Tailoring the Shape of Oxidic Nanoparticles:

Vanadium Oxide Nanotubes, Molybdenum Oxide Nanofibers, and Iron Oxide Microplatelets

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Introduction

The search for novel methods to synthesize nano-objects with controlled shape, size, and composition still remains a challenge. Especially nanoparticles with reduced dimensionality such as quantum dots (zero-dimensional), nanotubes and nanowires (1-dimensional), and layerlike entities (2-dimensional) have attracted much attention, because the anisotropy inherent in these systems provides unique properties, which are expected to be critical to the function and integration of nanoscale devices.

Here we present a compilation of different techniques for the synthesis of nanostructured transition metal oxides with anisotropic particle shapes. The main focus was directed towards the use of air-stable and cheap metal oxide precursors in order to allow a simple handling as well as a low-cost scale-up.

Synthesis

Vanadium Oxide Nanotubes

$VO(O^iPr)_3$, $VOCl_3$, V_2O_5, HVO_3 + $C_nH_{2n+1}NH_2$ (n = 4 – 22)

1) Hydrolysis
2) Aging at RT
3) Hydrothermal treatment (7d at 180°C)

$VO_{2.43\pm0.06}(C_nH_{2n+4}N)_{0.27\pm0.01}$

Molybdenum Oxide Nanofibers

$MoO_3\cdot 2H_2O$ + $C_{12}H_{25}NH_2$

Addition of Water/Ethanol
Hydrothermal treatment

$MoO_{3.25}\cdot[C_{12}H_{28}N]_{0.5}$

HNO_3

$MoO_3\cdot H_2O$

Iron Oxide Platelets

$FeCl_3$ + thme + $[N(CH_3)_4]OH$

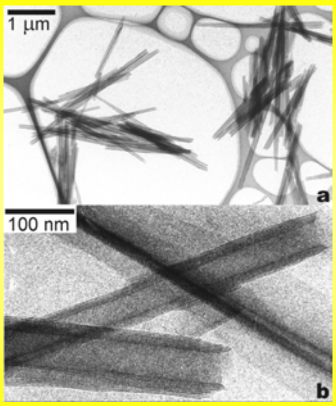
$[N(CH_3)_4]_2[OFe_6(H_3thme)_3(OCH_3)_3Cl_6\cdot MeOH$

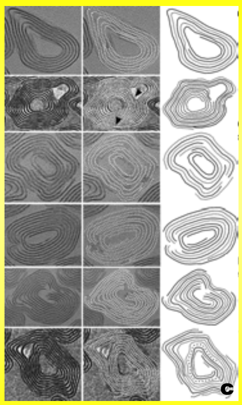
thme = 1,1,1-tris(hydroxymethyl)ethane

NaOH
HCl
Hydrothermal treatment

α-Fe_2O_3

Vanadium Oxide Nanotubes





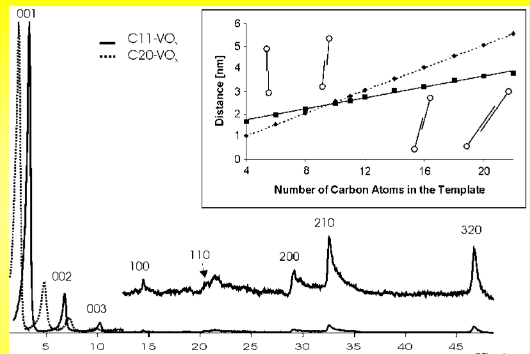
Representative TEM Images (left):

a and **b** (along the longitudinal projection direction):

- Exclusively multiwalled nanotubes
- Walls consist of equally spaced parallel lattice fringes, 2-30 layers
- Predominantly open tubes
- Outer diameters: 15-100 nm
- Inner diameters: 5-50 nm
- Length: 0.5-15 µm

c (cross-sectional TEM image):

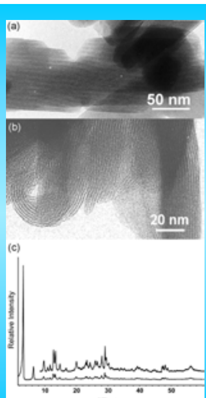
- Scroll-like morphology



XRD powder pattern:

The distance between the layers generating the reflections *00l* increases proportional to the length of the carbon chain in the alkylamine (inset).

