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Fabrication of Anisotropic Magnetic Nanostructures by Soft Chemical Approach

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Anisotropic magnetic nanostructures including Co nanorods and Ni nanocubes were prepared by soft chemical approaches. Co nanorods were produced by a reverse micelle of cetyltrimethylammonium bromide (CTAB), using 1-hexanol as a co-surfactant and octane as an oil phase. To this solution, aqueous solution containing $CoCl_2$ or reducing agent (N_2H_5OH) was added. It was found that the molar ratio of water to surfactant highly affected the size and shape of the products. Powder x-ray diffraction (XRD) pattern and transmission electron microscopy (TEM) images indicate that the products are *hcp* Co nanorods with the length of ca.700 nm and the diameter of ca.50 nm. Selected area electron diffraction pattern showed that the semi-crystalline characteristic of the Co nanorods. The formation mechanism of the Co nanorods in reverse micelles is discussed further. To prepare Ni nanocubes, we employed the solvothermal route in which tetrahydrofuran (THF) was used as the solvent, and tri-octylphosphine oxide (TOPO) and oleic acid as stabilizers. XRD and TEM results indicated that the products were face-centered cubic (*fcc*) Ni nanocrystals with anisotropic structures such as cubic and rhombus.
Key words: Anisotropic nanostructure, Cobalt, Nickel, synthesis

1. INTRODUCTION

In recent years, magnetic nanoscale materials have been attracting more of interest because of their potential applications in ultrahigh density magnetic storage devices. [1-2] Considerable progress on the fabrication of magnetic nanoscale materials was achieved. For instance, mono-disperse FePt nanocrystals and high quality hematite nanoparticles were produced by using iron carbonyl as a precursor. [1,3] High crystalline $CoPt_3$ alloys were also prepared in the presence of 1-adamantanecarboxylic acid and hexa-decylamine (HDA).[4] In general, physical and chemical properties of metal nanoparticles are highly dependent on the shape and size of the nanocrystals, contaminants, and the interaction of surface and ligands.[5] Therefore the morphology control of metal nanocrystals has been becoming an focusing and foundation for further application.[4-8] In the past decades, metal nanorods and nanowires were generally prepared by arc-charge in solid-liquid phase, a pulsed sonochemistry, some template routes including DNA, carbon nanotube and mesoporous silica. Anisotropic magnetic nanocrystals were also developed very recently.[9,10] Alivisatos and co-workers reported that the synthesis of Co with various shapes, including rods, plate and particles, all made by relatively simple variations in surfactant composition and time variations of monomer concentration.[11] Chaudret and co-workers demonstrated the formation of Ni nanorods in the presence of relevant amount of HDA.[12] However, magnetic nanorods with uniform size is still an challenge in shape control of nanoscale materials. Especially, there are relatively few reports on Co nanorods to date.[2,13] In addition, nanocube is one of interesting morphologies due to their potential as building blocks for mag-optic nanodevices. Xia and co-workers reported Ag nanobcubes and Au nanoboxes which derived from Ag nanocubes in gold solution.[14] Very recently, Zeng et al fabricated Co_3O_4 nanocubes at 90℃,[15] while Li and co-workers gave a size series of CaF_2 nanocubes prepared by the hydrothermal procedure[16] and Murphy fabricated Cu_2O nanocubes.[17] However, to our best knowledge, there has not yet been report on Ni nanocubes to date. In this contribution, reverse micelle method, which is similar to the literature reported synthesis of copper nanoparticles,[18] is used to fabricate Co nanorods, while a new strategy to produce nickel nanocubes is also presented.

2. EXPERIMENTAL

All chemicals used in the experiments were analytical level, and no further purification was done before being used.

Co nanorods were fabricated by the solvothermal reduction process of the reverse micelle consisted of surfactants of CTAB, an oil phase of heptane, co-surfactant of hexanol and an aqueous phase containing 0.5 M $CoCl_2$. The size of the reverse micelle is determined by the molar ratio of water to surfactants ($\omega = [H_2O]/[CTAB]$). For example, ω=11, high aspect Co naonrods were obtained whereas the aspect ratio obviously decreases if ω decreases to 8. In a typical synthetic procedure, the reverse micelle was vigorously stirred for 15 min, and then to the micelle, 0.5mL of hydrazine (N_2H_5OH) was added dropwise. Consequently, the mixture was swiftly transferred into teflon-line autoclave, sealed and kept at 100℃ for 12h. The system was then cooled to room temperature naturally. The precipitates were collected upon adding methanol/chloroform 1:1 and washed with methanol and distilled water in sequence to remove possible excess of N_2H_5OH and by-products. The resulting black powder was dried in vacuum at 60℃ for 12h, and was used for the characterization.

