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# Enhanced magnetoresistance and surface state of $CrO_2$ particles improved by chemical process

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**Abstract**

The paper presents an approach to enhance a magnetoresistance (MR) effect in $CrO_2$ powder compact by an oxidization reaction process. An aqueous potassium permanganate ($KMnO_4$) was used to react with the $CrO_2$ particles coated naturally with $Cr_2O_3$ layer. The experiment indicates that the strong oxidant can effectively adjust thickness of the natural $Cr_2O_3$ layer, and thereby change the surface state of the $CrO_2$ particles. Structural and magnetic properties for the improved $CrO_2$ particles have been characterized by X-ray diffractometer (XRD), X-ray photoelectron spectroscopy (XPS) and SQUID magnetometer. The results exhibit that the magnetotransport behavior of $CrO_2$ particles depends sensitively on the chemical reaction time. An optimal reaction process yields an obvious increase up to −33% in magnetoresistance at a temperature of 5 K for the chemical treated $CrO_2$ powder, compared to MR = -27% for the original $CrO_2$ powder. The mechanism of magnetotransport is assumed to originate from the spin-dependent tunneling in the granular system, which is consistent with our experimental results. The simple chemical approach has a potential to achieve an enhanced magnetoresistance in a metallic particle system by adjusting the surface state of the magnetic nanoparticle.

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*Keywords:* Magnetoresistance; Spin-dependent tunnelling; Potassium permanganate

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## 1. Introduction

Recently, chromium dioxide ($CrO_2$) has received much attention due to its half-metallic properties [1,2]. The nearly perfect spin polarization of $CrO_2$ has been proposed to be an ideal material for the magnetic tunneling devices [3,4]. Previous investigations have indicated that the polycrystalline film and powder compact of $CrO_2$ can yield a large negative magnetoresistance (MR) at low temperature [5,6]. The large MR is attributed to spin dependent intergranular tunneling effect [7,8]. Here, either the grain boundary or surface layer is believed to play a role of tunneling barrier in the intergranular tunneling process. As a tunneling barrier, the native and stable $Cr_2O_3$ phase on the surface of $CrO_2$, has been characterized by Hwang et al. [8] and Dai et al. [9] Since a surface state/layer on the metallic particles plays a crucial role in the electronic tunneling process, many emphases have been placed on surface natures of $CrO_2$ particles in the past decade [10,11]. If the tunneling barrier is too thick, tunneling MR will decrease dramatically. Since $Cr_2O_3$ is a stable thermodynamic oxide, it is difficult to reduce the antiferromagnetic $Cr_2O_3$ by physical process. In this paper, we introduce a simple and effective method to change $Cr_2O_3$ oxide layer, i.e. a strong oxidant potassium permanganate ($KMnO_4$) is used to react with $Cr_2O_3$. The electrical and magnetotransport property has been systemically studied with different reaction times. Here, an enhanced MR in the improved

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$CrO_2$ particles has been observed at low temperature. It is believed that the increase in MR is associated with an optimal thickness of $Cr_2O_3$ surface layer, depending on the chemical reaction time and temperature.

## 2. Experimental

In this experiment, we used an aqueous potassium permanganate ($KMnO_4$) to react an original $CrO_2$ powder that was supplied by Micro Magnetics, USA, and was acicular single-domain particles with an average length of 400 nm and an aspect ratio of about 9:1. The reaction was carried out in 0.01 mol/l mol concentration and at bath temperature of 50 °C.

