

2005

CoFe₂O₄ nanostructures with high coercivity

J S. Jung

J H. Lim

K H. Choi

S L. Oh

Y R. Kim

See next page for additional authors

Follow this and additional works at: https://scholarworks.uno.edu/phys_facpubs



Part of the [Nanoscience and Nanotechnology Commons](#), and the [Physics Commons](#)

Recommended Citation

J. Appl. Phys. 97, 10F306 (2005)

This Article is brought to you for free and open access by the Department of Physics at ScholarWorks@UNO. It has been accepted for inclusion in Physics Faculty Publications by an authorized administrator of ScholarWorks@UNO. For more information, please contact scholarworks@uno.edu.

Authors

J S. Jung, J H. Lim, K H. Choi, S L. Oh, Y R. Kim, S H. Lee, D A. Smith, K L. Stokes, L Malkinski, and C J. O'Connor

CoFe₂O₄ nanostructures with high coercivity

J.-S. Jung^{a)} and J.-H. Lim

Department of Chemistry, Kangnung National University, Kangnung 210-702, Korea

K.-H. Choi, S.-L. Oh, Y.-R. Kim, and S.-H. Lee

Department of Chemistry, Yonsei University 120-749, Korea

D. A. Smith, K. L. Stokes, L. Malkinski, and C. J. O'Connor

Advanced Materials Research Institute, University of New Orleans, New Orleans, Louisiana 70148

(Presented on 8 November 2004; published online 10 May 2005)

Nanometer-sized ferrite magnetic materials are the subject of intense research interest due to their potential applications in high-density magnetic information storage. One of the most explored ferrite materials is the cobalt ferrite (CoFe₂O₄). We have synthesized cobalt ferrite nanowires using cobalt ferrite nanoparticles in a porous anodic alumina template (AAT). The process of embedding ferrimagnetic particles into the pores was assisted by the magnetic field of a permanent magnet placed in vacuum directly under the substrate. Particles synthesized in the template were subsequently annealed at 600 °C for 2 h in Ar gas forming arrays of cobalt ferrite nanowires inside the AAT. The morphology of the ferrite before and after annealing was observed using a field-emission scanning electron microscope. The crystallographic structure of the nanowires was analyzed using x-ray diffraction and transmission electron microscopy. The magnetization was measured by a superconducting quantum interference device. The coercivity of the annealed ferrite in the form of nanowires is significantly larger than that of the separate ferrite nanoparticles in the pores. This effect is due to the clustering of nanoparticles when the organic solvent is removed by high-temperature annealing as well as an improvement in the crystallinity of the ferrite by reduction of defects. The Faraday spectra of the nanowires were measured before and after annealing. A significant peak was observed at 725 nm. The nanowire/AAT composite material had a Verdet constant of 0.1 min/(Oe cm) at the peak. It is important to mention that not only the properties but also the form of the material—a regular array of pillars—may be important for microelectronic or information storage applications. © 2005 American Institute of Physics.

[DOI: 10.1063/1.1852851]

In the past decade, one-dimensional (1D) nanostructured materials, including nanotubes,¹ nanorods,² and nanowires,³ have attracted much attention because of both their interesting physical properties and their wide range of potential applications in nanodevices.^{4,5} In particular, the fabrication of ordered magnetic metal oxide nanowire arrays has attracted considerable scientific and commercial attention due to their potential utilization in magnetic recording.^{6,7} High coercivity and high remanence have been reported in Co-ferrite thin films and nanopowders.^{8,9} Generally high coercivity is achieved in the magnetic materials with uniaxial anisotropy and high magnetocrystalline energy. Therefore, achieving Co-ferrite nanowires is not only interesting for high coercivity magnetic materials, but is also interesting for fundamental research of the synthetic method. Among the various methods for preparing magnetic nanowires, one of the most widespread is the template method.^{10,11} For example, a hard-template process such as that using the anodic alumina template (AAT) is an effective approach for fabrication of magnetic metal oxide nanowires because of its uniform and nearly parallel porous structure. In the present work, we have

combined the concept of building blocks by using nanoparticles and template preparation of nanowires to fabricate CoFe₂O₄ nanowire arrays.

