ELSEVIER

Journal of Alloys and Compounds 434–435 (2007) 646–649

Journal of ALLOYS AND COMPOUNDS

www.elsevier.com/locate/jallcom

Complex formation processes at the surface of Cu–O composite nanoparticles with and without external magnetic field

Shizuka Kitashima [a], Atsushi Kuroda [a], Katsumasa Hirose [a], Mamoru Senna [a,*], Anatoly Ye. Yermakov [b], Mikhail A. Uimin [b]

[a] *Faculty of Science and Technology, Keio University, Yokohama 223-8522, Japan*
[b] *Institute of Metal Physics, Ural Branch of RAS, Ekaterinburg 620219, Russia*

Abstract

Effects of preliminary magnetization on Cu–O nanoparticles (CNPs) and their electronic structures were examined in conjunction with their near-surface reactivity. CNPs were exposed to the external magnetic field, H ($\leq$4 kOe), in a glove box of Ar atmosphere at room temperature. The absorption intensity of UV/vis diffuse reflectance spectra of CNPs at the wavelength between 500 nm and 800 nm increased with magnetization. In order to elucidate the chemical consequences from magnetization, the reaction processes of CNPs at the boundary to the cyclohexane solution of acetyl pyridine (Apy) were examined by monitoring the decrease in the UV absorption band intensity at 279.5 nm due to π–π^* transition using a flow cell. The decrease in the UV absorption intensity is correlated with the increase in the extent of the reaction. We observed the two-step reaction process with a faster initial decay and a slower later one. We found the application of the magnetic field creates new active centers for the present coordination reaction. These magnetically acquired active centers are associated with the latter, more sluggish step of the two-step reaction. All these magnetic effects are consistently explained by the delocalization of the 3d electrons of Cu due to the partial change from antiferromagnetic to ferromagnetic states.

Keywords: Oxide materials; Nano-structured materials; Gas–solid reaction; Liquid–solid reaction; Magnetization

1. Introduction

Nano-structured materials with strong correlation among spin, charge and lattice attract increasing interests in the materials community, represented by high-temperature superconductivity [1] in cupric system and colossal magnetoresistance [2,3] in manganites. Yermakov et al. [4,5] have studied enhanced activity of copper oxide nanoparticles (CNPs) by a weak stationary external magnetic field on the dehydrogenation of 2,3,5-trimetyl-1,4-hydroquinone (TMHQ), adsorption of ammonia, and copper phthalocyanine formation where CNPs serve as a catalyst and an adsorbent, simultaneously.

We have also demonstrated the effects of weak magnetic field up to 4 kOe to which the reactant CNPs were exposed and subjected to the reaction of Cu(II) ammonium complex formation [6]. CNPs were surrounded by aqueous solution in the previous study. This might change the surface oxidation state constantly with the progress of the reaction to make the reaction mechanisms significantly more complicated. We therefore chose, in this study, a reaction with a non-aqueous solution, i.e. the surface compounding from a cyclohexane solution of acetyl pyridine (Apy) in contact with CNPs.

2. Experimental

Nanoparticles, CNPs, comprising Cu, Cu_2O and CuO were prepared by gas-condensation of copper metal vapor in controlled gaseous media containing argon and oxygen. The phase composition (Cu, Cu_2O, and CuO) of the three kinds of nanoparticles, determined by X-ray diffraction (XRD; Rigaku, Rint2000) is given in Table 1. The electronic states of CNPs were determined by ultraviolet–visible diffuse reflectance spectroscopy (UV/vis DR; JASCO, V-550). Sample nanoparticles were subjected to the static magnetic field up to 4 kOe and 23 h in a glove box of Ar atmosphere at room temperature. Magnetic measurements were performed by a SQUID magnetometer (MPMS-5).

CNPs were subsequently packed into a filter cartridge (0.20 μm pore size) in a circulating flow-cell system for in situ spectroscopy. The reaction kinetics were monitored continuously as a consumption of Apy by the decrease of the UV absorption band intensity of Apy, at 279.5 nm due to π–π^* transition.

