

Synthesis of decanoic acid-modified iron oxide nanocrystals using supercritical carbon dioxide as reaction medium

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Abstract

In the synthesis of surface modified nanocrystals (NCs), simple and green chemistry approach to reduce the liquid waste, especially solvent less process, has been desired. In this study, we applied supercritical CO₂ technology, which are substantially solvent less process, to the synthesis of surface-modified iron oxide NCs. The synthesis was performed at 30.0 ± 0.8 MPa of CO₂, 18 h and 100°C, where iron(III) acetylacetonate, pure water and decanoic acid were used as starting materials. As a result, supercritical CO₂ medium gave the NCs of α -Fe₂O₃ and γ -Fe₂O₃ with the unimodal size distribution where the mean size was 7.8 ± 2.0 nm. Additionally, they were self-assembled on the TEM substrate and the mean nearest-neighbor spacing was closed to the chain length of decanoic acid. Furthermore, FT-IR and TG analysis supported that decanoic acid chemically attach to the surface of iron oxide NCs that were dispersed to cyclohexane. These results suggest that supercritical CO₂ medium could be new appealing reaction field to fabricate the densely modified NCs without the liquid waste.

Keywords

supercritical carbon dioxide, iron oxide nanocrystals, surface modification

1. Introduction

The surface modified NCs has been typically synthesized using wet based methods such as sol-gel [1], hot-injection [2], heat-up [3] and hydrothermal [4] methods because the solvent is required to dissolve precursors and surfactants uniformly and to control the reaction of them [5]. However, wet based methods cause the large amount of liquid waste for the synthesis and washing [2–4], where the disposal and the regeneration cost of them is known as the critical issue. Whereas the synthesis in supercritical carbon dioxide (scCO₂) can be new appealing

candidate to fabricate surface modified NCs. scCO_2 has unique properties such as high solubility of the metal organic precursor [6] and diffusivity, which allows the formation of homogenous phase [7], while the synthesis in scCO_2 is substantially solventless reaction process. Additionally, scCO_2 can be used as not only synthesis but also washing and drying solvent for the particle production [7,8]. These characteristics allow the simple fabrication process without liquid waste, thus, scCO_2 medium has been applied for the synthesis of inorganic materials such as metal oxide [9], metal hydroxide [8] and metal sulfate [10]. However, in the most of case, the products were observed as aggregates or the submicron sized particles after the synthesis in scCO_2 [9,11]. This is probably due to the characteristic of scCO_2 that is non-polar solvent. Non-polar properties of scCO_2 have low compatibility with metal oxide surface (generally is hydrophilic), which typically results in the accelerated aggregation.

Introduction of organic surfactant to the synthesis in scCO_2 is expected to overcome this serious problem because surface modification can change surface properties of metal oxide from hydrophilic to hydrophobic that is compatible to scCO_2 [12]. Additionally, reduction of surface energy and steric repulsion between particles can be achieved by surface modification [12,13]. Furthermore, scCO_2 has high ability to dissolve organic surfactant that is typically used for the synthesis of surface modified NCs such as saturated and unsaturated fatty acid [5,14–16]. Therefore, scCO_2 with organic surfactant has the potential to directly synthesize the surface modified NCs with good monodispersity. However, the report concerned with the synthesis in scCO_2 is limited to the metal oxide without surface modification [8,11,17], thus, the direct synthesis of surface modified NCs in scCO_2 was attempted in this work.

In this contribution, we report a novel simple synthesis using scCO_2 as reaction medium for surface modified NCs. As a model material, we chose iron oxide that is applied as catalyst [18], drug carrier [19], and in magnetic recording device [20] due to its appealing catalytic and magnetic properties. Iron(III) acetylacetonate and decanoic acid of fatty acid were used as precursor and surfactant, respectively. Herein, hydrolysis or thermolysis of iron precursor were popular reaction to synthesize iron oxide NCs for conventional hydrothermal and heat-up methods [3,12]. Thermolysis reaction of the iron precursor requires high temperature above 300°C , where such severe environment easily produce the byproduct sourced from the thermal decomposition of high boiling solvent [21]. On the other hand, hydrolysis reaction of iron precursor easily proceed under 100°C and yield the well crystalline nanoparticles [22], therefore, small amount of water was used as a starting material to utilize hydrolysis reaction for the synthesis of iron oxide NCs in this study.