Ni nanocubes were obtained by the reduction of nickel salt in the presence of trioctylphosphine oxide (TOPO) and oleic acid in tetrahydrofuran (THF). The stock solution was freshly synthesized by dissolving 0.3-0.6 g of $Ni(acac)_2 \cdot 2H_2O$ in 3ml of THF, and this stock solution was injected in a 12ml of THF including 0.1-0.3g of TOPO, and 2-4 ml 85% N_2H_5OH at 60℃ under vigorous stirring. After 30 min, the reaction mixture was transferred into 100ml of teflon-line autoclave and heated at 70℃ for 12h. The autoclave was then cooled to room temperature naturally. The post-isolative process of nanocubes is similar with in the case of nanorods, as described above. The resulting products are black powders with the amount of 30-60mg.

Powder x-ray diffraction (XRD) patterns were collected on a Rigaku Dmax/2000 diffractometer under Cu $K\alpha$ radiation. The size and size distribution of nanocrystals was determined by transmission electron microscopy (TEM, JEOL 200CX).

3. RESULTS AND DISCUSSION

As well known, the reverse micelle provides plenty of templates with capsule-like structures, which can be used as to produce anisotropic nanostrucures. In such templates, the rod-like or linear nanostructures can be formed by controlling the components of the reverse micelle and a suitable reaction condition. Here we combined the reverse micelle with solvothermal process to fabricate Co nanorods. XRD pattern (Fig. 1) gave the evidence that *hcp* Co was formed after the solvothermal reaction process. Generally nanosized Co particles is easily oxidized if exposed to air. However, the XRD data gives no obvious feature of cobalt oxides. It should be ascribed to the protection of the surfactants on the surface of nanocrystals. TEM images of cobalt nanorods prepared with ω =10 (Fig. 2) show that the size of nanorods is ca. 500-700nm in length, and ca. 40-60nm in diameter. An enlarged image (Fig.2b) of Co nanorods shows that some surfactants are present, indicating a semi-crystalline structure. It is agreement with of the result of the selected-area electron diffraction (the inset in Fig 2b). It is most likely that the excess amount of surfactants could affect the crystallinity of nanorods to some extent. Certainly the crystalline nature of nanorods the is also related to the growth mechanism (see below).

Actually, the formation of Co nanorods is dependent on the reverse micelle components, reaction temperature and time. By controlling the concentration of cobalt ion, the diameter of Co nanorods is expected to be adjusted. When the molar ratio of water to surfactants ω = 11, higher aspect ratio of nanorods were prepared (Fig 3a). However, if ω was down to 8, the aspect ratio of nanorods was also decreased obviously, as shown in Fig.3b. In addition, the reaction temperature also strongly affects the formation of nanorods. When we set the temperature at 120℃ for certain time, only cobalt nanoparticles with an average size of 10nm were obtained (Fig.3c), as that in non-reversed micelle using only CTAB as a stabilizer. Therefore we can conclude that the ratio of water to surfactants, which determines the size of the droplet in reverse micelle, plays an important role to decide the morphologies of the products.

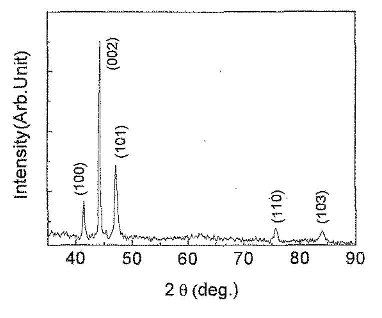

Fig. 1. XRD pattern of Co nanorods with the molar

Note that some TEM images give the evidence of the growth mechanism of Co nanorods in the revere micelle. In our experiment, shuttle-like structures were observed on the tip of the nanorods, as seen in Fig. 4. This phenomenon indicates that the growth process is directed and controlled by the surfactants, that is, the nuclei occurred at first, and continue to grow under the direction of surfactants. Similar behaviors have been observed in the gas deposition synthesis of metal and semiconductor nanowires.[19-21]

In the process of producing Ni nanocrystals, we systematically tested some surfactants including phosphines, primary and secondary amines, fatty acid and combinations of these compounds for the

