Magnetic superlattices and their nanoscale phase transition effects

Jinwoo Cheon*, Jong-II Park†, Jin-sil Choi*, Young-wook Jun*, Sehun Kim†, Min Gyu Kim†, Young-Min Kim†, and Youn Joong Kim‡

*Department of Chemistry and Nano-Medical National Core Research Center, Yonsei University, Seoul 120-749, Korea; †Department of Chemistry, Korea Advanced Institute of Science and Technology, Daejeon 305-701, Korea; ‡Department of Chemistry, Nano-Material and Environmental Science, Korea Basic Science Institute, Daejeon 305-335, Korea

Edited by Louis E. Brus, Columbia University, New York, NY, and approved December 29, 2005 (received for review October 11, 2005)

The systematic assembly of nanoscale constituents into highly ordered superlattices is of significant interest because of the potential of their multifunctionalities and the discovery of new collective properties. However, successful exploration of such superlattice-associated nanoscale phenomena is still elusive. Here, we present magnetic superlattices of Co and Fe3O4 nanoparticles with multidimensional symmetry of either AB (NaCl) or AB2 (AlB2). The discovery of significant enhancement (~25 times) of ferrimagnetism is further revealed by forming previously undescribed superlattices of magnetically soft–hard Fe3O4@CoFe2O4 through the confined geometrical effect of thermally driven intrasuperlattice phase transition between the nanoparticulate components.

Results and Discussion

Early investigations of nanoparticle assembly have focused on the fabrication of ordered monomeric nanoparticle superlattices with specific packing symmetry (e.g., fcc, hcp) (1–4), and the novel properties arising from these assemblies have been elucidated, such as metal–insulator transitions (2) and band-gap engineering (3). Researchers have further explored ordered binary superlattice systems composed of nanoparticle components that are isostructural with binary crystals of either NaCl or AlB2. The discovery of significant enhancement (~25 times) of ferrimagnetism is further revealed by forming previously undescribed superlattices of magnetically soft–hard Fe3O4@CoFe2O4 through the confined geometrical effect of thermally driven intrasuperlattice phase transition between the nanoparticulate components.

When hard spheres of two different sizes are mixed together, these spheres tend to assemble into a new structure with maximum packing density (11–13). Two crucial parameters determine the binary assembly pattern of the spheres: (i) the size ratio (γ = Rsmall/Rlarge) and (ii) the stoichiometric ratio between two spheres, although the binary organization of colloidal nanoparticle systems can be predicted by such hard sphere assembly approximations (5–10, 14), other parameters such as interparticle potentials also contribute to the determination of assembly patterns (10, 14).

Binary superlattices of magnetic Fe3O4 and Co nanoparticles were examined with careful consideration of such size ratio and stoichiometric ratio effects. The Fe3O4 nanoparticles used are highly monodispersed (σ ~ 5%), and the size can be tuned from 8.0 nm to 15.7 and 18.0 nm (Fig. 1 A–C) Fe3O4 nanoparticles of 8.0 (A), 18.0 (B), and 15.7 (C) nm. (D) Co nanoparticles of 7.5 nm. (E–G) Binary assemblies of Fe3O4 and Co nanoparticles. The assembly patterns are systematically modulated as random mixtures (γ ~ 0.94) (E), well organized binary superlattices (γ ~ 0.42) (F), and phase-separated arrays (γ ~ 0.48) (G).

Conflict of interest statement: No conflicts declared.

This paper was submitted directly (Track II) to the PNAS office.

Abbreviation: TEM, transmission electron microscopic.

1To whom correspondence should be addressed. E-mail: jcheon@yonsei.ac.kr.

© 2006 by The National Academy of Sciences of the USA
match the \([001]_{\text{SL}}, [111]_{\text{SL}}, \text{and} [110]_{\text{SL}}\) projection of the AB structure. TEM analyses suggest our binary superlattices are of AB symmetry. Each Co nanoparticle is surrounded by six equidistant Fe\(_3\)O\(_4\) nanoparticles situated at the corner of an octahedron (yellow squares), as is the case for each Fe\(_3\)O\(_4\) nanoparticle surrounded by six Co nanoparticles. Our superlattices have periodicitites with interplanar distances of 15.6 nm for \((200)_{\text{SL}}\) and 22.2 nm for \((110)_{\text{SL}}\), which is consistent with the Fourier transform of the TEM image (D Inset). The inner spots marked m and n spots are contributed from \([200]_{\text{SL}}\) and \([110]_{\text{SL}}\) reflections, respectively.