---

* Corresponding author.
E-mail address: senna@applc.keio.ac.jp (M. Senna).

0925-8388/$ – see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.jallcom.2006.08.239

Table 1
Phase composition (Cu, Cu_2O, CuO) of CNPs determined by X-ray analysis

Sample	Composition (wt.%)		
	Cu	Cu_2O	CuO
CNPs-1	3.3	46.2	50.5
CNPs-2	0	65.6	34.4
CNPs-3	0	97.0	3.0

3. Results and discussion

3.1. Properties of CNPs

As shown in Fig. 1, CNPs are spherical with their particle size ranging between 20 nm and 50 nm. UV/vis diffuse reflectance (DR) spectra of CNPs-1 are shown in Fig. 2. The KM intensity of spectra between 500 nm and 850 nm increased after the exposure to about 4 kOe magnetic field at room temperature. The intensity in the absorbance increased with increasing exposure time to the magnetic field. This is also the case with other CNPs as shown in Fig. 3. For the CNPs with their metallic Cu fraction exceeding 10% and no CuO, the increase in the magnetization was not observed. By comparison with the UV/vis DR spectrum for bulk Cu_2O, we attribute the spectrum of CNPs between 200 nm and 480 nm to the coexistence of Cu_2O. However, bulk Cu_2O absorption band between 480 nm and 630 nm was not observed in CNPs. The difference may, at least partly, be associated with the nano-size effect of band gap [7–14], i.e. the blue shift of the absorption edge [15], or the oxygen vacancies. At the same time, we have yet to account for the possible contributions from other ingredients, CuO, $Cu(OH)_2$, as well as those from unknown oxygen vacancy [15,16].

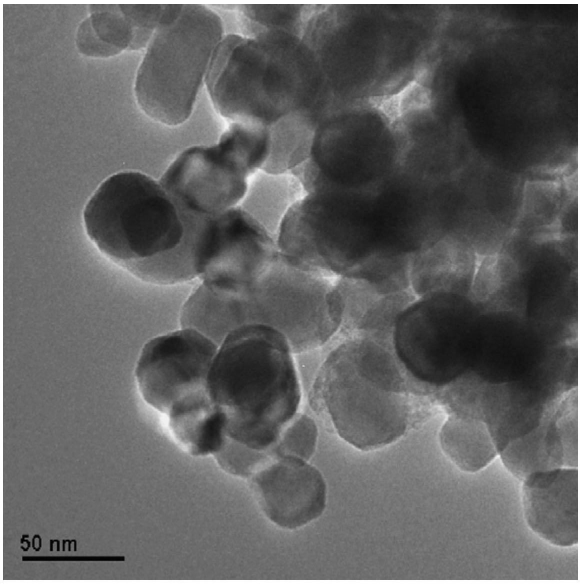

Fig. 1. TEM image of CNPs-1. The particle size ranges between 20 nm and 50 nm.

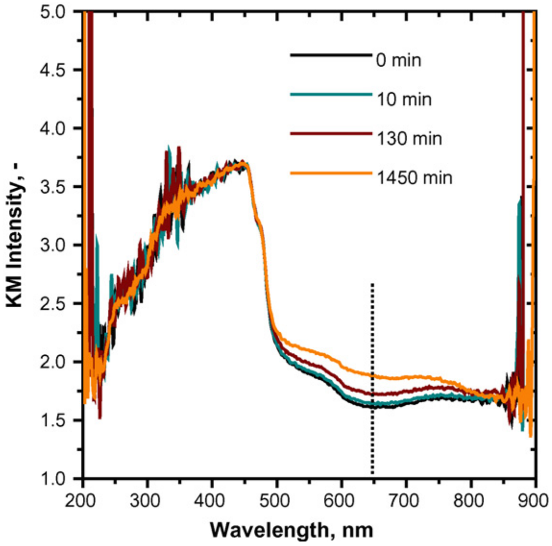

Fig. 2. Changes in UV/vis DR spectra of CNPs-1 produced by a 4 kOe magnetic field.

