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Applied Surface Science 181 (2001) 173–178

applied
surface science

www.elsevier.com/locate/apsusc

Self-assembled (SA) bilayer molecular coating on magnetic nanoparticles

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Received 26 March 2001; accepted 26 June 2001

Abstract

Protectively and functionally coated magnetic nanoparticles are of special interest because of their important technological applications in diverse fields, ranging from biotechnology to transportation. In this paper, monolayer and bilayer surfactant coating on magnetite (Fe_3O_4) nanoparticles has been obtained using the self-assembly method. Magnetic properties such as magnetization, ZFC and FC curves, blocking temperature, hysteresis loop, coercivity and remanent magnetization of the SAM and bilayer coated magnetite nanoparticles have been investigated. The results show the efficacy of our synthesis approach not only to protect magnetic nanoparticles via surfactant-mediated self-assembly but also their stable suspension in a variety of appropriate liquid media. The superparamagnetic nature of the magnetic nanoparticles remains unchanged with self-assembled coatings and paves the way for their use in colloid suspension for device applications. © 2001 Published by Elsevier Science B.V.

Keywords: Self-assembly; Coating; Magnetite; Nanoparticles

1. Introduction

Interfacial and surface interactions with nanostructured materials are becoming increasingly important subjects in recent years. The ability to control physical and chemical properties of the surfaces is crucial for many applications [1–3]. Self-assembled monolayer (SAM) as a suitable technique for such studies has been paid increasingly more attention in wide variety of fields ranging from biology to materials science [1,4,5,7,11]. SAMs are defined as monomolecular films of suitable bi-functional molecules (e.g. a surfactant) formed spontaneously on a substrate upon

exposure to molecular (surfactant) solution. The principal driving force for the formation of these films is specific for the interactions between the surfactant head group and the substrate surface. Provided these interactions are strong, SAMs form stable films. Depending on the structure of the surfactant, these films can be disordered (liquid-like) or well packed, resembling the organization of crystals. The degree of order in monolayers is a product of many factors, including geometric considerations, electrostatic and dipole–dipole interactions within the monolayers, affinity of the head group of the surfactant to the surface, etc. Many studies of SAM coatings of various organic molecules on flat polished metallic and metal oxide surfaces and nanoparticles have been reported [6]. In comparison, publications describing the synthesis and characterization of self-assembled *multiple* coatings on nanoparticles remain an emerging field in

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the light of the renewed significance of nanostructured materials and devices. A notable exception in magnetic oxides is included in the work of Shen et al. [7] on magnetite stabilization using bilayer coatings. This work presents an extension of their work to incorporate additional physical and magnetic measurements. This approach is also being extended to other functional oxides including dielectric and ferroelectrics.

Coating of surfaces can often change the intrinsic physical–chemical properties of the nanoparticles. The study of coatings on the surface of nanostructured powders is of great interest, because the coating can alter the charge, functionality, and reactivity of the surface, and enhance the stability and dispersibility of the nanoparticles [7–10]. The coated magnetic nanoparticles are of special interest because of their important technological applications in disparate fields ranging from magnetic recording to bio-diagnostics and therapeutics.

In this paper, SAM and bilayer coatings on nanostructured magnetite particles have been investigated. Nanostructured Fe_3O_4 particles were prepared by coprecipitation of acidic solutions of Fe(II) and Fe(III). Fatty acids of lauric acid and decanoic acid were applied as surfactants. The size and size distribution of the coated powders, the magnetic properties, surfactant coverage on the particles were measured by transmission electron microscopy (TEM), superconducting quantum interference device (SQUID) magnetometry and thermogravimetric analysis (TGA), respectively.

2. Experimental

Iron(II) ferrous chloride, iron(III) ferric chloride and ammonium hydroxide (29.4%) were obtained from Fisher Scientific. Lauric acid ($\text{CH}_3(\text{CH}_2)_{10}\text{COOH}$) (99.5%) and decanoic acid ($\text{CH}_3(\text{CH}_2)_8\text{COOH}$) (99%) were received from Aldrich Chemical. All chemicals were used as received.

