Flame Synthesis of Metal-Oxide Nanostructures

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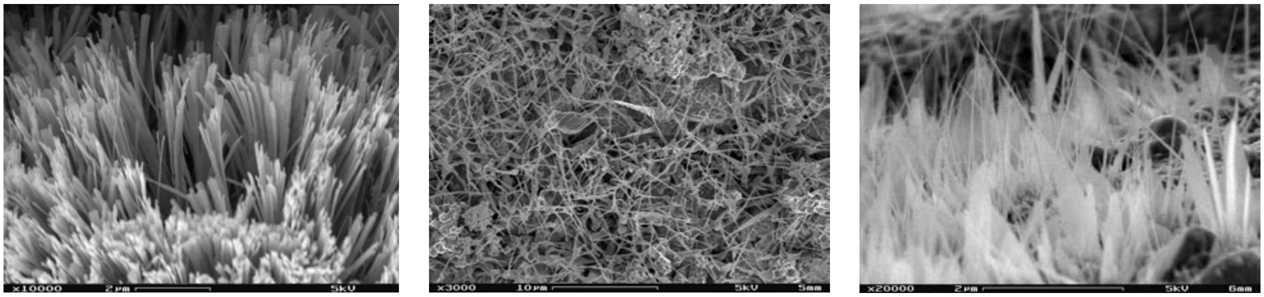
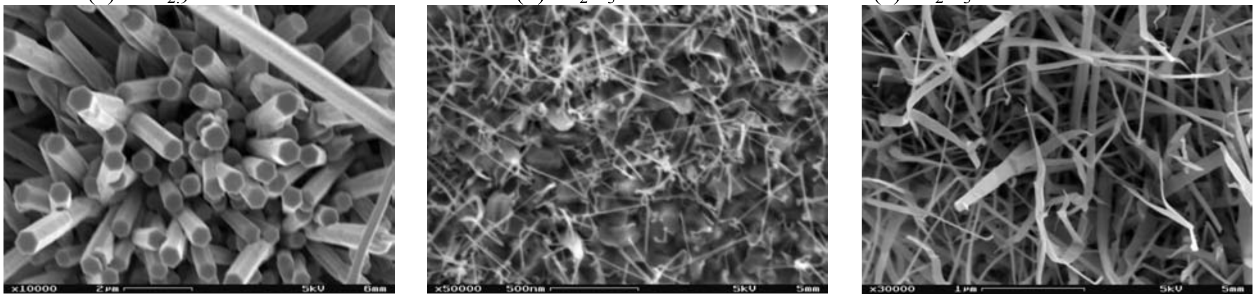
Over the past half-decade, research in functional oxide-based one-dimensional nanostructures has attracted considerable attention due to their unique and innovative applications in optics, optoelectronics, catalysis, and piezoelectricity. Semiconducting oxide nanowires constitute a unique group of 1D nanomaterials, which have well-defined and uniform shapes, controlled crystallographic and surface structures, stable surfaces, and dislocation-free single-crystal volumes.[1] Rod and ribbon-like morphologies appear to be an exclusive and common structural characteristic for the family of semiconducting oxides with cations of different valence states and materials of distinct crystallographic structures.[1] As a result, field effect transistors, ultra-sensitive nano-size gas sensors, nanoresonators, and nanocatilevers become realizable based on these individual nanostructures.

Many approaches have been used to prepare nano-wires/rods, such as vapor-liquid-solid growth, solution-liquid-solid methods, template mediate growth, electron beam lithography, scanning tunneling microscopy techniques, and others depending on the expected properties. However, these methods can be either technically complex, incompatible with complementary metal-oxide-semiconductor technology, or incapable of pattern growth. As such, efforts to develop a simple method for the production of metal-oxide nanowires for device applications without the above mentioned disadvantages are still required. Our team has developed a novel ***combustion-based*** technique to directly synthesize monocrystalline oxide nano- wires/rods from microsized metal grains at high rates under atmospheric conditions. Apart from manipulating aerothermochemical conditions, our process further utilizes ***electric and magnetic fields*** to control nano- and micro-morphologies of the nanostructured elements. Combustion synthesis has demonstrated a history of scalability and offers the potential for high-volume commercial production, at reduced costs. The robustness of flame systems to harvest various morphologies and micro-structures of metal oxide nanostructures is evinced in our results (see Fig.1).



