



Completely Filling Anodic Aluminum Oxide with Maghemite Nanoparticles by Dip Coating and Their Magnetic Properties

Il Seo,^a Chang-Woo Kwon,^b Hyun Ho Lee,^c Yong-Sang Kim,^a Ki-Bum Kim,^{b,*} and Tae-Sik Yoon^{a,z}

^aDepartment of Nano Science and Engineering and ^cDepartment of Chemical Engineering, Myongji University, Gyeonggi 449-728, Korea

^bDepartment of Materials Science and Engineering, Seoul National University, Seoul 151-742, Korea

Anodic aluminum oxide (AAO) nanotemplates were completely filled with maghemite ($\gamma\text{-Fe}_2\text{O}_3$) nanoparticles by a dip-coating process and their magnetic properties were investigated. Maghemite particles with ~ 20 nm diameter and stabilized by oleic acid were selectively deposited into AAO pores with ~ 100 nm diameter. The multiple layers of particles were obtained by repeating the procedures of dip coating and removing oleic acids from the particles. The magnetic moment of AAO with particles increased in proportion to the number of layers. These results demonstrate the possibility of integrating nanoparticles into nanotemplates and controlling their properties.

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The colloidal nanoparticles, synthesized through the chemical reaction in a suitable solvent and stabilized by a surfactant, can be formed with a narrow size distribution and assembled to form two- and three-dimensionally ordered structures on the substrate upon evaporation of the solvent.¹⁻³ To form the particle layer structures on the substrates, especially for the device applications, several processes have been suggested such as Langmuir-Blodgett,^{4,5} spin coating,^{6,7} and adsorption by dip-coating methods.⁸⁻¹² Furthermore, the delivery of nanoparticles on nanotemplates and nanopatterned substrates has been actively pursued.¹³⁻¹⁵ As an example of the possible applications, a patterned magnetic medium with magnetic particles has been actively investigated to continuously increase the area density of magnetic storage.¹⁶ Biosensors with a patterned magnetic layer were proposed for selective sensing of biomaterials attached to magnetic materials.¹⁷

We perform a simple and low cost dip-coating process for depositing magnetic maghemite particles into well-ordered anodic aluminum oxide (AAO) nanotemplates to fabricate a nanopatterned structure with particles. In this article, we report the selective formation of single and multiple layers of particles inside the AAO pores by employing repeated dip-coating and subsequent annealing procedures. Their magnetic properties were also investigated. This approach demonstrates an economically viable way to integrate the magnetic nanoparticles in nanometer-scale templates with the simple dip-coating process. This can be utilized for practical applications such as patterned magnetic media with ferromagnetic nanoparticles, patterned magnetic sensors, and so on.

The AAO templates were prepared by a two-step anodization of the Al plate as previously reported.¹⁸ The first anodization was performed at a constant voltage of 50 V in 0.3 M oxalic acid at 15°C for 4 h after degreasing an Al plate in acetone and following electropolishing in a mixed solution of perchloric acid and ethanol under a constant voltage of 15 V at 3°C for 2 min. Then the anodic oxide was removed by submerging in phosphoric acid and chromic acid at 60°C for 2 h. The second anodization was carried out to form the pores with a diameter of ~ 30 nm, and then the pore-widening step was done in a 0.5 M phosphoric acid for 1 h. The final pore size of the AAO templates was ~ 100 nm diameter.

The magnetic maghemite ($\gamma\text{-Fe}_2\text{O}_3$) nanoparticles with ~ 20 nm diameter, which is stabilized by a surfactant of oleic acid ($\text{C}_{18}\text{H}_{34}\text{O}_2$), were synthesized by following the method developed by Hyeon et al.³ During the particle synthesis, the oleic acid encapsulated the particle surface to prevent the aggregation of particles in

the solution, whose hydrophilic head was attached to the particle and whose hydrophobic tail faced the solvent. Therefore, the particles had a hydrophobic character and were well dispersed in a nonpolar solvent. Here, we dissolved the particles in octane (C_8H_{18}) with a concentration of $1.2 \times 10^{13}/\text{mL}$ for the uniform assembly, which was measured by an inductively coupled plasma spectrometer.

