Novel Flame-Gradient Method for Synthesis of Metal Oxide Nanomaterials

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ABSTRACT

The formation of 1-D and 3-D transition metal oxide nanostructures on molybdenum, iron, and tungsten probes inserted in a counterflow flame is studied experimentally. The unique thermal profile and chemical composition of the generated flame tends to convert almost pure bulk (99.9%) transition metal materials into 1-D and 3-D architectures. The synthesized Mo, Fe, and W oxide structures exhibit unique morphological characteristics. The application of Mo probes results in the formation of micron size hollow and solid Mo-oxide channels. The use of W probes results in the synthesis of 1-D carbon-oxide nanowires. The formation of iron-oxide nanorods is observed on iron probes.

Keywords: Transition Metal Oxides, Nanostructures, Combustion Synthesis, Electron Microscopy

1   INTRODUCTION

Flames have been successfully employed for growth of a variety of nano- and micro-materials such as fullerenes [1-3], carbon nanotubes [4-6], carbon whiskers, diamond crystals and other nanomaterials such as carbides and oxides of various metals [7-10]. In recent years, much effort has been devoted to the study of transition metal oxides and related materials. Through the simple conversion of transition metals to metal oxides, chemical, mechanical, and electronic properties are greatly enhanced. A variety of uses facilitates the development of novel synthesis methods for the generation of unique 1-D and 3-D transition metal oxides and related materials with desirable structure, chemical activity, and physical properties.

It has been shown that molybdenum oxides possess unique catalytic and electronic properties and have potential applications in chemical synthesis, petroleum refining, recording media and sensors [11-13]. For catalytic applications several techniques have been developed to synthesize nanodispersed molybdenum oxides directly on alumina and silica support surfaces [11]. A number of studies have been devoted to the growth of MoO_2 nanoparticles and wires on various substrates. For instance, Zhou and co-workers [14] have reported the formation of MoO_2 nanowire arrays formed by employing a high temperature heating process in a restricted vacuum chamber.

Iron oxides are widespread in nature and can be synthesized and structurally modified in the laboratory with controllable shapes and sizes for a variety of applications in electronics, medicine, chemistry, and biology [15]. Recently, much attention has been given to the controlled synthesis of one-dimensional iron oxide nanostructures [16-18] such as nanowires and nanorods. These materials have wide potential applications as catalysts, pigments, sensors, ferro fluids, magnetic recording and imaging materials. Fe-oxide nanorods, nanowires, and nanotubes have been synthesized by various methods, including aqueous chemistry, deposition in aluminum and silicon oxide templates, and pulsed laser deposition [19].

Recent reports announce that tungsten oxide materials are of great significance as important components. Their importance stems from the fact that they possess unique photocatalyst, electrochromic, gaschromic, and opto-chromic properties. Materials with these properties are key components in information displays, sensor devices, and "smart" windows [20]. Tungsten oxide possesses the interesting property of electrochromism, a permanent, reversible color change upon the application of electrical fields. Structures with a pointy and elongated characteristic such as nanotubes, nanorods, and micro-rods are considered to be excellent field emission electron sources, chiefly due to their high aspect ratio defined by the natural geometry of the one-dimensional structures.

Different methods have been employed for the synthesis of tungsten oxide structures that can be produced with a variety of shapes and morphologies, including nanorods, whiskers, films, nanowires, or selectively modified structures such as nanowire networks [20-22]. The fascinating properties of transition oxide materials have fostered the development of new growth methods and lead to the discovery of new potential applications. In this paper we report the studies on l flame-gradient synthesis of metal oxide nanomaterials.

