

## Preparation of rod-type ferric oxyhydroxide particles by forced hydrolysis in the presence of a cationic surfactant

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Nanosized rod-type ferric oxyhydroxide particles were prepared by forced hydrolysis in the presence of cetyltrimethyl ammonium bromide (CTAB). Selective adsorption of CTAB on the surface of particles induces the anisotropic growth of the particles. The resulting particles were characterized using XRD, TEM, SEM, TG-DTA and BET.

**Key words:** Iron oxide, forced hydrolysis, morphology, CTAB, surfactant.

### Introduction

The preparation of inorganic particles with a controlled size, shape, and internal structure is one of the most interesting fields in nanoscale materials research because the nanoscale structure of particles strongly influences their properties [1-3]. In recent years, various nanostructured materials including a mesostructured structure [4, 5], a wire-type [6, 7], a tube-type [8, 9] and a hollow sphere shape [10] have been prepared by a wet chemical method in which organic materials were employed as structure-directing materials. In these methods, surfactants or polymers were employed as a stabilizer, a capping agent, and a template, which can induce size restriction, anisotropic growth, and solidification with a periodic structure.

Cetyltrimethyl ammonium bromide (CTAB) is a cationic surfactant widely used for the synthesis of inorganic materials with a controlled structure. Mobil oil corporation researchers discovered the M41S family of mesoporous silica using electrostatic interaction between CTAB and the anionic precursor of inorganic materials and the self-assembling process of CTAB [11]. A 1-dimensional semiconductor [12], a metal [13, 14], and a metal oxide [15] have been synthesized by a solution-based method using CTAB. Sun et al. prepared ZnO nanorods from zinc powders by a hydrothermal method in the presence of CTAB [15]. According to the proposed mechanism, the presence of CTAB favors the erosion process and leads to the oriented growth of ZnO nanorods.

Ferric oxyhydroxides or oxides have been used in many fields of industrial application such as pigments, catalysts, gas sensors, and absorbents. Forced hydrolysis

of  $\text{Fe}^{3+}$  ions in aqueous solution is a simple method for the preparation of iron oxyhydroxides or oxides. Matijevec and other many researchers have investigated the relation between the experimental conditions (pH, temperature, concentration of ferric ions, aging time, additives) and the characteristics of the resulting particles such as shape, size, crystallinity etc [16-18]. Kandori et al. prepared nanoporous hematite by forced hydrolysis in the presence of polyethylene glycol (PEG) [19]. They discovered that hematite formed with PEG was hydrohematite with a crystal lattice distortion and that PEG act as a prominent templating agent.

In this study, rod-type ferric oxyhydroxide particles were prepared by forced hydrolysis of ferric nitrate aqueous solution in the presence of CTAB. In addition, the effect of CTAB and ammonium hydroxide on the formation of rod-type ferric oxyhydroxide particles will be discussed.

### Experimental

The synthesis of rod-type particles was carried out as follows. 2.28 g of CTAB were dissolved in 200 ml of deionized water. A ferric nitrate aqueous solution (10.01 g  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}/50$  ml) was poured into this solution with vigorous stirring. After 15 minute, 10 ml of 2.5% ammonia aqueous solution was added drop by drop under the same conditions. Precipitation was not observed in this step. After 1h, the solution was put into a polypropylene bottle and keep in a convection oven preheated to 80°C. After 2days of aging, a brown precipitate was formed. The supernatant solution was decanted and the particles collected were dried at 80°C for 1day.

