

# Synthesis and characterization of magnetic Co nanoparticles: A comparison study of three different capping surfactants

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## Abstract

This paper compares the performance of three long-chain acids—oleic and elaidic (both olefinic) and stearic (aliphatic)—as a capping agent in the synthesis of magnetic Co nanoparticles. The particles were formed through thermal decomposition of dicobalt octacarbonyl in toluene in the presence of the long-chain acid, and characterized by TEM, high-resolution TEM, and SQUID measurements. Infrared spectra revealed that some of the added olefinic acid was transformed from *cis*- to *trans*-configuration (for oleic acid) or from *trans*- to *cis*- (for elaidic acid) to facilitate the formation of a densely packed monolayer on the surface of Co nanoparticles. As compared to aliphatic acids, olefinic acids are advantageous for dense packing on small particles with high surface curvatures due to a bent shape of the *cis*-isomer. The presence of an olefinic acid is able to control particle growth, stabilize the colloidal suspension, and prevent the final product from oxidation by air. Our results indicate that oleic acid, elaidic acid, and a mixture of oleic/stearic acids or elaidic/stearic acids have roughly the same performance in serving as a capping agent for the synthesis of Co nanoparticles with a spherical shape and narrow size distribution.

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**Keywords:** Cobalt nanoparticle; Capping agent; Olefinic acid; Aliphatic acid; Isomeric transformation

## 1. Introduction

Metal nanoparticles with well-defined sizes and shapes have received much attention in recent years due to their peculiar electronic, optical, catalytic, and magnetic properties [1]. In particular, those with magnetic activities have attracted a great deal of interest because nanoscale magnetic particles allow one to investigate how atomic magnetism and bulk magnetism are correlated [2]. Magnetic measurements on small particles indicate that the magnetic moment of a nanoparticle can be enhanced by a factor of 1.3 per atom as compared to the bulk material [3]. Magnetic nanoparticles are also attractive for a range of applications that include magnetic information storage [4], magnetic refrigeration [5], and biomedical research such as

magnetic resonance imaging (MRI) contrast enhancement and hypothermia treatment [6–8].

Over the past decade, many different physical and chemical methods—for example, metal evaporation and solution-phase reduction of a metal salt or decomposition of an organometallic precursor—have been developed to synthesize magnetic nanoparticles [9–13]. Different from other systems, the strong magnetic interactions between magnetic nanoparticles in addition to their tendency to be oxidized in air have made it difficult to obtain stable colloids. To prepare stable magnetic colloids, a surfactant has to be added as a capping agent in order to control the particle growth and limit oxidation [14]. To this end, Sun and Murray have demonstrated the synthesis of Co nanoparticles in the presence of an organic surfactant such as oleic acid, lauric acid, trioctylphosphonic acid, and pyridine [15]. Kang and co-workers have also showed that magnetic  $\text{CoFe}_2\text{O}_4$  nanoparticles capped with oleic acid could be reversibly transferred between water and organic phases with the assistance of  $(\text{CH}_3\text{CH}_2)_3\text{N}$  [16]. However,

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the difference between these capping agents in controlling size distribution and air stability of Co nanoparticles was not reported. Herein we compare a number of surfactants for the synthesis of magnetic Co nanoparticles via thermal decomposition of an organic precursor, dicobalt octacarbonyl, at an elevated temperature. We specifically investigated the isomerization of oleic acid and elaidic acid and found that their *cis*-isomer with a bent shape is critical to the formation of a dense packing on the surface of a small particle typically characterized by a high curvature. As long as there is olefinic acid in the reaction solution, an effective coating can always be formed on the surface of Co nanoparticles, leading to a spherical morphology and a narrow size distribution for the product. This includes the use of a pure olefinic (oleic or elaidic) acid or a mixture of olefinic and aliphatic acids.

## 2. Experimental

Dicobalt octacarbonyl, oleic acid, elaidic acid, stearic acid, and toluene were obtained from Aldrich. All chemicals were used without further purification.

Cobalt nanoparticles were prepared through thermal decomposition of dicobalt octacarbonyl,  $\text{Co}_2(\text{CO})_8$ , in toluene. To prevent the product from aggregation, a surfactant has to be added at the beginning of each synthesis. In a typical experiment, a certain amount (as determined by the ratio between Co and the surfactant) of the surfactant was added to 20 mL dry toluene under vigorous magnetic stirring. 0.45 g  $\text{Co}_2(\text{CO})_8$  was then introduced into the reaction mixture and sonicated for 1 min to obtain a dark brown, transparent solution. Finally the reaction container was immersed in a pre-heated oil bath and the reaction was allowed to proceed under refluxing for 4 h. The solution turned into black in 10 min once the reaction had started.

