Magnetic properties in a partially oxidized nanocomposite of Cu–CuCl

Qi Li1, Shi-Wei Zhang1, Yan Zhang2 and Chinping Chen2

1 State Key Laboratory for Structural Chemistry of Unstable and Stable Species, College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, People’s Republic of China
2 Department of Physics, Peking University, Beijing 100871, People’s Republic of China

E-mail: zhangsw@pku.edu.cn and cpchen@pku.edu.cn

Received 16 May 2006, in final form 21 July 2006
Published 15 September 2006
Online at stacks.iop.org/Nano/17/4981

Abstract
Magnetism of a very thin antiferromagnetic (AFM) surface CuO has been investigated with partially oxidized nanocomposites of Cu–CuCl, ∼200 nm. The samples are characterized by x-ray diffraction, x-ray photoelectron spectroscopy, x-ray-excited Auger electron spectroscopy, transmission electron microscopy and magnetic measurements. The characterizations indicate that the composites have a core–shell structure. Before oxidation, it is (Cu)core/(CuCl)shell, and after oxidation it is (Cu)core/(Cu2O + CuCl + minute CuO)shell. The magnetic measurements have revealed that a ferromagnetic (FM)-like open hysteresis exists at temperatures below the freezing point, T_F. In the high field region, a paramagnetic (PM) response appears without showing any sign of saturation. Also, the field dependent magnetization (M–H) measurement is PM-like at T > T_F. These interesting magnetic properties are shown to arise from the AFM CuO on the outer surface. They are attributed to the uncompensated surface spins of Cu2+ and the effect of random surface potential. More interestingly, the magnetic susceptibility is greatly enhanced in the presence of Cl− anions at T < T_F, according to the field-cooled/zero-field-cooled (FC/ZFC) measurements. This further supports the point that the disorder or frustration effect of the impurity would reduce the AFM ordering of CuO and increase the level of uncompensated spins.

1. Introduction
The magnetic properties of mesoscopic or nanoscaled material have become increasingly important due to their application potential in many areas, such as ultra-high density magnetic recording [1], spintronics, etc [2]. With the progress in technology, various shapes of nanoscaled magnetic materials, such as nanorods, nanowires, etc, have been fabricated or synthesized. To understand the nanomagnetics of these materials is, therefore, a critical issue not only for the fundamental interest but also for practical purposes [3–5]. Investigation of the magnetism of nanoscaled particles (NPs) has long been of interest [6, 7]. In particular, many studies have reported on the magnetic properties of AFM NPs, including NiO [8–10], CoO [11–13], ferritin [14, 15], α-Fe2O3 [16, 17] and ferrihydrites [18, 19]. There are several properties observed with the AFM NPs which are not yet fully understood [20, 21]. Among them, the substantially large moment and the FM-like magnetism associated with the AFM NPs are interesting points for further studies [9]. The surface effect is very important to the magnetic behaviour of NPs due to the existence of random surface potential or the surface anisotropy. In two previous experiments [9, 22], a core–shell model emphasizing the surface effect was applied to explain the magnetic properties associated with the NPs. The surface spin glass state would result in a marked effect on the magnetic moment not only for the ferro- or ferri-NPs, but also for the AFM NPs. A very recent experiment demonstrated that a very thin layer, ∼1 nm, of AFM CoO surrounding a FM Co core does not exhibit an exchange biased behaviour, whereas such an effect has been observed with a thicker CoO layer, ∼3 nm [13]. This indicates that for a CoO layer to show an AFM property, the thickness
the NPs are characterized to show a core–shell structure, addition, the size dependent magnetic moment of NiO NPs of the surface effect has already been demonstrated. In explanation for the underlying mechanism, the importance structure [23]. Although, there is still a need for a satisfactory investigation on the magnetic properties of partially oxidized, with respect to oxygen. In this paper, we report a detailed have been reported [ 24, 25], which are attributed to the large coercivity and a shifted loop [9].

