

# Controlled Synthesis of Cobalt Flowerlike Architectures by a Facile Hydrothermal Route

Ya-jing Zhang,<sup>\*,[a]</sup> Ying Zhang,<sup>[a]</sup> Zhen-hua Wang,<sup>[a]</sup> Da Li,<sup>[a]</sup> Tie-yu Cui,<sup>[a]</sup> Wei Liu,<sup>[a]</sup> and Zhi-dong Zhang<sup>[a]</sup>

**Keywords:** Hydrothermal synthesis / Cobalt / Nanostructures / Magnetic properties

Cobalt flowerlike architectures composed of hexagonal nanoplatelets have been synthesized by a simple hydrothermal reduction method. The architectures are fabricated by the reaction of  $\text{CoCl}_2$  with  $\text{NaOH}$  at 140–180 °C in the presence of sodium dodecyl benzenesulfonate (SDBS), with  $\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$  as reducing agent. The diameters of the flowers range from 8 to 10  $\mu\text{m}$ , and the average thickness of the hexagonal sheets is about 100 nm. Higher reaction temperatures and the proper concentration of sodium hydroxide ( $\text{NaOH}$ ) are key requirements for the fabrication of the flowerlike architectures. A growth mechanism for these architectures is pro-

posed on the basis of the characterization by X-ray diffraction, scanning electron microscopy (SEM), and transmission electron microscopy (TEM). The magnetic hysteresis loops at 5 K and 295 K of the cobalt flowerlike architectures show ferromagnetic characteristics with coercivities of 371 Oe and 197 Oe, respectively. Our work may shed light on the designed fabrication of complex 3D architectures of other materials.

(© Wiley-VCH Verlag GmbH & Co. KGaA, 69451 Weinheim, Germany, 2008)

## Introduction

It is well known that assemblies of metallic and inorganic nanobuilding blocks yield collective physical properties, depending on their size, spacing, and high-order structure.<sup>[1,2]</sup> Therefore, considerable attention has been paid to synthesize and investigate nanomaterials with hierarchical architectures, because of their novel properties and potential application in optics, electronics, magnetism, and biology.<sup>[3]</sup> Because their properties have a close relationship with their morphologies, a wide variety of hierarchical architectures, which are composed of low-dimensional nanostructured building blocks, including 2D nanoplatelets, nanosheets and nanodisks,<sup>[4]</sup> 1D nanobelts, nanowires, nanorods and tubes, and 0D nanoparticles,<sup>[5]</sup> have been extensively investigated. For example, two kinds of morphologies of 3D flowerlike  $\beta$ -NiS architectures, nanorods or nanoneedles, were synthesized, and their morphologies can be modified conveniently by varying the reaction temperature;<sup>[6]</sup> 3D flowerlike bismuth tungstate structures, assembled by nanosheets composed of numerous square nanoplatelets, were obtained by varying the amount of surfactant of poly(vinylpyrrolidone) (PVP);<sup>[4c]</sup> weak ferromagnetic cobalt nanoparticles self-assembled into braceletlike rings with discrete

particle count, when dispersed by *C*-undecylcalixresorcinarene.<sup>[7]</sup> A lot of wet chemical processes for the fabrication of hierarchical nanomaterials,<sup>[8–10]</sup> based on different driving mechanisms including surface tension, capillary effects, electric and magnetic forces, and hydrophobic interactions, have been developed. Among all approaches, the hydrothermal process has been considered as one of the most promising routes because it is simple and inexpensive for large-scale preparation. However, as these processes are complicated and the structures of the products are usually unpredictable, the controlled synthesis of hierarchical structured nanomaterials is still an intensive challenge.

Cobalt nanomaterials have received increasing attention due to their important applications in the fields of high-density data storage, medical diagnosis, and catalysis.<sup>[10a,11,12]</sup> Cobalt nanocrystals (below their critical size) are superparamagnetic at room temperature due to their small sizes, and thus they cannot be used in many fields. It is known that the magnetic anisotropy can be increased by increasing the shape anisotropy of magnetic materials. As a result, great efforts have been focused on the controlled synthesis of cobalt nanostructures with a high aspect ratio and their multidimensional assemblies. 1D cobalt nanowires/nanobelts/nanorods,<sup>[13–18]</sup> 2D cobalt nanoplatelets/nanodisks and superlattices have been prepared for enhancing the magnetic anisotropy.<sup>[19,20]</sup> For instance, cobalt nanodisks and their assembly of ribbons were obtained by rapid decomposition of carbonylcobalt in the presence of trioctylphosphane and oleic acid.<sup>[19]</sup> Cobalt nanobelts and nanowires were obtained by a surfactant- and complex-as-

