Controlled Synthesis of V-shaped SnO2 Nanorods

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This report details the preparation of V-shaped SnO2 nanorods with an angle of 112.1° between the arms. The nanorods were produced by heating 1,10 phenanthroline (phen)-capped Sn nanoparticles (2−5 nm) in a NaCl flux. The use of both phen and NaCl flux were indispensable in forming long V-shaped structures. XRD, SEM, TEM, and HRTEM characterizations of the nanorods confirmed that the rods were crystalline SnO2 with a twin structure (twin plane of (101) and twin direction of [10$\bar{1}$]) at the V-junction. The diameters of the nanorods were nearly monodispersed with mean values of 48.4 and 13.2 nm depending on the synthesis conditions.

1. Introduction

While semiconductor crystals can be obtained in the nanometer length scale and in various geometries,[1,2] the one-dimensional (1D) variants warrant special attention because the anisotropy in quantum confinement potentials can be used to produce unusual optical, magnetic, and electronic properties.[3,4] SnO2, an inexpensive large band-gap (3.6 eV) semiconductor, is currently used for a wide range of applications, most notably catalysis, gas sensing, and electrochemical- or photoelectrochemical-based energy conversions.[5−10] The material performance is expected to increase with the decrease in length scale because most applications are based on surface or interfacial phenomena. As the properties of nanoscale materials are strongly dependent on their size and shape, it is extremely desirable to be able to exercise size and morphology control in any synthesis.[1,2,11] Evaporation of bulk Sn, SnO, or SnO2 at 1000−1350 °C in N2 has been used to produce ultralong SnO2 nanobelts or nanowires[7,8] suitable for NO2, CO, and O2 sensing in high-performance miniaturized gas sensors.[9,10] The chemical synthesis of SnO2 nanorods was only reported recently, using the heat treatment of microemulsion-derived precursors.[5,6] The SnO2 nanorods or nanobelts in these reports were either long with polydisperse diameters[5,7,8] or short (∼ 15−200 nm) with more monodisperse diameters (∼ 8−15 nm).[6]

