High thermal stability of the ferrimagnetic moment in exchange biased FeO(core)/spinel(shell) nanocubes

H.T. Hai*, H. Kura, M. Takahashi and T. Ogawa
Graduate School of Engineering, Department of Electronic Engineering, Tohoku University, 6-6-05 Aza-Aoba, Aramaki, Aoba-ku, Sendai 980-8579, Japan

E-mail: phai@ecei.tohoku.ac.jp

Abstract. We demonstrate herein a basic approach to a new type of exchange-coupled iron oxide-based core/shell nanocubes consisting of an antiferromagnetic (AFM) core of ferrous oxide (wustite, FeO) surrounded by a ferrimagnetic (FM) shell of ferrite (spinel, $\gamma$-Fe$_2$O$_3$ or Fe$_3$O$_4$). By coupling with AFM core, effective blocking temperature of FM moments is strongly enhanced up to Néel temperature ($T_N$ =198 K) of AFM core. This is assigned to contribution of an extra anisotropy induced by exchange bias at the interface between AFM and FM components in the nanocubes. Because of this special coupling structure, the high stability of FM moments can be achieved even at very small volume fraction of AFM with respect to FM matrix, thus significantly eliminate contribution of AFM to the magnetization of whole coupling system, suggesting a new hybrid structure for magnetic devices applications.

1. Introduction

Interest in magnetic nanoparticles has increased in the past few years by virtue of their potential for applications in fields such as ultrahigh-density recording media and medicine [1, 2]. Most applications reply on the magnetic order of the nanoparticles being stable with time evolution. However, with decreasing particle size, the magnetic anisotropy energy per particle responsible for holding the magnetic moment along magnetic anisotropy direction becomes comparable to the thermal energy. This brings about the thermal fluctuations of the magnetic moment, and the nanoparticles lose their stable magnetization state and show superparamagnetic. Thus, the demand for further miniaturization comes into conflict with the superparamagnetism caused by the reduction of the anisotropy energy per particles. It has been demonstrated that the magnetic coupling of ferromagnetic nanoparticles with an AFM matrix is a source of a large effective additional anisotropy [3-6]. This leads to a marked improvement in the thermal stability of the moments of the FM nanoparticles. This mechanism provides a way to artificially control the superparamagnetic limit in isolated nanoparticles. Herein, we show a simple approach to a new type of strongly exchange-coupled iron oxide-based core/shell nanocubes consisting of an AFM core of FeO, which is surrounded by a ferrimagnetic (FM) shell of spinel. The AFM/FM structure presented here is fundamentally interesting since it is inverted in respect to the classical and mostly studied FM/AFM paradigm based on a metallic particle covered by a thin oxide layer, Co/CoO [3]. Furthermore, the FeO and spinel components are highly compatible not only compositional but also structurally with a small lattice mismatch (~3%) [7], which is expected to provide a better structural perfection of the AFM constituent and a better control of its finite size. In this study, thermal stability of FM moment in 16 nm FeO (core)/spinel (shell) nanocubes...
with different FeO sizes was investigated. The advantage of this AFM/FM coupling system with respect to thermal stability of FM component as compared to single FM or classical FM/AFM coupling systems was also discussed.

2. Experiment

The 16 nm FeO (core)/spinel (shell) nanocubes were synthesized by the following method reported elsewhere [8]. Size of FeO core was atomically controlled by slow oxidation of the as-synthesized nanocubes at low temperature of 80°C in air ambient, and vigorous agitation condition and estimated using a simple calculation based on the saturation magnetizations of the nanocubes [8]. Herein, it was assumed that the nanocubes have perfect cubic cores and that the spinel phase in the nanocubes is $\gamma$-Fe$_2$O$_3$ and is preferentially distributed in the shells.

Transmission electron microscopy (TEM, Jeol-3010 at 200 kV) was employed to determine the morphology, particle size and size distribution of nanocubes. A superconducting interference device (SQUID; Quantum Design MPMS-5) with fields up to 40 kOe and temperatures from 5 K to 300 K was employed for magnetic measurements. Samples for the magnetic characterization were prepared by adding the hot dispersion of the nanocubes in tetracosane (melting point: 65°C) with 0.1 % volume fraction into a quartz tube ($\Phi$ X 75 mm) and rapidly solidifying using liquid nitrogen. The tube was then sealed in a glovebox using Araldite and the diamagnetic background from the quartz tube was subtracted. Mass of Fe in the samples was determined by x-ray fluorescence (Rigaku RIX 2100) [8].

