Rapid Combustion Synthesis of Zinc Oxide Nanostructures

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ABSTRACT

Zinc oxide nanostructures were grown on the surface of a Zn probe using the flame synthesis method. A sleeve surrounding the zinc probe is employed to protect the wire from melting inside the high temperature region of the flame. Different morphologies of Zn oxide structures are prepared by varying the size diameter of the sleeve. The synthesized structures include cylindrical, polyhedral, and complex 3D structures. The polyhedral structures have cubical, hexagonal, and pentagonal cross sections. Results indicated that the structures grown using the sleeve with larger size diameter window opening have higher length-to-diameter aspect ratio. The nanorods are single crystalline with hexagonal wurzite (ZnO) internal structure. Scanning electron microscopy (SEM), transmission electron microscopy (TEM), and selected area diffraction pattern (SADP) were used to characterize the synthesized structures. Moreover, the growth mechanism of ZnO nanostructures is briefly discussed

1   INTRODUCTION

Zinc Oxide nanostructures have been considered promising candidates for applications in photocatalysts, gas sensors, field emission devices, biological probes, and solar cells [1-3]. These applications are possible due to zinc oxides' unique mechanical, thermal, and electronic properties. High heat capacity and heat conductivity, along with low thermal expansion and high melting temperature of zinc oxides make this compound very unique. At the present time, different 1D and 3D nanostructured ZnO crystals have been formed such as nanorods [3], nanowires [4], nanoribbons [5], nanospings [6], nanocombs [7], nanobridges [8], and nanonails [9]. Different methods have been developed and employed to produce ZnO nanostructures, including chemical vapour deposition (CVD) and plasma enhanced CVD [4, 10], vapour-phase transport [5], thermal evaporation [7] reactive magnetic sputtering [11], spray pyrolysis [12], sol-gel techniques [13], and electrochemical deposition [14] for the synthesis of Zn oxide nanostructures. However, these methods are complex and composed of multi-step processes.

Recently, flames have emerged as a unique single-step, rapid, and inexpensive process for the synthesis of various types of nanomaterials. The flame synthesis method offers unique advantages over currently employed methods, including growth at atmospheric pressure (simple experimental setup), high temperature meduim, and large growth rates in a process consisting of only a few minutes. Previous works have shown that combustion-based synthesis methods are successful in preparing unique 1D and 3D transition metal oxide (TMO) nanostructures using Mo and W as the metal source [15,16].

2   EXPERIMENTAL SETUP

A stable counter-flow flame is utilized for the synthesis of zinc oxide nanostructures. The flame is formed by two opposite impinging streams of gases that form a stable stagnation plane and a diffusion flame established on the fuel side. The fuel ($96\%CH_4 + 4\%C_2H_2$) is introduced from top nozzle and the oxidizer ($50\%O_2 + 50\%N_2$) is supplied from the bottom nozzle (Fig. 1a). The experiments were conducted with constant fuel and oxidizer strain rate equal to 20 s^{-1}. The flow of gases is controlled by electronic mass flow meters providing accuracy within 1.5%. A 1.0mm diameter Zn probe with a purity of ~99.99% (Sigma-Aldrich corporation) is used as the metal source. The metallic probe, inside a sleeve, is inserted into the oxygen-rich flame zone to synthesize the Zn oxide nanostructures. Due to the low melting point of Zn (~ 419°C) the probe was sequestered inside the sleeve to protect it from the high temperature zone of the flame. The window size of the sleeve was changed to synthesize Zn oxide structures of various morphologies on the surface of the Zn probe.

3   RESULTS AND DISCUSSION

The counter-flow flame is characterized by strong axial gradients of chemical species and temperature (Fig. 1). The temperature gradients reach ~2000 K/cm and the chemical species rapidly change from a hydrocarbon-rich zone on the fuel side to the oxygen rich zone on the oxidizer side of the flame. The window size on the sleeve controls the flow of high temperature gases. Consequently, the probe position (Z height) in the flame and the window size of the sleeve strongly influence the synthesis processes. Z represents the distance from the edge of the fuel nozzle to the center of the window of the sleeve. The sleeve containing the Zn wire inside was positioned in the flame so that the gases flow perpendicularly. Window openings with various diameters are used to control the growth of the nanostructures.