Transmission electron microscopy (TEM) images were obtained using a JOEL 1200EX-II microscope operated at 80 kV. All samples for TEM studies were prepared at room

temperature by drying small droplets of the reaction solution on copper grids coated with amorphous carbon films (Ted Pella, Redding, CA). To investigate magnetic properties, dry samples of the Co nanoparticles in the powder form were prepared by completely evaporating the solvent (toluene) under ambient conditions. Magnetization was measured using a superconducting quantum interference device (SQUID) MPMS-5S magnetometer (Quantum Design, San Diego, CA). Approximately 100 mg samples were placed in a gelatin capsule and then loaded into the SQUID. Helium gas was flowed through the system during the measurement to prevent oxidation. All infrared spectra were taken with KBr pellets using a Perkin Elmer 1640 FTIR spectrophotometer.

## 3. Results and discussion

Colloidal stability is usually achieved by overcoming attractive interactions such as the van der Waals force (and magnetic dipole interaction for magnetic particles) with a repulsive barrier through capping by a surfactant [17]. A number of organic surfactants have been used to control particle size and prevent colloidal particles from aggregation. Because Co is a relatively reactive metal, a dense coverage by the organic surfactant is crucial to preventing the particles from being oxidized by air. Oleic acid is an excellent capping agent that can bind strongly to the surface of metals with native oxides through the carboxyl group. It has been widely used in the synthesis of colloidal nanoparticles from a large number of metals. In comparison, surfactants with a similar composition (e.g., elaidic and stearic acids) have been hardly explored for such an application. As shown in Fig. 1, oleic acid, elaidic acid, and stearic acid all contain 16  $\text{CH}_2$  ( $n = 1-2$ ) units, forming an extended chain with a methyl ( $-\text{CH}_3$ ) group at one end and a polar, carboxyl group at the other. These surfactants are very similar in chemical composition but different in molecular structure, making them a good system to

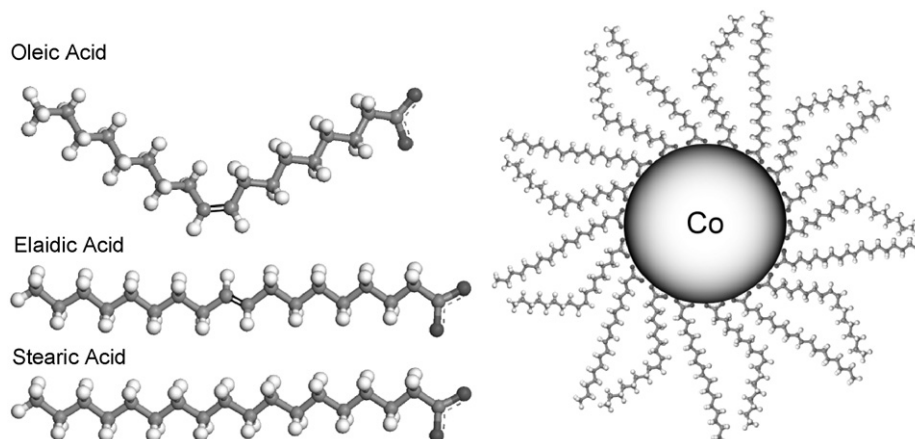


Fig. 1. Schematic drawings of oleic, elaidic, and stearic acids, together with a spherical Co nanoparticle whose surface is capped with a densely packed monolayer consisting of both oleic and elaidic acids (note that the particle size and molecular length are on different scales).

examine and compare the effect of molecular structure on the capping and stabilization of colloidal nanoparticles.

### 3.1. Synthesis with the addition of oleic acid as a capping agent

Fig. 2A and B shows TEM images of Co nanoparticles synthesized with oleic acid added as a capping agent. The nanoparticles had a spherical shape and characterized by a narrow size distribution (<6%); both attributes enabled the particles to self-assemble into a regular 2D array on the TEM grid during solvent evaporation. The edge-to-edge separation between adjacent particles was  $\sim 5$  nm (a value that is roughly twice as the length of an oleic acid molecule), indicating that the oleic acid formed a dense monolayer on the surface of each particle. This monolayer was “hard” enough to prevent adjacent particles from being crushed into physical touch by the capillary forces typically involved in solvent evaporation. In our synthesis, we used toluene as the solvent to achieve a relatively high reaction temperature. The use of a high reaction temperature would provide sufficient thermal energy for the atoms to diffuse to the site with the lowest free energy and thus generate a spherical morphology for the final product. When we prepared TEM sample by drop casting the colloidal suspension onto a carbon-coated TEM grid at room temperature, the slow evaporation rate of toluene

also facilitated the spherical particles to organize into a 2D hexagonal array.