The AAO templates were vertically dipped and pulled out with a speed of 0.1 mm/s after a duration time of 1 min in the solution, and were dried in room-temperature air to deposit the particles inside the pores of the AAO templates. During the process of dip coating, the particles adsorbed on the surface of the templates and assembled when the solvent evaporated.^{8,9,12} The adsorbed particles were driven into the pores, especially on the templates with pore patterns, by capillary force during the solvent evaporation.¹³ As well as simply repeating the dip coating, the dip-coated templates were annealed at 200°C for 1 h in air, during which the oleic acid molecules desorbed from the particle layer.¹⁹ Then the templates were subsequently dipped into the solution for additional adsorption of particles onto the particle layer. The dipping and annealing procedures were repeated three and five times, respectively, to form the multiple layers of the particles inside the pores. The maghemite particles were characterized by transmission electron microscopy (TEM). The morphologies of the particle layers were analyzed using plan-view and oblique-angle-view scanning electron microscopy (SEM). Oblique-angle-view images were obtained by folding and tilting AAO templates formed on the Al plate. A desorption of oleic acid from the particle layer was confirmed by Fourier transform infrared (FTIR) spectrophotometry. The magnetic properties of the AAO templates with maghemite particles were characterized by a vibrating-sample magnetometer (VSM). The AAO samples for VSM measurement were prepared by cutting the Al plate to a thickness of 0.25 mm and an area of 1 cm^2 .

Figure 1 shows a TEM image and a diffraction pattern of as-synthesized maghemite nanoparticles placed on the carbon-coated TEM grid. The diameter of the particle is approximately 20 nm and its phase is maghemite in accordance with the report by Hyeon et al.³

These particles are deposited into AAO templates by a dip-coating process. Figure 2 shows the plan-view and oblique-angle-view SEM images of maghemite particles inside the AAO templates after dip coating once [(a) and (b)] and after repeating five times [(c)]. As we previously reported, the particles are uniformly and selectively deposited inside the pores and assembled at the bottom of the pores forming a single layer.¹⁵ The selective assembly of the particles inside the patterns is obtained by the capillary-force-driven particle migration into the pores.¹³ The capillary force at the edge of

* Electrochemical Society Active Member.

^z E-mail: tsyoon@mju.ac.kr

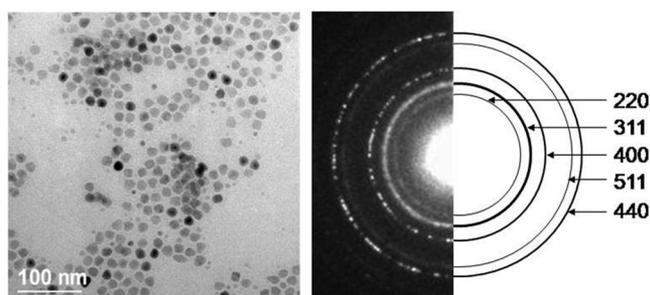


Figure 1. TEM image and diffraction patterns of maghemite ($\gamma\text{-Fe}_2\text{O}_3$) nanoparticles.

the solution interface with the template surface is expressed as $F_c = 2\pi r \sigma \sin \varphi$, where σ is the surface tension of a solution, r is the particle-solution contact-line radius that equals the particle radius when the solution meniscus moves down to a thickness of particle radius, and φ is the angle between the radial axis of the particle and solution. A magnitude of capillary force for a 20 nm diameter particle in the octane solution with the surface energy roughly assumed to be 21.62 mN/m of octane solvent, and with φ of 90° assumed to be complete wetting between the nonpolar octane solvent and the hydrophobic tail of oleic acid covering the particle surface, is $\sim 330kT/\text{nm}$, which is high enough to drive the particles into pores.

Because the bottom of the pores is round, some pores appear to have multilayers in the oblique-angle-view images. However, most of them have a single layer. The particles do not form multiple layers of particles but only a single layer, even after the multiple dip-coating procedures. One of the probable reasons for a self-limited single-layer formation is that the surfactants covering the particle surface prevent the additional adsorption of particles from the solution onto the particle layer in the pores. The self-limited single-layer formation was previously reported on planar Si and SiO_2 substrates.⁸ This self-limited single-layer formation occurs similarly in the pores where the particles are driven by the capillary force.^{13,15} When repeating dip-coating procedures, the particles driven into the pores may not adsorb on the particle layer because the surfactants (oleic acid) on the particle surface inhibit the adsorption on the particle layer but escape from the pores before the solvent is completely dried.

To form multiple layers through desorbing the oleic acid from the particle layer, the desorption of oleic acid after annealing the particle layers at 200°C for 1 h was confirmed by using FTIR analysis. For comparison, three samples were prepared on a slide glass; the first one is pure oleic acid, the second is a maghemite particle layer, and the third is a maghemite particle layer after annealing at 200°C for 1 h. In Fig. 3, the peaks from oleic acid match well with the reports of Wu et al.²⁰ and Shukla et al.²¹ The peaks at 2926 and 2856 cm^{-1} are attributed to the asymmetric and symmetric CH_2 stretches, respectively. The peaks at 1730 , 1460 , 1260 , and 967 cm^{-1} are matched with the bands of the $\text{C}=\text{O}$ stretch, the in-plane O–H band, the C–O stretch, and the out-of-plane O–H stretch, respectively. Among these, the peaks at 2926 , 2856 , and 1730 cm^{-1} are clearly observed from the particle layer, indicating that the oleic acids are attached on the surface of particles. These peaks disappear after annealing the particle layer at 200°C for 1 h, as shown in Fig. 3. This clarifies that the oleic acids were desorbed from the surface of particles by the annealing process.

