Electrochemical Syntheses and Electrochromic Properties of Chromium Cyanide Magnetic Thin Films

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Electrochemical preparation method and electrochromic properties of the mixed valence chromium cyanide thin film, which is one of the ferrimagnet with highest critical temperature (T_c) among molecule-based magnets, were described. The difference in the ability of the ligand substitution reaction between Cr^{II} and Cr^{III} was utilized to synthesize the prussian blue analogs. The obtained magnetic material exhibited an excellent electrochromic properties. This indicates the compound has a potential for future display devices, as well as tunable molecule-based magnetic devices.

There has been a great interest in the study of the magnetic properties of molecule-based compounds exhibiting the spontaneous magnetization below T_c.[1-15] Several kinds of compounds with a high critical temperature are recently reported.[5,7,12] Our objectives are the design and synthesis of the molecule-based magnets whose magnetic properties can be controlled by external stimuli.[12-15] In order to electrolytically control the magnetic properties we have focused on the prussian blue analogs. This is because the oxidation states of this types of compound can be controlled by electrochemical method.[16] In our preceding paper we have reported that the magnet of chromium cyanides could be synthesized as a thin film by an electrochemical method.[12] In this article the principle and the applicability of this technique are described. Furthermore, the electrochromic properties of the synthesized compound were reported.

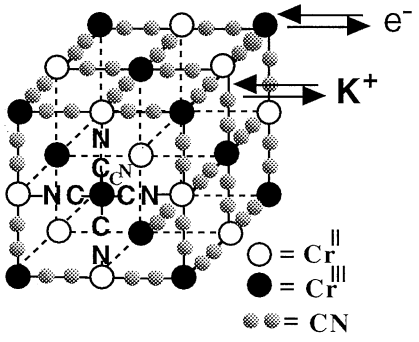

Figure 1. Unit cell of chromium cyanide. Water molecules and defects were omitted for clarity. The electrochemical redox of the Cr ions involves the uptake or removal of K^+ in interstitial sites, so as to compensate the negative charge of the electron.

The key to the electrochemical syntheses of chromium cyanides (Figure 1) is the difference in the ability of the ligand substitution reaction between Cr^{II} and Cr^{III}. The mixing of the aqueous solutions of Cr^{III} and $[Cr^{III}(CN)_6]^{3-}$ gave no precipitate of the chromium cyanides, because Cr^{III} ions are substitution inert species. When an electrode in the solution was cathodically biased, the inert Cr^{III} (or $[Cr^{III}(CN)_6]^{3-}$) ions are reduced to be Cr^{II}. The labile Cr^{II} ions react with $[Cr^{III}(CN)_6]^{3-}$ (or $[Cr^{II}(CN)_6]^{4-}$), resulting in the formation of the chromium cyanides. It is important to note that the electrochemical method can be widely applied to the synthesis of other molecule-based magnetic materials. Actually we have succeeded in synthesizing oxalate-bridged mixed valence magnetic thin films, $NBu_4Fe[Fe(ox)_3]$ (NBu_4^+ = tetra(n-butyl)ammonium ion; ox^{2-} = oxalate ion),[10] by using Fe^{III} and $[Fe^{III}(ox)_3]^{3-}$ instead of Cr^{III} and $[Cr^{III}(CN)_6]^{3-}$.

In order to investigate the process of the electrochemical synthesis described above, FT-IR spectrum was measured just after the film $\{Cr^{II}_{1.5}[Cr^{III}(CN)_6]$ with $T_c = 240$ K$\}$ preparation at -840 mV vs. saturated calomel electrode (SCE). The spectrum showed two peaks, i.e. 2187 cm^{-1} (the stretching mode of CN with Cr^{III}-CN-Cr^{II} structure) and 2071 cm^{-1} (the stretching mode of CN with Cr^{II}-CN-Cr^{II} structure). The peak at 2071 cm^{-1} was gradually decreased on drying the material and, finally, it disappeared completely. These observations suggest that both Cr^{III} and $[Cr^{III}(CN)_6]^{3-}$ ions are reduced during the electrochemical synthesis at -840 mV and, after the deposition, the Cr^{II} ions coordinated to carbon end are oxidized due to their strong reducing power, leading to the stable compound with the structure of Cr^{III}-CN-Cr^{II}. The thermogravimetric analysis measured from 30°C to 420°C in N_2 gas flow shows two step loss of H_2O before the decomposition of the compound. The two step decrease implies that there are two kinds of H_2O in this compound, i.e. H_2O molecules coordinated to Cr^{II} and those at interstitial sites.[6]

The elctrochromic properties of the compound were investigated in 1 mol dm^{-3} KCl aqueous solution. The SnO_2 (10 Ω / grid) glass with the chromium cyanide film was attached onto the electrochemical cell and used as the working electrode. The counter and reference electrodes were Pt and SCE, respectively. The optically transparent SnO_2 electrode allowed to monitor the change in color during a redox reaction. The compound exhibited a voltammometric peak around -0.84 V vs.

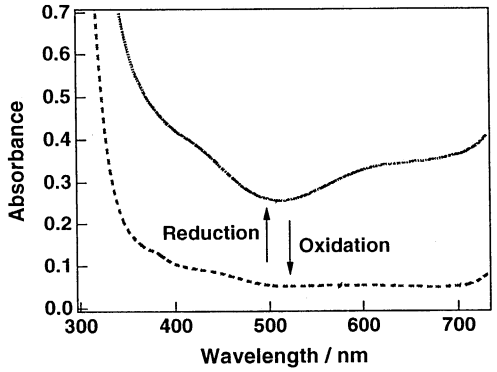

Figure 2. Electrochromic properties of the chromium cyanide thin film at room temperature; ----- before reduction, ——— after reduction. The absorption spectra of the reduced form were measured at -0.95 V vs. SCE.

