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Photoreduction of Prussian Blue Intercalated into Titania Nanosheet Ultrathin Films

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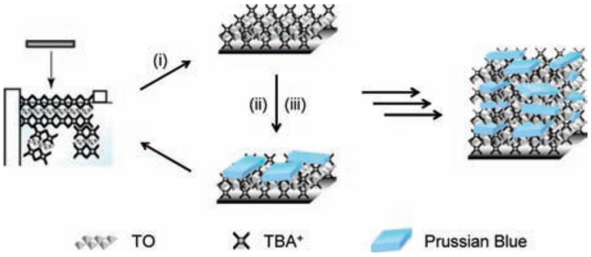
Photomagnetism has been one of the most attractive topics for the molecule-based magnetism community.[1] In principle, this phenomenon is attributed to photoinduced electron transfer, leading to changes in the spin state. For example, in Co−Fe Prussian Blue, excitation of an intervalence charge transfer band results in trapping the metastable high-spin state.[2] Previously, we have demonstrated a photomagnetic effect in the composite system of semiconductive CdS and magnetic Prussian Blue nanoparticles.[3] Upon UV excitation, generated electrons in the conduction band of CdS were injected into Prussian Blue. As a result, ferromagnetic Prussian Blue was reduced to paramagnetic Prussian White.

As part of our investigation for hybrid photomagnets, we have proposed the utility of the modified Langmuir−Blodgett (LB) technique.[4,5] Briefly, negatively charged clay platelets are hybridized with cationic amphiphiles at the air−water interface. Thus formed monolayers are transferred onto a solid support, whose surface can be exchangeable with other cations. Based on this strategy, we have prepared Prussian Blue ultrathin films and observed the following two phenomena: the highly efficient photochromism-induced magnetization changes[4] and the anisotropic photoinduced magnetization effect in Co−Fe Prussian Blue.[5] Since numerous inorganic layered compounds are known,[6] these materials could also be incorporated into the LB films. Among them, semiconductive layered titanates are a fascinating material because of exfoliation into single nanosheets.[7] The delaminated titania nanosheets form a densely packed film at the air−water interface and can be transferred onto a solid support.[8]

Herein, we report photoreduction of Prussian Blue intercalated into titania nanosheet ultrathin films. The titania thin films were prepared by the modified LB method using a titania suspension and tetrabutylammonium cations as the subphase and the confinement agent, respectively. Prussian Blue was deposited onto the titania films by a sequential adsorption technique. It was revealed that the hybrid ultrathin films could be prepared in a layer-by-layer manner. In the ultrathin films, Prussian Blue was reduced to Prussian White as a consequence of injecting photoexcited electrons from titania nanosheets. Spectroscopic investigation revealed that this reaction could proceed only in the presence of scavenging interlayer water molecules.

A typical protocol for preparation of the hybrid magnetic films is shown in Scheme 1. The titania (TO) nanosheets with the composition of $Ti_{0.91}O_2$ was prepared according to a previous report.[9] The solution of tetrabutylammonium bromide (TBA^+Br^-, 500 μL, 1 mM) was spread on the subphase of TO nanosheets suspension (8 ppm, pH 9.5) for confinement at the air−water interface. Floating TO/TBA^+ films were compressed up to a surface pressure of 15 mN m^{-1} and then transferred by a horizontal dipping method. The Prussian Blue layer was deposited onto the transferred film by successive immersion into $FeCl_2$ solution (1 mM, 1 min) and $K_3[Fe(CN)_6]$ solution (1 mM, 1 min). Multilayered films were fabricated by repeating this cycle.

Scheme 1. Preparation of the Ultrathin Films[a]



[a] (i) Transferring TO nanosheets/TBA^+ films at 15 mN m^{-1} onto a solid support, (ii) immersing into $FeCl_2 \cdot 4H_2O$ aqueous solution (1 mM, 1 min), and (iii) dipping into $K_3[Fe(CN)_6]$ aqueous solution (1 mM, 1 min). Cycling this protocol produces the multilayered ultrathin films.

The surface pressure−area ($\pi - A$) isotherms of TO nanosheets indicate formation of stable films at the air−water interface with the aid of TBA^+ cations. That is, TO nanosheets can be transferred by the LB technique. Formation of multilayered ultrathin films was monitored by UV−vis and FT-IR absorption spectra measured in the preparation process. Characteristic peaks for TO nanosheets and Prussian Blue were observed at 263 nm in UV−vis and 2074 cm^{-1} in FT-IR spectra, respectively. Moreover, plots of absorbance of these peaks *vs* a cycle number show a linear relationship, which confirm reproducible formation of the ultrathin films. Structural analyses were performed utilizing atomic force microscopy (AFM) and X-ray diffraction (XRD). AFM topographic images demonstrate that TO nanosheets are densely packed in the ultrathin films. In addition, XRD patterns gave two diffraction peaks at $2\theta = 7.2°$ and 15.2° ascribed to (010) and (020) reflections of TO nanosheets, respectively. The thickness of the Prussian Blue layer is estimated to 0.50 nm when considering the basal spacing of the ultrathin films (1.23 nm) and the thickness of TO nanosheets (0.73 nm).

Photoinduced electron transfer was examined with changes in FT-IR spectra upon light-irradiation measurement at room temperature. Before irradiation, an intense peak centered at 2074 cm^{-1} was observed, which is assigned to the bridged CN stretching vibration of $Fe^{II}-CN-Fe^{III}$ species. Upon UV irradiation (320 nm) in air, this peak shifted toward 2063 cm^{-1} due to producing $Fe^{II}-CN-Fe^{II}$ species, indicating that Prussian Blue is reduced to Prussian White.[10] The resulting metastable state relaxed to the initial state on exposure to air for several hours. It should be noted that when irradiating *in vacuo*, the above-mentioned spectral shift was not observed.

