

Hydrothermal Synthesis of Radicals-containing Vanadium Oxides that Exhibited Room-Temperature Ferromagnetic Semiconductor

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Introduction

Room-temperature ferromagnetic semiconductors are much more desirable for spintronics devices. Among various types of semiconductors, dilute ferromagnetic oxides are one of the most promising host compounds to realize a higher Curie temperature.¹ For example, Co-doped TiO₂ films² and Li-doped VO_x nanotubes³ were found to be ferromagnetic at room temperature. However, it presents a great challenge for the development of hybrid-semiconductor that has ferromagnetic hysteresis at room temperature. In this report, we address a new ideal that organic radical spins within host lattice of oxides would be an alternative candidate for mediating semiconductor spintronics devices operable at room temperature.

Experimental

The MV⁺@VO_x ribbon-like fibers were obtained by a simple mild hydrothermal method. Initially, the MVCdI₄ compound, a precursor of MV²⁺, was prepared in our previous works. A reaction mixture of α-V₂O₅, MVCdI₄ and water in molar ratio of 4:1:4000 was seriously controlled pH < 2 with HCl (%) solution, and then heated at 200 °C for 96 h in a 23 mL Teflon lined stainless steel autoclave. The deep-yellow fibers were isolated by filtration from the reaction mixture, washed with water and acetone, and dried in air. At higher pH > 2 condition, no reaction product was found in the hydrothermal synthesis. On the basis of the analysis of EA and ICP-MASS, the elemental composition is (MV⁺)_{0.061}VO_{2.48}. The thermogravimetric analysis (TGA) in nitrogen reveals that the MV⁺ molecules are liberated below 400 °C, a weigh loss of 11.2 % consistent with the weigh percent of MV⁺ per formula unit. No weight loss was further observed in the temperature range 400 – 600 °C.

Results and Discussion

Our promising strategy for preparation of intrinsic ferromagnetism is to design 1D hybrid-semiconductors that redox organic-radical molecules are intercalated into semiconductor oxides. The redox molecules trapped in crystalline oxide are thought to enrich electrical transport through the surface of the oxides. Moreover, the radical spin-ordering in oxides might create a spin-polarization band at the Fermi level (Fig. 1). Such an attractive radical-triggered semiconductor might lead to versatile system not only for spintronics, but also as chemical and biological sensors.

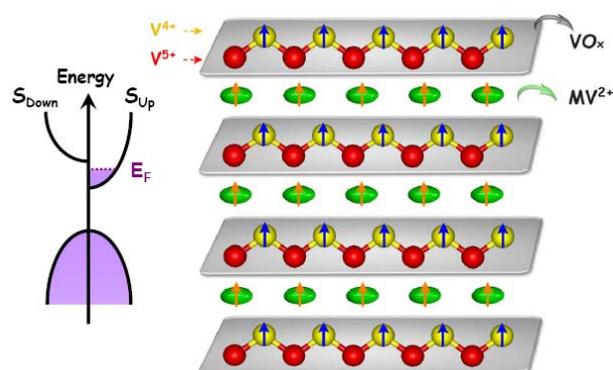


Figure 1 Schematics for radical spin-ordering in oxides. An intrinsic ferromagnetism might rise from the spin-polarization when the mixed-valence VO_x layers doped with methyl viologen radical cations (MV⁺).

The organic dopant used here possesses bipyridinium moieties (N,N'-dimethyl-4,4'-bipyridinium; so-called methyl viologen MV²⁺), a redox-active functional group that can be switched between its oxidized (MV²⁺) and reduced (MV⁺ and MV⁰) states. We suppose that the strongly oxidizing character of the oxide could induce the radical MV⁺ forms entrapped into the lattice host. The subject (MV⁺@VO_x) of this intercalation of methyl viologen into vanadium oxides was performed by hydrothermal method in acid condition (pH = 2.0). ‡

The fiber or ribbon-like morphologies for MV⁺@VO_x have been investigated through scanning electron microscopy (SEM). SEM images reveals that the as-synthesized fibers are tens of micrometers long, typical 500 – 3000 nm width and 60 – 300 nm thickness. Moreover, a highly ordered layer phase for MV⁺@VO_x has been characterized by synchrotron X-ray diffraction (XRD) patterns. The space group of MV⁺@VO_x is monoclinic C 2/m with cell parameters of $a = 21.2233(5)$, $b = 3.58434(8)$, $c = 6.3170(2)$, $\beta = 94.697(2)$ Å and $V = 478.93(2)$ Å³. A set of peaks characteristic of (h00) reflections is apparently investigated. The layer spacing of the phase is thus determined to be 10.61 Å from the (200) reflection, suggesting that the MV⁺ molecules are oriented parallel to the plane of the VO_x layers.

