Synthesis of Niobium Pentoxide Micro/Nanorods in a Counter-Flow Flame

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The rapid and catalyst-free flame synthesis of $\alpha$-Nb$_2$O$_5$ micro/nanorods is reported. The synthesis is performed using 1mm diameter Nb probes (~99.9 purity) as a metal source inserted in the oxygen-rich zone of a counter-flow flame. The fuel stream (96%CH$_4$ + 4%C$_2$H$_2$) flows from the top nozzle and the oxidizer stream (50%O$_2$ + 50%N$_2$) to the bottom nozzle. Probes were introduced radially into the flame parallel to the nozzles’ planes. The Nb probes were inserted at two different heights of $Z=12$ mm and $Z=13$ mm. $Z$ represents the distance between the fuel (top) nozzle and the center of the probe. Niobium oxide structures grow nearly instantaneously forming a white semi-oval layer of material surrounding the surface of the Nb probe. The morphology of the oxide layer strongly depends on the position of the probe inside the flame (temperature and oxygen content). At $Z=12$ mm the Nb oxide layer is composed of coalesced microrods with a diameter of ~ 1µm. At $Z=13$ mm the formed Nb oxide layer is composed of individual and coalesced micro/nanorods with diameters ranging from 50 nm to 1 µm. The HR-TEM and SAED images reveal that grown nano/microrods are highly crystallized, monoclinic crystals with growth direction of [110]. The growth mechanism is discussed.

1. Introduction

Flame synthesis methods are broadly employed in manufacturing of commercial nanoparticles such as carbon blacks, fumed silica, and optical fibers (Kammler et al. 2001). Efficient flame synthesis of several types of nano- and micro-materials including fullerenes (Howard et al. 1991), multi- and single-walled carbon nanotubes (Li et al. 2007), carbon diamond nanocrystals (Shenderova et al. 2002; Vander Wal 2000), and other nanomaterials such as metal oxides (Merchan-Merchan and Farmahini Farahani 2013; Xu et al. 2006; Xu et al. 2007; Rao and Zheng 2011; Merchan-Merchan et al. 2011), has been recently reported. Research interest in the flame synthesis is shifting to the synthesis of one-dimensional (1D) and three-dimensional (3D) transition metal nano/microstructures that exhibit unique physical and electronic properties.

Transition metal oxide (TMOs) structures have received significant attention due to their promising properties and applications. Among TMOs, niobium-oxide micro/nanostructures have wide applications in areas such as sensors (Arshak et al. 2008), solar cells (Aegerter et al. 2001), ferroelectric compounds (Uekawa et al. 2003), capacitors (Kim et al. 2005), lithium-ion batteries (Viet et al. 2010), optic glasses (Lin et al. 2003; Lai et al. 2005), catalysts (Paulis et al. 1999), electron emitters (Varghese et al. 2008) and electrochromic devices (Avellaneda et al. 1998). The Nb$_2$O$_5$ compound exhibits higher chemical stability and corrosion resistance than other niobium oxides. Different applications require different dimensionalities and structures. For instance, enlargement of surface area is favorable for catalyst activity and charge capacity (Lim et al. 2012), high length-to-width aspect ratio is favorable in polymer technology (Viswanathamurthi et al. 2003), highly ordered porous structures with controllable pore size and high aspect ratio have gained significant interest for various nano-bioapplications (Choi et al. 2007), and semiconductors with wider bag gap are the more favored options for electrochemical devices (Hara et al. 2000).
Since niobium oxides show favorable characteristics many research groups have employed various methods to fabricate niobium oxide nanostructures. For instance, the sol-gel method (Aegerter 2001; Avellaneda et al. 1998), magnetron sputtering (Lai et al. 2005), chemical vapor deposition (CVD) (O'Neill et al. 2003), anodization (Karlinsey 2005; Lim et al. 2012), plasma (Mozetič et al. 2005; Cevelar and Mozetič 2007) and pulse laser decomposition (Gimon-Kinsel and Jr. 1999) have all been used to synthesize and control the morphologies and properties of niobium oxides. Compared to other currently employed methods, flame synthesis is a single-step process with no need for catalysts resulting in rapid and inexpensive growth of micro/nanomaterials. Therefore, this method is a unique and cost effective synthesis technique.

In recent years research efforts in the area of flame synthesis of Nb oxide and related nanostructures have been focused on the type of catalyst and method of delivery into the flame medium in order to increase the rate of growth. The techniques of flame spray pyrolysis and vapor-fed to deliver the catalytic particles and source of the metallic material into the flame volume has also been studied. Additionally, the application of various flame types including premixed, diffusion, and inverse diffusion for the synthesis of Nb oxide and related structures has been studied (Guenin et al. 1988; Kachelmyer et al. 1995; Phanichphant et al. 2011).

