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## Boomerang-shaped VO<sub>x</sub> belts: Twinning within isolated nanocrystals

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**ABSTRACT** A hydrothermal method was used to synthesize new types of vanadium oxide belts exhibiting a boomerang shape. Scanning force microscopy (SFM) and transmission electron microscopy (TEM) analysis revealed a layered structure closely corresponding to that in known V<sub>2</sub>O<sub>5</sub> nanofibers. Most strikingly, selected area electron diffraction (SAED) provided clear evidence that the unique structure of the belts originates from twinning along the [130] direction. This result constitutes the first observation of twins within individual nano-sized crystals.

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### 1 Introduction

Low-temperature, solution-phase synthesis represents an attractive approach towards nano-scale one-dimensional (1-D) materials of high crystalline order [1]. In contrast to pulsed laser vaporization [2] and chemical vapour deposition [3], which are frequently used to produce carbon nanotubes or semiconductor nanowires [4], solvothermal methods work at relatively low temperatures of typically 100–200 °C. The latter methodology has proven highly versatile for the production of a wide range of 1D single-crystalline materials, including vanadium pentoxide (V<sub>2</sub>O<sub>5</sub>) [5], molybdenum trioxide (MoO<sub>3</sub>) [6], cadmium sulphide (CdS) [7], bismuth (Bi) [8], and perovskite manganites (La<sub>0.5</sub>(Ba, Sr)<sub>0.5</sub>MnO<sub>3</sub>) [9]. Among these, the vanadium oxide system is of special interest due to the variety of different structural morphologies that can be obtained in this manner [10]. Depending on the presence of additives (as a structural template and/or a reducing agent), as well as the reaction temperature and time, formation

of vanadium oxide nanofibres [5] or nanotubes [11] has been observed. In the present Communication, we report on a new type of nano-structured vanadium oxide, namely VO<sub>x</sub> nanobelts of boomerang shape, obtained via controlled hydrothermal synthesis using a vanadyl-ester as organic precursor. Microscopic analysis of these nano-sized crystals revealed that their remarkable structure originates from twinning, a phenomenon which had up to now been documented only in the bulk [12].

### 2 Experimental

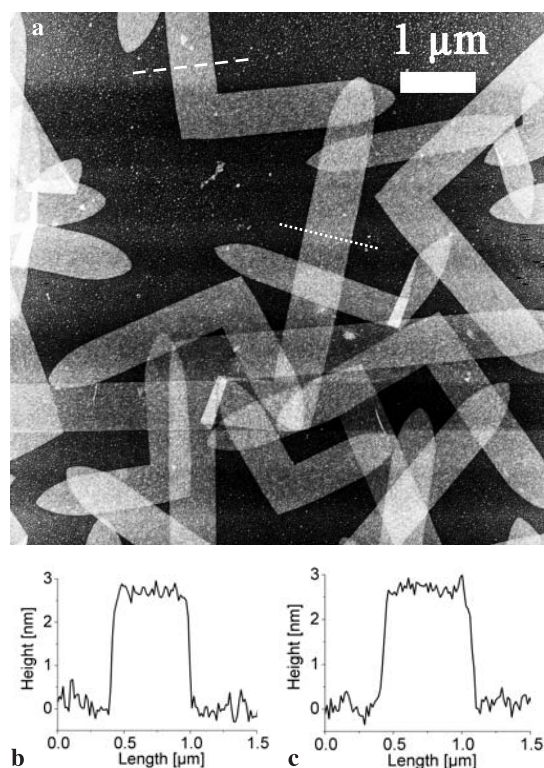
For hydrothermal synthesis, 150 μl of vanadium-oxytriisopropoxide (Aldrich) was added to 15 ml of ultra-pure water at room temperature. The mixture was stirred for 3 min at 70–80 °C until the formed, orange-colored gel had been completely dissolved. Then the solution was transferred into an autoclave cell (Teflon) of 20 ml volume, and kept for 3.5 h at 180 °C. The VO<sub>x</sub> nanobelts were deposited on Si/SiO<sub>2</sub> wafers that had previously been surface-modified by

treatment with N-[3-(trimethoxysilyl)propyl]ethylene-diamine (Aldrich, 10 μl in 10 ml of water, 2 min at room temperature). After diluting the VO<sub>x</sub> suspension 1 : 10 with pure water, the pre-treated wafer was kept for 20 s in this solution. For the TEM investigations, the nanobelts were deposited on Formvar-coated copper-grids (300 mesh, SPI Supplies) by the same procedure as used for Si/SiO<sub>2</sub> wafers. Scanning force microscopy was carried out with a DI Nanoscope IIIa, using standard silicon cantilevers in tapping mode. TEM and SAED experiments were obtained in a Philips CM30/ST (300 kV) equipped with a LaB<sub>6</sub> cathode. The SAED patterns were performed with the aid of a diaphragm which limited the diffraction to a selected area of 250 nm in diameter. TEM and SAED patterns were registered with a Multiscan CCD Camera (Gatan, Software: Digital Micrograph 3.6.1).