A few reports have appeared recently on building complex structures from nanorods: the multiarmed CdS and MnS,[12,13] the arrow-, teardrop-, and tetrapod-shaped CdSe,[14] and the fork-shaped α-MoO3.[15] It is believed that these complex nanorod-derived structures could offer new opportunities in tailoring the properties of discrete 1D nanostructures and in 3D organization of nanostructured materials.[12−15] The V-shaped nanowires are of particular interest because the sudden break in lattice periodicity at the junction offers good lateral confinement, and enhanced excitonic optical response has been demonstrated by a number of GaAs quantum wires showing high photoluminescence.[16−17]
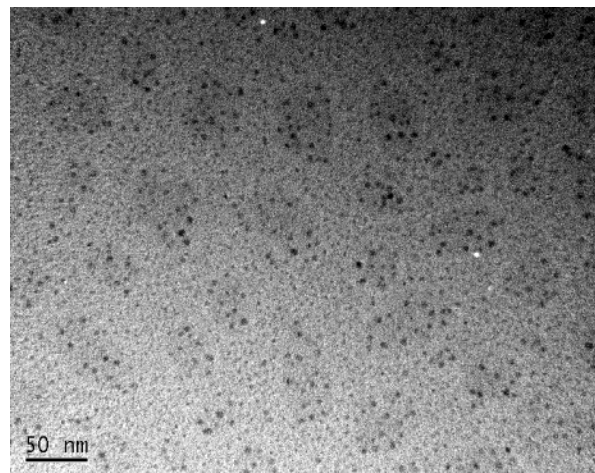
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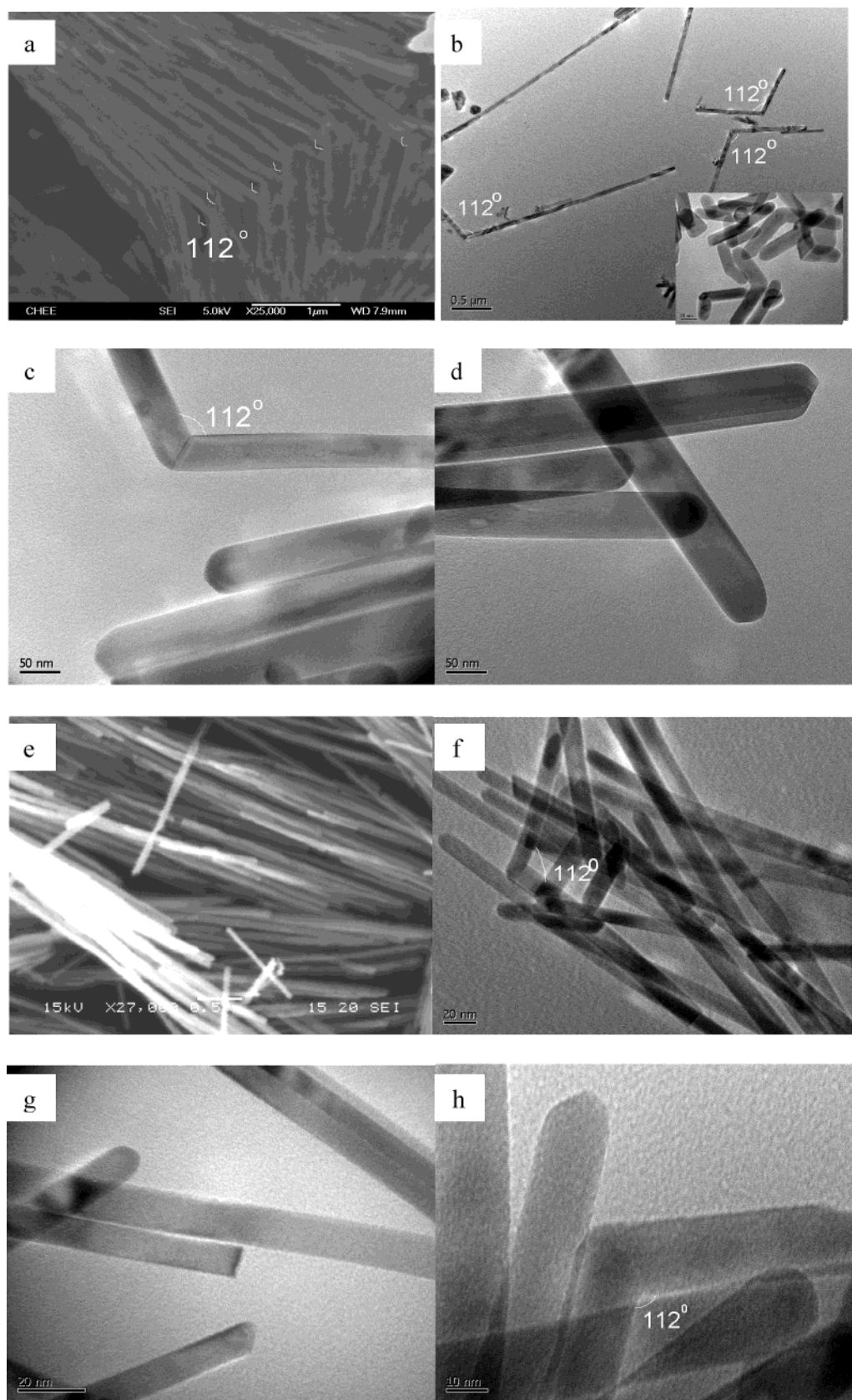‡ Singapore-MIT Alliance, NUS.

Figure 1. TEM image of 2−5 nm phen-stabilized Sn nanoparticles from the NaBH4 reduction of (phen)SnCl4 aqueous solution. (phen = 1,10-phenanthroline).

In this work, we report, for the first time, a chemical synthesis method for producing V-shaped (112.1°) SnO2 nanorods with a twin structure at the V-junction and a very large aspect ratio (100−1000) for the arms. The diameters of the rods can be controlled to be around either 48 or 13 nm. The V-shaped SnO2 nanorods are nearly diameter-monodispersed without any size- and shape-sorting. These intriguing geometrical constructs may be of interest for the fabrication of complex nanodevices.