2. Experimental

2.1. Materials

Iron(III) acetylacetonate [Fe(acac)₃] (purity > 99 %) and decanoic acid (purity > 98.0 %,) were purchased from Wako Pure Chemical Industries, Ltd. CO₂ (purity > 99.9 %) and nitrogen (N₂, purity > 99.95 %) were supplied by Fujii Bussan Co., Ltd. Ultra-pure water was prepared using Direct-Q UV3 Water Purification System supplied by EMD Millipore Corp. and the resistivity was confirmed to be 18.2 MΩ cm.

2.2. Synthesis procedure

The high-pressure system shown in Fig. 1 was developed to synthesize surface modified NCs in scCO₂. The 0.53 g of Fe(acac)₃, 1.29 g of decanoic acid and 0.45 g of water were transferred to the 76 mL volume of a reaction vessel (TSC-CO₂-008; Taiatsu Glass Corp.). These amount of Fe(acac)₃, decanoic acid and water correspond to the molality of 0.03, 0.15 and 0.50 mol/kg in scCO₂, respectively, where the molality of them were calculated using the volume of the vessel and CO₂ density at the reaction condition. The mixture was stirred for 1 min at the ambient condition. Subsequently, CO₂ was flowed under 0.5 MPa for 1 min to displace the air in the vessel and liquified CO₂ was introduced into the vessel using the HPLC pump (PU-4386; JASCO Co., Ltd.) until reaching 6.6 to 7.0 MPa. After reaching the appropriate pressure, the vessel was sunk in the oil bath stirrer, which resulted in the target temperature of 100°C and the pressure of 30.0 ± 0.8 MPa. The vessel was left in the oil bath stirrer for 18 h while the enclosed materials were vigorously stirred. After the time passed, the vessel was pulled up and was depressurized at a rate of approximately 0.5 MPa min⁻¹ using a metering valve. After depressurization, the vessel was quenched in a water bath at room temperature.

The products were collected by rinsing the vessel successively with cyclohexane/ethanol mixture whose the volume ratio was 1:4. The products were centrifuged and washed with a mixture of cyclohexane and ethanol (1:4) to eliminate the unreacted precursor and surfactant. The solid products were dried in a vacuum oven at room temperature for 24 h.

2.3 Characterization

The particle yield Y was defined as follows.

$$Y = \frac{W_{collect}}{W_{theory}} \quad (1)$$

where $W_{collect}$ is the weight of final products after washing and drying and W_{theory} is the maximum particle weight of Fe₂O₃ when the reaction is complete. X-ray diffraction patterns of the products were obtained by X-ray diffractometer (XRD) (MiniFlex600-C; Rigaku Corp.) using Cu Kα radiation. The products were observed by transmission electron microscopy (TEM) (H-7650; Hitachi Corp.) operated at 100 kV. High resolution TEM (HR-TEM) images and electron diffraction pattern were acquired using a JEOL JEM-2010F electron microscope

operated at 200 kV. The solid products for TEM and HR-TEM analysis were dispersed in cyclohexane before transferred onto the copper grids with organic membrane. The mean size, with their standard deviation, of the particles were determined by observing approximately 200 particles for TEM analysis. Thermogravimetric variation were analyzed from room temperature to 600°C at a ramp rate of 10°C min⁻¹ and at N₂ atmosphere using thermogravimetric analyzer (TGA) (TGA-50; Shimadzu Corp.). The absorbed state of organic surfactant on the iron oxide surface was investigated using a fourier transform infrared spectrometer (FT-IR) (FT-IR4100; JASCO Co., Ltd.).

