One-dimensional twisted and tubular structures of zinc oxide by semiconductor-catalyzed vapor–liquid–solid synthesis

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Abstract
The exploration of unconventional catalysts for the vapor–liquid–solid synthesis of one-dimensional materials promises to yield new morphologies and functionality. Here, we show, for the model ZnO system, that unusual nanostructures can be produced via a semiconductor (Ge) catalyst. As well as the usual straight nanowires, we describe two other distinct morphologies: twisted nanowires and twisted nanotubes. The twisted nanotubes show large hollow cores and surprisingly high twisting rates, up to 9°/μm, that cannot be easily explained through the Eshelby twist model. A combination of ex situ and in situ transmission electron microscopy measurements suggest that the hollow core results from a competition between growth and etching at the Ge-ZnO interface during synthesis. The twisting rate is consistent with a softening of elastic rigidity. These results indicate that the use of unconventional, nonmetallic catalysts provides opportunities to synthesize unusual oxide nanostructures with potentially useful properties.

Supplementary material for this article is available online

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(Some figures may appear in colour only in the online journal)

1. Introduction

One-dimensional (1D) metal oxide nanostructures with several different morphologies have been synthesized via the vapor–liquid–solid (VLS) mechanism using metal catalysts [1, 2]. Gold (Au) is the most common choice. However, the use of a metal as the catalyst presents two problems for metal oxide nanostructure growth. Metal catalysts, especially Au, are known to dope the nanostructure or diffuse into it during growth [3, 4], especially at high temperatures. This may create mid-gap non-radiative levels and hence degrade important physical properties. Other catalyst metals may have a strong interaction with metals that are of most interest in complex oxides. This may hinder growth since the synthesis process requires a catalyst that can act as a reservoir for all the metals involved. These issues have led to an active search for alternative catalysts for the VLS synthesis of oxide nanowires (NWs) [5]. Recent studies demonstrate that a semiconductor, germanium (Ge), can act as an effective catalyst for growth of zinc oxide (ZnO) NWs [6, 7]. Ge is an intrinsically interesting catalyst for oxide NWs because it is easily oxidized to form volatile species such as GeO₂, a process that we might expect would keep the liquid surface open to accommodate the continuously arriving metal precursors. The use of Ge
catalysts may therefore broaden the synthesis space and the opportunities to create new types of metal oxide 1D nanostructures. Compared to conventional metal catalysts such as Au, Ge catalysts are unusual in showing an extremely large contact angle at the VLS interface [6, 7]. The reason for this effect and its influence on growth is not known.

Here, we observe unusual structures in a metal oxide and examine how a Ge catalyst facilitates their formation. We are particularly interested in synthesis of nanostructures that are hollow and/or twisted due to their intriguing growth modes [8, 9] and properties [10–12]. Hollow nanotubes (NTs) have been synthesized in polycrystalline form, for example, by using sacrificial templates [13] or by exploiting the Kirkendall effect [14]. Single crystal NTs, especially those with a periodic spiral structure, are mostly found in layered materials [9], including chiral carbon and MoS2. Tubular and twisted structures in non-layered materials often form in the presence of an axial screw dislocation [15]. The strain field created around the disrupted region causes the crystal to twist around its axis, a phenomenon known as Eshelby twist [16]. The presence of the dislocation may also drive another effect, the Frank open-core mechanism [17, 18], in which a hollow core is energetically favorable whenever eliminating the highly strained material at the dislocation core overcomes the energetic cost of introducing new inner surfaces. The coexistence of both mechanisms is known to create NTs that are both hollow and twisted [19] with a twisting rate of below 2° μm⁻¹ [18].

We find that Ge catalysts show complex behavior in which growth and etching processes take place simultaneously during the formation of ZnO nanostructures. The resulting nanostructures show a range of different morphologies with unexpected features. These include solid straight and twisted NWs, hollow structures with cores that are much larger than expected from the hollow-pipe mechanism, and hollow twisted structures with much higher twisting rates than can be explained by Eshelby twist—even though Eshelby’s model does account for the twisting rate in the twisted solid NWs. Using a combination of ex situ and in situ electron microscopy and spectroscopy to measure structural and compositional parameters and the effect of growth conditions, we propose how features of the Ge-catalyzed growth mechanism may explain both the large cores and the high twisting rates in the NTs. Our model is based on the idea that etching, enhanced at defective regions such as screw dislocation cores, is responsible for the large hollow cores seen in twisted NTs, and that catalyst diffusion under the growth conditions can explain the NT twisting anomaly via changes in mechanical properties. We suggest that, more generally, nanostructure formation processes in which there is a competition between growth and catalyst-induced etching may be useful for generating a wider range of structures and properties, and may lead to opportunities that are unavailable from VLS growth using conventional metal catalysts. The results emphasize the importance of exploring new catalysts as a strategy to gain more precise control over oxide nanowire growth.

