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Size-controlled synthesis of hematite mesocrystals

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Size-controlled hematite mesocrystals were prepared by forced hydrolysis of $FeCl_3$ via a facile hydrothermal process. The particle size of hematite mesocrystals were well-controlled by the ratio of ethanol to water. As the ratio of ethanol increased, the particle size of hematite mesocrystals increased from 0.5 to 1.5 μm without losing theirinternal mesocrystalline structure. The sizes of hematiteparticles werealso affected by the concentration of KOH and formic acid. Goethite rods were prepared with 0.26 M KOH.

1. Introduction

Mesocrystals exhibiting scattering properties similar to that of a single crystal are a new class of nanostructured materials composed of individual oriented nanocrystals[1, 2]. They are considered as intermediates between classical single crystals and polycrystals without mutual orientation of subunits[3]. Mesocrystals, hence, may combine the merits of both single crystals with highly ordered internal structure and polycrystals with high porosity and a large number of interfaces, which has sparked fundamental as well as technological interest. The size control of the mesocrystals is of great importance to their distinctive applications. For example, mesocrystals can be used as a precursor to prepare either the same kind of mesocrystals with various morphologies[4] or other kinds of mesocrystals[5]. If the size of mesocrystals precursor is controlled, the derived mesocrystals are also controlled. For controlling the size of mesocrystals, the basic principle is that the internal mesoscopic structure and external morphology of the mesocrystals should not be changed when the size of mesocrystals is changed. The synthetic conditions such as starting materials, pH value of the system, the ions, and organic additives are vital for preparing certain mesocrystals because the self-origination of subunits in mesocrystals is very sensitive to the environment. However, in many cases, when the parameters are changed to control the size, the mesocrystals may not be formed or the morphologies of mesocrystals are changed[6-9].

Various mesocrystals including α-Fe_2O_3[4], TiO_2[10], ZnO[11], $SrTiO_3$[12], and $CaCO_3$[13] have been prepared. For many of the mesocrystals, the internal structures are less known and the formation mechanisms are not quite clear. As the first reported three-dimensional mesocrystals[1, 6], the pseudo-cubic hematite (α-Fe_2O_3) particles have been thoroughly studied by

Sugimoto et al. on the formation mechanism[14, 15], effects of ions on the morphology[9] and the internal structures[16]. Therefore, the hematite particles are especially suited for the investigation of size-controlled synthesis of mesocrystals.

Hematite (α-Fe_2O_3) is thermodynamically stable, Crystallographic phase of iron oxide with a band gap of 2.2 eV. It has been extensively used in many industrial applications such as pigments, catalysts, optical devices, gas sensor sand raw materials for hard and soft magnets[17]. Sugimoto et al.[14] reported that the pseudo-cubic hematite particles were prepared through a two-step phase transformation, namely, from $Fe(OH)_3$ to β-$FeOOH$, and from β-$FeOOH$ to α-Fe_2O_3. The size of pseudo-cubic hematite particles was controlled by the temperature during the preparation of the $Fe(OH)_3$ gel or the added amount of seeds. However, for those preparations, due to the low temperature, the aging time for the formation of hematite particles was usually longer than 1 day. Recently a facile one-step hydrothermal process has been developed to prepare hematite particles with higher efficiency by forced hydrolysis of $FeCl_3$[4, 18]. So far, though many methods have been developed to control the size of various nanostructures[19], it remains a great challenge to control the size of hematite mesocrystals in a hydrothermal process.

Herein, size-controlled hexahedral hematite mesocrystals were prepared by forced hydrolysis of $FeCl_3$ via a hydrothermal process. Effects of the parameters (e.g. the ratio of ethanol to water, the concentration of KOH and formic acid) on the crystallinity and the morphology of the samples were investigated. The mechanism for controlling the size of hexahedral hematite particles has been proposed.

2. Experiment section

2.1. Preparation

2.1.1. Preparation of hematite particles

All the regents were purchased from Sinopharm Chemical Reagent Co. and used as received without further purification. In a typical procedure, 0.71 g anhydrous ferric chloride ($FeCl_3$) was dissolved in a solution containing various volume of ethanol and H_2O to get a suspension. The total nominal volume of ethanol and H_2O was kept to 70 ml. The as-prepared

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suspension was sealed within a Teflon-lined autoclave (100 ml) and heated at 150 °C for 6 h. The solid products were collected by centrifugation, washed with ethanol several times, and then dried in air at 80 °C for 6 h.