Fourier-transformed TEM images. From these observations, we conclude the binary superlattices are well organized AB structures with the lattice parameter of 31.2 nm.

We further investigated the effects of the relative stoichiometry of Fe\(_3\)O\(_4\) and Co nanoparticles on assembly patterns of binary superlattices. When Fe\(_3\)O\(_4\) nanoparticles and two molar excess of Co nanoparticle were mixed and cocrytallized, the resulting superlattices (Fig. 3E) revealed that the nanoparticles assembled into an AB\(_2\) rather than an AB structure. The structures show bilayers composed of a hexagonal close-packed layer of Fe\(_3\)O\(_4\) and a second layer of Co nanoparticles. The observed bilayer structure (Fig. 3E) is the hexagonal AB\(_2\) substructure (Fig. 3A–C) and has periodicitites with interplanar distances of 9.6 nm for \((200)_{\text{SL}}\) and 16.7 nm for \((110)_{\text{SL}}\). A small-angle diffraction pattern of our bilayer structure (Fig. 3D) shows discrete reflection spots from the hexagonally ordered structures. The inner hexagonal spots marked p and q positioned 30° apart from each other are contributions from the \((200)_{\text{SL}}\) and \((110)_{\text{SL}}\) reflections, respectively.

The formation of binary magnetic nanoparticle superlattices with well defined symmetry and stoichiometric composition prompted us to investigate their assembly-induced novel magnetic properties. Because each Fe\(_3\)O\(_4\) nanoparticle is surrounded by a highly symmetric arrangement of Co nanoparticles within a distance of \(\approx 1\) nm, nanoscale chemical and physical interactions between these two nanoparticles can be exploited to generate unique phase-transitional behaviors. The nanoscale transformation of as-assembled binary superlattices of Fe\(_3\)O\(_4\) and Co nanoparticles into core–shell type Fe\(_3\)O\(_4@\)CoFe\(_2\)O\(_4\) superlattices were thermally driven through intrasuperlattice redox chemical processes. Such core–shell type Fe\(_3\)O\(_4@\)CoFe\(_2\)O\(_4\) superlattice formation leads to significant changes in its magnetism when compared with those of as-assembled superlattices. As-assembled AB type superlattices (Fig. 4A) have magnetic coercivity \((H_c)\) values of 580 oersted (Oe) at 5 K (Fig. 4C), which is roughly in between the values for individual Co (780 Oe) and Fe\(_3\)O\(_4\) (200 Oe) nanoparticles. After thermal annealing pro-

![Fig. 2. Binary superlattices of Fe\(_3\)O\(_4\) and Co nanoparticles with AB symmetry and their structural characterizations. (A and B) The unit cell (A) and the extended cell (B) of the NaCl type AB binary structure. (C–H) TEM images of our binary superlattices (D, F, and H) and the corresponding AB structure (C, E, and G), respectively, which match the \([001]_{\text{SL}}, [111]_{\text{SL}}, \text{and} [110]_{\text{SL}}\) projection of the AB structure. TEM analyses suggest our binary superlattices are of AB symmetry. Each Co nanoparticle is surrounded by six equidistant Fe\(_3\)O\(_4\) nanoparticles situated at the corner of an octahedron (yellow squares), as is the case for each Fe\(_3\)O\(_4\) nanoparticle surrounded by six Co nanoparticles. Our superlattices have periodicitites with interplanar distances of 15.6 nm for \((200)_{\text{SL}}\) and 22.2 nm for \((110)_{\text{SL}}\), which is consistent with the Fourier transform of the TEM image (D Inset). The inner spots marked m and n spots are contributed from \([200]_{\text{SL}}\) and \([110]_{\text{SL}}\) reflections, respectively.](image)
processes at 400°C (Fig. 4B), however, the magnetic coercivity of AB structures increased dramatically to 15,000 Oe (∼25 times higher than the initial value) (Fig. 4D; refs. 17 and 18). However, such dramatic magnetic enhancement is not observed for phasesegregated mixtures of Fe3O4 and Co nanoparticles (see Fig. 7, which is published as supporting information on the PNAS web site), suggesting that symmetry and proximity effects between the two nanoparticle components are essential in inducing such nanoscale magnetic phenomena.

