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Synthesis and characterization of novel nanoscopic molybdenum oxide fibers

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A molybdenum oxide with high aspect ratio has been synthesized by a template-directed process. The reaction of molybdic acid and primary amines with long alkyl chains, followed by hydrothermal treatment, led to a lamellar molybdenum oxide–amine composite. The subsequent removal of the intercalated amines with nitric acid yielded a pure molybdenum oxide phase with a fibrous morphology. According to X-ray powder diffraction and chemical analysis, these fibers crystallize with the structure of α-$MoO_3 \cdot H_2O$. Electron microscopy investigations have revealed that the fibers are up to 15 μm long and that their diameters generally range from 50 to 150 nm. The presented synthesis approach uses a cheap and air-stable precursor and, thus, provides an advantageous access to gram quantities of this novel anisotropic nanomaterial.

Introduction

At present, a main objective of nanochemistry is the development of new "bottom-up" methods for synthesizing and characterizing chemical structures within the size range of about 1–100 nm in one, two or three dimensions.[1] Dimensionality is a crucial factor in determining the properties of nanomaterials[2] and, thus, the control of size and shape is of great interest with regard to specific applications of such materials as nanodevices. In particular, reduced dimensionality has attracted considerable attention. One-dimensional nanomaterials such as nanowires and nanotubes have one macroscopic dimension in the micron range, and the remaining two are in the nanometer region. General methods for the preparation of such nanostructures are not yet available, although different approaches have been pursued: lithographic techniques[3] as well as deposition within the pores of nanoporous membranes[4] have been used.

In the course of the exploration of novel approaches for the preparation of metastable oxide materials, the main interest is focused on soft-chemical routes.[5,6] In particular, host–guest compounds represent a new and promising class of material that can be used for the controlled preparation of complex organized structures or composites in the nanoscale regime.[7,8] The scientific and technological interest in layered materials has also included the development of novel synthesis routes to low-dimensional and porous molybdenum oxide derivatives, since these compounds offer promising catalytic properties[9] and a rich intercalation chemistry.[10–18] Recently, a review article summarized the growing family of molybdenum oxide–organodiamine compounds.[19]

In general, two different strategies can be applied for the preparation of molybdenum oxide–organic composite materials, namely either an intercalation route or a template approach. Hydrothermal reaction of molybdic acid or sodium molybdate with dodecyltrimethylammonium bromide yielded a lamellar composite material with the composition $[C_{12}H_{25}N(CH_3)_3]_{0.5}MoO_{3.25}$.[20,21] In a similar intercalation approach, ammonium molybdate was reacted with long chain quaternary ammonium surfactants at different pH values.[22] In the obtained layered molybdenum oxide–surfactant composites, the *d*-spacings of the layers (2.07–2.55 nm) were controlled by variation of the surfactant alkyl chain length. Using a template approach, triblock copolymer micelles have been used for the synthesis of porous, highly uniform, and hollow MoO_3 nanospheres.[23] Mesostructured molybdenum oxide toroids were prepared from a dimeric molybdenum ethoxide complex with a bridging dodecylimido group.[24] Although it was proposed[20] that the removal of the organic templates from the lamellar molybdenum oxide–surfactant composites may lead to the formation of mesoporous solids, in all cases the material collapsed completely upon removal of the template molecules.

Here, we report an efficient method to produce nanoscopic molybdenum oxide fibers.[25] The procedure is based on the intercalation of primary amines into the layered structure of molybdic acid and subsequent transformation of the lamellar molybdenum oxide–amine intermediate into the fibrous product.

Experimental

Materials

Sodium molybdate Na_2MoO_4, undecyl-, dodecyl- and hexadecylamine were obtained from Fluka (Switzerland) and used without further purification. Molybdic acid was synthesized by dissolving Na_2MoO_4 in 3 M perchloric acid.[26] For hydrothermal treatment, we used Parr Acid Digestion Bombs with 23 or 45 ml Teflon cups as autoclaves.

Synthesis

In a typical procedure, molybdic acid $MoO_3 \cdot 2H_2O$ (10 mmol) was mixed with the amine in 5 ml ethanol (molar ratio 2 : 1). After the addition of 15 ml distilled water, the yellow suspension was stirred at room temperature for 48 hours until a white precipitate was formed. The hydrothermal reaction of this composite was performed in an autoclave at

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120 °C for 3 to 5 days. After filtering and washing with ethanol and diethyl ether, a white powder resulted.

