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# Synthesis of Co submicrospheres self-assembled by Co nanosheets via a complexant-assisted hydrothermal approach

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# 1. Introduction

Magnetic nanostructures represent a particularly interesting class of materials for both fundamental scientific research and potential technological applications [1–3]. In recent years, controlling the morphologies and structures of magnetic nanomaterials has become the focus of intensive research, because the electronic, optical, catalytic, and magnetic properties of magnetic materials depend considerably on their size, shapes, and dimensionality [4-7]. As some of the most important magnetic materials, Co nanostructures have been of particular interest for their high saturation magnetization and magnetic coercivity, as well as their excellent catalytic properties [8-10]. In the past few years, much attention in this area has been paid to assembling low-dimensional Co nanostructures into three dimensional (3D) complex architectures, as a possible way to improve the magnetic anisotropy of the materials. To date, a number of 3D Co hierarchical architectures composed of nanosized subunits have been successfully fabricated by various methods [11-23]. Recently, Zhang et al. reported the synthesis of Co chains self-assembled by Co submicrospheres with the assistance of PVP in ethylene glycol solution [15]. Liu et al. demonstrated the fabrication of hierarchical Co nanoflowers composed of nanorods,

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## ABSTRACT

Co submicrospheres with the typical diameter of ca. 500 nm, and possessing beautiful morphologies composed of dense Co nanosheets ca. 10 nm thick, were synthesized by a facile and low-cost complexant-assisted hydrothermal approach. Magnetic measurement at room temperature indicated the coercivity of the submicrospheres reached 268 Oe, which was much higher than that of bulk Co and of some microstructure cobalt materials reported previously. Hexagonal close-packed (hcp) and face-centered cubic (fcc) cobalt phases in the materials were identified by X-ray diffractometer (XRD). It was revealed that the addition of the complexant sodium tartrate played a crucial role in the formation of the hierarchical architectures of the Co submicrospheres. We believe that the high coercivity of the synthesized submicrospheres may result from their special nano-micro structure, and we suggest that this low-cost and facile synthesis approach can be used for large-scale production of Co magnetic materials with special structures and morphologies, as well as excellent magnetic properties.

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through a solvothermal synthesis in polyol using Ru as the heterogeneous nucleation agent and hexadecylamine as the structure-directing agent [18]. Yang et al. prepared hexagonal Co microspheres composed of nanoflakes via a two-step process, in which cobalt bis (4-pyridine carboxylate) tetrahydrate was used as precursor of Co [19]. Obviously, noble metals, a considerable amount of surfactants, or some uncommonly used reagents are indispensable in most of these approaches, which makes the synthetic process less attractive because large-scale production of these microstructures will be costly.

In this study, we report the synthesis of Co submicrospheres with a typical diameter of ca. 500 nm, composed of Co nanosheets ca. 10 nm thick. The method was facile and low-cost, employing the complexant sodium tartrate (ST) to assist in the formation of hierarchical architectures. The prepared Co submicrospheres were characterized by X-ray diffractometry (XRD), scanning electron microscopy (SEM), X-ray energy-dispersive spectroscopy (EDS), and superconducting quantum interference device (SQUID) magnetometry. The effects of the complexant on the morphology of the final products, and the role of ST in the synthesis process, were also investigated.

# 2. Experimental section

All reagents were of analytic grade and double-distilled water was used throughout the experiment. In a typical synthetic

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process, 6 mmol  $CoCl_2 \cdot 6H_2O$  and 12 mmol ST were dissolved in 102 mL  $H_2O$ , followed by dropping 30 mL NaOH solution (5 M) and 16 mL hydrazine hydrate solution (50%) into the above solution under intense stirring. The total volume of the solution was ca. 150 mL and the final concentrations of  $CoCl_2$ , ST, NaOH, and hydrazine hydrate were 0.04, 0.08, 1, and 1 M, respectively. Afterwards, the solution was transferred into a Teflon-lined stainless steel autoclave, which was kept in an air oven at 393 K for 8 h. After the reaction, the solid precipitate in the bottom of Teflon cup was collected and washed with double-distilled water and acetone, then dried in a vacuum oven at 333 K for 12 h.