### 3 Results and Discussions

A representative scanning force microscopy (SFM) image of the VO<sub>x</sub> nanobelts on a Si/SiO<sub>2</sub> wafer is displayed in Fig. 1a, from which their regular boomerang (or “L”) shape is clearly apparent. Analysis of a larger number of belts has shown that the internal angle between their arms is identical, with a value of 96°. Although the belts are of equal shape, a distribution in the width and length of their arms is observed. For the present sample, the arm width amounts to 650 ± 50 nm and the length varies from 2–4.5 μm. The end regions of the belts are round-shaped, and terminated by a relatively sharp tip. Such tapering at the ends together with

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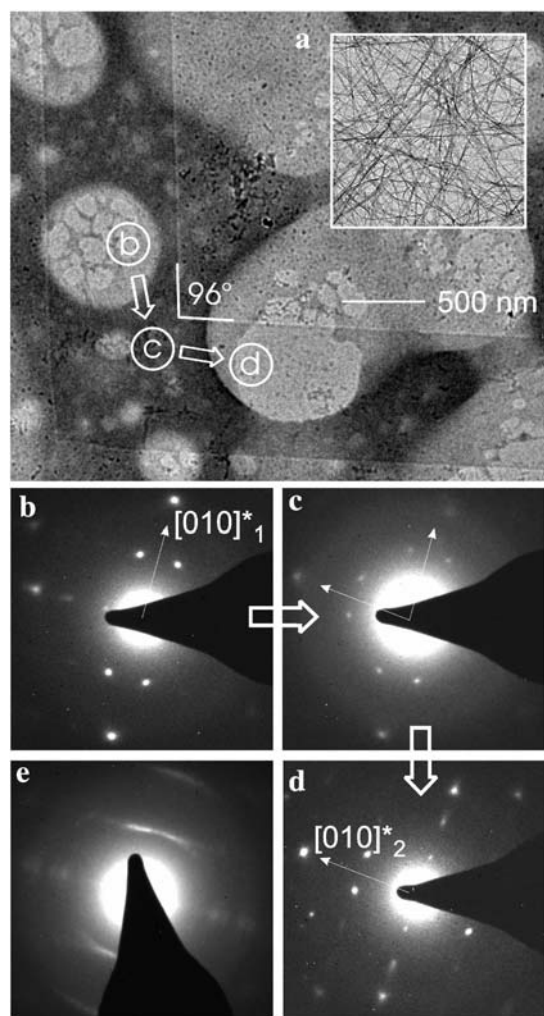
**FIGURE 1** a Scanning Force Microscopy image of boomerang-shaped  $\text{VO}_x$  nanobelts. The height-scale of the image is 10 nm. b, c Averaged cross sections of two nanobelts, as indicated in the SFM-image with a dashed line (b) and a dotted line (c), respectively

the fact that the two arms within each belt are of almost identical length, suggest that the crystal growth starts at the center of the kink, from where it simultaneously progresses along the two arm directions.

The nanobelts reveal a reproducible, uniform thickness of  $\sim 2.8$  nm, as exemplified by the cross-sectional profiles in Fig. 1b,c, which were obtained from two different objects. This regularity indicates a layered structure of the material [14–16]. In order to investigate the atomic structure of the nanobelts in detail, a combined study using Transmission Electron Microscopy (TEM) and Selected Area Electron Diffraction (SAED) has been performed. Figure 2a shows the TEM image of part of an isolated nanobelt deposited on a polymer (Formvar) support. The sharp Bragg intensities in the SAED patterns (Fig. 2b,d) recorded on its two separate arms (marked by “b” and “d” respectively in Fig. 2a) reflect a high crystalline order of the belts.

