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Room-Temperature Decay and Light Reactivation of High-T_c Ferromagnetism in an Oxide-Diluted Magnetic Semiconductor

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The manipulation of electron spins in diluted magnetic semiconductors (DMSs) is a central theme of the emerging field of spintronics.[1] Since ferromagnetism in III−V-based DMSs strongly depends on carrier−dopant magnetic exchange interactions, the electrical and optical manipulations of spins have been demonstrated in these systems by varying carrier concentration.[1,2] A conversion between paramagnetism and ferromagnetism, together with the variation of coercive force, has been achieved in (In, Mn)As/GaSb heterostructures with light illumination.[2a,b] However, the development of practical devices based on these DMSs has met the limitation of the cryogenic Curie temperatures (T_c) required for ferromagnetic ordering. The findings of high-T_c ferromagnetism in oxide-based DMSs offer opportunities for the development of practical semiconductor spintronics technologies.[3] In contrast with the carrier-mediated ferromagnetic order in III−V compounds, donor defects in oxide-based DMSs have been suggested to play a vital role in mediating ferromagnetic order.[4] In this communication, we report for the first time on light manipulation of high-T_c ferromagnetism in nanostructured oxide DMSs. This facile and effective light manipulation may find practical applications in future integrated magneto-optical nanoelectronics.

We pre-prepared oleic acid-capped Co^{2+}-doped TiO_2 nanocrystals (Co:TiO_2 NCs) by a hydrothermal route.[5] A UV pulsed laser of 248 nm was used to irradiate aged thin films, which were prepared by spin-coating these colloidal NCs on Si or quartz substrates followed by annealing in air, as shown in Figure 1. (See the experimental details in Supporting Information.) As described later, the ferromagnetism of the as-prepared films was found to decay with time at room temperature, and the lost ferromagnetic order in the aged films can be reactivated by the light illumination. These novel results are shown in Figure 2.

Figure 2A shows magnetization curves for a transparent thin film (10 layers, ∼0.3 μm in thickness) of 4.87% Co:TiO_2 NCs (∼5.3 nm in average diameter). The as-prepared film exhibited a hysteresis loop with a saturation magnetization $M_s = 0.08$ μ_B/Co and a coercive force $H_c = 80$ Oe (the blue curve). After the film was aged in air at room temperature for 1 year without any special treatment, we re-examined its magnetic characteristics and observed a distinct conversion from ferromagnetic to paramagnetic states, as shown by the blue arrow. This decay of ferromagnetism with aging time was observed repeatedly in other similar samples, revealing the significant instability of the magnetic order, which presents a great challenge to practical applications in spintronics.

To reactivate the magnetic order, the aged film was cut into two identical parts, which were irradiated in two different ways with identical excitation light intensity (∼50 mJ/cm^2). The first half was immerged in degassed alcohol, and then irradiated by UV light for 1 h under N_2 protection. Interestingly, after irradiation, a remarkable conversion from the paramagnetism to strong ferromagnetism took place, as demonstrated by the red arrow in Figure 2A. The 2-fold enhancement of saturation magnetization was obtained (0.18 μ_B/Co), whereas the coercive force exceptionally reduced nearly 4-fold (23 Oe), as compared to the values for the as-prepared film.

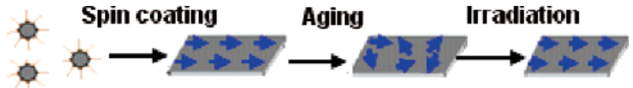

Figure 1. Schematic illustration of the preparation, room-temperature aging, and UV irradiation of Co:TiO_2 films as well as the changes in magnetic order owing to these manipulations.

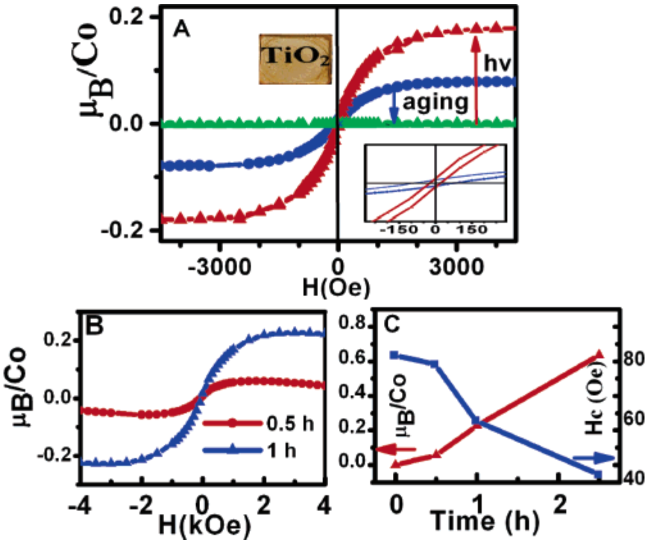

Figure 2. Room-temperature magnetization curves for 4.87% Co:TiO_2 NC thin films. (A) As-prepared (blue), aged in air at room temperature for 1 year (green) and UV-irradiated under poor oxygen conditions for 1 h (red); (B) irradiated in air; (C) dependences of M_s and H_c on irradiation time in the Co:TiO_2 film irradiated in air.