X-ray diffraction patterns were recorded using a Shimadzu XD-3A X-ray diffractometer with Cu K $\alpha$  radiation ( $\lambda = 1.5406$  Å). The morphology and elements of the sample were studied using a Hitachi 4800 field emission scanning electron microscope (FE-SEM) equipped with X-ray energy-dispersive spectroscopy. The *M*/*H* hysteresis loop was recorded with a Quantum Design MPMS XL-7 superconducting quantum interference device magnetometer.

30

40

50

2theta (degree)

60

70

#### 3. Results and discussion

The morphology and sizes of the samples were examined by FE-SEM. Fig. 1a, shows a low-magnification SEM image of the synthesized materials, in which the spherical particles can be clearly observed. It is important and interesting that the spherical particles are neither dense nor simply porous, but have a beautiful morphology and plentiful hierarchical architectures, as shown in Fig. 1b; the particles resemble peony flowers, and are composed of compact Co nanosheets ca. 10 nm thick.

The XRD pattern of the Co microspheres in Fig. 1c shows five peaks at  $2\theta = 41.6^{\circ}$ ,  $44.3^{\circ}$ ,  $47.4^{\circ}$ ,  $51.5^{\circ}$ , and  $75.9^{\circ}$ , suggesting the coexistence of hexagonal close-packed (hcp) and face-centered cubic (fcc) phases of Co in the samples [24]. The hcp and fcc phases of Co are close in energy because they differ only in the stacking sequence of the atomic planes in the cubic (111) direction; mixtures of these two phases have often been observed in samples prepared by wet-chemical methods [25,26]. The EDS pattern in Fig. 1d indicates that the sample is essentially pure Co. A small amount of oxygen (1.2 wt%) was also detected, which may

Co

Energy (keV)

9

6

12

15



Fig. 1. SEM images (a), (b), XRD and EDS patterns (c), (d) of the Co sample.

0

3

80

have resulted from partial oxidization and/or complexant residue on the sample's surface.

In a chemical reduction route, reduction temperature has a direct influence on the formation of crystal nuclei and the crystal growth rate of nano/micromaterials, thus also affecting the morphology and crystal structures of the products. In our study, when the reaction temperature was decreased to 363 K, the product was Co microspheres with a typical diameter of ca. 8 µm (Fig. 2a). Interestingly, numerous flying-saucer-like Co microcrystals were found embedded in the surface of these microspheres. We found the reduction reaction could even progress at room temperature (ca. 300K), but only some micron-sized Co spheres with relatively smooth surfaces were obtained (Fig. 2b). Increasing the temperature to 423 K resulted in the formation of Co submicrospheres structured by dense Co nanosheets, similar to those obtained at 393 K but not so beautiful or well architectured as the latter. It seems that a relatively high temperature is advantageous in the formation of Co submicrospheres composed of Co nanosheets, with the optimum temperature being ca. 393 K.

The crystal structures of the samples (as shown in Fig. 2d) obtained at different reaction temperatures were found to be almost the same. In our previous work, it was observed that the

crystal structures of the Co samples were highly related to the solvents used in the synthetic process, and the Co products tended to crystallize as mixed hcp and fcc phases in water solution [27]. This implied that the reaction temperature had little influence on the crystal structures, in spite of its great impact on the morphology of the samples.

