

Study of the structure and stability of cobalt nanoparticles for ferrofluidic applications

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We present X-ray absorption spectroscopy (XAS) data, ultraviolet photoelectron spectra (HeI) and metastable impact electron spectra (MIES) of cobalt nanoparticles (typically 4 to 10 nm), prepared by $\text{Co}_2(\text{CO})_8$ thermolysis and pre-stabilized by smooth oxidation. We find that the particles consist of a core-shell system with a dominantly f.c.c. core and a shell in which Co–C and Co–O coordination is likely to occur. This corresponds well to the results from electron spectroscopy, that stabilization occurs via formation of (Co–CO_x) and (Co–O) groups formed during the oxidation procedure and appears sensitive to the reaction conditions. Peptization of the pre-stabilized particles with KorantinSH surrounds the particles with a dense organic shell, stable up to about 250 °C. The carbonic acid molecules of the shell are oriented predominantly perpendicular to the surface of the particles, their carboxyl functional group linking the shell with the cobalt particles. This result is also supported by the XAS data, where it is observed that, during peptization, Co–C coordination is partly replaced by Co–O coordination. In order to arrive at these statements, auxiliary measurements on bare and gas-exposed cobalt films, also reported here, were required. Copyright © 2004 John Wiley & Sons, Ltd.

KEYWORDS: X-ray absorption spectroscopy (XAS); metastable impact electron spectroscopy (MIES); UPS; HeI; cobalt; nanoparticles; ferrofluid

INTRODUCTION

Magnetic fluids (MFs) with a narrow particle size distribution exhibit properties useful for a number of technical and biomedical applications. The magnetic properties of MFs depend strongly on the size of the particles and the concentration of the magnetic material in solution. The well-known magnetite (Fe_3O_4) MFs have good stability. However, their magnetic properties do not yet meet a number of demands. Consequently, stable MFs on the basis of nano-sized colloidal cobalt(0) particles are very interesting materials.

For the preparation of nanoscopic cobalt(0) particles the thermolysis of $\text{Co}_2(\text{CO})_8$ is a very convenient and generally applied method.¹ An important issue is the stability of the cobalt(0) particles against air and moisture: if their surface remains unprotected, the saturation magnetization of cobalt particles obtained by conventional thermolysis decays rapidly when exposed to air after peptization with, for instance, KorantinSH.¹ However, it was found that, after smooth oxidation with air, the particles can be isolated and peptized with the help of surfactants in order to give remarkably stable MFs which can be handled under ambient conditions.² Further work is required to elucidate the mechanism of pre-stabilization underlying the smooth oxidation procedure. Possible reaction paths leading to the stabilization include (i) the conversion of the C–O bonds resulting from the preparation steps into carbonaceous

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species, and (ii) the oxidation of cobalt surface atoms during the smooth oxidation procedure.

Understanding and controlling the effects of surface chemistry on the magnetic properties of nanoparticles (NPs) has become increasingly important for the technological application of magnetic particles, such as in high-density storage media, medical imaging, and drug delivery.³ For practical implementation of NPs in biomedical applications, such as in magnetically guided site-specific drug delivery and in magnetic resonance contrast-enhancement agents, the surface of the particles has to be modified with biocompatible ligands that also have the function of being drug-carrying vehicles. These particles, in turn, once internalized into the body, become encapsulated with biological ligands associated with the body's defense system. Understanding the changes in magnetic behavior caused by these chemical interactions at the surface is critical in developing nanoparticles in biomedical techniques.

Here, we have applied a combination of X-ray absorption spectroscopy (XAS), valence-band electron spectroscopies, metastable impact electron spectroscopy (MIES) and ultraviolet photoelectron spectroscopy (UPS(HeI))^{4,5} to obtain detailed information on the chemical composition and the structure of the pre-stabilized particles, prior to their peptization. The same techniques were also utilized to obtain information on the structure of the particles encapsulated after their peptization. This includes information on the functional group responsible for the chemical interaction between the shell and particles, and the orientation of the organic molecules with respect to the surface normal. Furthermore, the range of thermal stability of the peptized particles was studied. Auxiliary measurements on bare and gas-exposed cobalt films were made in order to arrive at an unambiguous interpretation of the experimental data gathered from the nanoscopic particles.

