Synthesis and Characterization of CoO, Co_3O_4, and Mixed Co/CoO Nanoparticules

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Very small nanometric oxide particles (CoO and Co_3O_4, around 2 nm in diameter) well dispersed inside a polymer matrix were prepared by solid-state oxidation of a metallic colloid precursor (1.6 nm Co particles). WAXS (wide-angle X-ray scattering) and HREM (high-resolution electronic microscopy) were used to observe very precisely the structural changes occurring during the oxidation process. With cobalt particles a few nanometers large, air oxidation at room temperature results in a surface passivation. Consequently the particles show a composite structure with a metallic core surrounded by an oxide surface layer. Preliminary magnetic measurements reveal that unidirectional exchange anisotropy between the metallic ferromagnetic core and the antiferromagnetic oxide layer occurs below 130 K.

Introduction

Nanostructured materials have been intensively studied in the past decade since their physical properties are entirely different from those of the bulk state.[1] This feature is particularly true when the size of the cluster reaches molecular dimension (typically 1−2 nm). For example, when reducing the dimension of a metallic system, the number of atoms in the cluster drops from few thousands to a few atoms and the quasicontinuous density of states is gradually replaced by a discrete energy level structure. In other words, the typical bulk cooperative properties, such as conductivity or magnetism, and their typical band structure transform to reach eventually into molecular species characterized by an energetically well-defined set of bonding and antibonding molecular orbitals.[2] This quantum size effect is a challenge for chemists and physicists. The synthesis of nanoparticles of uniform size and structure (quantum dots) might open the door to new generations of electronic and magnetic materials.

Despite the large amount of literature regarding nanoscaled particles, producing real nanometric clusters is not an easy task and generally requires sophisticated methods and equipment such as a low-pressure metal evaporation/condensation device or fast quenching of a hot metallic plasma generated by a pulsed laser method. Since these free clusters are extremely reactive, ultrahigh vacuum is needed and their study outside the production device is a serious problem.[3]

Inorganic and organometallic chemistry allow synthesis of a wide variety of nanoscaled metallic, oxide, or sulfide particles with quite simple and easy methods.[1,4] But usually clusters reach a few nanometers and are often agglomerated. Moreover, in each case, they are stabilized by ligands or surfactants which interact with the surface.

Recently, we have briefly described a new way of synthesizing cobalt particles of nearly uniform size dispersed inside a polymer matrix.[5] The metallic clusters are obtained by the decomposition of an organic precursor under dihydrogen in the presence of a polymer. It has been shown, depending on the experimental conditions, mainly on the nature of the polymer, that

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cobalt cluster size ranges between 1.6 and 5 nm. Clusters are well-dispersed inside the polymeric matrix, nonagglomerated, and their magnetic behavior is totally similar to that of free noninteracting clusters produced by vacuum cluster beam technology.[6] That proves, that, unlike for many ligands or surfactants, there is not a strong chemical interaction between the polymer and the particles. The polymer matrix simply sets up the cluster size and efficiently protects particles.

After producing monometallic systems, our goal is now to synthesize more complex compounds, and this paper deals with the synthesis of cobalt oxides by a well-controlled air oxidation of the cobalt nanoparticles. As for pure metallic particles, the literature dealing with nanometric ceramics in the range of several tens or hundreds of nanometers is very rich. Works about 5−10 nm oxide nanoparticles are still very rare,[4i−l] whereas synthesizing and studying free, nonagglomerated and quasi-monodispersed <5 nm nanometers oxides remains an almost unexplored field [except ref 4m,n]. As demonstrated in some other papers,[4e,5,7] wide-angle X-ray scattering (WAXS) may be one of the most powerful techniques to study the medium-range distance order (0−2 nm) in nanometric materials. We applied this method to study the oxidation kinetics and to characterize finely the oxidized product. The size distribution and the structural changes of the Co particles were also studied using electron microscopy (HREM) performed before and after oxidation.

Experimental Section

Synthesis. The organometallic precursor $(Co(\eta^3\text{-}C_8H_{13})(\eta^4\text{-}C_8H_{12})$ reacts in a THF solution with dihydrogen in the presence of a polymer to yield cobalt particles. When the reaction is carried out at 65 °C in the presence of poly(vinylpyrrolidone) (PVP) with 11 wt % of metal (11% Co, 89% PVP in the final product), the average particule size is around 1.6 nm with a very narrow distribution. This sample will be referenced as CoPVP1.6nm. When the reaction is performed in the presence of polydimethyl phenylenoxide (PPO), the particle size is larger, around 5 nm, this batch will be called CoPPO5nm. Oxidation was performed in air following an iterative procedure. For example, the sample is exposed to air for 3 h and immediately evaluated by the WAXS measurement. It is then exposed to air for 48 h more, followed by a new measurement and so on. High-temperature oxidations were done similarly from the 5-day-oxidized sample.

