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BRIEF COMMUNICATION

Atom Force Microscopic Characterization of Ultrafine Fe_3O_4 Powders

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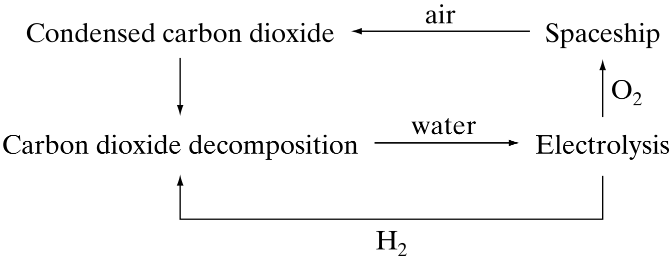
Ultrafine powders of Fe_3O_4 have been synthesized in different ways: hydrothermal air oxidation crystallization, high-temperature roasting decomposition, and supercritical fluid drying methods. These powders are characterized by atomic force microscopy and the results show that ultrafine Fe_3O_4 powders prepared in different ways exhibit different microstructures and different morphologies on the micrometer scale. © 1996 Academic Press, Inc.

INTRODUCTION

Recently, there has been increasing interest in the study of ultrafine Fe_3O_4 powders which can be reduced into $Fe_{3+\delta}O_4$ ($\delta > 0$) by H_2 gas at 573 K. These have potential application as high-activity and high-selectivity catalysts in decomposing carbon dioxide into carbon and oxygen (1). This process plays an important role in spaceships with an enclosed space that must support life. The process can be described as follows:



Atomic force microscopy (AFM) has been recently shown to be a powerful tool in the investigation of semiconductor ultrafine powders (2). Compared with other methods, such as scanning electron microscopy, and transmission electron microscopy (3, 4), atomic force microscopy has the advantage of convenient, *in situ,* real-time observation on the microstructures of ultrafine powders with high resolution. In this letter, we present our direct observation on microstructures of the ultrafine Fe_3O_4 powders prepared in different ways.

EXPERIMENTAL

1. Preparation of Ultrafine Fe_3O_4 Powders

Hydrothermal air oxidation crystallization. An $Fe(OH)_2$ suspension was obtained by mixing $FeSO_4$ and NaOH solutions at a molar ratio of 1 : 2. Before mixing, the O_2 dissolved in these solutions was eliminated by passing highly purified nitrogen over these solutions. The material was oxidized for 20 hr in air at 358 K, and then filtered and washed with water and dried under a nitrogen environment at 358 K. The obtained Fe_3O_4 powders were marked as Fe_3O_4-I.

Supercritical fluid drying. Excess ammonia solution was added to an $FeSO_4$ solution to form a gel; water molecules of the gel exchanged completely with anhydrous alcohol. The adduct was put into a high-pressure vessel and heated at a rate of 80°C/hr to supercritical condition to eliminate the alcohol solvent. The sample thus obtained was subjected to a flow of highly purified nitrogen gas for 1 hr. This sample was marked as Fe_3O_4-II.

High-temperature roasting decomposition. $FeC_2O_4 \cdot 2H_2O$ was dried for 2 hr under vacuum at 463 K, heated

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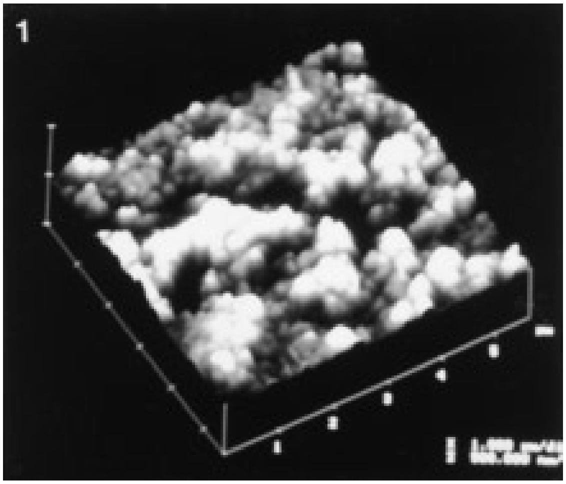