The multiple layers of particles completely filling the AAO pores were obtained by repeating the procedures of dip coating and annealing to desorb the oleic acid. Figure 4 shows the oblique-angle-view SEM images of maghemite particles in the pores after repeating dip coating and annealing at 200°C for 1 h three and five times, respectively. The multiple layers are clearly observed, and the number of layers increases with an increase in the number of dip-coating and annealing steps. The AAO pores are almost completely filled

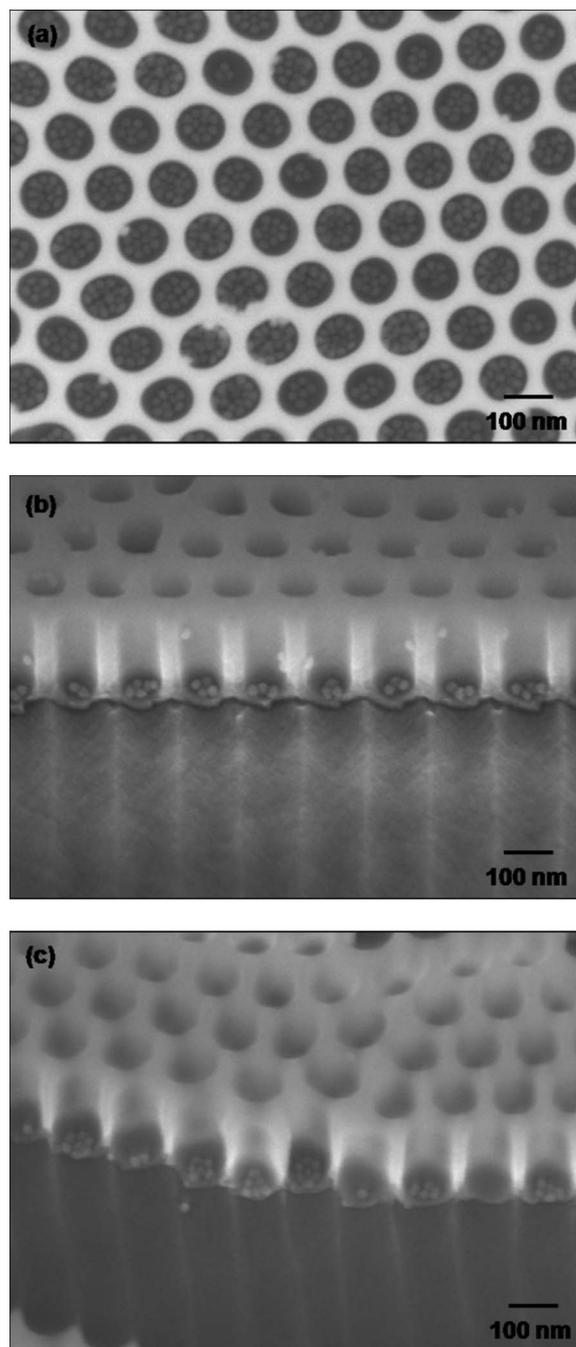


Figure 2. Plan-view and oblique-angle-view SEM images of maghemite particles in AAO templates after dip coating for [(a) and (b)] one and (c) five times, respectively.

with particles by repeating the steps five times (Fig. 4b). The particles can be selectively integrated into the nanopores as both the single layer and multiple layers completely filling the pores by the simple dip-coating process.

The magnetic moment of AAO templates with maghemite particles is shown in Fig. 5. The magnetic moment of AAO with a single layer of particles by dip coating once is the lowest, while the AAO with multiple layers after the dip-coating and annealing steps were repeated five times has the highest moment. The magnetic moment increases in proportion to the number of particle layers due to the increased total volume of particles. More particles have aligned magnetic orientation similar to the domain contribution be-