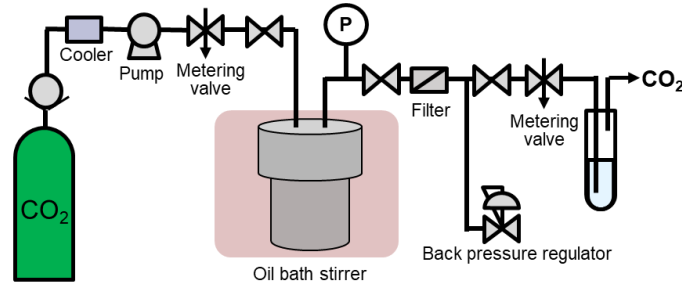


Fig. 1 Experimental apparatus for the synthesis of organic modified NCs

2.4 Phase equilibrium calculation

Phase equilibrium calculations were performed to predict the phase state of synthetic field. Peng Robison (PR) equation [23] were used to solve the water + scCO₂ equilibrium and to calculate water solubility to scCO₂. In the calculation, the below mixing rules were employed.

$$a_m = \sum_i \sum_j x_i x_j (a_i a_j)^{1/2} (1 - k_{ij}) \quad (2)$$

$$b_m = \sum_i \sum_j x_i x_j b_{ij} \quad (3)$$

$$b_{ij} = (b_i + b_j)/2 \quad (4)$$

where a_m and b_m is the mixture's parameter. a_i and a_j are parameters reflecting attracting forces of pure components i and j . b_i and b_j are size parameters of pure component i and j . To decide the binary interaction parameters k_{ij} and the temperature dependence of it, the data from S. Hou et al. [24] were used. Additionally, Chrastil's equation [25], expressed as follows, were used to calculate the decanoic acid and Fe(acac)₃(III) solubility to scCO₂.

$$\ln y = k \ln \rho_r + \frac{m}{T} + n \quad (5)$$

where k , m and n , are fitting parameters and ρ_r is the relative density of CO₂. For decanoic acid case, only the mol fraction data from 0.0 to 0.05 were used to fit the parameters, k , m and n [15]. To fit the parameters k , m and n for Fe(acac)₃(III), the data from M. Haruki et al. [6] were used.

3. Results and discussions

3.1 Phase equilibrium calculation

Fitted values, summarized in Table 1, were used to predict the phase state. Fig. 2a, b and c show Fe(acac)₃, water and decanoic acid solubility to scCO₂, respectively, where the initial concentration values of water, Fe(acac)₃ and decanoic acid in the synthesis were depicted as plots in the figures. The initial concentration value of Fe(acac)₃ is somewhat higher than the solubility. The initial concentration values of water and decanoic acid were significant lower than these solubility, indicating that water and decanoic acid is completely soluble to scCO₂ for the synthetic conditions.

Table 1 Fitted parameters in Eq. (2) with PR equation and in Eq. (5)

(a) Temperature dependence of binary interaction parameters in Eq. (2) with PR equation

| System | Temp. range (K) | Equation |
|--------------------------------|-----------------|----------------------------|
| CO ₂ (1) + water(2) | 323–398 | $k_{ij} = 0.5821 - 2120/T$ |

(b) Correlated results by Eq. (5)

| System | Temp. range (K) | k | m (K) | n |
|---|-----------------|-------|-------|------|
| CO ₂ (1) + Fe(acac) ₃ (2) | 313–333 | 4.55 | -4940 | 4.71 |
| CO ₂ (1) + decanoic acid(2) | 328–358 | 10.82 | -5618 | 9.21 |