EXPERIMENTAL DETAILS

Preparation of air-stable cobalt particles via thermolysis of $\text{Co}_2(\text{CO})_8$ in the presence of $\text{Al}(\text{C}_8\text{H}_{17})_3$

Air-stable cobalt(0) particles as precursors for preparing MFs were obtained via the thermal decomposition of $\text{Co}_2(\text{CO})_8$ in the presence of aluminum-organic compounds, and a subsequent modification of the protective shell by the smooth oxidation of the surface of Co–AlR₃ particles. These air-stable cobalt particles can be peptized in different carrier liquids by suitable surfactants.^{1,2}

Sample A: $\text{Co} : \text{Al}(\text{C}_8\text{H}_{17})_3 = 8 : 1$

Step 1: particle formation. In a 4000 ml three-necked flask fitted with an effective mechanical stirrer and a reflux condenser, 53 ml of $\text{Al}(\text{C}_8\text{H}_{17})_3$, dissolved in 3000 ml of toluene, was introduced under a flow of argon and heated to 60–70 °C (oil

bath). To this mixture, 171 g of dry $\text{Co}_2(\text{CO})_8$ was added in one go over a period of 1–2 minutes. The mixture was stirred continuously and gradually heated to 110 °C (toluene reflux). This temperature was maintained for 18 h (toluene reflux). As CO evolution proceeded, the color of the solution changed to dark brown, and a black slurry precipitated from the clear solution. The temperature of the oil bath was increased to 150 °C and maintained for 2 h. The contents of the flask were cooled to 20 °C and 8 ml of $\text{Al}(\text{C}_8\text{H}_{17})_3$ was added. After that the mixture was stirred overnight.

Step 2: smooth oxidation. After completing step 1 strictly under protecting gas (argon), a stream of synthetic dry air (20 vol.% O₂; 80 vol.% N₂) was slowly introduced into the liquid through a fine capillary that was immersed in the constantly stirred mixture. This was carried on for 16 h, while moderate stirring was continued. The precipitate was allowed to settle for 2 h. The supernatant was decanted, and the cobalt particles (now surface stabilized) were washed twice using 1.5–2 l toluene each time and isolated in wet form, i.e. as a suspension of cobalt in toluene.

Step 3: peptization of the cobalt particles in toluene. The wet Co particles were peptized (i.e. dispersed) in toluene by adding 10 ml of KorantinSH (surfactant) dropwise. In order to facilitate the particle peptization, the mixture was stirred very well and gradually heated to 60–70 °C during 0.5–2 h to obtain the cobalt magnetic fluid in toluene.

Sample B: $\text{Co} : \text{Al}(\text{C}_8\text{H}_{17})_3 = 5 : 1$

Step 1: particle formation. In a 500 ml three-necked flask fitted with an effective mechanical stirrer and a reflux condenser, 8.8 ml of $\text{Al}(\text{C}_8\text{H}_{17})_3$ dissolved in 300 ml of toluene was introduced under a flow of argon. To this mixture, 34.2 g dried $\text{Co}_2(\text{CO})_8$ were added at once (1–2 min). The mixture was stirred continuously and gradually heated to 110 °C (toluene reflux). This temperature was maintained for 18 h (toluene reflux). As CO evolution proceeded, the color of the solution changed to dark brown, and a black slurry precipitated from the clear solution.

The contents of the flask were cooled to 20 °C, 1.5 ml $\text{Al}(\text{C}_8\text{H}_{17})_3$ was added and the temperature of the oil bath increased to 110 °C and maintained for 3 h. After that the mixture was cooled to room temperature and stirred overnight.

Step 2: smooth oxidation. After completing step 1 strictly under protecting gas (argon), a stream of synthetic dry air (20 vol.% O₂; 80 vol.% N₂) was slowly introduced into the liquid through a fine capillary that was immersed in the constantly stirred mixture. This was carried on for 5 h, while moderate stirring was continued. The precipitate was allowed to settle for 2 h. The supernatant was decanted, and the cobalt particles were isolated in wet form (suspension in approximately 20 ml toluene).

Step 3: peptization of the cobalt particles in toluene. The wet cobalt particles were peptized in toluene by adding 0.5 ml of KorantinSH dropwise. In order to facilitate the particle peptization, the mixture was stirred very well and gradually

heated to 60–70 °C over 0.5–1 h to obtain the cobalt MF in toluene.

Experimental details of the XAS measurements

Cobalt K-edge X-ray absorption near-edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) measurements were carried out at beamline BN3 of the Electron Stretcher Accelerator ELSA (operating at 2.3 GeV energy) in Bonn using a modified Lemmonier-type double-crystal monochromator⁶ equipped with a set of Ge(220) crystals. Further details about the setup at this beamline are described elsewhere.⁷ The measurements were performed in a transition mode using ionization chambers filled with argon at 600 mbar pressure as intensity monitor and as detector. For magnetic nano-powder, samples were ground and fixed between two layers of self-adhesive Kapton tape. The MF was injected into a liquid cell, identical to the one used by Angermund *et al.*⁸ Sample preparation took place in the argon atmosphere of a glove-box for the air-sensitive samples. The thickness of the sample was optimized to result in an edge jump of approximately one. The XANES spectra were scanned three times from 7650 to 7850 eV in steps of 0.6 eV with 1000 ms integration time per step and then averaged. The EXAFS spectra were recorded twice and then averaged, the energy range of the scan was from 7500 to 8800 eV in steps of 1.2 eV and 1000 ms integration time per step. Energy calibration was performed relative to the spectrum of bulk h.c.p. cobalt, whose first inflection point was 7709 eV. Standard XANES data-handling routines were followed, including subtraction of a linear background fit to the pre-edge region. The spectra were normalized at 7820 eV. For evaluation of the EXAFS spectra, the UWXAFS program suite^{9–11} was used.

