Investigating oxidation growth routes in the flame synthesis of tungsten-oxide nanowires from tungsten substrates

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ABSTRACT

Tungsten-oxide nanowires are synthesized directly from the surface of tungsten substrate probes inserted into counter-flow diffusion-flames to correlate as-formed morphologies with local conditions because of the quasi-one-dimensionality of the flow field. Computational simulations aid in designing the flame structure for the experiments with respect to relevant chemical species and temperature. The tungsten substrates are inserted into the flame structure on either the air side or fuel side of the flame reaction zone, permitting evaluation of the roles of H_2O (or CO_2) versus O_2, which serve as reactant species in the growth of the resulting tungsten-oxide nanostructures. Furthermore, methane flames are compared with hydrogen flames, which only have H_2O (and no CO_2) as product species. The temperature profiles of the methane and hydrogen flames are purposefully matched to compare the effect of chemical species produced by the flame which serve as reactants for nanostructure growth. Single-crystalline, well-vertically-aligned, and dense $WO_{2.9}$ nanowires (diameters of 20–50 nm, lengths of $> 10\,\mu m$, and coverage density of 10^9–$10^{10}\,cm^{-2}$) are obtained at a gas-phase temperature of 1720 K on the air-side of the methane flame. Comparisons among the probed locations and flame species indicate that the CO_2 route is a heterogeneous one that helps in seeding the growth of nanowires at the nucleation stage, with subsequent vapor–solid growth occurring from other routes. Probing on the fuel side of the hydrogen flame isolates the H_2O route and confirms that it is able to produce tungsten-oxide nanowires, albeit at a very reduced rate and yield. Moreover, given the thermodynamic unfavorability of H_2O reaction with W to form gaseous W/O species, a self-photocatalytic mechanism is proposed where H_2O decomposes to reactive OH on the surface of WO_x, facilitating production of volatile W/O species for continued growth by the vapor–solid mechanism for the tungsten-oxide nanowires. The effect of gas-phase temperatures of 1280, 1500, and 1720 K are examined, with increasing temperatures corresponding to higher yield density because of increased nucleation and augmented formation of volatile W/O compounds.

1. Introduction

Transition metal-oxide nanomaterials have been widely investigated and implemented in various fields for the past few decades because of their useful physical and chemical properties, such as piezoelectric [1], catalytic [2], and magnetic [3]. Among them, tungsten oxides have attracted considerable attention owing to their unique electrochromic [4], photochromic [5], and gaschromic [6] performances. As such, synthesis of tungsten-oxide 1-D nanomaterials have been investigated using a variety of methods, including wet chemistry, thermal evaporation, chemical vapor deposition (CVD), sputtering, and flame synthesis. For example, hydrothermal method was used to produce WO_3 nanorods ($\sim$100 nm diameter and $\sim$2 μm length) by using aqueous solution containing 0.13 M of Na_2WO_4 and 0.26 M of NaCl at 180 °C for 24 h [7]. Solvothermal method was used to fabricate $W_{18}O_{49}$ nanowires ($\sim$6.2 nm diameter and $\sim$116 nm length) via the reaction between WCl_6 (0.014 M) and ethanol (99.8%) at 200 °C for 10 h [8]. Thermal evaporation of tungsten powder resulted in the growth of $W_{18}O_{49}$ nanowires (diameters of 10–50 nm and lengths of 500–1500 nm) on a tungsten plate at 650 °C and 20 Torr for 2 h [9]. By heating up a tungsten spiral coil in a vacuum chamber at $\sim$5.0 Pa [10], $WO_{2.9}$ nanorods (diameter of $\sim$45 nm, length of $\sim$300 nm and growth time of $\sim$10 min) were grown on a pretreated silicon wafer. Hot-wire CVD was employed to generate WO_3 nanorods (10–50 nm diameters, 50–200 nm lengths and 10 min growth time) with O_2 and Ar ($\sim$4% O_2) mixture as background gas under 150 Torr [11]. For CVD, the sources of W/O related species generally come from

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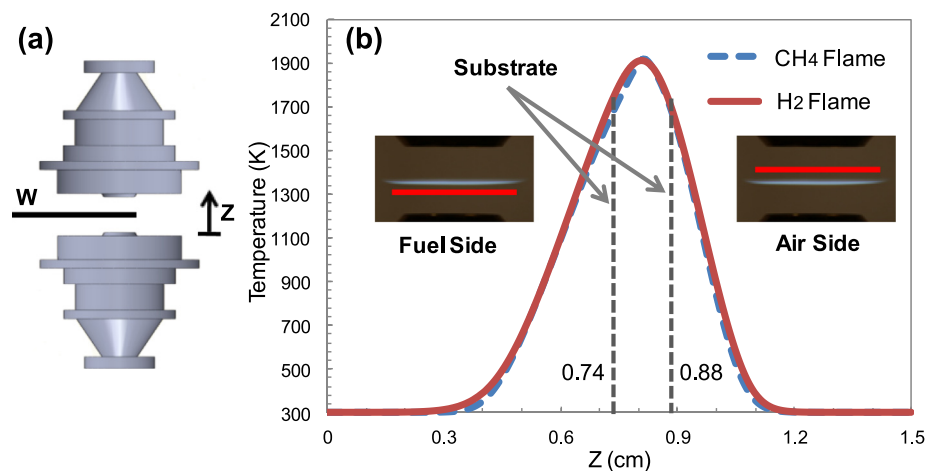*E-mail address:* sdytse@rutgers.edu (S.D. Tse).