Complexants have been widely utilized to modify the morphology of metallic nanomaterials prepared by chemical reduction of the corresponding metallic salts [7,12,26,28]. In the present study, when no complexant was used in the synthesis, the products were some dendrite-like Co microcrystals (Fig. 3a). When sodium citrate was substituted for ST as the complexant. the as-obtained Co products were similar in morphology to those obtained in the absence of the complexant, implying that sodium citrate had little effect on the morphology of the products. It should be mentioned that Li et al. and Xie et al. recently reported the aqueous phase synthesis of Co microspheres and Co nanowires with the assistance of citrate acid or citrate sodium [20,28]. But obviously, the reaction conditions in the present case were quite different. EDTA is another commonly used complexant that could be employed to control the morphology of the Co nanomaterials [7]. But we found that with EDTA as the complexant, only Co aggregates with irregular morphologies



Fig. 2. SEM images (a)–(c) and the crystal structures (d) of Co sample prepared at different reaction temperatures: (a) T = 300 K (b) T = 363 K (c) T = 423 K.



Fig. 3. SEM images of the samples prepared without complexing agent (a), and using sodium citrate (b), and EDTA (c) as complexing agents, respectively.



Fig. 4. SEM images of Co samples prepared at different molar ratios of ST to CoCl<sub>2</sub>: (a) 1:1, (b) 3:1.

were obtained (Fig. 3c). Based on these observations, it is clear that ST is crucial for the formation of the Co submicrospheres composed of Co nanosheets in our study. Moreover, we found the amount of ST in the synthesis also played an important role in determining the final morphology of the products. When the molar ratio of ST to CoCl<sub>2</sub> was decreased from 2:1 to 1:1, Co aggregates with irregular morphologies as well as Co nanoplatelets were obtained (Fig. 4a). When the molar ratio was increased to 3:1, Co submicrospheres composed of Co nanosheets could again be achieved (Fig. 4b). This suggests that a relatively high concentration of ST is favorable for the production of Co submicrospheres.

To further understand the role of ST in the synthesis, we carried out XRD analysis of a sample obtained at an early stage of the reaction process (the hydrothermal reaction proceeded for 2 h in total). The XRD result in Fig. 5a indicates that metallic Co coexisted with  $Co(OH)_2$  in the sample. We also designed another experiment, in which no  $N_2H_4$  was introduced into the synthesis while other experimental conditions were kept unchanged. All the diffraction peaks in the XRD pattern (Fig. 5b) of the corresponding

product can be assigned to  $Co(OH)_2$ , and the typical SEM images (Fig. 6) indicate that these  $Co(OH)_2$  products are numerous nanosheets ca. 20 nm thick and 50–200 nm in diameter.

The solubility product constant  $(K_{sp})$  of Co(OH)<sub>2</sub> is  $10^{-14.23}$ , while the complex stability constant of Co<sup>2+</sup>-tartaric acid is only  $10^{2.1}$  [29]. So, in a strong basic solution the Co<sup>2+</sup>–ST complex is not stable from a thermodynamics viewpoint, and the ST ligands will be replaced by OH<sup>-</sup>. Considering the XRD results in Fig. 5, it is reasonable to conclude that the actual precursor of Co was  $Co(OH)_2$  rather than  $Co^{2+}$ -ST complex. Recently, Zhang et al. proposed a mechanism to explain the formation of the flowerlike Co architecture [16], which included three steps: (1) Co(OH)<sub>2</sub> platelets were formed as an intermediate product: (2) Co products sustained the platelet structure of  $Co(OH)_2$  in the presence of the surfactant during chemical reduction; and (3) Co nanosheets diffused and assembled together as a result of strong magnetic interaction and of the drive of entropy. According to this mechanism, the formation of Co nanosheets is, in the present study, the key step in the production of Co submicrospheres. To clarify this, an additional experiment was done in which the as-



Fig. 5. XRD patterns of the samples obtained at the reaction time of 2h (a) and obtained in the absence of reducing agent (b).