For preparation of magnetite particles, 2 g ferrous chloride was dissolved in 5 ml 2 M HCl solution and 3.2 g ferric chloride in 20 ml 2 M HCl solution. Ferrous chloride and ferric chloride solution were combined in a beaker with a magnetic stirring bar placed in the beaker to stir vigorously. At the same

time, 30 ml ammonium hydroxide solution was added slowly into the beaker by a pipette and magnetite in the form of a black precipitate, formed immediately. Stirring was continued for 15 min after adding ammonia hydroxide. Stirring was then stopped and a strong magnet was used to settle the black precipitate. Most of the liquid was then decanted and disposed of, and the remaining solution was stirred further. The solution was centrifuged for 2 min at the speed of 1800 rpm and the solution was decanted. Centrifuging was repeated five times to remove excess ammonia from the remaining solution. Finally, a black precipitate (magnetite) was obtained [12,13].

For SAM coating on nanosize magnetite particles, the 2 g as-prepared black precipitate was dispersed in 40 ml deionized (DI) water. A 2.5 g of lauric acid was dissolved in 40 ml DI water at 70°C. Lauric acid solution was added to the dispersed iron particles solution with pipette and stirred at 70°C. The flocculation, which is the coated magnetite nanoparticles, formed immediately. A strong magnet was used to settle the flocculation and the solution was decanted. The precipitate was washed with acetone or DI water five times to remove the excess fatty acid and dried in an oven at 50°C for 12 h. This resulted in SAM coated iron oxide nanoparticles. For self-assembly of the secondary layer, half of the as-prepared monolayer coated iron oxide nanoparticles was redispersed in 40 ml DI water, and 1 g decanoic acid was dissolved in 20 ml DI water at 70°C. The decanoic acid solution was then dropped to the redispersed fluid with continuous stirring at 70°C. The later steps were the same as those for the SAM coatings. Finally, self-assembled bilayer coated magnetite nanoparticles were obtained after this process.

The size and morphology of the self-assembly coated magnetite nanoparticles were measured by an HF-2000 field emission gun transmission electron microscope (Hitachi, Japan). The size distribution was determined by measuring more than 400 particles from TEM images. Magnetic properties of SAM and bilayer coated nanoparticles were measured by SQUID (Quantum Design, MPMS). The magnetization and hysteresis loops were measured at the room temperature and at 10 K, respectively. Blocking temperature (T_B) was measured based on ZFC (zero field cooled) and FC (field cooled) measurements with M vs. T curves at external magnetic field of 1000 G.

Measurements were performed by cooling a sample in zero field down to 5 K whence a magnetic field of 1000 G was applied. After that, the sample was slowly warmed up to a temperature of 320 K in steps of 5 K with stabilization at each temperature and subsequent measurement of the magnetization (ZFC). Then, without turning off the magnetic field, the sample was cooled down to 5 K with measurement of magnetization at each intermediate temperature (FC). The temperature at which the two curves (ZFC and FC) merge is traditionally called blocking temperature T_B [4]. TGA measurements were performed by TGA 2850 thermogravimetric analyzer (TA instruments) under N_2 at the temperatures range 30–700°C with an increasing rate of 5°C to verify the coating formation on the surface of magnetite nanoparticles.

3. Results and discussion

The morphology and the size distribution of SAM coating on magnetite nanoparticles are shown in Figs. 1 and 2. It can be seen from Fig. 1 that the magnetic Fe_3O_4 nanoparticles are close to spherical. Fig. 2 indicates the size of the particles distributed from 4 to 16 nm. The size distribution fits a log-normal distribution. The mean particle size is about 9.6 nm with a standard deviation of about 2.5 nm.

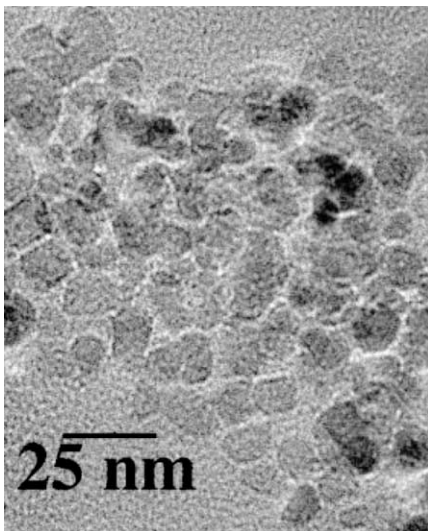


Fig. 1. TEM micrograph of SAM Fe_3O_4 nanoparticles.