In this paper, the synthesis of niobium pentoxide (Nb$_2$O$_5$) nano/micro structures in the counter-flow flame is discussed for the first time. The growth process of Nb$_2$O$_5$ requires a very brief process, lasting only a few minutes. A one-millimeter diameter high purity niobium probe introduced in the oxygen-rich part of the flame serves as the material source. Individual and coalesced micro/nanorods are rapidly formed on both sides (fuel and oxygen) of the Nb wire. Grown structures on each side have different morphologies, however, they grow based on the same growth mechanism. The morphology of the grown Nb oxide structures on the surface of the probe significantly depends on the flame height. The characterization of a strong axial gradient of both temperature and chemical species of the flame leads to formed nanomaterials with a morphology alteration. Nb$_2$O$_5$ structures grow through a basal growth mechanism due to the constant flow of oxygen onto the surface of the niobium metal. During the growth process highly dense adjacent nanorods tend to coalesce and form micro/nanorods. The flame temperature is sufficiently high to transform grown rods to monoclinic $\alpha$-Nb$_2$O$_5$. Scanning electron microscopy (SEM), transmission electron microscopy (TEM), high resolution TEM, selected area electron diffraction (SAED) pattern imaging, and X-ray diffraction (XRD) are employed to analyze grown structures.

2. Methods

Two opposite impinging streams of gases form a stable counter-flow flame. A diffusion flame with a stable stagnation plane on the fuel side is established. The fuel (96%CH$_4$ + 4%C$_2$H$_2$) is introduced from the top nozzle and the oxidizer (50%O$_2$ + 50%N$_2$) is supplied from the bottom nozzle (Fig. 1a). The top and bottom nozzles are separated by a constant distance of 25.4 mm (one inch). The experiments were conducted with constant fuel and oxidizer strain rates equal to 20 s$^{-1}$. The addition of acetylene (C$_2$H$_2$) in the fuel stream increases the flame temperature and affects growth of metal-oxide structures. The flows of gases are controlled with electronic mass flow meters providing accuracy within 1.5%. Niobium wires, with a purity of ~99.99% (Sigma Aldrich Corporation) and diameter of 1 mm, were introduced in the flame parallel to the nozzles’ planes. The variable Z height represents the distance from the edge of the fuel nozzle to the center of the Nb probe (Fig. 1a). The counter-flow flame is characterized by a high temperature gradient and rapid changes in concentration of combustion species (Fig. 1b) (Silvestrini et al. 2005). The Niobium probe was introduced in the flame at two axial position of Z=12 mm and Z=13 mm. At Z=12 mm temperature is approximately 2500°C and oxygen content is 0.015 mole, and at Z=13 temperature is approximately 2300°C and oxygen content of 0.1 mole.

In order to prepare samples for TEM analysis the synthesized structures were mechanically removed from the probe and mixed with methanol. The mixture was sonicated for a few minutes. The suspension fluid from the sonicated mixture was placed on a TEM copper-substrate/carbon film grid and dried. Further discussion of the experimental setup can be found in our previous reports on counter-flow flame synthesis of carbon and metal oxide nanostructures (Merchan-Merchan and Farmahini Farahani 2013; Merchan-Merchan et al. 2012; Merchan-Merchan et al. 2003).
3. Results and Discussion

The flame generated by the counter-flow burner is characterized by strong axial gradients of 2000 K/cm, consequently the probe position in the flame significantly affects the synthesis processes. Z represents the distance from the edge of the fuel nozzle to the center of the probe.

3.1. Structure at different positions in the flame volume

Figure 2a shows as-grown individual nanorods formed on the oxidizer side of the Nb probe at Z=12 mm. The nanorods have diameters of ~50-200 nm with height of more than 2 µm. The nanorods do not have uniform diameters as they taper towards the tip. Nanorods grow in different directions from the surface of the probe. In figure 2a the solid arrows point out a typical nanorod with variable diameter along the central rod axial axis. The flame temperature at Z=12 mm is ~2500°C and the surface of the niobium oxide layer appears to be covered with melted structures as highlighted by the dashed arrows in figure 2a. Besides the high flame temperature, exothermic reactions might occur over the formed rods and thus increasing their overall surface temperature. It has been shown that reactions such as surface quenching and radical recombination contribute to an increase in temperature over the surface of rods (Lin et al. 2011; Hsu et al. 2007) and result in the appearance of melted-like materials. Due to the high melting point of niobium (~2500°C) and Nb oxides (NbO: 1940°C, NbO$_2$:1900°C, and Nb$_2$O$_5$:1520°C), the possibility that the metallic probe could form vapors is eliminated. It is important to note that the temperature of the 1-mm probe used for Nb-oxide nanostructure synthesis is always much lower than the local flame temperature due to the radiant and conductive heat losses. Therefore, the growth mechanism of vapor-liquid-solid (VLS) or vapor-solid (VS) process does not apply here. Instead the rods grow by means of the basal attachment of Nb and O.

