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Synthesis and Magnetic Properties of CoO Nanoparticles

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Pure CoO nanoparticles in the 4.5−18 nm range have been prepared by the decomposition of Co(II) cupferronate in Decalin at 270 °C under solvothermal conditions. The particles have been characterized by X-ray diffraction, transmission electron microscopy, and cognate techniques. The particles are stable because of the organic coating that occurs in situ. The organic coating is readily removed by heating the particles to 260 °C without loss of the nanoparticulate nature. Magnetic measurements reveal the presence of ferromagnetic interactions at low temperatures in the small CoO nanoparticles (<16 nm). The small nanoparticles do not exhibit a distinct antiferromagnetic transition around 300 K as the bulk sample but instead show hysteresis below a blocking temperature of ∼10 K.

Introduction

CoO, crystallizing in the rock salt structure, is antiferromagnetic ($T_N \sim 298$ K) and electrically insulating.[1] Although there are a few reports in the literature on the preparation of CoO in bulk form, this material is difficult to obtain in pure form by simple methods, often being contaminated with Co_3O_4 or Co metal. Gravelle et al.[2] synthesized bulk CoO by heating an aqueous solution of $Co(OH)_2$ at 273 °C under vacuum, obtaining CoO mixed with Co_3O_4. El-shobaky et al.[3] prepared CoO_x ($x > 1$) by decomposing $Co(CO_3)_2$ under reduced pressure around 900 °C. CoO nanoparticles in the 10−80-nm range have been prepared by heating the gel precursor obtained by drying a solution of $Co(NO_3)_2$ and poly(vinyl alcohol) at 225 °C in a H_2 atmosphere.[4] Flipse et al.[5] have deposited CoO nanoparticles on a Si (100) substrate by spin coating an alcoholic solution of $Co(CH_3COO)_2$ followed by calcination in air at 477 °C. Decomposition of $Co_2(CO)_8$ in toluene in the presence of the surfactant Na(AOT) at 130 °C in air results in CoO nanocrystals mixed with Co and Co_3O_4.[6] Jana et al.[7] have recently obtained Co_3O_4 nanoparticles by the pyrolysis of fatty acid salts of cobalt in a hydrocarbon solvent under an argon atmosphere. Glaspell et al.[8] have recently prepared CoO nanoparticles from Co metal by laser vaporization condensation under carefully controlled partial pressures of O_2. Clearly, part of difficulty in preparing pure CoO is because of the greater stability of Co_3O_4 and the readily reducibility of CoO to Co metal. Nanocrystals of CoO are even more difficult to prepare because of the additional problems associated with surface oxidation.[8,9]

We have been successful in preparing pure CoO of different particle sizes in the nanometric range by using a simple procedure involving the decomposition of cobalt cupferronate in Decalin and other solvents under solvothermal conditions. Equally importantly, we have investigated the magnetic properties of CoO nanoparticles as a function of size. While bulk CoO is antiferromagnetic, with the susceptibility showing some direction dependence,[10] there have been conflicting reports on the magnetic properties of the nanoparticles. The reports vary from antiferromagnetism to room-temperature ferromagnetism.[11]

Experimental Section

Cobalt cupferronate, $Co(cup)_2$, was synthesized as follows. $Co(OAc)_2 \cdot 6H_2O$ (2 g) was dissolved in 150 mL of milli-Q water (0.5 M), and 2.5 g of Cupferron was dissolved in 100 mL of milli-Q water (0.16 M) by sonification, followed by filtration to get a clear light yellow colored solution. These solutions were cooled at 0 °C and the Cupferron solution added very slowly to the $Co(OAc)_2$ solution under vigorous stirring. After a few minutes a dark pink colored complex formed. It took another 20 min for completion of

