4 Experimental Section

4.1 Synthesis Techniques

4.1.1 General Techniques

Air- and moisture sensitive substances were handled under inert atmosphere, either working with Schlenk technique or with dry boxes. Argon (4.8 N) was used as inert gas, additionally cleaned by purification columns (HYDROSORB, OXISORB®-Glas) to remove residues of oxygen and nitrogen. The vacuum line was connected to a vacuum pump (Edwards) with a maximum vacuum of $5 \cdot 10^{-3}$ mbar.

4.1.2 Chemicals

Mono-n-dodecylphosphate was bought from Lancaster. All the other chemicals were obtained commercially from Fluka, Switzerland, and generally used without further purification. Exceptions are vanadium(V) oxytrichloride, and ethylenediamine which were distilled under intert atmosphere before use. Also anhydrous solvents like butanol, pentane, and toluene were dried with either sodium or CaH_2 and distilled.

Eicosylamine [1], molybdic acid [2], iron butoxide [3], and the iron(III)-tris(hydroxymethyl) ethane complex [4] were synthesized as reported in literature.

Glucopon 215 CS UP was supplied from Henkel KGaA, Düsseldorf.

4.1.3 Reaction Setups

For the hydrothermal treatment, steal autoclaves (Parr Acid Digestion Bombs) with Teflon cups (23 ml or 45 ml) were used. One single autoclave was heated in a small furnace from Berghof, whereas for the hydrothermal treatment of several samples at the same time, the autoclaves were put in a Venticell-furnace from MMM Medcenter.

4.2 Analysis and Characterization

4.2.1 X-ray Powder Diffraction

The X-ray powder diffraction (XRD) diagrams of all samples (except iron) were collected in transmission mode on a STOE powder diffractometer (STADI-P2, germanium monochromator; CuKα_1 = 1.54056 Å; position sensitive detector with $2\theta_{eff}$ = 40°, resolution about 0.01° in 2θ) using a Debye-Scherrer geometry. The samples were filled in a glass capillary (Mark Röhrchen; length = 80 mm; diameter = 0.3 mm).

The iron oxide samples were measured in reflection mode (CuKα radiation, germanium monochromator) on a BRUKER D8 diffractometer equipped with a scintillation counter and a secondary monochromator to suppress fluorescence radiation.

4.2.2 Transmission Electron Microscopy

Transmission electron microscopy (TEM) investigations were performed on a CM30ST microscope (Philips; LaB_6 cathode, operated at 300 kV). For the investigation of the longitudinal shape and structure, the nano-material was deposited onto a perforated carbon foil supported on a copper grid. In order to observe the structure of the VO_x-NTs perpendicular to the tube axis, a cross-sectional preparation technique was applied. The tubes were deposited on a Si-wafer coated with an epoxy resin and then covered with a second Si-wafer. Most of the tubes were now oriented flat between the wafers. This 'sandwich' was put into a copper tube (outer diameter: 3 mm), which was then filled with epoxy. After hardening of the resin, the resulting cylinder was cut into slices (thickness ≈ 300 µm) which were then mechanically abraded on both sides to a thickness between 100 and 150 µm. Subsequently, dimples (depth ≈ 40-60 µm) were ground into both sides of the slice (Dimple Grinder, Gatan). In the final preparation step, the specimen was etched on both sides with ion beams (PIMS, Gatan, argon ions, 4 keV) until a hole was created in the central area containing the tubes. At the thin specimen edge close to the hole, the tubes can be observed by TEM and their orientation quite often allows an investigation along the tube axis. The element specific images were obtained by means of the electron spectroscopic imaging technique with an energy filter (Gatan imaging filter) installed at a CM200 ST microscope (Philips; field emission gun, operated at 200 kV) [5,6].

4.2.3 Scanning Electron Microscopy

Scanning electron microscopy (SEM) investigations were made in the Laboratory of Electron Microscopy by Dr. Martin Müller on a Hitachi S-900 after coating the sample with either platinum (particle size 4 nm) or for higher resolution with tungsten (particle size 2 nm).

4.2.4 Chemical Analysis

C, H, and N analyses were carried out in the Organic Laboratory for Micro-Elemental Analysis by means of combustion test methods on a LECO CHN-900. Inorganic element analyses were performed in the group of Prof. Dr. D. Günther by inductive coupled plasma/optical emission spectroscopy (ICP-OES) on a Thermo Jarrell Ash IRIS.

4.2.5 Nitrogen Adsorption Measurements

Nitrogen adsorption was measured at 77.35 K with an ASAP 2010 Micromeritics apparatus after degassing the sample at 300°C for several hours under vacuum ($1.4 \cdot 10^{-3}$ Pa) by Benedikt Lindlar. For the determination of the surface area the BET method was used [7]. Barrett-Joyner-Halenda (BJH) calculations were made for the pore volume and pore size distribution for the adsorption portion of the isotherm.

4.2.6 Magnetic Measurements

Magnetic measurements were performed on a SQUID magnetometer (MPMS 5S, Quantum Design). Data was collected from room temperature down to 1.7 K and from -50 to 50kG. The samples (15-20 mg) were ground and transferred into a small glass tube, which was mounted in the magnetometer in a small quartz tube. This quartz sample holder was rotated by 360° during measurements. The diamagnetic contribution of the sample container was always considered. The gram susceptibility χ_g was calculated as follows:

$$\chi_g = M/(H \cdot m) \quad [cm^3/g]$$

with M = magnetic moment [emu], H = magnetic field [G], m = weight of the sample in gram.

Generally, the susceptibility is the sum of different contributions:

$\chi_{tot} = \chi_{dia} + \chi_{para} + \chi_{pauli}$

χ_{tot} = total susceptibility

χ_{dia} = diamagnetic contribution (independent of temperature)

χ_{para} = paramagnetic contribution (dependent on temperature)

χ_{pauli} = temperature-independent paramagnetic contribution (Pauli paramagnetism)

The total susceptibility is positive for paramagnetic substances and negative for diamagnetic substances.

4.3 Literature

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