

Synthesis and Characterization of Surface-modified FePt Nanocrystals by Supercritical Hydrothermal Method

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We have synthesized single nanosized FePt nanocrystals (NCs) by supercritical (sc-) hydrothermal synthesis. The synthesized FePt NCs were characterized by X-ray diffraction (XRD), transmission electron micrography (TEM), electron diffraction (ED), superconducting quantum interference device magnetometry (SQUID), and Fourier transform infrared spectroscopy (FTIR). Surface modification with oleic acid was also successful, and it gave spherical FePt NCs that had average particle size (APS) of 5.0 ± 1.5 nm. In addition, the surface-modified FePt NCs showed good dispersion into organic solvents. A dispersion in tetrahydrofuran (THF) was stable for at least 3 days. The dried surface-modified FePt NCs were easily oxidized in the atmosphere. This high reactivity to oxygen makes the characterization difficult and, at the same time, may indicate that quite a small amount of Fe NC is included in the reaction products.

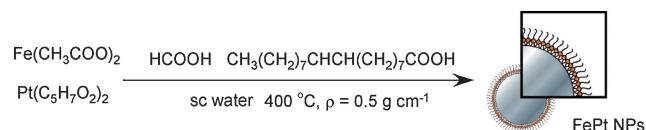
Alloys possibly exhibit benefits of all the contained metals. Sometimes alloy exhibits original unique properties that pure metals do not. These properties are attractive in terms of reduction of rare and noble metals usage. In addition, alloying may help the synthesis of nanoparticles (NPs) which consist of easily oxidized metals. Therefore, a lot of alloys, including their NPs, have been invented and applied as beneficial materials. Among them, FePt alloy which contains close to equal atomic percentage of Fe and Pt is an important class of magnetic materials.^{1–3} For instance, FePt NPs can be a magnetic recording material with quite high storage density. There have been a lot of studies to synthesize fine FePt NPs.^{4–8} However, a method for large-scale production of fine FePt NPs is still awaited.

When one thinks about metal NPs synthesis, the technique to avoid oxidation can be a key issue. Because metal NPs have very high surface/volume ratio, they easily aggregate to reduce total surface area and are rapidly oxidized to metal oxide NPs. In order to solve these problems, surface control of metal NPs and in situ surface-controlled synthesis of metal NPs are quite important issue to be studied. Recently, surface protection of metal NPs by graphite and/or graphene sheet seems promising to avoid oxidation of the surface of metal NPs.^{9–11} Further modification method of the graphite surface of the core-shell NPs to introduce functional reagent on them have been developed.^{12,13} Although this process is suitable to synthesize oxidation-resistant metal NPs, it is a dry process so that good control of the NPs size and morphology as well as dispersion of the NPs is difficult. At this point, the development of the solution-state synthesis of metal NPs seems still important.

Hydrothermal synthesis is a promising method to synthesize inorganic NPs, especially for metal oxides, with controlled size, morphology, and surface.¹⁴ We have developed in situ surface-modified supercritical (sc-) hydrothermal synthesis of metal oxide NPs.^{15,16} Since sc-hydrothermal reaction is very fast, it suits large-scale production of NPs, e.g., continuous production by utilizing flow-type reactors.¹⁷ This is a large advantage in the industrial production of NPs. Recently, a sc-hydrothermal method with effective reducing agent was also investigated to synthesize metal NPs.¹⁸ However, produced metal NPs were easily oxidized by water during the synthesis, washing, and storage processes. The oxidation made the characterization difficult to prove the production of easily oxidized metal NPs such as Fe NPs.

In this study, we performed sc-hydrothermal synthesis of FePt NPs. As mentioned above, iron alloys are more easily synthesized and more oxidation resistant than pure metal iron. Therefore, FePt NPs can be synthesized. Sc-hydrothermal synthesis using formic acid as reducing agent and oleic acid as surface modifier was performed. The oleic acid-capped FePt NPs showed quite stable dispersion in several organic solvents e.g., tetrahydrofuran (THF) and chloroform. The sc-hydrothermal synthesis is a rapid process, and one can evaluate continuous reactors for the sc-hydrothermal synthesis. Therefore, the method performed here would be a promising new method to synthesize FePt NPs with high efficiency.

The surface-modified FePt NPs were synthesized by sc-hydrothermal reaction. The method is concretely described in Supporting Information.²² Briefly, in an Ar-purged glove box, 2.5 mL of 0.01 M aqueous metal salt mixture and formic acid (concentration was set to 3 M, after the reaction system became homogeneous) and oleic acid (surface modifier, if necessary) were introduced into an autoclave made from Hastelloy C alloy (i.v. = 5.0 mL). Then the reactor was sealed and stored in a furnace (400 °C) for 10 min (Scheme 1). After the reaction, the reactor was removed from the furnace and immersed into a water bath to terminate the reaction. The reactor was opened in the glove box. With this procedure, the reactant and product could be treated in oxygen-free atmosphere to avoid unfavorable



Scheme 1. Schematic description for the synthesis of oleic acid-modified FePt nanocrystal.

