

Interaction of Fatty Acid Monolayers with Cobalt Nanoparticles

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ABSTRACT

Stable colloidal suspension of magnetic nanoparticles is challenging owing to both van der Waals forces and magnetic dipolar interactions. Thus, it is essential to coat magnetic nanoparticles with a surfactant during chemical synthesis in order to prepare well-dispersed nanoparticle colloid. In the present study, cobalt nanoparticles (~15 nm in size) were synthesized with the fatty acid (oleic acid) as a surfactant. The chemical interaction of the surfactant with the Co nanoparticles was studied by using Fourier transform infrared spectroscopy (FTIR) and X-ray photoelectron spectroscopy (XPS). The results indicated that oleic acid gets chemisorbed as a carboxylate on the Co nanoparticle surfaces, and the two oxygen atoms in the carboxylate are coordinated symmetrically to the Co atoms, leading to the formation of the covalent Co–O bond. This result has implications for the strong interaction between the surfactant and Co nanoparticle, which enhances the stability of Co colloid.

Introduction. Magnetic nanoparticles have attracted increasing interest among researchers of various fields due to their promising applications in high-density magnetic recording media¹ and biomedical, such as magnetic resonance imaging (MRI), cell and DNA separation, drug delivery, gene cloning, and hyperthermia for cancer therapy, etc.². To apply nanoparticles in various potential devices and architectures, it is very important to control the size and shape and to keep the thermal and chemical stability of the nanoparticles.^{3–5} As the size of nanoparticles decreases, the surface effect becomes more significant due to increase in the volume fraction of surface atoms within the whole particle.

In the past decade, colloidal solution synthesis has been widely used as an efficient route to control the particle size and shape. During the synthesis of colloids, surfactants are essential to disperse and stabilize nanoparticles in the solvent.^{6–9} For example, organic thiols are used to coat the surface of gold nanoparticles,^{10,11} and other analogous systems include carboxylic on Au,¹² carboxylates on Ag,^{13,14} poly(acrylic acid) on Cu,⁸ as well as oleic acid and trioctylphosphine on Co.¹⁵ Surface chemistry is of great importance to understand the chemical and physical properties of nanoparticles. For instance, the surfactant, which forms a covalent bonding to metal nanoparticles, can give an

enhanced stability of nanoparticles. Understanding the interaction between the surfactant and the nanoparticles is critical and essential to understanding synthesis and application of nanoparticles.

Co nanocrystals display a wealth of size-dependent structural, magnetic, electronic, and catalytic properties. In particular, the exponential dependence of the magnetization relaxation time on volume has spurred intensive studies of Co nanocrystal synthesis for magnetic storage purpose.¹⁶ It is very difficult to make isolated Co nanoparticles without a surfactant, in part because the forces between the particles are large. Although fatty acid, especially oleic acid is a commonly used surfactant to encapsulate the Co nanoparticles, few studies have been carried out on the chemical structure of the interface between the fatty acid and the Co nanoparticles. In the present work, Co nanoparticles coated with oleic acid are synthesized by the wet chemical method. The chemical structure of the surfactant adsorbed on the Co nanoparticles has been identified, and the interaction between the surfactant and the Co nanoparticles has shed more insight into the function of the molecules adsorbed on the particles.

Experimental Section. A typical detailed synthesis route is described elsewhere.^{1,16} In brief, 1.0 g Co (CH₃COO)₂·4H₂O and 1.5 mL oleic acid were dissolved and mixed in 40 mL diphenyl ether (DPE) and heated to 200 °C under N₂ atmosphere. In a separate flask, 4 g 1,2-dodecanediol was dissolved in 10 mL DPE and heated to 80 °C for 10 min to be used as a reducing solvent. After heating to 200 °C, 1

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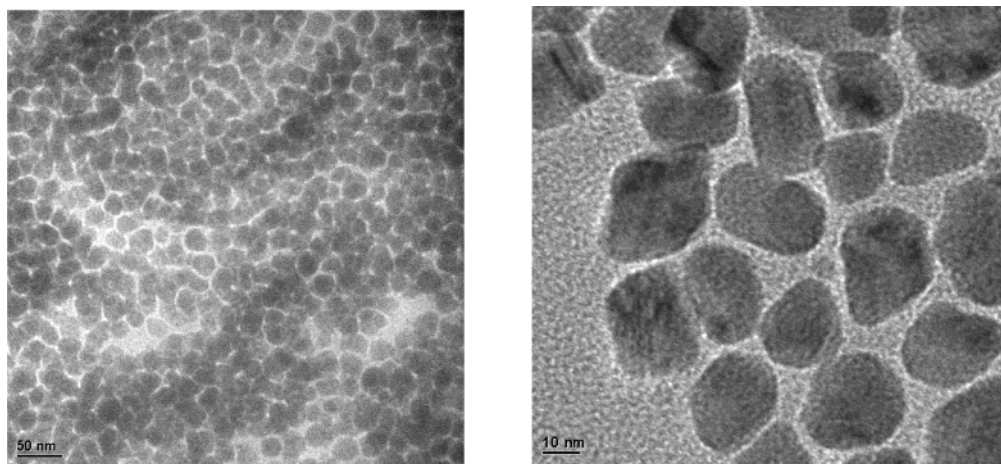


