ABSTRACT


Vanadium oxide nanostructures have been produced in a lot of variety including nanorods, nanowires, nanochannels, nanotubes, etc. They have been synthesized using hydrothermal, flame spray pyrolysis and other methods. However these methods are complicated and costly. A novel flame gradient method offers a simple and efficient approach with the capability of mass production with minimum contamination since precursors and dopants are not employed. The opposed flow oxygen enriched air-methane flame provides the high temperature chemically reactive environment that facilitates the synthesis of vanadium oxide nanostructures on the probe inserted in the flame. The material from the bottom part of the probe gets oxidized, ablated and vaporized in the flame environment and ultimately the vanadium oxide vapors crystallize on the upper part of the probe to form nanostructures. Morphology of the synthesized one-dimensional vanadium oxide nanostructures is controlled by careful manipulation of the governing parameters such as axial position of the probe inserted in the flame, flame composition, residence time and strain rate. The synthesized structures are observed under the compound microscope initially and later using a scanning electron microscope (SEM) for further intricate structural details. Energy dispersive X-ray spectroscopy (EDS) is performed in order to investigate the chemical composition of the synthesized structures. The formation of V₂O₅ microchannels, nanochips, nanowalls and nanowires is observed due to the variation of the governing parameters.
Opposed Flow Oxy-Fuel Diffusion Flame Synthesis of One-Dimensional Vanadium Oxide Nanostructures on Solid Support

by
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DEDICATION

This work is dedicated to my parents. Their love and constant support have been the strongest pillars helping me achieve my dreams.
BIOGRAPHY

The author was brought up in Mumbai, India. He completed his schooling and obtained the bachelor’s degree in Mechanical Engineering from Mumbai University, India. He developed strong interest in thermal science; especially towards combustion and heat transfer during his undergraduate studies. He later joined the Department of Mechanical and Aerospace Engineering at North Carolina State University, Raleigh to pursue his graduate studies.
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1. INTRODUCTION AND BACKGROUND

1.1 Metal oxide nanoparticles

Materials that have their dimensions of the order of nanometers are called nanomaterials. These materials have special properties owing to their nanoscale nature. Nanomaterials have a very high surface to volume ratio that gives rise to certain characteristic properties which are not exhibited when the material exists at macroscale. Metal oxide nanomaterials are oxides of metals existing at nanoscale dimensions. Metal oxide nanomaterials possess unique electric, magnetic, chemical, physical and optical properties [1]. They have potential applications in biological, chemical, opto-electric and semiconductor industries. These materials have been used in catalysis [2], gas sensors [3], electrodes of lithium-ion batteries [4], semiconductors [5], lasers [6] and also have several bio-medical applications [7-9]. Several methods have been employed for the synthesis of metal oxide nanostructures [6]; some of which are:

- chemical vapor deposition
- hydrothermal chemistry
- electrochemistry
- flame synthesis

The growth mechanisms for metal oxide nanomaterials are described primarily by three modes which are as follows [6]:

- vapor-liquid-solid (VLS)
- vapor-solid (VS)
- aqueous solution growth (ASG).
1.2 Flame synthesis of transition metal oxide nanoparticles

The synthesis of carbon nanostructures in flames has been extensively studied during the last two decades. This promoted the study of flames for the synthesis of transition metal oxide nanostructures. Both premixed and diffusion flames have been studied. In diffusion flames, the fuel and oxidizer diffuse into each other in the reaction zone producing the flame while fuel and oxidizer are mixed prior to their entry into the reaction zone in the case of premixed flames. Co-flow, inverse as well as counter flow configurations have been used in diffusion flames. In the co-flow and inverse flow configurations, the fuel and oxidizer flow in the same direction through concentric tubes. The difference is that in co-flow flames, the inner fuel flow is surrounded by oxidizer flow while in the inverse flow flames as the name suggests, the inner oxidizer flow is surrounded by the fuel flow. In the counter flow configuration, the fuel and oxidizer streams flow towards each other from opposite directions.