2   EXPERIMENTAL SETUP

Figure 1 shows the experimental setup used in the present study. A counter-flow burner forms two opposite streams of gases; the fuel (methane seeded with 4% of acetylene) is supplied from the top nozzle and the oxidizer

(50% O_2+50%N_2) is introduced from the bottom nozzle. The top and bottom nozzles have inside diameters of 40 mm. A detailed description of the burner is given by Beltrame et al. [23]. The experiments were conducted with constant fuel and oxidizer velocities and a strain rate equal to $20s^{-1}$.
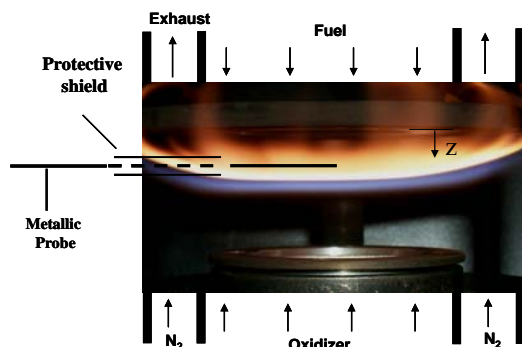

Fig. 1. Schematic of the experimental setup.

Transition metal probes of high purity such as iron, molybdenum, and tungsten were introduced through the flame-protecting shield into the flame medium. The position of the probe in the flame was measured in millimeters from the top nozzle and is denoted as the variable Z. Transmission Electron Microscope (TEM), Scanning Electron Microscope (SEM), X-ray energy dispersive spectroscopy (EDS), and Selected area electron diffraction pattern (SAED) microscopy were employed to characterize the structural and elemental composition of the synthesized structures.

3 RESULTS AND DISCUSSION

Transition metal probes of various types were tested for the bulk conversion of metals into 1-D and 3-D metal-oxide structures through an applied probe flame interaction. The synthesis results are expected to be affected by two main factors: (i) structural and thermal properties of the tested probes, (ii) the strong axial gradient of temperature and chemical species concentrations of the counterflow flame.

3.1 Synthesis of 3-D Mo-Oxide Channels

The introduction of a 1-mm Mo probe in the flame medium resulted in the formation of unique 3-D micron-sized structures. The 1.0 mm diameter molybdenum probe was exposed to the flame at a height of Z=11 mm. Performed SEM analysis revealed that the surface of the probe is covered with densely packed micron-size structures in the form of cubic whiskers with hollow rectangular shaped channels (Fig. 2). High resolution SEM of the flame exposed molybdenum probe showed that the formed structures are slender, prismatic, four-faced structures, and completely hollow with very large inside

cavities devoid of other materials (Fig. 2a and insert). The unique morphology with large cavities, nano-thick walls, sharp edges and high specific surface area gives the structure a significant importance, for example, in medical applications. The large cavities can also be used for a wide variety of applications such as the storage of fluids or nanoparticles, material reinforcements, or as a component in the fabrication of MEMs devices, etc.
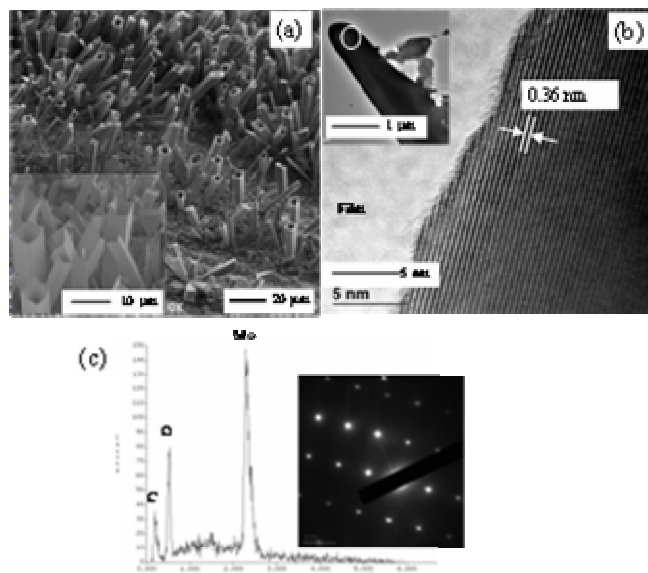

Figure 2. Molybdenum oxide hollow channels: (a) SEM image of the as-synthesized microstructures; (b) HR-TEM image showing highly ordered crystalline lattice (from circled area in insert); (c) EDS analysis results and diffraction pattern.

TEM imaging and high resolution TEM imaging were performed on the molybdenum oxide structures for further characterization and analysis. For TEM studies, the deposits were removed from the probe and dispersed on a TEM grid using methanol. High resolution TEM was employed to characterize the structure of the Mo based micro-channels. HR-TEM employed on the grown structures reveals the structural uniformity and highly ordered crystalline structure, as shown in Fig. 2(b).

