Ultrathin Films

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Sequential Assembly of Phototunable Ferromagnetic Ultrathin Films with Perpendicular Magnetic Anisotropy**

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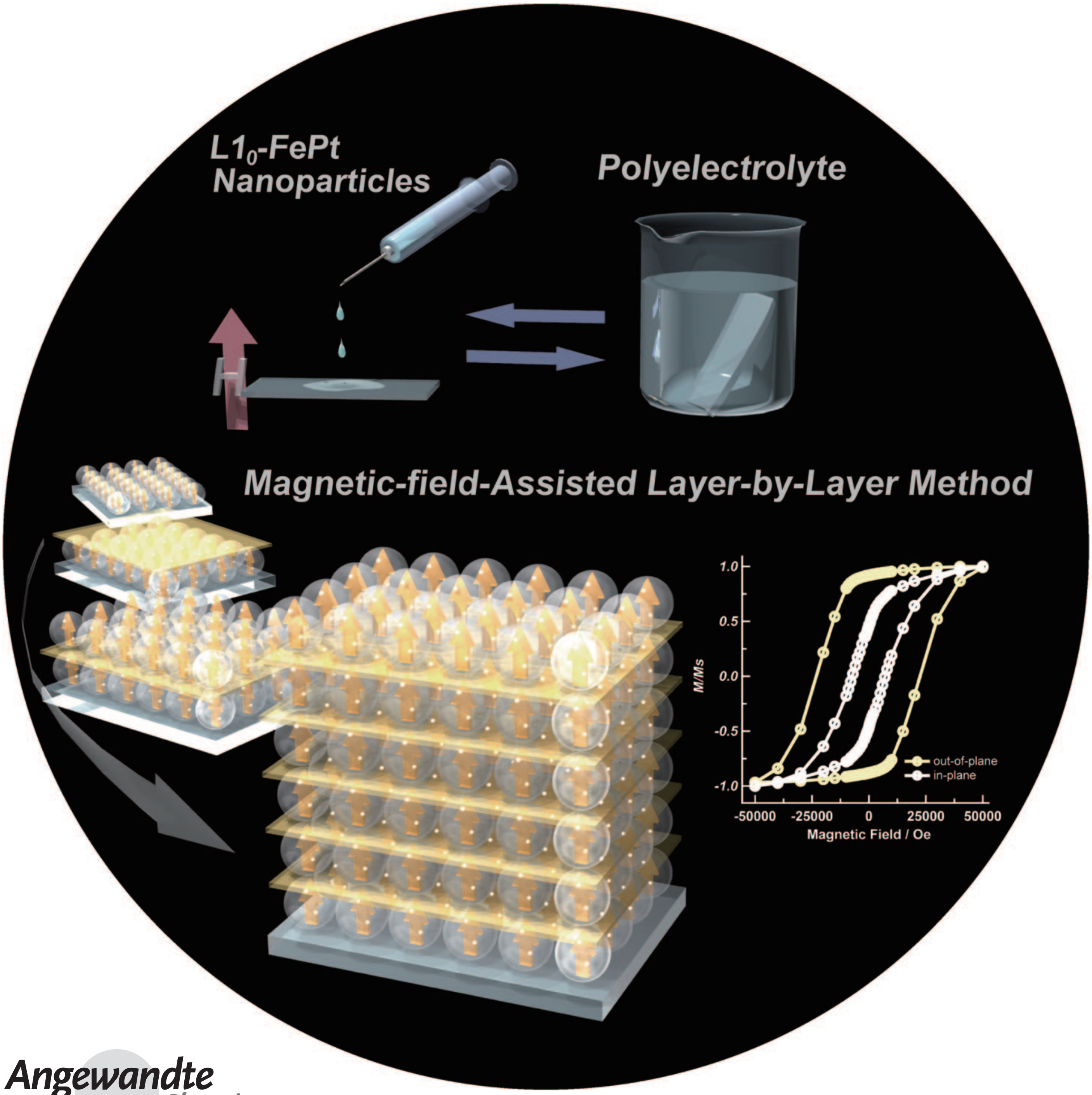

Since the discovery of photocontrollable magnetic compounds in 1996,[1] optically switchable magnetic materials have been attracting great interest because of the continued demand driving the development of optical-memory and -switching devices. Until now, although many interesting examples of photomagnetic phenomena have been reported, observations of photoswitching have been limited to low-temperature operation. In other words, in terms of practical application, the studies have not yet progressed beyond basic research. Here, we describe an optically controllable assembly of ferromagnetic FePt nanoparticles which we fabricated using a novel magnetic-field-assisted layer-by-layer method. As a result, we have realized significant perpendicular magnetic anisotropy in photocontrollable films at room temperature, which is one of the greatest challenges to be met before this technology can be used in practical applications. We believe this strategy is a giant step toward practical applications in optical magnetic recording systems.

