Preparation and characteristics of Co nanoporous magnetic materials synthesized by a template-free method

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Abstract. We report a template-free hydrogen reduction approach to prepare cobalt nanoporous magnetic materials with various morphologies employing Co3O4 as precursors, which were obtained by thermal-decomposing CoCO3 intermediates. The kinetic control of experimental parameters of synthetic CoCO3 intermediates by a facile solvent-thermal route can be an effective strategy to tune the morphology of Co nanoporous structures. The microstructures, crystal structures or thermal characteristics of products at different stages were investigated to reveal the formation mechanism of the Co nanoporous structures. Magnetic measurement showed that the Co nanoporous structures with rhomb-like and prism-like morphology exhibited saturation magnetization (Ms) of 149.2 emu/g and 141.8 emu/g, and coercivity (Hcj) of 508.4 Oe and 554.9 Oe, respectively. The as-prepared Co ferromagnetic materials exhibited remarkably high coercivity values mainly due to the three dimensional nanoporous structures.

1. Introduction

In the field of nanoscale materials with various morphologies, nanoporous materials with high specific surface area have been attracting intensive attention since porous materials usually exhibit unique physical properties different from solid structures, which make them critically important in technological applications such as catalysts [1, 2], sensors [3, 4], microwave absorbs [5], gas storage [6], ion transport membranes [7], super-capacitor electrodes [8, 9], and so on. Nanoporous metallic materials including nanoporous gold leaf [10], porous Pt–Co alloy nanowires [11], porous Au–Ag alloy nanotubes [12], and nanoporous films of noble metals (Au, Pd, Pt, Rh and Ru) [13] have been widely studied. Metallic nanostructured magnets with different morphologies have shown applications in the fields of high-density magnetic recording, medical diagnosis, magnet sensors, microwave absorption, etc. [14-19]. As important ferromagnetic materials, Co nano/micro-structures have also drawn extensive research attention for magnetic electronic devices due to its high saturation magnetization (Ms) and large anisotropy field [20]. Co nano/micro-structures such as flower-like Co spheres, hollow Co nanochains, Co nanoplatelets etc. have been investigated [21-23]. However, few contributions have been presented for Co nanoporous structures.

Template-based approaches were usually used to generate porous structures. Macroporous magnetic film was fabricated by the template-based electrochemical deposition employing assembled colloidal polystyrene spheres as template, but this approach is somewhat complicated and only
suitable for generating porous films [24]. Although microwave-assisted synthesis can prepare porous materials with narrow pore size distribution, this method was limited to metal-oxide materials (e.g., Fe₂O₃, Fe₃O₄, Co₃O₄) [25-28]. Other methods such as reaction-limited aggregation of nanoparticles [29, 30], fusion of metal nanoparticles during the reduction process [31], are employed to generate selected porous noble metallic structures. The above synthesis routes usually suffer from weak dispersity, low yield, and ineffective control over the morphology and size of spongy materials, which will affect their practical applications, and thus it is still a challenge to find new efficient routes to synthesize porous metallic materials.

In this study, we report a template-free hydrogen reduction approach to prepare Co nanoporous structures employing Co₃O₄ as precursor. Co₃O₄ precursors were obtained by thermal-decomposing of CoCO₃ intermediates with various morphologies prepared by a facile solvent-thermal approach. Monodispersed cobalt porous particles with continuous ligament-channel networks were successfully synthesized through a hydrogen reduction process. The magnetic properties of the Co nanoporous structures were investigated. The reported template-free method featured low cost, good structure stability, easy operation, and wide applicability, can provide a novel strategy to fabricate porous metallic materials.

2. Experimental

2.1. Synthesis of monodispersed Co nanoporous structures

1 g polyvinyl-pyrrolidone (PVP) was dissolved in 40 ml diethylene glycol (DEG) or the mixed solution of 38 ml DEG and 2ml deionized water, followed by the addition of 0.5 g Co(CH₃COO)₂·4H₂O ((Co(Ac)₂·4H₂O) under magnetic stirring. After they were completely dissolved, 0.3–1.8 g urea was added. The clear transparent solution was sealed into a 50 ml Teflon-lined autoclave and heated at 200 °C for 24 h. The pink products were centrifuged and washed with deionized water and ethanol, and then dried at 60 °C for 12 h. In this stage, the synthesis approach of CoCO₃ intermediates was developed on the base of the procedure reported by Li et al [32]. In ambient air, the as-prepared CoCO₃ samples were converted to nanoporous Co₃O₄ precursors by thermal decomposing at 400 °C for 1 h with a ramping rate of 1 °C min⁻¹. Then the Co₃O₄ precursors were placed in an alumina boat and treated at 300 °C for 2 h with a ramping rate of 2 °C min⁻¹, under H₂ flux in a quartz tube furnace.