Cobalt has two different crystal structures under ambient pressure: hexagonal-close-packed (hcp) at temperatures up till  $425^\circ\text{C}$ , and face-centered cubic (fcc) at temperatures above  $425^\circ\text{C}$ . For nanoparticles, a complex cubic primitive structure ( $P4_332$ ), with 20 atoms in each  $6.09\text{-}\text{\AA}$  cube was also observed by Sun and Murray [15]. This new phase, referred to as  $\epsilon\text{-Co}$ , is related to the beta phase of Mn. The high-resolution TEM image shown in Fig. 2C clearly indicates that the Co nanoparticles synthesized in toluene was a nearly perfect single crystal with a complex cubic structure associated with  $\epsilon\text{-Co}$ . The fringe spacing of  $0.2$  nm matches well the value derived from the electron diffraction pattern (Fig. 2D). The electron diffraction pattern could be indexed to  $\epsilon\text{-Co}$  with the strongest peak corresponding to  $\{221\}$ .

The TEM images in Fig. 2 clearly indicate that oleic acid can form a robust capping shell around each Co nanoparticle to minimize the oxidation and prevent irreversible aggregation of the particles. For the synthesis of Co nanoparticles with oleic acid as a capping agent, there exists a critical concentration below which oleic acid molecules could not form a densely packed monolayer on the particle surface. Consequently, black precipitates with irregular shapes were usually obtained, as in the case of nanoparticles synthesized with oleic acid/cobalt at a ratio

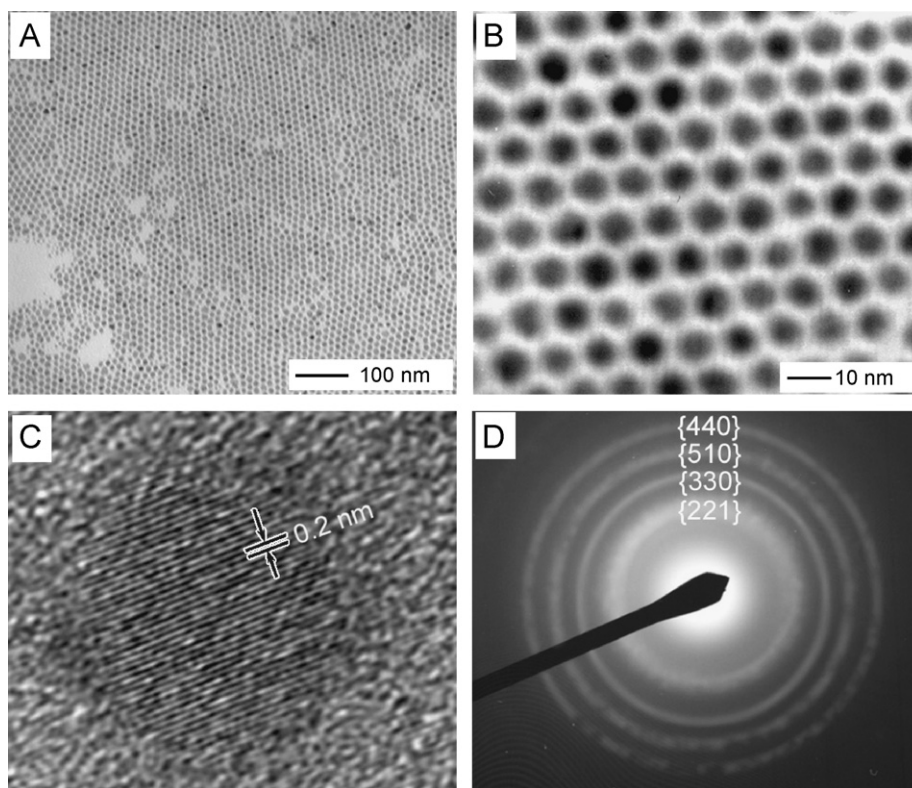


Fig. 2. (A, B) TEM images (at two different magnifications) of a regular 2D array of spherical Co nanoparticles synthesized with oleic acid added as a capping agent. The molar ratio of oleic acid to dicobalt octacarbonyl was 0.3 (i.e., oleic acid/cobalt = 0.6). (C) High-resolution TEM image of a single Co nanoparticle, with the lattice spacing matching the distance between  $\{221\}$  planes of  $\epsilon\text{-Co}$ . (D) Selected-area electron diffraction (SAED) pattern taken from an assembly of Co nanoparticles, with all rings indexed to diffractions from  $\epsilon\text{-Co}$ .