It can also be observed that the wall of the rectangular whisker is free of dislocations and structural defects. A lattice spacing of 0.36 nm was measured; it corresponds to ($\bar{1}11$) plane of a monoclinic MoO_2 cell. SAED pattern in Fig. 2(c) confirms the high degree of crystallinity of the material by showing a regular pattern of diffraction spots.

EDS analysis performed on the molybdenum oxide structures (Fig. 2c) show the presence of molybdenum, oxygen, and carbon. The carbon readings are attributed to the carbon tape used to hold the probe in place, and the presence of molybdenum and oxygen further confirms that the material is, in fact, an oxide of molybdenum.

3.2 Synthesis of Fe-Oxide Rod Structures

Iron has a moderate melting temperature the same cubic crystal structure as Mo and W. The introduction of iron probes in the flame medium resulted in the formation of a thin layer of material coating on the upper surface of the probe, as shown in Fig. 3(a).
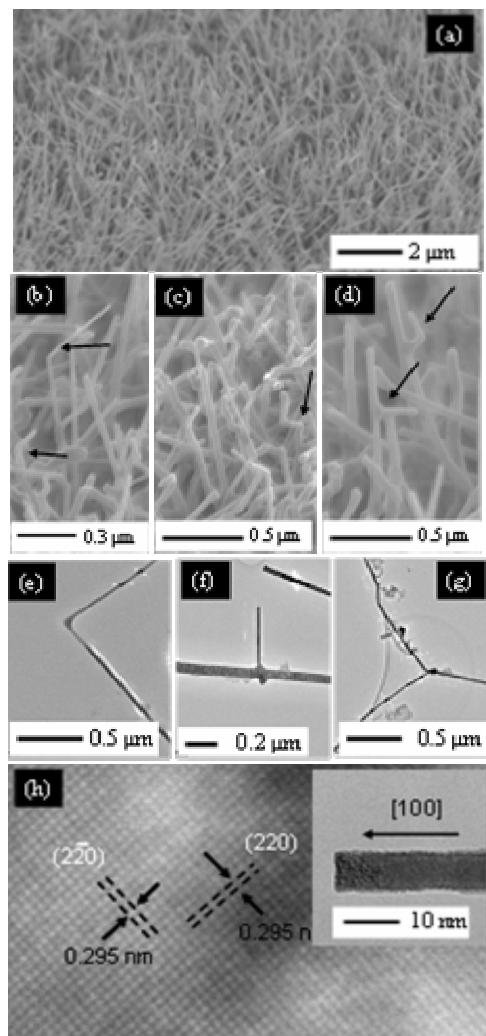

Figure 3. Iron oxide nanorods: (a-d) SEM image of as-synthesized nanorods with bending and branching phenomena highlighted with black and white circles, respectively; (e-g) TEM images further illustrating bending and branching; (h) high magnification TEM image showing highly ordered crystalline lattice.

Figure 3(a) represents a SEM image collected on the surface of a 1–mm diameter Fe probe exposed to the flame at a height of Z = 12.0 mm. The formed coat had a characteristic brownish color typical for iron oxide deposits. Higher resolution SEM imaging analysis revealed that the materials formed are composed of elongated 1-D