Firstly, we prepared 0.01 mol/l $KMnO_4$ solution 100 ml and dipped 1.5 g $CrO_2$ powders carefully into the initial solution while stirring continuously at a bath temperature of 50 °C. A 1–3 nm thick $Cr_2O_3$ layer on $CrO_2$ particles corresponds approximately to about 5% amount of the pure $CrO_2$ powders sample [9]. Namely, there is about 0.000493 mol $Cr_2O_3$ in 1.5 g $CrO_2$ powders. Subsequently, the reacted $CrO_2$ powders were washed with deionized water several times and then heated to 50 °C in order to evaporate the solvent. Finally, the prepared powders were pressed into pellets with a diameter of 10 mm and a thickness of 2 mm.The samples were coded with *t*0, *t*5, *t*, *t*, *t*20, *t*25 and *t*30, corresponding to different reaction time: 0, 5, 10, 15, 20, 25, and 30 min. The crystalline structure of the samples was determined using Rigaku D/MAX 2500/C X-ray diffractometer (XRD). Magnetic measurements were carried out using a SQUID magnetometer (Quantum Design MPMS XL). In the temperature range of $4\,K < T < 300\,K$, the electrical resistivity was measured by a standard four-probe method using Keithley 2400 Source-Meter and 2182 NanovoltMeter. Chemical element and valence state were determined using PHI-550 X-ray photoelectron spectroscopy (XPS).

## 3. Results and discussion

In order to adjust the stable trivalent $Cr_2O_3$ surface layer, a strong oxidant ($KMnO_4$) is used to react with $Cr_2O_3$. The chemical reaction can be expressed as follows:

$$2MnO_4^- + Cr_2O_3 + H_2O = 2MnO_2 + 2CrO_4^{2-} + 2H^+. \tag{1}$$

This chemical reaction indicates that the $KMnO_4$ oxidant can react effectively with $Cr_2O_3$, and finally convert $Cr^{3+}$to $Cr^{6+}$ ion that ultimately remains in the solution. In this experiment, the solution showed a weak acidity due to a pH value of 6 after reaction.

Fig. 1 shows the XRD patterns for the samples *t*0, *t*15 and *t*30, respectively. A weak $Cr_2O_3$ peak (1 0 4) appears near $2\theta \sim 33°$ in the sample *t*0 and *t*15, whereas the sample (*t*30) does not exhibit this peak. Therefore, the original $CrO_2$ powders are analyzed by XRD in a precision scan, i.e. a small scan step (0.002 °) and long scan time (0.1 °/min). The results are presented in the inset of Fig. 1. A very clear signal of $Cr_2O_3$ (1 0 4) peak has been observed in the samples t0 and t15, not in the sample t30. This means that the $Cr_2O_3$ on surface of the $CrO_2$ particle has been completely removed after an etching of 15 min. Fig. 2 presents the variation of electrical resistivity of the samples with reaction time at 290 K. Since the measured resistivity arises mainly from the insulating $Cr_2O_3$ layer on surface of $CrO_2$ particles, the resistivity decreases rapidly with the reaction, especially during initial reaction of 10 min. However, the change in resistivity is insensitive to the reaction time for a longer reaction time. As a result of the reaction, a desired thickness of the insulating $Cr_2O_3$ layers may be achieved by control of the reaction time.

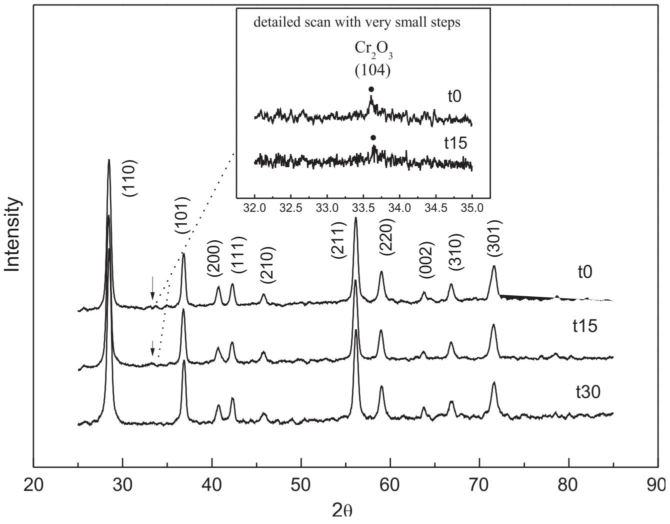

Fig. 1. X-ray diffraction patterns of $CrO_2$ particles for the sample *t*0, sample *t*15 and *t*30. Inset shows the detailed scan over the range $32° < 2\theta < 35°$.