2.1.2. Preparation of hematite particles and goethite rods

0.71 g $FeCl_3$ was dissolved in 10 ml anhydrous ethanol or H_2O to get a suspension. 60 mL KOH solution was mixed with the suspension. The as-prepared suspension was sealed within a Teflon-lined autoclave (100 ml) and heated at 150 °C for 6 h. The solid products were collected by centrifugation, washed with ethanol several times, and then dried in air at 80 °C for 6 h.

2.1.3. Preparation of aggregated hematite particles

0.71 g $FeCl_3$ was dissolved in a solution with 10 ml ethanol and 60 ml H_2O to get a suspension. Various amount of formic acid was added to the suspension. The as-prepared suspension was sealed within a Teflon-lined autoclave (100 ml) and heated at 150 °C for 6 h. The solid products were collected by centrifugation, washed with ethanol several times, and then dried in air at 80 °C for 6 h.

2.2. Characterization

Powder X-ray diffraction (XRD) was used to characterize the samples. Data were collected on a X'Pert PRO X-ray diffractometer with Cu Kα radiation (λ=1.54178 Å) at a beam current of 40 mA. The morphologies of the samples were investigated using a Hitachi S-4800 field-emission scanning electron microscope (FE-SEM) with cold field emitter. The particle size of the hematite mesocrystals was measured by FE-SEM images. In order to observe the internal structure of the particles, thin sections of the samples were prepared by an ultramicrotome processing using ULTRACUT UC7 (LEICA, Germany). The conditions of slicing speed and thickness were 1mm/sec and 60nm, respectively. Transmission electron microscopy (TEM) and high resolution transmission electron microscopy (HRTEM) were used to observe the morphology of the thin sections and investigate the crystallographic characteristics of the samples. TEM studies were carried out on a TecnaiF20 with accelerating voltage of 200 kV.

3. Results and discussion

3.1. Effects of the ratio of ethanol to water on the crystallinity, morphology and microstructure

Fig. 1 shows XRD patterns of the samples prepared with various volume of ethanol. The samples prepared with 0, 10, 30, 50 and 60 ml ethanol are pure hematite (see the curve a-e of Fig. 1). However, both the amorphous phase and hematite are detected in the sample prepared with 70 ml ethanol (see the curve f of Fig. 1). Based on the XRD data, the crystal size of the samples were calculated by using the peaks at 33°, 36°, 54°, 49°, 24°, 62°, 64° and 41° according to Scherrer equation. The average was applied as a result. The crystal sizes of the samples prepared with 0, 10, 30, 50 and 60 ml ethanol were 47, 44, 30, 26 and 24 nm, respectively, indicating that the crystal sizes of the samples decrease with increasing the volume of ethanol.

Fig. 2 shows FE-SEM images of the samples prepared with various volume of ethanol. Well-dispersed hexahedral particles

are obtained with 0, 10, 30 and 50 ml ethanol and no obvious morphology changes are detected for the samples (see Fig. 2a-d). The slightly aggregated hexahedral particles are obtained
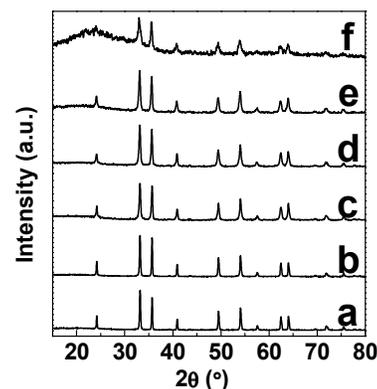

Figure 1. XRD patterns of the samples prepared with various volume of ethanol: (a) 0, (b) 10, (c) 30, (d) 50, (e) 60 and (f) 70 ml.

with 60 ml ethanol (see Fig. 2e). The severe aggregated particles are obtained with 70 ml ethanol and the shape of the particles is spherical instead of hexahedral (see Fig. 2f). From FE-SEM images, it can be seen that the particle size, which is ranged from 0.5 to 1.5 μm, increases when the volume of ethanol rises up from 0 to 50 ml, and then slightly decreases as the volume of ethanol increases to 60 ml.