Individual and coalesced nano/microrods grown on the surface of the probe inserted in the flame volume at Z=13 mm are shown in Fig. 2b. The grown rod-like structures have different size diameters ranging from ~ 50 nm to 1 µm. A close inspection of the thicker structures using TEM reveals that they are formed of various rod-like structures. It is also interesting to note that the diameters of selected individual nanorods (dashed arrows) closely approach those forming the microbundles (solid arrows). It appears that the microrods are formed by a coalescence of individual nanorods.
Close inspection of the grown structures at Z=13 mm shows a lack of the characteristics of melted-like material on their surfaces. This can be attributed to the lower temperature of the flame at Z=13 mm (~200°C lower than Z=12 mm). However, a strong flame temperature and oxygen concentration gradients are still present at this flame position and promote the growth of highly dense structures on the oxidizer side surface of the probe. Furthermore, structures grown at Z=13 mm have high aspect ratio which can be attributed to a higher oxygen concentration present at this flame position. Mozetic et al. (Mozetič et al. 2005) found that growth of the Nb oxide depends on oxygen concentration. Their study demonstrates that structures grown in low oxygen concentration are thicker in diameter. The counter-flow flame provides oxygen content of ~0.015 mole and 0.1 mole at Z=12 mm and Z=13 mm, respectively. Similar to Mozetic’s findings, our results also demonstrate thicker rods at lower oxygen concentration. Morphologies of the grown structures vary by the probe position inside the flame volume. Variation of TMO morphologies based on the probe flame positions and growth locations on the surface of probes were investigated by previous studies and have been confirmed (Merchan-Merchan et al. 2009a; Merchan-Merchan et al. 2011; Merchan-Merchan et al. 2006; Merchan-Merchan et al. 2009b). In this study, Nb$_2$O$_5$ rods grown on the oxidizer side have smaller diameters and a higher growth rate; structures grown in a flame region closer to the flame front (Z height) have sharper tips. Furthermore, structures grown at higher temperature (Z=12 mm) show melted-like morphology. Temperature and oxygen content difference at Z=12 and 13 mm is 200°C and 0.085 mole, respectively. The study of the characteristics of the grown structures suggests the higher oxygen concentration results in higher growth rate and thinner rods.

### 3.2. Characterization of grown structures

High resolution TEM, selected area electron diffraction pattern (SAED), and X-ray diffraction analysis (XRD) were employed to characterize the flame formed structures. Figure 3a represents a TEM image of nanorods with diameter of ~120 nm. The HR-TEM images (Fig. 3b) reveal highly crystallized structures and lattice fringes of 0.37 nm which closely correspond to \{110\} plane spacing. Figure 3c exhibits SAED pattern of a selected area in one of the nanorods in Fig. 3a. It reveals that the formed rods are single crystalline and free of crystal dislocation and defect. Additionally, the SAED pattern shows the rods are composed of crystalline monoclinic with growth direction of [110]. The X-Ray Diffraction analysis (Rigaku Ultima IV X-ray Diffractometer, CuKα 40 kV) was used to identify the crystalline structures and elemental ratio of the products (Fig. 3d). The main crystal structure closely correlates with α-Nb$_2$O$_5$ (PDF# 00-0371-1468) with monoclinic structure. Bansal (Bansal 1993) reported that Nb$_2$O$_5$ heated over 1000°C irreversibly transforms to monoclinic α-Nb$_2$O$_5$. In the same work it was explained that α-Nb$_2$O$_5$ has a white color appearance very much coinciding with the color of our synthesized Nb oxide materials.

The synthesized rods have average length of ~10 µm and 20 µm at Z=12 mm and Z=13 mm, respectively. Figure 3e depicts the size distribution of diameter of the synthesized rods at Z=12 mm and Z=13 mm. It can be
interpreted that most of grown rods have diameters in the range of 200 to 800 nm. Also, the histogram reveals that grown rods at lower Z have thicker diameter. Considering length of grown rods, it can be concluded that grown rods at Z=13 mm have higher length-to-diameter aspect ratio.