Experimental details of the MIES and UPS measurements

In MIES, metastable helium atoms ($2^3S/2^1S$) are utilized to eject electrons from the substrate surface. Details of the apparatus designed for performing the electron spectroscopic measurements with MIES and UPS(HeI) can be found elsewhere.^{12–14} Briefly, a cold-cathode helium gas discharge source serves both as the source for an intense metastable helium beam for MIES ($He^*(2^3S/2^1S)$ with 19.8/20.6 eV excitation energy) and as an HeI photon source for UPS (HeI with 21.2 eV). The contributions to the electron spectra from metastables and photons within the beam are separated by means of a time-of-flight technique combined with a double counter system allowing one to measure MIES and UPS spectra simultaneously. Electrons emitted in the direction normal to the surface are analysed. A detailed introduction to MIES and its various applications in molecular and surface spectroscopy can be found in recent reviews.^{4,5}

The energy scales in the figures are adjusted in such a way that electrons emitted from the Fermi level E_F —i.e. electrons with the maximum kinetic energy, show up at the fixed energy $E_B = 0$ eV. For photoelectrons and for electrons generated in

MIES by Auger deexcitation^{4,5} the E_B values are with respect to the Fermi level. With this choice, the low-energy cutoff gives the work function of the surface directly; changes in its position reflect directly the change of the work function occurring during the deposition of the stabilized platinum-colloids or during film heating.

For the characterization of the chemical composition of the bare surface and the films of nanoscopic particles the apparatus is equipped with a twin anode (Mg/Al) X-ray photoelectron spectroscopy (XPS) source.

RESULTS AND DISCUSSION

Investigation of the particle core

Figure 1 shows the cobalt K-edge XANES spectra of particles A (Co:Al ratio 8:1) and B (Co:Al ratio 5:1) before and after peptization, each compared with an h.c.p. cobalt reference foil. In all spectra, clear differences from the cobalt foil as well as the other spectra are visible, especially in the region of the absorption edge. In this region, two important features play a role for the interpretation of the spectra: the pre-edge shoulder at about 7709 eV; and the maximum of absorption ('white line'). The origin of the pre-edge shoulder, which appears in a number of 3d transition-metal spectra, is attributed to a mixing of p and d states.¹⁵ Therefore, it can be used as an indicator for the presence of chemical interaction which interferes notably with this overlap, thus allowing for the separation of effects related to both structural and chemical phase transformations. Comparison of the pre-edge intensity between the spectra of the h.c.p. cobalt foil and the pre-stabilized powder sample B suggests clearly that hardly any chemical interaction has occurred. Instead, the spectrum is dominated by the typical features for f.c.c. cobalt.^{1,16} (When comparing the calculated spectra displayed in these two references, it must be kept in mind that the Palshin *et al.*¹⁶ calculation uses a refined geometry input for the ϵ -Co phase that was not available when Bönemann *et al.*¹ reported their results). In contrast, the pre-stabilized sample A shows clear indications of chemical interaction. Note that the stronger indication for chemical interaction is found in a particle that has been synthesized using a larger Co:Al ratio, which is expected to be a larger particle.¹⁷ This observation indicates that the observed variation, which is also reflected in a change of magnetic properties,¹⁸ cannot be explained by the fact that the contribution of a surface coordination is smaller for a bigger particle. Instead, the formation of the particle shell must be influenced by a variation of the Co:Al ratio. A more systematic study of this effect is in progress.

The findings discussed so far are supported by the analysis of the EXAFS spectra of the corresponding samples, which are displayed in Fig. 2 and summarized in Table 1. When fitting sample B, no significant contribution of a soft backscatterer appears in either powder or MF within the limits of precision of the EXAFS analysis. However, the precision that can be