WAXS Study. Colloid samples were sealed in a Lindeman capillary. The scattering spectrum produced by the sample irradiated with graphite-monochromatized silver Kα radiation ($\lambda = 0.56083$ Å) was obtained using a dedicated diffractometer. A total of 580 intensity values were collected for equidistant s points ($s = 4\pi(\sin\theta/\lambda)$; $\Delta s = 0.035$) in the range $0° < \theta < 65°$. Data collection times were 20 h for every measurement except for the 3-h-oxidized sample, for which the measurement was done quickly, in 2 h, to limit sample evolution during data collection. Measurements of air and a Lindeman capillary filled with polymer only were carried out under exactly the same conditions. The raw sample scattered intensity (sample + air + capillary) was corrected for the scattering from air and capillary with polymer contribution by spectra subtraction taking into account absorption from sample. Polarization and self-absorption effects were corrected as well. The normalization factor was determined from Norman's and Krogh-Moe's methods.[8] The atomic scattering factors were taken from Cromer and Waber.[9] The experimental reduced radial distribution function (RDF), which shows the distribution of the interatomic distances, was calculated similarly, as given in ref 10.[10] Theoretical structural models were built up using the Xmlmctep program.[11] The theoretical reduced RDF was calculated for the structural models by Fourier transform of the theoretical intensities calculated using the Debye formula.[12]

TEM Study. The size distribution, morphology, and crystalline structure of the particles were studied by HREM performed on a Philips CM30/ST operating at 300 kV whose point resolution is 1.9 Å. To avoid any possible uncontrolled oxidation of the cobalt particles, the samples for HREM experiments were prepared in a glovebox under an argon atmosphere. The powder was dissolved in THF and the resulting solution was poured onto a copper grid covered by a thin carbon film. However, a very short exposure of the sample to air during the transfer to the microscope could not be avoided.

The size distribution of the colloids was measured from low-magnification micrographs highly underfocused in order to get Fresnel fringes surrounding the grains. Numerical image analyses were performed after digitizing the images and size histograms were calculated. HREM experiments were then used to determine the fine structure of the particles. These experiments generally revealed nonperfect lattices due either to nonoriented and/or highly distorted particles. However, since we were studying a very large number of particles, some of them were oriented with a zone axis parallel to the electron beam. In that case HREM lattice images were digitized and the interplanar angles and spacings were measured from the corresponding numerical diffractograms (Fourier transforms). The HREM experiments were not successful for high-temperature oxidations (>120 °C), since annealing made the dissolution of the polymer impossible in THF.

Magnetic Study. Magnetic studies were performed using a Quantum Design Squid magnetometer at 5−300 K and field up to 5 T.

Results

WAXS and TEM Study. CoPVP1.6nm and CoPVP5nm Metallic Colloids. Synthesis and structural and magnetic characterizations of these metallic colloids have been[5] or will be reported in other papers. However, in Figure 1a, it is clear that Copvp1.6nm is composed of almost monodispersed nanoparticles (average diameter of 16 Å[13a]) very well-dispersed inside the polymer matrix. On the other hand, the CoPPO5nm sample (Figure 1b) is composed with single-crystal aggregates, around 5 nm in average size. The exact structure of CoPVP1.6nm colloids is still under study. HREM experiments performed on such particles show a highly distorted lattice image (not shown), which

