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High Coercivity of Oleic Acid Capped CoFe$_2$O$_4$ Nanoparticles at Room Temperature

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High coercivity (9.47 kOe) has been obtained for oleic acid capped chemically synthesized CoFe$_2$O$_4$ nanoparticles of crystallite size ∼20 nm. X-ray diffraction analysis confirms the formation of spinel phase in these nanoparticles. Thermal annealing at various temperatures increases the particle size and ultimately shows bulk like properties at particle size ∼56 nm. The nature of bonding of oleic acid with CoFe$_2$O$_4$ nanoparticles and amount of oleic acid in the sample is determined by Fourier transform infrared spectroscopy and thermogrvimetric analysis, respectively. The Raman analysis suggests that the samples are under strain due to capping molecules. Cation distribution in the sample is studied using Mössbauer spectroscopy. Oleic acid concentration dependent studies show that the amount of capping molecules plays an important role in achieving such a high coercivity. On the basis of above observations, it has been proposed that very high coercivity (9.47 kOe) is the result of the magnetic anisotropy, strain, and disorder of the surface spins developed by covalently bonded oleic acid to the surface of CoFe$_2$O$_4$ nanoparticles.

1. Introduction

Magnetic nanoparticles have been widely investigated due to their potential applications in magneto-optical recording, magnetic data storage, drug delivery, MR contrasting, etc.[1–4] They possess different magnetic properties like anisotropy, coercivity, magnetization, blocking temperature, and so forth, which often differ from the bulk. The most remarkable size dependent property of the magnetic particles is an increase in the coercivity compared to that of bulk material as the particles decrease in size in the nanometer regime. Highest coercivity is reached at a critical size characteristic of the material, below which the coercivity again starts decreasing with decrease in the particle size. At sufficiently small size of the particles, the coercivity becomes zero and the particles are termed as superparamagnetic. Although superparamagnetic particles are quite useful in many technological applications, the low or zero coercivity of such particles prohibits their use as miniature elements for high density data storage. It is therefore interesting to explore the possibility by which one could combine nano size with large coercivity.

Bulk cobalt ferrite (CoFe$_2$O$_4$) has been under intense investigations in the past few decades due to its good mechanical hardness as well as chemical stability. It is a good candidate for magnetoelectronics applications due to large Kerr and Faraday rotations.[5,6] It has a coercivity of ∼0.75−0.98 kOe along with ∼80 emu/g magnetization at room temperature[7,8]

and is a good candidate for the magnetic recording application. Magnetic coercivity of any material depends on several factors like magnetocrystalline anisotropy, shape anisotropy, defects, strains, size, doping, nature of the surface, and interface.[9–16] A number of efforts have been made to increase the coercivity in cobalt ferrite using different strategies. All attempts so far to increase the coercivity at room temperature have led to 9.3 kOe as the highest coercivity for thin films deposited on SiO$_2$ single crystal substrate.[10] Such a large coercivity was a result of the presence of grains ∼50 nm in size and the lattice strain produced in these films. However, the maximum coercivity reported so far in the powders of CoFe$_2$O$_4$ is 5.3 kOe for the samples prepared by chemical route.[9] The large coercivity is reported to be due to small particle size and built up of a large residual strain. The maximum room temperature coercivity reported in CoFe$_2$O$_4$ particles synthesized by mechanical milling process is 5.1 kOe.[11] The large coercivity is attributed to the high strain and defects produced in CoFe$_2$O$_4$ powders by milling. Recently Cedeno-Mattei et al.[12] adopted an interesting factorial design to rapidly examine the effect of different variables on the final product and achieved the highest coercivity as large as 4.6 kOe in case of CoFe$_2$O$_4$ of about 20 nm size particles.

In this communication, we report high coercivity (9.47 kOe) at room temperature achieved in CoFe$_2$O$_4$ particles of about 20 nm average size. Theoretically, it was predicted that Cobalt ferrite particles ∼100 nm or smaller are single domain particles reaching superparamagnetic limit at ∼10 nm.[17] Chinnasamy et al.[13] experimentally reported that the critical size of single domain cobalt ferrite nanoparticles is ∼40 nm. It is therefore expected that 20 nm size particles would have low coercivity as well as magnetization. However as will be discussed below

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the use of oleic acid (C$_{17}$H$_{33}$COOH) as a capping agent during the synthesis of nanoparticles leads to the high coercivity. The oleic acid capped CoFe$_2$O$_4$ particles have been reported earlier.[18] However, the highest coercivity reported at room temperature was rather low (~1.25 kOe for 24 nm sized particles) in contrast to our results. It is therefore necessary to characterize the samples to understand the nature of chemical bonding on the active surface sites of nanocrystalline CoFe$_2$O$_4$, which might be responsible for the high coercivity. Various techniques like X-ray diffraction, transmission electron microscopy, Fourier transformed infrared spectroscopy, thermogravimetric analysis, and Raman and Mössbauer spectroscopy were employed to understand structural and microstructural changes, which have further been utilized in proposing a model.