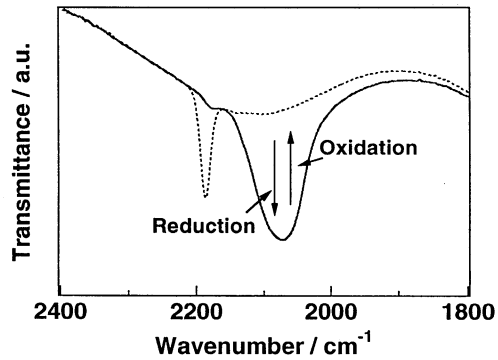

Figure 3. CN stretching peaks (at room temperature) before the reduction (-----) and after the reduction at -0.95 V vs. SCE (———). The CN stretching peak positions before and after the reduction were 2187 cm^{-1} and 2071 cm^{-1}, respectively. The CN stretching bands shifts towards the higher frequencies with the increase of the oxidation states, since an electron is removed from an antibonding orbital.[17]

SCE (sweep rate = 1 mV s^{-1}). The UV-VIS spectra obtained before and after the electrochemical reduction are depicted in Figure 2. The compound before the reduction seems to be almost colorless. Although there are absorption peaks at 380 nm and 560 nm, the bands cannot be observed clearly in the figure because of their small absorption coefficient. The absorption bands at 380 nm and at 560 nm are ascribable to the d-d band of Cr^{III} in the $[Cr^{III}(CN)_6]^{3-}$ and Cr^{II}, respectively. Note that the color of the thicker film was pale brown. When this material was reduced electrochemically, new bands appeared in UV-VIS region. The compound was colored green after reducing at -0.95 V vs. SCE. Furthermore, in near IR region a broad absorption band appeared. When the reduced compound was oxidized again in the KCl solution, the newly appeared absorption bands gradually decreased. Finally, the absorption spectra was restored to the initial one. The interconversion between colorless and green could be repeated almost reversibly. The reversible electrochromic properties could be observed for other chromium cyanide-based magnets. The CN stretching peaks of the colorless (before reduction) and green (after reduction) compounds were shown in Figure 3. The redox reaction of Cr at carbon ends results in the color change of the compound. The stability of the compound during the electrochemical treatment was investigated by repeating (50 times) the electrochemical reduction and oxidation around -0.84 V in the KCl aqueous solution. The peak current tends to slightly decrease with the increase in the number of the redox cycle. The average decrease in the peak current was about 0.6 % per cycle. The stability may be improved by optimizing the electrochemical conditions. Note that the thin film before reduction is colorless even at low temperature (below magnetic phase transition temperature), as well as at room temperature. The transparent magnetic thin film, as opposed to powder form, allows to regulate the polarization of light due to a magneto-optical effect.

In summary, the colorless chromium cyanide thin film was synthesized via electrochemical route. The electrochemical method can be widely applied to the synthesis of other molecule-based magnet. It was found that the optical property, as well as the magnetic one, could be controlled by electrochemical redox treatment. The chromiun cyanide, thus, provides a new type of compound whose optical, electrical and magnetic properties are coupled each other.

References and Notes

1 O. Kahn, D. Gatteschi, J. S. Miller, F. Palacio, "Magnetic Molecular Materials", Kluwer, London (1991), Vol. E198.
2 O. Kahn, "Molecular Magnetism", VCH, New York (1993).
3 J. S. Miller, and A. J. Epstein, *Angew. Chem., Int. Ed. Engl.*, **33**, 385 (1994).
4 D. Gatteschi, *Adv. Mater.*, **9**, 635 (1994).
5 J. M. Manriquez, G. T. Yee, R. S. Mclean, A. J. Epstein, and J. S. Miller, *Science,* **252**, 1415 (1991).
6 T. Mallah, S. Thiebaut, M. Verdaguer, and P. Veillet, *Science*, **262**, 1554 (1993).
7 S. Ferlay, T. Mallah, R. Ouahes, P. Veillet, and M. Verdaguer, *Nature,* **378**, 701 (1995).
8 W. R. Entley, and G. S. Girolami, *Inorg Chem.*, **33**, 5165 (1994).
9 W. R. Entley, and G. S. Girolami, *Science*, **268**, 397 (1995).
10 H. Tamaki, M. Mitsumi, K. Nakamura, N. Matsumoto, S. Kida, H. Okawa, and S. Iijima, *Chem. Lett.*, 1975 (1992).
11 Z. Gu. O. Sato, T. Iyoda, K. Hashimoto, and A. Fujishima, *Mol. Cryst. Liq. Cryst.*, **286**, 147 (1996).
12 O. Sato, T. Iyoda, A. Fujishima, and K. Hashimoto, *Science*, **271**, 49 (1996).
13 O. Sato, T. Iyoda, A. Fujishima, and K. Hashimoto, *Science*, **272**, 704 (1996).
14 O. Sato, Y. Einaga, T. Iyoda, A. Fujishima, and K. Hashimoto, *J. Electrochem. Soc.*, in press.
15 Z. Gu. O. Sato, T. Iyoda, K. Hashimoto, and A. Fujishima, *J. Phys. Chem.*, in press.
16 K. Itaya, I. Uchida, and V. D. Neff, *Acc. Chem. Res.*, **19**, 162 (1986).
17 K. Nakamoto, "Infrared and Raman Spectra of Inorganic and Coordination Compounds", Wiley, New York (1986).