(a) $WO_{2.9}$ nanowires. (b) Fe_2O_3 nanowires. (c) Fe_2O_3 nano- wires and ribbons.



(d) Zinc oxide nanorods. (e) Zinc oxide nanowires. (f) Zinc oxide nano-ribbons.

Figure 1. Nano-wires/rods and their aggregate morphologies, as produced by Tse's flame synthesis process.

Fundamentally, the large characteristic thermal and chemical gradients characterizing flames are especially advantageous for determining nano-wire/rod growth conditions in that a large parameter space of conditions can be found within a single flame. In comparison, systematic variation of parameters such as chemical species and temperature in a CVD reactor would be very time-consuming and tedious. Further utilization of ***advanced laser-diagnostics*** to determine the local in-situ temperature and gas-phase chemical species concentrations for given morphologies and growth rates not only reveal fundamental mechanisms, but also establish "universal" conditions which should be directly applicable as specific operating conditions for other methods of synthesis.

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[1] Wang, Z.L., "Self-assembled nanoarchitectures of polar nanobelts/nanowires," *J. Mater. Chem.* 15:1021-1024 (2005).

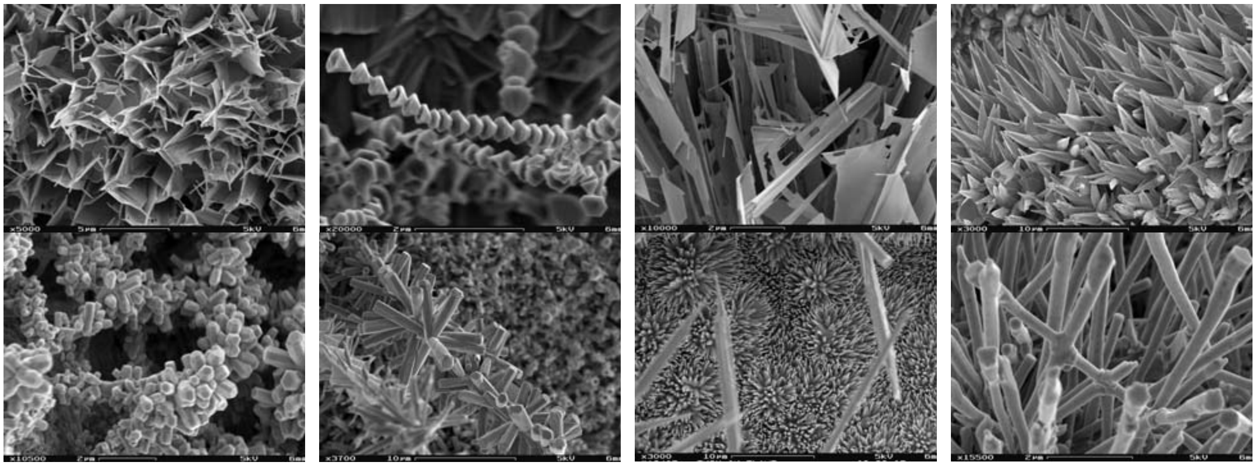
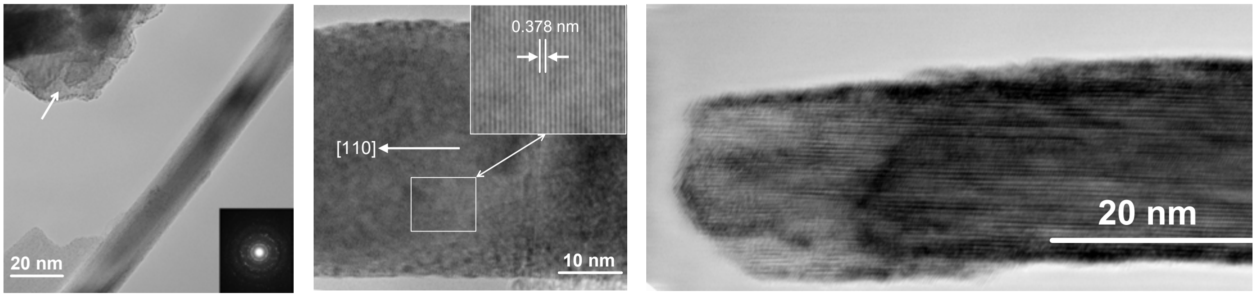


Figure 2. Various ZnO nanostructures grown in Tse's flame synthesis system.

