

Self-assembled nanoarchitectures of polar nanobelts/nanowires

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This article reviews the most recent progress in the synthesis of polar-surface dominated semiconducting and piezoelectric ZnO nanostructures: including nanosprings, nanohelices, nanorings, nanobows and nanodisks. These structures were formed by self-assembly of polar nanobelts/nanowires as driven by minimizing electrostatic energy owing to spontaneous polarization. The nanostructures could have novel applications in optoelectronics, sensors, transducers and resonators.

Since the discovery of oxide nanobelts of semiconducting oxides in 2001,¹ research in functional oxide based one-dimensional (1D) nanostructures has been rapidly expanded due to their unique and novel applications in optics, optoelectronics, catalysis and piezoelectricity.^{2,3} Semiconducting oxide nanobelts are a unique group of quasi-1D nanomaterials, which have a well-defined and uniform geometrical shape, a controlled crystallographic and surface structure, environmentally robust and stable surfaces, and a dislocation-free single-crystal volume. The belt-like morphology appears to be a unique and common structural characteristic for the family of semiconducting oxides with cations of different valence states and materials of distinct crystallographic structures. Field effect transistors⁴ and ultra-sensitive nano-size gas sensors,⁵ nanoresonators⁶ and nanocantilevers⁷

have been fabricated based on individual nanobelts. Thermal transport along the nanobelt has also been measured.⁸ Very recently, nanobelts, nanosprings⁹ and nanorings¹⁰ that exhibit piezoelectric properties have been synthesized, which could be candidates for nano-scale transducers, actuators and sensors.

The wurtzite structure is a unique family for functional materials, whose members include but are not limited to ZnO, GaN, AlN, CdSe and ZnS. Owing to the non-centro-symmetric structure, the wurtzite family is unique for optoelectronics, lasing, piezoelectricity and pyroelectricity. Zinc oxide (ZnO) is a versatile smart material that has key applications in catalysts, sensors, piezoelectric transducers,¹¹ transparent conductors¹² and surface acoustic wave devices.¹³ The structure of ZnO, for example, can be described as a number of alternating planes composed of tetrahedrally coordinated O²⁻ and Zn²⁺ ions, stacked alternately along the *c*-axis

(Fig. 1a). The oppositely charged ions produce positively charged Zn-(0001) and negatively charged O-(000 $\bar{1}$) polar surfaces, resulting in a normal dipole moment and spontaneous polarization along the *c*-axis (Fig. 1b). If the elastic deformation energy is largely suppressed by reducing the thickness of a nanobelt, the polar nanobelt could self-assemble into different shapes as driven by minimizing the electrostatic energy coming from the ionic charges on the polar surfaces (Fig. 1c and d), analogous to the charge configurations of a RNA molecule.

The synthesis is based on a solid-state thermal sublimation process (Fig. 2),¹ in which a pile of source materials, typically the powder form of oxides, is placed at the center of a tube furnace. The source materials are sublimated by raising the temperature; a re-deposit ion of the vapor phase at a lower temperature zone gives some novel nanostructures. By controlling the growth kinetics, local growth temperature and chemical composition of the source materials, a wide range of polar-surface dominated nanostructures of ZnO have been synthesized under well controlled conditions at high yield (Fig. 3).^{14,15}

Self-catalyzed growth on cation-terminated polar surface

The cation-terminated polar surface is chemically active in the growth of nanostructures. The Zn-terminated (0001) surface, for example, is catalytically active, while the O-terminated (000 $\bar{1}$)

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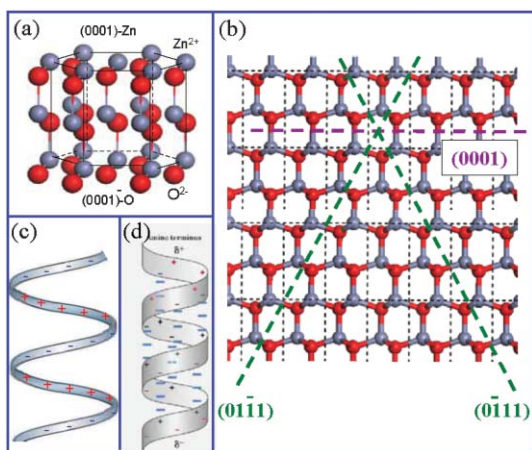


Fig. 1 (a) Structural model of ZnO. (b) The projected structure of ZnO along a -axis, showing the $\{0001\}$ and $\{01\bar{1}1\}$ polar-surfaces. (c) Spiral model of ZnO polar nanobelt. (d) Charge model of an RNA molecule.