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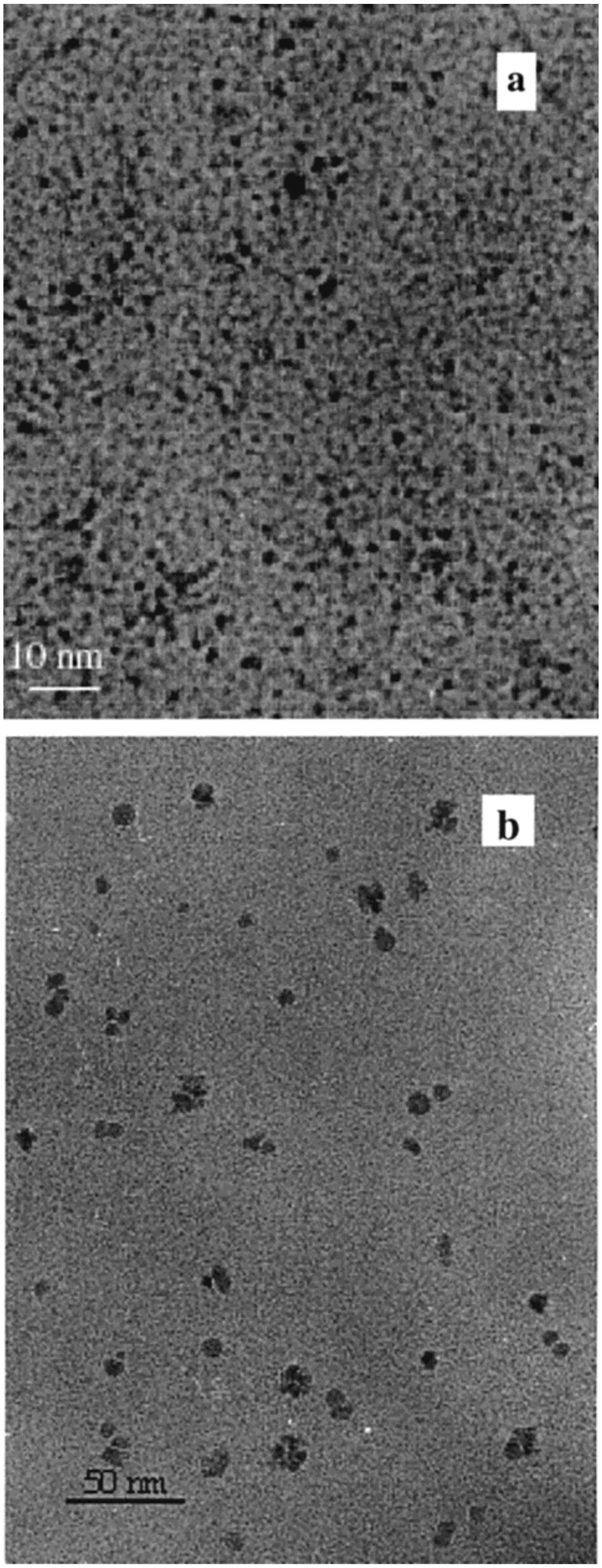

Figure 1. TEM image of CoPVP1.6nm sample (a) and CoPPO5nm sample (b).

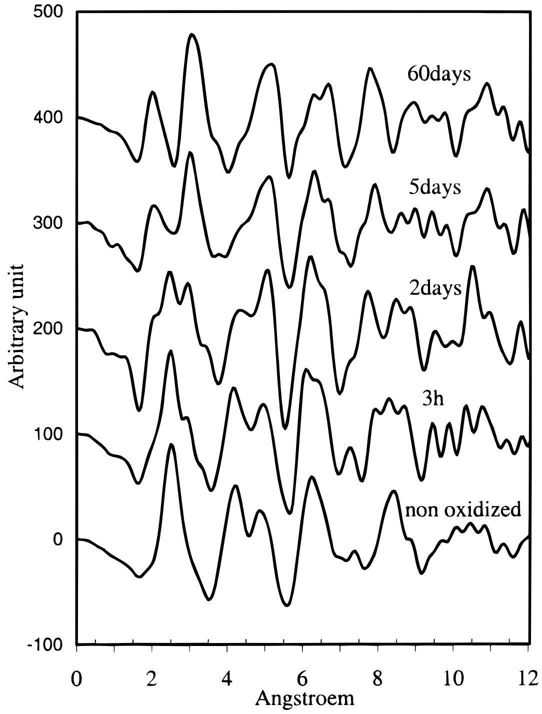

Figure 2. Reduced radial distribution function of CoPVP1.6nm colloid oxidized under air at 20 °C during increasing time.

might result from a nonperiodic structure (like an icosaedral one) or from a very perturbed distorted periodic structure. WAXS experiments show undoubtedly that it is a metallic structure. Indeed, the first pair correlation is located at 2.48 Å, which is characteristic of a Co···Co distance in a metallic state. The structure is surely not a classical compact one (hcp or fcc), but this point remains an open question which will be developed further. The CoPPO5nm colloid displays unambiguously an hcp structure as previously reported.[5b]

CoPVP1.6nm. Oxidation at Low Temperature; Formation of CoO Oxide. Figure 2 shows the evolution of the reduced RDF according to increasing oxidation periods from 3 h to 2 months at room temperature. Cobalt nanoparticles are quite well-protected by the PVP polymer. Indeed, after a 3 h oxidation the experimental RDF is mainly dominated by the metal influence. However, close to the characteristic metal peaks (for example, around the first Co···Co distance at 2.48 Å) some shoulders appear which are characteristic of an oxide (first Co···O distance at 2 Å and first Co···Co distance near 3 Å). A 48-h oxidation results in an approximately equal contribution of the metal and oxide phases. Oxidation during 5 days gives mainly an oxide, but the metallic pair contribution centered at 2.48 Å has not totally vanished. Sixty days are necessary to get a pure oxide.