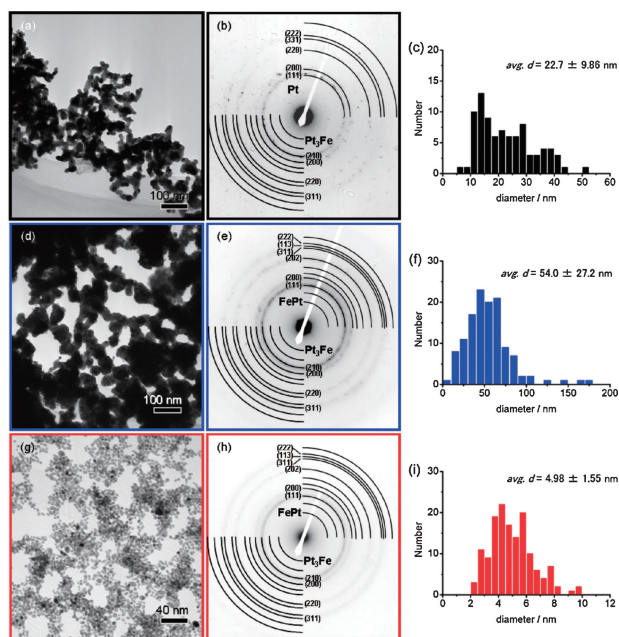


Figure 1. TEM images (a), (d), (g); ED patterns (b), (e), (h); and histogram (c), (f), (i) of the NCs synthesized in this study. The sample for (a), (b), and (c) was synthesized with 0.4 M formic acid (FA) and 0 M oleic acid (OA). The sample for (d), (e), and (f) was synthesized with 3 M FA and 0 M OA. The sample for (g), (h), and (i) was synthesized with 3 M FA and 0.2 M OA. As a reference, the diffraction patterns of JCPDS file for FePt (No. 21-1272), Pt₃Fe (No. 29-1423), and Pt (No. 04-0842) were also displayed in each ED pattern (detail see text).

oxidation of the reactant and product by oxygen. The reaction products were collected with methanol and washed by centrifuge three times. Washed powder was dispersed in water and freeze-dried. The obtained products were stored in the glove box. The products were characterized crystallographically by XRD and ED, morphologically by TEM, and magnetically by SQUID. The surface modification of the products was analyzed by FTIR.

Figure 1 depicts the TEM images and ED patterns of the NPs synthesized in this study. The X-ray diffraction patterns are depicted in Figure 2. Both the ED and XRD patterns of the NPs synthesized with 0.4 M formic acid showed good agreement with the diffraction patterns of JCPDS file for Pt₃Fe. Small peaks corresponding to Fe₃O₄ were also observed in the XRD pattern. These results suggest that the main product was Pt₃Fe with this condition. When the amount of formic acid was increased to 3 M, both the ED and XRD patterns still showed good agreement with the diffraction patterns of the JCPDS file for Pt₃Fe, but it also showed good agreement with the diffraction patterns of the JCPDS file for FePt as well. Especially in XRD patterns, it is observed that the peaks around 41, 47, and 70° shifted from Pt₃Fe to FePt position. The peaks corresponding to Fe₃O₄ are lessened. These imply that the product was mainly FePt (or a mixture of FePt and Pt₃Fe). When the surface modifier (oleic acid) was loaded, both the ED and XRD patterns showed good agreement with that of the JCPDS file for FePt. In addition, small peaks corresponding to Fe₃O₄ disappeared. This might result in the improvement of the yield of FePt by slowing down

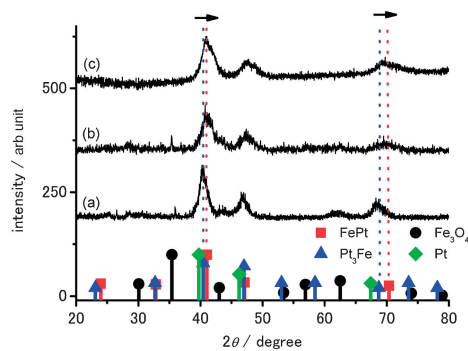


Figure 2. Powder XRD pattern of the NPs synthesized (a) with 0.4 M formic acid (FA) and 0 M oleic acid (OA), (b) with 3 M FA and 0 M OA, and (c) with 3 M FA and 0.2 M OA. The diffraction patterns of JCPDS files for FePt (No. 21-1272), Pt₃Fe (No. 29-1423), Fe₃O₄ (No. 79-0419), and Pt (No. 04-0842) were also depicted as reference.

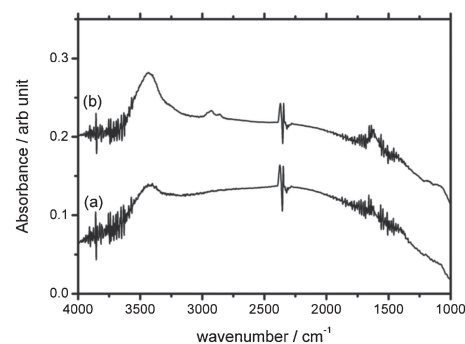


Figure 3. FTIR spectra of the NPs synthesized (a) with 3 M formic acid (FA) and 0 M oleic acid (OA), (b) with 3 M FA and 0.2 M OA.

the precipitation of Fe ions in the reaction system. According to the facts, it can be said that FePt NPs with small size and size distribution, i.e., APS = 4.98 ± 1.55 nm, were synthesized.