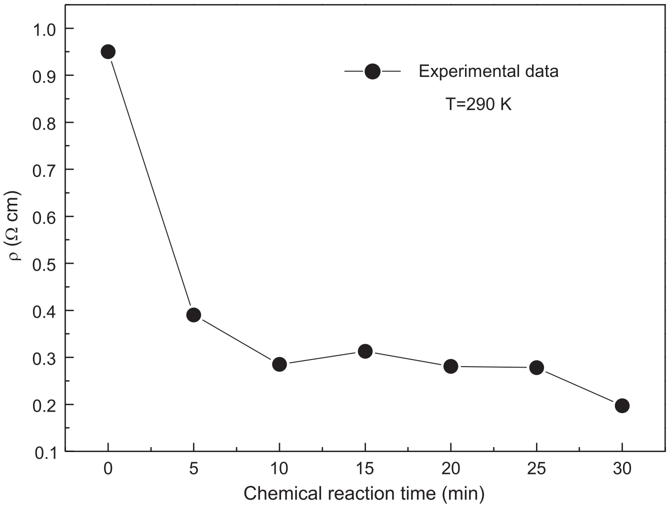

Fig. 2. Variation of resistivity with the chemical reaction time for $CrO_2$ particles at 290 K.

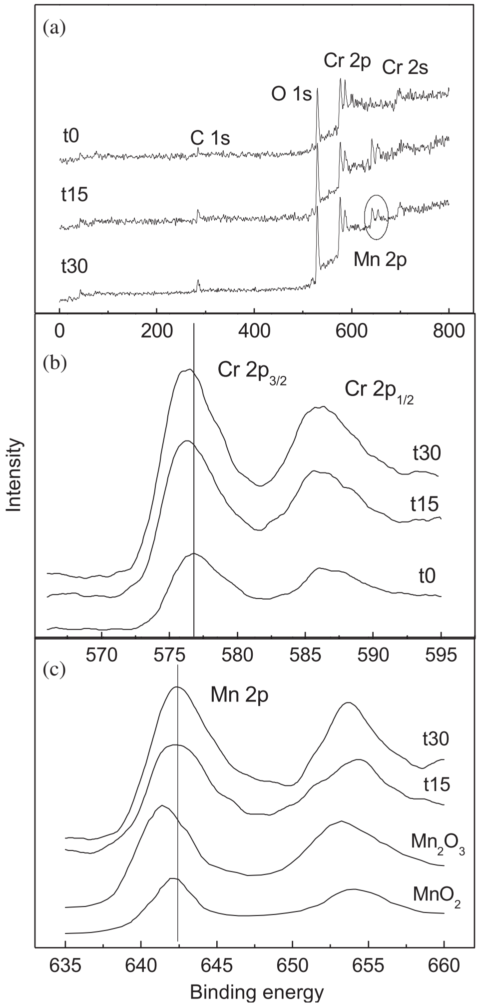

Fig. 3. Specific magnetization $M$ as a function of chemical reaction time at a low temperature of 5 K and applied field of 50 kOe. Inset shows the low field hysteresis loops for the CrO2 powder compacts ($H = 4000$ Oe).

X-ray photoelectron spectroscopy (XPS) patterns for the samples t0, t15 and t30 are illustrated in Fig. 3(a). Except for Cr, O and C element, no other elements have been found in the original $CrO_2$ particles. It is believed that the small amount of carbon C may arise from the contamination on the surface of $CrO_2$. Fig. 3(b) shows a magnified pattern of binding energy corresponding to Cr $2p_{3/2}$ state for the three samples. With the increase of the reaction time, the binding energy of Cr $2p_{3/2}$ gives rise to a drop from 576.8 eV (Sample t0) to 576.3 eV (Sample t15) and 576.2 eV (Sample t30). Obviously, the binding energy of Cr $2p_{3/2}$ for the sample t0 is in good agreement with previous reported (576.7-576.8 eV) of $Cr_2O_3$ [12,13]. Since XPS is sensitive with 1–2 nm into the particle surface, this is a convincing evidence that the $Cr_2O_3$ layer on the original $CrO_2$ particle has more than 2 nm in thickness. More importantly, both the sample t15 and t30 exhibit a almost same binding energy of Cr 2p, which is consistent with the binding energy (576.3–576.4 eV) of $CrO_2$ [12,14]. Remarkably, these results imply that $Cr_2O_3$ layer has been effectively removed from surface of the original CrO2 particles. Furthermore, a small amount of Mn element (~3 at%) is found in the sample t15 and t30, which is due to an incomplete washing in the two samples. The binding energy of Mn 2p state is also presented in Fig. 3(c). The Mn 2p state in the sample t15 and t30 are in good agreement with $MnO_2$.