2. Methods

2.1. Materials synthesis

We used thermal vapor transport to grow the Ge-catalyzed ZnO materials, with zinc oxide, black carbon and germanium oxide powders as precursors (10:10:1 molar ratio). The molar ratio of 1 GeO2:10 ZnO was chosen to ensure that the dominant vapor species is ZnO with GeO2 only contributing to forming the catalysts [6]. Other ratios such as 2 GeO2:10 ZnO and 4 GeO2:10 ZnO produced similar results. The mixed precursors (0.5 gram) were put at the central of a horizontal tube furnace, which was set at 975 °C–1000 °C. The growing substrates, which included silicon wafers, silicon nitride coated wafers and silicon nitride TEM grids, were put downstream, 10–12 cm away from the precursors. The estimated temperature at the substrates spans the range 500 °C–650 °C. Each growth is typically 15–30 min long, under a flow of 50–65 sccm N2/Ar as the carrier gas. After growth finishes, the furnace cap is opened and the carrier gas flow is changed to 200 sccm to facilitate quick cooling. We do not observe any significant difference in material morphologies, distribution and yield when using different substrates.

2.2. Ex situ electron microscopy characterization

SEM images and SEM-EDS spectroscopic data were obtained for nanostructures without removing them from the growth substrate, using a FEI FIB/SEM operated at 5–20 kV. TEM samples were prepared on copper grids by either dry or wet transfer. For dry transfer, copper grids were gently dragged over the growth substrates to collect the grown material. For wet transfer, the growth substrates were sonicated briefly in iso-propanol solution and the solution was drop-cast onto copper grids. Imaging and selected area diffraction were carried out on a JEOL 2010F TEM operated at 200 keV. Diffraction patterns of ZnO for different zone axes were simulated using Crystal Maker software. We note that perhaps because of their large sizes, Ge catalysts were easily broken off during the transfer processes. As a result, many TEM images in this study show only ZnO stems.

2.3. In situ environmental TEM (ETEM)

Ge-catalyzed ZnO nanostructures were grown directly onto TEM grids in which SiN membranes were supported on Si. The grids have multiple opened windows in the SiN where ZnO can grow away from the substrate. This configuration permitted observation of Ge–ZnO interactions in situ using the aberration-corrected Thermo Fisher Titan 80–300 ETEM [20] at Brookhaven National Laboratory, operated at 300 keV. Samples were heated using a Gatan double tilt heating holder and digermane (20% in He) was flowed into the sample area using a manual leak valve to a total pressure of 1–2 × 10⁻⁵ Torr. Note that the ETEM base pressure is 10⁻⁶ Torr. The electron dose rate (10⁻¹⁰–10⁻¹² electron nm⁻² s⁻¹) was monitored to assess its effect on the phenomena observed. The electron dose for data presented in figure 4 are specified in the corresponding movies in the supplementary data.
2.4. STEM-cathodoluminescence

STEM-CL images and spectra were collected in a JEOL 2011 TEM connected to a Gatan MonoCL3 + CL system with photomultiplier tube detector. The setup allows the collection of both CL maps in panchromatic/monochromatic modes and point spectra. Panchromatic CL map collects the light emission with a full range of wavelengths.

3. Results and discussion

3.1. Morphologies of Ge-catalyzed ZnO nanomaterials

Ge-catalyzed ZnO nanostructures were synthesized by a vapor transport method using zinc oxide, carbon black, and germanium oxide powders as precursors [6], as detailed in the Methods. A significant feature of the growth process is that Ge must be supplied continuously for growth to be sustained, as has been noted previously.

Figure 1 displays an overview of the range of ZnO nanostructures that result from this synthesis. We observed three distinct morphologies: straight NWs, twisted NWs, and twisted NTs. Unless broken, each morphology exhibits a large, approximately spherical catalyst particle at the tip. Energy dispersive spectroscopy (figure S1, supplementary data is available online at stacks.iop.org/NANO/32/075603/mmedia) confirms that all morphologies are composed of ZnO with catalyst particles of Ge. TEM images and diffraction patterns, shown for a representative NT in figure 1(d), reveal that both NWs and NTs have single crystalline wurtzite structure growing in the [0001] (c-axis) direction. Diameters range from 100 to 2000 nm and lengths can be up to 50 μm after 30 min of growth.

