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. Here we present a synthesis route to structured iron oxides using an iron-polyolate complex.

Synthesis

A simple procedure has been developed for the synthesis of colloidal iron oxide particles involving the use of a hexanuclear iron-polyolate complex as precursor [2]:

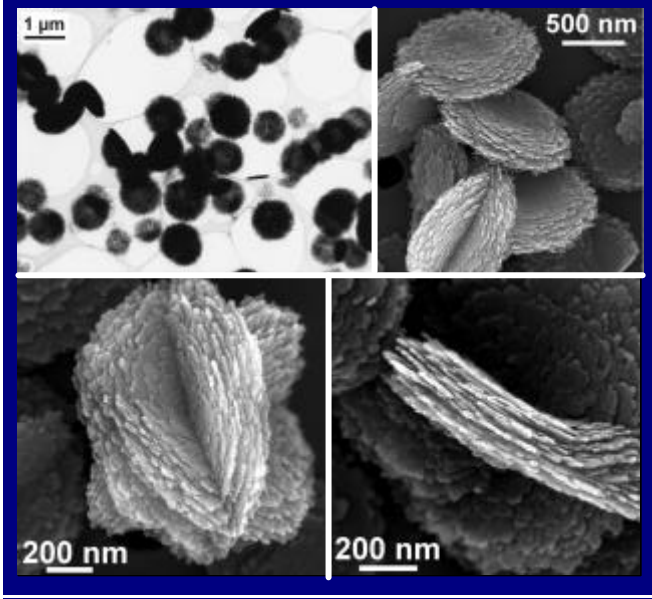
$FeCl_3$ + thme + $[N(CH_3)_4]OH$ ⟶ $[N(CH_3)_4]_2[OFe_6(H_{-3}thme)_3(OCH_3)_3Cl_6 \cdot MeOH$,

with thme = 1,1,1-tris(hydroxymethyl)ethane.

The hydrolysis and hydrothermal treatment of this complex yielded monodispersed hematite particles [3]:

$[N(CH_3)_4]_2[OFe_6(H_{-3}thme)_3(OCH_3)_3Cl_6 \cdot MeOH$ ⟶ (1) Dissolution in NaOH, additives; (2) Precipitation with HCl; (3) Hydrothermal treatment ⟶ α-Fe_2O_3

Reaction without any Additives:



TEM and SEM:

- Diameters ranging from 0.9 – 1.1 µm
- Small size distribution
- Layered structure consisting of stacked iron oxide platelets

HRTEM/ED:

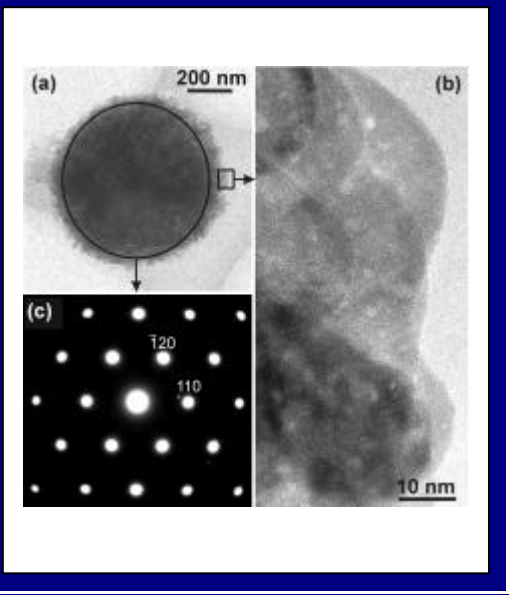
- HRTEM (b): poly crystalline
- ED (c): single crystalline

XRD:

- Hematite α-Fe_2O_3
- All reflections hkl with I = 0 are sharp

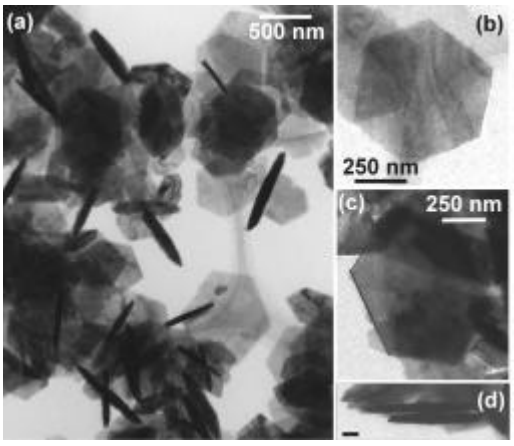
BET:

- BET-surface: 51 m^2/g
- Pore size distribution (BJH): 20-120 Å

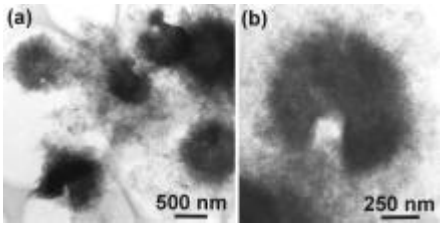


Reactions with Additives:

Final product in the presence of hydrazine:



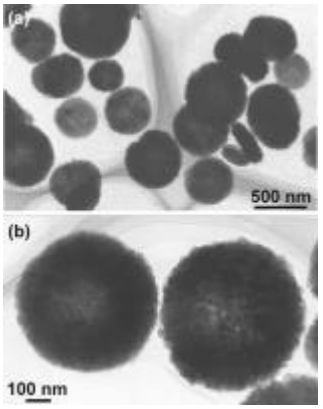
Final product in the presence of 1,2-hexadecanediol:



Analysis of the final products:

- ***Hydrazine:*** Hematite with hexagonal crystal shape
- ***1,2-Hexadecandioel:*** Hematite
- ***Sodium hexadecylsulfonate:*** Template intercalated: [Fe] = 10.93 %, [C] = 48.22 %, [H] = 7.45 %, [S] = 7.99 %

Final product in the presence of sodium hexadecylsulfonate:



Conclusion

This work presents a novel and reproducible route to iron oxide colloids using an iron-polyolate complex as precursor instead of inorganic salts. The air-stability and easy synthesis of this precursor provides an advantageous access to iron oxide colloids in gram quantities. The influence of different additives on particle size, shape and composition opens the possibility to tailor the final 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] M. Niederberger, F. Krumeich, M. Müller, R. Nesper, in preparation

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