The specific magnetization $M$ as a function of chemical reaction time is shown in Fig. 4. The measurement was performed at a temperature of 5 K and external magnetic field of 50 kOe. Clearly, there is a significant increase in the specific magnetization for the reaction time of 10 min. It is assumed that the enhanced $M$ is strongly dependent on the decreased thickness of $Cr_2O_3$ surface layer. It is worth noting that a tendency of the decrease in the specific magnetization $M$ appears in $t > 10$ min. Since the mol concentration ratio of $KMnO_4$ to $Cr_2O_3$ is 2:1, the *mol* concentration of $KMnO_4$ is very small after a reaction of 30 min.$KMnO_4$ is unable to react with $CrO_2$ drastically after $Cr_2O_3$ has been etched completely. At the same time, XPS of Cr valence state and resistivity measurements are hardly sensitive to etching time for $t > 10$ min. These results indicate that it is unlikely to produce any other phases after long time etching. We consider that the possible reason for decrease in magnetization $M$ is that a small amount of $KMnO_4$ destroys spin arrangement on surface of $CrO_2$. This leads to a disorder or spin canting in surface spin. Furthermore, the disorder or spin canting of surface spin may induce the large coercivity $H_c$. The increase in $H_c$ can be observed in sample $t30$, as presented in the inset of Fig. 4.

Fig. 5 gives the dependence of MR on the chemical reaction time at a low temperature of 5 K and applied field of 50 kOe. Due to a thick and natural $Cr_2O_3$ layer on the $CrO_2$ particle surface, the original $CrO_2$ particles has a MR = −27%, which is comparable to previous reported

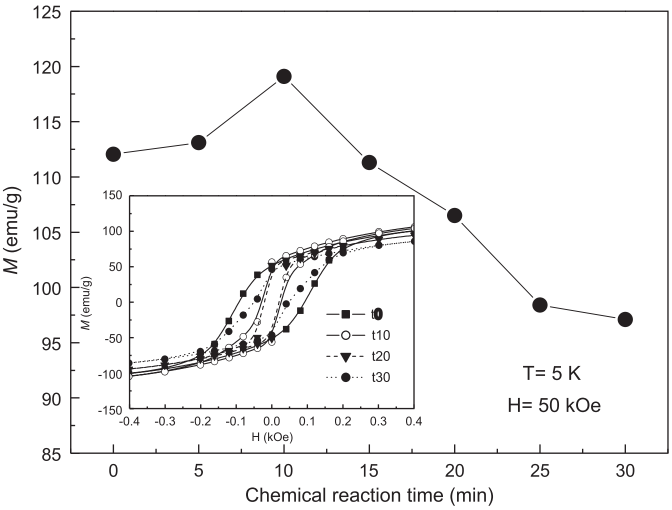

Fig. 4. (a) X-ray photoelectron spectroscopy of the sample $t0$, $t15$, and $t30$, (b) A magnified pattern of the binding energy for Cr 2p state, and (c) Binding energy for Mn 2p state.