2. Experimental Section

2.1 Synthesis of CoFe$_2$O$_4$ Nanoparticles. Cobalt ferrite nanoparticles have been synthesized by a wet chemical route. The aqueous solutions of 0.2 M CoCl$_2$·6H$_2$O and 0.4 M FeCl$_3$·6H$_2$O were mixed and stirred together for 30 min. Oleic acid (0.2 M) was added into the above solution as a capping agent, followed by the addition of an aqueous solution of 3 M NaOH. The pH of the solution was continuously monitored and maintained in the range of 11−12. The solution was heated to 353 K, and the solution was constantly stirred for one hour. The solution was then cooled to the room temperature. A blackish precipitate was separated and several times washed with water and ethanol. The precipitate dried in vacuum appeared black in color. This sample was labeled pristine. Parts of the sample were heated in the furnace at different temperatures for 10 h each. Following the same procedure, samples with two more oleic acid concentrations viz. 0.05 and 0.1 M were also synthesized in order to understand the role of capping molecules on magnetic properties of CoFe$_2$O$_4$ nanoparticles. A sample was also prepared without using oleic acid while keeping all other conditions same. This sample was annealed at 1473 K for 10 h.

2.2. Characterization. Structure of the powder samples were determined using Rigaku X-ray diffractometer with Cu Kα (1.542 A°) source. Transmission electron microscopy (TEM) of the pristine sample (as synthesized 0.2 M oleic acid) was performed on Tecnai 200 G2 with LaB$_6$ electron source. The sample for TEM analysis was prepared by depositing a drop of the pristine sample dispersed in solvent on a carbon coated copper grid. Magnetization of all the samples under the application of magnetic field up to 18 kOe was measured at room temperature using a LakeShore 7307 vibrating sample magnetometer (VSM). The percentage of oleic acid present on the surface of the nanoparticles is obtained by thermogravimetric analysis (TGA). Measurements of powder samples were carried out on Shimadzu DTH60 from room temperature to 1073 K with heating rate of 10 K/min. Fourier transform infrared spectroscopy (FTIR) of powder samples was performed with a Thermo SCIENTIFIC Nicolet - 6700 spectrometer. The Raman spectrometer used to record the room temperature spectra was LABRAM HR-800 equipped with an Ar$^+$ laser (488 nm, 10 mW) excitation source and CCD detector.

3. Results and Discussion

Figure 1A shows the X-ray diffraction (XRD) patterns of CoFe$_2$O$_4$ (a) pristine sample, (b) annealed at 573 K, (c) annealed at 973 K, and (d) uncapped sample annealed at 1473 K. The structure of all the CoFe$_2$O$_4$ powder samples by comparing with Joint Committee for Powder Diffraction Set (JCPDS) Data 22-1086 was found to be a spinel structure. In Figure 1A, the

standard peak positions of bulk CoFe$_2$O$_4$ are shown for comparison. The widths of the diffraction peaks decrease as the sample is annealed (a−d), indicating an increase of crystallite size. The average crystallite size calculated using Scherrer formula ($d = 0.9 \lambda/\beta \cos \theta_B$) for the pristine sample, annealed at 573, and annealed at 973 K are ~20, ~24, and ~44 nm, respectively. The crystallite size of the uncapped sample annealed at 1473 K is ~56 nm. There is no impurity or other phase-related peaks present, indicating that the samples are pure. The lattice constant is calculated for all the samples using Rietveld refinement. The graph is plotted for the pristine sample, the same sample annealed at 973 K, the uncapped sample annealed at 1473 K, and the standard bulk CoFe$_2$O$_4$ (JCPDS Data 22-1086) (Figure 1B). The value of lattice constant for bulk CoFe$_2$O$_4$ is 8.391 Å. The lattice constant increases from 8.370 to 8.380 Å as the annealing temperature increases up to 1473 K. The lattice constant of pristine sample is smaller by 0.021 Å than the standard bulk value. TEM of the pristine CoFe$_2$O$_4$ sample is shown in Figure 2. The particle size distribution shows that the average particle size is ~20 nm, which is in good agreement with the XRD results. However, there are some particles (<10 nm) in the superparamagnetic regime.

