Magnetically self-assembled SrFe₁₂O₁₉/Fe-Co core/shell particles

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ABSTRACT: Epitaxial growth to synthesize core/shell-structured materials is limited because large lattice mismatches are common between materials. Magnetically hard/soft, core/shell-structured materials can be potentially used for rare-earth free permanent magnets, but their synthesis presents a challenge. We report a wet chemistry method to synthesize core/shell structured particles consisting of a magnetically hard SrFe₁₂O₁₉ core and a soft Fe-Co shell, with a lattice mismatch of ~100%, which cannot be achieved by conventional epitaxial growth or other alternative methods. When decreasing the size of the magnetically soft Fe-Co nanoclusters to below 5 nm, we show that they can be magnetically attracted by the hard SrFe₁₂O₁₉ to form core/shell structured particles. An AC demagnetization experiment demonstrates the formation mechanism of the core/shell particles, and their magnetic hysteresis loop shows potential for use as rare-earth free permanent magnets.

1. Introduction

Core/shell hetero-structured materials with modulated composition have been of great interest because of their novel magnetic [1], catalytic [2], optical [3] and electronic properties [4]. Currently, most core/shell-structured materials are synthesized by epitaxial growth [5-7]. Unfortunately, differences in lattice constant, crystal structure and bonding between core and shell materials, limit the application of epitaxial growth [6, 8, 9]. The failure of epitaxial growth has stimulated discovery of other alternative methods, such as nonepitaxial growth [10] and anion coordination [11]. So far there is still no general method reported for the synthesis of core/shell-structured materials.

An important application is synthesis of magnetically hard/soft core/shell materials. This structure combines the large coercivity of the magnetically hard core and the large magnetic moment of the magnetically soft shell by exchange coupling [12-14], giving excellent magnetic properties. These have potential to replace rare-earth (RE) permanent magnets such as Nd₂Fe₁₂B and SmCo₅ with common, inexpensive materials. RE elements have limited accessibility, relatively high cost, and unacceptable environmental hazard in the extraction processes [15]. In this paper, we present a new coating concept of magnetic self-assembly and report a novel route to achieve magnetically hard/soft core/shell structured particles. The concept and approach are demonstrated using the synthesis of SrFe₁₂O₁₉/Fe-Co core/shell submicron particles.

2. Experiments

Hexagonal strontium ferrite (SrFe₁₂O₁₉ or SrM) submicron particles were synthesized by a traditional ceramic method [16] by firing a mixture of Fe₃O₄ [17] and SrCO₃ [18] nanoparticles. SrFe₁₂O₁₉ particles

(0.1 g) were dispersed into 60 mL ethylene glycol (EG) with ultrasonication for 30 min. Sodium acetate (NaOAc, 1 g), sodium hydroxide (NaOH, 4 g), iron (II) chloride tetrahydrate ($\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$, 0.4 g) and cobalt chloride hexahydrate ($\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, 0.1 g) were introduced into another 60 mL EG. The two aliquots of EG were mixed and vigorously stirred in a three-neck flask with a magnetic stir bar. The reaction system was at first heated to 100 °C for 30 min to completely dissolve all of the chemicals, then increased to 180 °C with an average heating rate of 2 °C/min, and finally held for 30 min to reduce Fe and Co salts into an Fe-Co alloy. After the reaction, the heating source was removed and the solvent was cooled down to room temperature. The products were separated with a rare-earth magnet and washed with ethanol 3 times. To protect the products from oxidation, the processes of chemicals introduction and mixing, chemical reaction, solvent cooling and product washing were conducted under N_2 environment.

3. Results and discussion

Two steps are involved in the synthesis of SrM/Fe-Co core/shell particles: i) Fe-Co alloy nanoclusters are synthesized by wet chemical reduction of their chloride salts; ii) as-synthesized Fe-Co nanoclusters self-assemble on the SrM surface by magnetic attraction. However, SrM can be reduced and decomposed by the reducing agent. The challenge here is to reduce iron and cobalt salts into an Fe-Co alloy, and at the same time, protect SrM from reduction. EG was chosen as the solvent and reducing agent [19-21]. Typically, Fe-Co particle synthesis by EG reduction is conducted at its boiling point (~200 °C) [19-21]. However, our experiments showed that EG can also reduce SrM at the boiling temperature. The reduction potential of EG can be regulated by controlling the reaction temperature [22]. Therefore, after all the chemicals (NaOH, NaOAc, FeCl_2 and CoCl_2) were introduced into a dispersion of SrM particles in EG, the reaction temperature was kept at 180 °C for 30 minutes. It was confirmed that an Fe-Co nanoparticle alloy was formed and less than 10% of SrM was lost under this reaction condition.