[a] Shenyang National Laboratory for Materials Science, Institute of Metal Research, and International Centre for Materials Physics, Chinese Academy of Sciences, Shenyang 110016, PR China  
E-mail: yjzhang@imr.ac.cn

Supporting information for this article is available on the WWW under <http://www.eurjic.org> or from the author.

sisted hydrothermal reduction process, respectively.<sup>[14,15]</sup> In addition, some cobalt hierarchical architectures were fabricated to this end. Cobalt chainlike structures composed of cobalt nano/microspheres or hollow spheres are further examples.<sup>[21–23]</sup> However, few efforts have been focused on fabricating cobalt 3D hierarchical structures. By a hydrothermal reduction approach, 3D cobalt microspheres composed of nanoplatelets were synthesized with surfactant sodium dodecyl benzenesulfonate (SDBS) and capping reagent sodium tartrate.<sup>[24]</sup> It is highly desirable to synthesize 3D cobalt hierarchical architectures.

Besides the technological application in high-density storage and catalysis, the synthetic method for obtaining cobalt 3D hierarchical structures is very interesting. Undoubtedly, simplifying the synthetic method as well as simultaneously controlling the structures will contribute to improving their magnetic properties, understanding the fabrication mechanism, and extending the potential application of hierarchical magnetic nanomaterials. In this study, 3D flowerlike hierarchical architectures consisting of cobalt hexagonal nanosheets were fabricated with SDBS by a simple hydrothermal reduction method. The effects of the reaction parameters, such as the reaction temperature and the amount of NaOH in the starting solution, on the morphologies of the products were investigated. On the basis of the evolution of the structure and the morphology with increasing reaction time, a growth mechanism of the 3D flowerlike cobalt architectures is proposed. Moreover, the magnetic measurements show that the flowers have ferromagnetic characteristics with a coercivity of 197 Oe at 295 K, which is greatly enhanced relative to their bulk counterpart.

## Results and Discussion

### Controlled Synthesis and Characterization of Cobalt Flowerlike Architectures

The  $\text{CoCl}_2$  and NaOH solution with SDBS was prepared in a beaker. After the addition of reducing agent  $\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$ , the solution was stirred and autoclaved for hydrothermal treatment. Typical XRD patterns of the products obtained after the hydrothermal treatment at 180 °C for 6–24 h are shown in Figure 1. The XRD pattern of the product obtained after the hydrothermal treatment at 180 °C for 24 h exhibits a predominant crystalline Co hexagonal phase, in consistent with the standard card JCPDS No.5–727 (space group  $P6_3/mmc$ ;  $a = 2.503 \text{ \AA}$ ;  $c = 4.060 \text{ \AA}$ ). The energy-dispersive spectrum (EDS) shown in Figure 2 confirms that the product is pure cobalt (the element Au originates from the thin Au layer sputtering on the sample in the test). The morphology and size of the samples were examined by scanning electron microscopy (SEM). Figure 3a shows the general morphologies of the product (180 °C, 24 h), revealing that it consists of relatively uniform flowerlike architectures with diameters of 8–10  $\mu\text{m}$ . Under the conditions reported, the products are all in this morphology. High-magnification SEM images in Figure 3b shows that each flowerlike structure is composed of many

hexagonal nanosheets with an average thickness of 100 nm. These results indicate that the flowerlike cobalt hierarchical structures can be synthesized by the present simple route of surfactant-assisted hydrothermal reduction. Interestingly, the flowerlike structure can still maintain its morphology even after sonication for 30 min, indicating that the structure is stable.

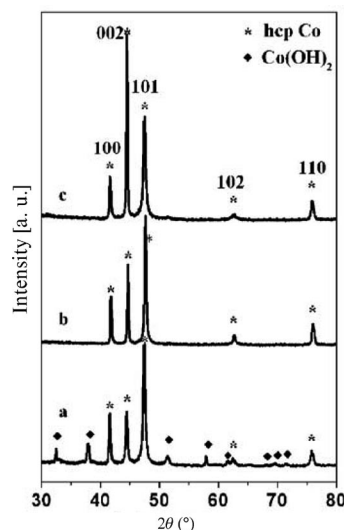


Figure 1. XRD patterns of the products collected at different stages of the reaction at 180 °C: after (a) 6 h, (b) 16 h, and (c) 24 h.