The flame aerosol process and the flame spray pyrolysis process are the two primary methods used for the flame synthesis of transition metal oxide nanoparticles. The main difference between these two methods is that the flame aerosol process includes gaseous delivery where the vaporized precursor is introduced in the flame, while in flame spray pyrolysis, atomized liquid precursor is sprayed into the flame. These methods along with plasma assisted flame synthesis approach have also been employed for the synthesis of one-dimensional nanostructures of transition metal oxides. The synthesized nanoparticles are thermophoretically collected and analyzed using transmission electron microscope (TEM) or are collected on substrates and analyzed using scanning electron microscope (SEM). Laser diagnostics are applied in some flame synthesis experiments to obtain the profiles of
temperature and chemical species. Table 1 provides examples of nanoparticles synthesized with premixed, co-flow and counter flow configurations.

Table 1. Summary of experimental studies of gas phase synthesis [10].

<table>
<thead>
<tr>
<th>Reactants</th>
<th>Particles Formed</th>
<th>Apparatus</th>
<th>Particle Retrieval Method</th>
<th>Particle Morphology</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Iron carbonyl/ hexamethyl-disiloxane/CH₄/O₂</td>
<td>Fe₂O₃</td>
<td>Premixed burner</td>
<td>Deposition directly on TEM grids</td>
<td>Fe₂O₃ encapsulated in SiO₂ spheres</td>
<td>[11]</td>
</tr>
<tr>
<td>TiCl₄/CH₄/ Ar/air</td>
<td>TiO₂</td>
<td>Co-flow diffusion burner</td>
<td>Deposit onto glass fiber filters</td>
<td>Agglomerates, primary particles ~11-105 nm</td>
<td>[12]</td>
</tr>
<tr>
<td>Al(CH₃)₃/CH₄/O₂/N₂</td>
<td>Al₂O₃</td>
<td>Counter flow diffusion flame</td>
<td>Deposition directly on TEM grids</td>
<td>Agglomerates, primary particles ~13-47 nm, sintered spheres ~ 20-60 nm</td>
<td>[13]</td>
</tr>
</tbody>
</table>

The advantages of flame synthesis over other methods are:

- The high temperature flame environment provides self-purity from microscopic organisms that can contaminate the particles during the experimentation.
- The flame itself provides the energy required to sustain the synthesis.
- In some cases the nanoparticles do not require any post processing like washing, etc which minimizes the waste.
- There is a great amount of flexibility offered in the gas phase synthesis that allows nanoparticle synthesis of about a few microns down to 10 nm.
• The apparatus is compact and not bulky.
• Time required for synthesis is greatly reduced
• The process is inexpensive.

1.2.1 Factors influencing the flame synthesis

Flame synthesis is influenced by flame temperature, residence time, reactant composition, reactant mixing and precursor additive among other factors. Flame temperature depends on burner geometry, reactant composition and reactant mixing. Increasing the oxygen supply promotes oxidation and increases flame temperature. The increase in temperature increases the precursor decomposition and sintering is also increased [10]. If the increase in temperature is coupled with higher residence time, larger primary particles are formed while lower residence time gives rise to agglomerates of smaller particles. Higher gas velocities influence turbulent mixing due to which the fuel consumption is increased. Diluents soak up the heat released due to combustion. Increasing the amount of diluents delivered reduces the flame temperature. As the flame temperature gets reduced, the particle growth rate decreases [10].

The flame temperature, reactant concentration and gas flow rate determine particle morphology and properties [10]. Processes such as homogeneous nucleation, surface growth, agglomeration and coalescence occur simultaneously as the synthesis takes place. Thus particle morphology steadily evolves. System conditions like temperature, reactant concentration and burner geometry greatly influence the processes of nucleation, deposition, agglomeration and coalescence. As the precursor concentration increases, the density of the
individual agglomerates formed is increased and greater number of sites are available for particle growth [10].

1.2.2 Flame aerosol process

In flame aerosol process, the vaporized precursor is introduced in the flame. Typical experimental setup consists of a reactor, burner, flow system for gas delivery and a filter system. The reactor consists of a precursor unit where the precursor is vaporized. The carrier gas is bubbled through the container filled with the liquid precursor. The gas lines and the container are heated to ensure vapor state of the precursor. This is then fed into the flame. Research has shown that factors such as the particle residence time and flame temperature play a crucial role in the characteristics of the synthesized powders [14]. Reactant mixing is observed to affect the particle size by one order of magnitude resulting in the formation of finer particles in inverted diffusion flame than in co-flow diffusion flame [12, 15]. Moreover the choice of the precursor becomes vital when considerable heat is produced by the combustion of precursor [14]. Additives play an important role to control the primary particle size and the extent of agglomeration [14].