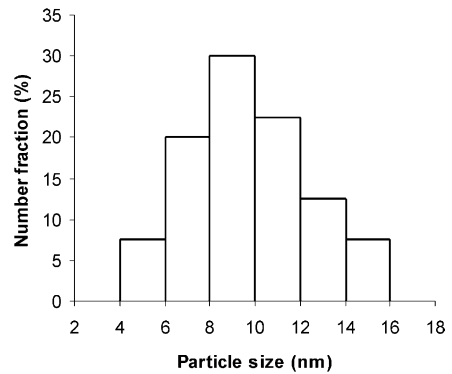


Fig. 2. The distribution of SAM Fe_3O_4 nanoparticles.

It is difficult to directly observe the coating on the surface of Fe_3O_4 nanoparticles from TEM micrographs. The indication of the coating formation on the surface of magnetite nanoparticles can be obtained from TGA measurements. Fig. 3 presents typical TGA heating and cooling curves of SAM and bilayer coated magnetite nanoparticles. The mass profile shows a major weight loss over temperature range 150–360°C for monolayer coated Fe_3O_4 nanoparticles. For bilayer coated Fe_3O_4 nanoparticles, the heating curve exhibits several major weight losses, revealing a different pattern from that observed for monolayer coated nanoparticles. The major weight loss between the temperature 150 and 360°C of the monolayer coated nanoparticles could be ascribed to the desorption and evaporation of the coating from the particle surface. The major weight losses between 150–250°C and 310–650°C of bilayer coated nanoparticles are due to desorption and evaporation of the secondary (outer) layer and the first layer (inner) of the coating, respectively. TGA results of monolayer coated nanoparticles and bilayer coated nanoparticles also indicate that desorption and evaporation of the secondary outer layer (150–250°C) is faster than that (150–360°C) of the first inner layer coated on the surface of the nanoparticles. It means that the strength of the bonding between the first layer and the second layer is weaker than that between the first layer and the surface of the nanoparticles.

Magnetization loops of non-coated Fe_3O_4 nanoparticles, SAM coated Fe_3O_4 nanoparticles and self-assembled bilayer coated Fe_3O_4 nanoparticles measured at the room temperature are depicted in Fig. 4.

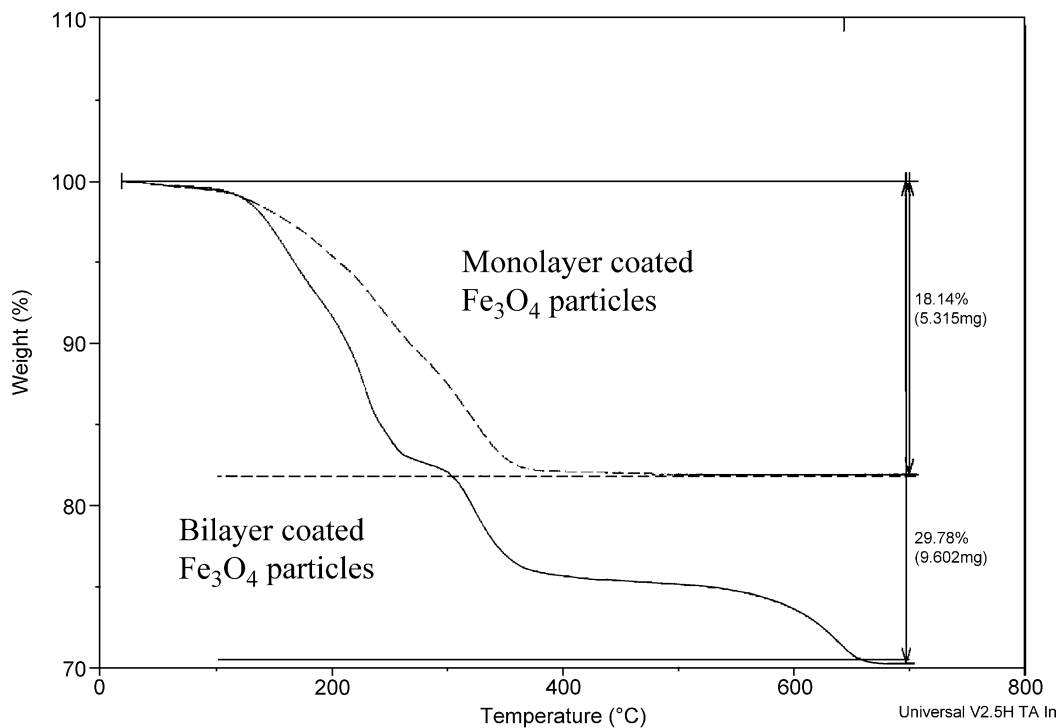


Fig. 3. Heating and cooling curves of SAM and bilayer coated Fe_3O_4 nanoparticles.