3. Results and discussion

Figure 1a shows low resolution TEM image of 16 nm as-synthesized FeO/spinel nanocubes. The nanocubes are highly monodispersed with small size deviation of 5 %. Size of FeO core as estimated from TEM image is about 10 nm. This is consistent with 3 nm penetration length of oxygen into FeO lattice from the nanocube surface at ordinary temperature as well as the value estimated using saturation magnetization ($M_s$) of the nanocubes. The high resolution TEM picture of an isolated 16 nm nanocube in figure 1b shows that it is highly crystallized, as indicated by clear atomic lattice planes. The $d$ spacing determined from HR-TEM image is about 0.21 nm match well with that between $<400>$ planes of spinel phase. Minimal lattice strain between FeO core and spinel shell could be observed, consistent with small lattice mismatch (~ 3%) of the constituents [7]. Consequently, structure matching of AFM core is expected to be well stabilized by spinel shell lattice. Figure 2a shows the temperature-dependent ZFC-FC susceptibility curves of the 16 nm as-synthesized core/shell nanocubes at different field-cool strengths in the range from 50 Oe to 1000 Oe. Both ZFC and FC curves exhibit the independent-applied field peaks at about 198 K, consistent with Néel temperature.
Interestingly, in addition to the AFM transition peak, a broad shoulder in the low temperature range below AFM transition point in the ZFC curves appears and shifts gradually toward lower temperature as increasing field cool strength, revealing a feature of superparamagnetic transition ($T_B$) of FM component in the nanocubes. Moreover, the decrease of $T_B$ from $T_N$ of FeO with increasing field cool strength suggests that by coupling with AFM core the spinel shell remains FM up to $T_N$ of FeO core. In this case, the nanoshell moments are prevented from thermal fluctuation over the magnetic anisotropy energy barrier for all temperature below $T_N$ of FeO, and thus the nanocubes remain magnetically stable below $T_N$. In fact, the highly thermal stability of FM moments in FC mode may be understood by high alignment of FM spins and uncompensated spins of AFM at interface. It is really interesting because even in ZFC mode highly thermal stabilization of FM moments is also achieved. In order to get insight, the loop shift ($H_{ex}$) and coercivity ($H_c$) of the as-synthesized 16 nm FeO(core)/spinel(shell) nanocubes were measured at 5 K after the field cool of 10 kOe from $T_i$ in the range from 5 K to 300 K.

($T_N$) of FeO phase. Interestingly, in addition to the AFM transition peak, a broad shoulder in the low temperature range below AFM transition point in the ZFC curves appears and shifts gradually toward lower temperature as increasing field cool strength, revealing a feature of superparamagnetic transition ($T_B$) of FM component in the nanocubes. Moreover, the decrease of $T_B$ from $T_N$ of FeO with increasing field cool strength suggests that by coupling with AFM core the spinel shell remains FM up to $T_N$ of FeO core. In this case, the nanoshell moments are prevented from thermal fluctuation over the magnetic anisotropy energy barrier for all temperature below $T_N$ of FeO, and thus the nanocubes remain magnetically stable below $T_N$. In fact, the highly thermal stability of FM moments in FC mode may be understood by high alignment of FM spins and uncompensated spins of AFM at interface. It is really interesting because even in ZFC mode highly thermal stabilization of FM moments is also achieved. In order to get insight, the loop shift ($H_{ex}$) and coercivity ($H_c$) of the as-synthesized 16 nm FeO(core)/spinel(shell) nanocubes were measured at 5 K after the field cool of 10 kOe from $T_i$ and shown in figure 2b. Even when the FC takes place from as low as $T_i = 50$ K, a large exchange bias (nearly a half of the maximum value) still remains, meanwhile a large coercivity (nearly 62 % of the maximum value) can be achieved even the FC starts from $T_i = 5$ K (or zero-field cooling). This means that even in ZFC procedure, a significantly additional anisotropy is still provided to the FM component in the exchange-bias coupling system, thus stabilizing their magnetic moment. The same dependence of $H_{ex}$ and $H_c$ on the temperature point ($T_i$) at which the FC starts is also observed in the Co/CoO exchange coupling system [9], somewhat attributed to single domain nature of FM component in the nanoparticles, and still an open question needs to be further studied in the future.

As revealed, $T_B$ of FM moment in an exchange-bias coupling system is equivalent with $T_N$ of AFM constituent. Subsequently $T_N$ is governed by its physical dimension due to the so-called “finite-size effect” [10]. Accordingly, study about thermal stability of FM moment in the nanocubes identifies with that about FeO core size-Néel temperature dependent.