Fig. 3a-b show FE-SEM images (high magnification) of the samples prepared with 10 ml and 50 ml ethanol, respectively. The hexahedral particles prepared with 10 ml ethanol show smooth surfaces and slightly rough corners (see Fig. 3a). They exhibit a rhombohedral shape with six equivalent facets with angles of 94° and 86°. The hexahedral particles prepared with 50 ml ethanol show rough surfaces and somewhat round corners (see Fig. 3b). Moreover, the particle size of 50 ml ethanol prepared sample is larger than that of 10 ml ethanol prepared sample. Fig. 3c, d show TEM image of thin sections of the hexahedral samples prepared with 10 ml and 50 ml ethanol, respectively. Small particles are observed in the thin sections. Some of them are marked in red. Fig. 3e, f and Fig. 3g, h show HRTEM images and the SAED pattern of samples prepared with 10 ml and 50 ml ethanol, respectively. The hexahedral particle is confirmed to be hematite, and the hexahedral particle has a single-crystal-like structure, suggesting the nature of mesocrystals. According to Fig. 3c - f, the hexahedral particles are composed of nanoparticles with high crystallinity and the crystals in the particle has same orientation, which confirms that the particle has mesocrystal structure. According to the SAED pattern (see Fig. 3g and h), the hexahedral particle of both samples are also proved to be hematite. It suggests that the particles size of hematite hexahedral particles increases without losing their internal mesocrystalline structure as the volume of ethanol increases.

3.2. Effects of the concentration of KOH on the morphology and crystallinity

Fig. 4 shows XRD patterns of the samples prepared with various concentration of KOH in the presence of 10 ml ethanol. All the diffraction peaks of the samples prepared with 0.04 M
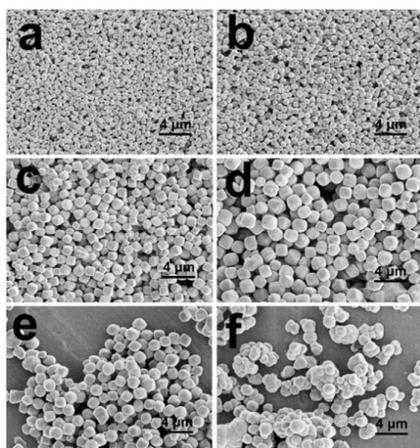

Figure 2. FE-SEM images of the samples prepared with various volume of ethanol: (a) 0, (b) 10, (c) 30, (d) 50, (e) 60 and (f) 70 ml.
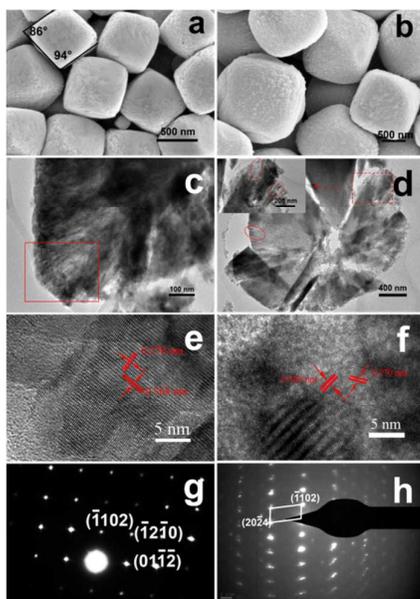

Figure 3. FE-SEM images (high magnification) of the samples prepared with 10 ml (a) and 50 ml (b) ethanol; TEM image (c), and HRTEM images (e) of the thin sections of the sample prepared with 10 ml ethanol; TEM image (d) and HRTEM images (f) of the thin sections of the sample prepared with 50 ml ethanol. SAED pattern of the samples prepared with 10 ml (g) and 50 ml (h) ethanol.

and 0.08 M KOH (see the curve a and b) are assigned to hematite (JCPDS No. 33-0664). The estimated crystal sizes of the samples prepared with 0.04 M and 0.08 M KOH are 39 and 42 nm, respectively, which were calculated as well according to Scherrer equation. Comparing with the crystal size of the sample prepared without KOH, which is 44 nm, it can be suggested that the crystal size is slightly affected when the

sample is prepared with low concentration of KOH. However, the sample prepared with 0.26 M KOH is assigned to goethite (JCPDS No. 29-0713). Fig. 5 shows FE-SEM images of the samples prepared with various concentration of KOH in the presence of 10 ml ethanol. The hexahedral particles are obtained with 0.04 M and 0.08 M KOH (see Fig. 5a and Fig. 5b). Moreover, the particle size of the sample prepared with 0.04 M KOH is larger than that of the sample prepared with 0.08 M KOH. The elongated rods and a small number of Y-shaped structures are obtained with 0.26 M KOH (see Fig. 5c).
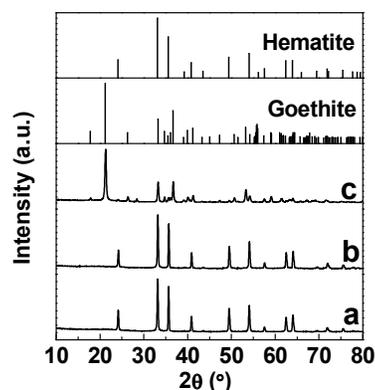