The controlled synthesis and assembly of magnetic-nanoparticle-based compounds are key to important new technologies.[2,3] In the course of developing such assemblies, it is also crucial to find a way of controlling the magnetic anisotropy of the nanoparticles, since it is expected that the application of perpendicular magnetization will enable the production of ultrahigh-density magnetic recording media. Previously, thin films that exhibit large perpendicular magnetic anisotropy have been realized by several dry processes[4–6] utilizing $L1_0$-FePt alloy, which is an excellent candidate for such applications because of its uniaxial magnetocrystalline anisotropy ($K_u = 7 \times 10^6\,\mathrm{J\,m^{-3}}$) and excellent chemical stability.[3] An alternative approach would be a solution-based process utilizing chemically synthesized nanoparticles. Such processes have great potential to realize the storage of one bit per one particle, which is the ultimate goal in the development of ultrahigh-density recording media. Although various methods for fabricating well-ordered nanoparticle assemblies by wet processes have been proposed,[7–9] no methods are known that enable the fabrication of nanoparticle assemblies featuring perpendicular magnetic anisotropy.

Herein we describe a novel method, referred to the magnetic-field-assisted layer-by-layer method, for the fabrication of ferromagnetic FePt nanoparticle assemblies which exhibit large perpendicular magnetic anisotropy. In the current system, we have modified the well-known layer-by-layer method[10] by simply applying a strong magnetic field during the deposition of the FePt nanoparticles. Another important advantage that can be gained by this technique is the strong possibility of introducing a second functionality, such as phototunability, into the magnetic nanoparticles by using functional molecules as organic components.[11,12]

Figure 1 a shows a transmission electron microscopy (TEM) image of $L1_0$-FePt nanoparticles deposited from water solution. The $L1_0$-FePt nanoparticles show good dispersibility even after ligand exchange, and the particles are uniform with a diameter of about 3.5 nm. The magnetization curves (M–H plots) measured at 300 K for a solution of $L1_0$-FePt nanoparticles dispersed in water show superparamagnetic-like behavior with no hysteresis curve (Figure 1 b), while a large hysteresis loop with coercivity (H_c) of 1.8 T was observed for powder $L1_0$-FePt nanoparticles (see Figure S1 in the Supporting Information). In this case, the M–H plots could be fitted by the curve given by Langevin's function, which expresses the superparamagnetic magnetization theoretically. This means that each $L1_0$-FePt nanoparticle in solution can be rotated by the applied magnetic field until its c axis (magnetic easy axis) is parallel to the direction of the magnetic field because each nanoparticle is magnetically isolated from the others.[13] Hence, it is expected that the application of an external magnetic field during the layer-by-layer deposition will result in the assembly of magnetic nanoparticles with oriented magnetic moments.

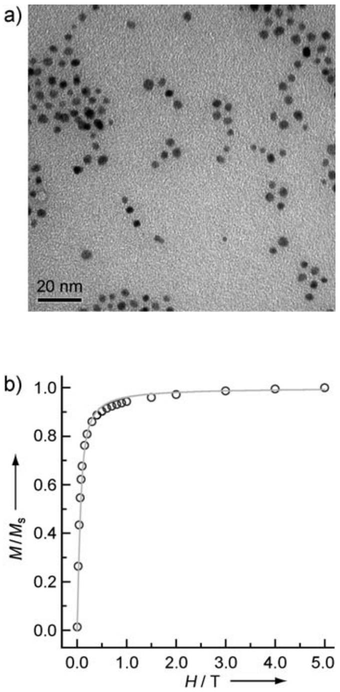

Figure 1. a) TEM image of $L1_0$-FePt nanoparticles deposited from a dispersion in water onto a collodion-coated copper grid; scale bar: 20 nm. b) Plot of normalized magnetization M/M_s versus applied magnetic field H at 300 K for $L1_0$-FePt nanoparticles dispersed in water solution (circles) and the fitted curve given by the Langevin function (solid line).

