Coating of Amorphous Iron Nanoparticles by Long-Chain Alcohols

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Coating of long-alkyl-chain alcohols on nanophased amorphous iron nanoparticles has been carried out using the self-assembled technique. The formation of chemical bonds between the substrate and the alcohols was demonstrated by FTIR and XPS measurements. The superparamagnetic nature of the small coated nanoparticles is detected in the magnetization measurements.

Introduction

The most favorable surfactant for metals, metal oxides, and ceramic materials is the thiol chromophore. It has been used in the coating of flat surfaces as well as isolated particles using both Langmuir−Blodgett and self-assembled methods.[1−9] Alcohols on the other hand have been used less frequently for coating particles and flat surfaces, perhaps due to weaker chemical bonds with the substrates.

Octadecyl alcohol[10] was coated on Fe, Ni, Cr, and Pt surfaces at elevated temperatures and did not form closed packed monolayers on Fe. Self-assembled monolayers of *n*-decanol[11] on a Au(111) film were studied by using the STM technique. The molecules were shown to be arranged in a hexagonally closed-packed array with an interchain spacing of 0.5 nm. Octadecyl alcohol[12] was also used in coating magnetite particles which had undergone a first layer coating by silica. This was done in order to produce a stable dispersion of the magnetic particles in a non-aqueous solution. More recently porous Si particles[13] were coated by alcohols and their luminescence was observed to be hardly affected by such coatings.

We have used amorphous iron and amorphous iron oxide[14,15] nanoparticles as substrates for self-assembled coatings with sodium dodecyl sulfate (SDS), octadecyltrichlorosilane (OTS) and long-chain thiols.[16−19] We have measured the magnetic properties, thermal stability, and reactivity of these coated particles. In this paper, we report the room-temperature coating of 1-octanol, 1-dodecanol, and 1-tridecanol on amorphous iron nanoparticles. The characterization of the coated particles was carried out by IR spectroscopy, XPS, and measurements of magnetization and floatability properties.

Experimental and Discussion

The amorphous iron nanoparticles were prepared according to the process outlined by Suslick.[20,21] In short, a 1 M solution[19] of $Fe(CO)_5$ in decane was sonicated under argon for 3 h to prepare the amorphous iron. The amorphous iron was coated with the alcohols by taking a 12:1 iron/alcohol molar ratio in 20 mL of ethanol. The washing and drying process was similar to that described for the thiols.[18]

To probe whether any interaction has occurred between the amorphous iron and the alcohols we measured the floatability[22] of the coated particles and compared the results with those of the uncoated iron nanoparticles. We also demonstrated the existence of the interaction by comparing the catalytic activity of bare amorphous iron nanoparticles toward H_2O_2 decomposition with that of the coated particles. Finally, to determine whether the interaction is merely a physical adsorption or chemical bonds are formed between the substrate and the alcohol, we have measured the infrared and X-ray photoelectron spectra and the magnetism of the coated particles and compared the results with those of the uncoated iron particles.

We have used floatability measurements (total floating and total sinking) to demonstrate that the alcohol molecules are adsorbed (physically or chemically) on the surface of the iron nanoparticles. In this method the coated particles were placed on the surfaces of a series of liquids with different surface tensions. The surface tension of each solution was measured in a torsion balance, according to the De Noüy method. The uncoated iron nanoparticles sink even in pure water. If the "critical spreading