The sleeve (with window opening size of 2.5mm) containing the Zn probe was first inserted at Z=11 mm height in the flame volume. Figure 2 represents a SEM image illustrating the as-grown structures on the surface of the Zn probe.
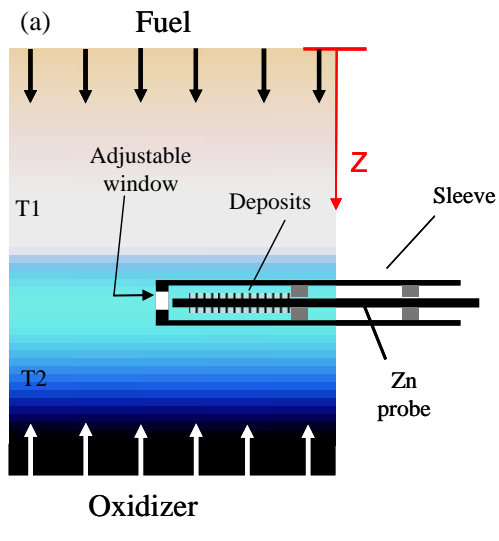
Figure 1: (a) Zn probe inside a chamber introduced to the oxygen zone of the flame for the synthesis of Zn oxide structures. Z represents the distance from the edge of the fuel nozzle to the surface of the probe; (b) flame temperature profile and chemical species of the flame predicted by a numerical simulation based on a multi-step reaction mechanism [17].

The structures appear to be growing in different directions and have approximately the same diameter. In order to characterize the internal structure of the formed materials, the deposits were mechanically removed from the surface of the probe and mixed with methanol.
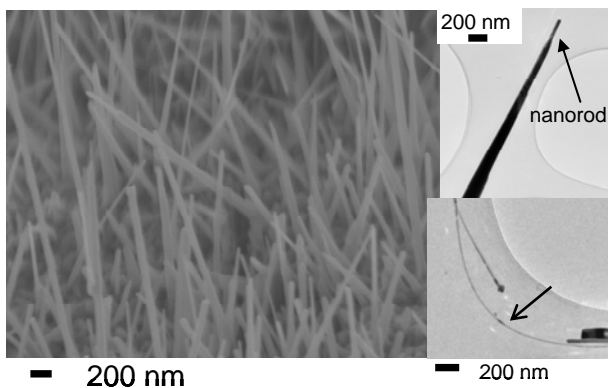

Figure 2: SEM image of ZnO nanorods formed using a window diameter of 2.5 mm and Z=11mm. The upper and lower insets represent TEM images of the nanorods.

The mixture was sonicated for a few minutes. A drop of the suspension was placed on a TEM copper-substrate/carbon film grid and dried. TEM analysis of the synthesized products shows that the structures contain sharp tip morphology and that they can be very flexible (black arrow Fig. 2 lower inset).