spin state between different configurations would result in a configuration in the whole particle. The irreversibility in the has a profound effect on the multiplicity of the AFM sublattice has been studied to show that the surface spin coordination has to exceed 1 nm. A similar result has also been reported in another experiment with $\text{Co}_{\text{core}}$/CuO$_{\text{shell}}$ NPs with a core–shell structure [23]. Although, there is still a need for a satisfactory explanation for the underlying mechanism, the importance of the surface effect has already been demonstrated. In addition, the size dependent magnetic moment of NiO NPs has been studied to show that the surface spin coordination has a profound effect on the multiplicity of the AFM sublattice configuration in the whole particle. The irreversibility in the spin state between different configurations would result in a large coercivity and a shifted loop [9].

Recently, some unique magnetic properties of CuO NPs have been reported [24, 25], which are attributed to the variation in unit cell and coordination style of surface copper with respect to oxygen. In this paper, we report a detailed investigation on the magnetic properties of partially oxidized, diamagnetic nanocomposites of Cu–CuCl. After the oxidation, the NPs are characterized to show a core–shell structure, $(\text{Cu})_{\text{core}}/(\text{CuCl} + \text{Cu}_2\text{O} + \text{minute CuO}_{\text{shell}})$. Since the Cu, CuCl, and Cu$_2$O are all diamagnetic, the observed magnetism is reasonably inferred to arise from the minute amount of AFM CuO residing over the surface. Therefore, the sample offers a good model system to study the magnetism of surface AFM CuO.

2. Synthesis and measurements

A typical sample was prepared by the following procedure. CuCl$_2$·6H$_2$O in a water solution was reduced to metal Cu NPs at $80^\circ$C by hydrazine hydrate. Afterwards, the precipitates of Cu NPs were washed several times with water to remove the unreacted hydrazine hydrate in the solution. A small amount of CuCl$_2$·6H$_2$O was then added again to form a CuCl shell enclosing the Cu NPs. Then, the Cu–CuCl composites were filtered out, washed three times with ethanol, and dried in vacuum. The final partially oxidized product was obtained through controlled air oxidation of the Cu–CuCl composite powder at room temperature after various days of oxidation, from 6 to 42 days. During the synthesis process, the CuCl shell is critical in order to obtain a sample with interesting magnetic properties, although the molar ratio of CuCl in the shell over the Cu in the core accounts for only 1%.

The samples thus obtained were characterized by several techniques. The crystal phase was analysed by x-ray diffraction (XRD) using a Rigaku diffractometer and Cu Kα radiation of $\lambda = 0.15418$ nm. The elements chemical state on the surface of the Cu–CuCl composites before and after oxidation was analysed by x-ray photoelectron spectroscopy (XPS) and x-ray-excited Auger spectroscopy (XAES). The XPS spectra were recorded using an Axis Ultra spectrometer (Kratos, UK) with monochromatic Al Kα radiation (1486.71 eV) at a power of 225 W (15 mA, 15 kV). To compensate for the surface charge effects, binding energies $E_b$ were calibrated using C 1s hydrocarbon peak at 284.8 eV. The XAES was performed on the same spectrometer, Axis Ultra spectrometer, with the same Al Kα radiation source. The structure of the nanocomposites was further investigated by a Hitachi H-9000 transmission electron microscope (TEM). The magnetic properties of these nanocomposite powders were measured using a Quantum Design SQUID magnetometer.

3. Results

The results of characterization of the sample phases, compositions, and structure, by XRD, XPS, XAES, and TEM are presented. The magnetic properties and the corresponding analyses are also given.

3.1. XRD analysis on Cu, Cu–CuCl and partially oxidized Cu–CuCl NPs

The XRD patterns for the Cu metal and the Cu–CuCl nanocomposites before and after 30 days of oxidation are presented in figure 1. The grain size $(D)$ was calculated from the width of the XRD peaks using the Debye–Scherer relation after correcting for instrumental broadening. It indicates that the composites are made up of cubic Cu $(D \approx 26.7$ nm), cubic Cu$_2$O $(D \approx 12.6$ nm) and cubic CuCl $(D \approx 24.8$ nm). It is worth noting that only the peak for Cu$_2$O shows up after oxidation, whereas there is no detectable CuO within the detection sensitivity of XRD. However, the characterization by XPS and XAES shows the presence of Cu$^{2+}$.