Magnetization measurements of the pristine and samples annealed at 373, 573, 773, and 973 K are shown in Figure 3, and magnetization values for all these samples are summarized in Table 1. It can be seen that for the pristine sample the magnetization value $M \sim 7.1$ emu/g is obtained with 18 kOe magnetic field and the huge coercivity viz. 9.47 kOe at room temperature. The value of coercivity is almost twice than what has been reported so far for the nanoparticles of CoFe$_2$O$_4$. Even after annealing the sample at 373 K, the coercivity value is substantially large (8.39 kOe) with concomitant small increase in the magnetization ($M \sim 7.8$ emu/g). Thus the chemical stability, thermal stability, and corresponding magnetic stability of the particles is quite good at moderate temperature. The coercivity, however, drops down dramatically at 573 K annealing temperature and magnetization goes on increasing as the annealing temperature increases. Decomposition of oleic acid starts due to annealing and particles coagulate with each other. Drop in the coercivity and increase in the magnetization as annealing temperature increases is a general trend as is obvious from Figure 4. When high magnetic field of 60 kOe is applied to the pristine sample the magnetization value increases to 18.3 emu/g and coercivity remains same at 9.47 kOe (Figure 5). It is observed that the hysteresis loop does not get saturated, consistent with some early observations on ultrafine particles of nickel ferrite coated with organic molecules.[19,20] It was shown that the spins remained at large angles even at as high as 68.5 kOe applied magnetic field.[19] The coating of capping molecules reduces the interparticle magnetic interaction. The low magnetization value of pristine sample is due to weak exchange interaction between particles. This reduction in interaction is due to organic capping molecules (oleic acid), which keep particles away from each other. Similar results were obtained by Berkowitz et al. in the case of NiFe$_2$O$_4$ ultrafine particles coated with oleic acid.[19] The hysteresis loops of uncapped sample and same sample annealed at 573, 973, 1473 K are shown in Supporting Information (Figure S1). The coercivity and magnetization values of 1473 K annealed uncapped sample are 0.94 kOe and 74.2 emu/g, respectively, which is well within the range of bulk reported values.[7,8]

Oleic acid (0.2 M) capped CoFe$_2$O$_4$ pristine particles of ~20 nm size have showed large coercivity. Magnetic coercivity of any material, a measure of the magnetic field strength required
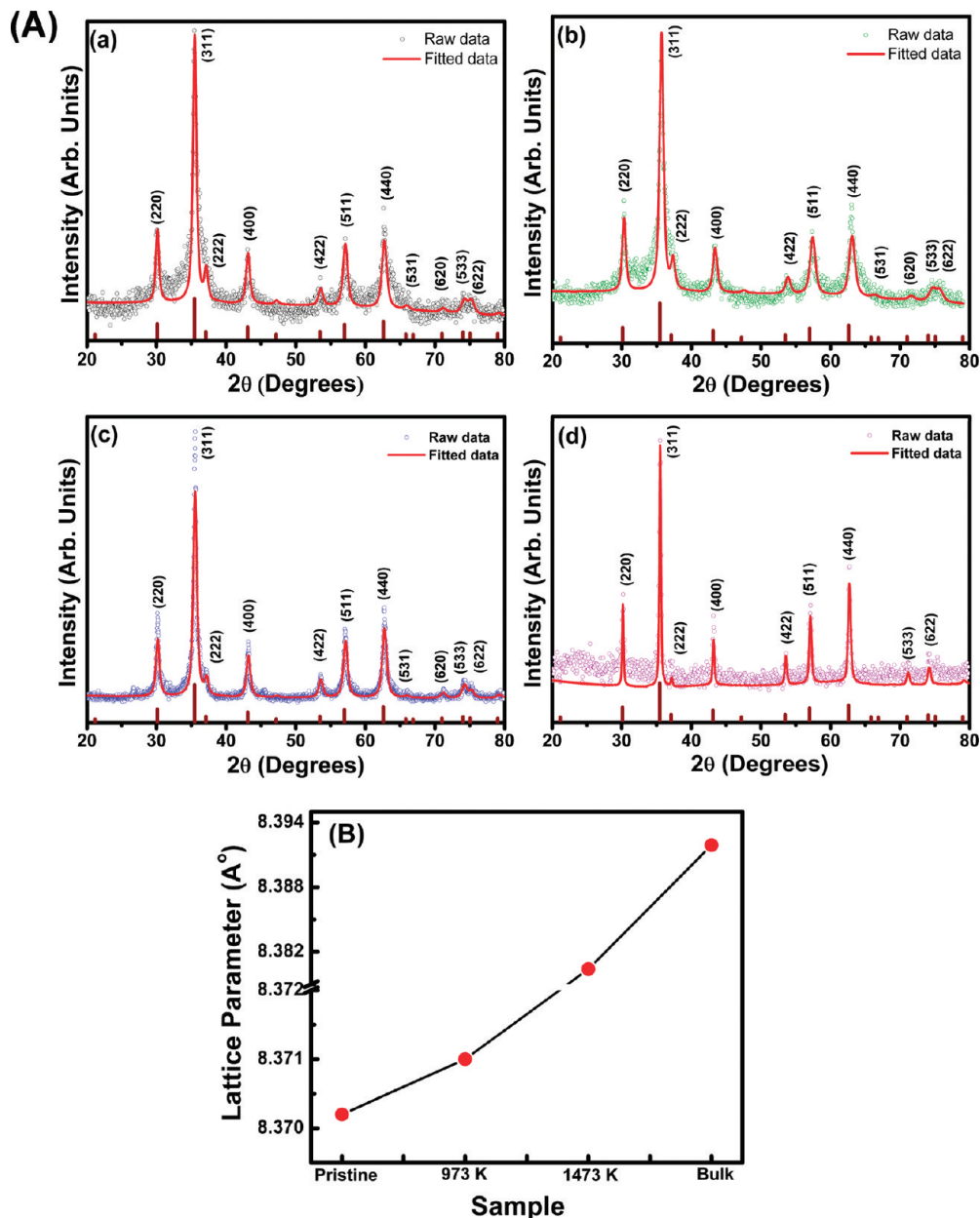
Figure 1. (A) XRD patterns of (0.2 M) oleic acid capped $CoFe_2O_4$ raw and fitted data (a) pristine, (b) 573 K, (c) 973 K, and (d) uncapped sample annealed at 1473 K along with standard bulk peak positions. (B) The plot of change in lattice parameters of pristine, 973 K annealed, and uncapped sample annealed at 1473 K with respect to bulk $CoFe_2O_4$.
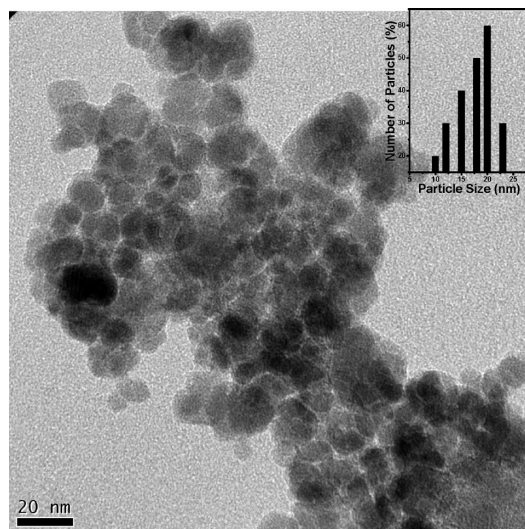
to change the direction of magnetization, as mentioned above, depends on several factors like magnetic anisotropy, defects, strain, size, doping, nature of the surface, and interface as well as interparticle interaction. In the case of the pristine $CoFe_2O_4$ particles synthesized by us, we have shown that the particles are single phase and pure. Energy dispersive X-ray Analysis and X-ray photoelectron spectroscopy analysis (not shown here) did not show any impurities in the sample. Therefore, the contribution to the high coercivity by impurities can be neglected.