Hexagonally ordered porous AAT was formed by anodization process, as described previously.¹² The cobalt ferrite nanoparticles were produced by a wet chemical technique that involves organic solution-phase decomposition of the cobalt and iron precursor at high temperature.¹³ To prepare cobalt ferrite nanowires, 10 mL of this cobalt ferrite nanoparticle solution was infiltrated into the alumina template by vacuum suction assisted by an applied magnetic field. The membrane was washed with hexane to remove any particles from the AAT surface and then dried under ambient atmosphere. To form the nanowire, the sample was annealed under Ar gas (99.999%) in a quartz tube at 600 °C for 2 h.

A Quantum Design MPMS-5S superconducting quantum interference device magnetometer was used for the magnetic measurements. A general discussion of the magnetic susceptibility measurements and calibration techniques is described in detail elsewhere.¹⁴ Transmission electron microscopy (TEM) imaging was performed on a JEOL 3010 microscope. Field-emission scanning electron microscopy (FESEM) imaging was performed on a Hitach S-4200 microscope. Pow-

^{a)}Electronic mail: jjscm@kangnung.ac.kr

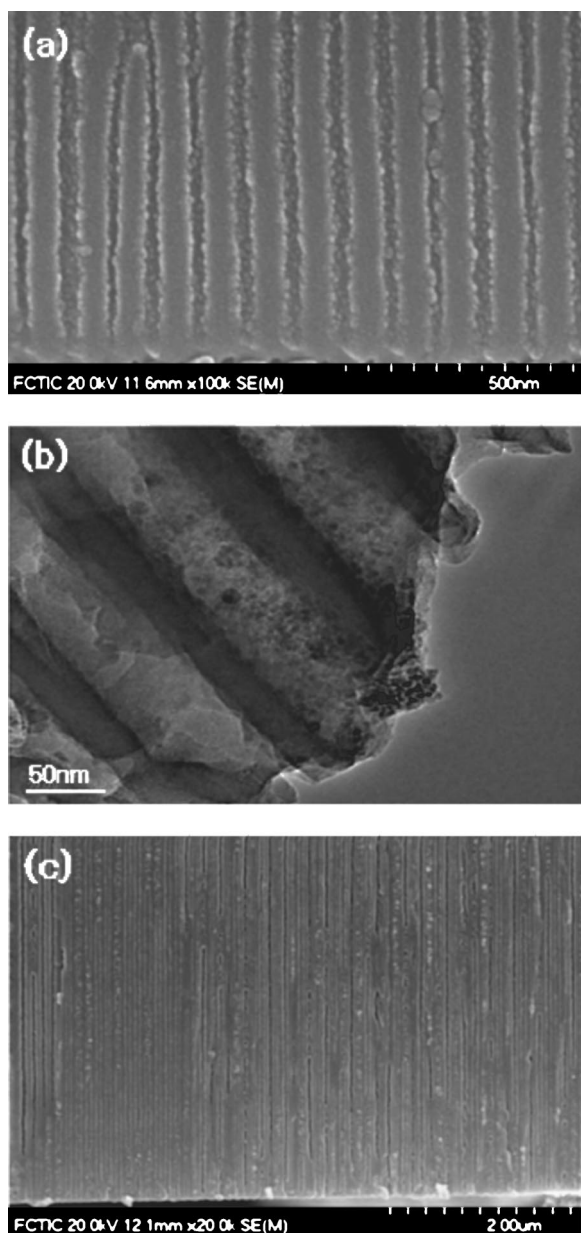


FIG. 1. (a) FESEM image of Co-ferrite in AAT, (b) TEM image of Co-ferrite in AAT, and (c) FESEM image of Co-ferrite in AAT after annealing at 600 °C for 2h.

der x-ray diffraction (XRD) data were collected on a Bruker D8 Advance system equipped with copper radiation and a graphite monochromator.