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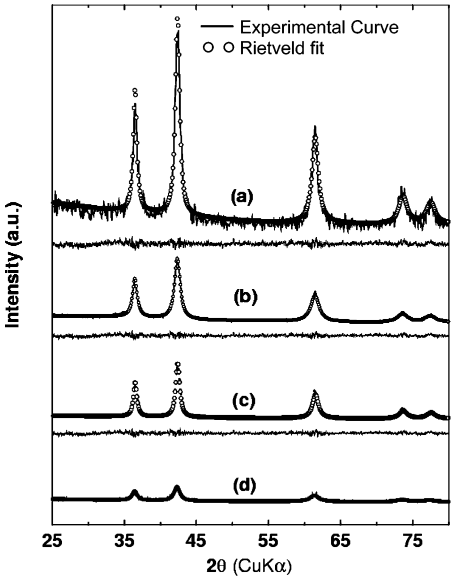

Figure 1. XRD patterns of the CoO nanoparticles with an average diameter of (a) 16, (b) 11.5, (c) 8.5, and (d) 4.5 nm along with the Rietveld fits. The difference plots for 16-, 11.5-, and 8.5-nm particles are shown below the corresponding curves. The difference plots have been multiplied by a constant factor to make them visible.

Table 1. Properties of CoO nanoparticles

reaction parameters[a]	average particle diameter from XRD peak broadening (nm)[b]	unit cell parameter $a = b = c$ (Å)
0.015 mmol, 48 h	4.5	4.293(3)
0.03 mmol, 48 h	8.5	4.265(3)
0.3 mmol, 48 h	11.5	4.264(3)
0.3 mmol, 120 h	16	4.263(2)
0.4 mmol, 120 h	18	4.263(2)

[a] Number of moles of Co(cup)$_2$ in 48 mL decalin is given along with the reaction time in hours. [b] The average uncertainty is around ±15% or less.

the reaction. The product was cooled at 0 °C for some time, filtered, thoroughly washed with milli-Q water, and dried at room temperature. The dried product was characterized by powder X-ray diffraction (XRD), IR spectroscopy, and thermogravimetric analysis (TGA).

The CoO nanoparticles were prepared by the decomposition of Co(cup)$_2$ in a hydrocarbon solvent. In a typical reaction, 0.5 g (0.3 mmol) of cobalt cupferronate [Co(cup)$_2$] were taken in 48 mL of Decalin and sealed in a Teflon-lined Stainless Steel autoclave of 80 mL capacity allowing 70% filling. The autoclave was kept inside a preheated air oven at 270 °C for 48 h. Then, it was allowed to cool to room temperature. A brownish-black solid insoluble in Decalin was obtained as the product. The excess solvent was removed, and the solid residue was washed with toluene for couple of times, followed by methanol. The sample was allowed to dry in an air oven at 50 °C for 1 h. Though it was noticed that the reaction finishes within 6 h, we have carried the reactions for a longer duration to improve the crystallinity of the product.

To vary the particle size, the concentration of the Co(cup)$_2$ and the reaction time were varied, keeping the amount of Decalin, the volume of the autoclave, and the reaction temperature constant. For example, four other conditions of preparation were as follows: 0.05 g (0.03 mmol) of Co(cup)$_2$, 48 h; 0.025 g (0.015 mmol) of Co(cup)$_2$, 48 h; 0.5 g (0.3 mmol) of Co(cup)$_2$, 120 h; and 0.065 g (0.4 mmol) of Co(cup)$_2$, 120 h. The decomposition of Co(cup)$_2$ was also carried out in tetralin and toluene at 270 °C under solvothermal conditions for the same duration of time. The nanoparticles synthesized in Decalin and tetralin could be readily dispersed in toluene by sonication.

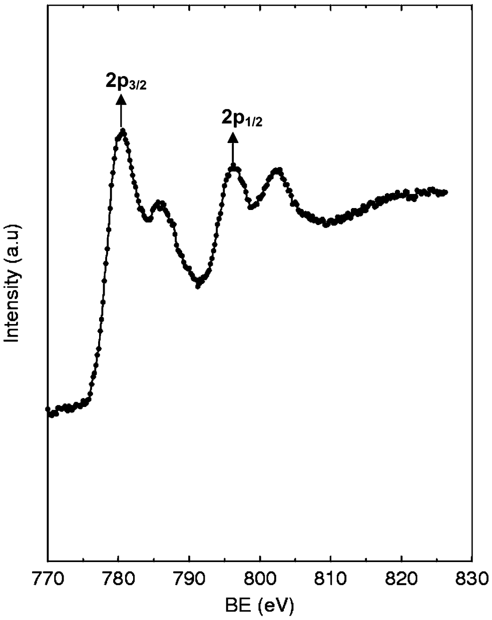

Figure 2. Co 2p core-level X-ray photoelectron spectrum of 11.5-nm CoO nanoparticles.