An X-Ray Diffraction (XRD) pattern was examined to investigate the crystallinity of the resulting particles which was taken on a Rigaku D/MAX RINT 2500 X-ray diffractometer operated at 40 kV and 100 mA using  $\text{CuK}\alpha$  radiation. The morphology of the particles was

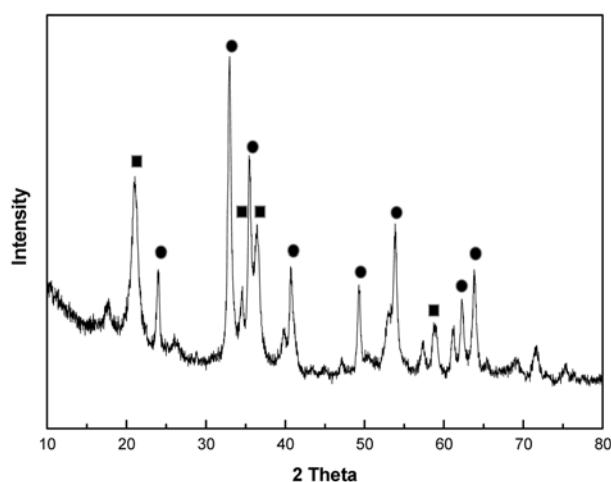
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examined by Transmission Electron Microscopy (TEM, Model 2000EX II, JEOL) operated at 200 kV. For the preparation of the samples for TEM observation, as-prepared powder was dispersed in ethanol by sonication for 5 minute. A drop of the dispersed samples was placed on the carbon-coated TEM grid. Field Emission Scanning electron microscopy (FE-SEM, Model JSM-6700F, JEOL) was used to investigate the morphology of dried particles. The samples were coated with platinum by sputtering for 150 seconds. The nitrogen adsorption and desorption isotherms at 77 K were measured using a Micrometrics ASAP 2000 system after the samples were vacuum-dried at 110 °C for 6 hours. Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) of the samples were carried out to confirm the adsorption of CTAB on the surface of particles using a Shimadzu TGA-50 thermal analyzer and Shimadzu DTA-50 differential thermal analyzer. The temperature was increased at a rate of 10 K  $\text{minute}^{-1}$  under a flowing  $\text{N}_2$  gas.

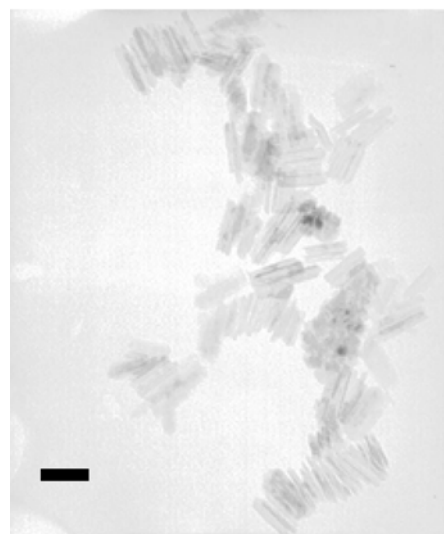
## Results and Discussion

An X-Ray diffraction pattern is presented in Fig. 1. Two phases of ferric oxyhydroxides were observed in the XRD pattern:  $\alpha\text{-FeOOH}$  (goethite) and  $\alpha\text{-Fe}_2\text{O}_3$  (hematite). Thermohydrolysis of ferric nitrate solution induces the formation of goethite followed by heterogeneous nucleation and growth of hematite on the surface of preformed goethite [20, 21].

A view of the resulting particles is shown in Fig. 2. In this micrograph, rod-type particles are observed. The mean size of the individual particle is about 30 nm in length and 10 nm in diameter. Many studies have reported various morphologies of the products prepared by forced hydrolysis of ferric ion solutions [22-24]. However, nanosized rod-type ferric oxyhydroxide particles have not been reported up to now. We believe



**Fig. 1.** XRD pattern of particles prepared by forced hydrolysis of 0.1 M ferric nitrate solution in the presence of CTAB. (■ : goethite ● : hematite)