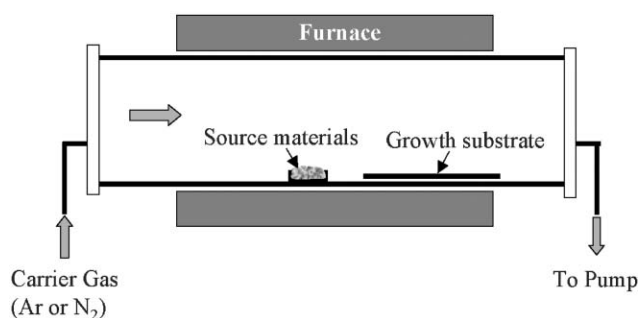


Fig. 2 Schematic of experimental set up for the synthesis of oxide nanostructures.

surface is inactive, resulting in the growth of a saw-tooth structure (Fig. 3a).¹⁶ This growth structure has also been observed for ZnS and CdSe.^{17,18} By forming a multiply twinned octahedral core, a fast growth along the $\{0001\}$ results in the tetraleg structure (Fig. 3b).¹⁹

Using NaAOT as templates, hexagonal disks and rings of ZnO have been grown using a solution-based synthesis (Fig. 3c).²⁰ The growth mechanism of the hexagonal disks is suggested due to the charge compensation of the anion AOT⁻ template at the Zn²⁺- $\{0001\}$ surface of ZnO; a fast growth along $\langle 2\bar{1}\bar{1}0 \rangle$ forms the hexagonal disks enclosed by the $\{10\bar{1}0\}$ facets. A higher density of defects at the center of the disk results in a higher local reaction/etching rate by NH₄⁺ and NH₃. A thickness-through hole as defined by the $\{10\bar{1}0\}$ facets at the center leads to the formation of a hexagonal ring.

Modifying the composition of the source materials can drastically change the morphology of the grown oxide

nanostructure. We used a mixture of ZnO and SnO₂ powders as the source material to grow a complex ZnO nanostructure.^{21,22} Fig. 3d shows an SEM image of the as-synthesized products with a uniform feature consisting of sets of central axial nanowires. The growth of the novel structure presented here can be separated into two stages. The first stage is a fast growth of the ZnO axial nanowire along $\{0001\}$. The growth rate is so high that a slow increase in the size of the Sn droplet has little influence on the diameter of the nanowire, thus the axial nanowire has a fairly uniform shape along the growth direction. The second stage of the growth is the nucleation and epitaxial growth of the nanoribbons due to the arrival of the tiny Sn droplets onto the ZnO nanowire surface. The Sn liquid droplets deposited onto the ZnO nanowire lead to the simultaneous growth of the ZnO nanoribbons along the six equivalent growth directions: $\pm[10\bar{1}0]$, $\pm[0\bar{1}10]$ and $\pm[\bar{1}100]$. Secondary growth along $\{0001\}$ results in the growth of the

aligned nanowires on the surfaces of the propellers.

Self-coiling of polar nanobelts/nanowires

ZnO has two polar surfaces: $\{0001\}$ and $\{01\bar{1}1\}$. The former is frequently observed, but the latter is rare. Recently, we have found that the ZnO nanowires dominated by $\{01\bar{1}1\}$ can form ultrasmall, deformation-free, single-crystal nanohelices or nanosprings (Fig. 3e).²³ The nanohelices are made of ~ 12 nm nanowires and have a uniform mean diameter of ~ 30 nm. The growth follows a hexagonal screw-coiling model, in which the growth of the nanowire is led by the Zn-terminated $\{0001\}$ front surface due to self-catalysis. A sequential and periodic 60° rotation in growth direction among the six equivalent directions of $\langle 0\bar{1}\bar{1}1 \rangle$ in an ordered and equally spaced distance results in the formation of the nanohelix. The sequential change in growth direction is to reduce the electrostatic interaction energy caused by the $\pm\{01\bar{1}1\}$ polar surfaces of the nanowire.