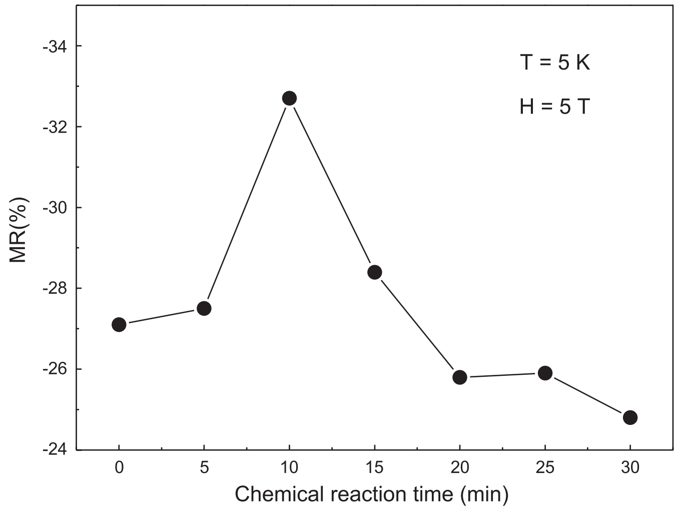

Fig. 5. Dependence of MR ratio for CrO$_2$ particle on chemical reaction time at $T = 5\,\mathrm{K}$ and applied field $H = 50\,\mathrm{kOe}$.

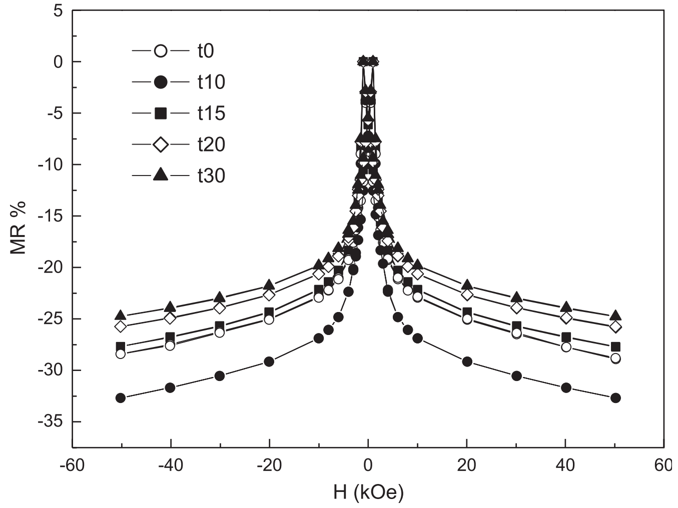

Fig. 6. MR ratio as a function of magnetic field $H$ at $T = 5\,\mathrm{K}$ and applied field up to 50 kOe.

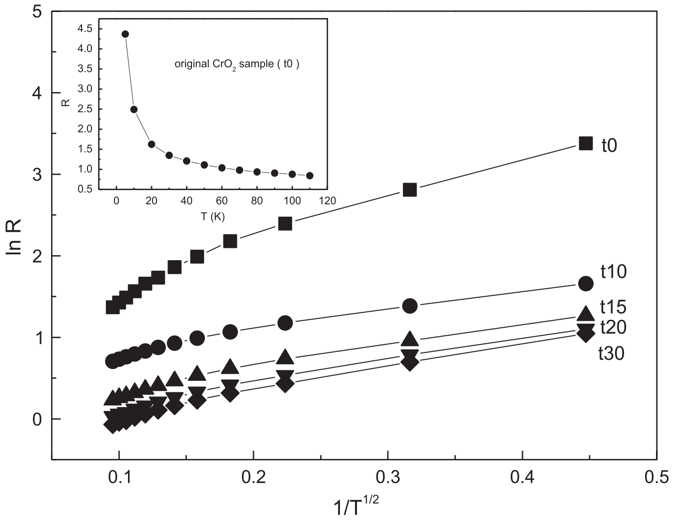

Fig. 7. The Ln R as a function of $T^{-1/2}$ for the sample $t0$, $t10$, $t15$, $t20$ and $t30$ in the temperature range from 4 to 110 K. Inset presents the resistance $R$ as a function of temperature for the sample $t0$.