The Ge catalysts have a diameter between 1 and 8 μm, typically 4 times the ZnO diameter for all morphologies [7] (figures 1(e)–(f)). While the physical mechanism for this large ratio is still unclear, we speculate that it is determined by the fluxes of the materials required for growth. The catalyst surface area [21] (as well as the pressure and sticking probabilities) determine the arrival rate of the vapor-phase species—in this case Zn, Ge and O—while the NW cross-sectional area and catalyst area influence their rate of removal by incorporation into the NW or back into the vapor phase. The need for flux balance during steady-state growth may therefore fix the geometrical relationship between catalyst and nanowire. The growth rate is 6–20 nm s⁻¹, which is comparable to previous reports using Ge catalyst [6, 7] (table S1, supplementary data). This is 5–10 times faster than Au-catalyzed ZnO NWs synthesized under similar conditions [5, 22]. The high growth rate may be related to the large surface area of the Ge catalysts, which, all other factors being equal, would increase the arrival rate of Zn atoms from the vapor phase and therefore contribute to faster NW formation. The percentage of structures with each morphology depends on the growth conditions (figure S3, supplementary data). At the cooler end of the substrate (500 °C–575 °C), solid NWs dominate (>80%) with twisted NWs and NTs being much less common (5%–10% each). In contrast,
twisted NTs are more frequently observed (30%) at the hotter end of the substrate (575 °C–650 °C). The observation of hollow and twisted structures (figures 1(b), (c)) suggests that axial screw dislocations are present [18, 23–26]. Indeed, diffraction-contrast TEM measurements confirm the existence of dislocations (figure S2, supplementary data).

Although these nanostructures appear to broadly follow the VLS growth mechanism, the diversity of hollow and twisted structures indicate that the growth may include aspects that are not part of the general VLS model [6, 7, 22, 27]. We therefore analyze in detail the twisted NTs and NWs to gain additional insight into their formation process.

### 3.2. Motif 1: hollow cores

The cleaved ends of NTs show that these structures have a range of internal diameters, as displayed in figures 2(a) and (b). Furthermore, we observe fully or partially hollow structures, and occasional structures that include a Ge particle within the cavity (figure S4, supplementary data). Figures 2(c), (d) show that there is no strong relationship between the inner \(r\) and outer \(R\) diameters, other than the obvious requirement that \(r < R\). Values of \(r/R\) range from 0.34 to 0.75 with a mean of 0.55.

These hollow structures are also twisted, as will be discussed in the following section. The presence of hollow cores in these NTs, especially given their twist, is immediately reminiscent of the open channels that are often associated with screw dislocations [18]. Such open cores are commonly explained by Frank’s elastic open-core mechanism [17, 18]. The model states that, in order to relieve the strain energy at the dislocated region, the disrupted core is removed at the penalty of introducing new surfaces (the surfaces of the hollow cavity). Minimization of energy under these circumstances leads to a 1D hollow structure with inner diameter given by equation (1):

\[
r_{\text{Frank}} = \left( \frac{\mu}{8\pi\gamma} \right) b^2,
\]

where \(b\) is the magnitude of the Burgers vector, \(\mu\) is the shear modulus, and \(\gamma\) is the surface energy. For ZnO with \(b_{\text{ZnO,NT}} \approx 2.0\) nm [18], \(\mu_{\text{ZnO}} = 51.0\) GPa [28], \(\gamma_{\text{ZnO}} = 0.31\) J.m\(^{-2}\) [18], the corresponding Frank’s hollow radius is \(r_{\text{Frank}} = 26\) nm. This is smaller than any of the inner radii observed for our NTs; figure 2(c) shows \(r_{\text{NT}}\) in the range

![Figure 2. Hollow structures. (a), (b) SEM images of NTs with thicker and thinner walls, respectively. (c) Relationship between NT inner and outer diameters \(r, R\). The red line indicates a linear fit. The NTs shown in figures 1(c), 2(a) and (b) are marked. (d) Distribution of ratios between inner and outer radii. A peak around 0.5 is visible but we note that small \(r/R\) may be less visible in images and large \(r/R\) may result in unstable NTs (see figure S4, supplementary data).](image-url)
50–500 nm, which is 2–6 times larger than predicted by Frank’s model. We will discuss the implications of these anomalously large cores in the following sections.

