Photoswitchable Magnetic Layer-by-Layer Films Consisting of Azobenzene Derivatives and Iron Oxide Nanoparticles

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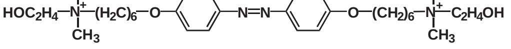
The photoswitchable magnetic thin films have been designed by alternate depositions of bipolar amphiphilic azobenzene and Fe_3O_4 nanoparticles by using the layer-by-layer adsorption technique. In these films, reversible photoisomerizations of the azobenzene chromophore affected the electrostatic interaction between the azobenzene chromophore and the surface of Fe_3O_4 nanoparticles. As a result, we have succeeded in controlling the magnetization of these films by photoillumination at room temperature.

Photoswitchable magnetic materials have attracted much attention in recent years.[1,2] To realize such a system, we have focused on the incorporation of organic photochromes into inorganic magnetic systems with nanometer orders.[3–5] Though several different methods were reported for the construction of such materials,[6,7] one of the easiest and most useful methods is layer-by-layer adsorption technique.[8] This method enabled to various composite materials which have anionic or cationic charges such as polyelectrolytes, bipolar amphiphiles, and colloidal particles with highly ordered structures and tunable thickness.[9] Here we designed a novel type of hybrid films consisting of cationic bipolar amphiphilic azobenzene, cationic poly(diallyldimethylammonium chroride) (PDDA)-coated Fe_3O_4 nanoparticles and anionic polyelectrolytes, polyacrylic acid (PAA), by using layer-by-layer adsorption technique. In this system, the magnetization values of these films were controllable by photoillumination at room temperature.

The cationic bipolar amphiphilic azobenzene, 4,4′-bis[[6-[(2-hydroxyethyl)dimethylammonio]hexyl]oxy]azobenzene dibromide ($Br^-N^+C_6AzoC_6N^+Br^-$), was synthesized as follows. 4,4′-Bis(6-bromohexyloxy)azobenzene was synthesized according to the literature[10] and then, quarternized in toluene with *N*,*N*-dimethylethanolamine for 4 h at 120 °C to form Br^-N^+-$C_6AzoC_6N^+Br^-$.



$Br^-N^+C_6AzoC_6N^+Br^-$

Chart 1.

The PDDA-coated Fe_3O_4 nanoparticles with the typical size of 10 nm were synthesized according to the literature,[11] and cationic water solution (PDDA:10 m M/Fe_3O_4:0.05 wt %) were prepared with a pH of 8.5.

The hybrid films were prepared as follows. Well-cleaned glass substrates were ultrasonicated for 10 min in a mixture of 1 g of potassium hydroxide, 60 mL of ethanol, and 40 mL of water. After this procedure, the substrates were rendered completely hydrophilic, and negative charges were induced. For precoating, the substrates were alternately immersed in water solution of PDDA (1 mM) and PSS (1 mM) for 5 min each. This procedure was repeated 5 times. After precoating, the substrates were immersed by turns in water solutions of PDDA-coated Fe_3O_4, PAA (10 mM), $Br^-N^+C_6AzoC_6N^+Br^-$ (1 mM) and PAA (10 mM) for 5 min each. This procedure was repeated 30 times. After each deposition, the substrates were rinsed 3 times in water for 1 min each.

The deposition cycles were monitored by UV–visible spectroscopy. The adsorption spectra with increasing number of the dipping cycles are shown in Figure 1. Each spectrum gave a intense absorption peak at 370 nm. This peak is ascribed to the π–π^* transition of the trans isomer of $N^+C_6AzoC_6N^+$. The absorption intensity increased with increasing number of dipping cycles. The inset of Figure 1 shows the maximum absorbance (at 370 nm) versus the number of dipping cycles. The absorbance at 370 nm increased linearly as the number of dipping cycles increased. This linearity indicates that the uniform depositions took place in each dipping cycles.

Photoisomerization of hybrid films of 30 cycles at room temperature was monitored by UV–visible absorption spectroscopy. The UV–vis spectral changes due to the photoisomerization are shown in Figure 2. Before light illumination, the films only consisted of the trans isomer of $N^+C_6AzoC_6N^+$, because it is thermodynamically more stable than cis isomer (Figure 2a). After UV illumination of the trans isomer for 10 min, the absorption at 370 nm which ascribed to the π–π^* transition of trans isomer was decreased (Figure 2b). This indicates that trans-to-cis photoisomerization occurred in the films. Following subsequent illumination with visible light for 10 min, the absorption at

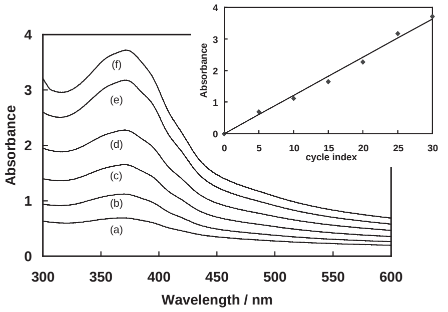


Figure 1. Optical adsorption spectra of the hybrid multilayered films [(a) 5 cycles, (b) 10 cycles, (c) 15 cycles, (d) 20 cycles, (e) 25 cycles, and (f) 30 cycles] with inset showing the linear relationship between number of deposition cycles and absorbance at 370 nm.