By stirring the molybdenum oxide–amine composite (2.5 g) in 10 ml 33% nitric acid (48 h at RT), the fibrous material was formed. The product was filtered, washed with ethanol and diethyl ether and then dried at 80 °C under vacuum (10^{-3} mbar).

Characterization

The X-ray powder diffraction (XRD) diagrams of all samples were measured in transmission mode (0.3 mm glass capillaries, $\mathrm{CuK}\alpha_1$ radiation) on a STOE STADI-P2 diffractometer equipped with a position sensitive detector (resolution $\sim 0.01°$ in 2θ). Transmission electron microscopy (TEM) investigations were performed on a CM30 ST microscope (Philips), operated at 300 kV. The material was deposited onto a perforated carbon foil supported on a copper grid. For scanning electron microscopy (SEM), performed on a Hitachi S-900, the sample was coated with platinum (particle size ~ 4 nm) or, for higher magnifications, with tungsten (particle size ~ 2 nm).

Nitrogen adsorption of the molybdenum oxide fibers was measured at 77.35 K with an ASAP 2010 Micromeritics apparatus. Prior to the measurement, the sample was degassed at 300 °C for several hours under vacuum (1.4×10^{-3} Pa). The surface area was determined by the BET method.[27]

C, H, and N analysis was carried out by means of combustion test methods on a LECO CHN-900. The molybdenum analysis was performed by inductive coupled plasma/optical emission spectroscopy (ICP-OES) on a Thermo Jarrell Ash IRIS.

Results and discussion

Synthesis and characterization

A novel fibrous molybdenum oxide material was synthesized *via* a soft chemistry route involving three steps: 1) molybdic acid ($MoO_3 \cdot 2H_2O$) and neutral primary amines with long alkyl chains ($C_nH_{2n+1}NH_2$ with $11 \leqslant n \leqslant 16$) were reacted; 2) the resulting composite was treated hydrothermally; 3) the reaction product was stirred in nitric acid.

In the first step of the synthesis, the molybdic acid was either mixed with a solution of the amine in ethanol or with the amine in pure, liquid form. After adding distilled water, aging at room temperature for at least 48 hours converted the yellow suspension into a white precipitate. For the subsequent hydrothermal treatment, the hydrolysis product was either taken directly or after filtering. Both procedures resulted in a lamellar structured molybdenum oxide–amine composite.

To investigate the influence of the amount of template on the morphology of the product, the initial molar molybdenum to template ratio (Mo/template) was varied from 4 to 1 whereas the amounts of water and ethanol for dissolution of the amine molecules were kept constant. After hydrolysis and aging at room temperature, a similar lamellar-structured molybdenum oxide–amine composite was obtained for Mo/template ratios ranging from 3 to 1. Further decrease of the template content, *i.e.*, Mo/template ratio = 4, inhibits the formation of the lamellar molybdenum oxide–amine intermediate. The yellow suspension kept its color during aging at room temperature for several days and, according to XRD measurements, the initial molybdic acid remained unreacted.

Various experiments were performed to investigate the effect of temperature and duration of hydrothermal processing on the morphology of the product. Independent of the duration (1 to 14 days), hydrothermal treatment at 100 °C or 120 °C showed no distinct effect on the obtained lamellar phase. In contrast to that, the morphology of the product strongly depended on reaction time, when heated at 150 °C. After 1 day, the white powder still consisted of a well-ordered lamellar structure, whereas a black powder was obtained after 7 days. XRD and TEM investigations showed a poorly structured lamellar phase. At even higher temperatures ($T = 180$ °C), the hydrothermal process yielded a black, crystalline product, which has not been further investigated yet.

TEM investigations of the intermediate product clearly reveal a lamellar morphology. A typical micrograph of this molybdenum oxide–amine composite is reproduced in Fig. 1a. The molybdenum oxide forms parallel layers, which appear with dark contrast in the TEM image, while the amine molecules are intercalated between these layers. Sometimes, these layers started to bend (Fig. 1b). The lamellar structure is confirmed by XRD measurements. The powder diffraction pattern (Fig. 1c) shows the highly intense and sharp reflections at low scattering angles that are typical for layered structures. The peak with highest intensity is located at a *d*-value between 2.6 and 3.2 nm and corresponds to the distance between the molybdenum oxide layers. The *d*-values of these 00l reflections