There are now other possibilities like magnetic anisotropy, strain, and interparticle interactions that need to be considered. The magnetic anisotropy calculated using the law of approach to saturation is given by[11]

$$M(H) = M_S\left(1 - \frac{0.07619K^2}{H^2M_S^2} - \frac{0.0384K^3}{H^3M_S^3}\right) \quad (1)$$

where $M(H)$ is the magnetization at an applied field of H, M_S is the saturation magnetization, and K is the magnetic anisotropy. K can be estimated by substituting the values from $M(H) - H$ curve in certain field range in eq 1. The value of K is found to be $\sim 7.03 \times 10^5$ J/m³ for the pristine sample at room temperature. It was found earlier[11] for cobalt ferrite nanoparticles with large coercivity (5.1 kOe) that K is 5.8×10^5 J/m³. The magnetocrystalline anisotropy of bulk $CoFe_2O_4$ is 2×10^5 J/m³.[21] The value of K is appreciably increased in pristine $CoFe_2O_4$ sample as compared to bulk value. The magnetocrystalline anisotropy of $CoFe_2O_4$ arises from the Co^{2+} ions that are present at B site (octahedral site) in inverse spinel structure. A change in the cation distribution leads to change in the magnetocrystalline anisotropy and magnetic coercivity. We checked the cation distribution in the pristine sample using Mössbauer spectroscopy at low (5 K) temperature and in the magnetic field

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Figure 2. Transmission electron micrograph of pristine (0.2 M) oleic acid capped CoFe$_2$O$_4$ pristine sample. The inset shows the particle size distribution.
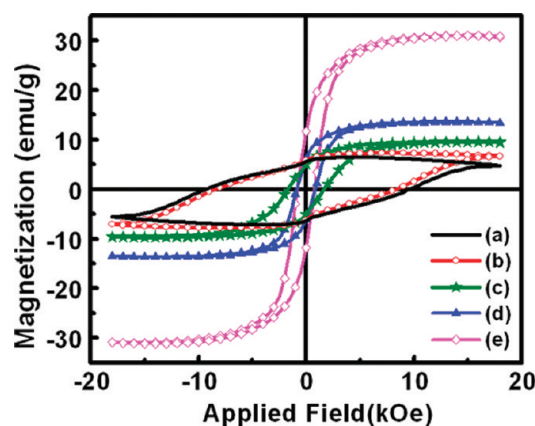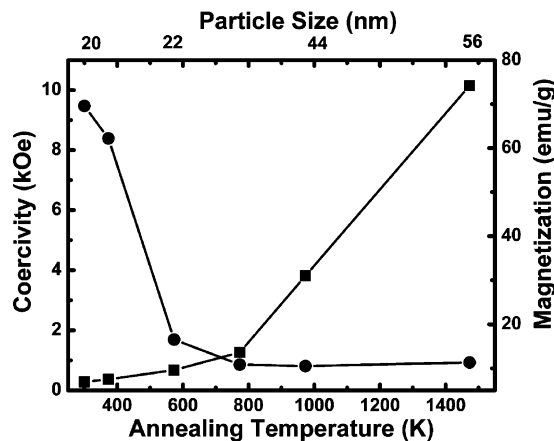

Figure 3. Room temperature magnetization plots of (0.2 M) oleic acid capped CoFe$_2$O$_4$ annealed at different temperatures: (a) pristine, (b) 373 K, (c) 573 K, (d) 773 K, and (e) 973 K.