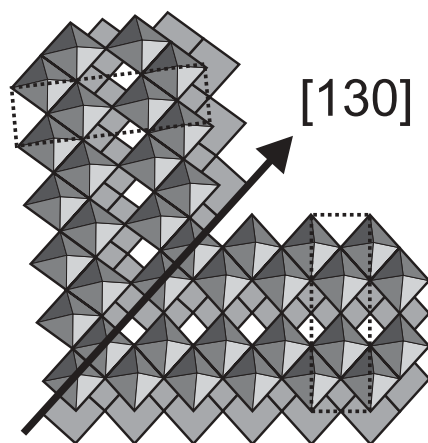
For the sake of comparison, diffraction patterns were also acquired from  $\text{V}_2\text{O}_5$  nanofibers (see TEM image in the inset of Fig. 2a), prepared via an ion-exchanger route from ammonium-metavanadate in aqueous solution at room temperature [13]. These fibers have a width of 10 nm and are 1.5 nm thick, while their length can reach up to  $20 \mu\text{m}$  depending on the ageing condition of the solution [13]. The diffraction pattern of a nearly isolated  $\text{V}_2\text{O}_5$  nanofiber, displayed in Fig. 2e, resembles that of the nanobelts, except that the spots are considerably broader compared to the former case. Both materials yield [001]-SAED patterns, which agree well with a corresponding simulation performed on the basis of a  $\text{V}_2\text{O}_5 \cdot n\text{H}_2\text{O}$  xerogel model [14]. In the following, this pattern will be used for indexation. It is noticed that the lattice parameters of the L-shaped  $\text{VO}_x$  nanobelts ( $a = 12.55 \text{ \AA}$ ,  $b = 3.76 \text{ \AA}$ ) are significantly larger than those reported for  $\text{V}_2\text{O}_5 \cdot n\text{H}_2\text{O}$  ( $a = 11.722(3) \text{ \AA}$ ,  $b = 3.570(3) \text{ \AA}$ ) [14].

To unravel the origin of the peculiar L-shape, the local SAED patterns obtained at different positions within a single  $\text{VO}_x$  nanobelt were examined. The diffraction pattern of Fig. 2c has been obtained from the “center” (kink position) of the belt (marked by



**FIGURE 2** a TEM-image of a boomerang-shaped  $\text{VO}_x$  nanobelt. Inset: TEM-image of a network sample of  $\text{V}_2\text{O}_5$  nanofiber with the same scale as in a. b–d Series of SAED diffraction patterns along the “L”, the position are marked in a. e SAED pattern of a nearly isolated  $\text{V}_2\text{O}_5$  nanofiber. The orientation has been adjusted to match that of b

“c” in Fig. 2a). Comparison with the diffraction patterns of the two arms (Fig. 2b,d) clearly shows that the central pattern corresponds to a superposition of the crystal orientations of the two arms. The L-shape of the VO<sub>x</sub> nanocrystals is consequently attributed to the presence of twins. The occurrence of twins is well-documented for bulk crystals formed under natural conditions, such as the Japanese twin of quartz [17]. Since the twin domains do not superimpose in [001] orientation of real space, double diffraction is not apparent in the SAED patterns. It is evident from Fig. 2c that both domains contribute separate reflections. Accordingly the twinning can be described as twinning by non-merohedry [18]. From the superimposed diffraction pattern (Fig. 2c), it is possible to identify the  $[310]_{1,2}^*$  direction as the axis of the twin. The angle between  $[010]_{1,2}^*$  directions of the single domains is found to be 84°, in accordance with the twinning axis. The small deviation from rectangular twinning is also known from the bulk of many other crystalline compounds, e.g. in TbVO<sub>4</sub> [19] and V<sub>2</sub>O<sub>5</sub> [12]. Significant is the correspondence of the angle of 84° between  $[010]_{1,2}^*$  in reciprocal space obtained in the superimposed diffraction pattern of a twinned region (Fig. 2c) with the angle of 96° in real space, as observed in the morphology (compare Figs. 1a, 2a). A precise determination of the twin element in real space would require high-resolution TEM images, which could not be obtained due to the rather small, homogeneous thickness of the VO<sub>x</sub> crystals. Nevertheless, a reasonable model of the real structure at the twin boundary can be developed by considering the geometry of the twinning as well as the good



**FIGURE 3** Model of the twin boundary region. The VO<sub>5</sub> pyramids show the upper layer, while the rhombi below reflect the lower layer with the apex of the pyramids pointing downwards. The arrow indicates the twinning-direction, while the dashed boxes reflect the unit cells of the two domains. The model resembles the observed angle of 96°

agreement between the diffraction pattern with simulations based on literature data [14–16]. Within this model (Fig. 3), the crystal consists of stacks of double layers made of joint VO<sub>5</sub>-pyramids, as proposed by Petkov et al. [14]. The twinning occurs along the [130] direction, which leads to the observed real space angle of ~96°. Noteworthy, the slight distortion that occurs at the twin boundary was also proposed for bulk V<sub>2</sub>O<sub>5</sub> [12].

#### 4 Summary

In summary, boomerang-shaped VO<sub>x</sub> nanobelts have been obtained by a hydrothermal process and characterized for the first time. Crystal twinning has been identified as the origin of their remarkable morphology. The observation of twinning within iso-

lated vanadium oxide nanocrystals contributes to the wealth of structures found for this material, and may be of importance for its application in catalysis or batteries.

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