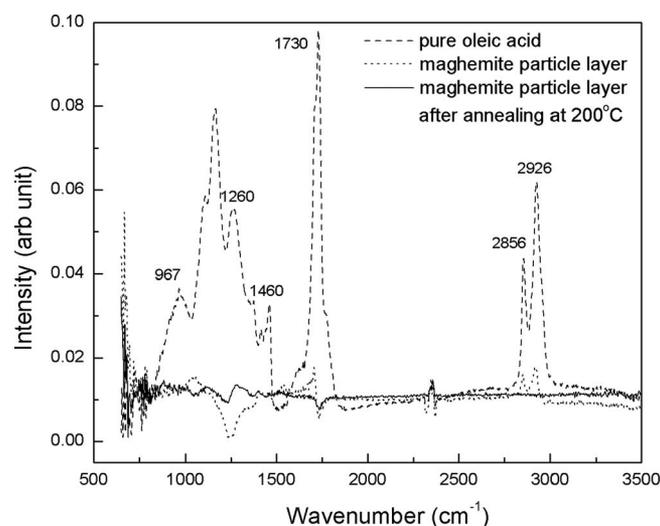


Figure 3. FTIR analysis of the desorption of oleic acid: (dashed) pure oleic acid, (dotted) maghemite particle layer, and (solid) maghemite particle layer after annealing at 200°C for 1 h.

ing weighted by its volume. This demonstrates that the magnetic properties of the nanostructure with nanoparticles can be controlled by tuning the number of particle layers.

In summary, both single and multiple layers of the particles completely filling the AAO templates could be obtained by employing the repeated dip-coating and subsequent annealing steps. The selective deposition of the particles inside the AAO pores results from the

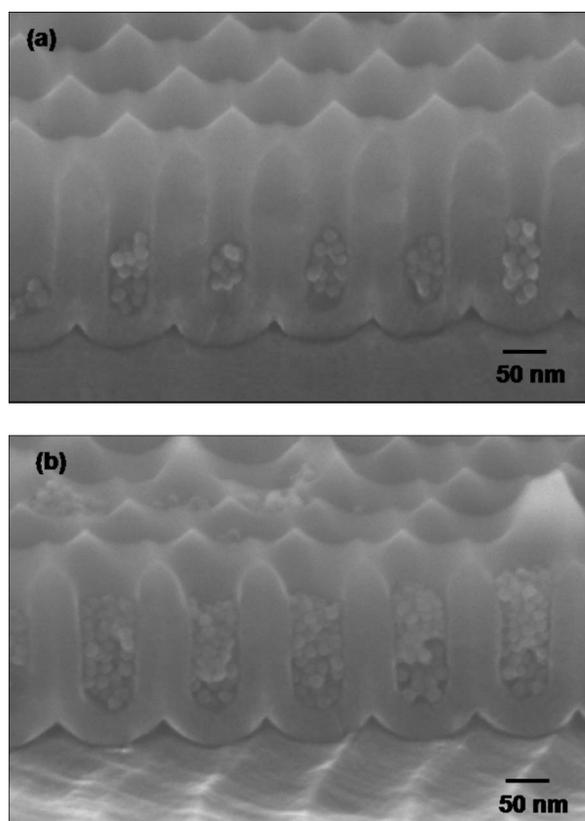


Figure 4. Oblique-angle-view SEM images of maghemite particles in AAO templates after dip-coating and subsequent annealing steps for (a) three and (b) five times, respectively.

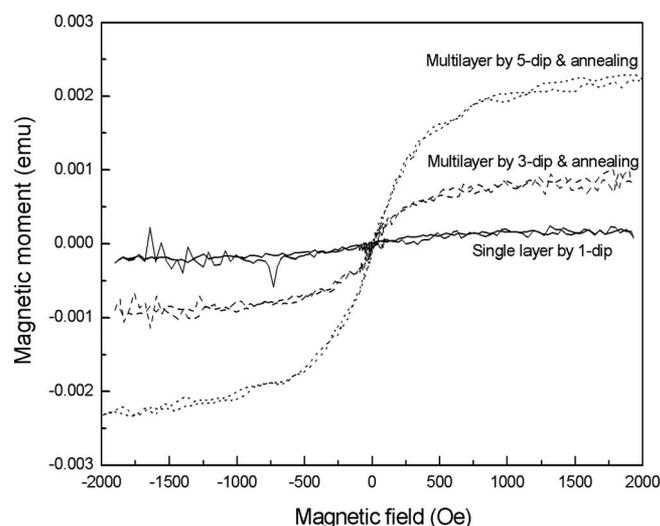


Figure 5. Magnetic moment of AAO templates with maghemite particles.

capillary force driving the particles into the pores when the solvent evaporates during the dip-coating process. After removing the surfactants of oleic acid from the particle layer in the pores, the subsequent dip coating forms the multiple layers. The number of particle layers inside the pores increases in proportion to the number of steps of dip coating and annealing. Also, the magnetic moment of AAO templates increases with the number of particle layers. This approach successfully integrates nanoparticles selectively in nanometer-scale templates with a simple dip-coating process and demonstrates the possibility to control the magnetic properties by changing the number of particles in the templates, which can be utilized for practical applications such as patterned magnetic media when using the ferromagnetic nanoparticles, patterned magnetic sensors, and so on.

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