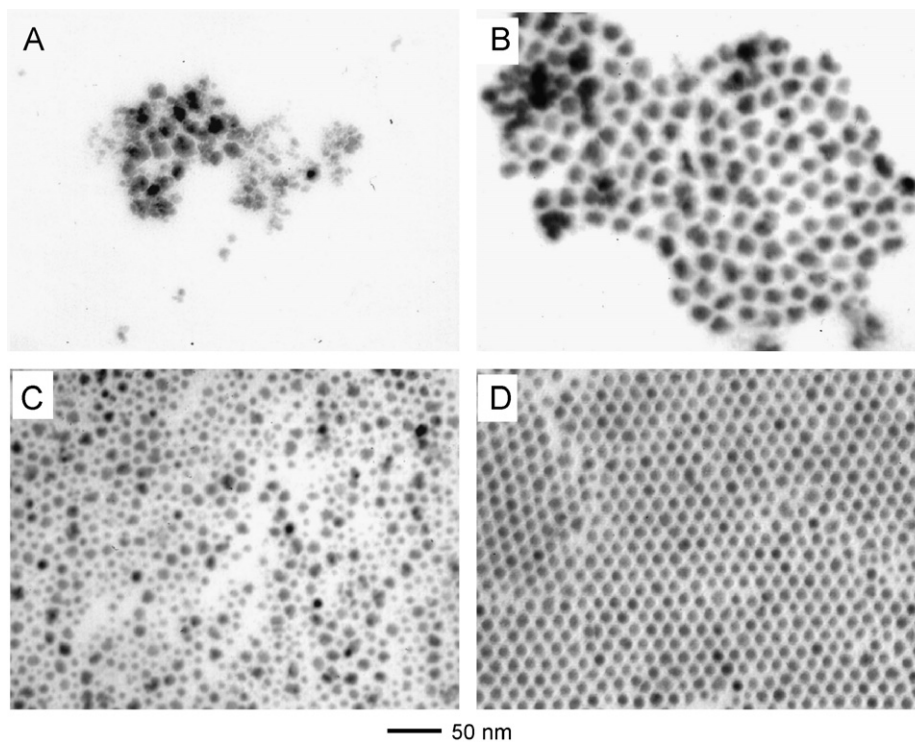


Fig. 3. TEM images of Co nanoparticles synthesized in the presence of oleic acid added as a capping agent (with molar ratio of oleic acid to cobalt being 0.6). These samples were taken after the reaction had proceeded for different periods of time: (A) 1, (B) 2, (C) 3, and (D) 4 h. Note that the Co nanoparticles were not uniform in either size or shape at the early stages of this synthesis.

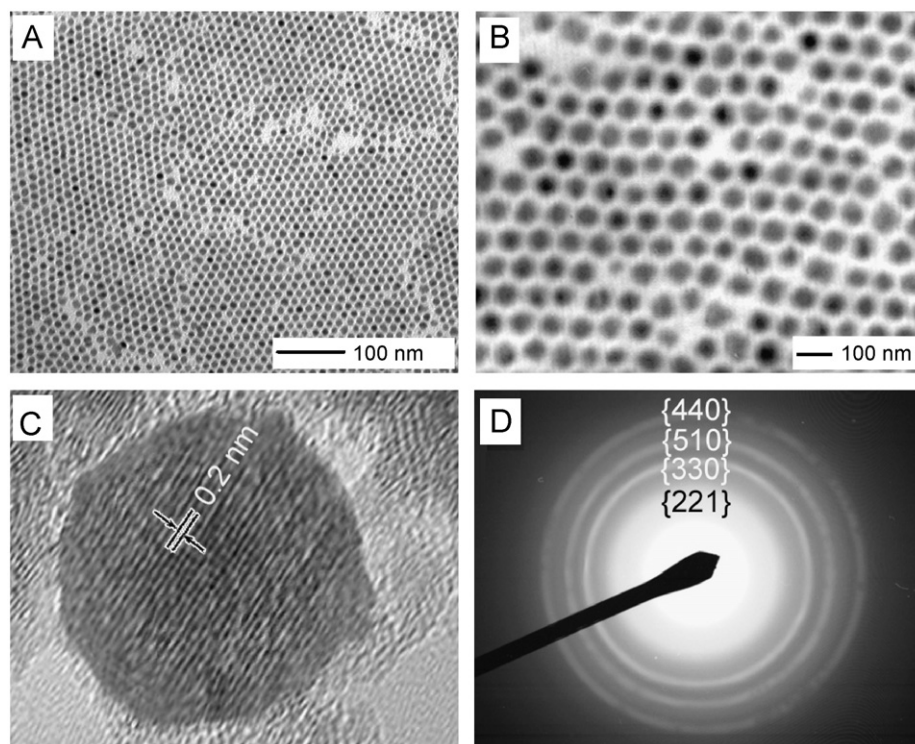


Fig. 4. (A, B) TEM images (two different magnifications) of a 2D array of Co nanoparticles synthesized with the oleic acid being replaced by elaidic acid at the same concentration as in Fig. 2. (C) High-resolution TEM image of a single Co nanoparticle. (D) SAED pattern taken from a random assembly of the same batch of Co nanoparticles. The synthesis was performed under the same conditions as those when oleic acid was added as the capping agent.

of 0.15. When the molar ratio was increased to 0.6, the capping agent was able to form a densely packed monolayer on the surface of the nanoparticles to stabilize them against agglomeration and prevent them from oxidation by air. The as-obtained Co nanoparticles could be easily dispersed in toluene to form a black and homogeneous suspension.