Figure 2a shows temperature-dependent ZFC-FC susceptibility curves of the 16 nm nanocubes with different FeO core sizes of 10 nm, 7 nm, 5 nm, and 0 nm (or single phase spinel nanocubes). Herein, the existence of FeO in the nanocubes was proved through observation of exchange-bias while size of FeO core was estimated using $M_s$ deduced from the hysteresis loops of the nanocubes (figure 3b) [8]. Indeed, the $H_{ex}$ is reduced to zero from 3.6 kOe of 10 nm FeO core while $M_s$ is increased up to 110 emu/g of the single phase spinel nanocubes as the spinel shell grows atomically on the expense of FeO core. The $T_N$ as indicated in the figure 3a are 198 K, 160 K, 136 K,
and 80 K for 10 nm, 7 nm, 5 nm, and 0 nm FeO core in the nanocubes respectively. These were confirmed by the temperature-dependent ZFC-FC susceptibility curves measured at different field-cool strengths and can be understood by the finite-size effect in AFM material [10]. Herein, slow reduction of \( T_N \) with FeO core size may be attributed to the lattice perfection of FeO core stabilized by spinel shell constituent. This result suggests that by implant of a small AFM core with size of 5 nm, 7 nm and 10 nm, \( T_B \) of FM shell component in the 16 nm FeO/spinel core-shell nanocubes was strongly enhanced up to 136 K, 160 K, and 198 K (\( T_N \) of FeO phase) as compared to 80 K of the 16 nm single spinel nanocubes (or no FeO core). This is very interesting because the reduction of volume of the FM spinel shells (or enlargement of FeO core size) in 16 nm nanocubes should bring about a reduction of \( T_B \) according to the Néel-Brown relaxation model for superparamagnetic nanoparticles [11]. In other words, the exchange-bias coupling induced at the interface between FM and AFM phases in the nanocubes presented herein provides a new approach for artificially controlling superparamagnetic limit of nanoparticles in addition to the traditional one completely basing on size of FM nanoparticles. Moreover, by considering the volume factions of spinel constituent with respect to FeO one in the 16 nm FeO/spinel nanocubes, the inverted paradigm AFM/FM exchange-bias coupling system presented herein exhibits an anomalous advantage as compared to the classical FM/AFM one because of highly thermal stability of FM moments achieved with minimum amount of AFM implant, thus strongly reduces mass contribution of AFM to magnetization of whole coupling system.

4. Conclusions

In summary, we have demonstrated a new type of exchange-bias coupled iron oxide-based core/shell nanocubes consisting of an AFM core (FeO) surrounded by a FM shell (spinel). An extra anisotropy induced by exchange bias at the interface between AFM and FM components in the nanocubes strongly enhances the effective blocking temperature of FM moment up to Néel temperature of FeO core. Well structure stabilized FeO core by spinel shell due to their small lattice mismatch (~ 3 %) leads to a slow reduction of Néel temperature, and thus blocking temperature of FM moment in spinel shell with FeO core size. Whereas the 16 nm single spinel nanocubes lose their magnetic moment at 80 K, the spinel shell in the 16 nm nanocubes with FeO core size of 5 nm, 7 nm,
and 10 nm remains ferrimagnetic up to about 136 K, 160 K, and 198 K respectively. This exchange-bias coupling system really provides and additional approach for artificially controlling superparamagnetic limit of nanoparticles and thus a new ideal for constructing new hybrid structure for magnetic device applications.

Acknowledgement

This work was supported by the Japan Society for the Promotion of Science (JSPS).

Reference

1. Kodama R H. 1999 J. Mag. Mag. Mater. 200 359.

2. Sun S H, Murray C B, Weller D, FolkS L and Moser A. 2000 Science 187 1989.

3. Meiklejohn W H and Bean C P. 1956 Phys. Rev. 102 1413.

4. Nogues J and Schuller I. 1999 J. Mag. Mag. Mater. 192 203.

5. Skumryev V, Stoyanov S, Zhang Y, Hadjipanayis G, Givord D and Nogues J. 2003 Nature 423 850.

6. Yamamoto Y, Nakagawa H and Hori H. 2007 J. Mag. Mag. Mater. 310 2384.

7. Cornell R M and Schwertmann. U., The Iron Oxides: Structure, Properties, Reactions, Occurrence and Uses (VCH, New York, 1996), pp. 28-29.

8. Hai H T, Yang H T, Kura H, Hasegawa D, Ogata Y, Takahashi M, OgawaT. 2010 J. Colloids and Inter. Sci. 346 37.

9. Riveiro J M, Toro D, Andres J A, Gonzalez J P, Munoz J A and Goff J P. 2005 App. Phys. Lett. 86 172503.

10. Ambrose T and Chien C L. 1996 Phys. Rev. Lett. 76 1743.

11. Néel L. 1949, Ann. Grophys 5 99.