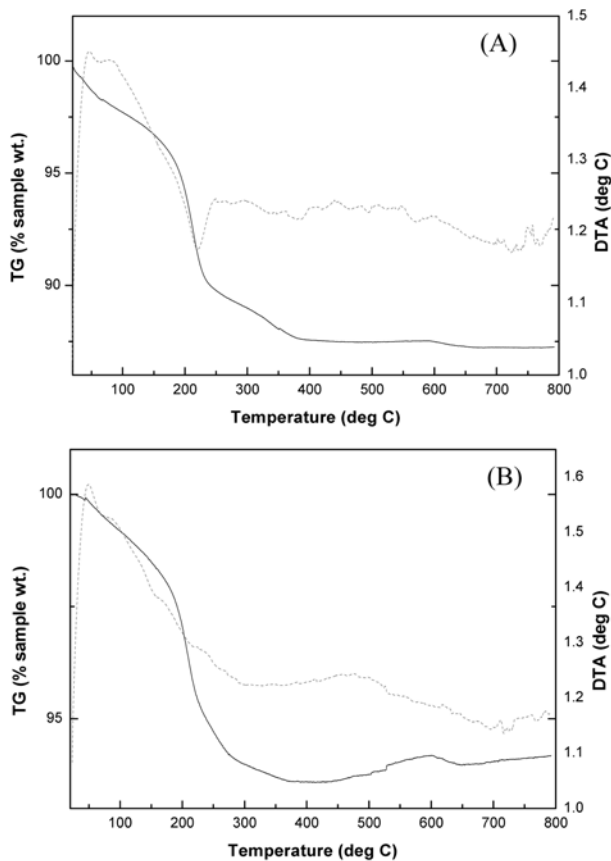


**Fig. 2.** TEM image of particles prepared by forced hydrolysis of 0.1 M ferric nitrate solution to which 2.5% ammonia was added before aging. (scale bar : 20 nm)

that CTAB is the most effective shape controller for these rod-type particles. The formation of rod-type particles can be attributed to the selective adsorption of CTAB on different crystal planes. The selective adsorption of organic surfactants or copolymers onto particular crystallographic facets has been developed as an effective means of controlling crystal shapes [25, 26]. El-Sayed and coworkers have reported on the structure of the capping agent and the shape formation mechanism of nanoparticles prepared in the presence of cationic surfactants or polymers [27, 28]. The adsorption of organic surfactants induces a change of growth kinetics and surface energy of crystal facets, which can ultimately lead to anisotropic growth of particles.

Figure 3 shows TG-DTA plots for the as-prepared and the washed particles. In the TGA plot for the as-prepared particles, there is a slow weight loss up to 180 °C, followed by a rapid weight loss in the range of 180~220 °C accompanied with an endothermic peak. Above 220 °C the weight slowly decreased until the temperature reached 380 °C. The weight loss from 180 °C to 380 °C is ascribed to the desorption and decomposition of surfactants [28]. The free surfactants in the solution are responsible for the first band, whose endothermic peak in the DTA plot is remarkably reduced in the case of washed particles as shown in Fig. 3(B). The slow weight loss is assigned to the bonded or the adsorbed surfactants on the surface of the rod-type particles.

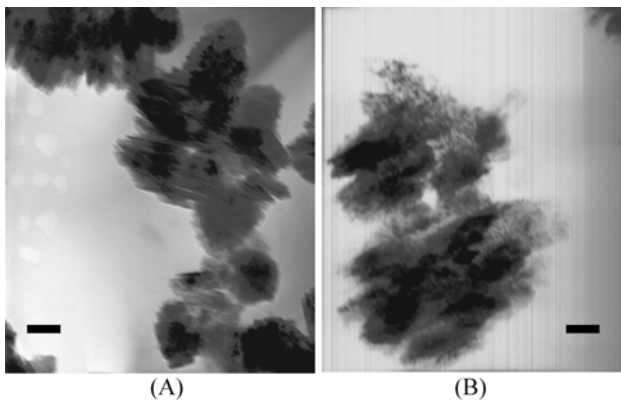
TEM images of particles resulting from the forced hydrolysis in the absence of CTAB and ammonium hydroxide are presented in Fig. 4. The resulting particles have an irregular shape, which is largely different from the morphology of particles produced in the presence of ammonium hydroxide and CTAB. This implies that the addition of ammonium hydroxide promotes the