Figure 1. TEM micrographs of cobalt nanoparticles. (a) Ensemble of cobalt nanoparticles, (b) high magnification image of cobalt nanoparticles. The film was drop-cast by putting a drop of hexane-dispersed Co nanoparticles on carbon-coated copper grid.

mL trioctylphosphine was added to the mixture and then heated to 250 °C. Subsequently, the reducing solvent was injected into the mixture. The mixture was held at 250 °C for 30 min until the reduction was complete (visually, the mixture became black from purple). After the reaction, the solution containing Co nanoparticles was cooled to room temperature. Ethanol was then added to precipitate Co nanoparticles. After washing several times with ethanol, the precipitated Co nanoparticles were collected for analysis. The morphology of the Co nanoparticles and the self-assembly of the nanoparticles was studied by a Hitachi HF-2000 cold field emission gun (cFEG) transmission electron microscope (TEM). For TEM observation, the nanoparticles were dispersed in hexane and then deposited on an amorphous carbon-supported Cu grid.

The infrared spectra (IR) were obtained with a NEXUS 870 Fourier transform spectrometer (Thermo Nicolet Corp.). A ZnSe crystal attachment together with the mercury cadmium telluride detector were used to record the attenuated total reflection (ATR) spectrum of pure liquid oleic acid. Each spectrum was obtained by averaging 64 interferograms with resolution of 4 cm^{-1} . The transmission spectra for the surfactant-coated Co nanoparticles were taken after making pellets with KBr powder.

X-ray photoelectron spectroscopy (XPS) analyses were performed with an Omicron ESCA probe, which was equipped with EA125 energy analyzer. Photoemission was stimulated by a monochromated Al $K\alpha$ radiation (1486.6 eV) with the operating power of 300 W. A low-energy electron flood gun was employed for charge neutralization. Survey scan and high-resolution scan were collected using pass energies of 50 and 25 eV, respectively. Binding energies of spectra were referenced to the C 1s binding energy set at 284.8 eV. Prior to XPS measurement, the powders were pressed to form a pellet, and then the pellet was put into the entry-load chamber to pump for 4 h.

Results and Discussion. Figure 1 shows TEM micrographs of cobalt nanoparticles coated with oleic acid. It can be seen that Co nanoparticles assemble very well. Each particle is separated from its neighbors by the organic ligand

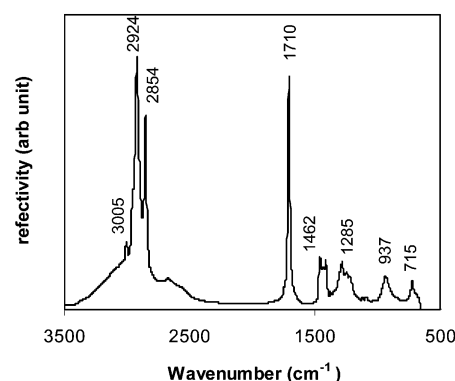


Figure 2. FTIR spectrum of neat/pure oleic acid. A ZnSe crystal attachment together with the mercury cadmium telluride detector was used to record the attenuated total reflection (ATR) spectrum of pure liquid oleic acid.

shell. The particle size is about 15~20 nm. The high-magnification TEM image (Figure 1b) shows that the particles are not fully spherical.

To better understand the adsorption mechanism of the oleic acid on the surface of cobalt nanoparticles, Fourier transform infrared (FTIR) measurements were carried out on the pure oleic acid and the composite Co nanoparticles capped with oleic acid, respectively. Figure 2 represents the typical IR spectrum of the pure oleic acid. The assignments of peaks are listed in Table 1. The broad feature between 3500 and 2500 cm^{-1} was undoubtedly due to the O–H stretch of the carboxylic acid. No other functional group had such a broad and intense band at high wavenumber. Two sharp bands at 2924 and 2854 cm^{-1} , which were superimposed on the O–H stretch, were attributed to the asymmetric CH_2 stretch and the symmetric CH_2 stretch, respectively. The intense peak at 1710 cm^{-1} was derived from the existence of the C=O stretch, and the band at 1285 cm^{-1} exhibited the presence of the C–O stretch.^{13,14} The O–H in-plane and out-of-plane bands appeared at 1462 and 937 cm^{-1} , respectively.