The insertion of a window size of 1mm diameter in the sleeve at Z =11 mm causes polyhedral structures with nanoscale dimensions to be synthesized, Fig. 3. The
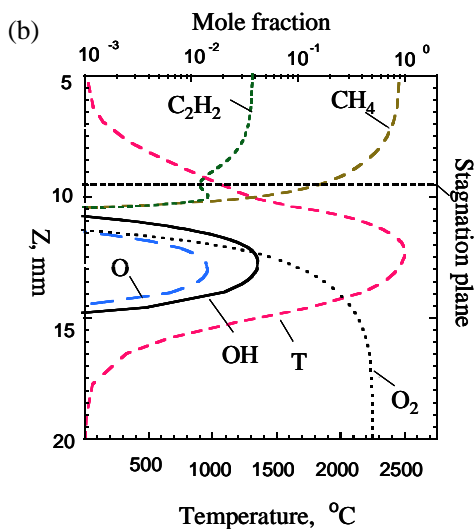
polyhedral nanorods have pentagonal, cubical, and hexagonal cross sections. The cross section ranges from ~50 to 200 nm and the lengths range from ~150 to 500 nm (Fig. 3). In order to determine the crystal structure of an individual polyhedral nanorod, TEM imaging and SAED analysis were conducted. SAED shows that the polyhedral rod (Fig. 3 lower inset) can be indexed as a single-crystalline hexagonal structure, growing along [0001] direction without any defect or dislocation.
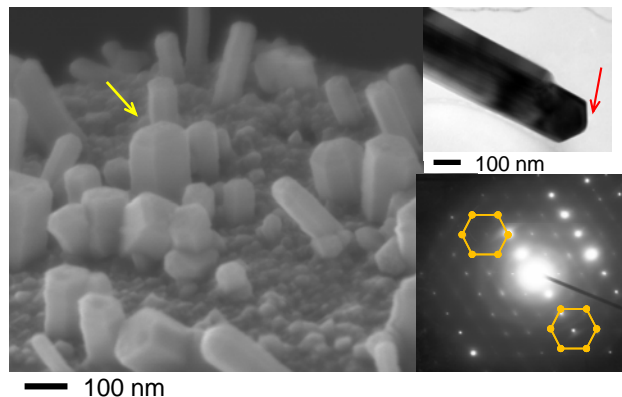

Figure 3: SEM and TEM images of Zn oxide nanorods containing pentagonal and hexagonal cross-sectional areas using a sleeve with a window diameter of 1mm. The yellow and red arrows point to the domed cap morphology at the tip of the structures. Inset shows SAED of the nanorod.

Additionally, top and bottom surfaces of the nanorod are a pair of (0001) and (000$\bar{1}$) c planes, while six side facets are {01$\bar{1}$0}.

From the synthesized structures it is evident that the diameter size of the window opening in the sleeve strongly

influences the morphology of the grown structures. As the diameter of the window opening increases, the mass flow of high temperature gases increases and leads to variation in synthesized structures. The nanostructures formed on the surface of the probe inserted in the flame medium with a larger window opening in the sleeve have a higher length-to-diameter aspect ratio. Saitoh *et al*. [18] prepare oriented ZnO whiskers using chemical vapour deposition technique. In the same work it was found that a higher vapourization temperature increases the aspect ratio of the formed structures.

In this study we propose that the growth mechanism is composed of two different processes: 1) Formation of vapors by the evaporation of the base metal as it is exposed to the flame medium. The Zn atoms are intercalated with oxygen atoms deriving from the flame to form Zn oxide nuclei. 2) Subsequent to formation of Zn oxide nuclei, elongated structures start to form through the vapor-solid (VS) growth mechanism. Experimental results suggest that Zn and oxygen both in the vapor form must combine and deposit along the surface of the probe to serve as the nuclei and the source for the growth of the Zn oxide structures. Due to the probe/flame interaction Zn atoms join oxygen atoms to form Zn oxide nuclei. The Zn oxide nuclei are deposited on the surface of the probe and/or the previously formed ZnO structures to further crystallize into 1-D or 3-D structures, Fig. 4a. Formation and transformation of the shape of structures depend upon the presence and on the degree of concentration of Zn oxide vapors (source). It is not clear what activates the growth of the nanorods on the tip of the larger crystals, but apparently the tip of the larger crystal serves as an auto-catalyst similar to the VLS growth model. As for the vapor-solid growth mechanism, it is common that nanorods gradually taper and possess a pointy tip (schematic in Fig. 4b). Upper inset in Fig. 2 shows a nanorod that gradually tapers towards its tip.
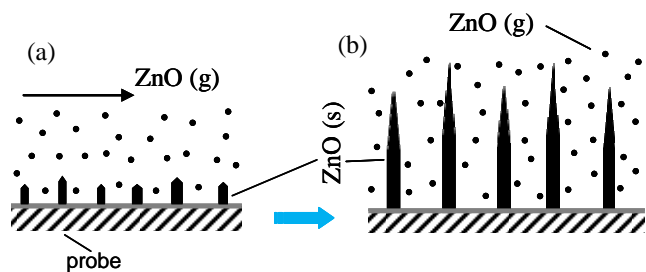

Figure 4: Proposed growth mechanism.