The results show that no hysteresis is detected and the magnetization does not saturate at 10 kG. The superparamagnetic behavior is indicated by zero coercivity and zero remanance on the magnetization curves for non-coated magnetite nanoparticles, monolayer coated and bilayer coated magnetite nanoparticles.

It can be seen from Fig. 4 that magnetization decreases with increasing the layers of the coating. This is because magnetization is proportional to the amount of weight for the same magnetic material. Increasing coating layer increases the amount of non-magnetic substance (fatty acids) on iron oxide. It means that the

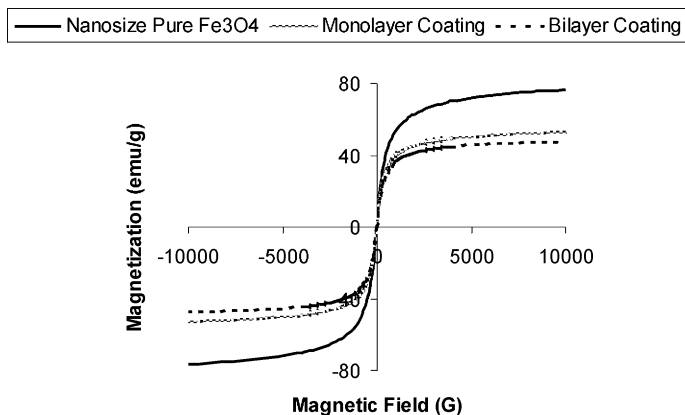


Fig. 4. Magnetization of non-coated iron oxide particles, monolayer and bilayer coated magnetite nanoparticles.

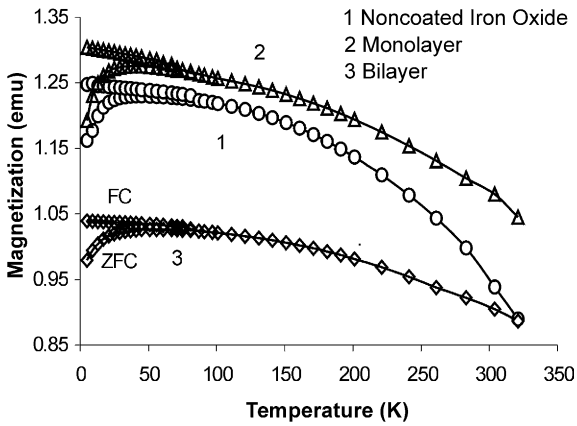


Fig. 5. The ZFC and FC curves for (1) non-coated; (2) monolayer coated; (3) bilayer coated magnetite nanoparticles.

more the layer of the coating, the less the amount of magnetite contained in the same weight of sample.

The M vs. T measurements (ZFC and FC curves) were carried out for non-coated magnetite nanoparticles, SAM and bilayer coated magnetite nanoparticles, and the blocking temperatures T_B were obtained. The magnetic blocking appears because below T_B , thermal energy is not enough to overcome the energy of magnetic anisotropy and magnetic interactions; thus the paramagnetism disappears. The general trend is that T_B shifts towards higher temperature when the strength of interactions between particles increases. The results of M vs. T measurements of non-coated magnetite nanoparticles, SAM and bilayer magnetite nanoparticles are shown in Fig. 5. Their blocking temperatures are about 80 K. The results indicate that there is no big difference in the blocking temperature for non-coated magnetite, SAM or bilayer coated magnetite. This may indicate that the average distance

between the magnetic nanoparticles does not change significantly. It seems that SA layer takes place on the surface of the some agglomerated nanoparticles and not on the surface of all individual magnetite nanoparticles. This is because if the layer covers each individual nanoparticle, the inter-particle separation increases, thus reducing the magnetic dipole–dipole interaction. This must lead to a significant shift in T_B for coated particles. So, increasing the layer of the coating must push blocking temperature T_B to lower temperatures. But in our measurements, blocking temperature of non-coated, monolayer coated and bilayer coated magnetite are almost the same. It can be seen from Fig. 5 that the loss of magnetization of non-coated magnetite is sharp with increasing temperature over 250 K, but is smooth for SAM coated magnetite and the loss of magnetization is the slowest for bilayer coated magnetite. This can be ascribed to the fact that the coating layer works as a heat resistance layer and lowers the heat transfer to the magnetite, thus reducing the loss of magnetization. The results of M vs. T of monolayer and bilayer coated magnetite nanoparticles indicate that demagnetization can be retarded by increasing the coating layer on the surface of magnetite nanoparticles at higher temperature.