We have recently synthesized ZnO nanobelts that are dominated by the $\{0001\}$ polar surface.⁹ The nanobelt grows along $[2\bar{1}\bar{1}0]$ (the a -axis), with its top/bottom surface $\pm\{0001\}$ and the side surfaces $\pm\{01\bar{1}0\}$. Due to the small thickness of 5–20 nm and large aspect ratio of $\sim 1 : 4$, the flexibility and toughness of the nanobelts are extremely high. From the model presented in Fig. 1b, $\{0001\}$ are polar-surfaces. A polar surface dominated nanobelt can be approximated to be a capacitor with two parallel charged plates. The polar nanobelt tends to roll over into an enclosed ring to reduce the electrostatic energy. A spiral shape is also possible for reducing the electrostatic energy (Fig. 3f).²⁴ If the surface charges are uncompensated during the growth, the spontaneous polarization induces electrostatic energy due to the dipole moment, but rolling up to form a circular ring would minimize or neutralize the overall dipole moment (see Fig. 1c), reducing the electrostatic energy. On the other hand, bending of the nanobelt produces elastic energy. The stable shape of the nanobelt is determined by the minimization of the total energy

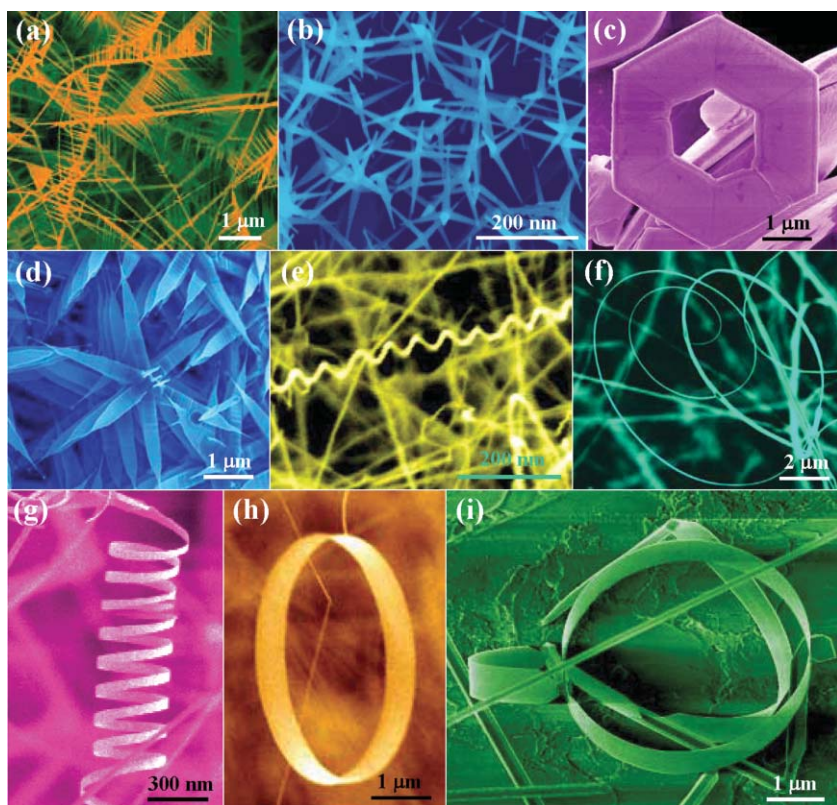


Fig. 3 A collection of polar-surface induced/dominated nanostructures of ZnO, synthesized under controlled conditions by thermal evaporation of solid powders unless notified otherwise: (a) nanocombs induced by asymmetric growth on the Zn-(0001) surface; (b) tetraleg structure due to catalytically active Zn-(0001) surfaces; (c) hexagonal disks/rings synthesized by solution based chemical synthesis; (d) nanopropellers created by fast growth along $\langle 0\bar{1}10 \rangle$ and c -axis; (e) deformation-free nanohelices as a result of block-by-block self-assembly; (f) spiral of a nanobelt with increased thickness along the length; (g) nanosprings; (h) single-crystal seamless nanoring formed by loop-by-loop coiling of a polar nanobelt; (i) a nanoarchitecture composed of a nanorod, nanobow and nanoring.

contributed by spontaneous polarization and elasticity.