2. Experimental Methods

To a suspension of 0.1 g 1,10-phenanthroline (phen, Nacalai Tesque) in 10 mL of water (phen: SnCl4 =1:1) was added 10 mL of 0.05 M SnCl4 (Riedel-de Haen, 99%). A clear solution was formed after a few minutes of stirring, indicating the formation of the coordination compound (phen)SnCl4. Then, 20 mL of 0.1 M NaBH4 (Fluka) aqueous solution was introduced dropwise (NaBH4:(phen)SnCl4 = 4:1). The mixture turned to pale yellow, indicating the formation of a sol of phen-capped Sn nanoparticles. The hydrosol was further stirred for 2 h before the Sn nanoparticles were spun down in an ultracentrifuge (15 000 rpm for 1 h).

Figure 2. (a) FE-SEM and (b, c, and d) TEM images of 48-nm diameter V-shaped SnO$_2$ nanorods; (e) SEM and (f, g, and h) TEM images of 13-nm V-shaped SnO$_2$ nanorods. The inset in (b) is the TEM image of prematurely grown SnO$_2$ nanorods after 5 min of molten salt analysis.

In a molar ratio of ∼1:10, 0.1 g phen-capped Sn nanoparticles were mixed with 0.5 g NaCl (Merck), ground into a fine powder, and heated at 850 °C for 45 min in a furnace. The melt was then naturally cooled to room temperature. The solidified mass

was washed several times with water and methanol (Merck), and dried at 130 °C for 3 h.

The obtained SnO$_2$ nanorods were characterized by scanning electron microscopy (SEM, JEOL JSM-5600LV) or field
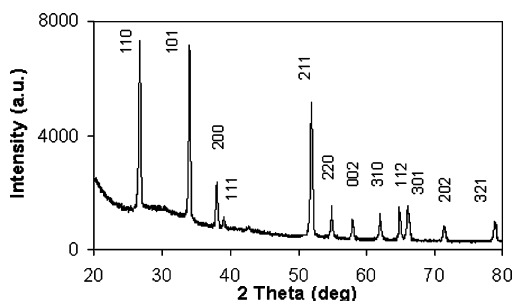
Figure 3. X-ray diffraction (XRD) patterns of 48-nm V-shaped SnO_2 nanorods. All peaks can be indexed to tetragonal SnO_2 with a rutile structure (JCPDS 21−1250).

emission scanning electron microscopy (FE-SEM, JEOL JSM-6700F), transmission electron microscopy, selected area electron diffraction (TEM/SAED, JEOL JEM-2010F), HRTEM (Philips FEG-CM200 and FEG-CM300), and powder X-ray diffraction (XRD, Siemens D6000).