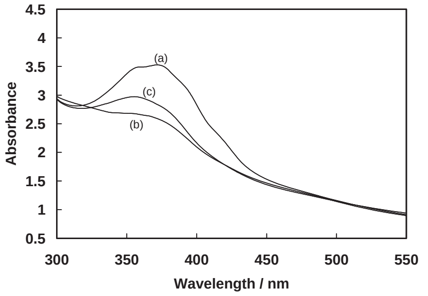


Figure 2. Changes in the optical adsorption spectra for the 30 cycles deposited films due to photoisomerization. The initial trans state (a) was first illuminated with UV light for 10 min (b). Then, it was subsequently illuminated with visible light for 10 min (c).

370 nm was increased to certain extent (Figure 2c). This indicates that cis-to-trans photoisomerization also occurred in the films, though it was incomplete. This incompleteness was due to the lower quantum efficiency of photoisomerization because the free volume for the photoisomerization was more restricted in these films than in solution. This photoisomerization cycle was repeated several times in the area from curve b to c. Similar results have been reported also in other layer-by-layer films consisting of bipolar amphiphilic azobenzene.[12]

The magnetic properties of 30 cycles of hybrid films were studied by SQUID measurements. The magnetization curves measured at 300 K are shown in the inset of Figure 3. A typical characteristic of superparamagnetic behavior, showing no coercivity and no remanence, was observed.

Subsequently, we investigated the influence of photoillumination on the magnetic properties of the films at 300 K (Figure 3). During the UV illumination, the initial magnetization value at 10 G increased from 20.0 to 20.6 emu/cm^2. Then, we illuminated the films with visible light. The magnetization value decreased from 20.6 to 20.2 emu/cm^2. After this process, UV-light increase and visible-light decrease of magnetization were repeated several times. The photoinduced changes in the magnetization values are estimated to be ca. 3% in the first cycle and ca. 2% after the second one. This decrease of the values after second cycle is also consistent with the decrease in the quantum efficiency for photoisomerization in these films.

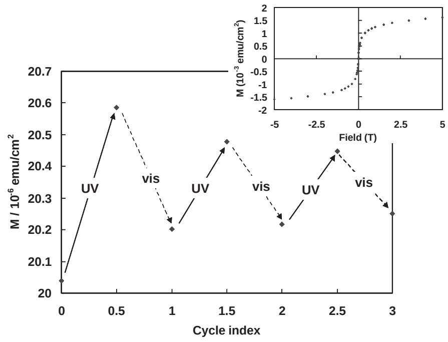


Figure 3. Changes in the magnetization for 30 cycles deposited films induced by alternating illumination with UV and visible light for 10 min each at 300 K with an external magnetic field of 10 G with inset showing the plot of magnetization M versus applied magnetic field at 300 K.

By analogy with our previous system,[3–5] it is proposed that photoinduced changes in the dipole moment due to the photoisomerization of the azobenzene chromophore affected the electrostatic interaction between the azobenzene chromophore and the surface of the Fe_3O_4 nanoparticles. As a result, changes in the magnetization of the films were observed. The reason for these smaller magnetization changes compared to our previous system[5] is that the electrostatic interaction is very small because of the existence of the polymer layers between the azobenzene chromophore and the Fe_3O_4 nanoparticles.

This explanation is also consistent with that by several physicists.[13–15] They discussed the relationship between the electronic polarizations (including the charge on the dipole moment) and the magnetization. The origins of the behavior of electromagnetic materials are the electric field induced g shift, the spin–orbit interactions, the exchange energies, and the electric field induced shift in the single ion anisotropy energy. The underlying electrodynamics are complicated by induced fields interacting with electric and magnetic moments. That is, the spin orientation is coupled to the electric multipole through the lattice. Morup et al. also discussed the existence of significant collective effects in a magnetic nanoparticle system and made several speculations regarding a spin-glass-like phase at low temperatures on dipole–dipole interacting systems.[15] Moreover, the surface magnetic phase diagram of the tetragonal manganites depends on the electrostatic interactions caused by the surface environment, such as surface termination.

In summary, we have succeeded in designing reversibly photocontrollable magnetic layer-by-layer films consisting of azobenzene derivatives and Fe_3O_4 nanoparticles. The photoinduced changes in the magnetization value of these films were observed at room temperature. Furthermore, it is expected that photocontrol of magnetization with larger value is possible by designing films which have thinner or no polymer layers between Fe_3O_4 nanoparticles and azobenzene derivatives.

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