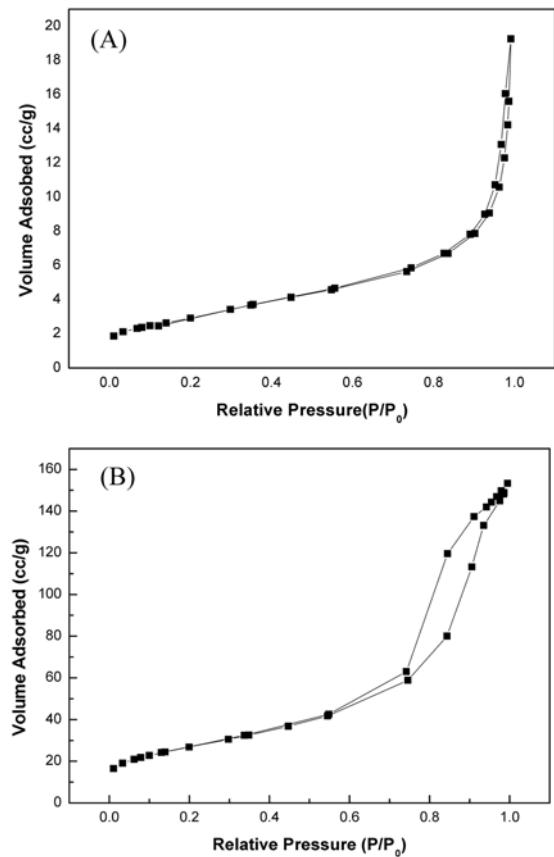
**Fig. 3.** (A) TG-DTA curve for powder obtained by forced hydrolysis of ferric nitrate solution with ammonia and CTAB (B) corresponding curve for washed powder.

selective adsorption of CTAB on the particle surface by affecting the hydrolysis and condensation steps of the precursor. Although it is hard to clearly understand the kinetics and thermodynamics of the particle formation at present stage, the adsorption of CTAB on the growing particles was enhanced because of the modification of the kinetics and thermodynamics in the solution.

To investigate the internal structure of the resulting particles, nitrogen adsorption-desorption isotherm and



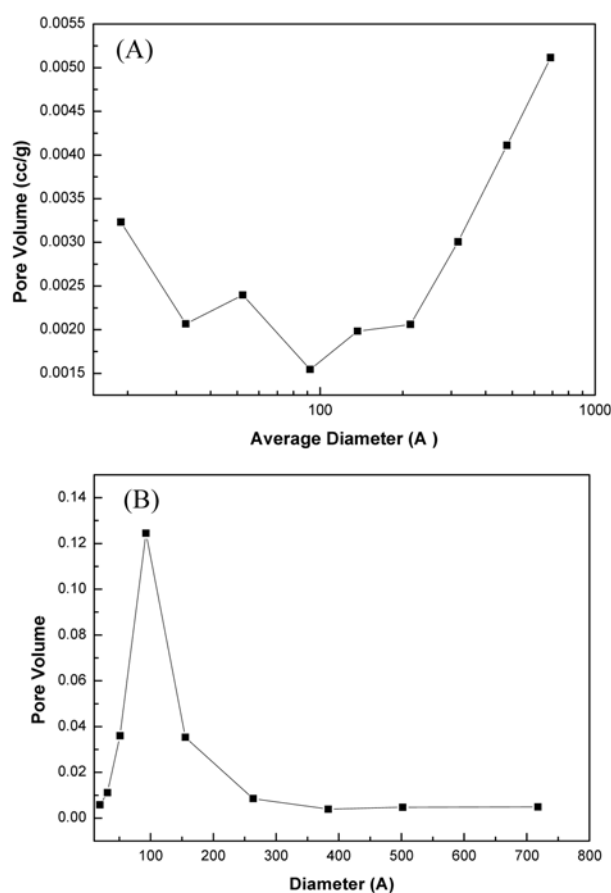
**Fig. 4.** TEM images of as-prepared particles prepared by forced hydrolysis of ferric nitrate solution in (A) the absence and (B) the presence of CTAB. (scale bar : 20 nm)