The application of external electric field charges the particles which are attracted towards oppositely charged electrodes and this promotes collision rate between various gaseous particles. The application of electric field influences flame temperature and structure of the flame which can be seen in the flattening of premixed oxy-methane flame which leads to an increase in the specific surface area of synthesized TiO$_2$ powder [14]. In addition, agglomeration of granular nanoparticles on appropriate substrates gives rise to thin films. Using premixed flames, thin films of SnO$_2$ are grown on commercial alumina chips which
have high sensing ability for ethanol vapor [16]. Scaled up flame aerosol process is currently used in the industry for large scale production.

1.2.3 Flame spray pyrolysis

In the flame spray pyrolysis process, the liquid precursor is sprayed through nozzle, atomized and is either mixed with oxygen producing a flame or is injected into a flame. The experimental setup for flame spray pyrolysis consists of a system for generation and spray of liquid droplets which usually include ultrasonic or gas assisted pressurized atomizers, oxidant to carry out oxidation and a heat source [14]. The heat source is provided by the combustion of liquid droplets or by the evaporation of liquid droplets to vapor followed by combustion. The quenching ability of the reactors is higher due to increased shear rates required to atomize the liquid. The composition of the liquid fuel and the liquid precursor play an important role in growth of particles. Burning rates, droplet lifetime and fuel atomization are important factors governing particle synthesis.

The use of organometallic precursors results in smaller particles with better homogeneity [17]. Increase in the oxygen flow rate invigorates the combustion and raises the flame temperature. This promotes the synthesis of smaller particles with higher specific surface areas [14]. Spheroidal and hexagonal ZnO nanoparticles ranging from 10 to 20 nm are synthesized using flame spray pyrolysis method with zinc naphthenate as a precursor dissolved in toluene/acetonitrile (80/20 volume %) [18]. Ethanol sensing films are produced by mixing these nanoparticles with organic paste.
1.3 Flame synthesis of one-dimensional transition metal oxide nanostructures

Synthesis of one-dimensional nanostructures of transition metal oxides has been a recent field of study. One-dimensional nanostructures include nanorods, nanotubes, nanowalls, nanoribbons, nanochannels and nanowires which are long enough to have their length as the predominant single dimension. Several methods such as vapor phase methods, solution phase methods, electrospinning, etc. have been developed. The successful application of the traditional flame synthesis methods such as flame aerosol and flame spray pyrolysis methods for the synthesis of transition metal oxide nanoparticles triggered the interest to explore their use for the synthesis of one-dimensional nanostructures of transition metal oxides. The flame synthesis includes gas phase synthesis and has also been extended to include synthesis using solid support. The precise control of factors such as flame temperature, residence time, reactant composition, reactant mixing and precursor additive affects the growth of the one-dimensional nanostructures. There is exhaustive research carried out on the flame synthesis of metal oxide nanoparticles as compared to one-dimensional metal oxide nanostructures. Flame aerosol and flame spray pyrolysis have been predominantly used for the synthesis of SnO$_2$ [19] and ZnO$_2$ nanorods [20], respectively. Plasma flame synthesis along with flame gradient method are recent additions to the flame synthesis techniques employed for growth of one-dimensional metal oxide nanostructures. These approaches have unique advantages over the traditional flame methods.

1.3.1 Flame aerosol process

The flame aerosol reactor consists of a precursor unit where volatile precursor is evaporated. SnO$_2$ nanorods are formed using flame aerosol process with the use of dopants species such
as chlorides of iron, lithium and zinc [19]. The precursor is then fed into the hydrogen-oxygen co-flow diffusion flame. Dopant concentrations and flame residence time affect the morphology of the synthesized nanowires. It is observed that the highest nanorod formation tendency is exhibited with Fe as the dopant species due to the high valency of Fe [19]. Increasing the Fe concentration and the flame residence time promotes the growth of SnO$_2$ nanorods. SnO$_2$ nanorods 200 nm in length and 20 nm in diameter are grown [19]. Using argon and methane alternatively as the carrier gas with dopant species of gold acetate and aluminum acetate, SnO$_2$ nanorods are also grown using flame aerosol method [21]. The use of methane provides greater control over high aspect ratio and average crystal size. Particle diameter increases from 19 nm using argon gas to 46 nm with the use of methane as the carrier gas thus increasing surface area.