The hysteresis loops of SAM and bilayer coated magnetite nanoparticles were measured at 10 K. The results are shown in Fig. 6. It indicates that SAM and bilayer coated magnetite nanoparticles exhibit hysteresis at the lower temperature. It means that they lose superparamagnetism at lower temperature. The coercivity of SAM coated magnetite nanoparticles is the same as that of self-assembled bilayer coated magnetite nanoparticles. The coercivity is 150 G at the temperature of 10 K. The remanent magnetization

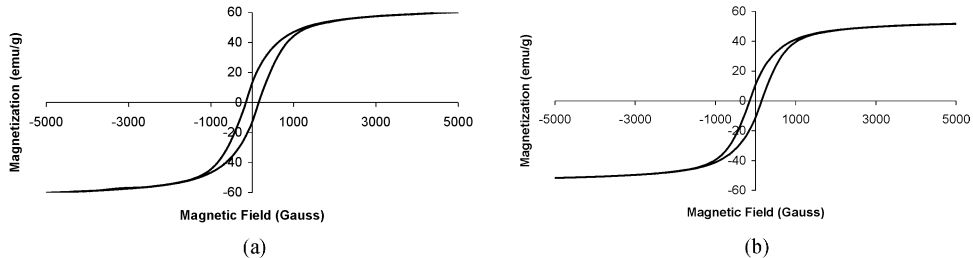


Fig. 6. Magnetization loop measurements for monolayer coated and bilayer coated Fe_3O_4 nanoparticles at the temperature of 10 K; (a) monolayer coated Fe_3O_4 ; (b) bilayer coated Fe_3O_4 .

of SAM coated magnetite nanoparticles (13.2 emu/g) is higher than that of self-assembled bilayer coated magnetite nanoparticles (11.1 emu/g). It can be inferred from the results that the number of coating layer has no effect on the coercivity of the self-assembled coated magnetite nanoparticles. It just affects the overall and remanent magnetization.

4. Summary and conclusions

SAM and bilayer coated nanoscale magnetite nanoparticles have been prepared by chemical co-precipitation method and studied for their physical and magnetic properties. SAM and bilayer coated Fe_3O_4 nanoparticles were obtained by using fatty acids (lauric acid and decanoic acid) as surfactants. TGA measurements verify the formation of the coating on the surface of magnetite nanoparticles. TGA result shows that the strength of bonding between the outer layer and the inner layer is weaker than that between the inner layer and the surface of magnetite nanoparticles. Desorption and evaporation of the outer layer is faster than that of the layer coated on the surface of the nanoparticles.

Measurements of the magnetic properties indicate that SAM and bilayer coated magnetite nanoparticles exhibit superparamagnetism above the blocking temperatures. The magnetization decreases with increasing the coating layers. The hysteresis loop measuring results reveal that coating layers have no effect on the coercivity of the self-assembled coated magnetite nanoparticles. It just affects the overall and remanent magnetization. There is no significant difference in the blocking temperature for non-coated magnetite, SAM and bilayer coated magnetite nanoparticles. SA layer appears to take place on the surface of some agglomerated nanoparticles and not on the surface of every individual magnetite nanoparticle. Demagnetization is retarded by increasing the layer of the coating on the

surface of magnetite nanoparticles at high temperature. Similar approach is being extended to other magnetic, dielectric and ferroelectric oxides in order to stabilize their suspensions for functionalization, colloid suspension and surface patterning.

Acknowledgements

This work is supported by NSF-DOE supported Institute for Environmental Catalysis (IEC) at Northwestern University, and the AFOSR-MURI Program: “Surface-templated, Bioinspired Synthesis and Fabrication of Functional Materials” monitored by Major Paul Trulove.

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