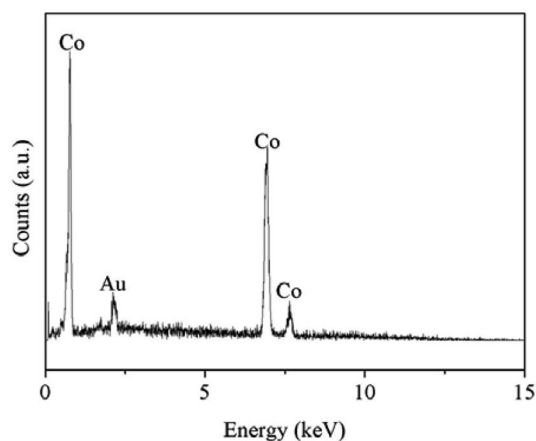


Figure 2. EDS pattern of the as-prepared cobalt flowerlike architectures at 180 °C after reaction for 24 h.

It was found that the morphologies of the products are greatly affected by the reaction temperature. When the reaction is performed at higher temperatures (ranging from 140 °C to 180 °C), the products are flowerlike hierarchical architectures, which are completely composed of hexagonal nanosheets with a thickness of 100 nm, similar to those obtained at 180 °C (Figure S1). However, it is interesting to note that when the reaction temperature is decreased to 120 °C, three different kinds of morphologies coexist in the product, as shown by the arrows in Figure 4a. One is the typical flowerlike architecture (similar to that shown in Figure 3), the second one is a spherical architecture, which is

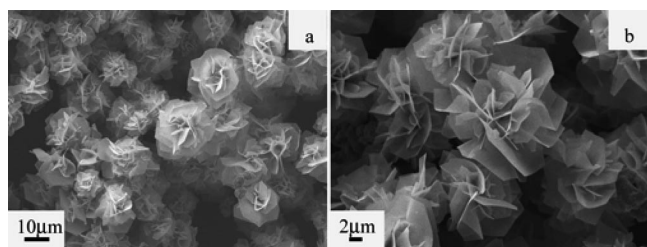


Figure 3. (a) Low-magnification and (b) high-magnification SEM images of the cobalt flowerlike architectures obtained at 180 °C after reaction for 24 h.

densely stacked by small hexagonal nanosheets (Figure 4b), another is monodisperse hexagonal sheets, with a diameter of 10  $\mu\text{m}$  and a thickness of about 200 nm. When the reaction temperature is decreased further to 100 °C, as shown in Figure 4c, the product is composed of irregular thin sheets in macroscale to nanoscale sizes, with widths of several hundred nanometers to a few micrometers. It is worth noting that most edges of the cobalt sheets have a tendency of curling, which may be due to their thin nature. The corresponding transmission electron microscopy (TEM) (Figure 4d) images and selected area electron diffraction (SAED) pattern (the inset in Figure 4d), demonstrate the sheet morphology of the products and indicate that the sheets are single crystals with a (0001) lattice plane as the basal plane. Due to the thin nature of and the magnetic interaction between the cobalt sheets, they tend to overlap.<sup>[20]</sup> In general, the morphology of the product depends strongly on the reaction temperature: lower temperature tends to generate cobalt sheets, while high temperature facilitates flowerlike architectures. This result is in agreement with other reports on the formation of CuO “dandelions”.<sup>[25]</sup> The results above suggest that the morphology of the product can be easily modified by changing the reaction temperature.

It was found that the surfactant SDBS is crucial for the growth of cobalt flowerlike architectures. In the absence of SDBS, the products are dominantly aggregations of spherical particles of various sizes (Figure S2). In order to investigate the influence of the surfactant, other surfactants have been examined. SDBS was substituted by sodium dodecyl sulfate (SDS) and cetyltrimethylammonium bromide (CTAB). No flowerlike architectures were observed in experiments with these surfactants. Furthermore, even upon varying the amount of the surfactants SDS or CTAB, the products were still spherical aggregations with irregular shapes (Figure S3). It is believed that the surfactant can selectively adsorb on a certain crystal facet of the as-prepared nanoparticles as well as prevent random aggregation of the nanoparticles, resulting in the assembled structures.<sup>[26,27]</sup> During the formation of the flowerlike architectures, SDBS possibly plays a role in both aspects. It is reasonable that the anionic surfactant has a stronger interaction with the cobalt ion relative to the cationic surfactant. The results reveal that not only the type but also the molecular structure of surfactant is important for the formation

