Complexant-assisted Fabrication of Flowery Assembly of Hexagonal Close-packed Cobalt Nanoplatelets

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Flowery assembly of hexagonal close-packed (hcp) cobalt nanoplatelets was fabricated in high yield via a simple one-pot method without any surfactants. The process involved the reduction of the precursor of cobalt dimethylglyoximate with hydrazine in a basic medium. Thus-prepared cobalt flowers exhibited a ferromagnetic characteristic with the coercivity of 308 Oe at room temperature, much higher than that of bulk counterpart.

Nanosized magnetic metals such as Fe, Co, and Ni have been paid great attention for their applications in a wide range of fields, such as magnetic recording, conduction, catalysis, and medical diagnosis.[1–4] Among them, Co is of particular interest owing to its multiple crystal structures (hcp, fcc, and epsilon) and structure-dependent magnetic and electronic properties.[5] Especially, hcp Co with the inherent anisotropic structure always shows high magnetic coercivity, which is the preferred structure for permanent magnet application.[6] Because of the close relationship between the properties and morphology of nanomaterials, great efforts have been devoted to the shape control of cobalt nanocrystals. For hcp Co, a series of differently shaped nanocrystals and their assembly structures have been created, such as nanodisks, nanobelts, nanowires, dendrite, hollow spheres, ribbons built by nanorods, superlattice self-assembled by nanocrystals, spheres assembled by nanoplatelets, flowers consisted of nanosheets, etc.[7–15] Most of these nanostructures were achieved with the assistance of surfactants or polymers. However, post-treatment of these organic molecules usually damaged their magnetic properties or destabilized the assembly architectures, which resulted in difficulties for their potential applications as nanodevices.[16] Currently, it is still challenging to the preparation of cobalt assembly nanostructures independent of any surfactants or polymers.

In this manuscript, we reported a simple surfactant-free method to the preparation of a new type of flowery crystallites of hcp Co, which were assembled by single crystalline nanoplatelets. The reaction process involved the hydrazine reduction of cobalt salts in a basic medium using dimethylglyoxime (dmgH) as complexant. The key factors affecting the formation of the flowery nanostructures and their magnetic properties at room temperature were investigated.

All chemicals were analytical grade and used without purification. A typical experiment was as following: 13 mL of ethanol solution containing 1 wt % dmgH was added dropwise into 28 mL of 14.4 mM aqueous solution of $CoCl_2 \cdot 6H_2O$. The solution turned from red to orange-brown, indicating the complexation of dmgH with Co^{2+}. Then, 2.0 mL of hydrated hydrazine (80%) and a certain amount of NaOH were added. In the final solution, the molar ratio of $CoCl_2$:dmgH:hydrazine was 1:2:6, and the pH value was above 12. The whole mixture was continuously stirred for another 30 min to give a homogenous solution. Subsequently, the solution was transferred into a 40-mL autoclave, sealed and maintained at 120 °C for 24 h. After the heating treatment was over, the resulted black powder was collected, rinsed with distilled water and ethanol by magnetic decantation for several times, and finally vacuum dried at 50 °C for 4 h.

X-ray diffraction (XRD) pattern of the sample was recorded on a Philips X'pert diffractometer with Cu Kα radiation ($\lambda = 1.5418$ Å). The morphology and structure of the sample were studied with field emission scanning electron microscopy (FE-SEM, JEOL JSM-6300F) and transmission electron microscopy (TEM, Hitachi, H-800) with an accelerating voltage of 200 kV. Magnetic–hysteresis (M–H) loops were recorded on a vibrating sample magnetometer (BHV-55).

Figure 1 showed the XRD pattern of the obtained sample, which could be indexed as the hcp cobalt (JCPDS: 05-0727). No impurities of cobalt oxides or cobalt hydroxides were observed, indicating that pure hcp phase cobalt was achieved by the present procedures. By comparing the weight of the product with the theoretic value, the yield of the hcp Co was estimated above 98%. It was noted that the relative intensity of (002) peak was strengthened compared with the standard pattern, implying the abundance of (001) planes in the product.

Morphology of the sample was studied by SEM and TEM. A panoramic SEM image of Figure 2a showed that the sample consisted of flowery crystallites with a size of about 5 μm, and the percent of the flowery structures in the product was above 90% from SEM observations, while a small number of isolated hexagonal platelets were also observed. Magnified image of Figure 2b indicated that the flower was assembled by platelet building blocks with the thickness of about 50–100 nm. TEM image of Figure 2c gave an isolated platelet which exhibited a hexagonal shape. The corresponding selected area electron diffraction (SAED) pattern revealed its single crystalline nature. According to the pattern spots, the top/bottom faces of the platelet were indexed as (001) planes of hcp Co. This result was consistent with the above XRD result with the intensified

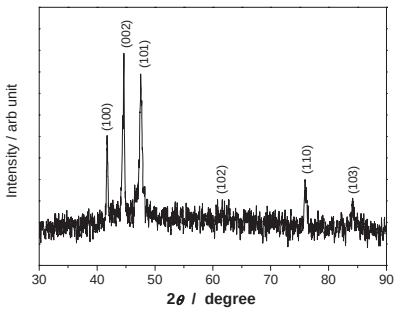

Figure 1. XRD pattern of the cobalt sample.