3. Results and Discussion

The $NaBH_4$ reduction of the phen−$SnCl_4$ complex was first used to obtain the starting material for the nanorods: 1,10-phenanthroline (phen)-capped Sn nanoparticles (2−5 nm). Phen was used here as a chelating agent for $SnCl_4$ and as a surface passivating agent for the nascent Sn nanoparticles formed upon reduction. The presence of phen on the Sn surface was confirmed by X-ray photoelectron spectroscopy (XPS), UV−visible spectroscopy, and Fourier Transform Infrared (FTIR) spectroscopy.[18] The phen-capped Sn nanoparticles were also nearly monodispersed without any observable agglomeration
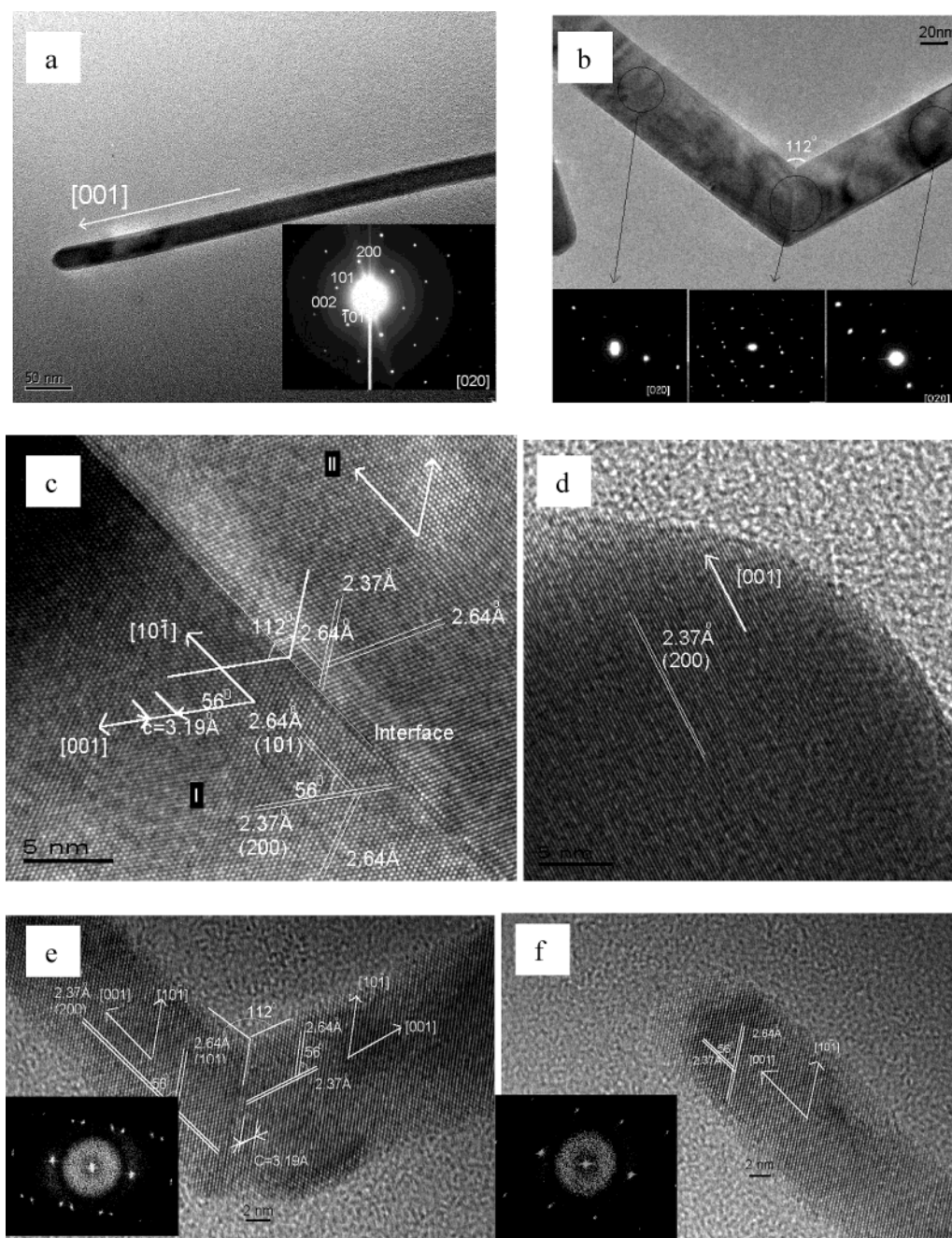

Figure 4. (a) TEM image of a free-standing SnO_2 nanorod with a SAED inset of the tip, (b) TEM image of the V-junction of a SnO_2 nanorod with insets of SAED patterns showing the junction and the arms. HRTEM images of (c) the V-junction of a 48-nm V-shaped SnO_2 nanorod, (d) the tip of a 48-nm V-shaped SnO_2 nanorod, (e) the V-junction of a 13-nm V-shaped SnO_2 nanorod, and (f) the tip of a 13-nm V-shaped SnO_2 nanorod.

both inside and outside of the phen domains, as shown by the TEM image of Figure 1.