Figure 3- (a) TEM image of a typical rod forming the Nb oxide layer synthesized in the flame; (b) HR-TEM image and of the highlighted section of the rod in (a); (c) SAED image of the highlighted section of the rod in (a); (d) XRD spectrum of synthesized niobium oxide layer closely corresponding to α-Nb$_2$O$_5$; (e) size distribution histogram of diameter of the rods at different Z heights.

3.2. Growth mechanism

Figure 4 schematically shows the growth process of Nb oxide nano/microrod on the surface of a Nb probe. Here the oxygen flux is supplied from the formed flame and the only supply of a metal source is the niobium probe. The metal oxide layer is instantly formed by introducing a niobium probe in the oxygen-rich part of the flame. The solids forming the layer have a white appearance. The continuous flux of O atoms causes supersaturation of the surface and leads to formation of an amorphous oxide layer, Fig. 4a.

As the probe/flame interaction time increases the supersaturation of the Nb surface causes spontaneous nucleation of niobium oxide crystals and crystallization of the amorphous layer, Fig. 4b. A few rod-like structures protrude from the amorphous metal oxide layer. Formations of an amorphous Nb oxide layer and its crystallization have been widely reported in the literature (Lin et al. 2011). The Nb oxide structures are able to grow due to the constant flow of oxygen onto the niobium metal and its surface. A significant change in the surface morphology of the grown layer is observed by increasing the probe-flame interaction time to 20 seconds, Fig. 4c. The density and size (diameter and length) of the Nb oxide structures increases significantly as the probe residence time inside the flame volume increases. The Nb oxide crystals grow in random directions by means of the basal attachment of Nb and O (basal growth), Fig. 4c.
As the exposure time of the probe-flame interaction was allowed to progress to 70 seconds, the morphology and physical characteristics of the Nb oxide layer significantly change (Fig. 4d). The Nb oxide layer is composed of a high density of structures that are closely packed. The nano/micro rods are several micrometers in length. Synthesis of niobium oxide at high temperature leads to transformation of all polymorphs to $\alpha$-Nb$_2$O$_5$. A similar growth process was observed in cold plasma treatment using a high neutral oxygen flux (Mozetič et al. 2005). The growth mechanism of the synthesis of the Nb oxide structures appears to involve several steps: 1) dissolution and diffusion of oxygen and oxygen radicals from the flame into the surface of the Nb probe forming a thin Nb oxide layer surrounding the surface of the probe; 2) nucleation of niobium oxide rods on the wire surface; 3) basal growth of nanorods; and 4) coalescence of nanorods which leads to formation of larger sized structures (bundles of nanorods).

Figure 4- Gradual growth of Nb$_2$O$_5$ rods; (a) It appears that for an almost instant probe-flame interaction (~ 2 sec.) a thin amorphous Nb oxide layer is already formed by diffusion and dissolution of atomic oxygen onto surface of the Nb probe; (b) nucleation of Nb$_2$O$_5$ on the surface of the Nb probe (~5 sec.); (c) growth of Nb$_2$O$_5$ nuclei into nanorods due to base attachment of Nb and O (~20 sec.); (d) coalescence of the nanorods (~70 seconds). The probe is inserted at Z =12 mm inside the flame volume.

4. Conclusions

A counter-flow flame is utilized for the rapid synthesis of the $\alpha$-Nb$_2$O$_5$ nano/micro sized structures. Niobium probes, with diameter of 1 mm and purity of ~99.99%, were inserted in the flame parallel to the nozzles’ planes. The introduction of a niobium probe inside the flame volume results in the formation of an oxide layer (white colored) coating the surface of the probe. The surface morphology of the oxide layer strongly depends on the flame position. At Z=12 mm the Nb oxide layer is composed of coalesced microrods with a diameter of ~ 1µm. At Z=13 mm metal oxide layers composed of individual and coalesced micro/nanorods with diameters ranging from 50 nm to 1µm were formed. The study of the characteristics of the grown structures suggests the higher oxygen concentration results in higher growth rate and thinner rods. In addition, the formed structures are composed of $\alpha$-Nb$_2$O$_5$ with the monoclinic structure. The growth mechanism proposes that crystallization consists of four steps: 1- diffusion of oxygen from flame into niobium surface; 2- nucleation of niobium oxide on the wire surface; 3- basal growth of nanorods; and 4- coalescence of nanorods and formation of larger sized structures (bundles of nanorods).

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References