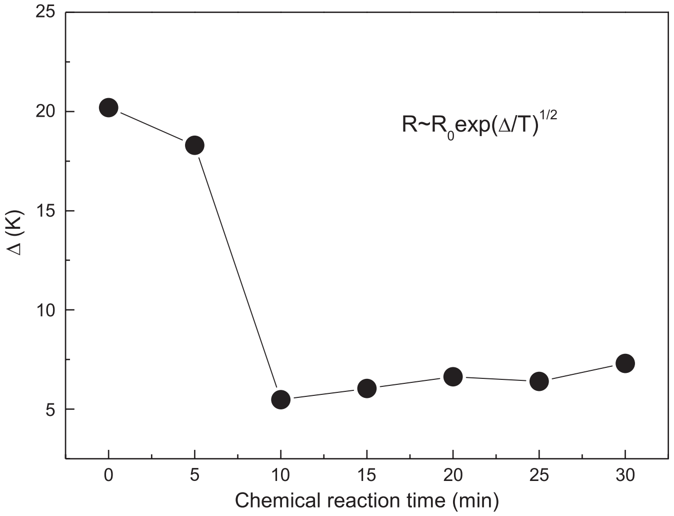

Fig. 8. Dependence of Δ on chemical reaction time for these CrO$_2$ samples.

results [7,9]. Apparently, the sample $t10$ exhibits a large MR (−33%) that increases by ~22%, compared to MR of the original particles. Fig. 6 shows the negative MR as a function of applied magnetic field for these samples. It is clear that low-field MR contributes predominately to overall magnetoresistance of the samples.

Previous research work has indicated that the low temperature magnetotransport mechanism in CrO$_2$ powder sample stems from spin-dependent tunneling effect [7,9]. Fig. 7 shows ln $R$ as a function of temperature $T^{-1/2}$ in the range from 4 to 110 K. The ln $R$ varies linearly with $T^{-1/2}$ at low temperatures. This is a typical temperature dependence of resistance in the materials in which the conduction is dominated with a tunneling process. Therefore, the resistance as a function of temperature can be expressed as [15,16]

$$R = R_0 \exp(\Delta/T)^{1/2} = R_0 \exp 2(2\kappa s E_c/T)^{1/2}, \qquad (2)$$

where Δ is proportional to the Coulomb charging energy $E_c$, tunneling barrier thickness $s$ and barrier height $\kappa$. Δ can be determined from the slopes of the linear region in Fig. 7. The dependence of Δ on the reaction time is illustrated in Fig. 8. Actually, the difference in the value of Δ reflects a difference in the barrier nature on the surface of CrO$_2$. For the original CrO$_2$, a large Δ value of 20.2 K reveals a thick Cr$_2$O$_3$ layer on the CrO$_2$ particles, whereas the Δ exhibits a minimum value ($\Delta = 5.48\,\mathrm{K}$) when the reaction time is 10 min. At the same time, we have noticed that a long time reaction ($t > 10\,\mathrm{min}$) do not give rise to an obvious change in Δ value. The spin-dependent tunneling conduction process is dominant at low temperature in these samples, which thereby is sensitive to the barrier thickness [17,18]. If the barrier thickness is too large, the tunneling conductance $G = e^2\eta^2/h^2$ [19], which is proportional to transmission coefficient $\eta^2$, will decrease due to a drop of $\eta^2$. This leads to a decrease in the tunneling magnetoresistance. As a result of the chemical treatment, a suitable $Cr_2O_3$ layer between $CrO_2$ particles yields an enhanced magnetoresistance for $t = 10$ min. But a long time reaction results in a reduction in MR, which is associated with the remove of $Cr_2O_3$ layer.

## 4. Conclusions

We have demonstrated a chemical approach to adjust/remove a natural $Cr_2O_3$ oxide layer on the surface of $CrO_2$ particle. The approach is based on the reaction between a strong oxidant $KMnO_4$ and $Cr_2O_3$ at 50 °C. The experimental results exhibit that magnetic and transport property relies strongly on the reaction time. A negative MR of −33% is measured at a temperature of 5 K and an applied field of 50 kOe for an improved $CrO_2$ sample. This results in an increase of 22% in MR, compared to the original $CrO_2$ powder sample with a thick $Cr_2O_3$ layer. The enhancement in MR is attributed to an appropriate barrier nature in the $CrO_2$ powder compacts. The assumption has been supported by XRD and XPS measurement. We believe that the work is significance of the control of oxide barrier layer on the surface of metallic particles.

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