1.3.2 Flame spray pyrolysis

In this method a liquid solvent containing appropriate precursors is atomized and sprayed into the flame through a nozzle. ZnO nanorods have been synthesized by flame spray pyrolysis method with a co-flow diffusion flame [20]. Indium, tin and lithium dopant species are used with concentration ranging from 1% to 10%. The effect of dopant concentrations on the metal oxide morphology is studied [20]. The nanorod formation is found to occur exclusively in the vapor phase. The nanorod formation mechanism depends on the dopant valency and their incorporation into the zinc crystal. Sn provides highest nanorod formation influence at lower concentrations than In. Lithium being of a lower valence does not alter the shape of ZnO. Flame spray pyrolysis has also been employed for the synthesis of SnO$_2$ nanorods inside Vycor tubing [22]. The synthesized nanorods are about 150 nm in diameter.
and their length ranges from 4 μm to about 200 μm. These homogenous structures are observed to grow preferentially as one-dimensional crystals [22]. These nanorods are observed to grow by layer-by-layer growth mechanism [22]. Limited research has been conducted in application of flame spray pyrolysis technique for the synthesis of one-dimensional metal oxide nanostructures.

1.3.3 Plasma assisted flame synthesis

The plasma assisted flame environment is utilized for the synthesis of metal oxide nanoparticles. The plasma assisted flame is able to achieve extremely high temperatures consequently accelerating the synthesis process and substantially reducing the production time. This approach is relatively recent compared to the traditional flame aerosol and flame spray pyrolysis methods.

1.3.3.1 Atmospheric microwave plasma torch flame method

ZnO nanorods are synthesized from Zn samples by their direct heating at atmospheric pressure in an oxygen microwave plasma torch flame [23]. The experimental setup as shown in Figure 1 consists of microwave generator, power monitor, waveguide, quartz tube, isolator, 3-stub tuner, oxygen source, mass flow controller and swirl gas inlet. In this method, the plasma is initiated by sparking a tungsten filament inserted into the waveguide in the quartz tube. The initiated plasma is then sustained by energy transferred from the microwaves generated by the microwave generator. Thus the oxygen swirl flowing at atmospheric pressure through the quartz tube is energized by the microwaves. The solid zinc
granules placed in the quartz tube melt and vaporize in the plasma torch flame and reactions occur in the plasma phase to form ZnO nanowires.

Fig. 1. Schematic diagram for experimental setup for ZnO nanorod formation by atmospheric microwave plasma torch flame [23].

The ZnO nanorod formation occurs by the vapor-liquid-solid growth mechanism [23]. Since the temperatures achieved in this method are very high, it is observed that ZnO nanorod formation occurs in less than one second.

1.3.3.2 Radio frequency thermal plasma flame synthesis

The radio frequency thermal plasma flame method has been developed to synthesize ZnO nanorods [24]. The experimental setup shown in Figure 2 consists of radio frequency source,
plasma generator, reactor and a collector. The plasma generator consists of the plasma forming gas argon, surrounded by the sheath of nitrogen and oxygen. The plasma torch is energized by the radio frequency generator. The zinc powder acts as the source for zinc. The plasma phase reactions trigger the synthesis of the nanorods which are deposited in the bottom collector.

Fig. 2. Schematic representation of the experimental setup for ZnO nanorod formation by radio frequency thermal plasma flame [24].

It is observed that oxygen partial pressure and zinc oxide supersaturation are important in the nanorod formation. Uniform ZnO nanorods with a high yield are reportedly obtained by this method [24].
1.3.4 Flame synthesis using flame gradient method

The flame gradient technique is based on incorporating the thermal and chemical gradients developed in flame. This method eliminates the need of dopants. The synthesis of particles in this method occurs in the flame volume which can be captured thermophoretically using a TEM grid. It also occurs on the solid support when it is inserted in the flame. The material feed probe is inserted in the flame at various axial locations within the flame. The thermophoretic sampling is carried out at various heights above the probe. Using this technique, ZnO nanorods are synthesized from zinc plated steel substrate inserted in a co-flow flame without the use of dopants [25]. From this method, ZnO nanowires are produced on the fuel as well as the oxidizer side of the flame. They are formed by vapor-solid growth mechanism. Nanorods of oxides of several metals such as iron [26] and molybdenum [27] have been synthesized using this technique on the solid support inserted in opposed flow diffusion flame. Additionally even volumetric flame synthesis has been carried out for molybdenum oxide [28].