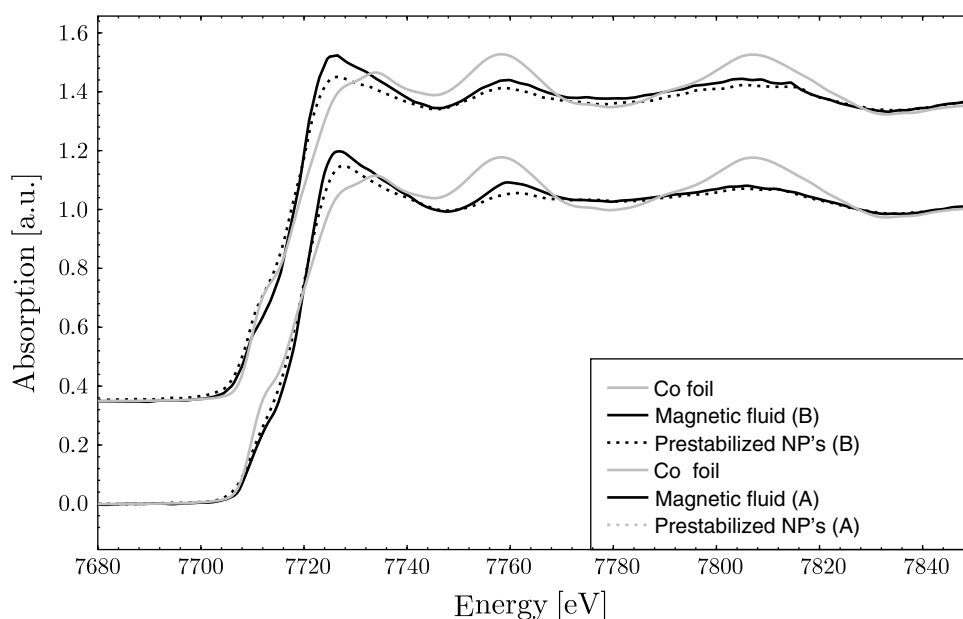


Figure 1. Cobalt K-edge XANES spectra of particles in sample A (Co:Al ratio 8:1) and B (Co:Al ratio 5:1) before and after peptization. Top: cobalt K-edge XANES of sample B after (solid line) and before (dotted line) peptization in comparison with h.c.p. cobalt reference foil. Bottom: as top, but for sample A.

Table 1. Results of the EXAFS analysis for the stable cobalt particles. The fit was done using $S_0^2 = 0.825$, a k weight of 3, the k range between 1.2 and 11.5, and the R range between 0.85 and 2.8

Sample	Backscatterer	R (Å)	N	σ^2 (Å ²)	E_0 (eV)
Pre-stabilized B	Co	2.50(1)	6.1(7)	0.009(1)	3.4(1.1)
Pre-stabilized A	Co	2.49(1)	4.5(7)	0.006(1)	3.1(8)
	C/O	1.96(1)	2.6(8)	0.020(2)	1.4(3)
Peptized B	Co	2.50(1)	6.9(3)	0.008(1)	2.6(6)
Peptized A	Co	2.49(1)	7.9(1.3)	0.010(1)	2.2(4)
	C/O	2.10(1)	2.5(5)	0.014(1)	12.0(4.7)

achieved in the EXAFS and XANES results still allows for a contribution of a few percent of the cobalt atoms which are coordinated to soft backscatterers. In contrast to this result for sample B, the analysis of sample A clearly indicates the presence of a soft backscatterer for both powder and MF. The distance between cobalt and this backscatterer before and after peptization varies considerably; in the first case it is about 1.96 Å, in the second it is 2.1 Å. Whereas scattering phase and amplitude are too similar to allow one to distinguish these types of atom, some information can be derived from the distances obtained in the fitting process: whereas 2.1 Å is a distance that is close to that encountered in CoO (2.13 Å) and CoCO₃, 1.96 Å is close to the Co–C distance encountered in Co₂C (1.92 Å), but also to the Co–O distance in Co₂O₃. Also, the Debye–Waller factors obtained from the fit for these paths are (even) bigger in the case of the pre-stabilized sample than in the MF. This may suggest that Co–C and Co–O are backscatterers in the pre-stabilized particle, whereas in the

MF oxygen at the larger distance, which is characteristic for CoO and/or CoCO₃, dominates over carbon. It should be stressed that in both cases Co–Co coordination dominates by far over coordination to a soft backscatterer (see Table 1). Some ordering of the particle core seems to go along with the peptization process, as indicated by the increasing Co–Co coordination numbers. The available data do not allow for a reliable and detailed comment on this effect so far. Further investigations are in progress.

If in fact for some of the cobalt atoms the nearest neighbor is changed from carbon to oxygen, one would expect the chemical interaction to increase and the white-line intensity at the cobalt K-edge to grow. Returning to Fig. 1, one observes exactly this change when comparing cobalt K-edge XANES spectra of the MF and the pre-stabilized powders. The high sensitivity towards the peptization process that is apparent in both the EXAFS and XANES spectra suggests strongly that the soft backscatterers are mainly located on the surface of the