For example, ZnO is a wide band-gap (3.37eV) semiconductor with a high exciton binding energy (60meV), and as such, is suitable for short-wavelength optoelectronics and transparent conducting windows for solar cells[2]. The piezoelectricity due to its non-centrosymmetric structure enables it to be an important material for electro-mechanical coupled sensors and actuators[3]. Structurally, ZnO can take on a wide range of novel structures, such as nanowires, nanorods, nanoribbons, and nanosprings that can be grown by tuning the growth rates along the growth directions[4]. Figure 2 presents some FESEM images of different ZnO nanostructures (i.e. nanoribbons, nanorods, nanocones, short interconnected nanorods, etc.) grown in our system. Note that these different morphologies correspond to different band-gaps, presumably due to the defects. As such, by adjusting local flame structure conditions, we can tailor the nano/micro-morphology to suit specific applications.

With respect to the nanowires, TEM imaging (Figs. 3 and 4) reveals that they are single-crystalline and dislocation free. Figure 3(a) shows a tungsten oxide nanowire with a diameter of ~20 nm. Its HRTEM image (Fig. 3(b)) confirms to it to be single-crystal $WO_{2.9}$, in terms of both *d*-spacings and SAED, with its growth direction along the [110] direction. Figure 4(a) shows a ZnO nanowire with a uniform diameter of ~40 nm. Its corresponding HRTEM is given in Fig. 4(b), from which the nanowire is confirmed to be single crystal ZnO, in terms of the *d*-spacings and SAED, with it growth direction along the $[11\bar{2}0]$ direction. The mechanism of formation of these nanowires appears to be by vapor-solid (VS) growth. In the vapor-liquid-solid (VLS) process, the growth is promoted by a liquid-solid interface, generally marked by the presence of droplets at the tips of the nanowires. The morphology of the nanowires are shown in Figs. 3(c) and 4(c), evincing no metal nanoparticle at its tip. The TEM images further reveal thickening by a ledge-growth mechanism, which is additional evidence for vapor-phase transport and deposition. Figures 3 and 4 show that our high-rate synthesis system can produce high-quality, single-crystal $WO_{2.9}$ and ZnO nanowires. ***Note that what could take over 12 hours by conventional thermal-evaporation methods would take us only minutes to produce.***



(a) 20nm nanowire with high aspect ratio.

(b) Single crystal and dislocation free – $WO_{2.9}$.

(c) Nanowire tip, with ledge growth suggesting VS mechanism.

Figure 3. Characteristics of flame-grown tungsten oxide nanowires.

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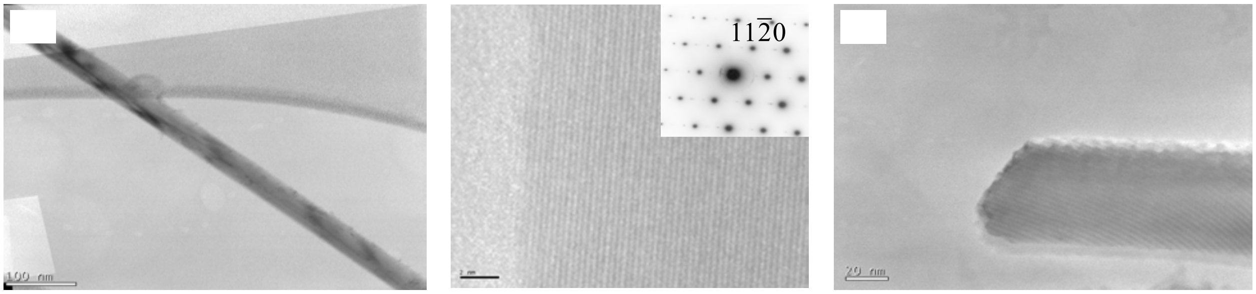
[2] Banerjee, D., Lao, J.Y., Wang, D.Z., Huang, J.Y., Steeves, D., Kimball, B., and Ren, Z.F., Synthesis and photoluminescence studies on ZnO nanowires, *Nanotechnology,* 15:404 (2004).