The scanning electron microscope (SEM) image in Figure 2a shows a large number of rodlike structures several micrometers to tens of micrometers in length in the final product. There was also an abundance of bent nanorods with relatively long straight sections. The transmission electron microscope (TEM) images in Figures 2b−d show several micrometer-long free-standing rods in isolation. The SnO_2 rods were about 48 nm in diameter, and most of them (85%) were V-shaped with an angle of about 112.1° between the two diverging arms. The surface of the nanorods and the junction between the two arms were both very smooth. The diameters of the rods were very uniform, showing a mean value of 48.4 nm and a standard deviation of 5.3 nm from counting the samples in Figure 2. The aspect ratio was fairly high, typically in the range of 100−1000. Powder X-ray diffraction (PXRD) in Figure 3 reveals that the SnO_2 nanorods were highly crystalline. All the diffraction peaks in the PXRD pattern could be indexed to a tetragonal rutile-structure with $a = 4.738$ Å and $c = 3.188$ Å (JCPDS 21-1250). The product obtained with only 5 min of heating had smaller diameters and shorter arms, but the V-shape architecture had already been established, as shown by the inset in Figure 2b. The rods apparently grew from the junction toward the tips of the divergent arms and the V-junction was not formed by merging two grown nanorods at the point of intersection.

If phen was completely washed off from the Sn nanoparticles, and the latter were mixed with NaCl and heated, no rodlike products were obtained. Phen was therefore contributing as a structure-directing agent in the growth process (Although phen is unstable at temperatures in excess of 500 °C, thermogravimetric analysis showed that some phen remained on the Sn surface for a period of time in the high-temperature NaCl flux). The shape control of transition metal nanocrystals has been reported previously, and was accomplished by selective area adsorption of stabilizing agents on the nanoparticle surface.[19,20] When extraneous phen (0.1 g) was ground with the mixture of phen-capped Sn and NaCl, SEM and TEM images in Figures 2e−h show that the resulting V-shaped SnO_2 nanorods had smaller diameters (mean $=13.2$ nm, $\sigma = 3.6$ nm). These observations underline the importance of phen in this preparation method. Organic ligands are known to inhibit particle nucleation and growth by presenting a strong steric hindrance to aggregation,[21] thereby indirectly promoting the formation of nanorods with narrow size and shape distribution.[22]

The TEM image in Figure 4a, with the inset of a selected area electron diffraction (SAED) pattern of the tip of a free-standing SnO_2 nanorod, shows that the tip was a nearly perfect single crystal. However, the SAED pattern of the junction in Figure 4b shows an overlap of two series of spots, a result of intersecting two arms of different orientations. The HRTEM images were processed by fast Fourier transform (FFT) to examine the V-shaped junctions of the 48- and 13-nm SnO_2 nanorods in detail (Figures 4c−f). From such analyses, it can be concluded that the V-shaped rods had a single twin structure at the junction. The twin plane was (101) and the twin direction was [10$\bar{1}$]. The twin boundary was very coherent, and the two arms were nearly symmetric with an angle of inclination of 112.1° between them. The (200) and (101) planes could be identified in each of the arms. The experimentally measured value between these planes (56.1°) agrees with the calculated value. The distance between two neighboring atoms in the (200) plane was equal to c (3.19 Å). It is clear that the preferential
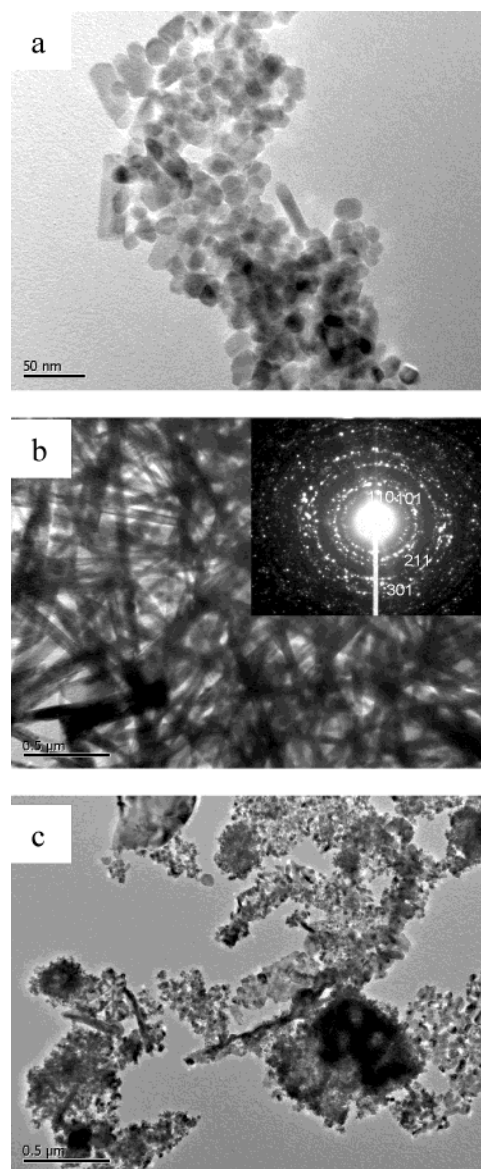
Figure 5. TEM images of products (a) without using a NaCl flux in the heat treatment, (b) agglomerated SnO_2 nanorods obtained by using an excess of NaCl flux (the inset shows the corresponding SAED pattern), and (c) from commercial Sn particles (100 nm, Aldrich) without a uniform phen coating.