TABLE 1: VSM Parameters such as Magnetization (*M*), Coercivity (*H*c) at Room Temperature for the (0.2 M) Oleic Acid Capped CoFe$_2$O$_4$ and Annealed at Different Temperatures under Applied Field of 18 kOe

CoFe$_2$O$_4$ sample	magnetization (M) (emu/g)	coercivity (H$_c$) (kOe)
pristine	7.1	9.47
373 K(annealed)	7.8	8.39
573 K (annealed)	9.9	1.69
773 K (annealed)	13.6	0.87
973 K (annealed)	31.0	0.81
1473 K (uncapped, annealed)	74.2	0.93

of 50 kOe (Supporting Information, Figure S2). (Detailed Mössbauer studies will be published somewhere else.) However, our Mössbauer analysis of pristine sample shows ~40% occupancy of A site (tetrahedral site) by Co^{2+} ions. The migration of Co^{2+} from B site to A site would decrease the magnetocrystalline anisotropy in CoFe$_2$O$_4$.[22] However, the total magnetic anisotropy is a combination of magnetocrystalline anisotropy and surface anisotropy, expressed as[23]

$$K = K_A + \left(\frac{6}{d}\right)K_S \qquad (2)$$

Figure 4. The change in magnetization and coercivity of (0.2 M) oleic acid capped CoFe$_2$O$_4$ sample with respect to annealing temperature.
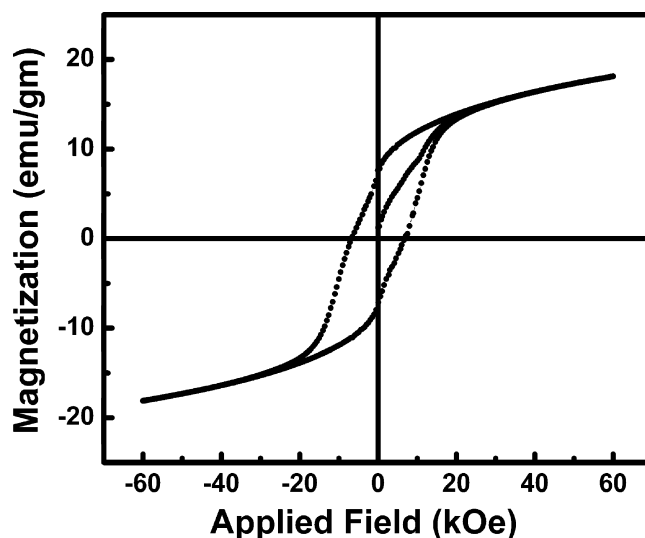
Figure 5. The magnetization plot of pristine sample at an applied magnetic field of 60 kOe.

where K is the total magnetic anisotropy, K_A is the magnetocrystalline anisotropy of material, d is the diameter of the particle, and K_S is the surface anisotropy. Surface anisotropy itself would depend upon the surface properties and surface coating. The surface of CoFe$_2$O$_4$ is coated with oleic acid. Therefore surface anisotropy may be developed through oleic acid molecules. As shown in Figure 3, there is a drastic reduction in the coercivity, as the oleic acid capping starts decomposing, it is very likely that surface anisotropy mainly arises due to the presence of oleic acid. Therefore, the enhancement in magnetic anisotropy would be a result from other factors like surface anisotropy and strain.