The samples were characterized by powder XRD using a Phillips X′Pert diffractometer employing the Bragg−Brentano configuration using Cu Kα radiation with the scan rate of 0.15° 2θ per min. The data were then rebinned into 0.05° steps. Core-level X-ray photoelectron spectra of the nanoparticles were recorded with a VSW Instrument using a monochromatized Mg Kα source. The resolution of the spectrum reported here is approximately 1 eV. To avoid charging effect, the nanoparticles were mixed with graphite powders. This method allows the nanoparticles to be finely dispersed and in intimate contact with conducting graphite. For transmission electron microscopy (TEM), toluene dispersions of the samples were dropped onto the holey carbon-coated Cu grids, allowing the grids to dry. The grids were examined using a JEOL (JEM3010) microscope operating with an accelerating voltage of 300 kV. IR spectra of the KBr pellets of nanoparticles were recorded with a Perkin-Elmer FTIR spectrophotometer. TGA was carried out using a Mettler Toledo Thermal Analyzer. Powder samples of the as-prepared nanoparticles were subject to the magnetic characterization using a Quantum Design SQUID magnetometer.

Results and Discussion

We have chosen the solvothermal procedure for the synthesis of CoO for two reasons, one of them being that the sealed autoclave acts as a pressure cooker, the autogenous pressure generated inside allowing the solvent to go far beyond the boiling point. The dependence of the autogenous pressure on the reaction temperature and free volume of the sealed vessel is documented.[12] The solvothermal environment also eliminates the need for an external inert gas supply and avoids the aerial oxidation of the nascent particles. Under the conditions of our experiments, the reaction temperature could be raised to 270 °C using Decalin as the solvent.

In Figure 1, we show typical X-ray diffraction patterns of the solid residues obtained from the thermal decomposition of Co(cup)$_2$ in Decalin at 270 °C. There is no evidence for impurities. Figure 1 also gives the Rietveld profile fits

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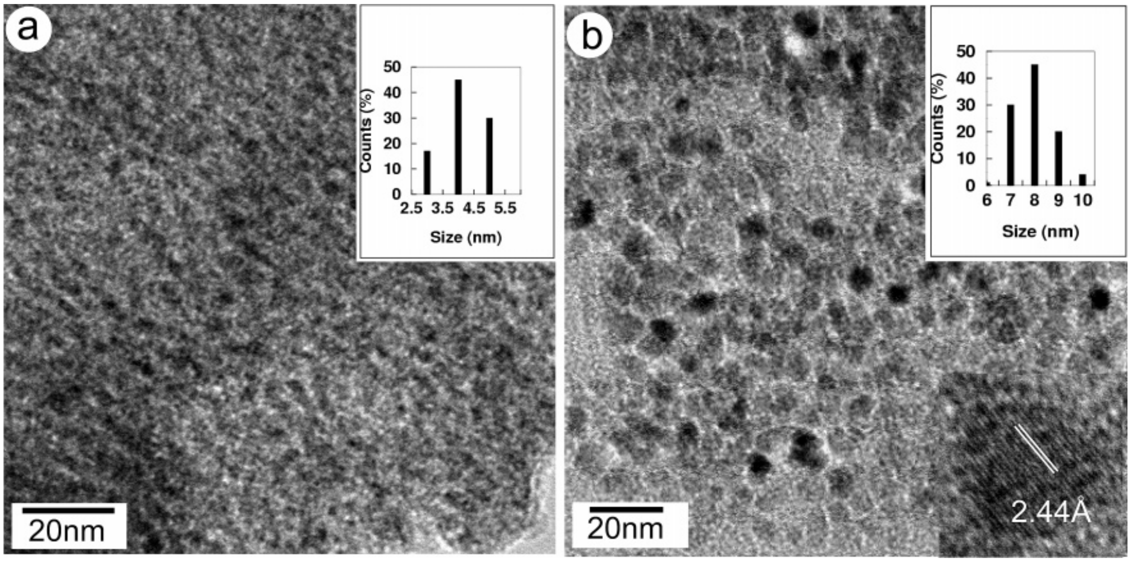