As depicted in Fig. 5A and B, the transformation processes can involve (i) dissolution and diffusion of Co atoms from Co nanoparticles into a Fe3O4 inverse spinel matrix and (ii) alloying of Co and Fe3O4 through exchange of Fe2+ in an O site with a Co atom through redox chemical reactions in which a Co atom is oxidized at the expense of an Fe2+, which ultimately results in the formation of the superlattices of core–shell type Fe3O4@CoFe2O4 nanoparticles.

The formation of core–shell type Fe3O4@CoFe2O4 nanoparticles resulting from such phase transformation processes was confirmed by elemental mapping analyses using high-resolution TEM. Because it is difficult to perform the elemental analyses with multilayers of nanoparticles, annealed nanoparticles were redispersed in toluene by using sonication and resampled on a TEM grid. Elemental mapping analyses based on Fe L-edge (color-coded as yellow; Fig. 6A) and Co L-edge (color-coded as cyan; Fig. 6B) electron energy loss spectroscopy show that the nanoparticles contain both iron and cobalt. An overlay of these two images (Fig. 6C and D) clearly indicates that the core region has high Fe content (yellow color). In contrast, the shell region shows green color resulting from color mixing between yellow (i.e., Fe) and cyan (i.e., Co), which is indicative of coexistence of Fe and Co at the shell region. These results strongly support that nanoparticles possess core–shell structure of Fe3O4@CoFe2O4 (Fig. 6D and E).

X-ray absorption spectroscopic analyses provide supporting evidence for such phase-transformation processes of the binary superlattices (Fig. 5C–E). In the Co K-edge x-ray absorption near-edge structure (XANES) spectra of our AB-type Fe3O4 and Co superlattices (Fig. 5C), the gradual decrease of the shoulder intensities at 7,712 eV (1 eV = 1.602 × 10⁻¹⁹ J) upon annealing at 300° and 400°C, respectively, suggests the disappearance of Co metallic species (19). The main-edge peak feature changes from a broad peak at 7,725 eV into two peaks at 7,723 and 7,728 eV and is indicative of formation of CoII species (20, 21). These spectral changes indicate that the metallic Co atoms are oxidized to Co2+ ions surrounded by Td or Oh oxygen lattices upon thermal annealing. The Fe K-edge XANES spectra (Fig. 5D) of as-assembled structures exhibit a pre-edge peak at 7,715 eV originating from Fe3+ in the Td site of the inverse spinel lattice and a broad main-edge peak at ∼7,130 eV due to Fe2+ and Fe3+ in the Oh ions.
Upon thermal annealing, the main-edge peak slightly shifts toward higher energy in both samples at 300°C and 400°C, suggesting an increase in oxidation state of Fe in Oh sites (21). Because the population of Fe$^{2+}$/H$_{11001}$ in the Oh site decreases as it is replaced by Co upon the formation of cobalt ferrite, it is reasonable to observe increment of average oxidation state of iron atoms in the Oh sites (21).

Extended x-ray absorption fine structure (EXAFS) analyses provide additional information on the local structural changes around Co atoms during the thermal annealing processes. In the Fourier-transformed Co K-edge EXAFS spectra of the AB-type superlattices (Fig. 5E), the peak at 2.0 Å, corresponding to fcc Co–Co at 2.0 Å in as-assembled superlattices, significantly decreased in intensity at 300°C and finally disappeared at 400°C. In contrast, the appearance of two new peaks at 1.7 and 2.6 Å is clearly seen, corresponding to Co(Oh)–O and Co(Oh)–Co(Oh) scattering of CoFe$_2$O$_4$, respectively.

Our observation of the nanoscale transformation of Co and Fe$_3$O$_4$ binary superlattices into core–shell type Fe$_3$O$_4$@CoFe$_2$O$_4$ superlattices explains the huge enhancements in their magnetism. The Co and Fe$_3$O$_4$ nanoparticles are a class of soft magnets, but when such soft–soft magnet superlattices are transformed into the core–shell type soft–hard Fe$_3$O$_4$@CoFe$_2$O$_4$ superlattices, it is possible to have a strong magnetic coupling between a hard magnet CoFe$_2$O$_4$ shell and the soft Fe$_3$O$_4$ core generated through an exchange-coupled magnetic system with high magnetic coercivity (8, 18).