One promising technique to obtain nanomagnetic arrays is by using the highly ordered arranged porous alumina template. A porous membrane of Al_2O_3 was formed with a regular hexagonal arrangement of pores of 60 nm in diameter and 100-nm spacing due to two-step electrochemical anodization aluminum process. Co-ferrite nanoparticles trapped inside porous AAT were distributed homogeneously throughout the AAT. Structural information was obtained from both electron and x-ray diffractions. From the FESEM and TEM micrographs in Fig. 1 one can see that the spherical nanoparticles of 8 nm in diameter uniformly fill the nanochannels within the AAT host. Figure 2 shows the XRD patterns of as-synthesized Co-ferrite particles and the nanostructure in AAT

before and after annealing. Although the background diffraction peaks of Al_2O_3 are present in Co-ferrite/AAT composite data, the main peaks correspond to a cubic spinel-type lattice. The average grain size calculated by the Scherrer formula is about 8 nm, which is consistent with the FESEM images.

Small size of the particles is needed to accommodate them inside the porous template. Because the particles are ferrimagnetic, the magnetic-field-assisted assembly of particles was very efficient and long pores in the AAT structure could be completely filled with the magnetic particles. The as-synthesized particles in the AAT show significant coercivity of 14 kOe at low temperatures, as shown in Fig. 3. However, at room temperature the coercivity is only about 100 Oe. The significant reduction in the coercivity can be explained by the vicinity of superparamagnetic limit. The average size of our particles is about 8 nm. Magnetization direction of isolated particles smaller than 8 nm can be randomized by thermal excitations at room temperature and such superparamagnetic particles have no coercivity.^{15,16} The particles inside the pores are separated by an organic coating and only weak dipolar interactions can exist among them. It was found¹⁷ that the coercivity of isolated Co-ferrite particles increases with the increasing diameter and reaches maximum value for the particles with diameters of about 40 nm. Magnetization vector rotation is considered to be the mechanism responsible for the coercivity of small particles. Particles larger than 40 nm divide into domains and domain-wall movements result in reduced coercivity with the increasing size.

The combustion of organic material surrounding Co-ferrite particles removes the barriers separating the particles and they aggregate forming pillars. These large clusters of nanoparticles are equivalent to polycrystalline particles with diameter of 60 nm and length of hundreds of nanometers. Such large objects do not exhibit superparamagnetic properties—they are unaffected by thermal excitations at room temperature. This results in significant increase of coercivity of the nanostructure up to 1600 Oe at room temperature, as presented in Fig. 3. This magnitude of coercivity is useful for applications and close to the values observed in the thin-film structures. For example, room-temperature coercivities of 510 Oe (Ref. 18)–1500 Oe (Ref. 19) were reported in the spin valves using Co-ferrite films. It seems that there is still a possibility to increase the coercivity of our structure. Some reports indicate that the coercivity of the ferrite films can be increased up to 18 kOe by high-temperature annealing²⁰ or by SiO_2 ²¹ doping.

In order to illustrate the potential applications of these structures for magnetophotonic or magneto-optical data storage applications, we have measured the Faraday rotation in the wavelength range of 500–1000 nm. The measurements were made at room temperature in the polar configuration²² with the magnetic field and light propagation perpendicular to the surface of the AAT composite. The Faraday rotation results are shown in Fig. 4. The spectra of the Co-ferrite nanocomposites show a shift from positive to negative rotation occurring at 625 nm and a broad negative peak at 725 nm. This is consistent with published results on Co fer-