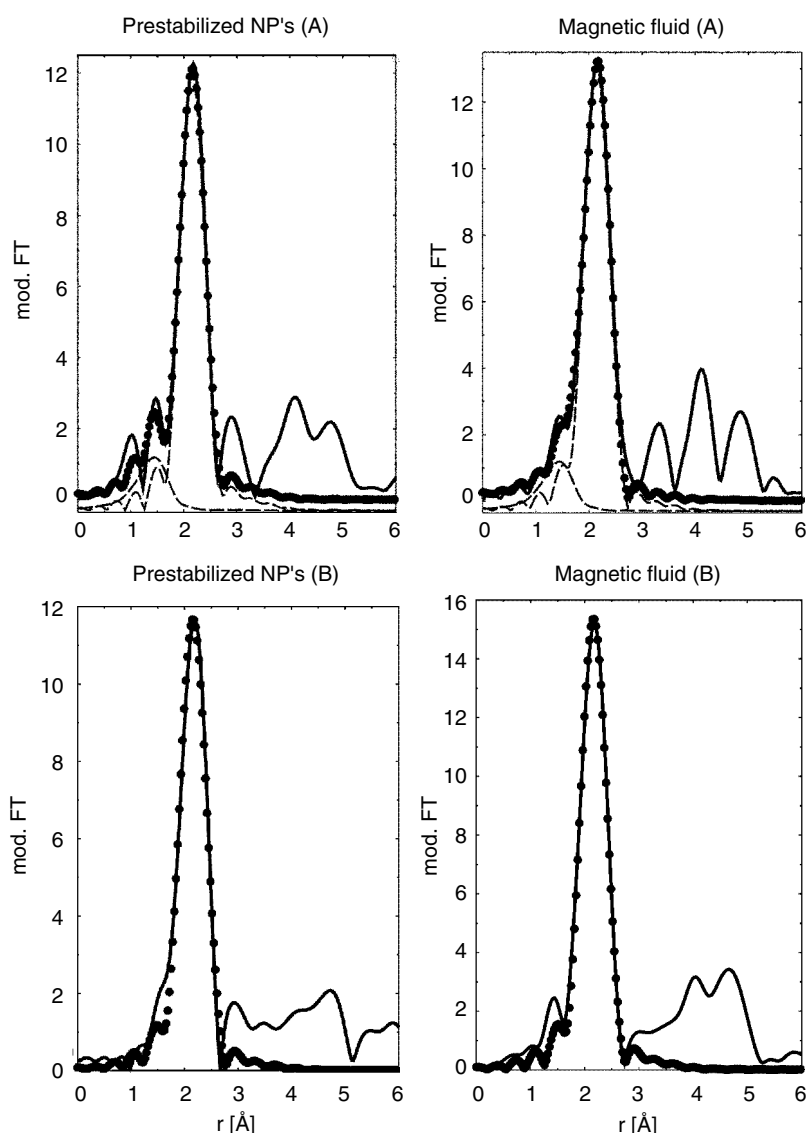


Figure 2. Modified Fourier transforms (solid lines) and fits (dots) for the samples. Broken lines show contributions of the different scattering paths where applicable.

respective particles, creating some shell layer on a metallic particle core.

Investigation of the particle shell

Studies on bare and gas-exposed cobalt films

In order to facilitate the interpretation of the results from pre-stabilized cobalt particles (this section) and those from the peptized particles (next section), cobalt films were produced on SiO_x substrates under the *in situ* control of MIES/UPS. These films were then exposed to O_2 , CO , and CO_2 , again under *in situ* control of MIES/UPS. A detailed presentation of the results will be the subject of a future publication;¹⁹ only a short summary will be presented here. Briefly, formation of Co–O bonds during the film oxidation produces MIES/UPS spectra that are very similar to those for the corresponding

O–Ni system.^{5,20} Five spectral features, A to E, can be resolved in the region between the Fermi energy E_F and about 13 eV; their positions are shown in Fig. 3. The identification of the emission seen between 0 and 5 eV as due to ionization of 3d Co^{2+} states¹⁹ is of particular importance for the interpretation of the spectra from the pre-stabilized and the peptized cobalt particles. CO adsorbs molecularly, manifesting itself in two peaks 5σ ; 1π (7.5 eV) and 4σ (10.7 eV) (Fig. 3). CO_2 is found to chemisorb dissociatively, producing MIES and UPS spectra very similar to those for CO.

Studies on the pre-stabilized cobalt particles

The pre-stabilized cobalt particles (see 'Experimental details' section) were deposited on SiO_x substrates from suspensions in toluene. Scanning Tunneling Microscopy (STM) indicated