### 3.3. Motif 2: axial twisting

The second striking feature of these Ge-catalyzed ZnO nanostructures is the twisting seen in NTs and some of the NWs. TEM provides a direct means of measuring the twisting rate in both NTs and NWs [18, 23–25]. As shown in figures 3(a), (b), selected-area diffraction patterns are collected at different locations along a nanostructure and matched to simulations with the orientation of the crystal at that location. The presence of different and alternating crystallographic orientations in the nanostructure is proof of its lographic orientation. The presence of different and alternating crystallographic orientations in the nanostructure is proof of its lographic orientation. The presence of different and alternating crystallographic orientations in the nanostructure is proof of its logographic orientation in the nanostructure is proof of its lographic orientation. The presence of different and alternating crystallographic orientations in the nanostructure is proof of its lographic orientation. The presence of different and alternating crystallographic orientations in the nanostructure is proof of its logographic orientation. The presence of different and alternating crystallographic orientations in the nanostructure is proof of its lographic orientation. The presence of different and alternating crystallographic orientations in the nanostructure is proof of its lographic orientation. The presence of different and alternating crystallographic orientations in the nanostructure is proof of its lographic orientation. The presence of different and alternating crystallographic orientations in the nanostructure is proof of its lographic orientation. The presence of different and alternating crystallographic orientations in the nanostructure is proof of its lographic orientation.

![Figure 3. 1D torsional structures of ZnO. (a) Low magnification TEM bright field image of a twisted ZnO NT having R = 155 nm and r = 65 nm. Areas marked as 1, 3 and 5 in blue have the same crystallographic orientation, the [10] zone axis (ZA), while 2, 4, and 6 in red have [1-100] ZA, as determined from the selected-area diffraction patterns in (b). The corresponding simplified schematics are illustrated below. The crystal rotates by 30° between each area leading to a measured twisting rate of 8.7°μm⁻¹ [23, 24]. (Note that the TEM image in (a) is rotated 25° clockwise with respect to the patterns in (b).) The inset of figure 3(a) is a higher magnification TEM image of the NT showing defect contrast that is consistent with twisting. (c) Twisting rate (radian/μm) as a function of inverse cross sectional area 1/πR² for twisted NWs (blue dots) and twisted NTs (red squares) measured by TEM. The NT shown in figures 3(a) and (b) is marked by a dotted circle. The linear fit for twisted NWs is consistent with the Eshelby model and yields a Burgers vector of ρ_{Twisted-Wire} = 2.3 nm.](image)

For 1D materials having an axial screw dislocation, Eshelby proposed that a pathway to compensate the strain energy in the dislocation core is to twist the entire structure. In the framework of continuum elasticity, the Eshelby twist is equivalent to an application of a torque, \( T \), exerted at two ends of a solid wire with a length, \( L \), that results in a torsional moment \( M_{Eshelby} = TL \) [16]. The Eshelby induced moment leads to a twisting angle \( \alpha \) (per unit length) of:

\[
\alpha_{Wire} = \frac{M_{Eshelby}}{\mu_{Wire} J_{Wire}} = \frac{M_{Eshelby}}{\mu_{Wire} \pi R^2}
\]

where \( J_{Wire} \) is the polar moment of inertia of a solid wire, \( J_{Wire} = \frac{3}{2} R^4 \), and \( \mu_{Wire} \) is the modulus of rigidity (shear modulus) of the wire. According to Eshelby [16], the torsion moment \( M_{Eshelby} \) is the result of energy balancing with the strain energy stored in the screw dislocation, therefore \( M_{Eshelby} = \frac{3}{2} \mu_{Wire} b R^2 \). Consequently, the Eshelby twisting rate \( \alpha_{Wire} \) (in units rad μm⁻¹) is:

\[
\alpha_{Wire} = \frac{\frac{3}{2} \mu_{Wire} b R^2}{\mu_{Wire} \pi R^2} = \frac{b}{\pi R^2}.
\]