Fig. 6. Typical SEM images of the Co sample obtained in the absence of reducing agent.

prepared Co(OH)<sub>2</sub> nanosheets (Fig. 6) were used instead of CoCl<sub>2</sub> as the reagent in the absence of ST. We found that no Co submicrospheres were produced without the assistance of ST; instead, the products were dendritic Co microcrystals (Fig. 7), quite similar in morphology to the sample obtained with CoCl<sub>2</sub> as the reagent in the absence of ST (Fig. 3a). Based on our experimental results, it is clear that ST played a key role in the second step, i.e., sustaining the nanosheet architecture and assisting in the formation of Co nanosheets, which would self-assemble into submicrospheres to lower the energy of the system, due to the high surface energy of the nanosheets and the strong magnetic interaction.

To determine the magnetic properties of the as-prepared Co submicrospheres, magnetic measurements were carried out at room temperature (300 K). The results are shown in Fig. 8, which demonstrates that the sample exhibits typical ferromagnetic properties at room temperature. The saturation magnetization  $(M_s)$  and remnant magnetization  $(M_r)$  of the sample are 157.2 and 11.0 emu/g, respectively.  $M_s$  is lower than that of bulk Co (168 emu/g), which may be attributed to the existence of oxides and/or organic residue on the surface of the sample [30]. As shown in Fig. 8b, the coercivity of the as-prepared Co microspheres composed of Co nanosheets at room temperature can reach 268 Oe, which is much higher than that of bulk Co (ca. tens of oersteds at room temperature [31]). The coercivity is also higher than those of recently reported Co chains self-assembled by Co submicrospheres (90Oe, 295 K [15]), and Co flowerlike architectures (197 Oe, 295 K [16]). It is widely acknowledged that the magnetization behavior of magnetic materials is closely associated with their shape and crystalline anisotropy [32]. The enhanced coercivity of the as-synthesized Co submicrospheres can be attributed to the high shape anisotropy of the Co nanosheets in the submicrospheres. However, this was still much lower than that of the flowerlike Co microcrystals composed of Co nanoplatelets reported in our early work (407.3 Oe, 300 K [7]), which may be due to the relatively small aspect ratio and low crystallinity of Co nanosheets in the asprepared Co submicrospheres.

## 4. Conclusion

In summary, Co submicrospheres self-assembled by dense Co nanosheets with a thickness of ca. 10 nm were synthesized via a



Fig. 7. SEM images of the Co sample prepared by using  $Co(OH)_2$  nanosheets as reagent in the absence of ST.



Fig. 8. Room-temperature magnetic hysteresis loops of the Co submicrospheres (a) and magnified magnetic hysteresis loops at the low field (b).

complexant-assisted hydrothermal approach, in which sodium tartrate was used to assist the formation of a hierarchical architecture. Magnetic measurement at room temperature indicated the coercivity of the as-prepared submicrospheres reached 268 Oe, which was much higher than the coercivity of either bulk Co or similar microstructures reported previously. It was revealed that complexant, sodium tartrate, was crucial for the formation of the Co submicrospheres. The facile complexantassisted solution route presented here used only low-cost inorganic reagents, making the method very suitable for largescale production of Co submicrospheres with hierarchical nanostructures.

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#### References

- [1] G.S. Chaubey, C. Barcena, N. Poudyal, C. Rong, J. Gao, S. Sun, J.P. Liu, J. Am. Chem. Soc. 129 (2007) 7215.
- A.-H. Liu, E.L. Salabas, F. Schüth, Angew. Chem. Int. Ed. 46 (2007) 1222.
- J.M. Thomas, E.T. Simpson, T. Kasama, R.E. Dunin-Borkowski, Acc. Chem. Res. 41 (2008) 665.
- [4] X.-W. Wei, G.-X. Zhu, Y.-J. Liu, Y.-H. Ni, Y. Song, Z. Xu, Chem. Mater. 20 (2008) 6248

