in an external magnetic field [20]. In these techniques, an external field was used to obtain chain-like nanowires and urchin-like nanoflowers. In addition, a method for reducing metal salts using hydrazine has been employed widely to synthesize nanoparticles in organic solvents [21,22]. Recently, Guo et al. utilized this reduction method to synthesize Ni and hollow cobalt mesospheres, thereby facilitating the assembly of a chain-like structure [23]. However, the high-yield synthesis of micrometer- and submicrometer-sized Ni via the assembly of small nanoparticles, while simultaneously controlling their shape, anisotropy, and magnetization, is still highly challenging. In our

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Table 1
Preparation conditions for different Ni samples. Volume of EG: 180 ml; reaction time: 60 min.

Sample	[NiCl ₂ ·6H ₂ O] (mg ml ⁻¹)	[N ₂ H ₄ ·H ₂ O](ml ml ⁻¹)	[PVP] (mg ml ⁻¹)
P0	10	0.05	0
P1	10	0.05	15
P2	10	0.05	30
P3	10	0.05	40
C1	5	0.025	7.5
C2	5	0.025	15
C3	20	0.05	15
C4	20	0.05	20

previous study [24], we successfully synthesized urchin-like chains, nanorings, and hexagonal plates by modulating the reaction conditions, such as the amount of NaOH and the order of adding the reactants.

In the present study, we report a simple method for the controllable fabrication of Ni nanoparticles and the formation of necklace chains, pinecones, and uniform dispersive microspheres via the assembly of nanoparticles. This morphology-controlled synthesis was achieved simply by modulating the amount of surfactant and the concentrations of the reactants in ethylene glycol (EG) solution in an ambient atmosphere. Furthermore, we propose a possible mechanism for the formation of different structures. We studied the morphology-dependent magnetic properties of the Ni assemblies.

2. Experiments

All of the chemicals used in the experiments were analytical grade purity and they were used without further purification. The growth of Ni particles with different structures was performed in a solution-phase system. During a typical synthesis experiment, 1.80 g NiCl₂·6H₂O and 2.70 g poly(vinyl pyrrolidone) (PVP, molecular weight M_w 10,000 g mol⁻¹) were dissolved in 180 mL EG with intensive stirring for 1 h, and a homogeneous transparent green solution was obtained. Next, 9.00 mL of hydrazine monohydrate (50 vol%) was added dropwise to the well-stirred mixture at room temperature, where the solution turned blue and turbid. Subsequently, the mixture was heated to the boiling point of EG solution and refluxed at ca 195 °C. Numerous bubbles were formed in the flask and a smell of ammonia could be distinguished. After refluxing for a specific period, the color of the solution changed from blue to dark blue, and a dark precipitate was obtained. Centrifugation was used to separate the precipitate, which was rinsed with absolute ethanol three times. The volatile solvent was evaporated under vacuum at 60 °C and a loose dark grey powder was finally obtained. To study the effects of the experimental conditions on the structures of the Ni products, different amounts of PVP and various concentrations of the reactants in the EG solution were tested, the details of which are shown in Table 1. The crystal structures of the Ni particles were analyzed using an X-ray diffractometer (XRD; XRD-6000, Shimadzu) with a Cu K α radiation source ($\lambda = 1.5481 \text{ \AA}$, 40.0 kV, 30.0 mA). Morphological analyses were performed using a scanning electron microscope (SEM; Hitachi, s-4800 with an accelerating voltage of 15 kV), which was equipped with an energy dispersion X-ray (EDX) spectroscopy analyzer. The magnetic properties of the samples were measured using a vibrating sample magnetometer (VSM, Lake Shore 7307).

3. Results and discussion

SEM images of some of the representative structures of the Ni products are shown in Fig. 1. Well-dispersed nanospheres that

measured ca 90 nm were observed in the products synthesized in the absence of PVP surfactant (Fig. 1a). When PVP was included in the reaction system, we obtained Ni pinecones, microspheres, and necklace chains via the assembly of small nanoparticles (Fig. 1b–d). The pinecone structures were formed via the assembly of ca 500 nm spheres and the necklace chains with lengths of up to 30 μm were assembled in a linear manner from ca 800 nm spheres. The pinecone structures and necklace chains were probably formed via the aggregation of Ni microspheres, which were attracted by magnetic forces. As reported previously, magnetic nanoparticles tend to form chains in solution systems because of internal attractive forces [21–25]. In the present system, however, the Ni nanoparticles appeared to remain well separated, which may be attributable to the steric effect of the EG molecules at the boiling temperature. In the absence of surfactant, the growth of the Ni nanoparticles via chemical reduction was random. Some dipolar interactions existed between the Ni nanoparticles, but these forces were too weak to facilitate their assembly into necklace chains or pinecone structures, thus only individual nanoparticles were formed. With PVP, however, the nanoparticles tended to assemble into microspheres before forming necklace chains or pinecone structures. To determine whether the necklace chains and pinecone structures were produced via the aggregation of magnetic microspheres, samples were treated by ultrasonication at 100 W for 1 h. The results indicated that the necklace chain and pinecone morphologies and structures were not destroyed by ultrasonication, thereby indicating that the necklace chains and pinecones were tightly integrated, rather than being loose aggregates of microspheres.

Fig. 2a shows the XRD patterns of nanospheres, pinecone structures, microspheres, and necklace chains. The peaks located at 44.53°, 51.82°, and 76.41° were well indexed to the (111), (200), and (220) planes of the face-centered cubic (FCC) Ni crystal structure (JCPDS 04-0850), and no impurity phases such as NiO or precursor compounds were detected. The purities of the prepared Ni samples were further verified by EDX spectroscopy, as shown in Fig. 2b, which produced appreciable signals only for Ni.

The influences of the experimental conditions on the structures of the final products were investigated systematically. The results showed that the amount of PVP, the concentrations of the reactants in EG solution, and the reaction time had key effects on the formation of different Ni structures.

The amount of PVP in EG solution was found to be particularly important in this synthesis method. Fig. 3 shows SEM images of the experiments conducted with fixed concentrations of Ni ions and hydrazine hydrate but various amounts of PVP. A series of Ni particles was prepared using PVP concentrations of 0, 15, 30, and 40 mg mL⁻¹. In the experiments, the Ni particle size was about 90 nm (Fig. 3a) without the addition of PVP, but the particle size increased to 500–800 nm as the amount of PVP increased (Fig. 3b–d), and the morphology changed from necklace chains assembled from spheres (Fig. 3b) into a mixture of shorter necklace chains and microspheres (Fig. 3c–d).

The experimental results demonstrate that PVP has significant effects on the formation of necklace chains. In the absence of PVP, only nanospheres were obtained, with no necklace chains. PVP is considered to be a protective polymer and it is used widely as a stabilizer to prevent nanoparticles from aggregating during the chemical preparation of noble metal nanoparticles, including silver [26], palladium [27], gold [28], and platinum [29]. In the absence of PVP, the Ni nanoparticles were distributed randomly after their formation. Thus, the absorption of PVP on the surfaces of the Ni nanoparticles also prevented their aggregation. The formation of the Ni chains may be attributable to the magnetic dipole–dipole interactions between neighboring particles, as discussed below.

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