Transformation of Co nanodisks to Co caterpillars

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Abstract

Co nanodisks and Co caterpillars were synthesized by novel wet chemistry method simply by controlling the concentration of cobalt ion. It was proven that both nanodisks and caterpillars had the same crystalline phase.

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1. Introduction

Nowadays, colloid chemistry is one of the important branches of chemistry in the synthesis of nanoparticles, which can control not only the metal nanoparticle sizes but also the shapes and morphologies of the nanoparticles. Shape control is an alternative tool to adjust chemical and physical properties, especially desirable magnetic characteristics of magnetic materials.

From 1995 to 2004, the reducing agent, hydrazine had the greatest potentiality for the synthesis of various cobalt materials by applying magnetic field, adjusting solvent polarity without the addition of capping agents \cite{1–4}. There are some resemblances among reaction conditions in these reports; however, little attention has been paid to the relationship of different shapes in cobalt materials. Besides, the nucleation and growth process of magnetic materials and self-assembly behaviour of cobalt materials from low-dimension to bulk in the only one system which lead to various anisotropic cobalt materials have not been reported, either.

In this article, the reaction at various cobalt salt concentrations and temperature yield products with different shapes like nanodisks and cobalt caterpillars by using cobalt nanoparticles as seed. A plausible mechanism for the formation of these cobalt materials is proposed.

2. Experimental

The shape-controlled syntheses of the cobalt materials were performed by seed-mediated method. Essentially, in the presence of cobalt seeds, cobalt ions were formed the green-blue complex of Co(N\textsubscript{2}H\textsubscript{4})\textsubscript{2+} with hydrazine immediately. The reaction did not complete until the complex disappeared after heating at 80°C. Cobalt seeds were prepared by the reduction of cobalt ion (0.445 mM, 9 mL) with ice-cold NaBH\textsubscript{4} (8 mM, 1 mL) in the presence of sodium citrate (0.194 g). The whole synthesis was carried out under nitrogen atmosphere, and the long aging time is needed for the complete degradation of the reducing powder of NaBH\textsubscript{4}.

3. Results and discussion

Cobalt nanodisks were formed in low cobalt salt concentration of \(2 \times 10^{-4} \text{M}\) even without addition of cobalt seeds. In Fig. 1 the standing shape confirms the formation of disk. Fig. 1(a) and (b) show cobalt nanodisks synthesized without addition of seeds are smaller than those synthesized with an addition of seeds because of seed catalytic effect. These cobalt disks actually resulted from the self assembly of much thinner disks in ways of

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side-to-side. As a complementary study, another experiment was performed to investigate the effect of the capping agent of the cobalt nanodisks. In comparison to the experimental method listed above, 0.05 g of polyvinylpyrrolidone (PVP) was added into cobalt salt solution beforehand. Obviously, much thinner disks with thickness less than 10 nm as shown in Fig. 1(c) were yielded, which indicated that those thick cobalt disks were composed of many thinner disks due to mutual magnetic attraction of thin Co disks. Transmission electron microscopy (TEM) image shows hexagonal symmetry and the disk plane corresponds to the (001) plane of an HCP structure corroborating the X-ray diffraction (XRD) data that the short axis was the [0001] direction. In Fig. 1(d) the selective-area electron diffraction pattern of individual flat-lying nanodisks showed regular hexagonal diffraction spot array.

In case of the increase of the Co$^{2+}$ concentration to $5 \times 10^{-3}$ M, cobalt caterpillars could be observed under the flask with the naked eye. Fig. 2 shows the XRD pattern of the cobalt caterpillars. The structure of cobalt caterpillars was hexagonal (standard cards JCPDS 5-0727, space group P6$_3$/mmc) with a unit cell of $a = 2.503$ Å, and $c = 4.060$ Å the same as that of nanodisks.

It was also obvious that the intensities of these diffraction peaks are not consistent with those in JCPDS card. As a result, the (002) peak was almost equivalent to the originally strongest (101) peak. This is probably caused by the preferred orientation of cobalt caterpillars. This result agreed with the recent report in which the samples were prepared under an external magnetic field [3].

In Fig. 3(c), the cobalt caterpillars were grown uniform and one directional with an average length of 90 $\mu$m and an average width of 2 $\mu$m. The inset shows the Chinese Cordyceps Sinensis comparable to these cobalt caterpillars. The cobalt caterpillars were composed of a lot of micro-sized spherical cobalt particles. The caterpillars were amazingly established by interior hierarchical porous architecture. The scanning electron microscopy image of Fig. 3(a) was grabbed thirty seconds after the cobalt complex gradually disappeared. The cobalt caterpillars looked like thinner disks aligned to form porous structure.

It is obvious that the porous cobalt network was initially formed instead of fine spherical nanoparticles as reported in literature [3]. After thirty minutes as shown in Fig. 3(b), the cobalt nanodisks aggregated to form spherical particles to reduce the magnetic energy. The porous structure was not filled up because of the constant release of nitrogen gas during reduction [5]. Then, porous structures covered by nanoparticles form spherical shapes which align one after
another in chains after three hours (Fig. 3(c)). Although cobalt caterpillars formed through an aggregation mechanism which induced larger vacancies, the magnetic force of cobalt helped to improve the regularity of crystalline phase in addition to van der Waals force as in other metals. Moreover, the reaction using the magnetic stir may also enhance such arrangement. In the TEM selected area electron diffraction pattern for cross section of Co caterpillars, the single crystalline pattern and diffraction points exhibit the shape of disks and rings correspond to the plate-like structures of the sample. The tailing phenomenon of diffraction pattern might be due to the slight deviation of plated-building blocks. In this case, the thermodynamic limit induces the system to yield spherically shaped particles despite the interior porous structure which are kinetically controlled. From the room temperature hysteresis loop of cobalt caterpillars, the saturation magnetization value for the samples was 149 emug\(^{-1}\) and the coercivity was about 135.5 Oe.

4. Conclusions

In conclusion, based on the above facts we were able to synthesize novel cobalt caterpillars with nanostructure similar to Chinese caterpillar fungus. The present study established one aqueous system to synthesize cobalt nanomaterials of different shapes and the promising technique can also be applied to produce other magnetic materials in future.

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References