Figure 3. TEM images of the CoO nanoparticles of (a) 4.5 and (b) 8.5 nm average diameters. The insets show the histograms of the particle size distributions (upper panels). The lower panel in b shows the HREM image of a single CoO nanoparticle.

obtained by using the Rietveld XND code.[13] The patterns could be indexed in the face-centered cubic cell with the *Fm*3*m* space group. In Table 1, we list the reaction conditions and the unit cell parameters from the Rietveld fitted X-ray diffraction profiles. By making use of the line widths from the Rietveld fits, particle sizes were estimated by using the Scherrer formula. The cubic lattice parameter increases slightly with the decrease in the particle size in the 4.5−18-nm range. We show in Figure 2 the core-level XP spectrum of the CoO nanoparticles in the Co 2p region. The peak at 780.2 eV is due to Co 2p$_{3/2}$ with the shake-up satellite at 786.1 eV, while the peak at 796.3 eV is due to Co 2p$_{1/2}$ with the satellite peak at 802.7 eV.[14,15] The presence of two peaks at 780.2 and 796.3 eV and a highly intense satellite is consistent with the presence of Co^{2+} in the high-spin (4$_{\mathrm{F}}$) state.[16] The absence of a feature at 778.1 eV indicates the nonexistence of Co metal impurity.

TEM images of the CoO nanoparticles with average diameters of 4.5 and 8.5 nm are shown in parts a and b of Figure 3a and b, respectively. The particles are reasonably monodisperse as can be seen from the size distributions shown in the insets of the Figure 3. The average particle sizes obtained from TEM are consistent with those estimated from the XRD peak broadening. The monodispersity of the nanoparticles decreases when the average size of the particles is large (16 and 18 nm). The single crystallinity of the particles was established by the high-resolution TEM (HRTEM) images. We show a HRTEM image of a 8-nm CoO particle as an inset in Figure 3b. The lattice spacing of 2.44 Å in the image corresponds to the interplanar separation between (111) lattice planes. We could prepare CoO nanoparticles with an average diameter of ∼12 nm using tetralin and toluene as solvents, but the size distributions were somewhat broad.

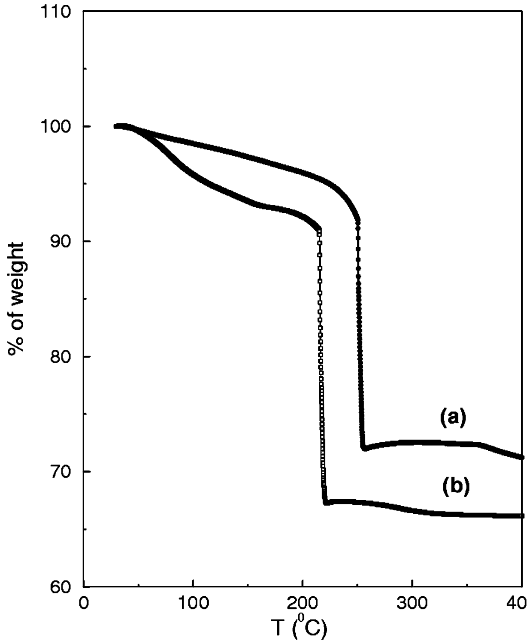

Figure 4. TGA curves of CoO nanoparticles (prepared in Decalin medium) of (a) 16 nm and (b) 4.5 nm, in nitrogen atmosphere (heating rate of 10 °C/min).