Molybdenum Oxide Nanofibers

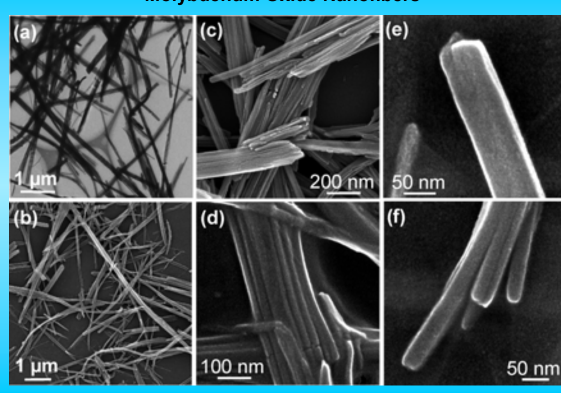


Characterization of the molybdenum oxide – amine composite:

(a) TEM image of the lamellar composite

(b) Sometimes the layers start to roll

(c) XRD powder pattern: The intense low-angle peaks correspond to the distance between the molybdenum oxide layers



Characterization of the molybdenum oxide nanofibers:

(a) Representative TEM image: The fiber length ranges from 350 nm to 14 µm, and the diameters vary from 20 to 280 nm

(b) Overview SEM image

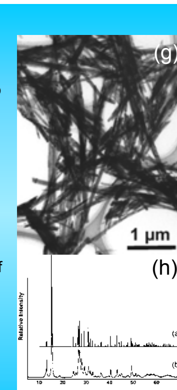
(c) Higher magnified area

(d) Close view of one bundle consisting of smaller filaments

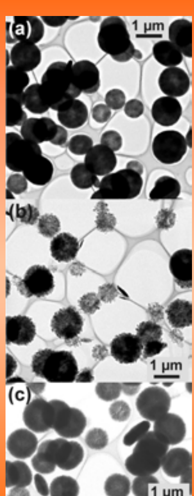
(e) and (f) Tips of a fiber consisting of smaller filaments

(g) TEM image of calcined fibers

(h) XRD powder pattern of the nanofibers (b) which matches with the theoretical pattern of α-molybdic acid $MoO_3\cdot H_2O$ (a)



Iron Oxide Microplatelets



On the left:

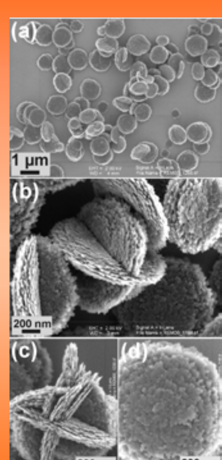
TEM images of the product obtained from the hydrolysis of the „Fe_6-complex" and hydrothermal treatment at

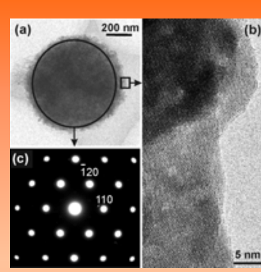
(a) 100°C for 3 days
(b) 180°C for 3 days
(c) 150°C for 24 h.

On the right:

SEM images of the product obtained after hydrothermal treatment at 150°C for 3 days:

(a) Overview
(b) Intergrown particles
(c) The particles exhibit a layered structure consisting of stacked discs
(d) Close view on one particle from above shows the polycrystalline nature of the particle

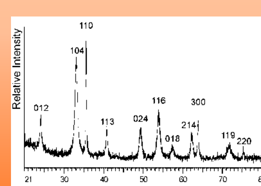




(a) TEM image of a single hematite particle

(b) HRTEM image showing the crystal structure as a hexagonal pattern of dark dots

(c) Electron diffraction pattern



XRD powder pattern of the hematite particles: The reflections *hkl* with *l=0* are sharper than the ones with *l≠0*

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