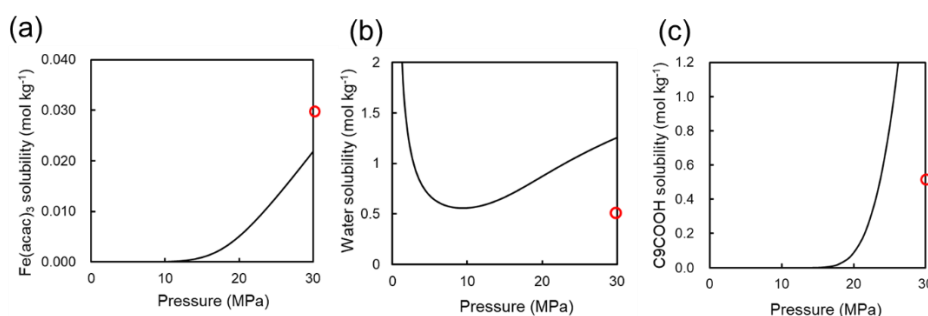


Fig. 2 Calculated line of solute solubility to scCO₂ for CO₂ + (a) Fe(acac)₃, (b) water and (c) decanoic acid system with the initial concentration values of each component in the synthesis (plot).

3.2 Synthesis of organic modified NCs

Table 2 shows experimental conditions and results. The particle yields were less than 1 % at N₂ atmosphere and at 30.0 MPa of CO₂ without water, as shown in run 1 and 2 from Table 2. On the other hand, they went beyond 50 % regardless of the existence of decanoic acid at CO₂ of 30.0 MPa with water. These results clearly indicate that water addition to scCO₂ medium accelerated the particle formation. Thermolysis rate of Fe(acac)₃ is known as very low, and the

calculated conversion at the reaction conditions (100°C, 18h) was negligible based on the report from G. Beech and R. Lintonbon [26]. Therefore, hydrolysis reaction should be key role to form iron oxide. However, water is not miscible with Fe(acac)₃ which suggests that water face the problem of diffusion limit at N₂ atmosphere. In contrast, scCO₂ have relatively high solubility of Fe(acac)₃, and water [27], as shown in Fig. 2a and b, thus, hydrolysis reaction of Fe(acac)₃ molecule could be accelerated in scCO₂, which plausibly promote the particle formation.

Table 2

Experimental conditions and results

| Products | Fe(acac) ₃ (g) | water (g) | Decanoic acid (g) | Atmosphere | Pressure (MPa) | Yield (%) |
|----------|------------------------------|-----------|----------------------|-----------------|-------------------|-----------|
| 1 | 0.530 | 0.45 | 1.29 | N ₂ | 0.1 | <1 |
| 2 | 0.530 | 0 | 1.29 | CO ₂ | 30.0 | <1 |
| 3 | 0.530 | 0.45 | 0 | CO ₂ | 30.0 | 52 |
| 4 | 0.530 | 0.45 | 1.29 | CO ₂ | 30.0 | 76 |

Fig. 3a, b and c show typical TEM images of the NCs prepared in scCO₂ with water. The products that were synthesized without decanoic acid were submicron sized aggregates (Fig. 3a), while the products that were synthesized with decanoic acid were self-assembled on the TEM substrate (Fig. 3b and c) where the mean nearest-neighbor spacing was calculated to be 2.4 ± 0.7 nm by observing about 100 spacing. The decanoic acid has a carbon chain length of 1.4 nm, thus, the distance between self-assembled NCs can be seen as approximately 2.8 nm [12]. This theoretical distance was somewhat closed to our observed distance of 2.4 ± 0.7 nm. Additionally, scCO₂ medium with decanoic acid gave the NCs with unimodal and narrow size distributions, as shown in Fig. 3d, and the mean size of NCs was 7.8 ± 2.0 nm. These results evidentially show that addition of decanoic acid to scCO₂ effectively modify the surface of NCs, which allows the inhibition of the aggregation in the synthetic field.