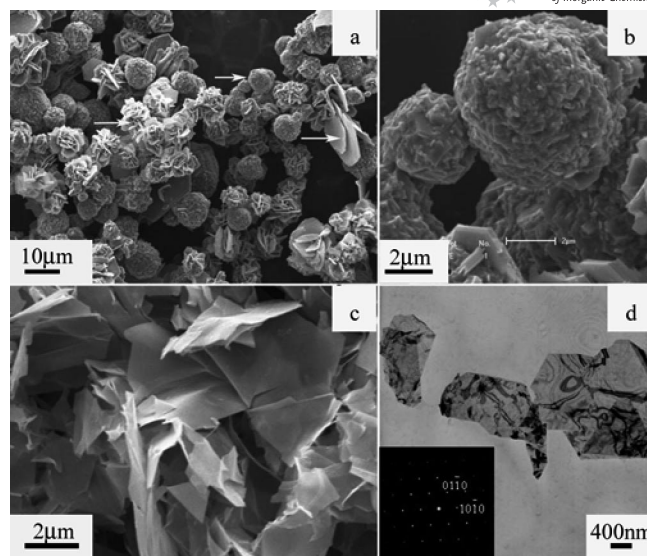


Figure 4. (a) Low-magnification and (b) high-magnification SEM images of the products prepared at 120 °C after reaction for 24 h, (c) SEM image and (d) TEM image of the products at 100 °C after reaction for 24 h (the inset in Figure 4d is the SAED of the cobalt nanosheets).

of the flowerlike architectures. In contrast to SDS, the surfactant SDBS favors the formation of flowerlike architectures, probably because of different interactions between the surfactant molecule and the cobalt ion.

To investigate the role of NaOH in the reaction, controlled experiments were carried out by keeping other parameters constant. When the concentration of NaOH was increased to 2–5 M, only irregular mesoscale sheets were observed. As shown in Figure 5, the size of the sheets increase with the concentration of NaOH. Xu et al. reported a similar result in the synthesis of metal (cobalt, nickel, copper) nanosheets in the presence of SDS.<sup>[20]</sup> It is understandable that the reaction rate is accelerated by increasing the NaOH concentration and the higher reaction rate favors the formation of larger sheet structure. This indicates that the NaOH concentration is a critical parameter for controlling the growth of flowerlike hierarchical architectures.

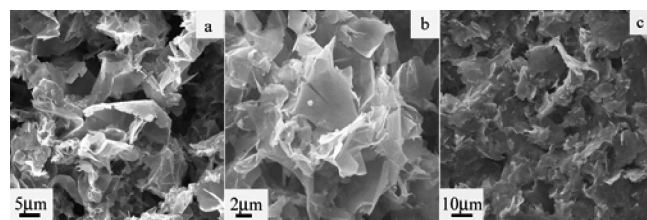


Figure 5. SEM images of the products prepared with different concentration of NaOH: (a) 2 M, (b) 3 M, (c) 5 M.

### Growth Mechanism for the Formation of Cobalt Flowerlike Architectures

To understand the growth mechanism of the flowerlike cobalt hierarchical architectures, systematical time-depend-

ent experiments illustrating the evolution of the structure and the morphology were carried out by XRD and SEM at various growth stages (6 h, 16 h, 24 h) of the hydrothermal process. When the reaction proceeds for 6 h, the XRD pattern (Figure 1a) shows that the product is a mixture of metallic Co and  $\text{Co}(\text{OH})_2$  (JCPDS NO. 30–443). The product exhibits an irregular morphology composed of a lot of tiny, close-stacked hexagonal sheets (Figure 6a). When the reaction time extends to 16 h, most of the product is metallic Co (Figure 1b) with flowerlike morphology (Figure 6b). When the reaction time is prolonged to 24 h, the reaction is complete. The product is metallic cobalt with flowerlike architectures consisting of many perfect hexagonal sheets (Figure 3). The reactions taking place during the hydrothermal process can be expressed as follows [Equation (1), Equation (2), and Equation (3)]:

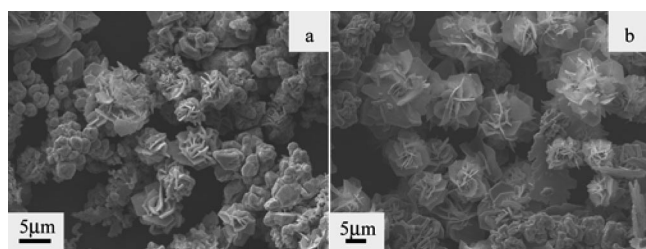
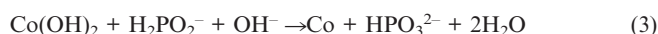
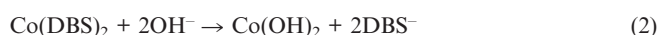


Figure 6. SEM images of the products recorded at different growth stages: (a) 6 h, (b) 16 h.