Figure 3 compares the experimental RDF for the 60-day-oxidized samples with the theoretical one calculated from a CoO oxide model. The same fitting procedure has also been done on reduced intensity in the reciprocal space[13b] (not shown). The quality of the fit is very good in both cases. Undoubtedly room-temperature oxidation

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(13) (a) The underfocusing to obtain Fresnel fringes could result in an overestimation of particle size (0.1−0.2 Å). Simulation of the magnetic behavior reported in ref 5a gives 1.5 nm (cluster of 150 ± 10 atoms). (b) Working in the real space on RDF is more convenient, but the quality of the fit is probably better appreciated with reduced intensity (reciprocal space) because it compares more directly with the theoretical model. (c) Magnetic preliminary measurements have been done on CoPVP1.6nm nanoparticles oxidized at room temperature (20 °C/60 days). Clearly these nanoparticles are not the pure stoichiometric antiferromagnetic CoO phase. It is well-known that cobalt monoxide can be very easily nonstoichiometric. Moreover, the fitting quality of WAXS investigation (Figure 3) is not as good as for Co_3O_4 (Figure 5). To our mind these oxidized nanoparticles shows undoubtedly the CoO rocksalt structure but are slightly polluted by Co^{3+} cation.

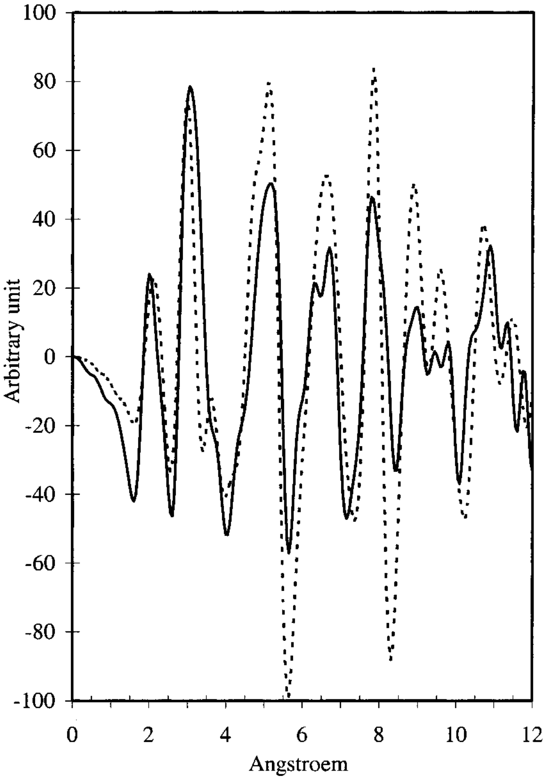

Figure 3. Reduced radial distribution function of CoPVP1.6nm colloid oxidized under air at 20 °C during 60 days (plain lines) compared to the theoretical ones calculated for a CoO model (dotted lines). CoO spherical model; $\phi = 1.4$ nm; 154 Co atoms, rock salt structure, $a = 0.420$ nm.

of these nanoparticles results in the bivalent cobalt oxide. However, some additional remarks can be done. The coherence length of cobalt particles before oxidation is shorter than the particle size, since beyond 8 Å the experimental RDF is almost flat (only noise remains). This feature is probably due to the highly distorted nature of these cobalt clusters, thus confirming HREM observations. However, beyond 2 days at 20 °C (Figures 2 and 3) the coherence length increases slightly to reach approximately the particle average size.

Figure 4 is a HREM micrograph of CoPVP1.6nm particles oxidized at 20 °C for 60 days with its Fourier transform inset. It evidences the two {111} planes and the {002} ones of the fcc CoO structure ($d_{002} = 2.13$ Å, $d_{111} = 2.46$ Å). Moreover, the size of the oxidized particles is found to be of the same magnitude order as the original cobalt particle size (15−20 Å), indicating that the 20 °C annealing does not induce any growth of the particles. However, as strongly suggested by WAXS experiments, we found that the oxidation of the highly disordered CoPVP1.6nm particles results in perfectly ordered fcc CoO particles.