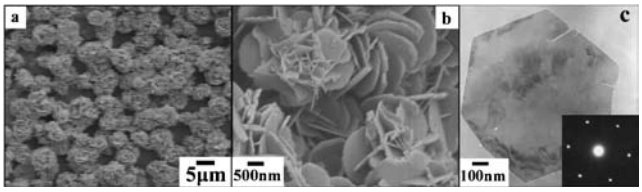

Figure 2. Morphology images of the hcp Co sample. (a) A panoramic SEM image, (b) A magnified SEM image of the flowers, (c) TEM image of an isolated platelet, inset was the corresponding SAED pattern.

(002) peak.

It was found that the complexant of dmgH was a crucial factor that affected the formation of the flowery crystallites. Control experiments demonstrated that without dmgH only irregular particles with the mixed phases of hcp and fcc were obtained. Replacing dmgH with other complexant of tartrate or citrate resulted in dendritic crystals of hcp Co. Here, dmgH was considered playing two important roles in the formation of the cobalt flowers. First, dmgH molecules coordinate with Co^{2+} and form the water-soluble complex of $Co(dmg)_2$.[17] Formation of the complex decreased the free Co^{2+} concentration in the solution, which resulted in a relatively slow reaction rate of the reduction of cobalt dimethylglyoximate with hydrazine. Such a slow reaction rate was considered favorable for the formation of the pure hcp Co and its subsequent anisotropic growth.[13] On the other hand, dmgH possibly acted as a structure-directing agent, which affected the shape of the cobalt particles. When $Co(dmg)_2$ precursor was reduced, the released dmgH species may be selectively adsorbed on the (001) planes of the cobalt crystals, limited them developing along the *c* axis and finally resulted in platelet-like product. When these platelets were formed, the interfacial tension and the hydrophilic surfaces of the particles may play a role in driving the platelets to aggregate, branching and fusing into flower architectures.[18,19]

Magnetic properties of as-prepared hcp Co flowers were measured with VSM at room temperature and 2 K with *M–H* loops shown in Figure 3. The sample exhibited a coercivity (*H*c) of 308 Oe and saturation magnetization (M_s) of 128 $emu \cdot g^{-1}$ at 300 K. At low temperature of 2 K, the values were 946 Oe and 141 $emu \cdot g^{-1}$. Such Hc value was much superior to the bulk cobalt (a few tens of Oersteds) and even higher than the previously reported hcp Co nanowires, for their smaller size and shape anisotropy.[9,20,21] However, this Hc value was lower

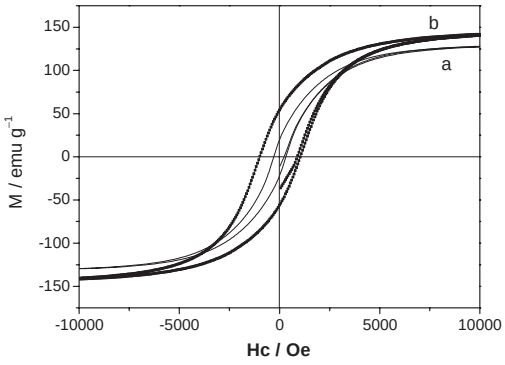

Figure 3. *M–H* loops of the cobalt flowers at different temperatures. (a) 300 K, (b) 2 K.

than that the one-dimensional nanocrystals which possessed much higher shape anisotropy. It was possibly due to the flowery assembly manner of the nanoplatelets, which had lower shape anisotropy as a total.[21] The decreased M_s value than that of bulk cobalt (168 $emu \cdot g^{-1}$) might be ascribed to the inevitable slight surface oxidation and the magnetic interaction between the platelets, which reduced the total magnetic moment at a given field.[22,23]

In summary, we reported the fabrication of flowery hcp Co crystallites assembled by single crystalline platelets through reducing cobalt dimethylglyoximate with hydrazine. It was found that the special complexant of dmgH played the crucial role for the formation of flowers. Thus-prepared cobalt crystallites exhibited a ferromagnetic characteristic with the coercivity of 308 Oe at room temperature. The present work provided an example for the fabrication of assembly nanostructure of hcp Co without any surfactants, and the flowery crystallites are expected to find applications in the fields of catalysis, energy storage, magnetism, etc.

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