nanostructures characterized by high aspect ratios (Fig. 3b-d). The diameters of the iron oxide nanorods vary from 10 to 100 nm with a typical length of a few microns. It can be observed from the SEM analysis that among the straight and uniform iron oxide structures, nanostructures with complex morphologies are also synthesized. The bending phenomena present in the structures are highlighted by the arrow in Fig. 3(b). Some of the structures also appear to be branched out in T- and Y-shapes, Figs. 3(b-c). In the area of nanomaterials, the modified "branched" and "bent" structures are excellent candidates for fabricating composite materials with enhanced mechanical or electronic properties due to the formation of a network-like phase within the matrix. TEM and high resolution TEM was applied in order to provide further insights into the structure, composition and morphology of the synthesized iron based nanorods. Representative TEM images of an iron oxide nanorod are shown in Fig. 3(e-h). TEM images of angled and branched iron oxide nanomaterials are shown in Figs. 3(e-g). These structurally modified structures possess the same ordered crystalline structure as the straight structures. The joints in the modified structures occur abruptly, followed within a few nanometers of the joint in either direction by a uniform, one-dimensional structure. The occurrence of the branching and bending structures increases with probe locations closer to the flame front. It is possible that bending and branching of nanowires is caused by minute temperature and flow velocity fluctuations. The highly ordered crystalline lattice of this nanorod obtained at higher magnification is displayed in Fig. 3(h). Two symmetric systems of crystallographic planes each forming an angle of 45° with the nanorod axis can be clearly observed. The crystalline structure has a characteristic lattice spacing of ~0.295 nm and can be correlated with the {220} interplanar spacing of cubic magnetite (Fe_3O_4).

3.3 Synthesis of 1-D W-Oxide Nanowires

Molybdenum and tungsten are hard, strong metals with a very high melting point. Despite these similarities these metals in the form of oxide structures exhibited quite distinct morphologies. The introduction of 1-mm probes made of W in the flame medium resulted in the formation of a unique 1-D type nanostructure, Fig. 4. The formed nanostructures have a rod-like shape with high aspect ratios. The structural characteristics of the nanowires grown on the 1-mm diameter probe are that they are up to 50 μm in length with diameters ranging from 10 to 100 nm. These structures are ideal candidates for gas sensing and electron emitter devices.

TEM and HR-TEM performed on the grown structures of the tungsten probe revealed structural uniformity and highly ordered 1-D tungsten based nanowires. High resolution TEM imaging of a selected nanowire revealed that the "core" inner dark material is a metal oxide sheathed by a "coat" layer of carbon material as shown in Fig. 4(b). TEM showed that the grown structures are essentially

nanowires. High resolution TEM of the nanowires shows that the "coat" is composed of a sheath of layered material with a planar spacing of 0.34 nm resembling the characteristics of graphite. High resolution TEM imaging of the inner "core" dark area shows the high degree of crystallinity present in the core of the nanowire. The inner metal oxide material has a lattice spacing of 0.38 nm that corresponds to (002) plane of a monoclinic WO_3.
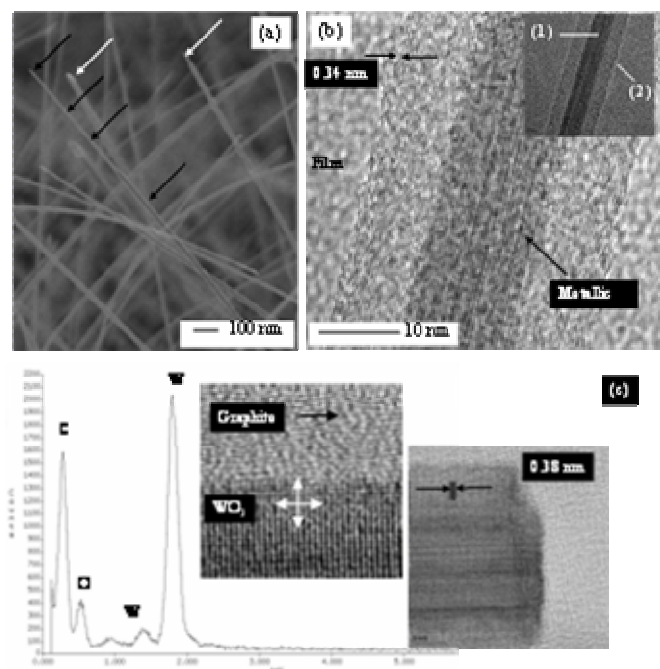

Figure 4. SEM images of tungsten-oxide nanorod layer formed on the surface of the tungsten probe: (a) low resolution SEM showing high density of the layer, (b) high resolution TEM image showing straight uniform nanorods composed of two types of materials, (c) EDS analysis conducted on the nanorods.

Conclusions

Herein we report the formation of molybdenum, iron, and tungsten oxide nanostructures with unique structural morphologies using the novel flame gradient synthesis method.

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