We plot the twisting rate \( \alpha \) as a function of \( 1/\pi R^2 \) in figure 3(c). Twisted NWs exhibit twisting rates consistent with equation (3). The slope of the linear fit yields a Burgers vector \( \rho_{Twisted-Wire} = 2.3 \) nm, approximately 4 times the lattice parameter in the [0001] orientation (\( c_{ZnO} = 0.53 \) nm) and of the same order as that seen in other NW studies (0.5–3.0 nm) [18, 19, 23–26]. However, twisted NTs do not follow the same relationship. Even if we include the hollow core by including the appropriate geometric correction to the polar moment of inertia [18, 29], the best fitting line yields a much larger, and likely physically unrealistic, Burgers vector of...
than expected from Frank oxidation and evaporation via the formation of volatile species. Furthermore, the twisted NWs show twisting rates that are consistent with physically reasonable Burgers vectors. However, three features of the Ge-catalyzed ZnO nanostructure growth require additional explanation. First, Ge must be supplied continuously if growth is to be sustained. Second, the diameter of the core (and even its presence) can vary along the length of the NT and the dimensions of the hollow cores can be several times larger than expected from Frank’s micropipe model. There is also a striking difference in the degree of faceting of the inner and outer walls. Third, the NTs show twisting rates that are several times larger than expected from Eshelby twist, even accounting for the hollow geometry. These anomalies suggest that ZnO growth using Ge catalysts is more complex than the VLS process that has been described in the case of metal catalyst counterparts.

We believe that the mobility and activity of Ge during growth can explain all the anomalous features of growth. The requirement for continuously supplying Ge suggests that Ge atoms leave the catalyst during growth, either by surface diffusion or (perhaps more likely at high temperature) by oxidation and evaporation via the formation of volatile species, such as GeO₂. These dynamics, in addition to the presence of Ge within the NT cavity (figure S4, supplementary data), hint at potential interactions between Ge and ZnO at elevated temperatures.

In order to assess such interactions directly, we examine the behavior of Ge and ZnO NWs via in situ ETEM. Figure 4 shows a series of images obtained during heating under vacuum of NWs that were still attached to their catalysts. Visible changes started to occur as the temperature was raised to 650 °C. A gap appeared at the Ge–ZnO interface, as displayed in figure 4(a), suggesting an etching reaction between Ge and ZnO. Another example is shown in figure 4(b) where residue of the catalyst particle created a pit in the body of the NW. The etching process can also take place in the interior of a nanowire. Figure 4(c) (see also movie 1, supplementary data) shows a Ge-containing particle within a hollow core. As etching continues, the core diameter increases and the particle is eventually consumed.

To investigate the reaction under more controlled conditions, we examined the effect of adding Ge to the surface of the pre-grown ZnO NWs. This was achieved by flowing digermane (Ge₂H₆), which cracks to deposit Ge on the NW surface as shown in figure 4(d) (see also figure S6, supplementary data and Experimental section for the deposition procedure). In figure 4(d), we see that these Ge particles can also etch the NW to leave a porous structure with interconnected etched pockets. The etching process is a solid-state reaction and, as shown in figure 4(e), is anisotropic with faceted etched regions visible (see also movie 2, supplementary data). As the process continues, the particles are consumed and the etching reaction eventually stops.

Figures 4(f)–(g) are two examples of atomic-resolution TEM images displaying the Ge-assisted ZnO etching process (see also movie 3, supplementary data). The reaction removes material at the area of contact, leaving a trace of empty volume behind that shows reduced contrast in the TEM image. The inset of figure 4(g) shows that the Ge-containing particle remains crystalline during the etching process. The fastest etching rate is measured in the [0001] direction, with a rate of 5–7 nm s⁻¹ (table S1, supplementary data). Recall that the rate of Ge-catalyzed ZnO growth is between 6 and 20 nm s⁻¹, also along the [0001] orientation. Thus, the rates of etching and growth for the Ge-assisted ZnO system are of the same order and take place over the same temperature range (600°C–650°C).

3.5. Proposed mechanism of anomalous motifs

The in situ observations imply a coexistence of growth and etching reactions during the formation of ZnO nanostructures from Ge catalysts. We suggest, based in particular on movie 2 (supplementary data), that the formation of unexpectedly large hollow cores takes place as etching occurs along the core of a dislocation that is already present in a solid NW. Etching processes are well known to occur more rapidly at locations with imperfect bonding such as the strained cores of dislocations [30]. The reactive Ge may even move along a narrow cavity first created by Frank’s micropipe mechanism. The higher etch rate we observe along the [0001] direction, even in the absence of defects (table S1, supplementary data), may contribute to the anisotropy. Accelerated etching along the center of the NW, with slower etching in the radial direction, would result in a large central hollow core. The core facets may also result from anisotropy in the etching process.