Li *et al*. [19] report the formation of micro- and nano-sized Zn oxide structures prepared by thermal evaporation that closely resemble our flame synthesized Zn oxide structures. In that study, the structures are grown in a tube chamber operating at ~1000°C with various oxygen percentages. It is proposed that at the applied temperature condition, Zn vapors are mass-produced from the Zn source material and later combine with the oxygen atoms in the gas-phase to form Zn oxide nuclei.

To support the above mechanism additional experiments were conducted by increasing the residence time of the probe/sleeve inside the flame volume. By increasing the residence time of the probe, the amount of Zn oxide vapors inside the sleeve should increase and should lead to crystal formation containing different characteristics on the surface of the Zn probe. Indeed, complex and unique structures are formed (Fig. 5).

Structures formed include bead-like crystals connected with small diameter nanorods, Fig. 5. As can be observed in the inset of Fig. 5, the 3D nanostructures are connected to each other by a single nanorod (~14 nm in diameter) as pointed out by the red arrows in the SEM image. HR-TEM of the nanorods shows that these structures are free of structural defects (lower inset in Fig. 5). Moreover, it can be observed (Fig. 5) that the elongated rod structures have several slender polyhedral structures that have diamond and rectangular shape (as if decorating the nanorod). This strongly supports the growth mechanism proposed above, specifically that the initial structures themselves play the role of support for the deposition of Zn oxides vapours to transform into various solid shapes. That is, as the reaction proceeds, a formed nanorod itself plays the role of support for the nucleation of other unique 1-D and/or 3D structures.
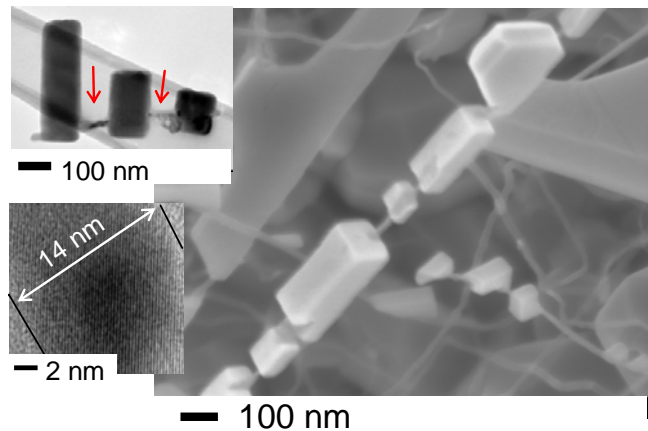

Figure 5: Zn oxide nanobead-like structures. Insets are TEM images of the bead-like structures and HR-TEM of the nanowire.

CONCLUSION

The synthesis of Zn oxide nanostructures is performed using Zn probes inserted in a counter-flow flame medium formed using methane/acetylene and oxygen-enriched air streams. The zinc probe was introduced in the flame medium by using a sleeve to prevent the zinc from melting in the flame. The probe position and the sleeve window opening play a key role for

the variation of the synthesized structures. Nanorods of approximately the same diameter with sharp-tips are grown on the surface of the probe using the sleeve window opening of 2.5mm. Hexagonal nanorods with cubical, pentagonal, and hexagonal cross sections are formed using a sleeve with a window opening of 1mm. Zinc vapors are formed due to the probe/flame interaction.. Zinc and oxygen atoms combine to form ZnO nuclei and these nuclei deposit on the surface of the probe to form the larger structures.

ACKNOWLEDGMENT

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