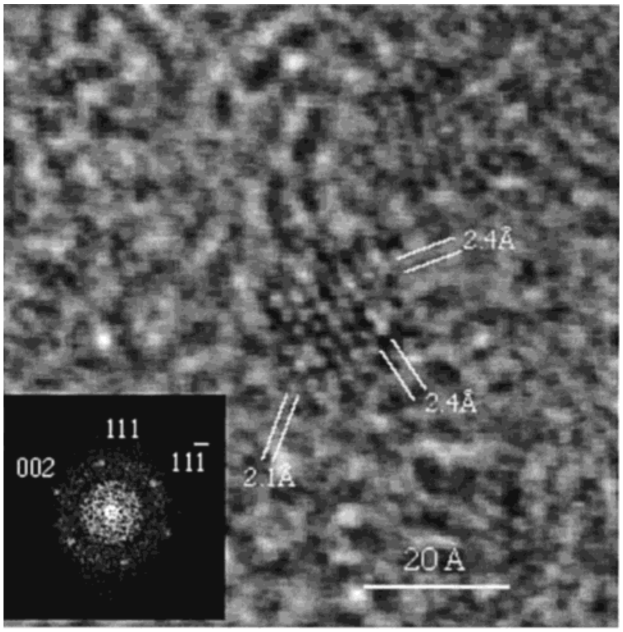

Figure 4. HREM image of CoPVP1.6nm sample oxidized 60 days at 20 °C. Fourier transform inset evidences the two {111} and the {002} planes of the fcc CoO structure ($d_{002} = 2.13$ Å, $d_{111} = 2.46$ Å).

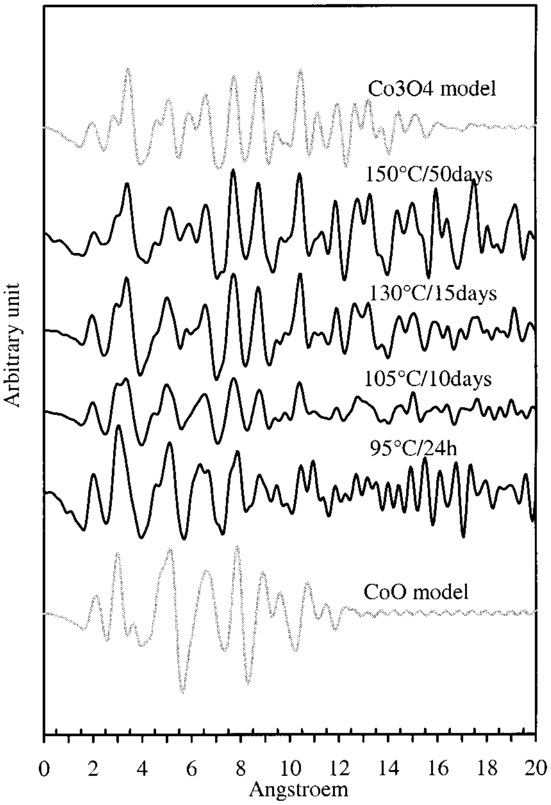

Figure 5. Reduced radial distribution function of CoPVP1.6nm colloid oxidized under air during increasing time and temperature compared with the theoretical models. CoO model same as in Figure 3. Co_3O_4 calculated from a spherical model; $\phi = 1.6$ nm; 151 Co atoms, spinel structure, $a = 0.809$ nm.

Oxidation at High Temperature: Formation of Co_3O_4 Oxide. The next figure (Figure 5) shows the progress of the oxidation reaction versus the temperature treatment, the 5-day room-temperature-oxidized sample being used as starting material. Treatment for 24 h at 95 °C produces little effect. The sample remains mainly in the CoO rocksalt form. After 14 days at 130 °C, the pure Co_3O_4 spinel oxide is formed. For this specific sample (oxidized 130 °C/15 days) both fitting procedures, in direct space and in reciprocal space, have been carried out (not shown) and are nearly perfect, which demonstrates that these particles consist of well-crystallized Co_3O_4 spinel oxide. The 130 °C oxidation treatment transforms half the Co^{2+} to Co^{3+} and results in a crystallization transformation as well.