We also closely monitored the evolution of Co nanoparticles during the course of a synthesis. Fig. 3 shows TEM images of the samples obtained after the reaction had proceeded for 1–4 h. In the early stage, particles with irregular shapes and a broad size distribution were observed. This was probably caused by the fact that thermal decomposition reaction was much faster than the diffusion of Co atoms. As a result, the Co atoms would nucleate to form clusters right after they were generated from thermal decomposition of the precursor. Due to the involvement of multiple nucleation events, it is expected for the immediate product to display a broad range of shapes and sizes. At a later stage, Ostwald ripening came into play, through which the bigger particles could grow at the expense of smaller ones. Meanwhile, the relatively high temperature could facilitate the diffusion of Co atoms and provide enough thermal energy for the particles to recrystallize into the lowest energy form, leading to the formation of single-crystal nanoparticles with a more or less spherical shape. This growth process for Co nanoparticles seems to differ from the observation by Papirer and co-workers who reported a constant number of growing particles during the entire decomposition process of  $\text{Co}_2(\text{CO})_8$  [17]. In contrast, our mechanism resembles the one proposed by Reiss who suggested that a narrow size distribution could be achieved through slow growth for the larger particles and fast growth for the small particles [18].

### 3.2. Replacement of oleic acid with elaidic acid as the capping agent

Oleic acid and elaidic acid are the *cis*- and *trans*-isomers of 9-octadecenoic acid. To test the capability of elaidic acid as a capping agent, we simply replaced the oleic acid with elaidic acid while other conditions were kept the same for a typical synthesis of Co nanoparticles. Fig. 4A and B shows TEM images of Co nanoparticles prepared with elaidic acid added as the capping agent. The average diameter of these particles was about 8.5 nm and they also assembled into ordered 2D arrays during TEM sample preparation. Again, both high-resolution TEM image (Fig. 4C) and electron diffraction pattern (Fig. 4D) suggest that the Co nanoparticles had the same crystal structure as those obtained using oleic acid as the capping agent.

To understand the observed similarity between oleic acid and elaidic acid in serving as the capping agent, we analyzed the samples with FTIR spectroscopy. Fig. 5 shows the absorption spectra taken from pure oleic acid, pure elaidic acid, and Co nanoparticles synthesized in the presence of oleic or elaidic acid (the free acids had been

removed through excessive washing of the samples with ethanol). Although the absorption bands of pure oleic acid and elaidic acid are different, Co nanoparticles capped by oleic acid and elaidic acid show nearly identical absorption spectra. The stretching mode of  $\text{C}=\text{O}$  in both pure acids was located at  $1715\text{ cm}^{-1}$ , and was shifted to  $1550\text{ cm}^{-1}$  after the acids had been immobilized onto the surface of Co nanoparticles. The *trans*  $\text{CH}=\text{CH}$  in-phase wag was found in the region of  $960\text{--}965\text{ cm}^{-1}$  for pure elaidic acid while the same peak appeared in the spectrum from Co nanoparticles prepared in the presence of oleic acid or elaidic acid. The *cis*  $\text{CH}=\text{CH}$  in-phase wag occurred over