Compared to flame aerosol, flame spray pyrolysis and plasma flame methods, flame gradient method is much simpler to control and inexpensive to employ. Flame gradient technique has been carried out using co-flow as well as counter flow diffusion flames. Co-flow flames possess chemical and thermal gradients varying in both the radial as well as the axial direction which complicates the experimental test of the variation in parameters to synthesize the nanostructures. Also changing the reactant composition for an air-methane co-flow diffusion flame greatly changes the height of the flame. This complexity in manipulation of parameters to study their effects on synthesis is reduced in the case of counter flow diffusion
flames where the thermal and chemical gradients vary in the axial direction which makes this kind of a flame essentially a one-dimensional flame.

1.4 Properties and applications of vanadium oxide nanostructures

The primary focus of the thesis is to employ the opposed flow diffusion flame to synthesize one-dimensional vanadium oxide nanostructures. Vanadium is a transition metal that maintains several oxidation states $V^{3+}$, $V^{4+}$, $V^{5+}$ producing various stable oxides. Vanadium pentoxide (V$_2$O$_5$) exhibits the maximum oxidation state for vanadium and is highly stable [29]. It exhibits unique properties based on its redox-chemistry as vanadium exists in multiple valence states [30]. The structural diversity of vanadium oxides allows for internal degrees of freedom within the structure bringing about sudden transitions from metal to insulator phase [31] or even become superconducting [32]. These peculiar metal-insulator phase transitions are particularly observed for VO$_2$ and V$_2$O$_5$ rendering these for use in the semiconductor industry. Due to the unique physiochemical properties, vanadium oxides find uses in electric-field effect transistors [33] and chemical sensors [34]. Vanadium pentoxide nanostructures are particularly used for a variety of applications such as:

- Catalysis [35].
- Field Effect Transistors [36].
- Sensors [37].
- Spintronic devices [38].
- Cathode material of lithium batteries with intercalations [39].
- Ceramics [40].
• Solar cells [41].
• Increasing the electrical conductivity and modulus of elasticity of polyvinyl chloride once added to it [42].

Vanadium oxide nanostructures have been usually synthesized using hydrothermal synthesis approach [43, 38] which avoids high temperatures which may cause difficulty in synthesis owing to the relatively low melting point of vanadium, 1910 °C and low melting points of vanadium oxides: 690 °C for V$_2$O$_5$ and 1967 °C for VO$_2$. Nanoparticles of vanadium oxide have been synthesized using flame spray pyrolysis [30] and of composites of mixed metal oxides such as V$_2$O$_5$/TiO$_2$ and V$_2$O$_5$/SiO$_2$ [44]. However one-dimensional vanadium oxide nanostructures have not yet been grown using any of the flame synthesis methods. The crystal structure of V$_2$O$_5$ is shown in Appendix A.

1.5 Thesis Objective and Outline

The primary objective of this thesis is to employ the opposed flow oxy-methane diffusion flame for the synthesis of one-dimensional vanadium oxide nanostructures. The solid support synthesis is investigated. The present work started with the successful implementation of the flame gradient technique for the solid support synthesis [26, 27]. This research seeks to extend this technique for the synthesis of one-dimensional vanadium oxide nanostructures. The research work initially included the design and assembling of the experimental setup, the details of which are covered in Chapter 2. The counter flow diffusion flame is employed for synthesis. Its governing equations and the theoretical description is provided in Chapter 3. This chapter also provides images of the flame for various compositions and strain rates which have been used in the experiment. The characteristic flame parameters which include
flame composition, residence time, probe position and strain rate have been varied and the corresponding morphological variations in the synthesized vanadium oxide structures are observed under the scanning electron microscope. The underlining mechanism of the material transport in the flame is explained. The results and discussions of the observed morphologies of the synthesized structures are presented in Chapter 4. This chapter also explains the crystal growth mechanism resulting in the synthesized structures. The conclusions derived from the experimental results and the available scope for future work are provided at the end of the thesis. There is ample scope for further investigation in this research so that this promising method becomes commercially viable.
2. EXPERIMENTAL SETUP

2.1 Burner and burner mount

A counter flow diffusion flame consists of two opposed flow streams of fuel and oxidizer. Methane is used as the fuel. The oxidizer consists of air with oxygen enrichment. The opposed jets of the reactants collide to create a stagnation plane and the flame exists at the stoichiometric contour. The counter flow diffusion flame burner is composed of bottom half and the top half as shown in the Figure 3.