3.2. Chemical reaction processes at the surface of CNPs

The temporal change in the UV absorption band intensity at 279.5 nm due to π–π^* transition exhibits pulsating absorbance intensity curves which are a typical feature of the flow-cell system where the solution was circulated. In the initial stage of the reaction, a virgin solution passes through the filtration cartridge where the predetermined amount of CNPs was packed, so that the absorption sharply decreases. The diluted solution is quickly mixed with a virgin, concentrated solution. The amplitude of pulsation decreases as the reaction proceeds and the change in the concentration before and after the encounter of the solution with CNPs decreases.

We then tried curve fitting for the locus of the crests of each pulsation by a nonlinear least-squares method. The kinetic

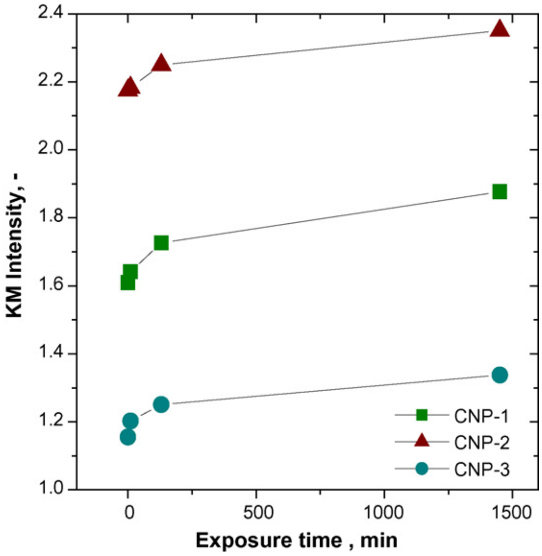

Fig. 3. KM intensity of UV/vis DR spectra at 650 nm for different exposure time: CNPs-1 at $H = 4$ kOe, CNPs-2 at $H = 4$ kOe, CNPs-3 at $H = 3$ kOe.

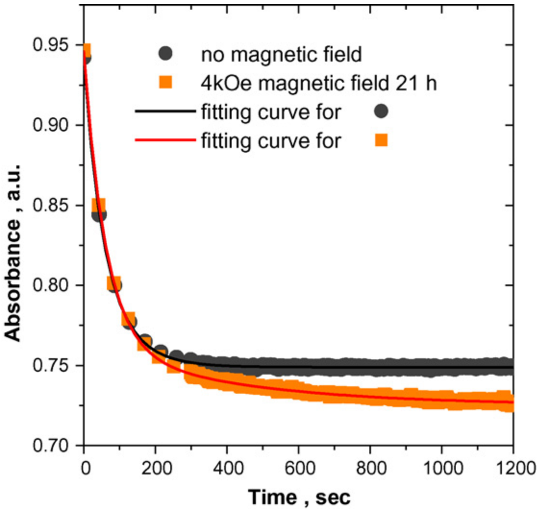

Fig. 4. Changes in the UV absorption band intensity of CNPs-1 at 279.5 nm due to π–π* transition produced by a 4 kOe magnetic field. The points are the locus of the crests of each pulsation. The solid lines are obtained by calculation.

curves made by this method fit the second order exponential with time, expressed as

$$A = A_1\,e^{-k_1 t} + A_2\,e^{-k_2 t} + \alpha \tag{1}$$

where A is absorbance, A_1 and A_2 are amplitude constants, t is reaction time, k_1 and k_2 are reaction rate constants, and α is a constant representing the asymptotic value to the absorption equilibrium. Fig. 4 exhibits the results with and without preliminary exposure to the magnetic field of 4 kOe for 21 h at room temperature. Curve fitting seems satisfactory since the solid lines by calculation coincide with the experimental points. From Eq. (1), we understand that the reaction comprises two parallel first-order kinetics. We may reasonably assume that the two processes correspond to two different types of the active species. The parameters obtained empirically from these kinetic curves are shown in Table 2.