On the basis of the results above, a growth mechanism is proposed, as illustrated in Figure 7. Three consecutive stages are included as follows: (1) Numerous cobalt hydroxide colloids are formed in the basic solution of  $\text{CoCl}_2$  (Figure 7, step a). (2) The cobalt hydroxide crystals appear under hydrothermal treatment. As a result of its intrinsic lamellar structure, cobalt hydroxide is prone to forming platelets.<sup>[28]</sup> Then, the  $\text{Co}(\text{OH})_2$  is reduced, and thus metallic cobalt nuclei that sustain the hexagonal sheet morphology of  $\text{Co}(\text{OH})_2$  are obtained (Figure 7, step b). (3) As the reaction proceeds further, these Co hexagonal sheets diffuse and aggregate together as a result of the strong magnetic interaction and the driving force of entropy.<sup>[27,29]</sup> Meanwhile, the small aggregations may serve as seeds and grow by the Ostwald ripening process. The flowerlike architectures are thus generated (Figure 7, step c).<sup>[30]</sup> It should be noted that the present mechanism for the generation of the flowerlike structures is different from that reported in our earlier work<sup>[23]</sup> and in another report,<sup>[24]</sup> in which cobalt hierarchical microspheres were reported to form by a typical Ostwald ripening process. A comparison of experimental parameters and results between the present study and that of Hou et al.<sup>[24]</sup> is presented in Table 1. In the work of Hou

et al.,<sup>[24]</sup> the cobalt complex is first formed with sodium tartrate, it is then reduced, and cobalt nanoplates directly form, possibly because SDBS kinetically controls the growth rates of the different faces of a cobalt nanocrystal, and finally spherical structures are generated, the process being driven by the interfacial tension and the hydrophilic surface of the cobalt plates. However, in our experiments without the capping agent, the formation mechanism of cobalt sheets is absolutely different. Here, at the beginning of the reaction,  $\text{Co}(\text{OH})_2$  is formed, which is then reduced to Co sheets, and the intrinsic lamellar structure of  $\text{Co}(\text{OH})_2$  plays a crucial role in forming Co nanosheets. The procedure for assembling cobalt nanosheets into flowers is also similar to that for the generation of cobalt spheres.<sup>[24]</sup> The average size of the flowers is larger than that of the spheres, which may be ascribed to the higher reaction temperature adopted here. In summary, the generation of flowerlike architectures occurs in two main steps: the first step [from  $\text{Co}(\text{OH})_2$  sheets to Co sheets] is the morphology maintenance process, and the second step is a typical Ostwald ripening process (from cobalt sheets to cobalt flowers).

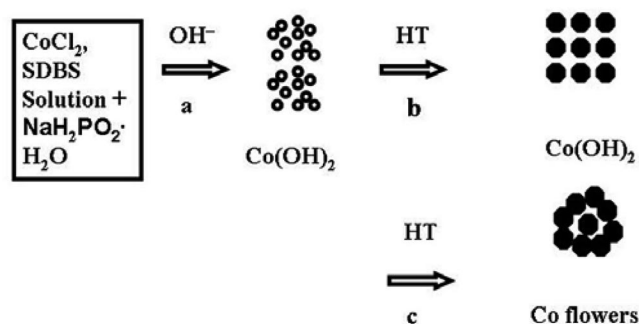


Figure 7. Schematic illustration of a possible formation procedure for the cobalt flowerlike architectures (HT: hydrothermal treatment.).