TGA (in a N$_2$ atmosphere) of the CoO nanoparticles of different sizes obtained by using Decalin as the solvent shows a large mass loss around 260 °C, due to decomposition of the organic coating on the particles (Figure 4). We observed a similar mass loss in the case of CoO particles prepared using tetralin and toluene as solvents. The IR spectra of the as-prepared CoO samples show evidence for the presence of an organic coating, probably of the solvent in mixture with nitrosobenzene.[17] Nitrosobenzene is known to be one of the products of the decomposition of the metal cupferronate. XRD patterns of the solid residues after the mass loss at 260 °C were characteristic of CoO and showed little

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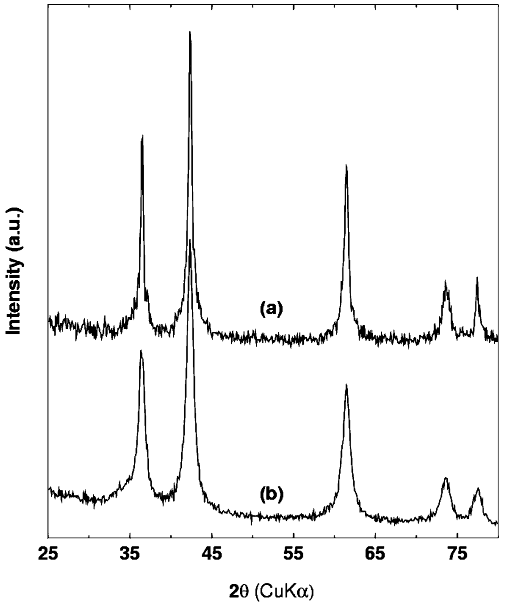

Figure 5. XRD patterns of the samples as obtained after heating (a) 16 and (b) 8.5 nm CoO under nitrogen atmosphere up to 260 °C by employing the heating rate of 10 °C/min.

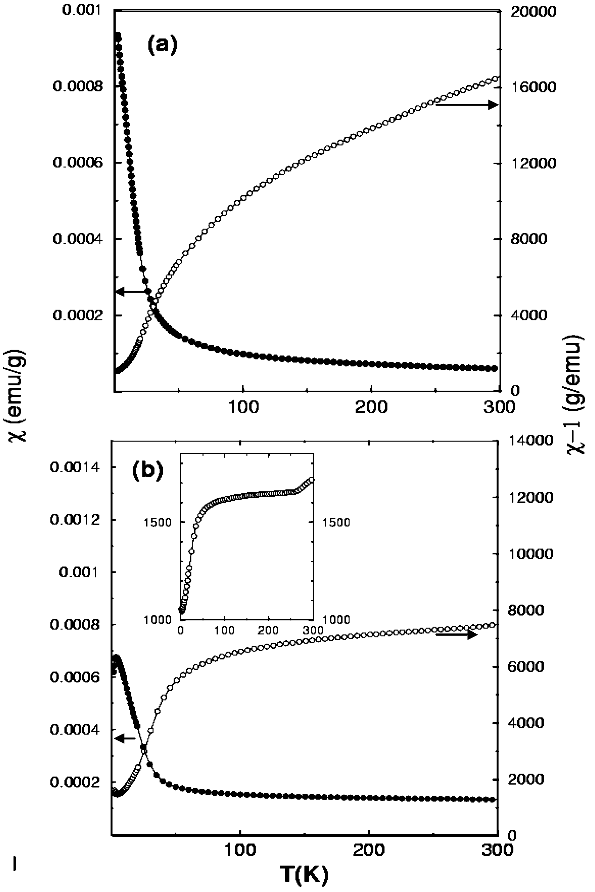

Figure 6. The temperature dependence of dc magnetic susceptibility (χ) and inverse magnetic susceptibility (χ^{-1}) of (a) 4.5 nm and (b) 11.5 nm CoO nanoparticles. The inset in b shows the inverse susceptibility vs temperature curve of 16 nm CoO.

change in the particle size (Figure 5). The presence of the organic coating helps to avoid the oxidation of the CoO nanoparticles.