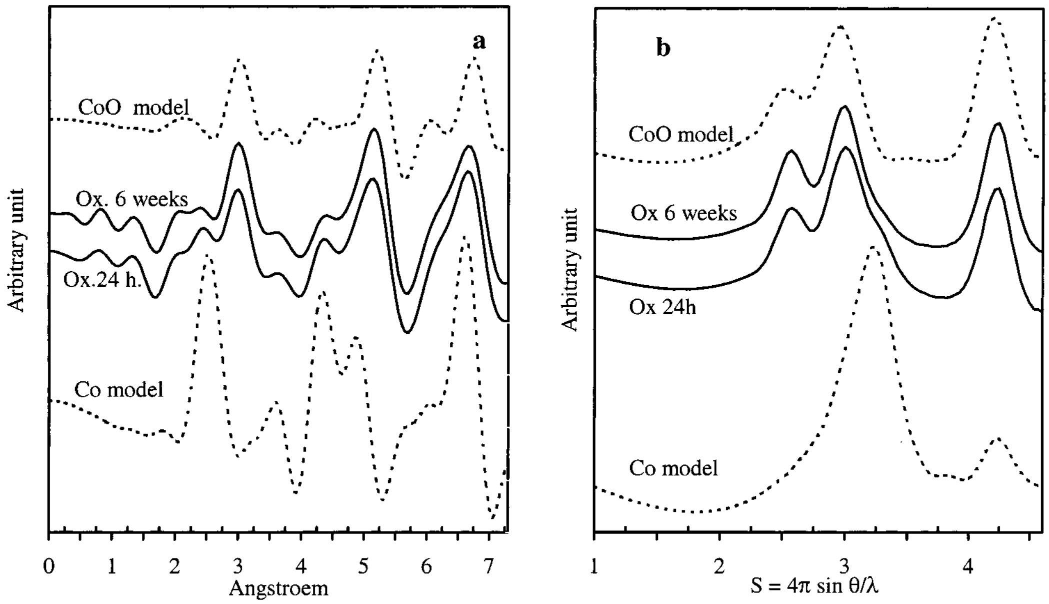

Figure 6. Reduced radial distribution function (a) and reduced intensity (b) of CoPPO5nm colloid oxidized under air at 20 °C during 24 h and 6 weeks (plain lines) compared with the theoretical ones calculated for Co and CoO models (dotted lines). CoO model, same as in Figure 3. Co model, hcp structure, $a = 0.207$ nm, $c = 0.4070$ nm, $\phi = 1.6$ nm.

As previously reported, the high-temperature annealing somewhat alters the polymer (probably reticulation) which becomes insoluble, thus making impossible any HREM investigation of these particles. It is therefore difficult to appreciate if the size of the Co_3O_4 particles oxidized at 130 °C has grown due to coalescence or not. However, a qualitative observation of the experimental RDF (Figure 5) shows that long-range pair correlation seems to be very weak after 18 Å. Consequently, to our mind, the size of these nanoparticles has aparently not increased a lot by coalescence after oxidation at 130 °C.

Oxidation at 150 °C during 50 days gives the same spinel oxide. Both RDF (see Figure 5) and reduced intensity (not shown) give results similar to those of the previous sample. No extra peaks are observed. The main difference is that, in this case, the coherence length, and so the particles size, is much larger than 20 Å, which demonstrates an important growth of the particles. This induces some discrepancy of peak intensities compared to the 130 °C oxidized samples. This behavior is not surprising, since some changes occur on the relative peak intensities when the size of the organized structures increases.

CoPPO5nm. Oxidation at Low Temperature; Formation of a Metal Oxide Composite Particle. In the case of bigger particles, CoPPO5nm, oxidation is not thoroughly completed at room temperature. Indeed, Figure 6 clearly shows that the experimental RDF and reduced intensity are mainly dominated by the CoO influence but with a nonnegligible metallic contribution. The polymer, PPO, does not protect the metallic colloid as efficiently as PVP, since, even after a short oxidation time (24 h), the CoO phase strongly dominates. WAXS measurements have been performed after oxidation for 24 h, 5 days, and 6 weeks. Surprisingly, even for very long oxidation periods the situation does not evolve much and after 6 weeks the metal contribution is still clearly visible. Reasonably good fit (not shown) can be obtained considering that approximately 80% of cobalt atoms are present in the cobaltous rocksalt phase, whereas 20% remains in the metal hcp form after 24 h oxidation. The same fitting procedure (not shown) performed on the 6-week-oxidized sample results in a metallic ratio around 10%. These values must be