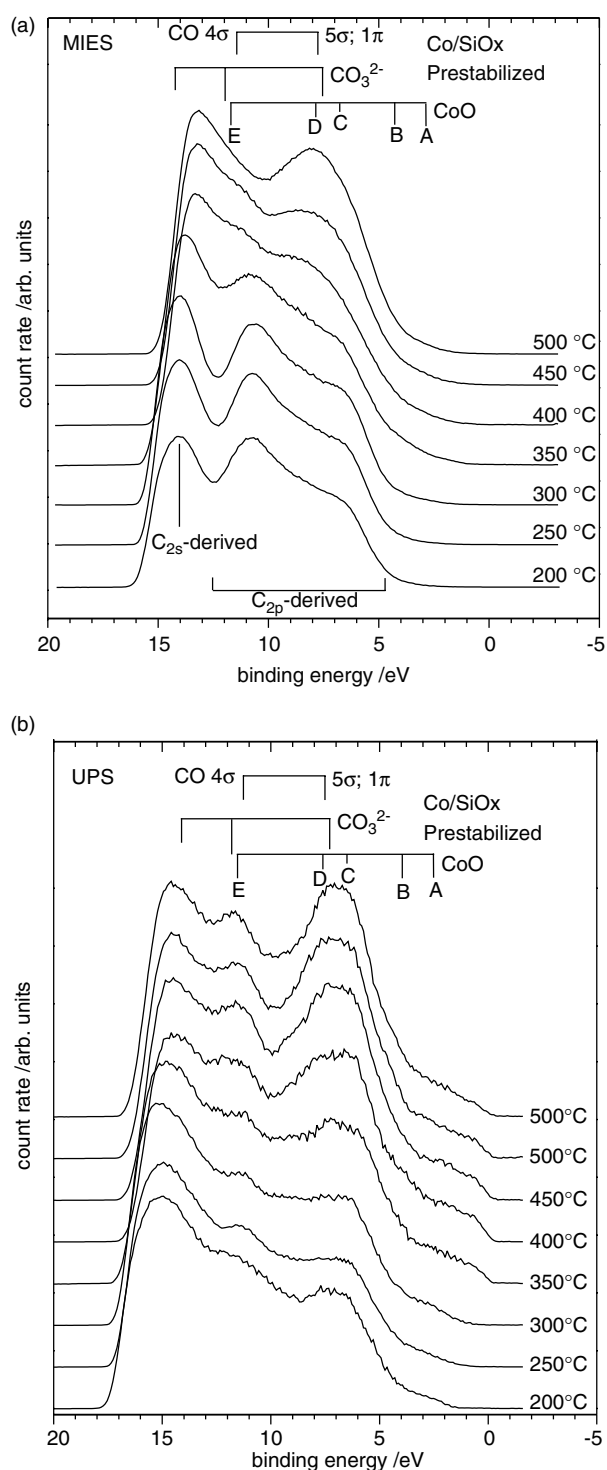


Figure 3. Spectra of pre-stabilized cobalt NPs as a function of the substrate temperature: (a) MIES; (b) UPS.

that a closed layer of the particles was obtained. Heating to about 250 °C was required to remove surface contaminations that apparently originate from residual solvent molecules. Fig. 3 displays the MIES (a) and UPS (b) spectra of the surface-deposited pre-stabilized cobalt particles as a function of surface temperature. Also shown are the energetic positions

of the main structures in the results of the previous section. For completeness we have also included the positions of the features due to carbonate (CO_3) groups as found at metallic surfaces.²¹

We concentrate on the UPS results of Fig. 3b: below 250 °C the emission seen between E_F and the valence band maximum is confined to the region between 2 and 5 eV, and can be attributed to the ionization of π molecular orbitals (MOs) from the aromatic rings of residual toluene solvent molecules on the surface of the particles (see below). Above 350 °C the emission fills the entire region between 0 and 5 eV, and cannot be attributed anymore to the ionization of organic molecules. The results from oxygen-exposed planar cobalt films suggest that it is due to 3d Co^{2+} ionization, i.e. stems from cobalt species in an oxidic and/or CO_x environment. This is supported by the emission seen in the range 5 to 17 eV: three structures are seen at $E_B = 7.1, 11.8,$ and 13.9 eV in the UPS spectra above 250 °C. On the one hand, the available film results do not allow for a unique identification of the species terminating the particles surface. On the other hand, it appears safe to state that the formation of Co–O and Co– CO_x bonds contributes to a large extent to the pre-stabilization of the cobalt particles' surface. From the fact that the intensity in the energy range from 0 to 5 eV, attributable to A;B, is relatively low, we conclude that, under the present preparation conditions, most of the intensity observed in the valence-band region (about 70%) is due to Co– CO_x bonds, not Co–O bonds. On the other hand, the MIES spectra do not show the features caused by Co– CO_x bonds and Co–O bonds very clearly, probably because the uppermost layer still contains some fragments of the solvent molecules, present prior to the heating.

Studies on peptized cobalt particles

Figure 4 shows the MIES (a) and UPS (b) results for pre-stabilized cobalt particles, peptized by KorantinSH (see 'Experimental details' section) and suspended on an SiO_x substrate from toluene solution. XPS and STM/atomic force microscopy measurements indicate that a dense film of peptized particles was produced.