The average primary particle diameters of the NPs were calculated from half-width of the XRD peaks by Scherrer's equation. The diameter was $d = 13.8$, 9.94 , and 8.14 nm, for Pt₃Fe, unmodified FePt, and surface-modified FePt NPs, respectively. Comparing the diameters obtained from TEM images and XRD patterns, it is suggested that the oleic acid actually avoided the aggregation and/or agglomeration of synthesized NPs and that the oleic acid-modified NPs were single crystal, i.e., they are FePt NCs. In order to confirm the surface modification of FePt NCs, FTIR spectroscopy was employed to detect hydrocarbon in the NCs synthesized with oleic acid. The spectrum is shown in Figure 3. The spectrum of oleic acid-modified NCs had peaks corresponding to C–H stretching around $3000\text{--}2700\text{ cm}^{-1}$ whereas the spectrum of the NPs without surface modifier had no peak corresponding to organic compounds, only a broad peak of adsorbed water ($3700\text{--}3000\text{ cm}^{-1}$) was seen. However, the measurement was quite difficult because the oleic acid-modified NCs were quite easily oxidized in the atmosphere. Actually, when dried oleic acid-modified NCs powder was exposed to air (atomized), the powder exploded. This phenomenon can also be additional proof of the

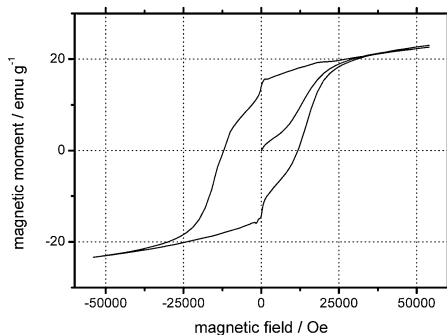


Figure 4. Magnetization as a function of field for the oleic acid-modified FePt NCs. The SQUID measurement was carried out at 300 K.

formation of small FePt particles, or a small amount of pure Fe NCs might be synthesized simultaneously. Then, even a small amount of Fe NC, Fe NC is extremely flammable, might ignite the whole to explosion.

We also measured magnetic properties of the oleic acid-modified NCs by SQUID. Figure 4 depicts the magnetization curve of the oleic acid-modified NCs. The obtained saturation magnetization (M_s) and coercivity (H_c) of the synthesized NCs was $M_s = 23.0 \text{ emu g}^{-1}$, $H_c = 12.1 \text{ kOe}$, respectively. Both saturation magnetization and coercivity of FePt depend on the size, crystal structure, and morphology, whereas the values measured for the synthesized NCs are reasonable to presume synthesized NCs are mainly composed of FePt. The values are comparable to those reported in the literature.^{1,19–21} In addition, energy-dispersive X-ray spectra (EDX) of the oleic acid-modified and unmodified FePt NPs were measured and depicted in Supporting Information.²² The EDX result supports the stoichiometry of the NPs, i.e., both NPs contain nearly equal atomic ratio of Fe and Pt.

Dispersion of the oleic acid-modified FePt NCs was also examined. As shown in Figure 5, oleic acid-modified FePt NCs showed stable dispersion. A small amount of precipitation was seen; however, most of the NCs dispersed very well in THF even after 3 days after the preparation. However, the NPs without surface modifier were totally precipitated. Actually, the affinity between the surface of the NCs and solvent molecules was increased by the surface modification. This good dispersion of oleic acid-modified NCs was also observed in CHCl_3 , CH_2Cl_2 , and DMSO.

In conclusion, FePt NCs were synthesized by sc-hydrothermal method. Surface modification by oleic acid was also successful, and it enabled us to obtain single nanosized ($\text{APS} = 5.0 \pm 1.5 \text{ nm}$) spherical FePt NC. The crystal structures of the synthesized FePt NCs were studied by XRD, ED, and TEM. In addition, the oleic acid-modified FePt NCs showed very good dispersion into organic solvents, e.g., the dispersion in THF was stable at least 3 days after the preparation. Because the oleic acid-modified FePt NCs in dry (powder) state was explosively burned in the atmosphere, further characterization in this study was very difficult. This high reactivity to oxygen may imply that the NPs include a small amount of single nanosized Fe.

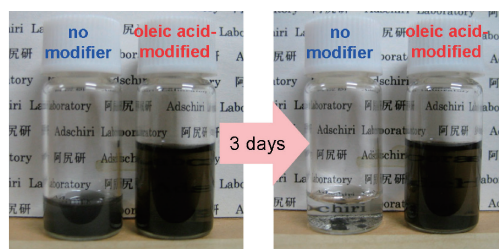


Figure 5. The images of the THF dispersions of the unmodified and oleic acid-modified FePt NPs. Left hand side image was taken just after and right hand side image was taken 3 days after the preparation.

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