3.2. Evidence for Cu$^{2+}$ in the partially oxidized sample by XPS and XAES

The XPS curves for the Cu–CuCl nanocomposites before and after 30 days of oxidation are shown in figure 2. The
curve for the sample before oxidation displays two symmetric peaks corresponding to the Cu 2p$_{1/2}$ (932.6 eV) and Cu 2p$_{3/2}$ (952.5 eV). On the other hand, in the curve for the partially oxidized sample, additional shoulders show up at 934.6 and 954.7 eV, i.e., a higher $E_b$ value than in the main peaks. These are due to the presence of CuO [26]. Furthermore, the accompanied shake-up satellite peaks approximately 9 eV higher than the shoulders are a signature for Cu$^{2+}$. Therefore, the XPS analysis confirms that CuO appears after the oxidation, and exists on the surface of the NPs. In addition, XAES for the oxidized sample is recorded and shown in the inset of figure 2. The peak maximum of Cu L$_{3VV}$ is at a kinetic energy of 916.3 eV ($E_b \sim 570.2$ eV), agreeing with the literature Cu$_2$O value. However, the peak shape is closer to that of CuO, confirming the presence of Cu$^{2+}$ on the surface [27]. From these analyses with XRD, XPS, and XAES, the composites should be a complex, which has a core of Cu, and a shell of Cu$_2$O and CuCl. In addition, a little CuO possibly exists on the outer surface.

3.3. Structure analysis by TEM

The structure of these composites was further characterized with TEM. Figure 3(a) shows the TEM images of the Cu NPs before oxidation. The shape is close to spherical with a uniformly dark shade and a sharp edge, indicating the uniformity in the composition. The particle size, $\sim$200 nm, is much larger than the grain size calculated from XRD, indicating the crystal structure is polycrystalline within the NPs. TEM images of the partially oxidized Cu–CuCl nanocomposites are shown in figure 3(b). It reveals the core–shell structure of the nanocomposites. The core appears with a much darker contrast than that of the shell, due to the difference in electron penetration efficiency. The shell appears to be fuzzy in a much lighter shade, almost the same as that of the background in the photo, but is still discernible. The shell contains diamagnetic compositions of Cu$_2$O and CuCl with a little AFM CuO. Its thickness is estimated to be 10–20 nm.

3.4. Temperature dependent magnetic susceptibility of partially oxidized Cu–CuCl nanocomposites

The temperature-dependent field-cooled (FC) and zero-field-cooled (ZFC) magnetic susceptibility, $\chi = M/H$, of the composite after 30 days of oxidation is shown in figure 4. The FC and ZFC curves exhibit a typical freezing behaviour at a temperature below the freezing temperature, $T_F \sim 6.4$ K, which is determined by the maximum in the ZFC curve. At $T < T_F$, $\chi_{ZFC}$ increases rapidly with decreasing temperature and becomes $\sim$17 times the value of $\chi_{ZFC}$. As mentioned above, the major composition of the sample is diamagnetic Cu, CuCl and Cu$_2$O, which do not exhibit large magnetic moments. Hence, the origin of the observed magnetism at $T < T_F$ with $\chi_{ZFC}$ is from the small amount of CuO on the surface. At about 8 K, which is above $T_F$, the FC and ZFC curves collapse. The susceptibility follows well-behaved Curie–Weiss law at $T > 70$ K. Inset (a) shows that $\chi$ follows a well-behaved Curie–Weiss law at $T > 70$ K. Inset (b) shows $\chi$ under FC for the samples after the various oxidation periods, (1) 6 days, (2) 24 days, (3) 36 days, (4) 42 days.
magnetization and coercive field at are observed. It shows a FM-like behaviour. The remanent \( Oe \) at 2 K and 0.

