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# Solid support flame synthesis of 1-D and 3-D tungsten-oxide nanostructures

Wilson Merchan-Merchan [a,*], Alexei V. Saveliev [b], Walmy Cuello Jimenez [a]

[a] School of Aerospace and Mechanical Engineering, University of Oklahoma, Norman, OK 73019, USA
[b] Department of Mechanical and Aerospace Engineering, North Carolina State University, Raleigh, NC 27695, USA

**Abstract**

In this paper we report the growth of 1-D and 3-D tungsten-oxide nanostructures on tungsten wire probes inserted in an opposed-flow oxy-fuel flame. The probe diameter and oxygen content in the oxidizer were varied to study their influence on the growth of tungsten-oxide nanostructures. The introduction of a 1-mm diameter W probe into the flame environment with an oxidizer composition of $50\%O_2 + 50\%N_2$, resulted in the formation of 1-D nanorods on the upper surface of the probe. The formation of triangular, rectangular, square, and cylindrical 3-D channels with completely hollow or semi-hollow morphology was achieved by reducing the probe diameter to 0.5 mm. Whereas, the increase of the $O_2$ content to 100% and the employment of a 1-mm probe resulted in the growth of ribbon-like micron-sized structures. The lattice spacing of $\sim$0.38 nm measured for the 1-D W-oxides closely matches a monoclinic $WO_3$ structure. X-ray photoelectron spectroscopy analysis revealed that the larger 3-D structures also consist of $WO_3$ confirming that the chemical composition of the structures remains the same while varying the probe and flame parameters. The proposed growth mechanism states that the 3-D $WO_3$ structures are formed through the lateral coalescence of 1-D W-oxide nanorods.


*Keywords:* Nanorods; Tungsten-oxide nanostructures; Counter-flow flame; Combustion; Synthesis

## 1. Introduction

Flame processes are widely employed in manufacturing of commercial nanoparticles such as carbon blacks, fumed silica, optical fibers, and pigmentary titania [1]. Efficient flame synthesis of several types of nano- and micro-materials including fullerenes [2,3], multi- and single-walled carbon nanotubes [4–10], carbon fibers [11], carbon whiskers, diamond nanocrystals [12], and other nanomaterials such as metal oxides [13–17], and carbides [18] have been recently reported. Research interest in the field is shifting to the synthesis of one-dimensional (1-D) and three-dimensional (3-D) nanostructures such as nanorods and nanowires that exhibit unique electronic and physical properties. In particular, 1-D nanostructures made of transition metal oxides (TMOs) are of great interest due to their rich collection of distinctive and interesting properties such as superconductivity, piezoelectric-

* Corresponding author. Address: University of Oklahoma, School of Aerospace & Mechanical Engineering, 865 Asp Ave., Felgar Hall, Room 208, Norman, OK 73019, USA. Fax: +1 405 325 1088.
*E-mail address:* wmerchan-merchan@ou.edu (W. Merchan-Merchan).

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ity, electrochromicity, photochromicity, and high magnetoresistance. Among the numerous TMOs, tungsten-oxides (W-oxides) are of special interest and of great importance due to their superconducting, photochromic, electrochromic, optochromic, and gaschromic properties [19–22]. W-oxides are chemically sensitive to gases, and also have a wide electronic band gap (3.15 eV) [23]. W-oxides have great potential for a wide range of applications including gas, humidity and temperature sensors [22]. Their optical properties make them suitable for construction of flat panel displays, photoelectrochromic smart windows, optical modulation devices, transparent conducting electrodes, and writing-reading-erasing optical devices [24,25,22]. Other remarkable applications of these novel structures include photocatalysis [26], microscopy, field emission [23,27], and potentially thin-film fuel cells [28].

Although unique properties and a vast variety of applications facilitate the development of novel synthesis methods, it has been reported that there is a lack of synthesis techniques of nanoscaled W-oxides [22,23,19]. Only recently, some research groups have started reporting on the fabrication of a diversity of shapes and morphologies of W-oxide nanostructures such as nanoparticles [29], nanorods [19], nanoribbons [30], films [31], nanotips [27], nanowires, and nanowire networks [16,22]. Despite the fact that some techniques have already been reported on W-oxide nanostructure synthesis, these methods can be either technically complex [22,20], incompatible with complementary metal-oxide semiconductor technology [32,17], or not capable of pattern growth [33,17]. Hence, efficient and simple techniques to synthesize W-oxide nanostructures for the previously mentioned potential applications are needed.

The present paper focuses on the development of a novel combustion-based synthesis method to synthesize crystalline W-oxide needle-like, ribbon-like, and hollow or semi-hollow structures with high aspect ratios on solid supports. The success of the flame media as a synthesis technique relies on the flexibility of a relatively inexpensive robust single-step process which has a potential for high-volume commercial production of various W-oxide nanostructures.

## 2. Experimental setup

The counter-flow flame geometry offers a highly stable one-dimensional reaction zone for the synthesis of carbon nanomaterials [3,34,35] and metal-oxide nanostructures [13–15]. The counter-flow flame is created by two opposite streams of gasses; the fuel ($96\%CH_4 + 4\%C_2H_2$) is supplied from the top nozzle, and the oxidizer ($50\% O_2 + 50\%N_2$) is introduced from the bottom nozzle both at a constant strain rate of $20\,s^{-1}$, Fig. 1. The addition of acetylene ($C_2H_2$) in the fuel stream increases the flame temperature and affects growth rates of metal-oxide structures. For all experiments the nozzles were separated by a constant distance of 25.4 mm. The tungsten probes with purity of 99.9% were introduced in the oxygen-rich zone of the flame at various axial positions $Z$ measured from the fuel nozzle. Experiments were conducted using 1.0 and 0.5 mm diameter probes. The synthesized materials were analyzed utilizing scanning and transmission electron microscopy (SEM and TEM, respectively). Energy dispersive X-ray spectroscopy (EDX), X-ray photoelectron spectroscopy (XPS), and selective area diffraction pattern (SAED) were employed to characterize the elemental composition and internal morphology of the synthesized structures. Further information on the experimental setup and the electron microscopy methods can be found in our previous reports on flame synthesis of carbon and metal-oxide nanostructures [3,13–15,36].

## 3. Results and discussion

The feasibility of the flame to convert bulk pure W material into 1-D and 3-D tungsten-oxide nanostructures was studied experimentally in the counter-flow flame where a strong axial temperature (up to 2000 K/cm) and chemical composition gradients exist. Thus, the position of the probe within a formed flame is one of the main factors affecting the results of nanomaterial synthesis.

### 3.1. Synthesis of one-dimensional tungsten-oxide nanorods

Tungsten probes of two different diameters were introduced in the high temperature zone of the opposed-flow flame for the synthesis of W-oxide nanostructures. For both tested probe sizes it was found that the introduction of the probes in the 1-D reaction zone of the counter-flow flame did not visibly disturb the flame nor did it create flame instabilities near the probe's surface or in the overall flame structure. The flow behavior in relation to the metal probe inserted in the flame medium can be considered as a flow around a stationary cylinder. Therefore, flow deceleration is small in the front of the cylindrical probe [37] and the flow continues to travel upwards around the smooth cylindrical surface. In contrast large flow field instabilities can be created behind the probes with the introduction of ribbon-like probes, even when the probes are micron size [37].

The introduction of 1.0 mm diameter tungsten probes in the high temperature flame medium at flame heights of $Z = 11$, 12, and 13 mm resulted in material deposition on the sides of the probe. A high density layer of synthesized material with