In order to further elucidate the effect of oleic acid on the surface of nanoparticles, we have varied the concentration of oleic acid (0.05, 0.1, and 0.2 M) and investigated the magnetic behavior of CoFe$_2$O$_4$ nanoparticles (Supporting Information, Figure S3). As the concentration of oleic acid increases, the coercivity also increases. Thus oleic acid concentration dependent magnetization measurements clearly indicate that the concentration of oleic acid is playing an important role in controlling the coercivity. Now it is necessary to determine the amount of oleic acid present as well as bonding nature of oleic acid on the surface of the nanoparticles. Therefore, we have performed TGA and FTIR analysis of all the samples.
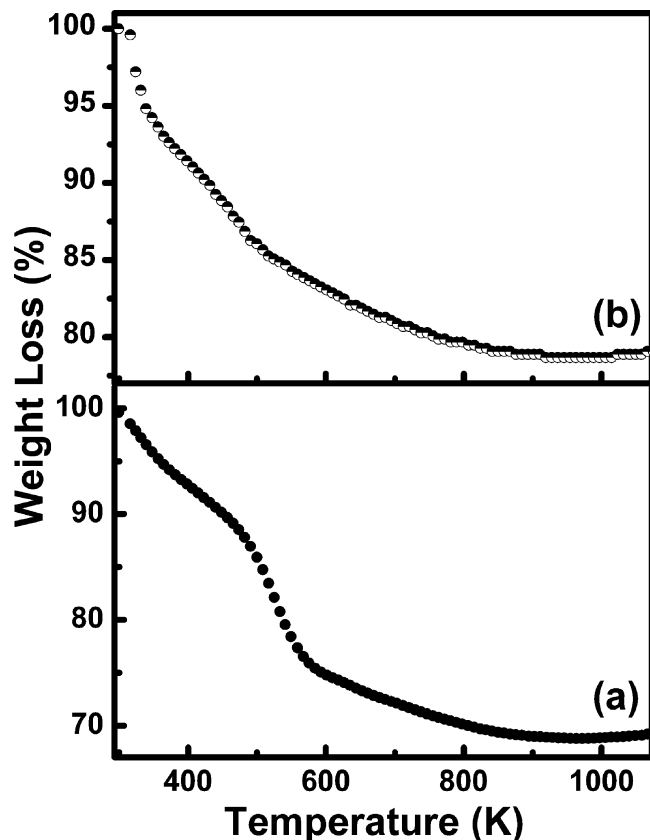
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Figure 6. TGA plots of (a) pristine and (b) uncapped CoFe$_2$O$_4$ sample.

Figure 7. FTIR spectra of (0.2 M) oleic acid capped CoFe$_2$O$_4$ annealed at different temperatures. (a) Oleic acid, (b) pristine, (c) 373 K, (d) 573 K, (e) 773 K, (f) 973 K, and (g) uncapped CoFe$_2$O$_4$.

Figure 6 shows TGA plots of pristine (a) and uncapped CoFe$_2$O$_4$ sample (b). In both of the samples, the initial weight loss up to ~473 K is due to moisture content in the sample. Above 473 K, decomposition of oleic acid starts[24-26] giving rise to significant weight loss, ~20% in the pristine sample. The weight loss obtained is used to estimate the number of oleic acid molecules per particle and could be calculated using following formula[27]

$$N = \frac{wN_A\rho\frac{4}{3}\pi R^3 \times 10^{-23}}{M} \qquad (3)$$

where N is the number of capping molecules (ligands) per particle, w is the weight loss in percent (%), N_A is Avogadro's number, ρ is the density of the nanoparticles (5.15 g/cm^3), R is the average radius of the CoFe$_2$O$_4$ particles (10 nm based on TEM analysis), and M is the molecular weight of the oleic acid (282.47 g/mol). The number of oleic acid ligands per particles in the pristine sample is ~9210. Using eq 3, we have also calculated the number of oleic acid molecules per square centimeter, which is ~7.3 × 10^{14}. TGA measurements are in well agreement with the results obtained by the other groups.[24-26] In uncapped CoFe$_2$O$_4$ sample [Figure 6(b)] continuous weight loss is observed after 473 K. Oleic acid concentration dependent TGA plots of CoFe$_2$O$_4$ nanoparticles are shown in Supporting Information (Figure S4). The percentage weight loss decreases as the concentration of capping molecules decreases in the synthesis which can be clearly seen from the plots (Figure S4).