At \( T \) loops close at about 25 kOe and 2.1 kOe measured at 2 and 6 K, data for the two samples. Likewise, the sample with Cl tends to enhance the magnetism. The inset shows the ZFC

without CuCl. This suggests that the presence of Cl enhances the susceptibility than the sample without Cl.−

3.5. Effect of Cl− anions on the magnetic property

Figure 6 shows the FC susceptibilities for the samples with and without CuCl. Both samples are after 30 days of oxidation. The sample with CuCl exhibits a much higher value of \( \chi \) at \( T < T_F \). At \( T = 2 \) K, it is \( \sim \)16 times the value for the sample without CuCl. This suggests that the presence of Cl− anions tends to enhance the magnetism. The inset shows the ZFC for the two samples. Likewise, the sample with Cl− has a more pronounced susceptibility than the sample without Cl−. At \( T = T_F \), the difference grows to be an order of magnitude.

3.6. Field dependent magnetization of partially oxidized Cu–CuCl nanocomposites

The field dependent magnetization (\( M–H \)) curves for \((Cu)_{core}/(Cu_2O + CuCl + minute CuO)_{shell}\) after 30 days of oxidation were measured at 2, 6 and 10 K, and are presented in figure 7. At \( T = 2 \) and 6 K, i.e. below \( T_F \), open hysteresis loops are observed. It shows a FM-like behaviour. The remanent magnetization and coercive field at \( T < T_F \) are 0.124 emu g\(^{-1}\), 5225 Oe at 2 K and 0.065 emu g\(^{-1}\), 508 Oe at 6 K. The open loops close at about 25 kOe and 2.1 kOe measured at 2 and 6 K, respectively. The much enhanced coercivity and remanence at 2 K in comparison with those at 6 K, clearly shown in the inset, is strongly correlated to \( \Delta M = M_{FC} - M_{ZFC} \) at the same temperatures, see figure 4 for the \( M_{FC} \) and \( M_{ZFC} \).\( \Delta M \sim 6.4 \) emu g\(^{-1}\) at 2 K, and 2.6 emu g\(^{-1}\) at 6 K. This indicates that the open hysteresis at \( T < T_F \) is attributed to the irreversibility of the surface moment, since \( \Delta M \) is arising from the surface magnetism. Above \( T_F \), the \( M–H \) curve reveals a linear PM behaviour. This is consistent with the result of FC and ZFC measurements, showing \( \Delta M = 0 \) at \( T > T_F \). The FC hysteresis loop was also measured at 2 K in order to investigate whether an exchange-biased effect exists. A field of 30 kOe was applied during the cooling process from 300 K down to 2 K. No such effect has been observed.

4. Discussion

The magnetic measurements along with the characterizations of the structure and composition have provided strong evidence that the observed magnetism arises from the surface. This indicates that the FM-like open hysteresis loop at \( T < T_F \) is attributed to the thin layer of AFM CuO over the surface surrounding the nano-sized diamagnetic core. More interestingly, the existence of Cl− anions greatly enhances the magnetism below \( T_F \).

In some of the previously reported experiments, the magnetization hysteresis loops have been observed with the nickel ferrite (NiFe\(_2\)O\(_4\)) [22], NiO [9], and CuO [24] nanoparticles. The FM-like irreversibility has been interpreted as due to the transition between multiple surface spin configurations resulting from the surface disorder state, which influences the magnetization reversal of the whole particle. In our experiment, the magnetism is a pure surface effect without interference from the background magnetism of the core. So, indeed, the surface effect plays an important role to cause the FM-like behaviour. The surface moment is expected to arise from the uncompensated surface spins of the AFM CuO.

Figure 7. Hysteresis loops of the powder sample at 2, 6 and 10 K with the cooling history of ZFC. The inset is for the loops in the low field region.
Magnetic properties in a partially oxidized nanocomposite of Cu–CuCl

analogy, the authors have ascribed it to the existence of a defect moment in the CoO shell. However, according to our experiment, the existence of the Cl\(^{-}\) impurity actually enhances the magnetism at \(T < T_F\).