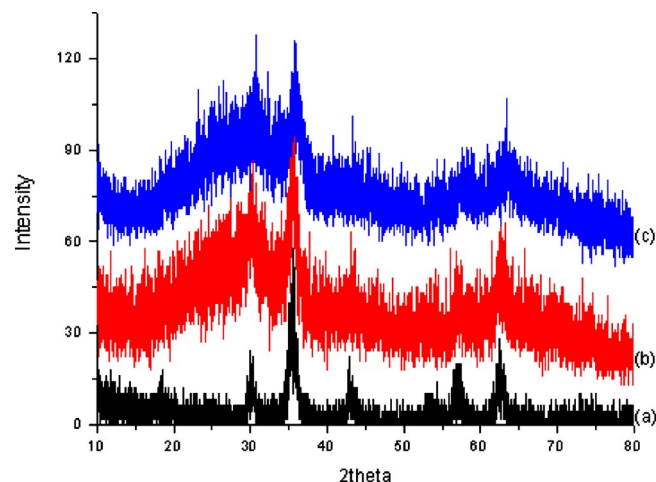


FIG. 2. XRD patterns of (a) Co-ferrite particles, (b) as-synthesized Co-ferrite in AAT, and (c) Co-ferrite in AAT after annealing at 600 °C.

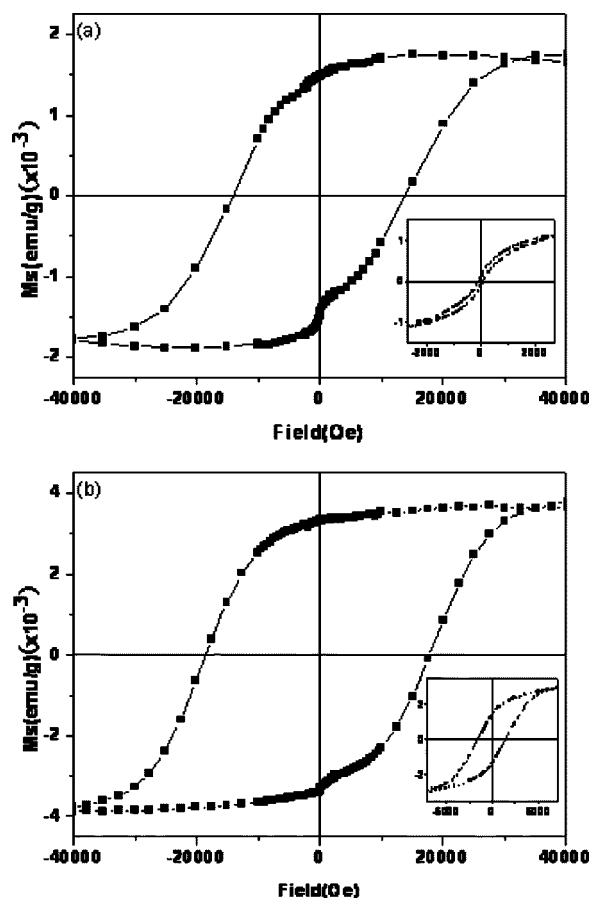


FIG. 3. Magnetization hysteresis loops for the as-synthesized particles in AAT (a) and particles annealed at 600 °C (b) measured at 5 K in the substrate plane. (The room-temperature hysteresis loops are displayed in the insets). The magnetization was calculated taking the collective mass of the particles and the substrate, so it does not reflect the exclusive magnetization of Co-ferrite but the magnetization of the whole structure.

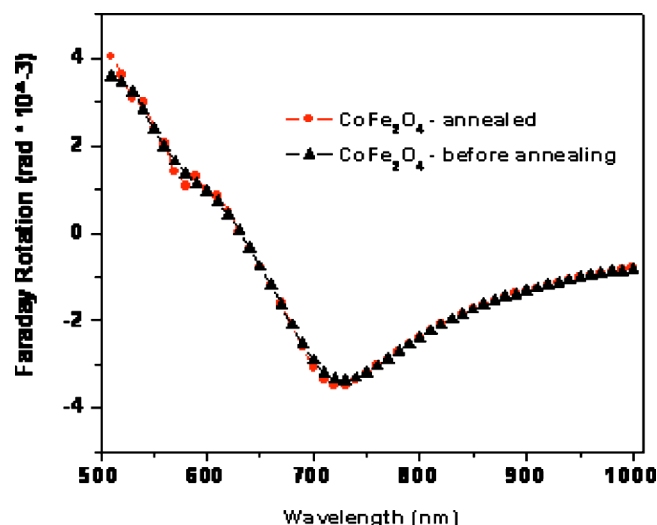


FIG. 4. Spectral Faraday rotation for the Co ferrite/AAT composite structure before and after annealing.