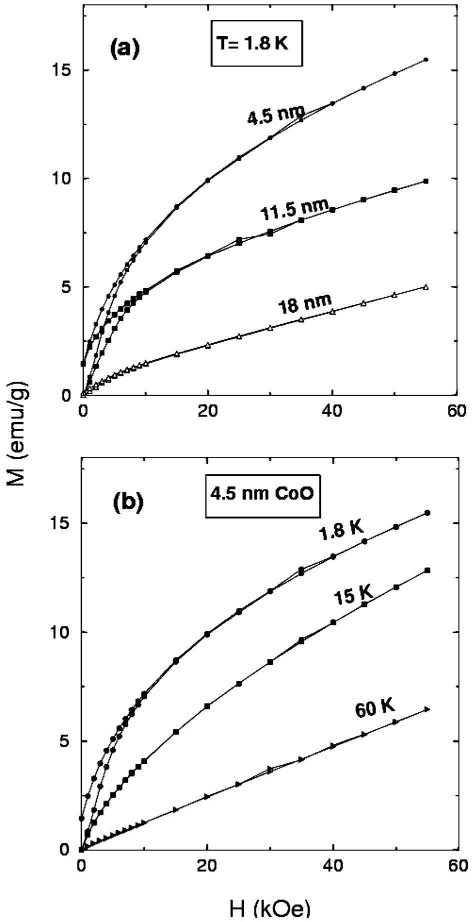

Figure 7. (a) M vs H at 1.8 K for 4.5-, 11.5-, and 18-nm CoO. (b) magnetization as the function of temperature for 4.5-nm CoO. All the data were acquired by applying a 1000-Oe field.

We show the temperature variation of susceptibility (χ) and the inverse susceptibility (χ^{-1}) of the 4.5- and 11.5-nm CoO nanoparticles in parts a and b of Figure 6 a and b, respectively. The inset in Figure 6b represents the inverse susceptibility (χ^{-1}) vs temperature data of the 16-nm particles. The 16-nm as well as the 18-nm samples show the presence of an antiferromagnetic transition (AFM) as evidenced by the broad peak around 300 K in the inverse susceptibility data. We do not see such a distinct AFM transition in the 11.5-, 8.5-, and 4.5-nm samples. The AFM transition is wiped out as the particle size decreases, probably due to the increased ferromagnetic interaction with decrease in particle size. Accordingly, the magnitude of the Curie–Weiss temperature (Θ_p) obtained from the extrapolation of the high-temperature inverse susceptibility data decreases with the increase in particle size. The Θ_p values are −1894, −1030, and −300 K, representing the 11.5-, 8.5-, and 4.5-nm samples, respectively, the magnetic moments being close to $5\mu_B$.

In Figure 7a, we show the variation of magnetization (M) with field (H) at 1.8 K for 4.5-, 11.5-, and 18-nm samples. The 4.5- and 11.5-nm samples show hysteresis at low temperature. Such hysteresis does not occur in the 18-nm sample. The temperature dependence of the magnetization of the 4.5 nm sample in Figure 7b shows that the hysteresis occurs only at low temperatures (<10 K), thereby establishing the presence of ferromagnetic interactions in CoO at low temperatures when the particle size is small (<16 nm). This is probably because of the uncompensated spins at the surface which increases as the particle size decreases.[4,5,18] We consider the small nanoparticles to be superparamagnetic showing magnetic hysteresis below a blocking temperature of ∼10 K. Accordingly, zero-field cooled susceptibility data show a peak around 10 K. It may be noted that, in the case of CoO thin films, magnetic hysteresis is found at 5 K as the film thickness decreases.[18] Support for this conclusion also comes from some of the recent work on Co_3O_4 nanoparticles.[19,20] Bulk Co_3O_4 shows an antiferromagnetic transition at ∼33 K, but nanoparticles show ferromagnetic features including hysteresis below 10 K. After we completed this work, we noticed a paper by Wang et al.[21] who have carried out a calorimetric study of CoO nanoparticles in the 10−320-K range. They prepared CoO nanoparticles by the decomposition of cobalt hydroxide in a H_2/Ar atmosphere. While we cannot be sure of whether surface oxidation was entirely avoided, it is noteworthy that this group found a broad maximum instead of sharp AFM transition in the 270-K region.

Conclusions

Stable nanoparticles of CoO in the size range of 4−18 nm have been prepared by decomposition of the cupferronate in Decalin under solvothermal conditions. The organic coating on the particles prevents surface oxidation of the nanoparticles, rendering them stable over long periods. It is interesting that nanoparticles with sizes less than 16 nm show ferromagnetic features below 10 K. The ferromagnetic interaction in small nanoparticles wipes out the sharp AFM transition around 300 K.

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