Hybrid multilayer films were fabricated by the layer-by-layer deposition of cationic polyelectrolyte azobenzene (poly-AZ, **1**) and $L1_0$-FePt nanoparticles. The preparation of

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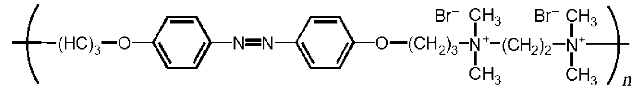

poly-AZ (**1**)

multilayer films of poly-AZ and FePt nanoparticles is shown schematically in Figure 2a. The deposition cycle was monitored by UV/Vis spectroscopy. Adsorption spectra recorded after increasing numbers of deposition cycles are shown in Figure 2b. Each spectrum has an intense absorption peak at 361 nm. This peak is ascribed to the π–π* transition of the *trans* isomer of poly-AZ. Figure 2c shows the maximum absorbance (at 361 nm) versus the number of dipping cycles. The absorbance at 361 nm increases linearly as the number of deposition cycles increases. This linearity indicates that uniform deposition took place during each cycle. Surface ζ potential measurements (shown in Figure S3 in the Supporting Information) also indicate that uniform layer-by-layer deposition was taking place.

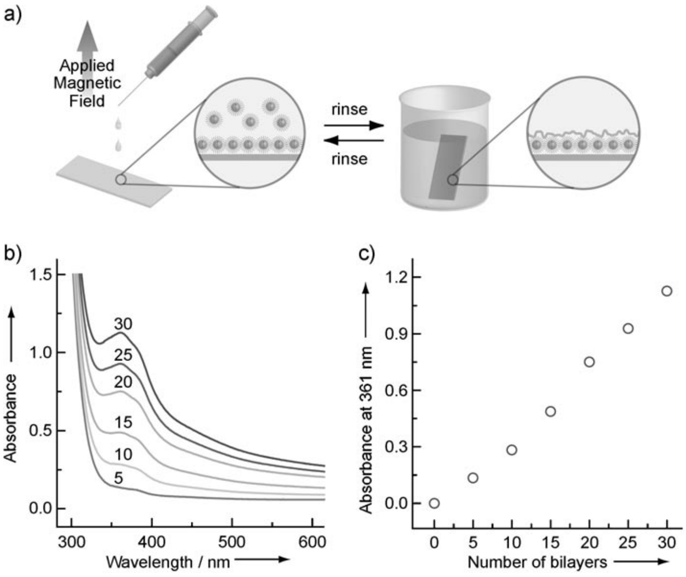

Figure 2. a) Schematic illustration of film preparation procedure. b) Changes in UV/Vis adsorption spectra for the hybrid films with increasing number of deposition cycles. c) Plot of maximum absorbance at 361 nm for the hybrid films versus the number of deposition cycles.

Subsequently, we focused on the magnetic anisotropy of the poly-AZ/FePt nanoparticle hybrid films. Figure 3 shows the *M*–*H* plots of the poly-AZ/FePt nanoparticle hybrid films. The external magnetic field was applied perpendicular (blue line) and parallel (orange line) to the film surface. Importantly, the poly-AZ/FePt nanoparticle hybrid films exhibited an extremely high coercivity of 2.4 T and a higher degree of squareness ($M_r/M_s = 92\,\%$) in the out-of-plane direction than in the in-plane direction ($H_c = 0.5$ T, $M_r/M_s = 40\,\%$). That is, the poly-AZ/FePt Nanoparticle hybrid films demonstrated a preferential orientation for their crystalline *c* axes in the direction perpendicular to the film surface. To the best of our knowledge, this is the first report of the solution-based fabrication of ultrathin films consisting of magnetic nanoparticles with such large perpendicular magnetic anistropy. Furthermore, the magnetic anistropy for the current system ($H_{c,\mathrm{easy}}/H_{c,\mathrm{hard}} = 0.20$) is comparable to the values obtained for the bulk systems realized previously ($H_{c,\mathrm{easy}}/H_{c,\mathrm{hard}} = 0.13$).[13]

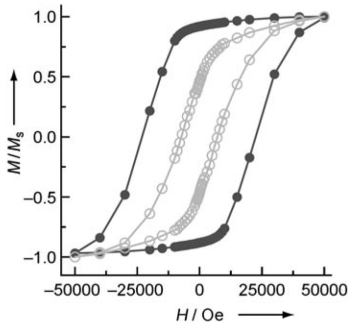

Figure 3. Plot of normalized magnetization M/M_s versus applied magnetic field H at 300 K for the hybrid films with the external magnetic field perpendicular (filled circles) and parallel (open circles) to the film surface.