growth direction for the rods was the [001] direction (*c*-axis) in the (200) plane.

Using phen-capped Sn nanoparticles without NaCl as a flux could only produce a few nanorods, as shown in the TEM image of Figure 5a. While phen was perhaps the primary structure-directing agent, the NaCl flux was equally indispensable in forming long V-shaped nanorods. These findings are consistent with the oft-cited salt effect in molten salt synthesis.[5,23,24] The presence of a flux can significantly reduce the viscosity of the melt, thereby increasing the mobility of the constituents. The interfacial energies between the constituents and the salt are minimized by adopting a particular growth direction. It was found experimentally that a 10:1 mole ratio of NaCl to Sn/phen was adequate for growing well-defined SnO_2 nanorods. If excessive NaCl (1.5 g) was used, the product in the TEM image of Figure 5b showed heavy aggregation of many nanorods.

The preparative procedure was repeated using commercial Sn nanoparticles (100 nm, Aldrich), phen, and NaCl. Only a few nanorods were formed as shown in the TEM image of

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Figure 5c, and the majority of the product was aggregates of SnO$_2$ particles. Therefore, nanorod formation was affected by the properties of Sn seeds, such as particle size and the extent of phen coverage. In this work, Sn was prepared from the in situ reduction of the (phen)SnCl$_4$ complex. The Sn nanoparticles so obtained were nearly monodispersed, with a particle size in the range of 2−5 nm and a uniform coating of phen on their surface. For the bigger commercial Sn particles (100 nm) where phen was only in contact with the particles through mechanical grinding, the effectiveness of phen as a structure-directing agent was greatly reduced. Nanorods that are formed from monodispersed particles have been known to display a more uniform morphology and aspect ratio.[25] The growth of Sn nanoparticles to nanorods in this work is believed to be promoted by the low-melting (232 °C) Sn nanoparticles acting as the self-catalyst in a vapor−liquid−solid (VLS) mechanism.[26] This was verified experimentally by the detection of a few isolated nanoparticles appearing near the tips of the rods in Figure 2b.[27] Current views consider the multiarmed nanorod structures to originate from the directed growth from a core area established early in the synthesis.[12,13] The formation of the core from individual nanoparticles is not known in detail. The experimental observation of V-junction formation as early as 5 min into the reaction basically supports the current views. The preferred growth directions are affected by the presence of the chelating agent (phen) and the molten salt (NaCl). A very long and highly symmetric V-shape structure with nearly unvarying rod diameter can then be formed after a sufficiently long growth time.

4. Conclusions

A chemical method for producing V-shaped SnO$_2$ nanorods with novel twin structures and large aspect ratios has been developed. The method involves the heating of phenathroline-capped Sn nanoparticles in a NaCl flux. Rods of different diameters (48.4 and 13.2 nm) could be obtained by varying the amount of phen present. This method should be explored further for the preparation of other semiconductor crystals requiring special morphology and diameter control.

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