Fig. 3. Schematic of the counter flow diffusion flame burner.
The burner is mounted on to a BISLIDE assembly (VELMEX Inc). The BISLIDE assembly is mounted on a machined aluminum plate. The plate is then secured vertically on the top half of a cabinet using strut channels. The bottom half consist of two concentric cylinders. The inner cylinder carries the oxidizer mixture of air and oxygen. It is filled with glass beads so that the flow is stabilized and large eddy formations are avoided. The oxidizer mixture is delivered to the flame from the fine wire mesh at the exit of the nozzle. This fine mesh ensures that the flow is laminar and that the exit velocity profile is radially uniform. The annular space between the two concentric cylinders carries inert nitrogen which forms the outer inert shroud around the flame and thus contains it from spreading to the outside. The honeycomb structure is fitted into this annular space at the exit to ensure that the nitrogen gas flow is laminar and exit velocity profile is radially uniform.

The top half consists of two concentric cylinders. The inner most carries the fuel gas consisting of methane. It is also filled with glass beads and there is a fine mesh at the fuel nozzle exit. Cooling water flows in the annular spaces developed between the first and second concentric cylinders and surrounds the ring of tubes that are contained between the two concentric cylinders. Exhaust gases from the combustion are driven upwards by buoyancy on account of their lowered density. These enter into the tubes contained between the two concentric cylinders. The cooling water forms a surrounding envelope for the exhaust gases and cools the hot exhaust gases. This ensures that the incoming fuel gas is not preheated and also that the cylinder walls are not overheated. Thus the experiment can run continuously without interruptions. The cooling water enters from the bottom and leaves from the top so as to avoid any air pockets from forming in the annular spaces which will
hinder the effective heat transfer from exhaust gas to the cooling water. The two halves of the burner are connected using nuts and bolts.

Using a 2.54 cm (1 inch) optical slab, the gap between the exit nozzles of the fuel and oxidizer is adjusted. Once the gap is achieved, the slab is removed and the nuts are tightened so that a fixed 2.54 cm (1 inch) gap between the exit nozzles of the fuel and oxidizer is set precisely. At the top of the top half of the burner is the exhaust outlet. This is connected to the stainless steel exhaust pipe using a hose clamp. The other end of the exhaust pipe is then connected to stainless steel reducer cup at its smaller diameter end using a hose clamp and this connection is sealed using aluminum foil. The larger diameter end of the reducer cup is connected to the suction pipe using a hose clamp and this connection is sealed using an aluminum foil.

The burner is mounted onto an angle plate using a flange at its bottom half. The angle plate is bent at right angles downwards. This vertical part of the angle plate is then fitted to the mounting slot on the BISLIDE. The entire burner can now be moved vertically using the BISLIDE. The BISLIDE when used for vertical motion is rated for a bending moment of 500 inch-lbs. Assuming the burner weight to be around 100 lbs, the moment applied when the burner is mounted exceeds this rated value. Therefore two plates are fitted at the top part of the top half of the burner below the exhaust outlet. These plates have 4 holes at their corners. One end of the loop ended stainless steel springs is inserted in these holes while the other end is inserted into holes in the upper surface of the cabinet roof. The weight of the burner when completely suspended from the springs without any BISLIDE connection is nearly half its original weight. Thus the burner is now suspended from the cabinet top using springs and mounted on the BISLIDE. Ensuring that the springs are always stretched, the burner can be
safely moved vertically covering a good measure of the available vertical travel on the BISLIDE.

The experimental setup is entirely mounted in the cabinet from Premier Metals. The primary components of the experiment as observed from the front which include the spring suspended burner mounted on BISLIDE, probe mount and probe holding assembly, cantilever panel mounted mass flow controllers and tube connections are shown in Figure 4.

Fig. 4. Experimental setup viewed from the front.