2.2. Characterization

The X-ray diffraction (XRD) pattern was obtained by a Rigaku Dmax-rc X-ray diffractometer with Ni filter CuK radiation (V = 40 kV, I = 50 mA) at a scanning rate of 4° min⁻¹. The microstructures of the resultant products were examined using a JSM-6700F field emission scanning electron microscope (FE-SEM) and a JEOL JEM-2100 high-resolution TEM (HR-TEM) operated at 200 kV. The thermal characteristics of CoCO₃ intermediates were measured by thermogravimetric (TG) analysis that was conducted on a diamond TG Perkin Elmer instrument at a heating rate of 10 °C min⁻¹ under air flux. The magnetization hysteresis curves of the nanoporous Co particles were recorded by a vibration sample magnetometer (Tamakawa, TM-VSM2014-MHR-Type).

3. Results and discussion

3.1. Structure and morphology

3.1.1. CoCO₃ intermediates. The different experimental parameters and the corresponding morphologies of CoCO₃ intermediates were listed in Table 1. As shown in Figure 1, all synthesized CoCO₃ particles are monodispersed with a narrow size distribution. Sample 1 showed the rhomb-like particles with a diameter of ca. 1-1.3 μm (Figure 1(a)). When the addition amount of urea decreased from 1.8 g to 0.6 g in solution, dumbbell-like structure (S2) aggregating from two solid spheres
Two individual solid spheres were fused into a dumbbell-like CoCO$_3$ particle during the growth stage of crystal driven by magnetic dipole attraction under the solvent-thermal condition \[33\]. Further decreasing the urea amount to 0.3 g, only a small amount of dumbbell-like CoCO$_3$ (S3) particles were obtained. When 2 ml deionized water was added to 38 ml DEG solution (total 40 ml) and the other experimental parameters were the same as S1 and S2, respectively, Figure 1 (b) and (d) revealed that the rhomb shaped (S4) and cube-like (S5) CoCO$_3$ particles were obtained, and the CoCO$_3$ particles have bigger size (1.5-2 $\mu$m) than S1 and S2. In contrast, when the urea amount was decreased to 0.3 g and the other experimental parameters were kept the same as S4 and S5, the prism-like CoCO$_3$ particles (S6) with length of ca. 2 $\mu$m and width of ca. 900 nm could be prepared (Figure1 (e)). The above results indicated that the addition of deionized water in the reaction system plays an important role in controlling the morphology and accelerating the crystallization of CoCO$_3$ in addition to the effect of urea. XRD measurements confirmed that all pink products synthesized in the solvent-thermal process are rhombohedral CoCO$_3$. As represented in Figure 1 (f), all diffraction peaks of the rhomb-like particles (S1) could match well with rhombohedral CoCO$_3$ with the cell constants of $a = 4.662$ Å and $c = 14.96$ Å (JCPDS 11-0692), and no peak of any other phase is detected, confirming the generation of pure CoCO$_3$.

In the solvent-thermal condition, the decomposition of urea at elevated temperature generates CO$_2$ and NH$_3$, and then CO$_2$ gas dissolves in the solution to form CO$_3^{2-}$ anions, which react with Co$^{2+}$ to form CoCO$_3$. When 2 ml deionized water was added into the reaction solution, the rhomb shaped (S4), cube-like (S5) and prism-like (S6) CoCO$_3$ particles with well crystallization were obtained due to the decrease of viscosity in the reaction system, which might lead to the diffusion of ions or subunits more easily and accelerate the anisotropic growth of CoCO$_3$ particles \[34\]. In contrast, CoCO$_3$ particles tend to grow more slowly without the addition of deionized water resulting in a relatively smooth surface. For example, the rhomb-like particles (S1) was likely to have an initial agglomeration stage, and then a slow Ostwald ripening process, in which the formed sphere-like particles with smooth surface have a relatively small surface energy and are thermodynamically favoured \[35\]. Besides, PVP plays an important role as the surface modifier to control the size and agglomeration of particles. PVP physically absorbed on the surface of the subunits can prohibit the growth of the grain as well as link the subunits to form more stable spheres during the reaction process \[36\], and thus the application of PVP can lead to narrow size distribution and monodispersed feature.

Table 1. Different samples and corresponding designed experimental parameters and morphologies.

| Samples | Co(Ac)$_2$·4H$_2$O (g) | Urea (g) | DEG (ml) | Time (h) | Morphology       |
|---------|------------------------|----------|----------|----------|------------------|
| S1      | 0.5                    | 1.8      | 40       | 24       | Rhomb-like       |
| S2      | 0.5                    | 0.6      | 40       | 24       | Dumbbell-like    |
| S3      | 0.5                    | 0.3      | 40       | 24       | Dumbbell-like    |
| S4      | 0.5                    | 1.8      | 38       | 24       | Rhomb shaped     |
| S5      | 0.5                    | 0.6      | 38       | 24       | Cube-like        |
| S6      | 0.5                    | 0.3      | 38       | 24       | Prism-like       |
Figure 1. (a)-(e) SEM images of the CoCO₃ intermediates at different urea and deionized water content. (a) S1 with rhomb-like, (b) S4 with rhomb shaped, (c) S2 with dumbbell-like, (d) S5 with cube-like, (e) S6 with prism-like morphology. The insets of (a), (c), (e) are the magnification SEM images, and the black scale bar is equal to 500 nm. (f) XRD pattern of CoCO₃.