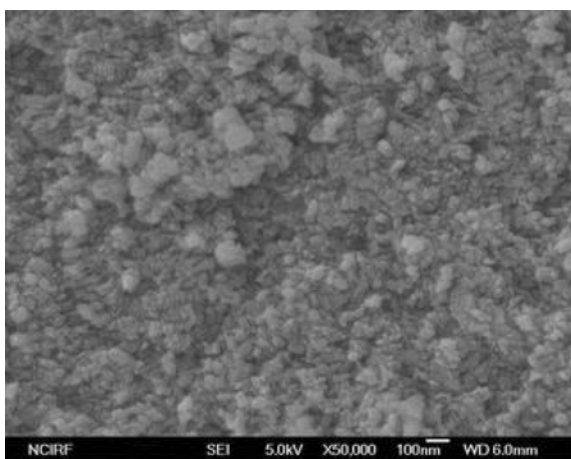
**Fig. 5.** Nitrogen adsorption-desorption isotherms of particles prepared by forced hydrolysis: (A) 0.1 M aqueous solution of ferric nitrate; (B) ferric nitrate solution with CTAB into which ammonia was added before aging in ethanol and ultrasonication was executed on this solution.

BJH (Barret-Joyner-Halenda) pore diameter distribution were examined. Figure 5(A) and 6(A) show the adsorption-desorption isotherm of the particles prepared in the absence of CTAB and ammonium hydroxide, which indicates that nonporous particles were prepared. By contrast to this result, when ferric nitrate solution with CTAB was aged after the ammonium hydroxide addition, the mesoporous particles with a narrow pore size distribution were obtained as shown in Fig. 5(B) and 6(B). The BET surface area and average pore diameter of the particles prepared with ammonium hydroxide and CTAB are  $91.77 \text{ cm}^2/\text{g}$  and  $7.8 \text{ nm}$ , respectively. The BET surface area is twice that of the particles prepared in the absence of CTAB and ammonium hydroxide. In spite of the narrow pore diameter distribution, the resulting particles have a disordered arrangement of pores in the solid material according to small angle X-ray scattering (SAXS) patterns.

Considering the average pore diameter and particle size, it is obvious that that mesopores in the powder are not located in the rod-type small particles. SEM image of dried powders is presented in Fig. 7. Agglomerated particles are observed, whose size and shape is different from those observed in Fig. 2. With regard to the



**Fig. 6.** BJH (Barret-Joyner-Halenda) pore diameter distribution of particles prepared by forced hydrolysis: (A) 0.1 M aqueous solution of ferric nitrate; (B) ferric nitrate solution with CTAB into which ammonia was added before aging.



**Fig. 7.** SEM image of goethite particles prepared with ammonia and CTAB.

above results, it can be inferred that the formation of mesopores may be ascribed to the voids between weakly agglomerated particles consisting of small rod-type particles. A relatively uniform pore diameter is attributed to the adsorption of the surfactant molecules on the surface of particles. Surfactant molecules adsorbed on

the particle surface may act as a 'spacer' among the neighboring particles and prevent the coalescence and the formation of hard agglomerates of individual particles.

## Conclusions

Nanosized rod-type ferric oxyhydroxide particles were prepared by forced hydrolysis of ferric nitrate aqueous solution in the presence of CTAB. Selective adsorption of CTAB on the surface of particle precursors is responsible for the formation of rod-like particles. Addition of ammonium hydroxide also plays an important role by enhancing the selective adsorption of CTAB on the surface of growing particles. After drying, weakly agglomerated particles with a disordered mesoporous structure and a narrow pore size distribution were obtained. These pores are attributed to the adsorption of CTAB on the particle surfaces, on which they act as a spacer among the neighboring particles. These agglomerated particles show a doubled BET surface area compared with resulting particles prepared by forced hydrolysis in the absence of surfactants. With this method, the synthesis of rod-type particles of other metal oxides is expected to be possible. Such materials with a uniform one-dimensional structure and richness of inorganic compositions have excellent potential for applications in optical devices and as electronic materials.