The light induction of the ferromagnetism can also be accomplished by direct light illumination in air. Figure 2B shows the irradiation effect in air with illumination time (t) varied. For $t = 0.5$ h, a ferromagnetic order has also developed, with $M_s = 0.057$ μ_B/Co. When the irradiation lasted for 1 h, the M_s increased to 0.23 μ_B/Co. The dependences of M_s and H_c on irradiation time are shown in Figure 2C. It is shown that the M_s value rapidly increases and the H_c value markedly decreases with increasing t, reaching $M_s =$ 0.63 μ_B/Co (8 times larger than the value for the as-prepared sample) and $H_c = 32$ Oe at $t = 2.5$ h. These results indicate that the light activation of ferromagnetism is insensitive to oxygen in air.

The irradiated films were also aged for 4 months at room temperature in air and N_2 (Figure S1). The decay of UV-activated ferromagnetism was also observed for aging in air. In contrast, when aged in N_2, the films show highly stable ferromagnetism, which indicates that the decay of ferromagnetism may arise from the absorption of O_2 in air.

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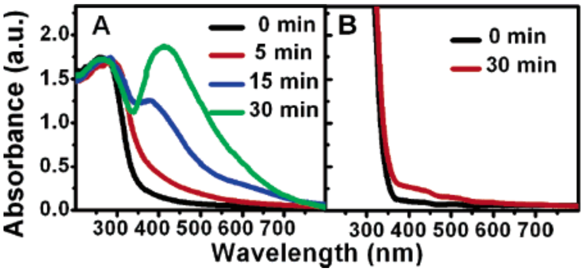

Figure 3. Room-temperature absorption spectra for the transparent Co:TiO_2 film (A) and pure TiO_2 film (B) irradiated for 0−30 min.

The nearly identical X-ray diffraction patterns for the films irradiated for 0 and 1.5 h were observed (Figure S2). The resistivity of the films was also unvaried with irradiation. These measurements indicate that the low irradiation energy of 50 mJ/cm^2 is too low to result in the change in crystallographic properties, such as the formation of ferromagnetic second phases. Moreover, UV irradiation was performed in air, so UV-induced photoreduction can be ruled out. In fact, the irradiated films remain in an insulating state ($>10^2$ Ωcm) (the scanning electron microscopy image of the film in Figure S3 shows no cracking defects). Therefore, we conclude that the irradiation-induced ferromagnetism is intrinsic.

The series of absorption spectra were performed on the irradiated transparent films. The change in the absorption spectra of the Co:TiO_2 film with irradiation time is shown in Figure 3A. A wide absorption band in the visible region with a strong peak at ∼400 nm appeared and became stronger with the irradiation time. The weak absorption of trapped electrons around 400 nm was also detected for pure TiO_2 NC films.[6] Thus the photoinduced strong absorption ∼400 nm in the Co:TiO_2 film may be ascribed to the absorption of trapped electrons. In contrast, weak UV-induced trapped electron absorption was also observed in a pure TiO_2 NC film with 10 layers (∼0.4 μm) (Figure 3B). From the enhanced trapped electron absorption in the Co:TiO_2 film, we conclude that the doped Co^{2+} ions are substantial electron traps. In fact, the studies on the photocatalysis of transition-metal-doped TiO_2 showed that the metal centers act as electron traps.[7] The unchanged resistivity of the films after irradiation also shows that the photogenerated carriers are bound.

It is still a central problem to elucidate the origin of ferromagnetism in oxide-based DMSs (ODMSs). A bound magnetic polaron (BMP) model[4a] has recently attained a growing recognition owing to its successful applications in the conducting and insulating states of ODMSs.[4,8] However, the microscopic origins of BMPs in ODMSs need to be identified. BMPs can be produced via defect-bound carriers, which is confirmed in conducting Co^{2+}:ZnO films, where the carriers are introduced by interstitial Zn.[4c] For insulating nanostructured ODMS films, nanocrystal fusion may produce interfacial F^+ centers, which form BMPs in the nanocrystal interface.[8] This kind of interfacial F^+ BMPs leads to the ferromagnetic ordering in the as-prepared Co:TiO_2 nanocrystal films (Figure 2a). The room-temperature decay of the ferromagnetism in the aged films indicates that the interfacial BMPs are metastable, likely due to the attack from O_2.[8d,9] The reactivation of the ferromagnetism in the irradiated films should also be understood in the context of the BMP model since the irradiated films remain insulating. We suggest that the BMPs may form via photogenerated bound carriers (electrons) rather than the interfacial F^+ centers. This correlation is based on the consistent changes in both the concentration of the light-induced bound electrons and the M_s value with the irradiation time (Figures 2C and 3A). The decay of the irradiation-induced ferromagnetism with aging time (Figure S1) is also consistent with that of the irradiation-induced absorption of trapped electrons (Figure S4). Irradiation-induced F^+ centers were previously observed in oxides irradiated under vacuum.[10] In our case, UV irradiation was performed in air. Moreover, we found that the EPR signal of F^+ centers[8d] in annealed Co:TiO_2 NC powders became weaker after irradiation (Figure S5). Therefore, photoinduced F^+-mediated ferromagnetism can be ruled out in the irradiated films.

In conclusion, we present a novel route for manipulation of the ferromagnetic order in TiO_2 DMSs using UV laser irradiation. The ferromagnetic order of the NC films decays with aging in air at room temperature, which can be reactivated and enhanced by UV irradiation. Photoinduced trapped electrons were suggested to induce the ferromagnetic order in the context of the BMP model. The light manipulation may be a general method for tuning the magnetic properties of ODMS systems. For example, the irradiation-induced enhancement in ferromagnetism in Co-doped ZnO nanocrystal films was also observed.

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Supporting Information Available: Experimental procedure, representative XRD, SEM, absorption spectra, and EPR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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