Figure 3 reveals the IR spectrum obtained from the Co nanoparticles coated with oleic acid. With the surfactant, the asymmetric CH_2 stretch and the symmetric CH_2 stretch shifted to 2919 and 2850 cm^{-1} , respectively. The surfactant

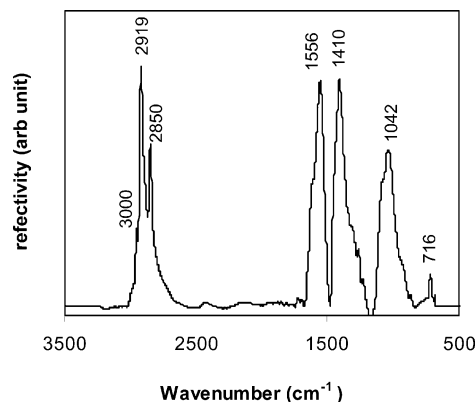


Figure 3. FTIR spectrum obtained from oleic acid coated Co nanoparticles. The main resonances are identified in the figure and discussed in the text with reference to *n*-alkane and C=O vibrations on Co solid surfaces.

Table 1. Vibrational Mode Assignments of Oleic Acid

peak (cm ⁻¹)	assignment
3500–2500	O–H stretch
3005	C–H stretch in C=C–H
2924	asymmetric CH ₂ stretch
2854	symmetric CH ₂ stretch
1710	C=O stretch
1462	in plane O–H band
1409	CH ₃ umbrella mode
1285	C–O stretch
937	out-of-plane O–H stretch
715	CH ₂ rocking

molecules in the adsorbed state were subject to the field of the solid surface. As a result, the characteristic bands shifted to a lower frequency region¹⁹ and indicate that the hydrocarbon chains in the monolayer surrounding the Co nanoparticles are in a close-packed, crystalline state. It is worth noting that the C=O stretch band of the carboxyl group, which is present at 1710 cm⁻¹ in the IR spectrum of pure liquid oleic acid, is absent in the spectrum of the coated Co nanoparticles. Instead, two new bands at 1556 and 1410 cm⁻¹ are characteristic of the asymmetric $\nu_{as}(\text{COO}^-)$ and the symmetric $\nu_s(\text{COO}^-)$ stretch. This reveals that oleic acid is chemisorbed as a carboxylate onto the Co nanoparticles, and the two oxygen atoms in the carboxylate are coordinated symmetrically to the Co atoms.

To further examine the chemical structure of the surfactant-coated Co nanoparticles, the XPS spectra of C1s, O1s, and Co2p core levels were obtained (Figure 4). Two C1s peaks at 284.8 and 288.2 eV are ascribed to the carbon atoms in the aliphatic chain (C–C) and the carboxylate (–COO⁻) moiety, respectively, which is consistent with the data obtained from carboxylates in the previous literature.^{17,18} No C1s peak corresponding to carboxylic carbon (–COOH) appeared in the spectrum, indicating the absence of free acid on the coated Co nanoparticles. This is also confirmed by the feature of the O1s peak at 531.2 eV (Figure 4b). A single and symmetric O1s peak reveals the presence of two symmetric oxygen atoms in the carboxylate (COO⁻) moiety and the absence of the C=O bond in the coated Co

