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ScienceDirect
Proceedings of the Combustion Institute 33 (2011) 1883–1890
Proceedings of the Combustion Institute
www.elsevier.com/locate/proci

Synthesis of tailored WO_3 and WO_x ($2.9 < x < 3$) nanoparticles by adjusting the combustion conditions in a $H_2/O_2/Ar$ premixed flame reactor

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Abstract

Flame synthesis of WO_3 and WO_x ($2.9 < x < 3$) nanoparticles is carried out by adding a dilute concentration of WF_6 as precursor in a low-pressure $H_2/O_2/Ar$ premixed flame reactor. The reactor is equipped with molecular-beam sampling and particle mass spectroscopy (PMS) to determine particle composition and sizes as a function of height above burner. Varying the H_2/O_2 ratio allowed us to tune the stoichiometry of the product. With a H_2/O_2 ratio of 0.67 white colored stoichiometric WO_3 is formed, whereas the H_2/O_2 ratio >0.8 yields blue colored non-stoichiometric WO_x ($2.9 < x < 3$) nanoparticles. The size of nanoparticles can be controlled by varying the residence time in the high-temperature zone of the reactor as observed by molecular-beam sampling with subsequent analysis using PMS. Transmission electron microscopy (TEM) images of as-synthesized nanoparticles show that particles are non-agglomerated and have an almost spherical morphology. The X-ray diffraction (XRD) pattern of the as-synthesized material indicates that the powders exhibit poor crystallinity, however, subsequent thermal annealing of the sample in air changes its structure from amorphous to crystalline phase. It is observed that particles with sub-stoichiometric composition (WO_x) show higher conductivity compared to the stoichiometric WO_3 sample.

Keywords: Premixed flame; Tungsten oxide; Nanoparticle synthesis; Particle size and morphology; Stoichiometry tuning

1. Introduction

Gas-phase combustion synthesis of nanoscale inorganic particles is very appealing because it provides materials with high purity, is cost efficient, and can be scaled up to industrial scale [1–4]. Different type of metal, metal oxides, and mixed oxides particles have been synthesized in flames [5–9]. Nanomaterials show different behavior from bulk material with the same chemical composition due to higher atom concentration on the surface, arising from increased surface-area-to-volume ratios. It is observed that the properties of nanomaterials depend on their size, morphology, crystallinity, and composition. Therefore, the properties of nanomaterials can be engineered by changing synthesis conditions

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doi:10.1016/j.proci.2010.06.162

such as temperature, pressure, residence time, precursor and the concentration of different species. The stoichiometry of some metal oxide particles can be controlled by varying the fuel/oxygen mixture in the flame [10] owing to the fact, that many metals show different oxidation states [11–13]. Metal oxide particle synthesized in flames can even exhibit several metastable crystal structures [14,15] depending on the temperature–time history during the synthesis.

Tungsten oxide is a very promising candidate for gas sensing applications with a good selectivity for sensing of ozone, air pollutants such as CO/CO_2, NO/NO_2 and ethanol [16–18]. It is also a promising material for the construction of humidity-insensitive sensors as it has a minor tendency only to form hydroxides. Thus, it overcomes one of the major disadvantages of conventional metal-oxide gas sensors [19]. The sensing behavior of WO_3 is a function of its physico-chemical properties such as surface area, crystallinity, stoichiometry, and phase composition. Tungsten oxide can also alter its optical properties in response to electrical fields and therefore can be used in solid oxide electrochromic windows [20]. It is also reported as a stable electrode material for use in photoelectrolysis [21,22]. The photoelectrolytic behavior of tungsten oxide depends on the oxidation states of tungsten. For example, Derrington et al. [23] reported that WO_x anodes show a photoelectric behavior that varies with x. Tungsten oxide nanoparticles and thin films are reported to be synthesized by a wide range of methods, such as sol–gel synthesis, chemical vapor deposition, rf-sputtering, and various precipitation techniques [24–28], but flame synthesis of tungsten oxide particles provides an unparalleled flexibility in comparison to other techniques. For the application fields mentioned above it is important to provide materials synthesis methods that allow to generate products with the desired properties.

In the present study, high purity tungsten oxide nanoparticles are synthesized in a premixed H_2/O_2/Ar flat flame with dilute concentrations of WF_6 as a carbon-free precursor. The H_2/O_2 ratio and the residence time for particle formation and growth are systematically modified to analyze their effect on the physical and chemical properties of the particles. The synthesized particles are characterized with particle mass spectrometry (PMS), X-ray diffraction (XRD), transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS), and impedance spectroscopy (IS).

2. Experimental

The experimental setup for the synthesis of flame-made tungsten-oxide nanoparticles is schematically shown in Fig. 1. The setup is divided into three segments that operate at different pressures. In the first segment, the combustion chamber, a water-cooled sintered-bronze burner head is used to stabilize the premixed H_2/O_2/Ar flame at 30 mbar. The burner head can be moved horizontally in order to vary the residence time of the particle-laden gas flow that is available for particle formation and growth before reaching the sampling location where a pneumatically assisted TEM sampling device is used for thermophoretic deposition of particles on TEM grids. At almost the same position a fixed sampling orifice transfers a continuous gas stream into the second segment, the expansion chamber, with a pressure of 10^{-4} to 10^{-3} mbar. A supersonic expansion into the low-pressure chamber reduces temperature and density of the particle-laden gas rapidly when entering this segment. Therefore, all chemical and physical processes that could further affect the particles stop immediately due to the rapid change to free-molecular conditions.

The center of the supersonic free jet is extracted by a 0.7 mm skimmer into the analysis chamber (10^{-6} mbar), resulting in a particle-laden molecular beam that contains charged and uncharged particles. In the particle mass spectrometer (PMS, c.f. Fig. 2) the beam is directed through an electric field between two parallel electrodes. Depending on their kinetic energy, the charged particles are separated by the electric field between the electrodes and the well-focused centered beam is converted into a fan. The current of the deflected charged particles is then measured with a Faraday cup at an off-axis position. The particles with different sizes are directed to the detector by varying the deflection voltage. The resulting current versus deflection voltage curve (Fig. 3) can be converted into a particle size distribution (Fig. 4) assuming that the material has bulk density. The PMS is used for the quasi-in-situ investigation of the particle size distribution, which is illustrated schematically in Fig. 2 and has been described in detail in [29].

In order to synthesize tungsten oxide nanoparticles, a lean, premixed low-pressure H_2/O_2/Ar flat flame is stabilized on a burner head by feeding the flame with WF_6 vapor (Air Liquide, 99% purity, 1% in argon). The concentration of WF_6 in the total gas mixture is kept constant at 524 ppm. All gas flows are controlled by mass flow controllers and mixed before passing through the burner matrix. The inlet gas velocity across the burner matrix is kept constant at 1.32 ms^{-1}, while the H_2/O_2 ratio is varied between 0.67 and 1.6 (equivalence ratio $\phi = 0.33$–0.8) with a total volumetric dilution of $Ar/(H_2 + O_2) = 0.51$ at a constant reactor pressure of 30 mbar. The distance between the movable burner head and a fixed sampling orifice was varied between 150 and 200 mm.

The effects of changing experimental parameters on the properties of the nanoparticles were analyzed with different methods. Quasi-in-situ