Photomagnetic Co–Fe Prussian Blue Thin Films Fabricated by the Modified Langmuir–Blodgett Technique

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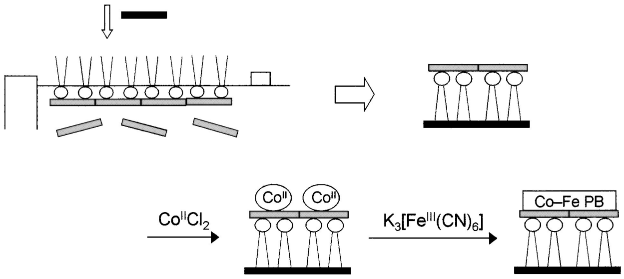
Co–Fe Prussian blue thin films have been prepared by means of a modified Langmuir–Blodgett technique, in which the hybrid monolayer composed of amphiphiles and clay platelets plays a template role for the formation Co–Fe Prussian blue thin films. Photoinduced magnetization was observed in the thin films as observed in the bulk Co–Fe Prussian blue. To the best of our knowledge, this is the first example of successful formation of Co–Fe Prussian blue thin films, which possess the ordered structure and, in addition, exhibit photoinduced magnetization.

Among the numerous number of cyano-bridged solid-state compounds, Prussian blue and its analogues have been extensively explored because of their interesting magnetic properties.[1] They also have some remarkable features: (1) It is easy to prepare. Only mixing aqueous solutions of MCl_2 and $A_3[M'(CN)_6]$ leads to M′–M Prussian blue (M, M′: metal, A: alkali cation). (2) They form a 3-D network, in other words, a cubic system. In particular, Co–Fe Prussian blue, which represents the Prussian blue analogue with Fe–CN–Co structures, exhibits photoinduced magnetization effects.[1a,2] In the application for devices, it is required to prepare thin films of Co–Fe Prussian blue. However, up to now, Co–Fe Prussian blue thin films have been prepared mainly by electrochemical methods.[3] With regard to uniformity of the films, there are few reports that demonstrate successful formation of the ordered thin films of Co–Fe Prussian blue.[4] Moreover, to the best of our knowledge, there are no attempts to examine photoinduced magnetization behavior in such ordered thin films.

The Langmuir–Blodgett (LB) technique is one of the most useful and well-known methods to prepare a thin film, in which the number of layers and their sequence can be controlled at the molecular level.[5] Recently, there have been reported a novel fabrication method for the hybrid film, which is based on the LB technique.[6] The difference between the conventional and the novel methods is the use of clay minerals. The hybrid films thus prepared are found to possess some remarkable features: (1) The layered structure of the film is quite stable because of the existence of the rigid clay layers. (2) It is able to introduce thin layers of cationic compound into the film by a cation-exchange reaction with clay layers. (3) The cations in the adsorbed layer are sandwiched in noncentrosymmetric fashion. Therefore, it is effective to prepare thin films to adopt this modified LB method.

In this work, we have prepared Co–Fe Prussian blue thin films by means of the above method. In this case, the transferred hybrid monolayer plays a template role in formation of Co–Fe Prussian blue thin films. Moreover, it is expected to obtain the ordered films, in contrast to electrochemical methods.

Montmorillonite (Kunipia P) is a smectite clay and used as the building block. The amphiphilic ammonium salt of dimethyldidodecylammonium bromide (DDAB) was dissolved in chloroform (2.0×10^{-3} M) and then spread onto a surface of the clay suspension at 90 ppm. The hybrid monolayer compressed up to a surface pressure of $10\,mN\,m^{-1}$ was transferred as X-type films onto a hydrophobic surface of a substrate by horizontal dipping. The average transfer ratios for the upstroke were 1.2 and those for the downstroke were 0. The surface of the transferred monolayer was rinsed with pure water and then it was dipped into an aqueous $CoCl_2$ solution (10 mM) for 2 min. After rinsing the surface with pure water, it was immersed in an aqueous $K_3[Fe(CN)_6]$ solution (10 mM) for 2 min to form a Co–Fe Prussian blue layer on the surface of the hybrid monolayer. The surface was rinsed with pure water and dried by blasting with N_2. The hybrid film of DDAB, the clay platelets, and Co–Fe Prussian blue were fabricated by repeating this cycle (Scheme 1).



Scheme 1. Preparation of Co–Fe Prussian blue thin films.

The formation of the hybrid film was monitored by the IR spectra measured in the process of the film preparation at room temperature. Each spectrum gave five characteristic peaks at 2957, 2924, 2851, 2160, and 2095 cm^{-1}. These peaks are assigned to the stretching vibration band of CH_3 antisymmetric, CH_2 antisymmetric, CH_2 symmetric, CN (Fe^{III}–CN–Co^{II})[7], and CN (Fe^{II}–CN–Co^{II})[7], respectively. Absorbances of each peak increased in a regular way as the layer number increased. This suggests that formation of the hybrid film is reproducible and also successful.