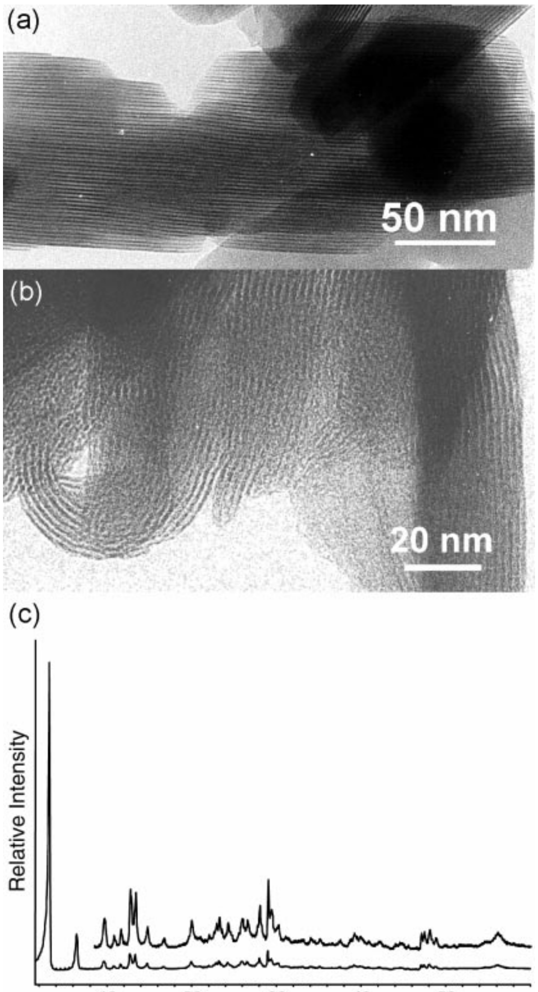

Fig. 1 (a) TEM image of the molybdenum oxide–amine composite, obtained from the hydrothermal treatment at 120 °C for 7 days of molybdic acid and dodecylamine in ethanol and distilled water, showing the layered structure of the lamellar phase. (b) TEM image of a lamellar molybdenum oxide–dodecylamine composite after hydrothermal treatment at 100 °C for 3 days, demonstrating layers that started to roll. (c) X-Ray powder diffraction pattern of a lamellar molybdenum oxide–dodecylamine composite after hydrothermal treatment. The 001 reflection, representing the distance between the molybdenum oxide layers, corresponds to a *d*-value of 2.76 nm. The enlarged section shows the characteristic reflections generated by the structure within the layers.

Table 1 Results of elemental analysis

	Mo	C	H	N	O
Molybdenum oxide–dodecylamine composite $[C_{12}H_{28}N]_{0.5}\cdot MoO_{3.25}$					
Measured	39.47	30.28	5.95	2.90	21.40[a]
Calculated	39.79	29.89	5.85	2.90	21.57
$MoO_3\cdot H_2O$ fibers					
Measured	58.38	0.72	1.27	0.03	39.6[a]
Calculated	59.24	0	1.24	0	39.52

[a] The amount of oxygen was calculated with respect to 100%.

depend on the alkyl chain length of the intercalated amine template. This observation indicates that the template molecules are indeed located in between the molybdenum oxide layers. At higher scattering angles, less intense reflections indicate crystallinity of the MoO_3 layers. A reliable determination of this structure has not been achieved yet.

According to elemental analysis, the composition of the layered molybdenum oxide–amine composite can be expressed by the general formula $[C_{12}H_{28}N]_{0.5}MoO_{3.25}$ (Table 1), which is in excellent agreement with the previously reported lamellar molybdenum oxide–surfactant composite $[C_{12}H_{25}N(CH_3)_3]_{0.5}MoO_{3.25}$.[20]

To remove the template molecules, the lamellar molybdenum oxide–amine composite was reacted with acid in the final synthesis step. The most suitable method involves the treatment of the composite with 33% HNO_3. Stirring at room temperature for 48 hours yielded a template-free molybdenum oxide. The concentration of the acid was about 13- to 15-fold excess with respect to the nitrogen content of the composite. Filtering and washing of the white precipitate with ethanol and diethyl ether gave a fibrous powder which was difficult to grind in a mortar.

The final product almost exclusively consisted of molybdenum oxide fibers (Fig. 2a and b). Fig. 2a shows a typical TEM image of this material representing a general view of the ribbon-like morphology. In some regions, the molybdenum oxide fibers are curved and tangled together forming bundles. The fibers exhibit a wide range of lengths and widths. Their diameters vary between 20 and 280 nm and their lengths range from 350 nm to 15 µm. In general, the majority of the fibers have an approximate diameter of 140 nm and the average length lies at 5 µm. SEM micrographs (Fig. 2b) prove the almost exclusive presence of molybdenum oxide fibers.