Table 1. A comparison of experimental parameters and results between the product in ref.<sup>[24]</sup> (sample 1) and the present product (sample 2).

| Sample | Reaction system                                                                                                                         | Temperature | Morphology        | Size    |
|--------|-----------------------------------------------------------------------------------------------------------------------------------------|-------------|-------------------|---------|
| 1      | $\text{CoCl}_2 + \text{Na}_2\text{-C}_4\text{H}_4\text{O}_6$<br>$\text{NaH}_2\text{PO}_2$<br>SDBS<br>$\text{NaOH} + \text{H}_2\text{O}$ | 110 °C      | cobalt<br>spheres | 2.8 μm  |
| 2      | $\text{CoCl}_2$<br>$\text{NaH}_2\text{PO}_2$<br>SDBS<br>$\text{NaOH} + \text{H}_2\text{O}$                                              | 180 °C      | cobalt<br>flowers | 8–10 μm |

## Magnetic Properties

The magnetic hysteresis loops of the cobalt flowerlike architectures obtained after hydrothermal treatment at 180 °C for 24 h were measured at 5 K and 295 K. The hysteresis loops were recorded at each temperature after a mag-

netic field of 20 kOe was applied. As shown in Figure 8, the coercivities at 5 K and 295 K are 371 Oe and 197 Oe, respectively. Relative to bulk cobalt (a few tens of Oe<sup>[16]</sup>) and cobalt hollow spheres (66 Oe, 300 K<sup>[21]</sup>), the coercivity at room temperature is enhanced, which can probably be attributed to the high shape anisotropy of the hexagonal sheets on the flowerlike architectures. However, although their morphologies are similar, the coercivity (371 Oe) of the present product at 5 K is much lower than that of the reported spheres (590 Oe, 5 K),<sup>[24]</sup> which might be because of the larger size of the present product (Table 1) and the higher reaction temperature. The saturation magnetization at 295 K of the flowerlike structures is 150.4 emu/g, which is slightly lower than that of its bulk counterpart (168 emu/g).<sup>[14]</sup> The result is consistent with other previous reports, which was ascribed to the reduction of the saturation magnetization because of the existence of impurities,<sup>[31]</sup> surface antiferromagnetic oxidation,<sup>[31]</sup> and surface spin disorder.<sup>[32]</sup> In the present case, all of these factors may be responsible for the reduction of the saturation magnetization.

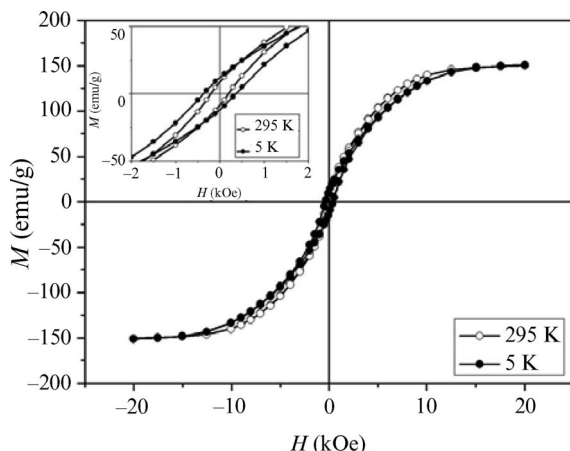


Figure 8. Magnetic hysteresis loops at 5 K (solid circles) and 295 K (open circles) of the product obtained at 180 °C after reaction for 24 h. The inset shows the low-field part of the hysteresis loops.

## Conclusions

Mesoscale formation of cobalt flowerlike hierarchical architectures self-assembled by hexagonal nanosheets has been fabricated in a controlled manner by a hydrothermal process in the presence of SDBS. It has been found that the surfactant SDBS, the reaction temperature, and the concentration of NaOH are key parameters for the fabrication of the complex 3D structures. The growth mechanism for the formation of the flowerlike architectures has been elucidated: the intermediate product  $\text{Co}(\text{OH})_2$  plays a critical role in the generation of sheet-shaped cobalt, and then the cobalt nanoplates assemble into flowers. The products exhibit ferromagnetic behavior. Such a simple and mild synthetic approach can be extended to the controlled synthesis of 3D hierarchical architectures of other materials.

## Experimental Section

All reagents used were commercial products of analytical pure grade, and they were used without further purification. In a typical procedure,  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  (0.238 g, 1 mmol), dodecyl benzenesulfonate (SDBS) (0.116 g, 0.5 mmol), and NaOH (1.6 g, 40 mmol) were first dissolved in distilled water (40 mL), and the solution was constantly stirred for 15 min at room temperature. After addition of  $\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$  (1.7 g, 16 mmol), the solution was constantly stirred for another 15 min. Then the solution was transferred into a 50 mL Teflon-lined stainless steel autoclave. The autoclave was sealed and maintained at 180 °C for 6–24 h and then cooled to room temperature naturally. The product was filtered off, washed with distilled water and ethanol for several times, finally dried in a vacuum oven at 60 °C for 4 h. Control experiments were carried out by adjusting the reaction temperature (100–180 °C) and the amount of NaOH (1–5 M), while keeping other reaction parameters unchanged.