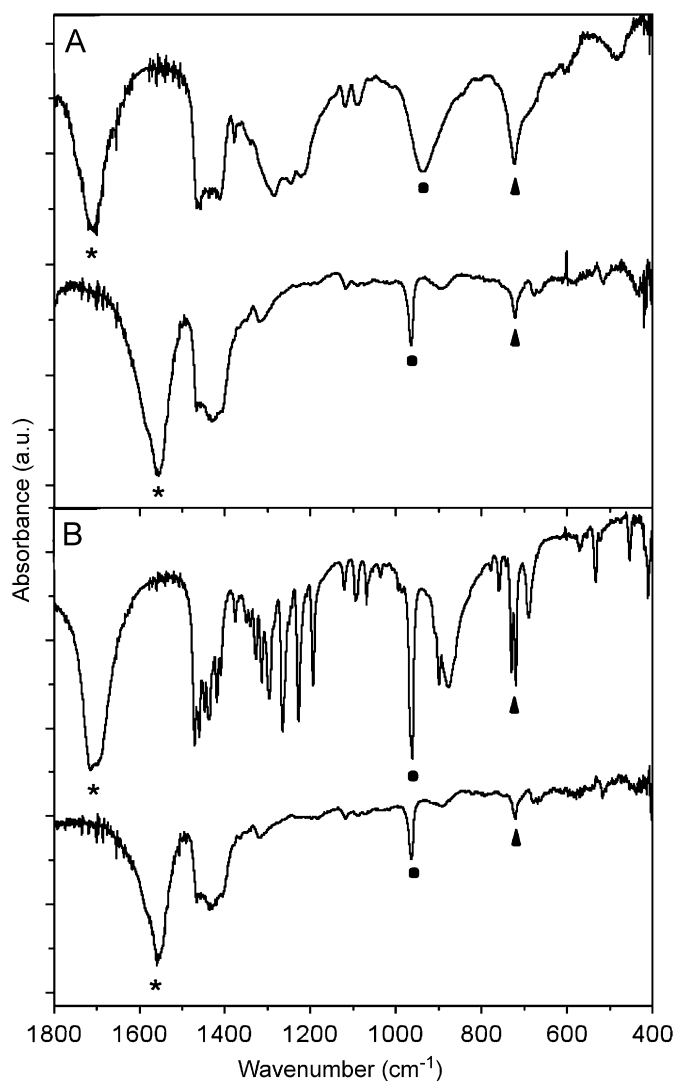


Fig. 5. FT-IR spectra of Co nanoparticles synthesized with (A) oleic acid, and (B) elaidic acid added as the capping agent. The upper trace of spectrum in each box was recorded from the pure acid before it was used in the synthesis, while the lower trace was obtained from Co nanoparticles capped by that acid. Note that the spectra for both oleic and elaidic acids on the surfaces of Co nanoparticles had similar features because the transformation of configurations should reach the same equilibrium if the reaction temperature was the same. The star symbols indicate the stretching mode of  $\text{C}=\text{O}$ ; the circles represent the in-phase wagging mode of *trans*- $\text{CH}=\text{CH}$ ; and the triangular symbols correspond to the in-phase wagging mode of *cis*- $\text{CH}=\text{CH}$ .

a broader spectral region ( $683\text{--}611\text{ cm}^{-1}$ ) for both samples of Co nanoparticles prepared with oleic acid or elaidic acid.

We believe this similarity was caused by the thermal transformation between oleic acid and elaidic acid at the reaction temperature [19]. Although a pure *cis*- or *trans*-isomer of 9-octadecenoic acid was added into the reaction solution, the transformation between *cis*- and *trans*-forms should lead to the same thermodynamic equilibrium after the reaction had proceeded for a certain period of time. Together, the *cis*- and *trans*-isomers could form a densely packed monolayer on the surface of a Co nanoparticle, as illustrated in Fig. 1. In oleic acid (the *cis*-isomer), the double bond is located at the half way of the hydrocarbon chain and the two half chains are bent with an angle of about  $120^\circ$ . The approximate geometry of an oleic acid can be considered as a cone if we assume the hydrocarbon chain can freely rotate against an axis normal to the surface

of a particle. In comparison, the “zigzag” configuration of elaidic acid (the *trans*-isomer) should behave like a linear chain and thus a cylinder under the free rotation assumption. Due to the high curvature of a small particle, the packing of pure cones or cylinders alone could not effectively cover the surface of a nanosphere. In contrast, a combination of these two differently shaped molecules (*cis*- and *trans*-forms) would allow for the formation of a dense coating layer on the nanoparticle surface. This explains why both oleic and elaidic acids are effective in serving as a capping agent.

### 3.3. Can stearic acid serve as an effective capping reagent?

Once we have understood how an olefinic acid works in the capping process, it is not hard to appreciate why stearic acid is not an effective capping agent. We have confirmed