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(1) Ulman, A. *An Introduction to Ultrathin Organic Films From Langmuir−Blodgett to Self-Assembly;* Academic Press: Boston, MA, 1991.
(2) Ulman, A. *Chem. Rev.* **1996**, *96*, 1533.
(3) Hostetler, M. J.; Stokes, J. J.; Murray, R. W. *Langmuir* **1996**, *12*, 3604.
(4) Weisbecker, C. S.; Merritt, M. V.; Whitesides, G. M. *Langmuir* **1996**, *12*, 3763.
(5) Nuzzo, R. G.; Allara, D. L. *J. Am.. Chem. Soc.* **1983**, *105*, 4481.
(6) Sandroff, C. J.; Garoff, S.; Leung, K. P. *Chem. Phys. Lett.* **1983**, *96*, 547.
(7) Laibinis, P. E.; Whiteside, G. M.; Allara, D. L.; Tao, Y.-T.; Parikh, A. N.; Nuzzo, R. G. *J. Am. Chem. Soc.* **1991**, *113*, 7152.
(8) Delmarche, E.; Michel, B.; Kang, H.; Gerber, Ch. *Langmuir* **1994**, *10*, 4103.
(9) Poirier, G. E.; Pylant, E. D. *Science* **1996**, *272*, 1145.
(10) Bascom, W. D. *J. Colloid Interface Sci.* **1968**, *26* (1), 89.
(11) Yeo, Y. H.; McGonigal, G. C.; Yackoboski, K.; Guo, C. X.; Thomson, D. J., *J. Am. Chem. Soc.* **1992**, *96*, 6110.
(12) Philipse, A. P.; van Bruggen, M. P. B.; Pathmamanoharan, C. *Langmuir* **1994**, *10*, 92.
(13) Namyong, K. Y.; Laibinis, P. E. *J. Am. Chem. Soc.* **1997,** *119* (9), 2297.
(14) Cao, X.; Koltypin, Yu.; Kataby, G.; Prozorov, R.; Gedanken, A. *J. Mater. Res.* **1995**, *10*, 2952.
(15) Cao, X.; Prozorov, R.; Koltypin, Yu; Kataby, G.; Felner, I.; Gedanken, A. *J. Mater. Res.* **1997**, *12*, 402.
(16) Rozenfeld, O.; Koltypin, Y.; Bamnolker, H.; Margel, S.; Gedanken, A. *Langmuir* **1994**, *10*, 3919.
(17) Kataby, G.; Koltypin, Y.; Cao, X.; Gedanken, A. *J. Cryst. Growth* **1996**, *166*, 760.
(18) Kataby, G.; Prozorov, T.; Koltypin, Y.; Cohen, H.; Sukenik, C. N.; Ulman, A.; Gedanken, A. *Langmuir* **1997**, *13*, 6151.
(19) Prozorov, T.; Kataby, G.; Prozorov, R.; Nitzan, B.; Gedanken, A. Submitted to *Chem. Mater.*
(20) Suslick, K. S.; Choe, S.-B.; Cichowlas, A. A.; Grinstaff, M. W. *Nature* **1991**, *353*, 414.
(21) Grinstaff, M. W.; Cichowlas, A. A.; Choe, S.-B.; Suslick, K. S.; *Ultrasonics* **1992**, *30*, 168.
(22) Marmur, A.; Chen, W.; Zografi, G. *J. Colloid Interface Sci.* **1986**, *113*, 114.

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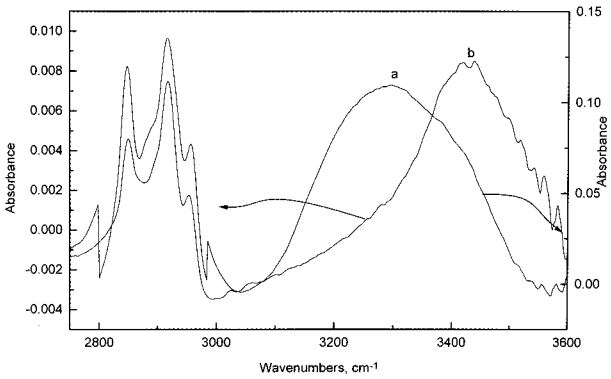

Figure 1. FTIR absorbance of (a) 1-tridecanol-coated amorphous iron and (b) 1-tridecanol.