The phases of all products were identified with a Rigaku D/max 2500pc X-ray diffractometer (XRD) with  $\text{Cu-K}\alpha$  radiation ( $\lambda = 1.54156 \text{ \AA}$ ) at a scan rate of  $0.04^\circ \text{ s}^{-1}$ . The morphology was investigated with a Shimadzu SSX-550 scanning electron microscope equipped with an EDS system operated at an acceleration voltage of 15.0 kV. Transmission electron microscopy (TEM) was carried with a TECNAI 20 instrument having an emission voltage of 200 kV. Magnetic hysteresis loops were measured by using a MPMS-7 superconducting quantum interference device (SQUID) magnetometer at fields up to 20 kOe.

**Supporting Information** (see footnote on the first page of this article): SEM images of the products at 140 °C and 160 °C; SEM image of the product at 180 °C in the absence of SDBS; SEM images of the products at 180 °C with SDS and CTAB.

## Acknowledgments

This work has been supported by the National Natural Science Foundation of China under Grant No. 50331030.

- [1] a) C. P. Collier, T. Vossmeier, J. R. Heath, *Ann. Rev. Phys. Chem.* **1998**, *49*, 371–404; b) M. P. Pileni, *J. Phys. Chem. B* **2001**, *105*, 3358–3371.
- [2] a) B. Kim, S. L. Tripp, A. Wei, *J. Am. Chem. Soc.* **2001**, *123*, 7955–7956; b) A. Wei, B. Kim, B. Sadler, S. L. Tripp, *Chem-PhysChem* **2001**, *2*, 743–745.
- [3] H. G. Yang, H. C. Zeng, *Angew. Chem. Int. Ed.* **2004**, *43*, 5930–5933.
- [4] a) V. F. Puentes, K. M. Krishnan, A. P. Alivisatos, *Science* **2001**, *291*, 2115–2117; b) M. Ruben, U. Ziener, J. M. Lehn, V. Ksenofontov, P. Gutlich, G. B. M. Vaughan, *Chem. Eur. J.* **2005**, *11*, 94–100; c) Y. Y. Li, J. P. Liu, X. T. Huang, G. Y. Li, *Cryst. Growth Des.* **2007**, *7*, 1350–1355; d) M. H. Cao, X. Y. He, J. Chen, C. W. Hu, *Cryst. Growth Des.* **2007**, *7*, 170–174.
- [5] a) M. H. Huang, S. Mao, H. Feick, H. Yan, Y. Wu, H. Kind, E. Weber, R. Russo, P. Yang, *Science* **2001**, *292*, 1897–1899; b) Y. Huang, X. F. Duan, Q. Q. Wei, C. M. Lieber, *Science* **2001**, *291*, 630–633; c) T. Yonezawa, S. Onoue, N. Kimizuka, *Adv. Mater.* **2001**, *13*, 140–142; d) S. Park, J. H. Lim, S. W. Chung, C. A. Mirkin, *Science* **2004**, *303*, 348–351; e) T. D. Ewers, A. K. Sra, B. C. Norris, R. E. Cable, C. H. Cheng, D. F. Shantz, R. E. Schaak, *Chem. Mater.* **2005**, *17*, 514–520; f) H. T. Shi, L. M. Qi, H. M. Cheng, B. Y. Zhu, *Adv. Mater.* **2003**, *15*, 1647–1651.
- [6] H. B. Li, L. L. Chai, X. Q. Wang, X. Y. Wu, G. C. Xi, Y. K. Liu, Y. T. Qian, *Cryst. Growth Des.* **2007**, *9*, 1918–1922.
- [7] S. L. Tripp, S. V. Puzstay, A. E. Ribbe, A. Wei, *J. Am. Chem. Soc.* **2002**, *124*, 7914–7915.