The X-ray diffraction (XRD) pattern for the hybrid film (100 hybrid layers) gave four diffraction peaks at $2\theta = 3.94$, 7.87, 16.1, 19.9, and 24.5° (Figure 1). This indicates that the hybrid film possesses layered structure. In addition, the thickness of one hybrid layer (DDAB/clay/Co–Fe Prussian blue) is calculated to be 2.24 nm. Considering the thickness of DDAB and clay platelets, the thickness of Co–Fe Prussian blue layers is estimated to be 0.44 nm. In this case, it is supposed that one layer of Co–Fe Prussian blue is adsorbed.

Magnetic properties of the hybrid film were investigated with SQUID. A Hg–Xe lamp was used as the light source and filtered red light ($\lambda > 550$ nm) was guided by an optical fiber into SQUID for illumination of the hybrid films. The field-cooled magnetization (FCM) curve at an external magnetic field of 10 G for the hybrid film is shown in Figure 2. The hybrid film exhibited a ferrimagnetic interaction below $T_C = 15$ K before illumination. Subsequent red light illumination at 5 K, the magnetization value increased rapidly and then gradually saturated after 90 min. The magnetization value at 5 K increased by 60%, compared with the initial one. The photoinduced magnetization value was reverted to its initial one by the thermal treatment at 200 K. These indicate that the photoinduced magnetization effect occurs even in the ordered thin film. To the best of our knowledge, this is the first example of demonstrating the successful fabrication of the Co–Fe Prussian blue thin films, which exhibit the photoinduced magnetization effect.

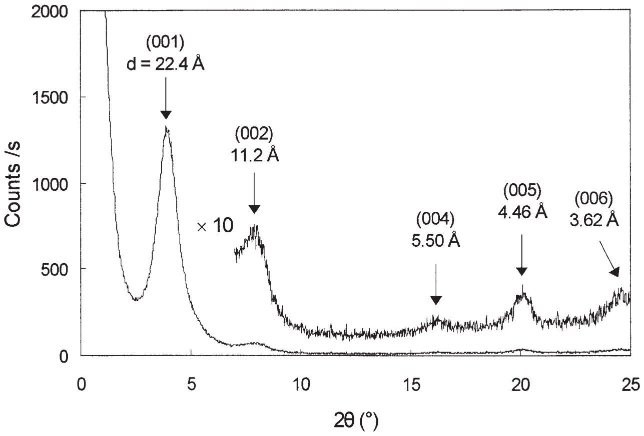


Figure 1. XRD pattern for the hybrid film (100 layer).

In the case of the bulk Co–Fe Prussian blue, the mechanism of the photoinduced magnetization effect has already discussed by mainly monitoring the changes in the IR spectra at 12 K.[2] Briefly, after red light illumination, the intensity of the peak at 2130 cm^{-1} decreased and that at 2165 cm^{-1} increased. The peaks at around 2165 and 2130 cm^{-1} are assigned to Fe^{III}–CN–Co^{II} (high spin) and Fe^{II}–CN–Co^{III} (low spin), respectively.[2b] This means that red light illumination induced the internal charge transfer (i.e. from the initial state Fe^{II}–CN–Co^{III} (low spin) to the metastable state Fe^{III}–CN–Co^{II} (high spin)). In the present system, similar spectral changes were observed in the IR spectra measured at 8 K. That is, by red light illumination, the intensity of the peak at 2130 cm^{-1} decreased and that at 2165 cm^{-1} increased. It is suggested that the efficiency of the internal charge transfer is reduced owing to the lowering the dimension of Co–Fe Prussian blue. Therefore, the number of the generated Co^{II} (high spin) ions by red light illumination was smaller than that of the bulk Co–Fe Prussian blue. In conclusion, the photoinduced magnetization effect was observed even in the ordered Co–Fe Prussian blue thin films prepared by a modified LB technique.

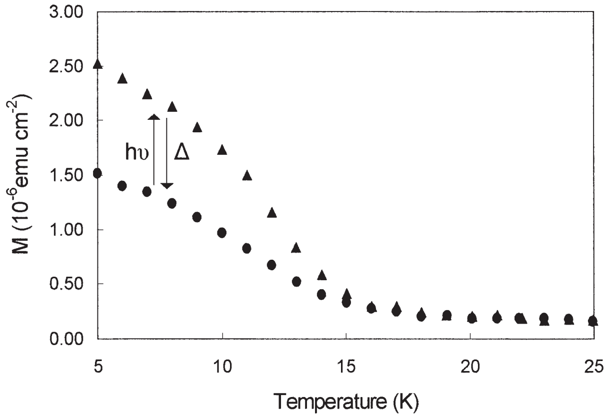


Figure 2. FCM curves for the hybrid films before (●) and after red light illumination (▲). Photoinduced state is backed to the initial state by thermal treatment at 200 K.

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