A remarkable feature is that the intensity further decreases gradually when the samples were preliminarily exposed to the magnetic field. The result is well reproducible, and other CNPs yielded similar results. We further notice that value α decreases significantly by preliminary application of the magnetic field. By assuming that the difference in the constants between the sample with and without magnetization, α and α_0, respectively, correspond to the amount of the active site, V_a, acquired after the exposure to the magnetic field, V_a is expressed as

$$V_a = s\Delta\alpha = s(\alpha_0 - \alpha) \tag{2}$$

where s is a proportionality constant. In the case of the exposure to 4 kOe field for 21 h, V_a amounts to 3.84×10^{-6} mol/g, by assuming that an Apy molecule reacts to one active site. This corresponds to 12.3% of the *a priori* existing active sites. It is important to emphasize that the application of the magnetic field creates new active centers for the present coordination reaction,

Table 2

Parameters in the kinetics for CNPs-1; amplitude constant of first term, A_1, and of second term, A_2, reaction rate constant of first term, k_1, and of second term, k_2, asymptotic absorbance, α

Applied field	Amplitude constant (a.u.)				Reaction rate constant ($\times 10^{-3}\,s^{-1}$)				Asymptotic value (a.u.)		
	Intact		Magnetic field		Intact		Magnetic field		Intact	Magnetic field	
	$A_{0,1}$	$A_{0,2}$	A_1	A_2	$k_{0,1}$	$k_{0,2}$	k_1	k_2	α_0	α	$\Delta\alpha/\alpha_0$
4k Oe 18 h	0.1826 ± 0.0012	0.0480 ± 0.0012	0.2008 ± 0.0005	0.0495 ± 0.0004	16.30 ± 0.12	4.57 ± 0.06	13.02 ± 0.05	2.20 ± 0.03	0.634 ± 0.000	0.620 ± 0.000	0.022 ± 0.000
4 kOe 21 h	0.1199 ± 0.0214	0.0732 ± 0.0215	0.1828 ± 0.0010	0.0380 ± 0.0010	19.88 ± 1.49	11.15 ± 0.79	16.47 ± 0.17	2.44 ± 0.06	0.749 ± 0.000	0.725 ± 0.000	0.032 ± 0.000

Here suffix “0” means a result obtained by measurement without magnetic field.

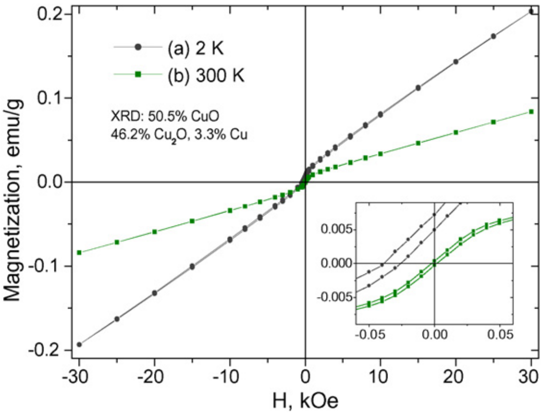

Fig. 5. Hysteresis loops of CNPs-1: (a) 2 K and (b) 300 K. The inset is enlarged figure around zero field.

which are associated with the latter, more sluggish step of the two-step reaction.

3.3. *Effects of magnetization on the chemical states of CNPs*

Magnetic properties of the present CNPs were examined by a SQUID magnetometer at different temperatures (2 K and 300 K) with the maximum applied field up to 3 T or 30 kOe, as shown in Fig. 5. The essential feature of the magnetic behavior of CNPs is the appearance of ferromagnetic regions under the magnetic field as low as a few kOe, by observing the magnetic hysteresis even at room temperature. Furthermore, the hysteresis loop becomes shifted to negative field at 2 K. The occurrence of this shift can be explained by the presence of an exchange interaction between the antiferromagnetic and ferromagnetic phases. We suspect that oxygen vacancies in the off-stoichiometric oxide state, CuO_{1-x}, are the main origin of ferromagnetic contribution in antiferromagnetic matrix of CuO [5,16–18]. These ferromagnetic regions were not observed in the bulk sample of the stoichiometric composition. From the analogy of well-established theoretical background of colossal magnetoresistance [3,19], Yermakov et al. in their previous report [4] adopted the key role of the small ferromagnetic drop or ferron [19] in the antiferromagnetic matrix of CuO, and associated spin flip on the effect of magnetic field for the chemical reaction involving CuO. As a consequence, Cu 3d-electrons would be delocalized by applied magnetic field. The increase of delocalized electrons implies the weakening of the electron shield or the ligand field of Cu, and hence, allowing further coordination of the ligands, Apy.

