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Multiple-diffusion flame synthesis of pure anatase and carbon-coated titanium dioxide nanoparticles

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ABSTRACT

A multi-element diffusion flame burner (MEDB) is useful in the study of flame synthesis of nanomaterials. Here, the growth of pure anatase and carbon-coated titanium dioxide (TiO_2) using an MEDB is demonstrated. Hydrogen (H_2), oxygen (O_2), and argon (Ar) are utilized to establish the flame, whereas titanium tetraisopropoxide is used as the precursor for TiO_2. The nanoparticles are characterized using high-resolution transmission electron microscopy, with elemental mapping (of C, O, and Ti), X-ray diffraction, Raman spectroscopy, and thermogravimetric analysis. The growth of pure anatase TiO_2 nanoparticles occurs when Ar and H_2 are used as the precursor carrier gas, while the growth of carbon-coated nanoparticles ensues when Ar and ethylene (C_2H_4) are used as the precursor carrier gas. A uniform coating of 3–5 nm of carbon is observed around TiO_2 particles. The growth of highly crystalline TiO_2 nanoparticles is dependent on the gas flow rate of the precursor carrier and amorphous particles are observed at high flow rates. Carbon coating occurs only on crystalline nanoparticles, suggesting a possible growth mechanism of carbon-coated TiO_2 nanoparticles.

1. Introduction

Flame synthesis, a $15 billion/year industry [1], is a cost-effective manufacturing process for nanoparticles. Nanoparticles commonly produced using flames by industry leaders Cabot, Cristal Global, DuPont, and Evonik include carbon black, fumed SiO_2, and TiO_2 [2]. A key challenge facing the industry is that flame reactors are usually built for a single product, while the possibility of modifying the reactor's operational parameters, including temperature, the fuel-to-oxidizer ratio, and the precursor loading rate, is limited. These operational parameters play a critical role in the growth of nanoparticles [3,4]. It is, therefore, important to develop flame reactors that will allow for a wide range of growth parameters and that can be easily scaled, specifically for the production of advanced materials, particularly next-generation metal oxides [5–7].

One such development is the use of multiple-diffusion flames or commonly known as a multi-element diffusion flame burner (MEDB, Hencken Burner). It is comprised of an array of needle tubes [8] that can be used either for the delivery of a fuel (normal-diffusion) or an oxidizer (inverse-diffusion). A honeycomb is used to align the needle tubes, which are surrounded by open cells for the transport of an oxidizer (normal-diffusion) or fuel (inverse-diffusion). This configuration results in many small and tightly spaced diffusion flames. The use of an MEDB offers several key advantages. First, uniform temperature and chemical species profiles are obtained downstream from the flame, which is critical in controlling the growth of nanomaterials. Second, since the mixing of the fuel, oxidizer, and precursor occurs external to the burner, unwanted reactions occurring prior to the establishment of the flame are avoided. Third, by using diffusion flames, many of the limitations related to premixed flames such as flashback and flame speed are avoided. This enables the burner to operate under a wide range of fuel-rich or fuel-lean conditions. Last, the burner can be readily scaled for large-scale production of nanomaterials. For these reasons, the use of MEDB has attracted the attention of combustion synthesis researchers (Table 1).

Wooldridge et al. [8] first reported the growth of nanomaterials using an MEDB. Silica (SiO_2) nanoparticles were synthesized at various global equivalence ratios (0.47–2.16), with silane as the precursor. Detailed temperature measurements were made to show that the temperature profiles were uniform in the radial direction and at various heights above the burner. Hall et al. [9] reported the growth of metallic tin, tin monoxide (SnO), and tin dioxide (SnO_2) using tetramethyltin as the precursor. Miller et al. [10] and Bakrania et al. [11–14] expanded the work on SnO_2 by introducing several metal additives. Solid-phase metal acetates of gold (Au), aluminum (Al), copper (Cu), and palladium (Pd), were introduced as precursors to form various tin-based nanocomposites. Of

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Table 1
A list of nanomaterials that were synthesized using multiple-diffusion flames.

Author	Nanomaterial	Fuel/oxidizer/φ	Metal precursor or growth material	Nanomaterial type
Wooldridge et al. [8]	SiO_2	SiH_4, H_2, Ar/O_2, Ar/0.47–2.16	Silane	Particles
Hall et al. [9]	Sn, SnO, SnO_2	H_2/O_2, Ar	Tetramethyltin	Particles
Miller et al. [10] Bakrania et al. [11–14]	SnO_2 with Al, Au, Cu and Pd	H_2/O_2, Ar	Tetramethyltin, metal (Al, Au, Cu and Pd) acetates	Particles
Bumbalough et al. [15]	CeO_2	H_2/O_2, N_2/0.92–1.32	Cerium acetate hydrate	Particles
Rao and Zheng [16]	α-Fe_2O_3	CH_4, H_2/Air/0.4–1.2	Growth on iron wires and foils	Flakes
Rao and Zheng [18]	γ-Fe_2O_3	CH_4, H_2/Air/1.6	Vapor from a steel wire mesh	Wires
Rao and Zheng [16]	CuO	CH_4, H_2/Air	Growth on copper wires and foils	Needles
Rao and Zheng [17]	$W_{18}O_{49}$ and WO_3	CH_4, H_2/Air/0.9,1.6	Vapor from a tungsten wire mesh	Wires, tubes, belts, and cones
Cai et al. [19]	α-MoO_3	CH_4, H_2/Air/0.8–1.4	Vapor from a molybdenum wire mesh	Single, branched, and flower-like belt arrays
Memon et al. [20]	Carbon nanotube	C_2H_4, Ar/O_2,Ar	Growth on nickel/titanium substrates	Tubes
Memon et al. [20,21]	Few-layer graphene	H_2, CH_4, Ar/O_2, Ar/$\sim$3	Growth on copper, nickel, and cobalt foils	Film
This work	TiO_2 with carbon	H_2/O_2, Ar/0.5	Titanium tetraisopropoxide	Particles

particular interest was the Au/SnO_2 nanocomposite [14], which was used for CO gas sensing. Additionally, using the same experimental setup, Bumbalough et al. [15] demonstrated the growth of cerium dioxide (CeO_2) by using cerium acetate hydrate as the precursor.