If the nanobelt is rolled uniradically loop-by-loop, the repulsive force between the charged surfaces stretches the nanohelix, while the elastic deformation force pulls the loops together; the balance between the two forms the nanohelix/nanospring (Fig. 3g).²⁴ The nanohelix has a uniform shape with radius of ~ 500 – 800 nm and evenly distributed pitches. Each is made of a uniformly deformed single-crystal ZnO nanobelt.

The nanohelices and nanospirals are made of polar nanobelts whose polarization is perpendicular to the spiralling axis. If the polarization is rotated 90° and points parallel to the spiral axis, a seamless nanoring is formed through a loop-by-loop self-coiling process (Fig. 3h).¹⁰ The polar nanobelt, which is the building block of the nanoring,

grows along $[10\bar{1}0]$, with side surfaces $\pm(1\bar{2}10)$ and top/bottom surfaces $\pm(0001)$, and have a typical width of ~ 15 nm and thickness ~ 10 nm. The nanobelt has polar charges on its top and bottom surfaces. If the surface charges are uncompensated during growth, the nanobelt may tend to fold itself as its length gets longer to minimize the area of the polar surface. One possible way is to interface the positively charged Zn-(0001) plane (top surface) with the negatively charged O-(000 $\bar{1}$) plane (bottom surface), resulting in neutralization of the local polar charges and the reduced surface area, thus forming a loop with an overlapped end. The long-range electrostatic interaction is likely to be the initial driving force for folding the nanobelt to form the first loop for the subsequent growth. As the growth continues, the nanobelt may be naturally

attracted onto the rim of the nanoring due to electrostatic interaction and extends parallel to the rim of the nanoring to neutralize the local polar charge and reduce the surface area, resulting in the formation of a self-coiled, co-axial, uni-radius, multi-looped nanoring structure. The reduced surface area and the formation of chemical bonds (short-range force) between the loops stabilize the coiled structure. A uni-radius and perfectly aligned coiling is energetically favorable because of the complete neutralization of the local polar charges inside the nanoring and the reduced surface area. This is a loop-by-loop self-coiling process of a nanobelt, which is called the “slinky” growth model. The charge distributed on the surface of the coiling nanobelt is similar to the charge distribution on the RNA helix (see Fig. 1d).

In this review, we have presented a few polar-surface dominated growth phenomena of zinc oxide. Due to the three types of fastest growth directions: $\langle 0001 \rangle$, $\langle 01\bar{1}0 \rangle$, $\langle 2\bar{1}\bar{1}0 \rangle$ and the polar surface induced phenomena, a diverse group of nanostructures has been grown for ZnO. The growth of several features can proceed simultaneously or one after the other, resulting in truly unique nanoarchitecture (Fig. 3i). The physics model presented here can be general for polar surface dominated growth. For applications in nanotechnology, ZnO has three key advantages. First, it is semiconductor, with a direct wide band gap of 3.37 eV and a large excitation binding energy (60 meV). It is an important functional oxide, exhibiting near-UV emission and transparent conductivity at room temperature and higher. Secondly, due to the non-central symmetry, it is piezoelectric, which is a key phenomenon in building electromechanical coupled sensors and transducers at nano-scale. The piezoelectric coefficient of a polar nanobelt is about three times of that of the bulk,²⁵ it is a candidate for nano-scale electromechanical coupling devices. Finally, ZnO is bio-safe and biocompatible, and it can be used for biomedical applications without coating. With these three unique characteristics, ZnO could be one of the most important nanomaterials in future research and applications. The diversity of nanostructures presented here for ZnO

should open many fields of research in nanotechnology.

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