It was reported that Fe-Co particles over 30 nm were formed without NaOAc [23]. As soon as the Fe-Co nucleus is formed in the solvent, NaOAc is assumed to adhere to the surface of Fe-Co nucleus, thereby inhibiting nucleus growth. This results in formation of Fe-Co nanoclusters of 2-3 nm, which is a precondition for the formation of magnetically self-assembled SrM/Fe-Co core/shell particles. Our experimental results also showed that when the Fe-Co particle size was over 50 nm, the magnetic attraction was not strong enough for them to self-assemble on the SrM surface to form a shell.

Figure 1a shows a transmission electron microscope (TEM) image of an as-prepared SrM particle. For effective exchange coupling to occur between hard and soft phases, the dimension of the soft phase should be smaller than twice the domain wall thickness of the hard phase [12-14], less than 28 nm in the case of SrM [24]. A TEM image of a SrM/Fe-Co core/shell particle is shown in Fig. 1b. The surface of the SrM is decorated with Fe-Co nanoclusters with thickness of ~15 nm. A representative TEM image of several SrM/Fe-Co(~15 nm) core/shell particles in lower magnification is also shown (Supporting Information Fig. S1). The surface is not uniformly covered as confirmed by tilt-angle TEM images (Supporting Information Fig. S2) and may be a result of the uneven magnetic field distribution. Energy dispersive X-ray (EDX) spectrometry of these SrM/Fe-Co core/shell particles was checked by TEM (Supporting Information Fig. S3). The line scan across a particle shows that the Sr signal was almost zero and the Fe and Co signals were relatively high at both ends of the selected particle. This result indicates the existence of Fe-Co nanoclusters on the surface of SrM.

Fig. 1. TEM images of SrM and SrM/Fe-Co core/shell and Fe-Co particle. (a) as-prepared SrM particle. (b) SrM/Fe-Co(~ 15 nm) core/shell particle. (c) SrM particle (after demagnetization of core/shell particles). (d) Fe-Co nanoclusters (after demagnetization of core/shell particles). The TEM samples were prepared by dispersing particles in ethanol under ultrasonication, and then dropped on amorphous carbon-coated TEM grids. All TEM images were acquired by TECNAI FEI 20 Transmission Electron Microscope at 200 kV. The demagnetization was conducted by Microsense Model 3473-70 VSM at room temperature with AC-Demagnetization.

Alternating current (AC) demagnetization was applied to the core/shell particles using a vibrating sample magnetometer (VSM), and TEM images were taken after that. After demagnetization, the SrM surface became bare as shown in Fig. 1c. Isolated Fe-Co nanoclusters, formerly attached to the SrM core particles, are shown in Fig. 1d. The demagnetization test confirms that the magnetic attraction between the magnetically hard SrM and soft Fe-Co is the origin for the formation of core/shell structured particles, rather than epitaxial growth or some other process. To better explain the formation process of magnetically self-assembled core/shell structured particles, a schematic diagram is shown in Fig. 2. As soon as randomly distributed Fe-Co nanoclusters are formed in the solvent, they are magnetically attracted to nearby SrM particles. This interaction leads to the formation of core/shell structured particles. It is unnecessary for the magnetically attracted soft phase to be a single layer of nanoclusters.

Fig. 2. The schematic of the formation process of SrM/Fe-Co core/shell particles by magnetic self-assembly.