In addition to nanoparticles from different chemical precursors, multiple-diffusion flames have been successfully used to grow nanomaterials directly on a substrate. Rao and Zheng [16] reported the growth of iron-oxide (α-Fe_2O_3) nanoflakes and copper-oxide (CuO) nanoneedles directly on iron and copper foils, respectively. The growth conditions for α-Fe_2O_3 were investigated over a wide range of global equivalence ratios (0.4–1.2) and temperatures (700–1000 °C). In addition to the direct growth of nanomaterials on a substrate, Rao and Zheng [17,18] also reported the growth of nanomaterials by placing various metal meshes above the burner as a precursor source. The vapor generated from these meshes was used to deposit nanomaterials on various substrates. The growth of tungsten oxide [17] ($W_{18}O_{49}$ and WO_3) nanostructures, including wires, tubes, belts, and cones, using this method was reported. The structure was found to be strongly dependent on the substrate and flame condition (lean vs. rich). Similarly, the growth of γ-Fe_2O_3 nanowires [18] was reported using a plain steel mesh as the precursor source, with the material deposited on a silicon wafer and iron foil. These flame-produced γ-Fe_2O_3 nanowires exhibited superior crystallinity and enhanced magnetic properties. Lastly, Cai et al. [19], using the same method, reported the growth of various molybdenum oxide (α-MoO_3) nanostructures, such as single, branched, and flower-like nanobelt arrays. A number of parameters, including temperature, equivalence ratio, and substrate, impacted the growth of the α-MoO_3 structures.

Typically, MEDB operates in a normal mode during where fuel flows through each tube and is surrounded by an oxidizer. However, this burner can also operate in an inverse configuration during which the oxidizer flows through the tube and is surrounded by fuel. Using the inverse configuration of multiple-diffusion flames, Memon et al. [20,21] demonstrated the growth of carbon nanomaterials. The growth of few-layer graphene (FLG) was demonstrated on copper, nickel, and cobalt foils, using hydrogen and methane as the fuel with an equivalence ratio of around 3. Additionally, the synthesis of carbon nanotubes (CNTs) [20] was reported using the same multiple inverse-diffusion flame setup.

In this work, multiple-diffusion flames were used to grow TiO_2 nanoparticles. TiO_2-based nanoparticles are interesting because of their possible applications in photocatalytic splitting of water [22], dye-sensitized solar cells [23], air/water purification [24], and catalyzing many chemical reactions [5]. The commonly observed phases of TiO_2 include the anatase and rutile phases. Rutile TiO_2 is widely produced in industry for pigment applications, while anatase TiO_2 is more photocatalytic.

A number of flame synthesis configurations have been used for the synthesis of TiO_2 nanoparticles, which have been summarized in Table 2. A co-flow diffusion flame [30] has been widely used for the growth of TiO_2 particles. Other burner configurations include: counterflow diffusion [28], premixed [38], premixed stagnation (atmospheric [33] and low pressure [34]), and swirl [41]. A variety of fuels have also been used at a wide range of temperatures. Commonly used precursors were titanium chloride ($TiCl_4$) and titanium tetraisopropoxide (TTIP). For collecting the particles, simple methods, such as placing a substrate downstream from the flame, to more complex methods, such as using a critical-flow nozzle [37] have been employed. The use of a substrate or nozzle has a quenching effect that can freeze particle growth [32,36,37,41]. The experimental setup, along with the various operating conditions, strongly influence the crystalline phase, morphology, and size of nanoparticles. Table 2 does not cover the use of flame spray pyrolysis (FSP) for TiO_2 production, which can be found in other papers [2,5].

When TiO_2 is coated with carbon, its photocatalytic efficiency is improved due to absorbance in the visible light range. Khan et al. [42] first reported the growth of carbon-modified TiO_2 (primarily in the rutile phase) by the combustion of Ti metal in natural gas. The flame temperature was held at 850 °C and the resulting photocatalyst exhibited increased efficiency for water splitting. Kammler and Pratsinis [43] reported the growth of TiO_2 coated with carbon using a diffusion flame with acetylene as the fuel and titanium tetraisopropoxide (TTIP) as the precursor. The particle surface area varied from 29 to 62 m^2/g and the rutile-phase content varied from 17 to 68 wt.%. Bhanwala et al. [40] reported the growth of carbon-coated TiO_2 using a laminar diffusion flame, with liquid petroleum gas (LPG) as the fuel and titanium chloride ($TiCl_4$) as the precursor. X-ray diffraction (XRD) results showed that the flow rate of LPG had a strong influence on the rutile-phase content (13.3–28.3 wt.%), surface area (19.8–38.8 m^2/g), and average particle size (48–93 nm). A number of methods that do not involve flame synthesis have also been used to prepare carbon-coated TiO_2 nanoparticles, one of them being placing commercially available TiO_2 particles with glucose and then heating them in a furnace at 800 °C [44]. However, a key advantage of a flame-based process is the one-step approach to producing both the TiO_2 nanoparticles and the carbon coating. The goal of this work is to investigate the growth of carbon-coated TiO_2 nanoparticles in the anatase phase by changing the precursor carrier gas in a MEDB.