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## References

1. A.P. Alivisatos, *Science* 271 (1996) 933-937.
2. K.K. Rangan, P.N. Trikalitis, and M.G. Kanatzidis, *J. Am. Chem. Soc.* 122 (2000) 10230-10231.
3. T.P. Raming, A.J.A. Winnubst, C.M. van Kats, and A.P. Philipse, *J. Colloid Interface Sci.* 249 (2002) 346-350.
4. P. Yang, D. Zhao, D.I. Margolese, B.F. Chmelka, and G.D. Stucky, *Chem. Mater.* 11 (1999) 2813-2826.
5. A. Lezau, M. Trudeau, G.M. Tsoi, L.E. Wenger, and D. Antonelli, *J. Phys. Chem. B* 108 (2004) 5211-5216.
6. Q. Zhao, L. Hou, and R. Huang, *Inorg. Chem. Commun.* 6 (2003) 971-977.
7. N.R. Jana, L. Gearheart, and C.J. Murphy, *Adv. Mater.* 13 (2001) 1389-1393.
8. M. Yada, M. Mihara, S. Mouri, M. Kuroki, and T. Kijima, *Adv. Mater.* 14 (2002) 309-313.
9. Y. Ono, K. Nakashima, M. Sano, Y. Kanekiyo, K. Inoue, J. Hojo, and S. Shinkai, *Chem. Commun.* 14 (1998) 1477-1478.
10. J.H. Park, S.Y. Bae, and S.G. Oh, *Chem. Lett.* 32 (2003) 598-599.
11. J.S. Beck, J.C. Vartuli, W.J. Roth, M.E. Leonowicz, C.T.

- Kresge, K.D. Schmitt, C.T. Chu, D.H. Olson, E.W. Sheppard, S.B. McCullen, J.B. Higgins, and J.L. Schlenker, *J. Am. Chem. Soc.* 114 (1992) 10834-10844.
12. Y. Liu, D. Hou, and G. Wang, *Chem. Phys. Lett.* 379 (2003) 67-73.
  13. N.R. Jana, L. Gearheart, and C.J. Murphy, *J. Phys. Chem. B* 105 (2001) 4065-4067.
  14. B. Nikoobakht, and M.A. El-Sayed, *Chem. Mater.* 15 (2003) 1957-1962.
  15. X.M. Sun, X. Chen, Z.X. Deng, and Y.D. Li, *Mater. Chem. Phys.* 78 (2002) 99-104.
  16. E. Matijevic, and P. Scheiner, *J. Colloid Interface Sci.* 63 (1978) 509-524.
  17. S. Music, S. Krehula, and S. Popovic, *Mater. Lett.* 58 (2004) 2640-2645.
  18. K. Kandori, Y. Nakamoto, A. Yasukawa, and T. Ishikawa, *J. Colloid Interface Sci.* 202 (1998) 499-506.
  19. K. Kandori, N. Okamoto, and T. Ishikawa, *Langmuir* 18 (2002) 2895-2900.
  20. J.P. Jolivet, *Metal oxide chemistry and synthesis*, John Wiley & Sons, Ltd. (1994).
  21. M. Ocana, M. Morales, and C. Serna, *J. Colloid Interface Sci.* 171 (1995) 85-91.
  22. E. Matijevic, *Ann. Rev. Mater. Sci.* 15 (1985) 483-516.
  23. E. Matijevic, *Langmuir* 2 (1986) 12-20.
  24. K. Kandori, Y. Nakamoto, A. Yasukawa, and T. Ishikawa, *J. Colloid Interface Sci.* 202 (1998) 499-506.
  25. L. Feng, L. Jiang, A. Mai, and D. Zhu, *J. Colloid Interface Sci.* 278 (2004) 372-375.
  26. Y. Sun, Y. Yin, B.T. Mayers, T. Herricks, and Y. Xia, *Chem. Mater.* 14 (2002) 4736-4745.
  27. J.M. Petroski, Z.L. Wang, T.C. Green, and M.A. El-Sayed, *J. Phys. Chem. B* 102 (1998) 3316-3320.
  28. B. Nikoobakht, and M.A. El-Sayed, *Langmuir* 17 (2001) 6368-6374.