- [8] a) X. W. Teng, H. Yang, *Nano Lett.* **2005**, *5*, 885–891; b) X. S. Fang, C. H. Ye, L. D. Zhang, J. X. Zhang, J. W. Zhao, P. Yan, *Small* **2005**, *1*, 422–428.
- [9] a) L. Manna, D. J. Milliron, A. Meisel, E. C. Scher, A. P. Alivisatos, *Nat. Mater.* **2003**, *2*, 382–385; b) H. Q. Yan, R. R. He, J. Johnson, M. Law, R. J. Saykally, P. D. Yang, *J. Am. Chem. Soc.* **2003**, *125*, 4728–4729; c) F. Gao, Q. Y. Lu, S. H. Xie, D. Y. Zhao, *Adv. Mater.* **2002**, *14*, 1537–1540.
- [10] a) C. B. Murray, C. R. Kagan, M. G. Bawendi, *Science* **1995**, *270*, 1335–1338; b) J. Liu, Q. Wu, Y. Ding, *Cryst. Growth Des.* **2005**, *5*, 445–449.
- [11] S. H. Sun, *Adv. Mater.* **2006**, *18*, 393–403.
- [12] A. P. Alivisatos, *Science* **1996**, *271*, 933–937.
- [13] F. Dumestre, B. Chaudret, C. Amiens, M. Respaud, P. Fejes, P. Renaud, P. Zurcher, *Angew. Chem. Int. Ed.* **2003**, *42*, 5213–5216.
- [14] Q. Xie, Y. T. Qian, S. Y. Zhang, S. Q. Fu, W. C. Yu, *Eur. J. Inorg. Chem.* **2006**, *37*, 2454–2459.
- [15] Q. Xie, Z. Dai, W. W. Huang, J. B. Liang, C. L. Jiang, Y. T. Qian, *Nanotechnology* **2005**, *16*, 2958–2962.
- [16] H. Q. Cao, Z. Xu, H. Sang, D. Sheng, C. Y. Tie, *Adv. Mater.* **2001**, *13*, 121–123.
- [17] Y. Henry, K. Qunadjela, L. Piroux, S. Dubois, J. M. George, J. L. Duvail, *Eur. Phys. J. B* **2001**, *20*, 35–54.
- [18] F. Dumestre, B. Chaudret, C. Amiens, M. C. Fromen, M. J. Casanove, P. Renaud, P. Zurcher, *Angew. Chem. Int. Ed.* **2002**, *41*, 4286–4289.
- [19] V. F. Puentes, D. Zanchet, C. K. Erdonmez, A. P. Alivisatos, *J. Am. Chem. Soc.* **2002**, *124*, 12874–12880.
- [20] R. Xu, T. Xie, Y. G. Zhao, Y. D. Li, *Cryst. Growth Des.* **2007**, *7*, 1904–1911.
- [21] L. Guo, F. Liang, X. G. Wen, S. H. Yang, L. He, W. Z. Zheng, C. P. Chen, Q. P. Zhong, *Adv. Funct. Mater.* **2007**, *17*, 425–430.
- [22] C. M. Liu, L. Guo, R. M. Wang, Y. Deng, H. B. Xu, S. H. Yang, *Chem. Commun.* **2004**, 2726–2727.
- [23] Y. J. Zhang, S. Ma, D. Li, Z. H. Wang, Z. D. Zhang, *Mater. Res. Bull.*, DOI: 10.1016/j.materresbull.2007.11.010.
- [24] Y. L. Hou, H. Kondoh, T. Ohta, *Chem. Mater.* **2005**, *17*, 3994–3996.
- [25] B. Liu, H. C. Zeng, *J. Am. Chem. Soc.* **2004**, *126*, 8124–8125.
- [26] Z. P. Zhang, X. Q. Shao, H. D. Yu, Y. B. Wang, M. Y. Han, *Chem. Mater.* **2005**, *17*, 332–336.
- [27] Z. Zhang, H. Sun, X. Shao, D. Li, H. Yu, M. Han, *Adv. Mater.* **2005**, *17*, 42–47.
- [28] Y. L. Hou, H. Kondoh, M. Shimojo, T. Kogure, T. Ohta, *J. Phys. Chem. B* **2005**, *109*, 19094–19098.
- [29] N. Vandewalle, M. Ausloos, *Phys. Rev. E* **1997**, *55*, 94–98.
- [30] A. R. Roosen, W. C. Carter, *Phys. A* **1998**, *261*, 232–247.
- [31] L. Zhang, A. Manthiram, *Phys. Rev. B* **1996**, *54*, 3462–3467.
- [32] D. Lin, A. C. Nunes, C. F. Majkrzak, A. E. Berkowitz, *J. Magn. Magn. Mater.* **1995**, *145*, 343–348.

Received: March 27, 2008  
Published Online: May 6, 2008