- [5] T. Wang, Y. Wang, Y. Fu, T. Hasegawa, H. Oshima, K. Itoh, K. Nishio, H. Masuda, F.S. Li, H. Saito, S. Ishio, Nanotechnology 19 (2008) 455703.
- M. Guang, J. Sun, C. Gao, X. Li, Z. Xu, Chem. Phys. Chem. 8 (2008) 2182.
- H. Li, S. Liao, J. Phys. D: Appl. Phys. 41 (2008) 065004.
- V.F. Puntes, K.M. Krishnan, A.P. Alivisatos, Science 291 (2001) 2115. [8]
- [9] A. Javey, H. Dai, J. Am. Chem. Soc. 127 (2005) 11942.
- [10] S.H. Sun, Adv. Mater. 18 (2006) 393.
- [11] Y. Hou, H. Kondoh, T. Ohta, Chem. Mater. 17 (2005) 3994.
- [12] X. Ni, D. Li, Y. Zhang, H. Zheng, Chem. Lett. 36 (2007) 908.
- Y.J. Zhang, S. Ma, D. Li, Z.H. Wang, Z.D. Zhang, Mater. Res. Bull. 43 (2008) 1957. [13] X. Wang, F. Yuan, P. Hu, L. Yu, L. Bai, J. Phys. Chem. C 112 (2008) 8773. 14
- Y.-J. Zhang, Q. Yao, Y. Zhang, T.-Y. Cui, D. Li, W. Liu, W. Lawrence, Z.-D. Zhang,
- Cryst. Growth Des. 8 (2008) 3206. [16] Y.-J. Zhang, Y. Zhang, Z.-H. Wang, D. Li, T.-Y. Cui, W. Liu, Z.-D. Zhang, Eur. J.
- Inorg. Chem. (2008) 2733. [17] H. Qi, W. Zhang, X. Wang, H. Li, J. Chen, K. Peng, M. Shao, Catal. Commun. 10
- (2009) 1178. [18]
- Q. Liu, X. Guo, Y. Li, W. Shen, J. Phys. Chem. C 113 (2009) 3436.
- [19] X. Yang, Q.-W. Chen, J.-Z. Zhang, Mater. Chem. Phys. 113 (2009) 675. [20] Y. Li, J. Zhao, X. Su, Y. Zhu, Y. Wang, L. Tang, Z. Wang, Colloids Surf. A:
- Physicochem. Eng. Aspects 336 (2009) 41.
- [21] Y. Zhu, Q. Yang, H. Zheng, W. Yu, Y. Qian, Mater. Chem. Phys. 91 (2005) 293. [22] J. Zhang, Z. Dai, J. Bao, N. Zhang, M.A. López-Quintela, J. Colloid Interface Sci.
- 305 (2007) 339.
- [23] R.-H. Wang, J.-S. Jiang, M. Hu, Mater. Res. Bull. 44 (2009) 1468.
- [24] Y. Zhu, H. Zheng, Q. Yang, A. Pan, Z. Yang, Y. Qian, J. Cryst. Growth 260 (2004) 427
- [25] C.B. Murray, S. Sun, H. Doyle, T. Betley, MRS Bull. 26 (2001) 985.
- [26] Y. Zhu, Q. Yang, H. Zheng, W. Yu, Y. Qian, Mater. Chem. Phys. 91 (2005) 293.
- [27] H. Li, Shijun Liao, J. Magn. Magn. Mater. 321 (2009) 2566.
- [28] Q. Xie, Y. Qian, S. Zhang, S. Fu, W. Yu, Eur. J. Inorg. Chem. (2006) 2454.
- [29] J.A. Dean, Lange's Chemistry Handbook, 13th ed., McGraw-Hill Book Company, 1985, pp 8.9 and 8.102.
- [30] L. Zhang, A. Manthiram, Phys. Rev. B 54 (1996) 3462.
- [31] H. Cao, Z. Xu, H. Sang., D. Sheng, C.Y. Tie, Adv. Mater. 13 (2001) 121.
- [32] D.L. Leslie-Pelecky, R.D. Rieke, Chem. Mater. 8 (1996) 1770.