Chemical bonding of oleic acid with particles was investigated using FTIR. Figure 7 illustrates the FTIR spectra of oleic acid, pristine sample, same sample annealed at 373, 573, 773, and 973 K, and uncapped CoFe$_2$O$_4$ sample. Oleic acid (sample a)
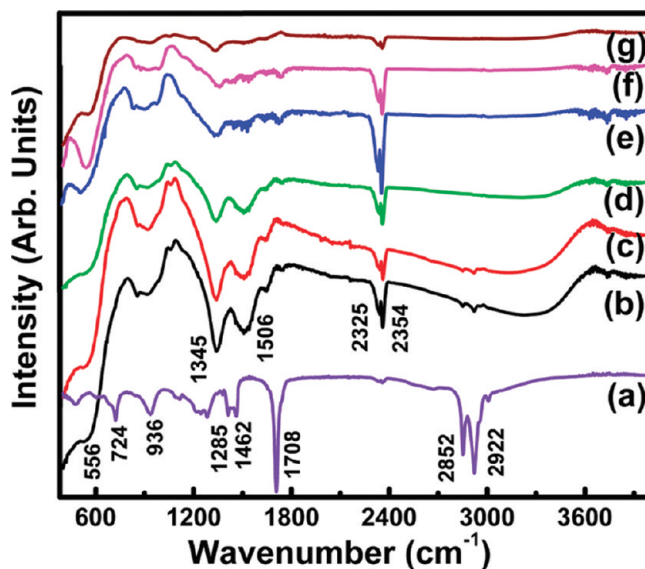
shows vibration bands at 2922 and 2852 cm^{-1} that are attributed to the CH$_2$ asymmetric and CH$_2$ symmetric stretch. In the same sample, peaks obtained at 1708 and 1285 cm^{-1} are due to C=O and C—O stretch, respectively.[28] Two bands at 1462 and 936 cm^{-1} are attributed to in-plane and out-of-plane O—H. In sample (b) pristine CoFe$_2$O$_4$ and (c) same sample annealed at 373 K, a broad peak is observed at 3405 cm^{-1}, which is assigned to O—H. It indicates that some water molecules are adsorbed on the sample from air. In (b) and (c), the peaks due to —CH$_2$ stretch have shifted to 2918 and 2848 cm^{-1} with respect to pure oleic acid due to absorption of oleic acid on the surface of CoFe$_2$O$_4$ nanoparticles. The intense peak obtained at 1708 cm^{-1} in oleic acid is not present in oleic acid-capped CoFe$_2$O$_4$ pristine sample. It indicates that no free pure liquid oleic acid is present in the sample. Two new intense and broad peaks appear at 1506 and 1345 cm^{-1}, which are characteristic of COO$^-$ asymmetric and COO$^-$ symmetric stretch.[29] The wavenumber separation (Δ) between COO$^-$ asymmetric and COO$^-$ symmetric is ~161 cm^{-1} and is ascribed to bridging bidentate, where the COO group is covalently bonded to Co and Fe surface atoms of CoFe$_2$O$_4$.[29] It was recently reported by Wu et al.[29] that the largest Δ (200–300 cm^{-1}) corresponds to the moderate interaction, the Δ (110–200 cm^{-1}) corresponds to a bridging bidentate, and smallest Δ (<110 cm^{-1}) corresponds to the chelating bidentate. It indicates that oleic acid is chemisorbed as carboxylate onto the CoFe$_2$O$_4$ nanoparticles. It revels that the two oxygen atoms in carboxylate are coordinated to the surface Co and Fe atoms in CoFe$_2$O$_4$ sample.[28] The covalent bonding of COO group with surface atoms creates strain and disorder of surface spins, which lead to very high coercivity in pristine sample at room temperature. The nature of binding of oleic acid depends on the processing method and leads to show different properties. The peak obtained at 556 cm^{-1} in all CoFe$_2$O$_4$ samples is attributed to Fe—O[26] or Co—O bond. In all other samples, the adsorbed water content (i.e., O—H bond) and presence of capping molecules goes on vanishing as the annealing temperature increases. For the sake of comparison, the FTIR spectra of CoFe$_2$O$_4$ nanoparticles capped with different concentration of oleic acid (0.2, 0.1, and 0.05 M) are given in the Supporting Information (Figure S5). The intensity of the COO peak

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SCHEME 1: Schematic Diagram of Oleic Acid Capped CoFe$_2$O$_4$ Nanoparticles and the Representation of the Steric Hindrance at the Surface of Nanoparticles
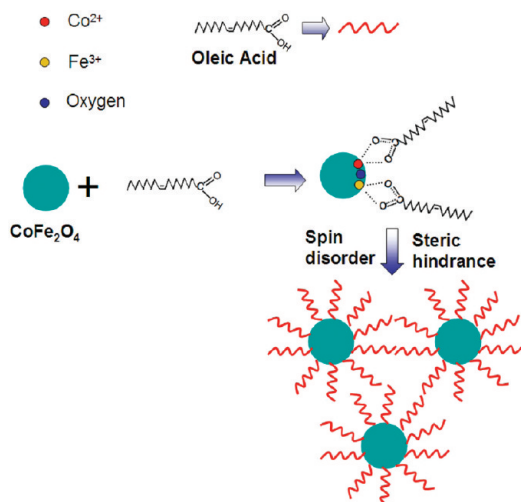
decreases as the oleic acid concentration decreases and ultimately coercivity also decreases.

To explain the observed high coercivity, we propose a model (Scheme 1). The oleic acid molecules bind strongly to the CoFe$_2$O$_4$ surface atoms. The strong binding of oleic acid is confirmed by FTIR analysis. The molecules also pose a steric hindrance, creating substantial anisotropy. Therefore application of an external magnetic field cannot easily reorient the spins even after a very strong magnetic field. This is evident from the absence of saturation as shown Figure 5. Drastic effect on magnetization and coercivity has been observed as the pristine sample annealed from 373 to 1473 K (Figure 3) or concentration of oleic acid is varied (Supporting Information, Figure S3). Thus oleic acid has played an important role in arresting the spins on the particle surface[19,20]and creating large surface anisotropy. Surface spins remain at large angles[19] and strong magnetic field is required to orient them in the direction of magnetic field. We also observe that the presence of oleic acid is responsible for inducing strain contributing to the coercivity.