rite thin films.²³ No change in the spectrum is observed due to annealing. This indicates that the as-synthesized nanoparticles are highly crystalline and the primary effect of annealing is the coalescence of the particles inside the channels which results in an increased coercivity, but does not affect the magneto-optical properties.

In summary, we were successful in the fabrication of a regular array of pillars of Co-ferrite with the diameters of 60 nm and with 100-nm spacing by the field-assisted assembly of spherical nanoparticles with the diameter of about 8 nm. The annealed nanostructures exhibit magnetic properties comparable with those of continuous Co-ferrite films.

This work was supported by the RRC program and the NRL(M1-302-00-0027 of MOST, DARPA(MDA972-04-1-0029) and from the Louisiana Board of Regents [LEQSF(2003-06) RD-B-13].

¹J. T. Hu, T. W. Odom, and C. M. Lieber, *Acc. Chem. Res.* **32**, 435 (1999).

²V. F. Puentes *et al.*, *Science* **291**, 2115 (2001).

³J. D. Holmes *et al.*, *Science* **287**, 1471 (2000).

⁴J. F. Wang *et al.*, *Science* **293**, 1445 (2001).

⁵H. Kind *et al.*, *Adv. Mater. (Weinheim, Ger.)* **14**, 158 (2002).

⁶R. J. Tonucci *et al.*, *Science* **258**, 783 (1992).

⁷T. W. Whitney *et al.*, *Science* **261**, 1316 (1993).

⁸J. Ding *et al.*, *Appl. Phys. Lett.* **65**, 3135 (1994).

⁹J. Ding *et al.*, *Solid State Commun.* **95**, 102 (1995).

¹⁰C. R. Martin, *Science* **266**, 1961 (1994).

¹¹K. Nielsch *et al.*, *Adv. Mater. (Weinheim, Ger.)* **12**, 582 (2000).

¹²H. Masuda and K. Fukuda, *Science* **268**, 1466 (1995).

¹³S. Sun *et al.*, *J. Am. Chem. Soc.* **126**, 273 (2004).

¹⁴C. J. O'Connor, *Prog. Inorg. Chem.* **29**, 203 (1982).

¹⁵A. R. Sufi *et al.*, *IEEE Trans. Magn.* **39**, 2198 (2003).

¹⁶A. R. Sufi *et al.*, *Appl. Phys. Lett.* **80**, 1616 (2002).

¹⁷C. N. Chinnasamy *et al.*, *Appl. Phys. Lett.* **82**, 2862 (2003).

¹⁸K. V. O'Donovan *et al.*, *J. Appl. Phys.* **95**, 7507 (2004).

¹⁹M. J. Carey *et al.*, *Appl. Phys. Lett.* **81**, 1044 (2002).

²⁰P. C. Dorsey, P. Lubitz, D. B. Chrisy, and J. S. Horowitz, *J. Appl. Phys.* **79**, 6338 (1996).

²¹J. Ding, Y. J. Chen, Y. Shi, and S. Wang, *Appl. Phys. Lett.* **77**, 3621 (2000).

²²Y. A. Barnakov, B. L. Scott, L. A. Kelly, W. Reddy, and K. L. Stokes, *J. Phys. Chem. Solids* **65**, 1005 (2004).

²³E. Takeda, N. Todoroki, Y. Kitano, M. Abe, M. Inoue, T. Fujii, and K. Arai, *J. Appl. Phys.* **87**, 6782 (2000).