Fig. 1. (a) Schematic of the quasi-1D counter-flow diffusion flame setup. (b) The temperature profiles of CH$_4$ flame (dash line) and H$_2$ flame (solid line); insets show that the temperature is 1720 K for the probe position at $z = 0.74$ cm (fuel-side) or $z = 0.88$ cm (air-side).

either the thermal oxidation of tungsten filaments or the decomposition/reaction of volatile precursors (e.g., tungsten hexafluoride (WF$_6$) and tungsten carbonyl (W(CO)$_6$)) [12]. Although these various methods have been successful, they may require vacuum systems [11], complex pretreatments [10], and/or expensive/volatile precursors [12]. Moreover, the growth rates can be very low (e.g., 1–10 nm/min) resulting in long processing times which can limit their feasibility in applications [7–12].

Flame synthesis is a widely used method in industry for manufacturing nanopowders, especially metal oxides and carbon-based materials, at high growth rate, high-volume production, and low cost [13–22]. At the lab-scale, various compositions and morphologies have been achieved [23–27], with the possibility of scaling for production capability. For example, Fe$_2$O$_3$ nanoflakes (thicknesses of 20–40 nm, lengths of > 20 μm, 20 minutes growth duration, and growth temperature of 700–1000 °C) have been rapidly produced by utilizing a flat diffusion flame [28]. Amorphous silica nanowire arrays (diameter of ∼20 nm and lengths of 110–600 nm) have been grown on plain glass substrates (without any pre-treatments, no catalytic nanoparticles, and at a temperature of 550 °C) using flame spray pyrolysis with ultra-high growth rates of 11–30 nm/s under the ambient environment [29]. WO$_3$ nanorods (diameters < 100 nm and lengths > 50 μm) have been produced by inserting a tungsten probe (1 mm diameter) into a counter-flow diffusion flame at gas-phase temperature of 2400 °C for 2 min [30]. W$_{18}$O$_{49}$ nanowires (10–400 diameters and 0.6–16.7 nm/s growth rates) has been grown on tungsten foil by placing by placing a tungsten wire mesh as the source material downstream of a Hencken-like burner [31].

By placing a metal probe/mesh in the flame structure or post-flame gases, the high-temperature combustion reactants/products contain oxidizing species that can oxidize the metal source, producing volatile metal-oxides that can condense into metal-oxide nanowires, for example, by the vapor-solid (VS) mechanism, at a substrate. However, the role of local gas-phase conditions, i.e., temperature, and O$_2$, H$_2$O, and CO$_2$ concentrations, involved in the growth of the metal-oxide nanowires and their resultant morphology, is far from well known. Here, the quasi-1D counter-flow diffusion flame would be especially advantageous if utilized to probe local conditions using a suitable metal probe on which metal-oxide nanowires can grow depending on the location of insertion into the flame structure. See Fig. 1. Knowing the gas-phase temperature and relevant species concentrations at the probed location, along with pyrometry determining the

substrate temperature, growth conditions can be correlated with as-synthesized morphology as revealed by ex-situ characterization. Moreover, different locations in the flame structure can be probed (e.g., fuel-side of the reaction zone versus air-side of the reaction zone) which have the same gas-phase temperature (e.g., both at 1720 K) but very different species concentrations. In this way, it becomes possible to compare the gas-phase growth conditions between oxygen-excess air-side and carbon/hydrogen-rich fuel-side at the same temperature. Moreover, by comparing a hydrogen (H$_2$) flame with a methane (CH$_4$) flame with approximately the same temperature profile, the difference between the H$_2$O and CO$_2$ oxidation routes of the metal substrate can be assessed, as only H$_2$O exists with no CO$_2$ in the hydrogen flame structure. The synthesis of tungsten-oxide nanowires is specifically investigated in this work, although the procedure may be applied for understanding of growth mechanisms in the synthesis of other metal-oxide or carbon-based nanostructures.

2. Experiment

As shown in the schematic of experimental setup, Fig. 1a, a quasi-1D counter-flow diffusion flame is utilized to grow tungsten-oxide nanowires directly on the surface of a tungsten substrate probe (purity of 99.95% and diameter of 0.5 mm). The probe serves as both the metal source as well as the depositing substrate; the detailed description can be found in Ref. [32]. Briefly, two separate diffusion flames with air as oxidizer are utilized in this work, i.e., CH$_4$ diffusion flame (nitrogen-diluted CH$_4$ as the fuel, 50% N$_2$/50% CH$_4$) and H$_2$ diffusion flame (nitrogen-diluted hydrogen as the fuel, 63.5% N$_2$/36.5% H$_2$). The tungsten substrate probe is inserted into the flame structure at various axial locations, z, which is referenced from the edge of the bottom burner's outlet nozzle. Since the quasi-1D flame is aerodynamically well defined, the experimental flame structure can be simulated and verified with detailed chemical kinetics and transport using GRI-Mech 1.2 [33]. As shown in Fig. 1b, the CH$_4$ and H$_2$ diffusion flames are purposefully constructed with approximately the same temperature profile to compare the effects of CO$_2$ route versus H$_2$O route on the oxidation and growth of tungsten oxide nanowires. From insets of Fig. 1b, the tungsten probe can be radially-inserted at either fuel-side or air-side of the flame reaction zone, but can still experience the same gas-phase temperature because of the symmetry of the diffusion flame structure. For example, the temperature is 1720 K at both $z = 0.74$ cm and $z = 0.88$ cm. After 10 min, the tungsten probe