Table 1. Characterization of Coatings by Floating Measurements

coating	surface tension float (dyn/cm)	surface tension sink (dyn/cm)	transition region (dyn/cm)
1-octanol	46.4	41.6	4.8
1-dodecanol	46.4	33.9	12.5
1-tridecanol	46.4	33.9	12.5

Table 2. Characterization of Coatings by FTIR

coatings	absorption, cm^{-1}	absorption width, cm^{-1}
1-octanol	2921.5	25.6
1-dodecanol	2919.8	22
1-tridecanol	2918.6	21.4

concentration" of these coated particles is higher than the surface tension of the liquid, they will sink; otherwise, they will float. In Table 1, we present the results of the floatability measurements of amorphous iron coated with different alcohols. Above a surface tension of 46.4 dyn/cm all the particles float. The existence of a transition region, in which a fraction of the particles sinks, is due to variations in the surface energies of the coatings and the degree of the coating. The results shown in Table 1 demonstrate that the coating of 1-octanol is superior to those of 1-dodecanol and 1-tridecanol. It means that the coating is not dependent on the length of the surfactant, and this is surprising. It is clear, however, that the floatability properties of the alcohol-coated particles are very different from those of the bare iron particles, indicating the existence of a coating on the surface.

Amorphous iron is known to catalyze the decomposition of H_2O_2 to oxygen and water. We have compared the rate of decomposition of H_2O_2 during catalysis by bare iron particles with that of the alcohol-coated iron particles. The results show that, after an incubation period, the rate of decomposition catalyzed by the bare iron particles is faster than that of the coated particles, although indirectly they are pointing to the existence of long-chain alcohols on the iron surface.

The nature of the interaction between the amorphous iron substrate and the coating alcohols was investigated by FTIR and XPS measurements. In Figure 1 we present the FTIR spectrum of tridecanol and the amorphous iron-coated tridecanol in the 2700−3600 cm^{-1} range. The room-temperature FTIR spectra were recorded on a Nicolet (Impact 410) spectrometer. The measurements were performed on KBr pellets each containing 1 mg of coated amorphous iron and 180 mg of KBr (FTIR grade). The absorption peaks at 2848.2 and 2918.6 cm^{-1} correspond to the CH_2 symmetric and antisymmetric stretching bands of the 1-tridecanol coating.

FTIR absorption frequencies and widths of CH_2 bands[23,24] can be used to evaluate the degree of order of the various coatings. The location of the absorption peaks of the CH_2 stretching mode, as well as the width of this band, is shown in Table 2 for the three different coatings. On the basis of the widths of the 2919-cm^{-1} bands, 1-octanol is the least organized coating. This is not surprising due to the more restricted interaction between the chains. If we compare, however, these widths to those for thiol-coated amorphous iron, the numbers for the C13 are almost identical. The most important evidence for the formation of a chemical bond between the alcohol and the iron is found in the O−H stretching mode region, 3000−3500 cm^{-1}. The O−H stretching vibration of the tridecanol at 3288 cm^{-1} disappears completely. The band peaking at 3420−3430 cm^{-1} is due to water molecules related to the KBr powder.