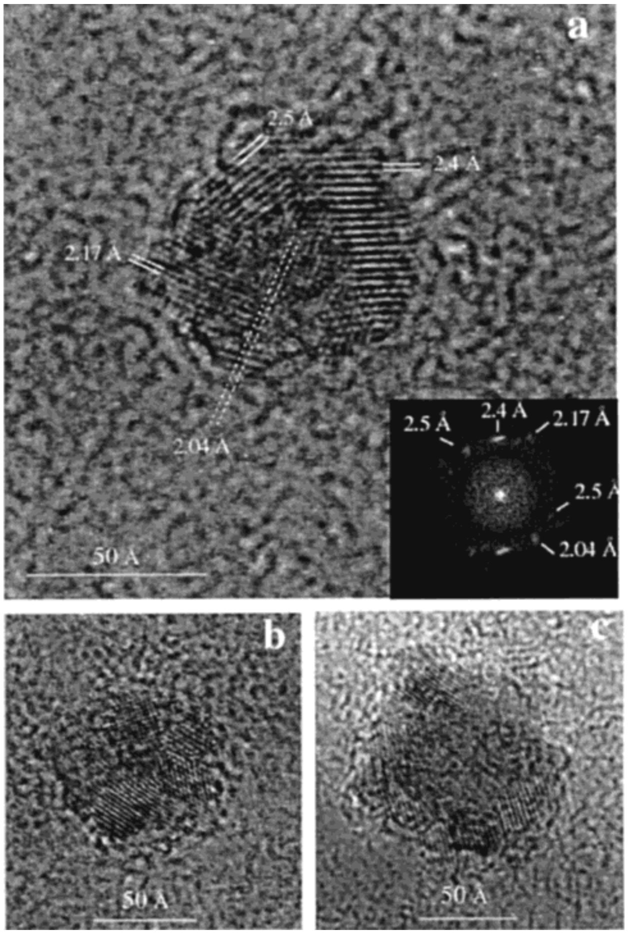

Figure 7. (a) HREM image of CoPPO5nm sample oxidized at 20 °C. Fourier transform (inset) evidences the presence of a lattice distance which corresponds to the (0002) planes of the metallic hcp Co structure ($d_{0002} = 2.04$ Å) and others coming from a fcc CoO structure. Panels b and c deal respectively with one of the smallest and the biggest particle.

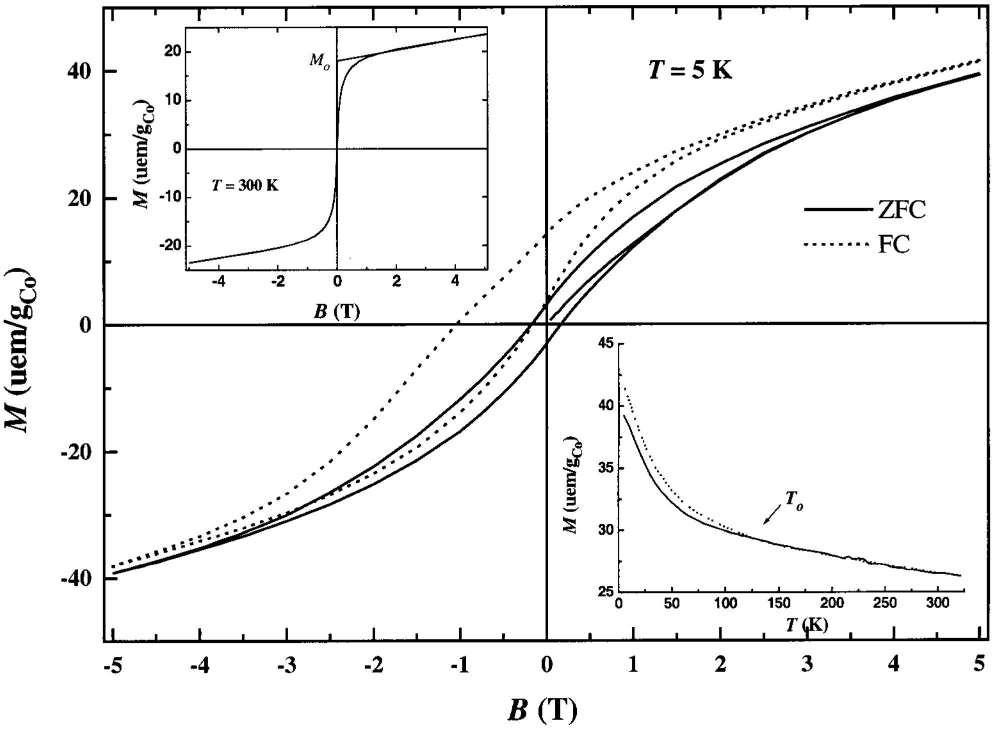

Figure 8. Hysteresis loops measured at 5 K after a zero field cooling and a field cooling at 5 K. The lower inset shows the high field magnetization ($B = 5$ T) measured after a zero field or a field cooled process. Under T_o, exchange phenomena are present. The upper inset shows the hysteresis loops measured at 300 K which allows evaluation of the spontaneous magnetization of the ferromagetic part of the sample (M_o).

considered simply as coarse estimation and not as an analytical result, because the fitting procedure is not perfect, but also because the two models (CoO and Co) are independent and the interactions between the two phases, such as the Co/CoO interface, are not taken into account.