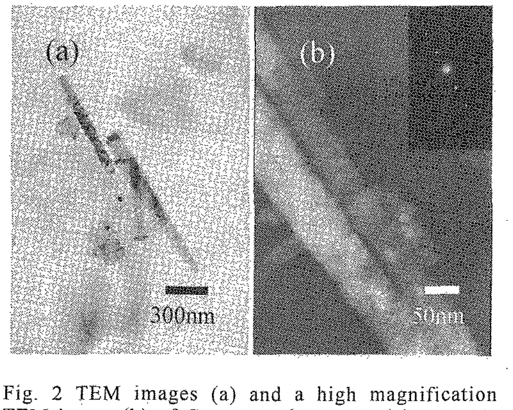

Fig. 2 TEM images (a) and a high magnification TEM image (b) of Co nanorods prepared by ω= 10, the inset is a selected-area electron diffraction pattern.

synthesis of Ni nanocrystals. We found that Ni nanocubes could be prepared when THF was used as the reaction solvent, and TOPO and oleic acid as stabilizers. XRD pattern of the sample (Fig. 5a) shows that Ni nanocrystals are face-centered cubic (*fcc*) structures. TEM image (Fig. 5b) shows the morphology of Ni nanocrystals are anisotropic such as cubic and rhombus. As for the formation mechanism of Ni nanocubes, it should be likely attributed to the combination interaction of excess amount of surfactants (TOPO) and oleic acid in THF. In other case of TOPO and Oleic acid, the solvent is ethyldiamine, the products are only Ni nanoparticles with the diameter of more than 20 nm.[22] The size of Ni cubes are expected

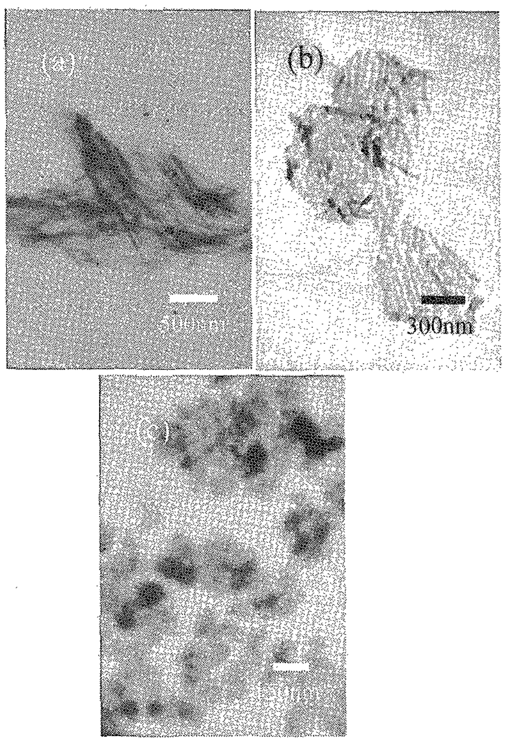

Fig. 3 TEM images of Co Nanorods with (a) ω =11, (b) ω =8, (c) prepared at 120 ℃ and ω = 8.

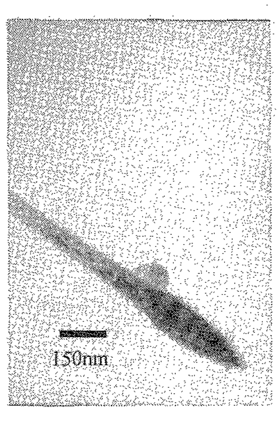

Fig.4 The formation mechanism of Co nanorods, this is the tip of a Co nanorod.

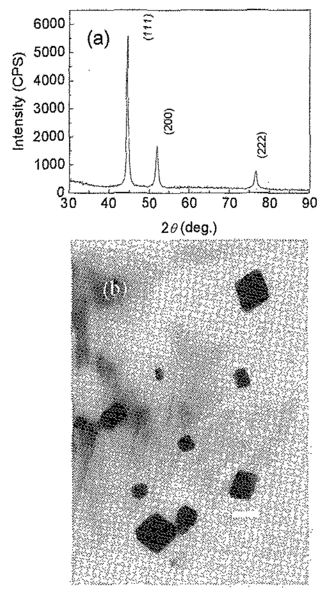

Fig. 5 XRD pattern (a) and TEM image (b) of Ni cubes.

to be controlled by tailoring the reaction condition including the concentration of surfactants, reaction temperature and time. Further study on the formation mechanism of Ni nanocubes is under way.

4. CONCLUSIONS

We have prepared Co nanorods by the reverse micelle in the solvothermal reduction process. It was found that the components of reverse micelles and reaction temperature, specially the ratio of water to surfactants (ω), highly affected the morphology of Co nanocrystals. When ω is set at 10~11, Co nanords with higher aspect ratio were obtained. In addition, in the presence of TOPO and Oleic acid, Ni nanocubes were produced in THF for the fist time.

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