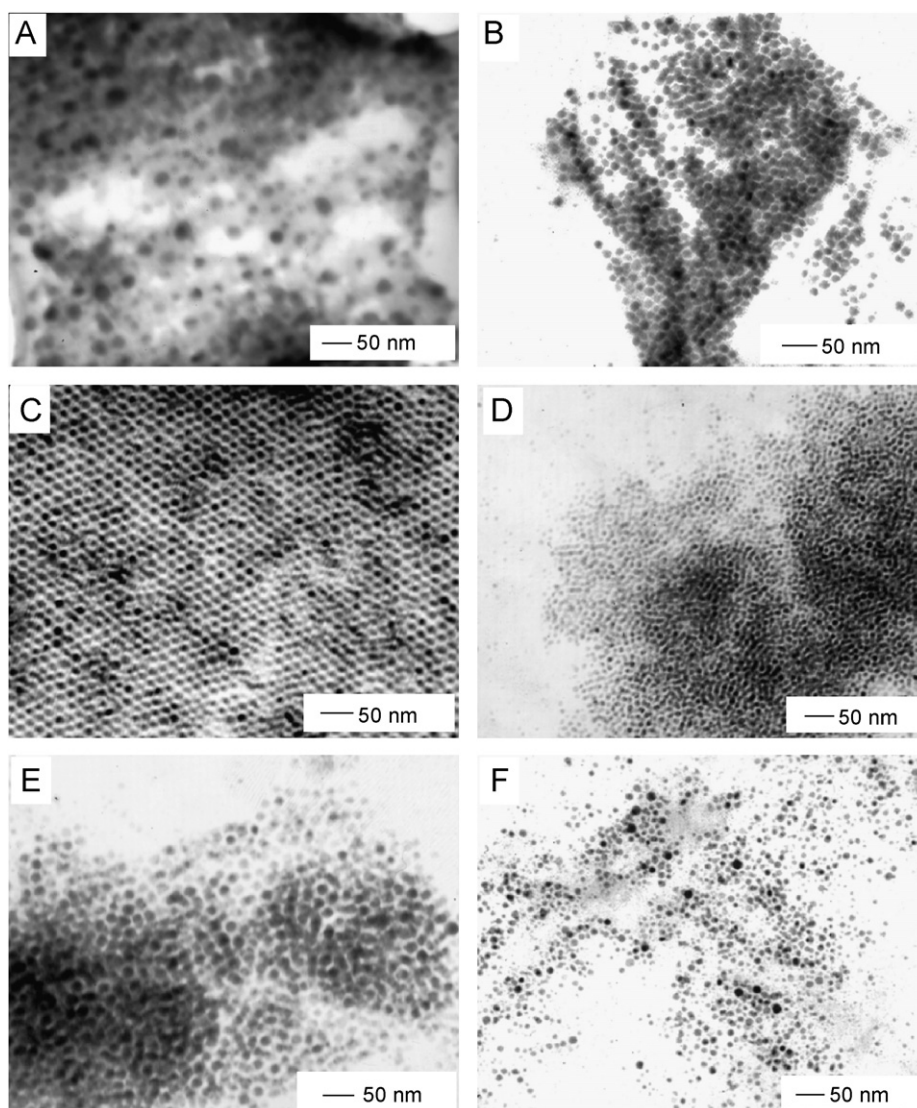


Fig. 6. (A, B) TEM images of Co nanoparticles synthesized with stearic acid added as a capping agent and at two different acid:cobalt ratios: (A) 0.2, and (B) 0.6. (C–F) TEM images of Co nanoparticles synthesized in the presence of a mixture of oleic acid and stearic acid. The ratio between carboxyl group (from both acids) and cobalt was kept at 0.6 for all syntheses. The molar ratio of stearic acid to oleic acid was varied as follows: (C) 1, (D) 2, (E) 4, and (F) 5. Note that uniform Co nanoparticles could still be obtained when the molar fraction of steric acid in the mixture was as high as 80% (sample-E).

this by replacing the oleic acid with stearic acid while other parameters were kept the same. Fig. 6A and B shows TEM images of Co nanoparticles synthesized in the presence of two different amounts of stearic acid. Again, the amount of surfactants added is very crucial to the formation of Co nanoparticles with a narrow size distribution. Too much surfactant would impede the diffusion process and result in a broad size distribution for the final product. When a right amount of stearic acid was used, we could obtain Co nanoparticles (Fig. 6B) with a relatively narrow size distribution, but the sample does not look as good as those obtained in the presence of an olefinic acid.

We believe the poor performance of stearic acid can be mainly attributed to its linear conformation. In addition, there might be other factors involved. Unlike oleic or elaidic acid, there is no C=C double bond in the chain of stearic acid. It is possible that the interaction of double bonds between olefinic acids could assist the formation of a densely packed layer on the surface of a Co nanoparticle. The overlap of double bonds between adjacent molecules would enhance the hardness of the capping layer. Since the densely packed surface layer is “harder” than those formed from aliphatic acids, the distance between adjacent particles will be precisely determined, allowing the particles to self-organize into ordered arrays. This was confirmed from the control experiments using a mixture of oleic acid and stearic acid as the capping agents to form Co nanoparticles. Fig. 6C–F shows the Co nanoparticles

synthesized with oleic acid and stearic acid added at different ratios. With the decrease of the molar ratio between oleic acid and stearic acid, less densely packed particles were observed on TEM grids even though they were still relatively uniform in size.

### 3.4. Magnetic measurements

Fig. 7A and B shows the hysteresis loops measured at 5 and 300 K, respectively, for Co nanoparticles synthesized with oleic acid added as a capping agent. The Co nanoparticles coated with oleic acid were below the critical size at which the particles are single crystals and each of them contains only one magnetic domain. As a result, the magnetic nanoparticles are expected to exist in the so-called superparamagnetism state. The recorded hysteresis loops also revealed weak interaction between the superparamagnetic particles. At low temperatures, the particles did not have enough energy to overcome their coercive field, so change of external magnetic field would not align all the magnetic domains of the nanoparticles. Accordingly, a small hysteresis was observed. As temperature increased, the thermal energy progressively overcame the magnetic interactions and the hysteresis disappeared at 300 K, and the magnetic interaction between particles was essentially negligible.

The temperature dependence of the magnetization was studied in a 10,000 Oe field between 5 and 300 K using