The MIES spectra can be subdivided into two regions. Region I ($E_B = 0$ to 4 eV): below 250 °C substrate temperature very little emission can be noticed in the region between E_F and the top of the valence band, 4.5 eV below E_F . Taking into account a work function of 3 eV, we obtain 7.5 eV as an estimate for the width of the band gap.¹⁴ This particular electronic structure is typical for films of organic molecules, as discussed in detail by Harada *et al.*⁴ Only, if emission from π MOs of aromatic molecules were to contribute significantly to the spectra would spectral features be seen between $E_B = 4.5$ and 6 eV, as exemplified for ionization of benzene and its derivatives.^{12,22–24} As can be seen in particular in the UPS results, emission at E_F becomes visible beyond about 250 °C, indicating that the film, by partial thermal decomposition, becomes sufficiently thin to allow electrons, ejected from the surface of the pre-stabilized cobalt particles,

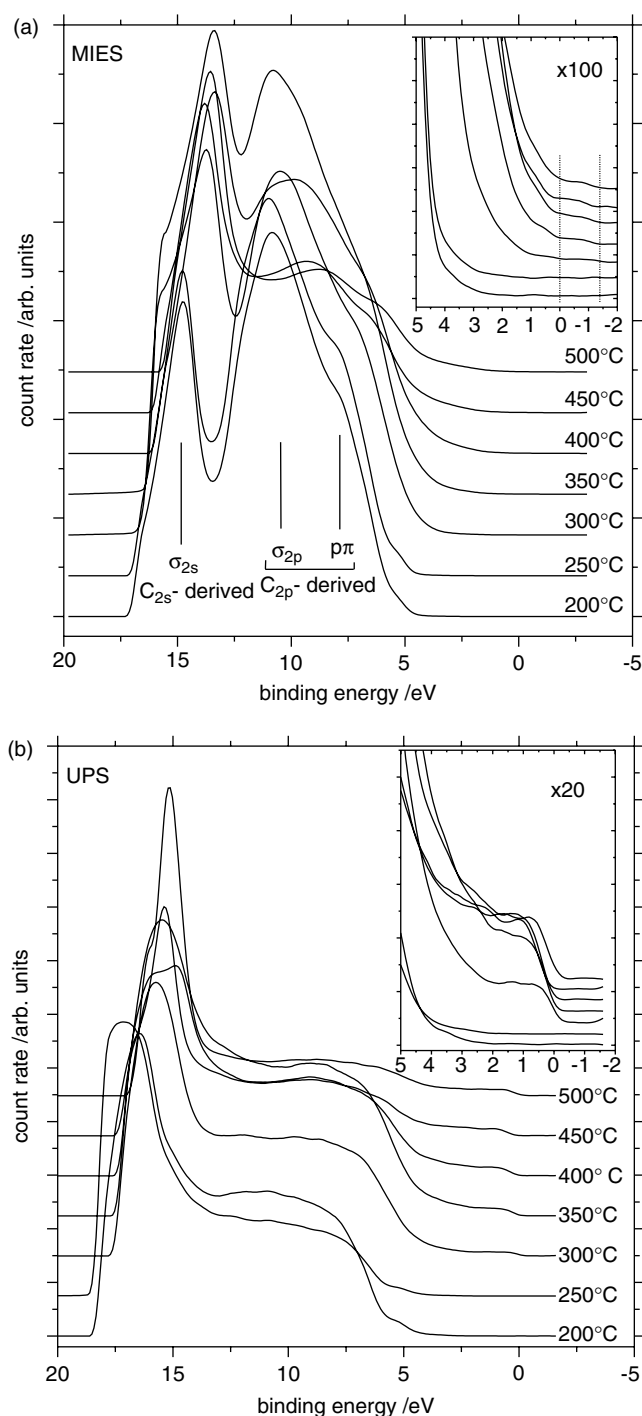


Figure 4. Spectra of the cobalt NPs peptized by KorantinSH versus substrate temperature: (a) MIES; (b) UPS.

to contribute to the spectral emission. On the other hand, no significant changes are to be seen in the spectra below 250 °C, suggesting that, up to this point, the organic shell remains thermally stable.

Region II ($E_B > 5$ to 15 eV): emission from organic molecules is seen typically,⁴ and is normally due to C 2p-derived MOs (5 to 12 eV) and C 2s-derived MOs (13 to

15 eV). For *n*-alkanes the MOs can be classified into three types: $p\pi$ consists of the C 2p_z and H 1s atomic orbitals (AOs; pseudo- π character), spreading essentially normal to the plane of the molecular frame. σ_{2p} is made up from the C 2p_{x,y} and H 1s AOs, and σ_{2s} is composed of the C 2s and H 1s AOs. All *n*-alkanes have an energy gap of about 4 eV width between the $p\pi$; σ_{2p} and σ_{2s} MOs. The shape of the spectral structures in region II is dependent on the particular configuration of the molecular frame of the molecule under consideration, as well as from attached ligands and/or functional groups. In the particular case under study, detailed information on the spectral features in region II can be obtained as follows: chemical intuition suggests that the long-chain carbonic acids should be oriented perpendicular to the cobalt particles' surface, with their functional carboxyl (COO) group establishing the bond between the carbonic acid and the particle surface. Thus, MIES can be expected to probe the MOs of the *n*-alkane chains, whereas those of the functional group are shielded from access by the He*. The interaction will be selective because of their particular spatial structure; in the present case, the MOs expected to interact efficiently with the He* are the σ_{2p} MOs with a large charge density at terminating hydrogen atoms.⁴ On the contrary, for organic chains lying flat on the surface, $p\pi$ emission at energies close to the top of the valence band would be expected to dominate the spectra.⁴