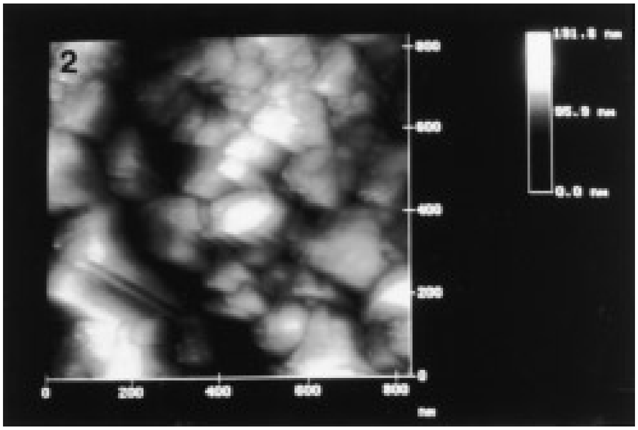

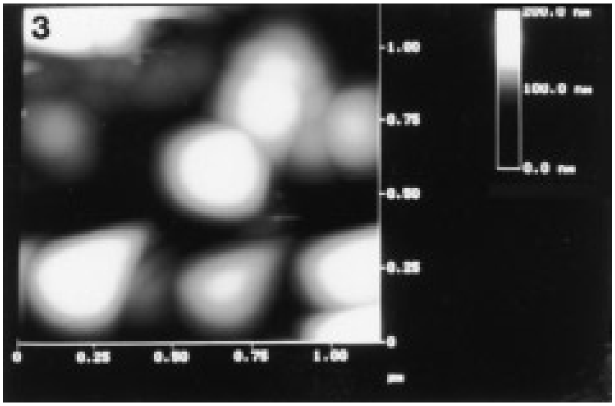

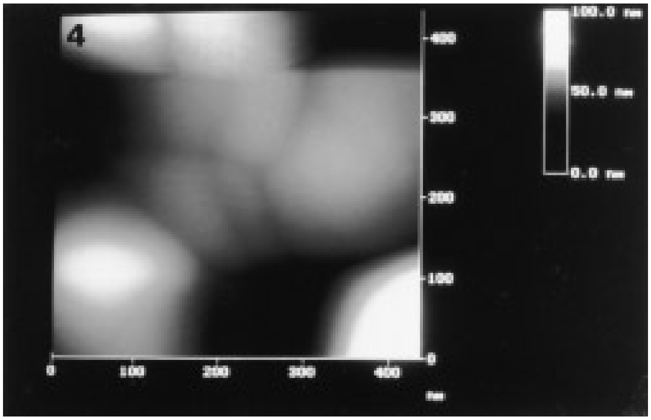

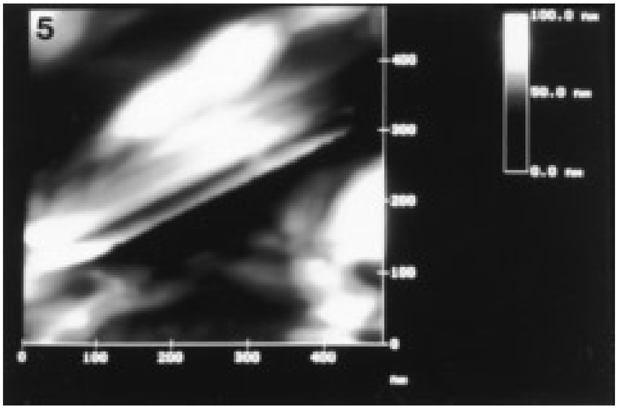

FIG. 1. 3D AFM topographic image of Fe_3O_4-I powders in large scale (5.6 × 5.6 μm^2) which exhibits the inhomogeneous distribution of the Fe_3O_4-I powders.