3.1.2. Nanoporous Co₃O₄ precursors. Rhomb-like (S1) and prism-like (S6) intermediates were chosen to prepare nanoporous Co₃O₄ precursors by thermally decomposing in air. The thermal behaviors of the carbonate samples have been examined by TG analysis. As present in Figure 2, the total weight losses of S1 and S6 were determined to be 40.07 wt% and 35.78 wt%, respectively. The weight loss at low temperature was mainly attributed to the removal of absorbed surfactants and water on the samples. After that, a drastic decrease in the dominant weight loss profile demonstrates a rapid decomposition process of CoCO₃ to Co₃O₄ and CO₂. Before the thermal-decomposing of CoCO₃, S1 showed higher weight loss (8.35 wt%) than that (3.62 wt%) of S6, probably due to the more surfactant attachment on the surface of S1 than S6 prepared in the present of water. In the thermal-decomposing process, the weight losses of S1 and S6 were 31.72% and 32.16%, respectively, approaching to the theoretical value (32.51%) of the decomposition of CoCO₃. In addition, the starting temperature of CoCO₃ decomposing for S6 is higher than that of S1 while the completion temperature is almost the same (ca. 400°C), probably attributing to the relatively larger particle size of S6. Therefore, 400°C was chosen as the calcination temperature to prepare nanoporous Co₃O₄.

After being annealed in air at 400 °C for 2h, the as-prepared carbonate intermediates were completely converted to phase-pure spinel Co₃O₄ (XRD in Figure 3(i)). All diffraction peaks could be indexed to the pure cubic phase of Co₃O₄ (lattice constant a₀ = 8.0837 Å; JCPDS PDF file no. 42-1467). From the panoramic SEM images (Figure 3(a), (d)), the original morphologies of CoCO₃ intermediates (S1, S2, and S6) were reserved well, while the higher magnification images for individual particle (Figure 3(b), (e), and (g)) show that Co₃O₄ remained an intact three-dimensional framework with porous structure after CO₂ gas released during the thermal decomposition process. Close inspections in Figure 3(c), (f) and (h) reveal that the wormhole-like mesoporous are actually disordered channels enclosed by solid ligaments, which consist of one or several interconnected particles. Fundamentally, the heat treatment caused the diffusion and aggregation of Co₃O₄ nuclei.
under the thrust of surface-energy reduction, leading to the formation of ligament islands and pore channels.

![Figure 2. Thermo-gravimetric (TG) curves of rhomb-like (S1) and prism-like (S6) samples.](image)

To further reveal the porous structure, TEM characterizations were performed on the prism-like Co$_3$O$_4$ sample. The apparent contrast between the white part and the black ligaments also confirms the nanoporous wormhole-like characteristic (Figure 4(a)), and the corresponding selected area electron diffraction (SAED) pattern (inset of Figure 4(a)) presents the polycrystalline nature of the porous structure. HRTEM image taken from the edge of S6 is shown in Figure 4(b). The typical lattice fringe spacings were measured to be 0.466 nm and 0.285 nm, corresponding to the (111) and (220) crystal planes of cubic Co$_3$O$_4$, meanwhile the pore with diameter of ca. 7 nm was observed.

![Figure 3. SEM images of as-prepared nanoporous Co$_3$O$_4$ precursors with rhomb-like (a, b and c), dumbbell-like (d, e, f), and prism-like (g, h) morphology. (i) XRD pattern of Co$_3$O$_4$.](image)
Figure 4. (a) and (b) HRTEM images of the prism-like Co$_3$O$_4$ precursor. The inset of (a) is the corresponding SAED pattern.

3.1.3. Co nanoporous structures. Monodispersed Co nanoporous particles were synthesized after the porous Co$_3$O$_4$ precursors were reduced by hydrogen. Figure 5 shows the XRD patterns of Co products obtained by the reduction treatment at 300 °C, 400 °C and 480 °C for 2h, respectively. When the reduction temperature was 300 °C, four obvious diffraction peaks can be indexed to the (100), (002), (101), and (110) facets of hexagonal-close-packed (hcp) Co phase (Figure 5(a)). If the temperature was increased to 400 °C, a weak diffraction peak of (200) assigned to centered cubic (fcc) Co phase appeared (Figure 5(b)), indicating that a phase transition began to occur. Further increasing the temperature, the phase transition became more obvious suggesting from the more intensity diffraction peak of (200) (Figure 5(c)). Generally, metallic cobalt has two different crystal structures: hcp and fcc structure. The fcc Co structure is a metastable epsilon phase, which is believed to be a third polymorph of elemental cobalt, therefore, the fcc Co phase appeared mainly due to the high reduction temperature.