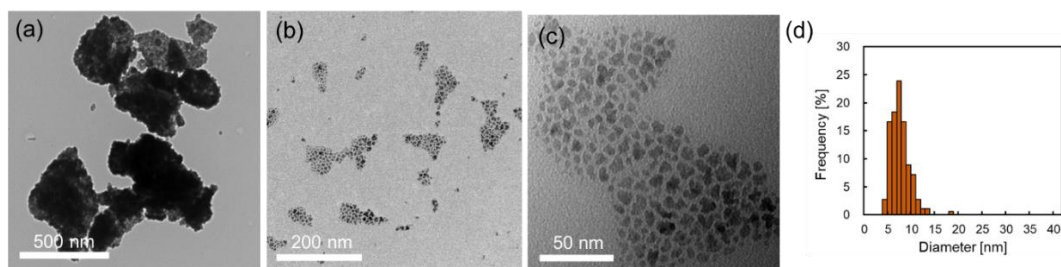


Fig. 3 (a-c) The typical TEM images of NCs synthesized in scCO₂ (a) without decanoic acid and (b and c) with decanoic acid. (d) Size distribution histogram of NCs synthesized in scCO₂ with decanoic acid.

HR-TEM, TEM electron diffraction and XRD analysis were performed to analyze the crystallinity and crystal structure of NCs synthesized in scCO₂ with decanoic acid, as shown in Fig. 4a, b and c. In the electron diffraction pattern, scattered diffraction spots and the Debye-Scherrer ring were observed, indicating that the obtained NCs have a good crystallinity. The good crystallinity of NCs was further confirmed by observing the atomic arrangement from the HR-TEM image shown in Fig. 3b. However, prepared NCs showed broad XRD peaks (Fig. 4c), which may be because of the very small particle size (the NCs can only be called as quasicrystal) [28]. Table 3 shows the lattice spacings calculated by the electron diffraction pattern (shown in Fig. 4a) of obtained NCs, where each lattice spacing was assigned to the crystal structure of α -Fe₂O₃ (ICSD:22505) and γ -Fe₂O₃ (ICSD:79196).

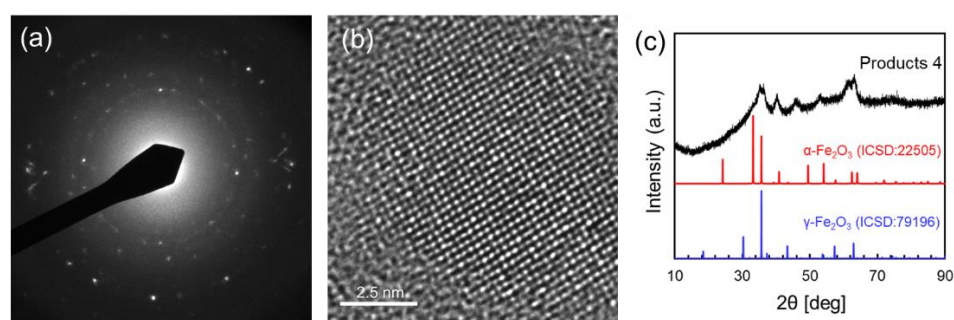


Fig. 4 (a) The electron diffraction pattern, (b) the high resolution TEM image and (c) the XRD pattern of NCs synthesized in scCO₂ with decanoic acid (Products 4 listed in Table 2).

Table 3

Lattice spacings and assigned structures of NCs synthesized in scCO₂ with decanoic acid.

| No | Lattice spacing ^a [nm] | Assigned structure ^b |
|----|-----------------------------------|---|
| 1 | 0.295 | γ -Fe ₂ O ₃ |
| 2 | 0.249 | α -Fe ₂ O ₃ γ -Fe ₂ O ₃ |
| 3 | 0.224 | α -Fe ₂ O ₃ |
| 4 | 0.203 | γ -Fe ₂ O ₃ |
| 5 | 0.168 | α -Fe ₂ O ₃ γ -Fe ₂ O ₃ |
| 6 | 0.148 | α -Fe ₂ O ₃ γ -Fe ₂ O ₃ |

^aLattice spacings were calculated by TEM electron diffraction pattern. ^b The lattice spacings were assigned to the crystal structure of α -Fe₂O₃ (ICSD:22505) and γ -Fe₂O₃ (ICSD:79196).