The transport of Ge into the NT interior may also explain the anomalous twisting of the NTs. We first note that if the hollow cores are caused by etching, the Burgers vector of the screw dislocation is likely to be the same as that of the unetched NWs, i.e. 2.3 nm (figure 3(c)). Without any external forces, the only mechanical application on the NT is the Eshelby induced moment $M_{\text{Eshelby}}$, which is unchanged and stored within the twisted structure before the etching event. The resultant twisting rate for the NT is

$$\alpha_{\text{Tube}} = \frac{M_{\text{Eshelby}}}{\mu_{\text{Tube}} J_{\text{Tube}}} = \frac{1}{\mu_{\text{Tube}}} \frac{\mu_{\text{Wire}} b R^2}{2 (R^4 - r^4)}, \quad (4)$$

where $J_{\text{Tube}}$ is the polar moment of inertia of a hollow tube, $J_{\text{Tube}} = \frac{1}{2} (R^4 - r^4)$, and $\mu_{\text{Tube}}$ is the modulus of rigidity. Equation (4) can be rewritten as:

$$\alpha_{\text{Tube}} = b \left( \frac{\mu_{\text{Wire}}}{\mu_{\text{Tube}}} \right) \frac{R^2}{\pi (R^4 - r^4)} = b \frac{K_{\text{Rigidity}}}{K_{\text{Geometry}}}, \quad (5)$$

$b$ is the twisting rate for the NT.
where \( b = 2.3 \text{ nm} \) (figure 3(c)), \( K_{\text{Rigidity}} = \left( \frac{E_{\text{max}}}{E_{\text{ZnO}}} \right) \) is the ratio of moduli of rigidity (or shear moduli) of as-synthesized NWs and etch-induced NTs, and \( K_{\text{Geometry}} = \left( \frac{R^2}{\pi (R^2 - r^2)} \right) \) is the geometry corrected factor. \( K_{\text{Geometry}} \) is known, based on measured outer and inner radii of the NTs \((R \text{ and } r)\). Thus on the right hand side of equation (5), the only unknown variable is \( K_{\text{Rigidity}} \).

We plot the calculated \( \alpha_{\text{Tube}} \) as a function of \( K_{\text{Geometry}} \) for several values of \( K_{\text{Rigidity}} \) in figure 5. The measured twist angles of the NTs (the data shown in figure 3(c)) are most consistent with \( K_{\text{Rigidity}} = 3-4 \), and the possibility that the anomalous twisting results from a Ge-induced softening of the ZnO in NTs. The close proximity of Ge and ZnO in the NT core may facilitate the diffusion of Ge atoms into the ZnO (figure S4, supplementary data). It is known that high concentrations of Ge, up to 17 at\%, can be incorporated into ZnO without apparent phase separation [31]. Furthermore, several
4. Conclusion

We have shown the role of an unconventional, non-metal catalyst in controlling metal oxide morphologies, using Ge-catalyzed growth of 1D ZnO as a model system. The VLS synthesis results in a variety of intriguing structures including straight NWs, twisted NWs, and twisted NTs, as characterized by electron microscopy and spectroscopy. In situ TEM reveals a competition between etching and growth at the Ge-ZnO interface, including an enhanced etch rate along the defective core of the nanostructure. We propose that this mixed growth and etching process can explain the formation of hollow core NTs, and we speculate that the presence of Ge within these cores may explain the anomalously large twisting rate. We believe that the observed phenomenon, where there is a coexistence of material addition and removal at the interface, is quite general, and could be realized in other metal oxide nanosystems by an appropriate choice of catalysts.

The structure and properties of highly twisted structures, especially of non-layered materials, is fundamentally intriguing. For instance, the twisted NTs that exhibit inner facets and a smooth outer wall may serve as an ultraviolet lasing medium [39] with optical features distinct from those of ZnO NWs with hexagonal or rectangular cross-sections. The large built-in torsional strain of the twisted ZnO NWs and NTs may lead to enhanced piezoelectric properties [40]. In addition, the possibility exists to create a homojunction between a twisted NW and twisted NT by choice of synthesis parameters, perhaps yielding new properties and potentially useful applications.

These results underscore the critical importance of testing new catalysts for controlling 1D oxide nanostuctures via VLS, establish a foundation to explore various pathways for oxide NWs and NTs synthesis, and emphasize the importance of in situ measurements to investigate these structures.

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Conflict of interest

The authors declare no conflict of interest.

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