An intriguing feature for MV⁺@VO_x is the coexistence of the two cooperative unpaired electrons of V⁴⁺ (d¹) atoms and viologen radicals in the same cell, which has been proved by electron spin resonance (EPR) spectra (Fig. 2). The g values

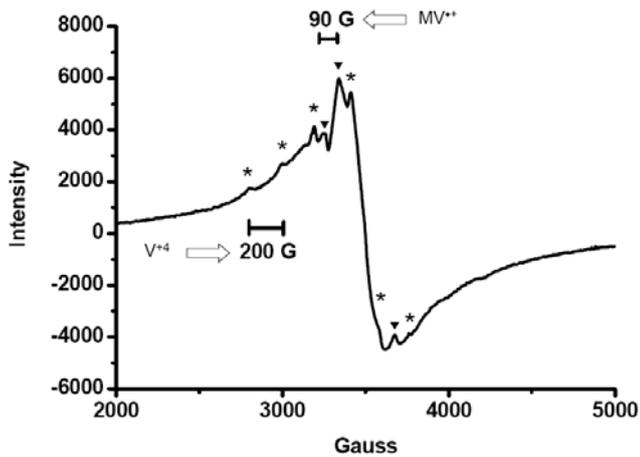


Figure 2. Electron spin resonance (EPR) spectrum for the $MV^{+}@VO_x$ fibers at 77 K by purging Ar gas

of EPR spectra are more difficult to interpret under air condition. Upon purging with argon gas, their two corresponding g values are almost seen in EPR spectra at 77 K; the resonance at $g = 2.009$ with peak width 90 gauss is attributed to viologen radicals, whereas one at $g = 1.947$ with peak width 200 gauss is to V^{4+} atom.

Electrical conduction of crystalline $MV^{+}@VO_x$ fibers has been conducted by four-probe measurements. Individual $MV^{+}@VO_x$ fiber was deposited on prefabricated electrode arrays with electrode separation of *ca.* 0.125 mm. In this specific case, a single fiber was in contact with the electrode pair. The conductivity is estimated to be *ca.* 3.0 S/cm at room temperature, such a high conductivity is similar to that of V_2O_5 nanowires.⁴ The resistance R change is closed to linear plotted in Figure 3 as $\ln(T/R)$ versus reciprocal temperature in the temperature range of 75 – 300 K. This linearity profile of the $\ln(T/R)$ versus $1000/T$ plot is typical of semiconductor behavior. A decline in conductivity with decreasing temperature is consistent with thermally activated hopping transport. According to the formula for small polaron hopping in the transition oxides, a fit to a thermally activated temperature-dependence yields a gap of 0.04 eV which is significantly smaller than the value of 0.21 and 0.11 eV obtained for nanowires and xerogel of V_2O_5 ⁵ respectively. Figure 4 shows the field-dependent magnetization ($M - H$) hysteresis loops taken at 10, 100, 200, and 300 K with sweeping magnetic field between -2000 to +2000 Oe. The $M - H$ responses are found to be nonlinear and hysteretic, a typical behavior of ferromagnetic magnetization. However, the profound hysteresis loops for $MV^{+}@VO_x$ fibers are substantially different with those of lithium-doped VO_x nanotubes reported by L. Krusin-Elbaum *et al.*³ It is notable that the saturation is not observed above 500 Oe, and the magnetizations linearly increase with increasing applied field. This behavior highlights the stronger anisotropy of $MV^{+}@VO_x$ fibers. Even more interesting phenomena is that all of the $M - H$ loops exhibit the same profile of hysteresis with a significant step within +125 and -125 Oe. Due to the fact that the radical-triggered ferromagnetic behavior is

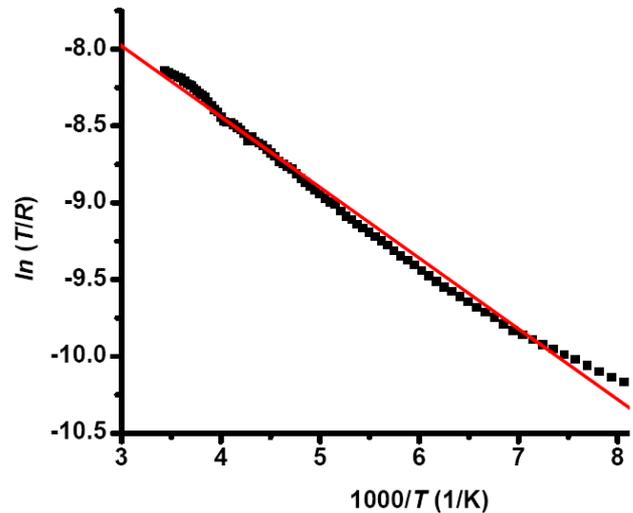


Figure 3. Temperature dependence of individual fiber resistance. $\ln(T/R)$ versus reciprocal temperature in the range of 75 – 300 K.

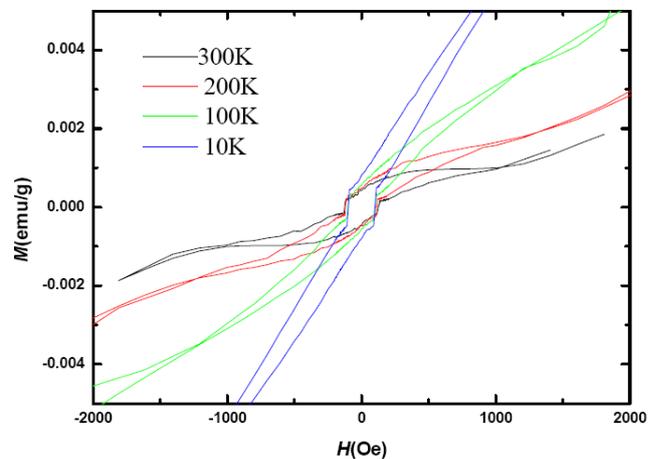


Figure 4. Typical ferromagnetic magnetization M versus applied magnetic field H hysteresis ($M - H$) loops taken at 10, 100, 200, and 300 K with sweeping magnetic field between -2000 to +2000 Oe,

rare phenomenon in the series of dilute ferromagnetic oxides, the radical-containing hybrid-semiconductors would be an important milestone towards the spintronics devices operable at room temperature.

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