4. Conclusion

Application of the external static magnetic field as low as 4 kOe on the nanoparticles prepared by a gas-condensation method comprising Cu, Cu_2O and CuO significantly increases the intensity of UV/vis DR spectrum, and the extent of the chemical reaction with acetyl pyridine in the solution of cyclohexane. The kinetic curves for the present reaction were analyzed by the two-step first-order exponential equation. Active centers for the present coordination reaction were increased and intensified by the magnetic field, to increase the rate of the latter, more sluggish step of the two-step reaction in particular. The mechanism of the magnetic effect is consistently explained by the delocalization of Cu 3d-electrons by applied magnetic field to weaken the electron shield and hence, intensified the ligand field strength of Cu.

References

[1] E. Dagotto, T. Hotta, A. Moreo, Phys. Rep. 344 (2001) 1–153.
[2] A.S. Moskvin, Phys. B 252 (1998) 186–197.
[3] Y. Tokura, Y. Tomioka, J. Magn. Magn. Mater. 200 (1999) 1–23.
[4] A.Y. Yermakov, T.A. Feduschak, M.A. Uimin, et al., Solid State Ionics 172 (2004) 317–323.
[5] A.Y. Yermakov, T.A. Feduschak, V.S. Sedoi, M.A. Uimin, A.A. Mysik, J. Magn. Magn. Mater. 272–276 (2004) 2445–2447.
[6] K. Hirose, et al., J. Metastable Nanocryst. Mater. 24-25 (2005) 499–502.
[7] A.E. Rakhshani, J. Varghese, Phys. Stat. Sol. A 101 (1987) 479–486.
[8] P.J. Sebastian, J. Quintana, F. Avila, X. Mathew, Surf. Eng. 16 (2000) 47–49.
[9] T. Maruyama, Sol. Energy Mater. Sol. Cells 56 (1998) 85–92.
[10] T. Mahalingam, J.S.P. Chitra, S. Rajendran, M. Jayachandran, M.J. Chockalingam, J. Cryst. Growth 216 (2000) 304–310.
[11] W. Klein, H. Schmitt, M. Boffgen, Thin Solid Films 191 (1990) 247–254.
[12] K. Santra, C.K. Sarkar, M.K. Mukherjee, B. Gosh, Thin Solid Films 213 (1992) 226–229.
[13] X. Mathew, N.R. Mathews, P.J. Sebastian, Sol. Energy Mater. Sol. Cells 70 (2001) 277–286.
[14] A.E. Rakhshani, A.A. Al-Jassar, J. Varghese, Thin Solid Films 148 (1987) 191–201.
[15] K. Borgohain, N. Murase, S. Mahamuni, J. Appl. Phys. 92 (3) (2002) 1292–1297.
[16] A.Y. Yermakov, M.A. Uimin, V.R. Galakhov, A.A. Mysik, O.V. Koryakova, V.G. Kharchuk, V.A. Vykhodetz, V.S. Gaviko, K. Kuepper, S. Robin, M. Neumann, Proceedings of the International Symposium on Metastable, Mechanically Alloyed and Nanocrystaline Materials, ISMANAM2004, Sendai, Japan, August 22–26, 2004, p. 44.
[17] L.A. Errico, M. Renteria, M. Weissmann, Phys. Rev. B 72 (18) (2005) 184425.
[18] A.Y. Yermakov, T.A. Feduschak, V.S. Sedoi, M.A. Uimin, A.A. Mysik, A.V. Korolyov, Proceedings of the International Symposium on Innovative Materials Processing by Controlling Chemical Reaction Field, IMP2002, Miyagi, Japan, November 27–29, 2002, pp. 93–96.
[19] E.L. Nagaev, Colossal Magnetoresistance and Phase Separation in Magnetic Semiconductors, Imperial College Press, London, 2002.