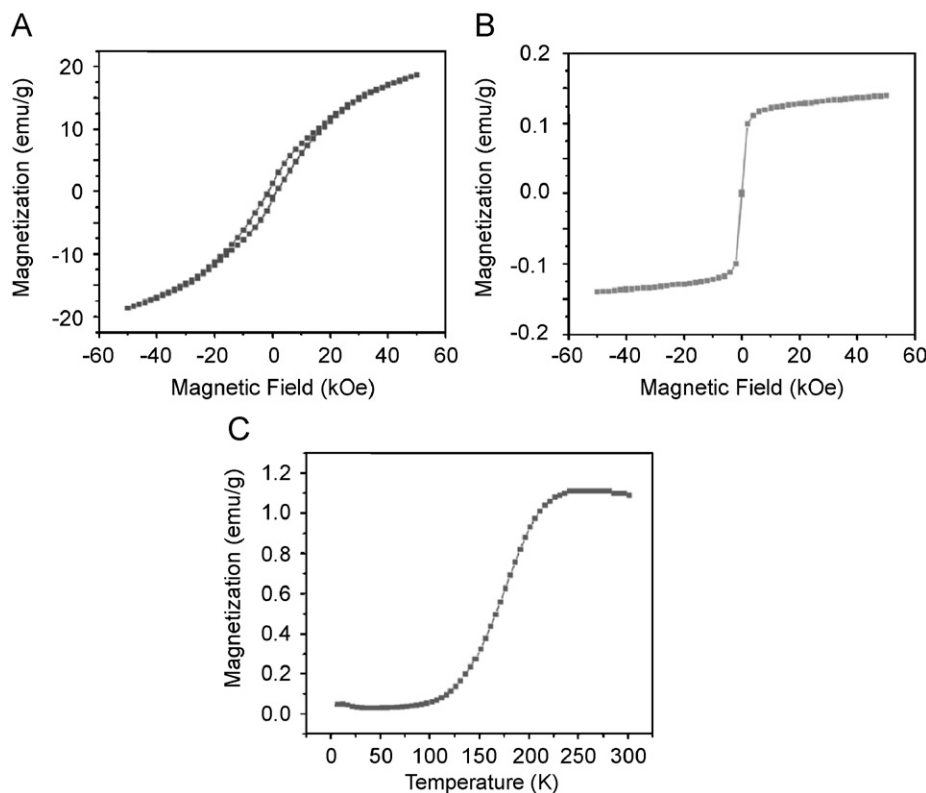


Fig. 7. (A, B) Hysteresis loops for the magnetization of Co nanoparticles (synthesized with oleic acid as the capping agent) recorded at 5 and 300 K, respectively. (C) Magnetization curves (ZFC) for the same batch of sample in the temperature range from 5 to 300 K.

zero-field-cooling (ZFC) procedure. At room temperature, thermal energy was high enough to overcome the coercive field of the particles so the magnetic domains of isolated particles were oriented in random directions. When an external field was applied to the randomly oriented particles, the magnetic field forced the particles to align. As the temperature decreased, the moments of individual particles were frozen. The increase of temperature allowed the nanoparticles to gain enough energy to orientate their magnetic polarization along the external field. As shown in Fig. 7C, the particle domains were realigned at about 100 K. The magnetization reached its maximum value at about 230 K where all magnetic moments were aligned in the same direction as the applied field, and the weak external field was enhanced.

### 3.5. Magnetic gel

Olefinic acid has an unsaturated double bond, which can be polymerized by heating or in the presence of a free radical initiator. When a relatively high concentration of oleic or elaidic acid is used, the free acids in the solvent can be polymerized together with those on the surfaces of Co nanoparticles to generate a three-dimensional (3D) polymer network [20]. As a result, the as-obtained colloidal dispersion can be converted into a magnetic gel. Fig. 8 shows a photograph of a reaction container in the upside-down orientation. The black magnetic gel at the bottom of the vial was formed by heating the reaction mixture (oleic acid/Co = 1.3) for a total of 5 h before cooling down to room temperature. Since each Co nanoparticle has multiple double bonds immobilized on its surface, it can serve as a point for cross-linking to generate a 3D network of polymer matrix impregnated with magnetic Co nanoparticles.

## 4. Conclusion

Oleic acid has been widely used as a capping agent to stabilize metal colloids since it can easily form a densely packed monolayer on the surface of a small particle characterized by a high curvature. FTIR spectra taken from Co nanoparticles synthesized in the presence of oleic acid indicate that some of the acid had been transformed from a *cis*- to a *trans*-configuration (elaidic acid) during the synthesis. It is a combination of both *cis*- and *trans*-isomers that leads to the formation a densely packed monolayer on the particle surface. For this reason, the oleic acid can be replaced with elaidic acid without compromising the quality of the final product. In addition to oleic acid, stearic acid was also examined as a capping agent to synthesize Co nanoparticles. It was found that stearic acid alone was capable of promoting the formation of Co nanoparticles with a relatively narrow size distribution and stabilizing the product against agglomeration. However, a “hard” capping shell could not be formed on the particle surface, and accordingly, those nanoparticles would not be



Fig. 8. Photograph of an upside-down vial containing a black gel containing Co nanoparticles and a cross-linked network of oleic acids. In this case, a relatively high concentration of oleic acid (oleic acid/cobalt = 1.3) was used.

able to self-assemble into ordered arrays during the evaporation of solvent. This can be remedied by using a mixture of stearic acid and oleic or elaidic acid. Due to the existence of double bonds in olefinic acids, it was possible to form magnetic gels by polymerizing and cross-linking the double bonds.

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