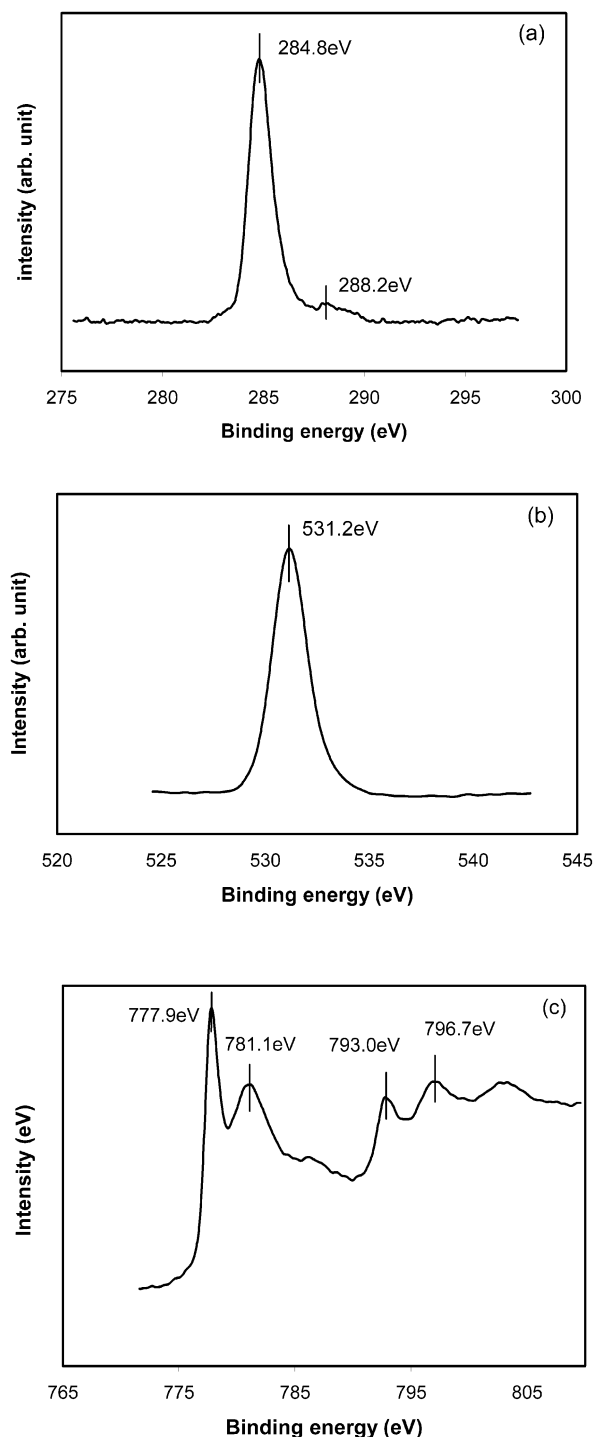


Figure 4. XPS spectra obtained from the oleic acid coated Co nanoparticles: (a) C1s core level, (b) O1s core level, (c) Co 2p core level.

nanoparticles. The Co 2p doublet with the binding energies of 781.1 and 796.7 eV implies the Co–O bond formation in the carboxylate, while the Co2p doublet with the binding energies of 777.9 and 793.0 eV corresponds to the metallic Co atoms underneath the chemisorbed carboxylate.

It is known from the previous investigations,^{19,20} when carboxylic acids adsorb from solution to the metal surface, there may exist two different bonding types of carboxylate groups to the metal, i.e., either a bidentate bond through two

equivalent oxygen atoms or a monodentate bond with inequivalent oxygen atoms. In case of the monodentate bond, the C=O bond is still present and the acid hydrogen is substituted by metal atoms. In this way, the IR spectrum would have displayed a strong band at 1700~1730 cm⁻¹, and the O 1s XP spectrum would have presented another peak at around 533 eV in addition to the one at around 531 eV. In fact, the present study demonstrates that the IR band at 1700 cm⁻¹ disappears after the oleic acid has been adsorbed on the surface of Co nanoparticles. In addition, the O1s XPS spectrum that was obtained from the coated Co nanoparticles illustrates a single peak instead of two non-equivalent peaks. Therefore, it can be inferred that the carboxylate group is bound to the surface of Co nanoparticles symmetrically through its two oxygen atoms.

Furthermore, based upon previous studies of carboxylates,²¹⁻²³ the interaction between the carboxylate head and the metal atom is categorized as four types: monodentate, bridging bidentate, chelating bidentate, and ionic interaction. The wavenumber separation, Δ , between the $\nu_{\text{as}}(\text{COO}^-)$ and $\nu_{\text{s}}(\text{COO}^-)$ IR bands can be used to diagnose the type of the interaction between the carboxylate head and the metal atom. The largest Δ (200~320 cm⁻¹) is corresponding to the monodentate interaction and the smallest Δ (<110 cm⁻¹) is for the chelating bidentate. The medium range Δ (140~190 cm⁻¹) is for the bridging bidentate. In the present work, the Δ (1556-1410 = 146 cm⁻¹) is ascribed to bridging bidentate, where the interaction between the COO group and the Co atom is covalent.

Summary. The experimental results showed that the C=O stretch band of carboxyl group, which is present at 1710 cm⁻¹ in the IR spectrum of pure liquid oleic acid, is absent in the spectrum of the coated Co nanoparticles. Instead, two new bands at 1556 and 1410 cm⁻¹ are characteristic features of the asymmetric $\nu_{\text{as}}(\text{COO}^-)$ and the symmetric $\nu_{\text{s}}(\text{COO}^-)$ stretch. This indicates that oleic acid is chemisorbed as a carboxylate onto the Co nanoparticles, and the two oxygen atoms in the carboxylate are coordinated symmetrically to the Co atoms. A single and symmetric O1s peak indicates the presence of two symmetric oxygen atoms in the carboxylate (COO⁻) moiety and the absence of the C=O bond in the coated Co nanoparticles. The Co 2p doublet with the binding energies of 781.1 eV and 796.7 eV implied

the formation of the Co-O bond in the carboxylate. Because oleic acid is widely used as a surfactant in colloids synthesis, this study can help to better understand the interaction and the chemistry between the surfactant and the metal nanoparticles.

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