In summary, we have demonstrated the fabrication of highly ordered binary magnetic nanoparticle assemblies with controlled packing geometry through size ratio and stoichiometric effects. The binary superlattices show a unique ferrimagnetic phase transformation behavior through nanoscale redox chemical reactions, which leads to a magnetically soft–hard core–shell type nano-alloy system. The assembly-induced phase transformation strategy presented here can potentially be extended not only for high-performance integrated magnetic systems such as high-density information storage devices and magnetic sensors, but also for the fabrication of new types of ordered nanosystems with multifunctionalities and enhanced properties.
and CoFe$_2$O$_4$. Cheon et al. Synthesis of Co Nanoparticles and Fe$_3$O$_4$ Nanoparticles. Methods and A nanoparticle. These observations support that the core consists of iron-rich materials (i.e., Fe$_3$O$_4$) and the shell is comprised of materials containing iron and cobalt (i.e., CoFe$_2$O$_4$).

**Methods**

**Synthesis of Co Nanoparticles and Fe$_3$O$_4$ Nanoparticles.** For the synthesis of monodispersed Co nanoparticles (7.5 nm), 4 ml of 0.5 M Co$_2$(CO)$_8$ was injected into refluxing toluene containing 0.080 g of NaAOT and allowed to react for 6 h. After precipitation by addition of ethanol, Co nanocrystals were redissolved in 40 ml of toluene. Fe$_3$O$_4$ nanoparticles of 8.0, 15.7, and 18.0 nm were synthesized by the thermal decomposition of iron pentacarbonyl [Fe(CO)$_5$; 1 mmol] in a hot octyl ether solution containing 3 mmol of lauric acid under aerobic condition (15). After injection of the precursor solution into hot surfactant solution at 293°C, large nanoparticles were allowed to grow for an appropriate time (1 h for 8.0 nm, 1.5 h for 15.7 nm, and 2 h for 18.0 nm) and then cooled to room temperature. Ethanol was added to precipitate nanoparticles from the solution. The particles were separated by centrifugation and dispersed in toluene.

**Binary Structures of Co Nanoparticles and Fe$_3$O$_4$ Nanoparticles.** Separately prepared Fe$_3$O$_4$ and Co nanoparticles were dissolved in toluene (2 mg/ml). Nanoparticle solutions with molar ratios of 1:1 for AB and 1:2 for AB$_2$ were mixed together, which was followed by slow evaporation (~10 min) on a carbon-coated Cu grid attached on a glass slide in a Petri dish under an inert Ar atmosphere of 1 atm at room temperature. TEM analysis were performed on EM 912Ω (Zeiss, Korea Basic Science Institute) operated 120 kV whose point resolution is 3.7 Å and ARM 1300S (JEOL, Korea Basic Science Institute) operated at 1,250 kV with a point resolution of 1.2 Å.

**Formation of Fe$_3$O$_4$@CoFe$_2$O$_4$ from AB Superlattices.** AB superlattices are formed on a TEM grid or a Si wafer (1 cm$^2$) by slow evaporation of the mixed solution of Fe$_3$O$_4$ and Co nanoparticles (~2 ml) under Ar atmosphere. Thermal transformation processes were conducted on a hot plate preheated to a constant temperature of 300° or 400°C under Ar gas for 1 h. The annealed sample was sealed with polyimide tape (KAPTON-500H, 125-μm thickness) in a glove box to prevent any contamination and analyzed by superconducting quantum interference device, electron energy loss spectroscopy (EELS), and x-ray absorption spectroscopy. EELS mapping analyses were performed through standard three-windows methods with the energy window of 30 eV. Co K-edge, Fe K-edge x-ray absorption spectra were obtained in reflection mode at beamline 7C of Pohang Light Source with a ring current of 120 ~ 170 mA at 2.5 GeV.

We thank J. M. Oh and H. C. Kim (Korea Basic Science Institute). This work is supported in part by Nano Science and Technology Grant M1-0213-12-0001, National Core Research Center Grant R15-2004-024-02002-0, R & D Program of Fusion Strategies for Advanced Technologies Grant M1-0326-11-0006, NCI Center for Nanotechnology Excellence, Center for Nanotubes and Nanostructured Composites, and the BK 21 Project.

A. Phase separated mixtures of Co and Fe$_3$O$_4$ nanoparticles

\[ H_c = 500 \text{ Oe} \]

B. After annealing at 400 °C

\[ H_c = 550 \text{ Oe} \]