FIG. 2. AFM image of Fe_3O_4-I powders at high resolution (800 × 800 nm). We can see clearly the aggregates of Fe_3O_4-I powders and the size of the aggregates.

FIG. 3. AFM image of Fe_3O_4-II powders (1.2 × 1.2 μm) which shows the individual cone-like particles and the clusters of Fe_3O_4-II powders.

FIG. 4. AFM image of clusters of Fe_3O_4-II powders (400 × 400 nm).

FIG. 5. AFM image of Fe_3O_4-III powders (450 × 450 nm) which displays a striped microstructure.

gradually to 923 K, and then kept for 10 hr under these conditions, after which it was cooled to ordinary temperature. These powders were designated as Fe_3O_4-III.

2. Atomic Force Microscopic Measurements

The AFM measurements were carried out on a commercial system (Nanoscope III, Digital Instruments, Santa Barbara). Two different scanners were used for surface inspection: one at 12.5 μm for large-scale observation and the other at 0.7 μm for nanometer-scale measurements. The tip was made of microfabricated silicon nitride (Si_3N_4), attached to a 200-μm cantilever with a force constant of about 0.12 N/m. A typical operating force between tip and samples was on the order of 10^{-8} N. All images were taken at room temperature in air. The ultrafine Fe_3O_4 powders were fixed by adhesive paper on the surface of a freshly cleaved mica substrate.

RESULTS AND DISCUSSION

A topographic view of ultrafine Fe_3O_4 powders prepared by the hydrothermal air oxidation crystallization method (sample Fe_3O_4-I) on a large scale (5.6 μm × 5.6 μm) is shown in Fig. 1, which gives the morphology of sample Fe_3O_4-I powders in a large area. The image was gray-scale-encoded; that is, darker regions are deeper than lighter ones, and the same brightness corresponds to the same height. We observed that the distribution of Fe_3O_4-I powders is not homogeneous and some powders aggregated tightly. Further information can be obtained from Fig. 2 (800 × 800 nm), which shows the size and microstructure of Fe_3O_4-I aggregates. The size of the aggregates is within the range of 100 ~ 200 nm and the shapes of the aggregates are irregular.

A typical image of sample Fe_3O_4-II powders which were prepared by supercritical fluid drying is shown in Fig. 3 (1.2 × 1.2 μm image). Some cone-like and spherical particles can be seen individually in the image; the diameters of the particles are roughly 200 ~ 250 nm. It should be noted here that in imaging, rotation of the scan direction and changes of the scan frequency did not affect the structure of Fe_3O_4 particles, ruling out the possibility that scanning influenced the shapes of these particles or caused some imaging artifact. Morever, we also found clusters of Fe_3O_4 particles in Fig. 3. The cluster of Fe_3O_4 particles can be seen clearly in Fig. 4 (400 × 400 nm).

Figure 5 shows the image (500 × 500 nm) of Fe_3O_4-III powders prepared by the high-temperature roasting decomposition method. The image exhibits a layered striped microstructure which shows that Fe_3O_4-III powders are not formed as nanometer crystals and are obviously different from those observed in the images of Fe_3O_4-I and Fe_3O_4-II powders.

From the above-mentioned atomic force microscopic images, we found that Fe_3O_4 powders prepared in different ways exhibited different shapes and different microstructures. The powders prepared by the supercritical fluid drying method are fine nano-crystals of Fe_3O_4, while the powders prepared by other two methods are not. Thus in order to gain nanometer crystals of Fe_3O_4, the supercritical fluid drying method should be used. This work also shows that atomic force microscopy is a powerful tool in the investigation of the microstructure of ultrafine powders. Further investigation is in progress on the difference in catalytic capabilities of $Fe_{3+\delta}O_4$ reduced from Fe_3O_4 powders prepared in different ways.

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