Template-Directed Synthesis of Structured Iron Oxides

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Introduction

In the nano regime magnetic, optical, electronic, and catalytic properties strongly depend on the morphology. The control over particle size, size distribution, shape, and composition is an important goal in the synthesis of structured materials. Although many preparation techniques have been elaborated [1], it is still rather difficult to produce large quantities of such nano-materials. The application of surfactant-mediated synthesis procedures, which involve the precipitation of various precursors from homogeneous solutions in the presence of different additives, has proved to be a promising strategy towards tailoring such materials.

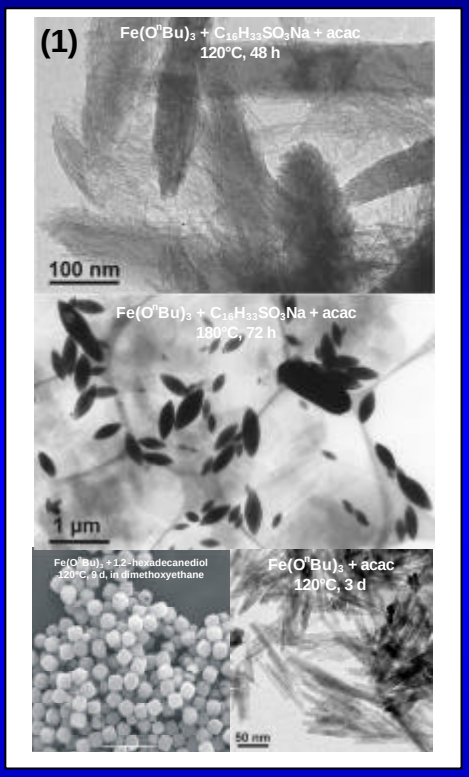
General Synthesis Procedure

Here we present the template-directed synthesis of structured iron oxides using two different iron oxide precursors, either iron(III) n-butoxide or the air-stable hexanuclear iron complex $[N(CH_3)_4]_2[OFe_6(H_{-3}thme)_3(OCH_3)_3Cl_6 \cdot MeOH$ (thme = 1,1,1-tris(hydroxymethyl)ethane) [2].

1) $Fe(O^nBu)_3$ + Template $\xrightarrow[\text{2) Hydrothermal Treatment}]{\text{1) Hydrolysis}}$ FeO_x

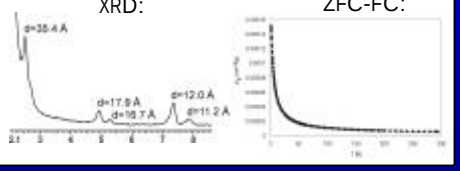
2) $[N(CH_3)_4]_2[OFe_6(H_{-3}thme)_3(OCH_3)_3Cl_6 \cdot MeOH$ + Template $\xrightarrow[\text{3) Hydrothermal Treatment}]{\text{1) Dissolution in NaOH; 2) Precipitation with HCl}}$ FeO_y

Experiments with Iron n-Butoxide



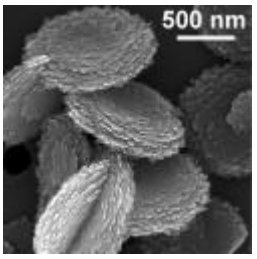
Analysis of (1)

XRD: ZFC-FC:

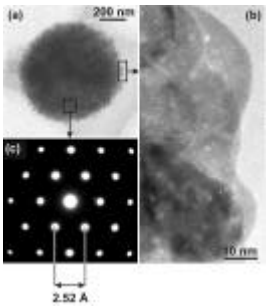


Experiments with $[N(CH_3)_4]_2[OFe_6(H_{-3}thme)_3(OCH_3)_3Cl_6 \cdot MeOH$

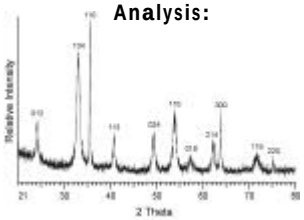
SEM image of the disc-like hematite particles obtained without the use of any templates:



Polycrystalline HRTEM (b) and mono-crystalline ED (c) of one single particle (a):



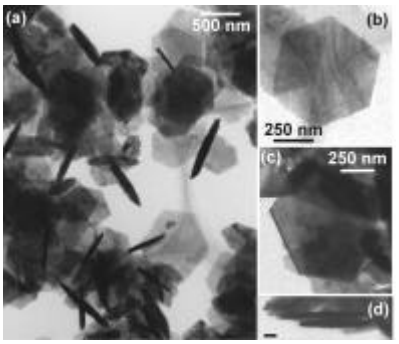
Analysis:



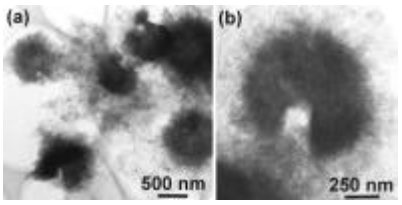
BET measurements: 51 m^2/g
BJH (adsorption): 20-120 Å

TEM images of the products obtained with additives

Hematite colloids produced in the presence of hydrazine:

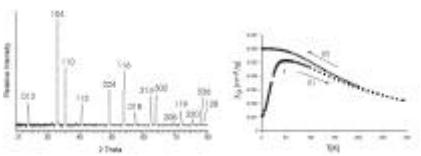


Hematite particles synthesized in the presence of 1,2-hexadecanediol:



Analysis of the hydrazine-product:

XRD: ZFC-FC:



Discussion

In additon to the well-known synthesis routes to structured iron oxides using inorganic salts (e.g. [3]), we developed a novel approach involving the hydrolysis of an iron alkoxide or an iron-polyolate complex. Due to its air-stability and easy synthesis the use of $[N(CH_3)_4]_2[OFe_6(H_{-3}thme)_3(OCH_3)_3Cl_6 \cdot MeOH$ in particular provides an advantageous access to monodispersed iron oxide colloids in gram quantities [4].

The influence of different organic additives such as long-chain surfactant molecules with neutral or charged functional head groups and redox-active agents on particle size, shape and composition opens the possibility to tailor the material to a certain extent.

Literature

[1] Matijevic, E. *Chem. Mater.* **1993**, *5*, 412
[2] Cornia, A.; Gatteschi, D.; Hegetschweiler, K.; Hausherr-Primo, L.; Gramlich, V. *Inorg. Chem.* **1996**, *35*, 4414
[3] Tolbert S. H., Sieger P., Stucky G. D., Aubin S. M. J., Wu C.-C., Hendrickson, *J. Am. Chem. Soc.* **1997**, *119*, 8652
[4] M. Niederberger, F. Krumeich, M. Müller, R. Nesper, in preparation

Acknowledgements

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