SEM images at higher magnification illustrate several other notable features of the molybdenum oxide fibers. Fig. 2c shows that the fibers have many discontinuities and defects along their axis, giving rise to a rough surface. A closer examination of the material reveals that the shape of the fibers is a flat needle rather than a round cylinder. In addition, they seem to consist of smaller anisotropic particles that are agglomerated into bundles. This is clearly seen in the SEM micrograph at higher resolution in Fig. 2d, which affords a more detailed view of one single bundle. The overall diameter of this bundle is about 180 nm. It is made up of agglomerated smaller filaments with diameters ranging from 20 to 50 nm. Fig. 2e and f depict the tips of two molybdenum oxide fibers. Fig. 2e illustrates that the fiber is neither round nor rotationally symmetric. Instead it seems as if two single filaments are agglomerated vertically to form a T-like angular particle. In Fig. 2f the tip of a bundle of fibers is represented, giving evidence that the bundle with an average diameter of 115 nm is composed of at least 5 smaller filaments with quite similar diameters of about 40 nm.

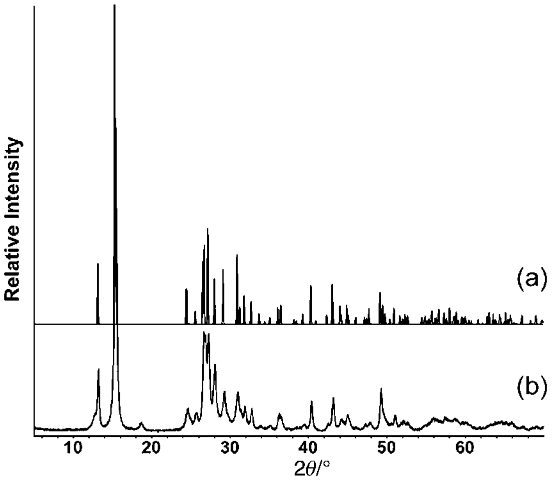

Fig. 3 (a) The theoretical XRD pattern of α-molybdic acid $MoO_3\cdot H_2O$. (b) XRD pattern of the fibrous molybdenum oxide.

The X-ray powder diffraction pattern of the fibrous material (Fig. 3b) is in good agreement with the theoretical X-ray powder pattern of white α-molybdic acid $MoO_3\cdot H_2O$[28,29] shown in Fig. 3a. The relatively sharp high angle peaks indicate rather good crystallinity. The elemental analysis is consistent with the composition of the fibrous product as $MoO_3\cdot H_2O$ (Table 1). The amount of organic residues in the final material is about 1%.

The absence of a porous structure is also confirmed by nitrogen adsorption and desorption isotherms. The calcined

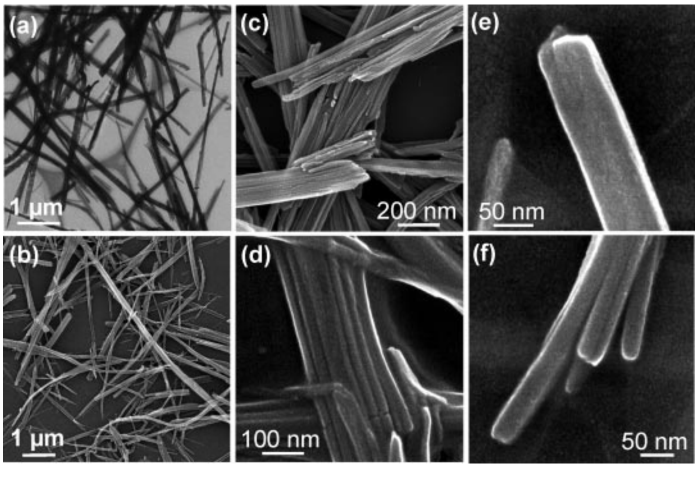

Fig. 2 Molybdenum oxide fibers obtained by the treatment of a molybdenum oxide–dodecylamine composite at room temperature with nitric acid for 56 h (a) or 24 h (b–f), respectively. (a) Representative TEM image. The fiber length ranges from 350 nm to 14 µm and the diameters vary from 20 to 280 nm. Hardly any by-product can be seen. (b)–(f) SEM images: (b) survey; (c) higher magnified area; (d) close view of one bundle (diameter ~ 180 nm) consisting of smaller filaments; (e)–(f) tip of a fiber composed of several filaments.