The XPS spectra of uncoated and alcohol-coated iron are shown in Figure 2. The spectra are of the Fe(2p)[25−27] photoelectrons of bare amorphous iron and the alcohol-coated iron particles, respectively. The spectrum of the bare iron is much broader than the corresponding spectrum of the coated particles, due to the partial oxidation of the iron in the uncoated particles. The XPS of the crystalline iron should exhibit a peak at 707 eV, and the Fe_2O_3 peak is reported at 710.9. If the observed shoulder at 707 eV is indeed due to zerovalent iron, then its disappearance in the alcohol-coated iron must be due to bonding to the tridecanol. The peak detected at 719 eV, in the bare particles, assigned to Fe_2O_3, undergoes a red shift to 716 eV upon its coating by the tridecanol. We conclude at this stage that the oxidized surface layer and zerovalent iron atoms that are found on the surface or close to the surface are both bonding the tridecanol molecules. The remaining question is whether the alcohol is mostly bonded through Fe−O(−O−) bonds or through Fe−O bonds. The O(1s)[25−27] XPS spectrum does not provide a conclusive answer to this question. The spectra, depicted in Figure 3, show that the most intense peak, which appears at 530.1 eV in the bare iron, undergoes a slight red shift upon its coating with tridecanol to 529.95 eV. This fits very well the reported binding energies for Fe_2O_3 (530.2 eV) and for Fe−O*(−O−H) (530.1 eV). In other words a red shift of 0.1 eV can be explained by formation of the Fe−O(−O) bonds. However, it is also consistent with a surface composed only of Fe−O−C−C... bonds, as the binding energies of the Fe_2O_3 almost coincide with those of the Fe−O(−O−) moiety. This explanation would require the elimination of a water molecule when the alcohol forms a bond with the oxidized iron oxide (Fe_2O_3) on the surface and the elimination of a hydrogen atom when it interacts with the bare iron atom. The IR spectrum of the alcohol-coated iron particles shows two relatively strong bands at 1045 and 1093 cm^{-1}. The IR spectrum of Fe−O(−O−H) reveals a broad absorption feature peaked at 1120 cm^{-1}. This is an unassigned band which we tend to attribute to the O−O stretching mode. We conclude therefore that the alcohols are bonded to the surface of the iron particles through two channels, the first being through the Fe−O−O bonds which are due to the oxidized iron layer on the surface and the second, the predominant bonding, being through direct Fe−O−C bonds resulting from the zero valence iron atoms on the surface.

The results of magnetization loop measurements of the 1-octanol-, 1-dodecanol-, and 1-tridecanol-coated amorphous iron particles are depicted in Figure 4. The iron concentration was determined by ICPAES measurements (Spectroflame, Spectro, Kleve, Germany). The magnetization loop measurements were conducted at room temperature using an Oxford Instrument vibrating sample magnetometer (VSM). Saturation is not detected for any of the samples even at 15 KG. Similarly, we do not observe hysteresis for any of the three samples. This behavior is typical for a superparamagnetic[28−31] species. The loops shown in Figure 4 demonstrate shapes characteristic for paramagnetic particles and can be fitted to the Langevin[31−33] function. The

(23) Brandriss, S.; Margel, S. *Langmuir* **1993**, *9*, 1232.
(24) Tillman, N.; Ulman, A.; Schildkraut, S.; Penner, T. L. *J. Am. Chem. Soc.* **1988**, *110*, 6136.
(25) Maschhoff, B. L.; Armstrong, N. R. *Langmuir* **1991**, *7*, 693−703.
(26) Abdel-Samad, H.; Watson, P. R. *Appl. Surf. Sci.* **1997**, *108*, 371−377.
(27) Zaera, F. *J. Vac. Sci. Technol., A* **1989**, *7* (3), 640.
(28) Ishikawa, T.; Cai, W. Y.; Kandor, K. *J. Chem. Soc., Faraday Trans.* **1992**, *88*, 1173.
(29) Moumen, N.; Veillet, P.; Pielini, M. P. *J. Magn. Magn. Mater.* **1995**, *149*, 67−71.
(30) Murad, E. *Phys. Chem. Miner.* **1996**, *23*, 248−262.
(31) Morup, S. *Europhys. Lett.* **1994**, *28*, 671−676.
(32) El-Hilo, M.; O'Grady, K.; Chantrell, R. W. *J. Magn. Magn. Mater.* **1992**, *114*, 295.
(33) Moumen, N.; Pielini, M. P. *J. Phys. Chem.* **1996**, *100*, 1867−1873.