Powder X-ray diffraction (XRD) patterns were used to determine the phase of both core and core/shell particles. Fig. 3a shows the XRD pattern of pure SrM core particles. The XRD pattern of SrM/Fe-Co(~ 15 nm) core/shell particles is presented in Fig. 3b, and the peaks for SrM in Fig. 3b match well with those in Fig. 3a. This indicates that the SrM phase is well maintained during the reduction reaction. At the same time, an Fe-Co peak was also detected in Fig. 3b, which confirms the existence of the soft phase in the core/shell particles. The broader peak from Fe-Co compared to those from SrM is attributed to the small Fe-Co particle size [25].

Fig. 3. Powder X-ray diffraction patterns of SrM core and SrM/Fe-Co(~ 15 nm) core/shell particles. (a) XRD pattern of SrM particles. (b) XRD pattern of SrM/Fe-Co(~ 15 nm) core/shell particles. Both samples were measured at room temperature by Bruker D8 XRD with the wavelength of $1.54 \text{ \AA}$ from Cu K α radiation, and SrM/Fe-Co particles were protected from air during measurement.

The magnetic hysteresis loops for SrM core and SrM/Fe-Co(**~15 nm**) core/shell particles are shown in Fig. 4. The saturation magnetization of SrM/Fe-Co core/shell particles increased from 65.3 emu/g to 80.5 emu/g, while the coercivity decreased from 5.75 kOe to 3.81 kOe compared to the SrM core particles. The magnetic hysteresis loop of the core/shell particles shows a negligible kink, and generally follows the Stoner-Wohlfarth model [26] for uniaxial, isotropic, non-interacting particles, which suggests exchange coupling exists between the magnetically hard phase of SrM and soft phase of Fe-Co. The magnetic properties can be regulated by the shell thickness. **To decrease the shell thickness, the concentration of iron and cobalt precursors was decreased to the half of above the experiment. The corresponding TEM image is shown in Fig. 5, and the Fe-Co shell thickness is ~7 nm. The magnetic hysteresis loop of SrM/Fe-Co(~7 nm) is also shown in Fig. 4, with magnetization of 72.1 emu/g and coercivity of 4.71 kOe.**

Fig. 4. Magnetic hysteresis loops of SrM core and SrM/Fe-Co core/shell particles. The samples were measured at room temperature by Microsense Model 3473-70 VSM with applied field up to 2.1 T shown in x axis. The y axis shows the magnetization (σ) of measured samples. The sample of SrM/Fe-Co core/shell particles was protected from air.

Fig. 5. TEM image of SrM/Fe-Co(~7 nm) core/shell nanoparticle.

Pure Fe-Co nanoclusters were synthesized with the same method mentioned above, but no SrM particles added. The magnetization of Fe-Co nanoclusters was characterized to be 181 emu/g, and the magnetization of SrM was 65 emu/g as shown in Fig. 4. Based on the equation [14, 27]:

$$\sigma_{\text{ex}} = \sigma_s * \chi + \sigma_h * (1 - \chi) \quad \text{Eq. (1)}$$

where σ_{ex} is the magnetization of an exchange coupled magnet, σ_s is the magnetization of the soft phase, σ_h is the magnetization of the hard phase and χ is the mass percentage of the soft phase, the Fe-Co mass percentage in the samples of SrM/Fe-Co(~7 nm) and SrM/Fe-Co(~15 nm) was calculated to be 6.1% and 13.0%, respectively.

Besides the percentage of hard and soft phases, shape anisotropy is another possible factor that affects the coercivity of exchange coupled composite [28-31]. However, our core and core/shell particles are magnetically hard materials, which led to a much smaller effect of shape anisotropy than magnetocrystalline anisotropy (intrinsic property) on the total coercivity.

4. Conclusion

We have reported a new method to synthesize core/shell structured particles by magnetic self-assembly. By combining two materials in this way, the lattice mismatch that prevents epitaxial growth can be overcome. These core/shell-structured particles have significantly better magnetic properties because of exchange coupling [12-14], making them excellent candidates for RE-free permanent magnets made from abundant and inexpensive elements. Moreover, this discovery might also be employed to fabricate completely new architectures for other applications.

Based on the proposed magnetic self-assembly mechanism, it can be speculated that a higher remanent magnetization of the hard phase may result in a thicker layer of the soft phase nanoclusters. However, further experiment is needed to confirm the speculation.

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