We also investigated the photoresponsiveness of the poly-AZ/FePt nanoparticle hybrid films. The photoisomerization of the hybrid films in the solid state at room temperature was monitored by UV/Vis absorption spectroscopy (Figure 4a). The reversible spectral changes indicate high-efficiency reversible photoisomerization, even in the solid state. Subsequently, we investigated the influence of photoillumination on the magnetic properties of the poly-AZ/FePt nanoparticle hybrid films at 300 K (Figure 4b) with an external magnetic field of 5 T applied perpendicular to the film surface. An increase of about 5 % for the initial saturation magnetization value was observed during the UV illumination, and recovery to the initial value was observed during the illumination with visible light. After this process, the UV-light-induced increases and the visible-light-induced decreases in magnetization were repeated without any attenuation. Even when the external magnetic field was applied parallel to the film surface, very similar phenomena were observed, with almost the same rates of change in the magnetization.

From the above observations, we propose that the photoisomerization of poly-AZ caused the changes in the electrostatic field around the FePt nanoparticles. As a result, changes in magnetization were induced by electronic polarization on the surfaces of the FePt nanoparticles. From Mössbauer studies, it was observed that organic-ligand-coated FePt nanoparticles exhibit two magnetic phases: one is a hyperfine interaction in the bulklike core, while the other is a dipolar surface layer resulting from dipolar charges on the organic ligands. These differences in the magnetic phase between the particle cores and the particle surfaces form electronic shell structures with significant gradients in their electronic charge densities.[12c,14] In a previous report, we observed photoinduced changes in the hyperfine fields of the surface-layer phase on azobenzene-passivated FePt nanoparticles.[12c] These

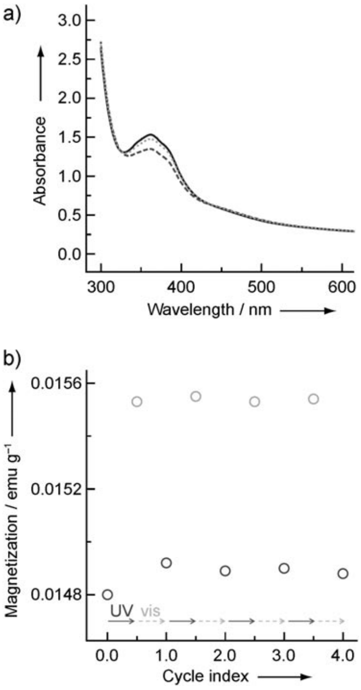

Figure 4. a) Changes in the optical absorption spectra of the hybrid films resulting from to photoisomerization. The initial *trans* state (solid line) was first illuminated with UV light for 1 min (dashed line). It was then illuminated with visible light for 1 min (dotted line). b) Changes in magnetization by photoillumination at 300 K under an external magnetic field of 5 T perpendicular to the film surface.

photoinduced changes in the hyperfine field mean that the photoisomerization of the azo ligands had induced electronic polarization on the surfaces of the FePt nanoparticles. As a result, changes in the magnetic properties of the composite nanoparticles were caused by photoinduced changes in the electronic charge density on the surface iron atoms.

In conclusion, we have introduced a new way for generating an assembly of ferromagnetic FePt nanoparticles with large perpendicular magnetic anisotropy, which we have called the magnetic-field-assisted layer-by-layer deposition method. As a result, large perpendicular magnetic anisotropy has been observed in layer-by-layer films consisting of $L1_0$-FePt naoparticles and organic polymers. This is the first example of the fabrication of ultrathin films consisting of magnetic nanoparticles with large perpendicular magnetic anistropy through a solution-based process. Furthermore, we have also succeeded in introducing phototunability into these films by the use of photochromic molecules as polymer layers. We believe that this novel strategy will open up great possibilities for practical applications in optical magnetic recording systems.

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