The FT-IR and TG analysis were applied to characterize the surfactant attached on the surface of NCs synthesized in scCO₂ with decanoic acid. Fig. 5a shows FT-IR spectra of obtained NCs and pure decanoic acid. The characteristic bands at 2850 and 2920 cm⁻¹ were assigned to asymmetric and symmetric stretching modes of -CH₂- in the alkyl chains of

monocarboxylic acid.[29] However, the bands that is assigned to the free carboxyl group (-COOH) of monocarboxylic acid was not observed while the band of free carboxyl group (-COOH) is normally detected at about 1700 cm^{-1} [29]. Furthermore, bands at approximately 1530 and 1400 cm^{-1} can be assigned to the asymmetric and symmetric stretching modes of carboxylate group (-COO^-) of the monocarboxylic acid [29]. These results evidentially show that decanoic acid do not physical absorb to the surface but chemically attach to the surface of iron oxide NCs [14]. Fig. 5b shows the TGA results for the obtained NCs. Increase of weight loss was accelerated from the approximately 300°C , which also supports that decanoic acid chemically attached to the surface of iron oxide NCs because increase of weight loss should be stopped at near boiling point of decanoic acid (corresponding to 243°C) in the case of physical absorption [30,31]. Herein, chemical-bonded and densely surfactant on the surface typically enables the good dispersion of NCs in organic solvent which are essential for the self-assemble on the substrate [12]. In this study, we could observe the good dispersed NCs with a concentration of 0.2% (w/v) in cyclohexane, shown in Fig. 5c. It was also confirmed that the NCs were self-assembled on the TEM substrate shown in Fig. 3b and c by dripping the obtained NCs dispersed in cyclohexane onto TEM grid.

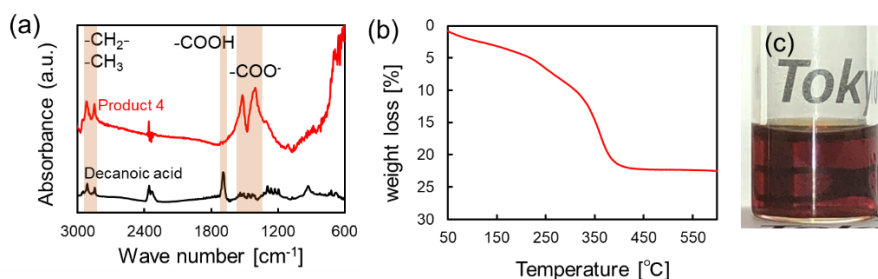


Fig. 5 (a) FT-IR spectra of NCs synthesized in scCO_2 with decanoic acid and pure decanoic acid. (b) TG spectra of NCs synthesized in scCO_2 with decanoic acid. (c) The optical images of the obtained NCs (products 4 listed in Table 2) with a concentration of 0.2% (w/v) in cyclohexane.

4. Conclusion

In this study, we tried to synthesize the surface modified iron oxide nanocrystals (NCs) in scCO_2 to demonstrate the feasibility of scCO_2 as the reaction field for the synthesis of them. To investigate the effects of scCO_2 , the synthesis was performed at N_2 atmosphere and at $30.0 \pm 0.8\text{ MPa}$ of CO_2 , where iron(III) acetylacetonate, pure water and decanoic acid were used as starting materials. As a result, the particle yield of the solid materials significantly increased by using scCO_2 compared with the test at N_2 atmosphere. Moreover, addition of surfactant to scCO_2 was revealed to drastically inhibit the aggregation of NCs, which allowed the formation of single-nano sized crystals with the unimodal size distribution. Furthermore, FT-IR and TG

analysis supported that decanoic acid chemically attach to the surface of the NCs that were dispersed to cyclohexane. These results suggest that scCO₂ medium could be new appealing reaction field to fabricate the densely modified NCs without liquid waste.

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