A HREM image obtained on such oxidized particles is reported in Figure 7a with its corresponding Fourier transform inset. The numerical diffractogram reveals the presence of a lattice distance which corresponds to the (0002) planes of the metallic hcp Co structure (d_{0002}= 2.03 Å) and other distances resulting from a fcc CoO structure. The HREM image shows that the particles consist of a 25 Å diameter Co core surrounded by the CoO oxide, the total diameter being 75 Å. Considering a spherical particle, these measurements indicate that only about 3.5% of the particle volume remains in the metallic phase. Similar results have been obtained for a representative number of Co/CoO particles selected in the sample which are similar to the ones reported in Figure 7b,c. For the first one, a 15 Å Co core is measured, whereas the total diameter of the particle equals to 80 Å (Co/Co + CoO $\cong$ 1%). The second particle in Figure 7c is larger (115 Å in diameter) with a Co core diameter estimated to 35 Å (Co/Co + CoO $\cong$ 2.7%). In a few other much larger particles, this ratio is more important. These observations indicate that the oxidation of the particles produces an oxide shell which makes further oxidation of the Co core more difficult. The wider the original particle, the larger the resulting final Co core after oxidation. Co/Co + CoO $\cong$ 3% in volume means that approximately 6% of the cobalt atoms are present in the metallic form, which is slightly less than deduced from the WAXS estimation.

This unexpected composite structure is very interesting for the physics community since it allows a careful study of the magnetic coupling between the ferromagnetic core and the antiferromagnetic oxide layer.

Magnetic Study. Magnetic studies on CoO proved difficult, which is probably due to the nonstoichiometry of this phase,[13c] whereas Co_3O_4 displays an expected antiferromagnetic behavior. The most interesting magnetic measurements were performed on oxide-passivated Co nanoparticles (CoPPO5nm). Hysteresis loops were measured as a function of the temperature according to the zero field cooling (ZFC) and field cooling (FC) procedures. The latter corresponding to the cooling from 300 to 5 K (measurement temperature) in a magnetic field of 5 T. Figure 8 shows these two curves measured at $T = 5$ K. The ZFC loop is symmetrical in shape around the origin, whereas the FC loop is shifted along the applied field direction and expands toward the applied field direction. These last features clearly reveal the presence of unidirectional exchange anisotropy.[14] Low field susceptibility ($B = 1$ mT) and high field ZFC and FC magnetization ($B = 5$ T) measurements were performed. The former reveals a superparamagnetic behavior above the blocking temperature $T_{B-Ox} = 200$ K. Before passivation, the blocking temperature of the pure CoPPO5nm nanoparticles was over 300 K. The high field magnetization shows an enhanced signal in the FC process compared to the ZFC one for temperature below $T_o = 130$ K (see lower inset of Figure 8). They are identical above that temperature, showing that the shift along the applied field direction disappears.

We believe that the superparamagnetic behavior appearing at lower temperature for oxide-coated par-

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[14] Meiklejohn, W. H. *J. Appl. Phys.* **1962**, *33*, 1328.

ticles compared to the pure metal particles evidences a decrease of the ferromagnetic volume in each particle. After passivation the magnetization at 5 K falls down to 40 uem/g_{Co} instead of 160 uem/g_{Co} in the pure metallic phase.[15] At 300 K, the spontaneous magnetization M_o due to the ferromagnetic part of the sample is close to $M_o = 18$ uem/g_{Co}, which corresponds to a fraction of approximatively 12.5% of cobalt atoms in the metallic state. The oxidized outer layers create an antiferromagnetic shell surrounding the ferromagnetic core responsible for the unidirectional exchange anisotropy below T_o. This temperature is found to be between the Néel temperatures of CoO and of Co_3O_4, respectively, 290 and 40 K in bulk samples.[16] Usually, these ordering temperatures decrease with decreasing size or dimensionality.[17] In our case, the value of T_o seems to confirm the presence of a CoO type oxide. These results are in accordance with the previous evaluation from WAXS spectra.

Conclusion

Studies for the preparation of extremely small (<5 nm) nanoparticles of metal oxide[4m,n] are scarce. In this paper we describe the first careful study of a mild solid-state oxidation of cobalt nanoparticles resulting successively in CoO and Co_3O_4. Furthermore, when using larger particles, it is possible to obtain nanocomposites displaying interesting magnetic properties.

Since WAXS and HREM are very powerful tools to observe very precisely the structural changes occurring during oxidation reactions, we have been able to produce CoO and Co_3O_4 nanoparticles well-dispersed inside a polymer matrix. It is obvious that this procedure can be applied to many other nanometric oxide systems and may be widely developed. Indeed, transition metal oxides often display semiconducting properties, where the size-dependent behavior should be of a special interest in microelectronics.

As mentioned hereabove, when the cobalt particles are a little bigger than a few nanometers, air oxidation at room temperature gives rise to a surface passivation phenomenon, which results in a metallic core protected by an oxide surface layer. In the future, one of our main goals will be to separate the metal oxide nanocomposite colloids from its polymer matrix or to synthesize it alone (without any polymer) in order to obtain a granular material where metallic ferromagnetic cores are separated by an insulator antiferromagnetic oxide of a few nanometers. Indeed, lately spin-dependent electronic transport between two ferromagnets through an insulator junction has been intensively studied for tunneling magnetoresistance (TMR) applications.[18]

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