Indeed, inspection of the MIES spectra of *n*-alkanes deposited onto solid surfaces supports these considerations. The local distribution of MOs outside the molecular surface was probed by MIES for two molecular orientations of *n*-alkane chains, lying and standing on the substrate. Films of hexacosane (C₂₆H₅₄), hexatriacontane (C₃₆H₇₄), and tetratetracontane (C₄₄H₉₀) were prepared on a graphite substrate at 213 K and are known to lie flat on the substrate surface.⁴ Although the general structure of the spectra (a separation into two parts from contributions of C_{2p}-derived MOs (5–12 eV) and C_{2s}-derived MOs (13–15 eV)) is similar to ours, the relative intensities differ from those seen in Fig. 3a: the main contribution is seen close to the valence band maximum and originates from $p\pi$ MOs as the comparison with first principles calculations shows.⁴ On the other hand, the spectra obtained from 68 monolayers of C₃₆H₇₄ and 34 monolayers of C₄₄H₉₀ on copper, deposited at room temperature, are very similar to ours. In this case, the organic chains are known to stand upright from the surface, and the comparison with first principles calculations confirms that the emission is dominated by the contributions from those σ_{2p} MOs having a large charge density at the terminal hydrogen atoms.

As a consequence, the MIES spectra of the films discussed above can be regarded as fingerprints for the lying and standing orientations of alkyl chains, and, thus, can be used for the identification of the exposed part of surface molecules having long hydrocarbon units. In the present case, the 'fingerprint' spectra suggest that the emission seen in region II of Fig. 3a is due to the interaction of He* with *n*-alkane chains standing upright from the particles surface; in Fig. 3a we have identified the spectral features accordingly.

'Fingerprint' UPS spectra of organic molecules with carboxyl functional groups²⁵ indicate that the ionization of MOs of the COO functional group of KorantinSH would produce a contribution between $E_B = 4$ and 6 eV, which is not seen in the present case, neither with UPS, nor with MIES. This is strong evidence that the functional group is indeed oriented towards the particle surface, being responsible for the chemical interaction between particle and shell, and corresponds well to the partial substitution of Co–C by Co–O bonds obtained from the XAS results.

On the basis of the results presented in the 'Investigation of the particle core' section, an attempt can be made to identify the emission appearing in the band gap (between E_F and $E_B = 5$ eV) during thermal decomposition of the organic shell: it is rather similar to that seen from the pre-stabilized particles at the corresponding temperatures. Thus, we conclude that above 250 °C the surface of the pre-stabilized particles becomes accessible to our techniques; the emission seen in the band gap after partial decomposition of the shell of organic molecules is due to the ionization of C–O and/or CO_x groups that form the stabilizing layer of the pre-stabilized cobalt particles.

SUMMARY

Nanoscope cobalt particles (typically 4 to 10 nm), intended for ferrofluidic applications, were produced by thermolysis of Co₂(CO₈). They were isolated after their pre-stabilization by smooth oxidation in solution. We have measured and interpreted the cobalt K-edge X-ray absorption spectra (XANES, EXAFS), photoelectron spectra (UPS(HeI)) and the MIES spectra of the pre-stabilized cobalt particles and peptized particles. Auxiliary measurements on bare and gas-exposed cobalt films were carried out for comparison with the results obtained from the nanoscopic particles, and greatly contribute to their understanding and interpretation. The XAS results suggest that one is dealing with a core–shell system in which the core is formed by metallic cobalt, most likely in the f.c.c. phase. The shell properties are sensitive to the parameters of the synthesis and peptization. In qualitative agreement with the XANES spectra, the EXAFS analysis suggests that, in the course of the peptization process, Co–C coordination, which dominates in the shell of the pre-stabilized particles, may be substituted by Co–O coordination.

From the MIES and UPS results we conclude that the particles' stabilization against moisture results from the formation of Co–CO_x and Co–O groups at their surface during the oxidation procedure. Peptization of the pre-stabilized particles by KorantinSH leads to their encapsulation by a dense organic shell, stable up to about 250 °C. The carbonic acid molecules of the shell are oriented predominantly perpendicular to the surface of the particles, whereby the carboxyl functional groups link the shell and the

particles, and their alkyl chains are directed away from the particles surface.

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