[3] Gao, P.X., and Wang, Z.L., Nanoarchitectures of semiconducting and piezoelectric zinc oxide, *J. Appl. Physics,* 97:044304 (2005).

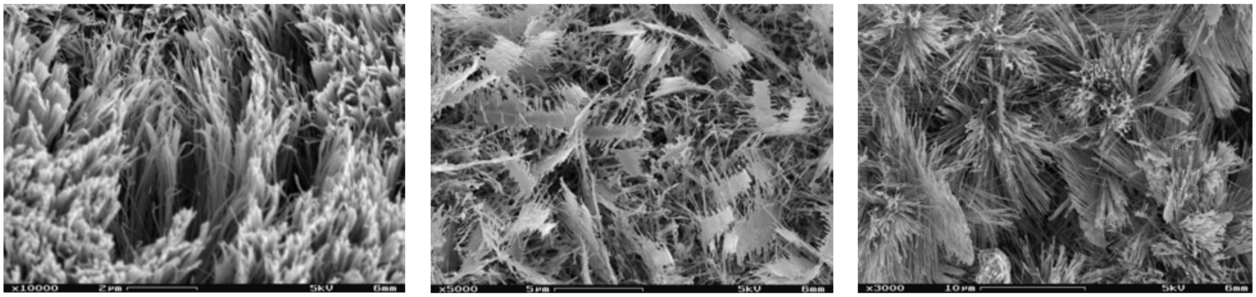
[4] Wang, Z. L., Zinc oxide nanostructures: growth, properties and applications, *J. Phys.: Condens. Matter.* 16, 2004:R829-R858 (2004).



(a) 40nm nanowire with high aspect ratio. (b) Single crystal and dislocation free – ZnO. (c) Nanowire tip, with ledge growth suggesting VS mechanism.

Figure 4. Characteristics of flame-grown zinc oxide nanowires.

The use of electrical force fields provides an advantageous tool to improve uniformity and productivity in gas-phase synthesis processes. Our preliminary results show that very different nano/micro-structures, as shown in Fig. 5, can result when voltage bias is applied to the substrate. The interplay of various transport mechanisms and resulting complex flows can make it difficult to isolate and study the fundamental processes involved with electric field control. Moving ions alter the electric field, coupling flow field and electric field, so that both should be considered simultaneously. As a result, experiments should be conducted which involve the simplest relationships between the flow field and the electric field. In conjunction, corresponding numerical studies become essential in providing better insight and understanding. However, such complementary studies have been lacking, despite detailed investigation of ion properties in flames[5] and the current state-of-the-art in laminar flame simulation. Much more study is needed.



(a) No voltage applied (b) -10V applied. (c) -100V applied.

Figure 5. Effect of bias voltage applied to substrate on tungsten oxide nanowire morphology. (Tse's work)

Another attractive aspect of our process is that we can readily synthesize various other crystalline nanowires/structures of metal oxides such as the perovskites: $BaTiO_3$, $SrTiO_3$, and $ZrTiO_3$. We can grow nanowires from powders of the perovskites in our unique process. By tuning the hydrogen concentration, H_2 reduction aids in initial nanoparticle formation of the base metals. The high characteristic temperature and H_2O concentration in the flame process induces nanowire growth without the help of catalysts (given the high melting temperatures of Zr [1855ºC] and Ti [1668ºC]) through the hydrolysis and hydrate species formation routes. Alternatively, we can start with mixed powders of Ba/Ti, Sr/Ti, and Zr/Ti deposited on a substrate. In the end, the growth mechanism is vapor-solid based, with key parameters being radical species present, oxidizer and water-vapor concentrations, substrate temperature, and gas-phase temperature. A positive temperature gradient extending outward from the (cooler) substrate surface into the (hotter) surrounding gas promotes vertical orientation of the nanowires.

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[5] Fialkov, A.B., Investigations on ions in flames, *Progress in Energy and Combustion Science* 23:399-528 (1997).