Figure 5. XRD patterns of Co products obtained by hydrogen-reduction treatment at 300 °C (a), 400 °C (b), and 480 °C (c) for 2h.

Figure 6 shows the SEM images of Co products derived from rhomb-like (S1), dumbbell-like (S2), and prism-like (S6) precursors. The resultant Co products preserved the ligament-channel framework, and there is a slight decrease in size due to the structure shrink. Close inspection (Figure 6 (b), (d), and (f)) reveals that the sponge-like porous morphologies are actually built from particle-like ligaments and there are a lot of holes on the surface of Co particles. The Co nanoporous particles formed through a three-step formation mechanism. When CoCO$_3$ intermediates were gradually heated, CO$_2$ started to release from the surface of particles. The CO$_2$ gas ran through channels originating from structure
defects or vacancies of oxygen and carbon atoms, and also the void space left from the assembly of inner particles for decreasing the surface energy at high temperature. The channels were reserved as an interconnected three-dimensional (3D) network after the Co$_3$O$_4$ crystallization. When reduction gas homogeneously flew through the porous Co$_3$O$_4$ precursors, by kinetically controlling the thermal reduction, the crystallization and growth of Co nanoparticles formed during the reduction process can be induced to constitute a 3D sponge-like structure with Co backbones. If the CoCO$_3$ intermediates were directly treated by thermal reduction at 300 °C without the first decomposition process, obvious cracks can be observed on Co particle surface, indicating that one-pot reaction was too violent to allow a well-defined complete porous Co structure.

![Figure 6. SEM images of (a, b) rhomb-like, (c, d) dumbbell-like and (e, f) prism-like cobalt nanoporous structures.](image)

3.2. Magnetic properties of Co nanoporous structures

The magnetic characterizations of Co nanoporous structures were performed at room temperature, and magnetic properties including saturation magnetization (M$_s$) and coercivity (H$_c$) of cobalt samples with different morphologies were close. The typical magnetization hysteresis (M-H) loops of the rhomb-like (H1) and prism-like (H6) morphology prepared with different contents of urea and DEG as reactants were shown in Figure 7. The porous cobalt samples with rhomb-like and prism-like structures exhibited M$_s$ of 149.2 and 141.8 emu/g, respectively. Comparing with M$_s$ value of bulk Co (168 emu/g) [37], the saturation magnetization of the as-prepared nanoporous cobalt structures are slightly reduced, but close to the other reported values of Co nano/micro-structures such as flower-like Co particles and hollow Co microspheres [38-39]. The decrease of M$_s$ is probably attributed to the existence of nonmagnetic or weak magnetic Co oxide shell due to the exposure of samples in air after synthesis. Moreover, the nanoporous structures have large surface area, which induced the enhancement of spin disorder on the surface [40], might be another reason for the reduction of ferromagnetism. However, H1 and H6 samples exhibited the remarkable large coercivity (H$_c$) of 508.4 and 554.9 Oe, respectively, which are higher than that of bulk cobalt (ca. 10 Oe) [41].

Generally, the magnetocrystalline anisotropy and the shape anisotropy of materials mainly contribute to coercivity. The experimental results suggest that the random and isotropic interactions of the nanoporous structures enhance the anisotropy fields of cobalt and more magnetic energy is demanded to change the magnetization direction of dipoles [42]. The coercivity value of Co samples is
higher due to the enhanced anisotropic field involving magnetocrystalline anisotropy and shape anisotropy of the nanoporous ferromagnetic material.

4. Conclusions
In conclusion, monodispersed cobalt nanoporous structures have been synthesized by a novel hydrogen reduction synthesis approach employing Co$_3$O$_4$ as precursors. The wormhole-like Co$_3$O$_4$ precursors were obtained by thermal-decomposing CoCO$_3$ intermediates with various morphologies prepared by a facile solvent-thermal approach. The products in every step were characterized by the X-ray diffraction (XRD), SEM, high-resolution transmission electron microscopy (HR-TEM), thermogravimetric (TG) analysis. The Co nanoporous structures with rhomb-like and prism-like morphology exhibited coercivity ($H_c$) of 508.4 Oe and 554.9 Oe, respectively. Compared with some other Co materials, the nanoporous cobalt exhibited higher coercivity values, mainly due to the three dimensional porous structure with an enhanced anisotropic field involving magnetocrystalline anisotropy and shape anisotropy of the nanoporous ferromagnetic material.

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