Figure 4. XRD patterns of the samples prepared various concentration of KOH in the presence of 10 ml ethanol with: (a) 0.04 M, (b) 0.08 M, (c) 0.26 M.
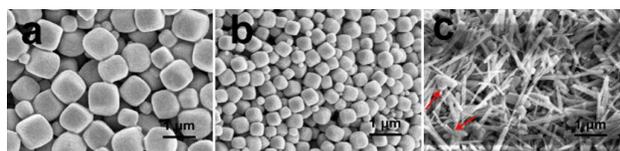

Figure 5. FE-SEM images of the samples prepared with various concentration of KOH in the presence of 10 ml ethanol: (a) 0.04 M, (b) 0.08 M, (c) 0.26 M.

Fig. 6 shows XRD pattern of the sample prepared with 0.26 M KOH in the absence of ethanol. All the diffraction peaks of the sample are indexed to goethite, indicating that goethite is obtained with 0.26 M KOH. Fig. 7 shows FE-SEM images of the samples prepared with various concentration of KOH in the absence of ethanol. The hexahedral particles are obtained with 0.04 M and 0.08 M KOH (see Fig. 7a and Fig. 7b). Moreover, the particle size of the sample prepared with 0.04 M KOH is
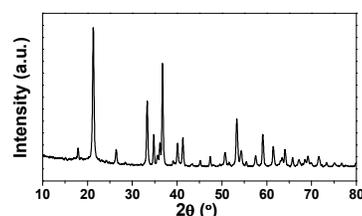

Figure 6. XRD pattern of the sample prepared with 0.26 M KOH in the absence of ethanol.

slightly larger than that of the sample prepared with 0.08 M KOH. The elongated rods, which are aligned and stacked together, are obtained with 0.26 M KOH (see Fig. 7c).
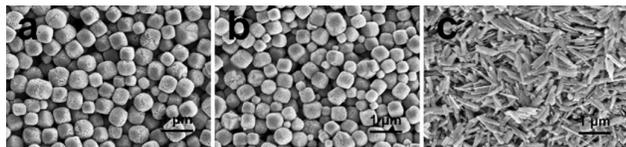

Figure 7. FE-SEM images of the samples prepared with various concentration of KOH in the absence of ethanol: (a) 0.04 M, (b) 0.08 M, (c) 0.26 M.

According to Fig. 4-7, some phenomenon are found by comparing the samples prepared with various concentration of KOH in the presence and in the absence of ethanol. Firstly, the particle size of the hexahedral particles prepared with 0.04 M KOH in the presence of 10 ml ethanol (see Fig. 5a) is much larger than that prepared with 0.04 M KOH in the absence of ethanol (see Fig. 7a), which confirms that the size of the hexahedral particles is promoted by adding ethanol. Secondly, the elongated rods and a small amount of Y-shaped structures are prepared with 0.26 M KOH in the presence of ethanol (see Fig. 5c), while the elongated rods, which are aligned and stacked together, are prepared with 0.26 M KOH in the absence of ethanol (see Fig. 7c).

3.3. Effects of the concentration of formic acid on the morphology and crystallinity

Fig. 8 show XRD patterns of the samples prepared with 0.095 M and 0.76 M formic acid in the presence of 10 ml ethanol. According to Fig. 8, the samples are assigned to pure hematite. The crystal sizes of the samples prepared with 0.095 M and 0.76 M formic acid are 50 and 29 nm (calculated according to Scherrer equation), respectively. Comparing with the crystal size of the sample prepared without formic acid, which is 44 nm, it can be suggested that the crystal size of the sample is slightly affected when the sample is prepared with low concentration of formic acid.

Fig. 9 shows FE-SEM images of the samples prepared with various concentration of formic acid in the presence of 10 ml ethanol. The aggregated hexahedral particles are prepared with 0.095 M and 0.19 M formic acid (see Fig. 9a-b), while the aggregated spherical particles are prepared with 0.285, 0.38 M, 0.57 M and 0.76 M formic acid (see Fig. 9c-f). The size of the aggregated particles prepared with 0.095 M and 0.19 M formic
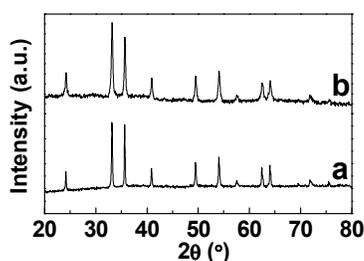