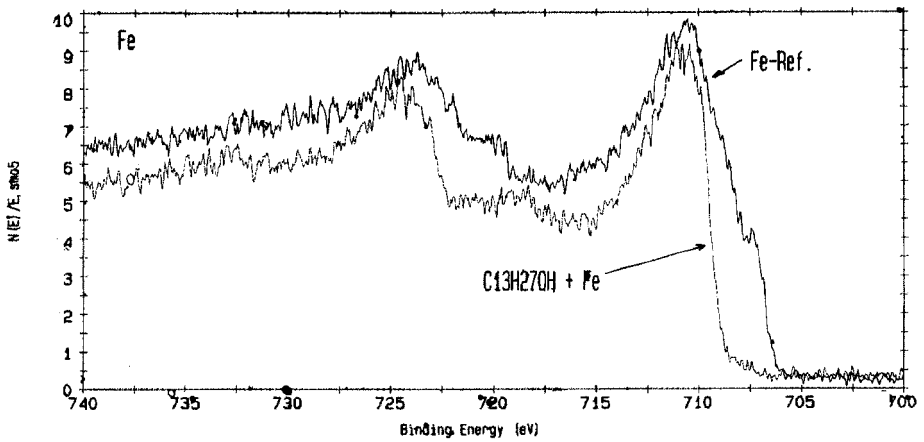

Figure 2. The Fe(2p) XPS spectrum of amorphous iron and 1-tridecanol-coated amorphous iron.

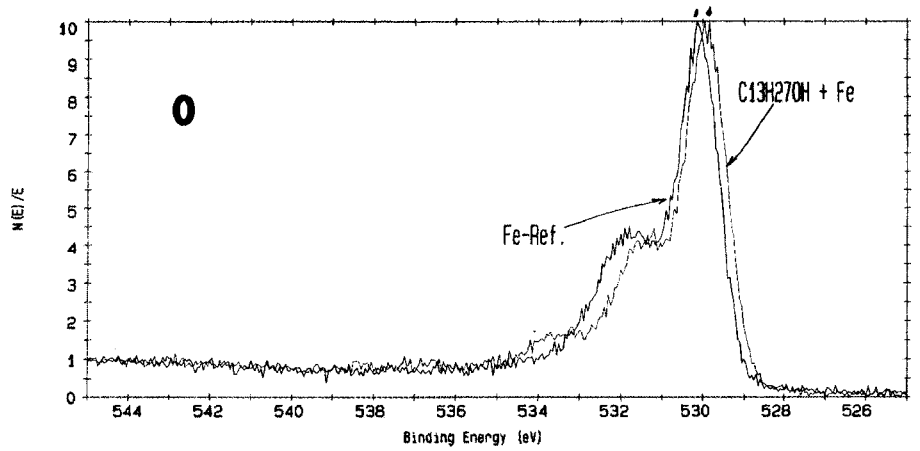

Figure 3. The O(1s) XPS spectrum of amorphous iron and 1-tridecanol-coated amorphous iron.