5. Conclusions

Complex Cu–CuCl composites with a core–shell structure have been synthesized. They consist of a Cu core, and a shell of Cu\(_2\)O and CuCl, along with a little CuO on the outer surface. The magnetism from a thin surface layer of AFM CuO contributes a substantial value of the total magnetic moment. Below the freezing temperature, \(T_F\), it shows a FM-like open hysteresis along with a PM response in the high field region. In the meantime, a PM-type \(M-H\) curve has been observed at \(T > T_F\). The observed magnetic moment on the particle’s surface can be explained by the uncompensated surface spin. In addition, the presence of Cl\(^{-}\) would greatly enhance the magnetism, possibly by adding surface disorder. The samples are unique in the magnetic properties of the AFM NPs and are helpful in understanding the nature of the magnetism in such particles.

Acknowledgment

This work was supported by NSFC of China (No. 20273001).

References

[1] Parekh V, Chunsheng E, Smith D, Ruiz A, Wolfe J C, Ruchhoeft P, Svedberg E, Khizroev S and Litvinov D 2006 Nanotechnology 17 2079
[2] Cerletti V, Coish W A, Giwat O and Loss D 2005 Nanotechnology 16 R27
[3] Bader S D 2006 Rev. Mod. Phys. 78 1
[4] Skomski R 2003 J. Phys.: Condens. Matter 15 R841
[5] Kodama R 1999 J. Magn. Magn. Mater. 200 359
[6] Speiloius D E 1999 J. Magn. Magn. Mater. 193 29
[7] Kodama R H and Berkowitz A E 1999 Phys. Rev. B 59 6321
[8] Richardson J T, Yiagas D L, Turk B, Forster K and Twigg M V 1991 J. Appl. Phys. 70 6977
[9] Kodama R H, Makhlouf S A and Berkowitz A E 1997 Phys. Rev. Lett. 79 1393
[10] Makhlouf S A, Parker F T, Spada F E and Berkowitz A E 1997 J. Appl. Phys. 81 5561
[11] Krivorotov I V, Yan H, Dahlberg E D and Stein A 2001 J. Magn. Magn. Mater. 226–230 1800
[12] Zhang L, Xue D and Gao C 2003 J. Magn. Magn. Mater. 267 111
[13] Tracy J B, Weiss D N, Dinega D P and Bawendi M G 2005 Phys. Rev. B 72 064404
[14] Gider S, Awschalom D D, Mann S and Chapekala M 1995 Science 268 77
[15] Makhlouf S A, Parker F T, Spada F E and Berkowitz A E 1997 Phys. Rev. B 55 R14717
[16] Ibrahim M M, Zhao J and Seehra M S 1992 J. Mater. Res. 7 1856
[17] Vasquez-Mansilla M, Zysler R D, Arciprete C, Dimitrijevits M, Rodriguez-Sierra D and Saragovi C 2001 J. Magn. Magn. Mater. 226 1907
[18] Jambor J L and Dutrizac J E 1998 Chem. Rev. 98 2549
[19] Seehra M S, Babu V S, Manivannan A and Lynn J W 2000 Phys. Rev. B 61 3513
[20] Morup S and Frandsen C 2004 Phys. Rev. Lett. 92 217201
[21] Tiwari S D and Rajeev K P 2005 Phys. Rev. B 72 104433
[22] Kodama R H and Berkowitz A E 1996 Phys. Rev. Lett. 77 394
[23] Skomski R, Stoyanov S, Zhong Y, Hadjipanayis G, Givord D and Norgues J 2003 Nature 423 850
[24] Pannusore A, Magrone H and Seehra M S 2001 Phys. Rev. B 64 174420
[25] Borzi R A, Stewart S J, Mercader R C, Punte G and Garcia F 2001 J. Magn. Magn. Mater. 226–230 1513
[26] Chang S S, Lee H J and Park H J 2005 Ceram. Int. 31 411
[27] Tu H B and Wang J Q 1996 Polv. Degrad. Stabil. 54 195
[28] Poulston S, Parlett P M, Stone P and Bowker M 1996 Surf. Interface Anal. 24 811