Fig. 4 Representative TEM image of molybdenum oxide fibers which have been heated at 400 °C for several hours in air.

molybdenum oxide fibers (300 °C) have a N_2 Brunauer–Emmett–Teller (BET) surface area of 35 $m^2 g^{-1}$. This is rather small compared with porous molybdenum oxides showing BET surfaces of 82[17] or 107 $m^2 g^{-1}$.[18]

Molybdenum oxides are important and effective catalysts in alcohol[30] and methane oxidation.[31] The novel particles with a filament-like shape in the nanoscale dimension have a large fraction of atoms exposed to the surface[32] and, therefore, they are especially promising with respect to the development of new catalytic characteristics. For catalytic applications, thermal stability of the material is indispensable and was therefore investigated. The fibers were thermally treated at 400 °C in air. After 3 hours, both the organic residues as well as the water molecules were removed and anhydrous MoO_3 was formed. However, the fibrous morphology has withstood this treatment and remains unaltered as shown in Fig. 4.

Discussion

Using an approach similar to the preparation of vanadium oxide nanotubes starting with layered vanadium pentoxide as the vanadium source,[33] we have shown that molybdic acid $MoO_3 \cdot 2H_2O$ represents a suitable precursor for the template-directed synthesis of nanostructured molybdenum oxides. The layered structure of this host compound enables direct intercalation of amine molecules due to strong interactions between the surfactant and the inorganic species.

It is interesting that the yellow molybdic acid $MoO_3 \cdot 2H_2O$ reacts to give the white precipitate at room temperature only in the presence of the amine molecules. Since the white lamellar product was also obtained by the reaction in anhydrous diethyl ether, the presence of water does not seem necessary to transform the molybdic acid into the white composite compound. The structure of yellow molybdic acid consists of $[MoO_5(H_2O)]$ octahedra connected to infinite layers, with water molecules intercalated in between the layers.[28] These two kinds of differently bound water molecules can be removed in two steps, which has been shown to occur topotactically.[34] So in the present case it seems likely that the color change from the yellow molybdic acid to the white composite is not caused by a hydrolysis reaction but by dehydration of $MoO_3 \cdot 2H_2O$ by which both water molecules are replaced by the amine molecules (Scheme 1).

By acid treatment of the molybdenum oxide–amine composite, the template molecules are substituted again by water molecules forming the white α-molybdic acid $MoO_3 \cdot H_2O$. The whole process can be summarized as a substitution of water molecules by amine molecules, followed by a re-substitution of these organic material again by water molecules. Since the XRD pattern of the lamellar molybdenum oxide–amine composite corresponds to none of the theoretical patterns of yellow $MoO_3 \cdot 2H_2O$, white $MoO_3 \cdot H_2O$ or anhydrous MoO_3, a structural rearrangement must have taken place during step (1), excluding a topotactical substitution process.

$$MoO_3 \cdot 2H_2O \xrightarrow{(1)} MoO_{3.25} \cdot [\text{amine}]_{0.5} \xrightarrow{(2)} MoO_3 \cdot H_2O$$

Scheme 1 Reaction scheme for the formation of the molybdenum oxide fibers: (1) addition of amines, ethanol and water followed by hydrothermal treatment; (2) reaction with HNO_3, *i.e.* removal of intercalated amines.

Removal of the template molecules from the molybdenum oxide–amine composite does not yield a mesoporous material. Instead, the reaction in nitric acid leads to a morphological transformation from the lamellar composite material into the fibrous particles, *i.e.*, transformation from a two-dimensional to a one-dimensional material. This process can be attributed to the loss of the organic intercalates, which probably induces a structural rearrangement. Since the final material also macroscopically shows the fibrous shape, it is interesting to note that this fibrous-like appearance is preserved from the macroscopic to the microscopic detail.

Conclusion

A template-directed process has been employed for the preparation of molybdenum oxide with a novel, fibrous morphology. This rather simple technique results in the production of gram quantities of this material. In general, the intercalation of template molecules leads to the structuring of the materials. In this case, the removal of the surfactant molecules directs a structural rearrangement, yielding a novel fibrous morphology.

Since transition metal alkoxides generally are rather expensive, the search for novel precursor materials is still interesting with regard to a cost-saving scale-up, especially interesting because of possible applications in catalysis. By using molybdic acid $MoO_3 \cdot 2H_2O$, it is possible to combine two main advantages: a) the precursor is cheap and easy to synthesize in large quantities, b) the air and moisture stability of the precursor offers easy handling without special precautions.

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