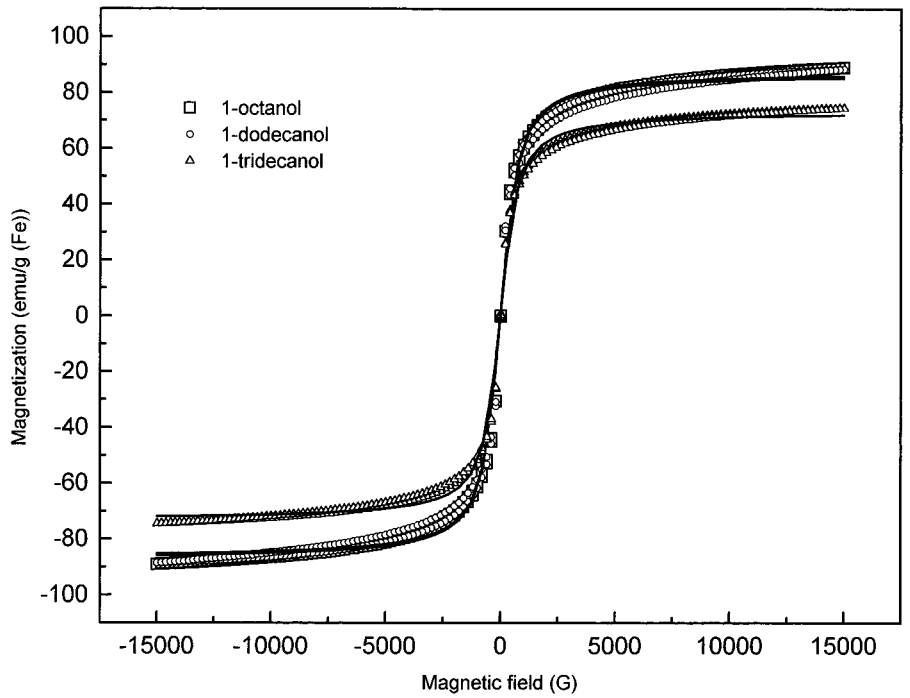

Figure 4. Magnetization loop of alcohol-coated amorphous iron particles. The circles, triangles, and squares present the experimental data. The full lines depict the calculated magnetization for each alcohol.

calculated data are presented in Figure 4, and a reasonable fit to the experimental results is obtained. Indeed, the least-squares fit is not perfect, the low-field slope is lower, and the high-field susceptibility of the calculated curve is also lower than the data. These deviations are due to the distribution of the iron particle sizes and possible dipole−dipole interactions between the particles.[31−33] Using low-field expansion of this function or a direct fit, we roughly estimate the magnetic particle size in our

materials for all three cases as 10−20 Å. This estimate is of course much smaller than that seen from direct TEM images. This is explained by taking into account agglomeration of magnetic particles. The magnetization measurements indicate that the 10−20-Å particles within the agglomerated particle are independent (i.e. there is no exchange interaction between them).

The dependence of the magnetization values on the length of the alkyl chain reveals the tridecanol-coated iron particles to have the largest magnetization. These results are contrary to those obtained for amorphous iron and amorphous Fe_2O_3-coated thiol particles, where the longer the alkyl chain, the weaker is the magnetization. Whether the differences in the magnetization loops of the alcohol-coated iron particles are meaningful or they are within the experimental error is now under careful study. However, the difference in magnetization values at large fields reflects differences due to the surfactant itself. The largest magnetization observed in tridecanol-coated material may be interpreted as a reduction of dipole fields due to magnetic particles separation. These results are contrary to those obtained for thiol-coated Fe and thiol-coated Fe_2O_3, where the largest magnetization is observed for the shortest thiol molecule. The magnetization of alcohol-coated iron is larger than that of thiol-coated particles (with the same surfactant to substrate molar ratio). When we compare the magnitude of the magnetism of dodecanethiol-coated iron and dodecanol-coated iron prepared with the same surfactant/substrate molar ratios, that of the alcohol is larger by a factor of about 2.5. We explain this as a result of a better coating obtained for the thiol which is better at shielding the magnetization of the iron core.

Several explanations are possible for the alkyl chain length dependence, although the complexity of the problem does not permit an unequivocal conclusion.

The straightforward factor, the difference in chemical bonding, may lead to different spin ordering on the particle surface. This may provoke a significant change in the magnetic surface anisotropy, thus being responsible for the observed effect.[34−36]

Another more speculative explanation may be a sign reversal (along the external field) of the effective internal dipole fields in the case of alcohol-coated iron. The direction of the internal dipole fields depends on the geometrical arrangements of the magnetic particles, the crystal, and the shape anisotropy. Thus, different surfactants may affect those properties and lead to the observed effects. Additional studies are now in progress to clarify this question.

We have demonstrated in this letter that alcohols can form a coating on amorphous iron nanoparticles through the formation of chemical bonds.

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(34) Jacobs, J. S.; Bean, C. P. In *Fine Particles, Thin Films and Exchange Anisotropy;* Jacobs, J. S., Bean, C. P., Eds.; Academic Press: New York, 1963.

(35) Slonczewski, J. C. *J. Magn. Magn. Mater.* **1992**, *117*, 368.

(36) Kodama, R. H.; Berkowitz, A. E.; Mcniff, E. J.; Foner, S. *J. Appl. Phys.* **1997**, *81*, 5552.