Figure 8. XRD patterns of the samples prepared with (a) 0.095 M and (b) 0.76 M formic acid in the presence of 10 ml ethanol.
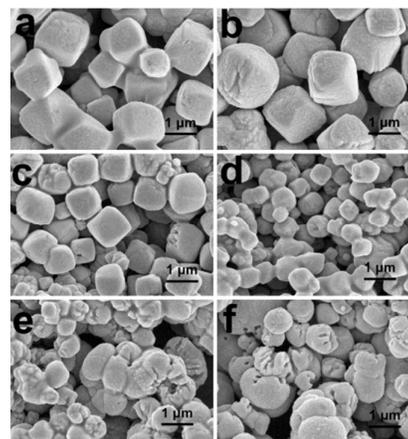

Figure 9. FE-SEM images of the samples prepared with various concentration of formic acid in the presence of 10 ml ethanol: (a) 0.095 M, (b) 0.19 M, (c) 0.285 M, (d) 0.38 M, (e) 0.57 M and (f) 0. 76 M.

acid is about 1 μm (see Fig. 9a-b). Comparing with the particle size of the sample prepared without formic acid, which is about 0.7 μm (see Fig. 2b), it can be suggested that the particle size of the sample increases when the samples is prepared with low concentration of formic acid.

3.4. The mechanism for controlling the size of hematite particles

As we know, in a homogeneous nucleation and growth process, the high nucleation rate produces smaller particles, while the low nucleation rate produces larger particles. In the present work, the nucleation rate of hematite particles is affected by the concentration of formic acid or KOH[14]. When the sample is prepared with low concentration of formic acid, the nucleation rate of hematite particles decreases, leading to the formation of larger hexahedral hematite particles (Fig. 9a-b).However, the HCOO$^-$ ions from formic acid may act as a competitive adsorbent of Cl$^-$, leading to the formation of aggregated hematite particles (see Fig. 9e-f). When the sample is prepared with low concentration of KOH, on the contrary, the nucleation rate of hematite particles increases, leading to the formation of smaller hexahedral hematite particles (see Fig. 5a-b). When the sample is prepared with higher concentration of KOH, goethite with a cicular morphology is formed because of the instinct crystal structure of goethite[20](see Fig. 5c and Fig. 7c). Due to the selective absorption of ethanol on the specific facets of goethite, a facet-mediated aggregation may occur to decrease the total free energy when the sample is prepared in the presence of ethanol[21], which results in the formation of the Y-shaped rods (see Fig. 5c). Therefore, well-defined hexahedral hematite particles can only be obtained in a very limited concentration range of formic acid and KOH.

It is noteworthy that hematite particles (containing some amorphous phase) are prepared with pure ethanol (see Fig. 1f and Fig. 2f), indicating that FeCl$_3$ (Lewis acid) can react with

ethanol (Lewis base) under hydrothermal/solvothermal condition. Moreover, in a $FeCl_3$ solution with various amount of ethanol, pH value of $FeCl_3$ solutions was found to decrease as the ratio of ethanol to water increases[22]. Therefore, ethanol employed as solvent may participate the hydrolysis reaction of $FeCl_3$ and make the pH value decreased during the hydrothermal/solvothermal process. As the ratio of ethanol to water increases, the nucleation rate of hexahedral hematite particles decreases, leading to the formation of larger hexahedral hematite particles (see and Fig. 2). However, no other ions are brought into the system as the ratio of ethanol to water increases. Therefore, the morphology and the internal mesocrystalline structure of hexahedral hematite particles are not significantly affected by the ratio of ethanol to water (see Fig. 3). Furthermore, the crystal growth of the nanocrystals within hexahedral hematite mesocrystals may be suppressed by the adsorption of ethanol. Therefore, the crystal size of hexahedral hematite particles decreases as the ratio of ethanol to water increases (see Fig. 1).

Conclusions

A facile hydrothermal process has been developed to prepare hexahedral hematite mesocrystals by forced hydrolysis of $FeCl_3$. As the ratio of ethanol to water increased, the particle size of hexahedral hematite mesocrystals increased from 0.5 to 1.5 μm without losing their internal mesocrystalline structure. The crystal size of hematite hexahedral mesocrystals decreased as the ratio of ethanol to water increased. The sizes of hexahedral hematite particles were also affected by the concentration of KOH and formic acid. Goethite rods were prepared with 0.26 M KOH. The aggregated hematite particles were prepared with high concentration of formic acid.

Acknowledgements

Notes and references

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