The presence of a strain in the pristine nanoparticles of CoFe$_2$O$_4$ has been observed through the Raman spectroscopy. In Figure 8, Raman spectra of (0.2 M) oleic acid capped pristine sample (a), pristine sample annealed at 573 K (b), 973 K (c), and uncapped sample annealed at 1473 K (d) have been plotted. The spectra could be deconvoluted into six components at 467, 503, 538, 575, 619, and 671 cm^{-1} for pristine, 463, 496, 546, 600, 646, and 688 cm^{-1} for 573 K annealed sample, 473, 571, 605, 632, 662, and 690 cm^{-1} for 973 K annealed sample, and 473, 529, 572, 607, 639, and 693 cm^{-1} for uncapped sample that is annealed at 1473 K. By comparing with the earlier work on CoFe$_2$O$_4$,[30,31] we have assigned the highest frequency Raman mode at 693 cm^{-1} in 1473 K annealed sample (as it is similar to bulk sample and is not expected to have strain effects due to surface/oleic acid) to tetrahedral position (identified with T site) and the one at 473 cm^{-1} to the octahedral site (identified with O site). All other modes are characteristics of the cubic inverse spinel O$_h^7$ (*Fd3m*) space group of CoFe$_2$O$_4$.[32−34] The peak at 693 cm^{-1} in the 1473 K sample (T site) appears to shift substantially toward a lower value reaching 671 cm^{-1} for the pristine sample. The shift of T site peak suggests that the pristine sample is under strain.[10] The full width at half-maximum (fwhm) of the T-site mode is 42.1 cm^{-1} for 1473
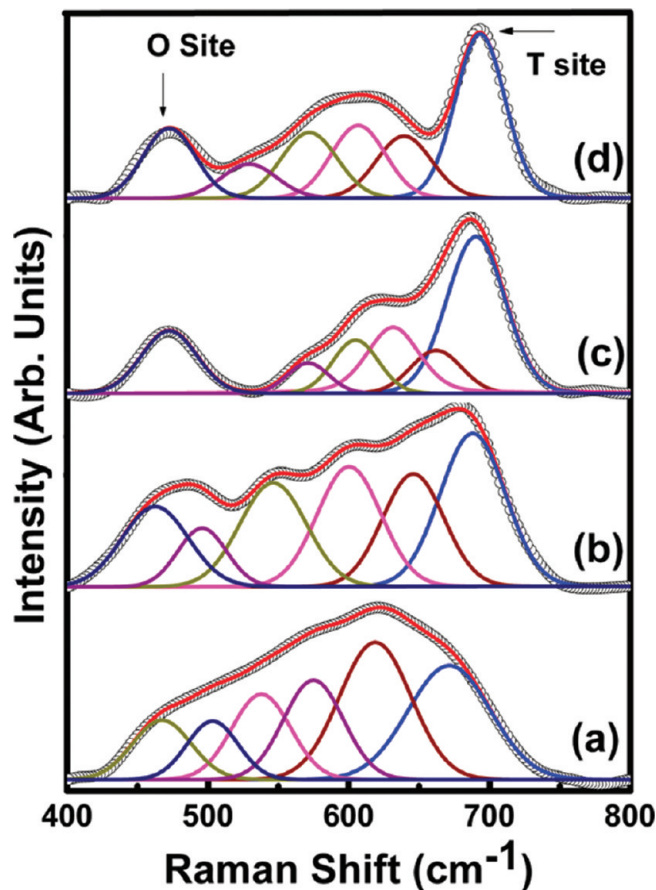
Figure 8. Raman spectra of (0.2 M) oleic acid capped CoFe$_2$O$_4$ sample (a) pristine and (b) annealed at 573 K, (c) 973 K, and (d) uncapped 1473 K annealed.

K annealed sample, which is increased to 68.9 cm^{-1} for pristine sample. The broadening of the Raman mode in the pristine sample is due to local disorder.[31] Also Raman spectrum of different concentration of oleic acid (0.2, 0.1, and 0.05 M) capped CoFe$_2$O$_4$ are shown in Supporting Information (Figure S6). For the sake of comparison, Raman spectra of uncapped CoFe$_2$O$_4$ annealed at different temperatures (573, 973, and 1473 K) are shown in the Supporting Information, (Figure S7).

4. Conclusions

In summary, cobalt ferrite nanoparticles of ∼20 nm size have been synthesized using a chemical route in which the particles are capped with oleic acid. Analysis of the sample using XRD and Mössbauer shows that the sample is in the mixed spinel state with ∼ 40% Co^{2+} ions occupying tetrahedral (A) site. High coercivity (9.47 kOe) has been observed at room temperature for the pristine sample (0.2 M oleic acid). TGA analysis and FTIR confirms the strong binding of oleic acid to surface of CoFe$_2$O$_4$ nanoparticles. Raman analysis suggests that the oleic acid capped CoFe$_2$O$_4$ sample is under strain. High coercivity was found to be a cumulative effect of disorder of surface spins, large strain, and surface anisotropy at the particle surface due to oleic acid.

Supporting Information Available: VSM measurements of uncapped $CoFe_2O_4$ annealed at different temperatures; Mössbauer studies of pristine $CoFe_2O_4$ sample; VSM, TGA, FTIR, and Raman measurements of $CoFe_2O_4$ nanoparticles coated with different concentration of oleic acid; Raman analysis of uncapped $CoFe_2O_4$ annealed at different temperatures. This material is available free of charge via the Internet at http://pubs.acs.org.

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