Generally, photoinduced electron transfer from TiO_2 requires scavenging reagents that reduce the generated holes in the valence

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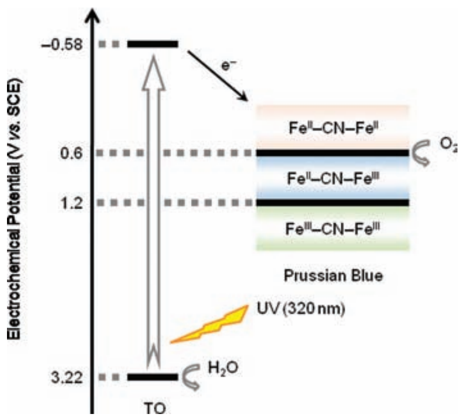
Scheme 2. Schematic Energy Diagram of Photoinduced Electron Process in the TO Nanosheets/Prussian Blue Ultrathin Films



band.[11] In other words, excited electrons are easily recombined with holes without the presence of scavenging agents. For example, in the case of electrochemically prepared TiO_2/Prussian Blue thin films, photoinduced electron transfer has been achieved in a mixture of water and methanol where methanol acts as the hole scavenger.[12] Note that, in this reported case, the electron transfer has not occurred without the presence of methanol (i.e., only water system).

Based on our results and the above report, the mechanism of photoreduction process is proposed as shown in Scheme 2. Upon band gap excitation of TO nanosheets, holes and electrons are generated in the valence band and the conduction band, respectively. The holes oxidize interlayer water molecules and protons are produced. On the contrary, the electrons are injected into Prussian Blue, resulting in reduction to Prussian White. Here, the produced protons migrate to a Prussian White lattice compensating for the charge balance. It should be mentioned why water molecules act as the hole scavenger in our case. It is well-known that an anatase-type TiO_2 has the band gap energy of 3.2 eV. In contrast, in TO nanosheets, the band gap energy has been estimated to be 3.8 eV.[13] According to Sasaki et al., the larger band gap energy of TO nanosheets is due to quantum size effects.[14] The lower edge of the conduction band for TO nanosheets is 0.1 V higher than that for anatase, and the upper edge of the valence band is 0.5 V lower. Therefore, an oxidative power of holes in TO nanosheets is stronger than that in an anatase, which enables oxididation of water molecules.

Figure 1 shows *MT* and *MH* plots for the TO nanosheets/Prussian Blue ultrathin films. Before UV irradiation, the rise in magnetization was observed below $T_C = 4.5$ K, which indicates the onset of a long-range ferromagnetic order. The lowering ordering temperature compared to the bulk Prussian Blue (5.6 K) is because the number of exchange pathways per magnetic ion is reduced. Upon irradiation, the magnetization value at 2 K declined by 53%, suggesting formation of paramagnetic Prussian White species. Subsequent exposure to air led to recovery in the magnetization value. In *MH* plots, after UV irradiation, a decrease in the corecivity from 40 to 10 G (instrumental resolution of SQUID magnetometer) was observed, which also supports reduction of Prussian Blue to Prussian White species. Again, subsequent exposure to air led to recovery in the magnetic property.

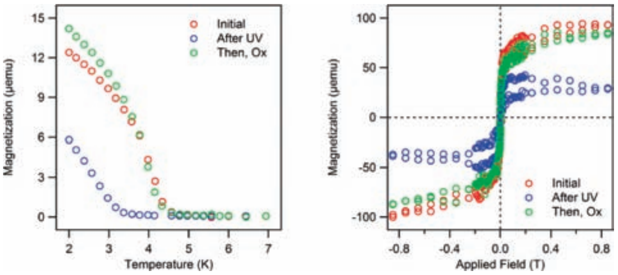


Figure 1. (Left) Plots of the magnetization *M vs* temperature *T* for the TO nanosheets/Prussian Blue ultrathin films (24 layer number) after field cooling in 10 G. (Right) Plots of the magnetization *M vs* the applied magnetic field *H* for the TO nanosheets/Prussian Blue ultrathin films (24 layer number) measured at 2 K.

In summary, we have prepared photomagnetic ultrathin films composed of titania nanosheets and Prussian Blue by the modified Langmuir−Blodgett technique. Upon band gap excitation of titania nanosheets, electron injection into Prussian Blue was achieved with scavenging interlayer water molecules, resulting in photoreduction to Prussian White. This phenomenon is due to the larger band gap energy of titania nanosheets, which, in turn, possesses a strong oxidation power of generated holes. The present work demonstrates utility of titania nanosheets for fabricating an innovative photofunctional material. Since the process proceeds at the interface between the materials, reducing the dimensionality of a magnetic material is an effective approach to observe such a photomagnetic effect. In addition, an anisotropic behavior is expected to be observed due to the low-dimensional nature, and this topic is now in progress in our group. Furthermore, the clever use of photosensitizers enables the design of a visible-light-sensitizing system.

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Supporting Information Available: Experimental details for synthesis and film preparation, surface pressure−area ($\pi - A$) isotherms, spectroscopic study (UV−vis and FT-IR), structural analysis (AFM and XRD). This material is available free of charge via the Internet at http://pubs.acs.org.

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