The cabinet is the primary load bearing frame of the entire experimental setup. It offers rigid support bars with ample slots for connections and has enough free space for mounting the apparatus. The cabinet at its base has 4 casters with swiveling front wheels and foot operated friction brake. In order to secure the cabinet in a fixed position, 4 leveling leg assemblies are
connected to the cabinet at its base. Each leveling leg assembly consists of a rubber cushioned base having an adjusting stud, one coupling nut, fully threaded stud and 2 heavy hexagonal nuts. The base of the cabinet has 4 threaded holes near its 4 corners each. In each corner hole, the fully threaded stud is inserted. It is turned until it protrudes sufficiently from the bottom of the hole. It is now fitted into the heavy hexagonal nut and the coupling nut through approximately half the length of the coupling nut. The heavy hexagonal nut is fitted onto the threaded stud of the rubber cushioned base and this is stud is now fitted into the coupling nut through the remaining half of its length. Once the coupling nut is fitted equally on both the threaded studs, the heavy hexagonal nuts are tightened to lock it in place. Now by turning the coupling nut the entire cabinet can be lifted off the ground and kept fixed in position for running the experiment. The relative horizontal tilt of the cabinet with respect to the ground is checked using a spirit level and adjusted using the coupling nuts. Similarly, the cabinet can be lowered until its wheels come in contact with the ground when it is required to move the experimental setup.

The components used for the experimental setup have been machined from the machine shop of the Department of Mechanical and Aerospace Engineering at North Carolina State University. SolidWorks Education Edition software has been used for all the machine designs of all the machined components in the experimental setup.

2.2 Flow control system

The flow control system primarily comprises of the piping and tubing systems, mass flow controllers, mass flow meter, pressure regulators, gas cylinders, rotameter, panels and valves. The central control for all the gases is located on the exhaust panel mounted on the exhaust
hood. The exhaust panel is a machined aluminum plate that is fixed to the exhaust hood. The side panel is a machined steel plate from Premier Metals fitted on the side of the cabinet. Polyethylene (PE), fluorinated ethylene propylene (FEP or Teflon) tubes from Thermo Fisher Scientific and high pressure braided polyvinyl chloride (PVC) tube from McMaster-Carr are used. The PE tubing is used for methane, acetylene, air and nitrogen gases while the FEP tubing is used for oxygen. The braided PVC tubing is used for the cooling water. The stainless steel, brass connections and valves are all obtained from Swagelok. The basic design of the flow control system showing the important gas flow line connections is provided in Figure 5.

Fig. 5. Schematic of the flow control system showing gas line connections.
The ball valves for methane, acetylene, nitrogen and oxygen gases are mounted on the exhaust panel. The side panel is further machined from the machine shop so that connectors for all the gases and toggle valves for methane, acetylene, oxygen and variable pressure valve for air are mounted on it. The tubing connections are used to connect these exhaust panel valves to the connectors mounted on the side panel. The tubing is further used to connect these connectors to the valves mounted on the side panel. In case of nitrogen, the tubing is used to connect the side panel connector to a nitrogen rotameter from Dwyer, mounted on an aluminum plate fitted at the base on the side of the cabinet.

The fuel gas cylinders for methane and acetylene are kept inside the fuel cylinder chambers. The pressure regulator consists of Microline custom made panel, mounted on the inside of the fuel cylinder chamber. The gas is then delivered through stainless steel pipe to the valve mounted on the exhaust panel. The oxygen and nitrogen cylinders are fastened to the optical table from Thorlabs, Inc. The pressure regulators are fitted on the cylinders and the tubes are used to connect the regulators to the valves mounted on the exhaust panel.

The compressed air is drawn from the air line using copper tube and is delivered to wall mounted air pressure regulator with filter. Now the air from its outlet is delivered using the tube to the connector and further to the variable flow valve mounted on the side panel. The mass flow controllers (MFCs) from Aalborg are used for controlling the flow rates for methane, acetylene and oxygen while the mass flow meter (MFM) is used for indicating the flow rate for air which is controlled using the variable flow valve. The cantilever shelf from Premier Metals is machined so that all mass flow controllers and the mass flow meter can be mounted on it. It is then fitted on the side bars of the cabinet facing inwards and above the side panel. Its machining is carried out precisely so that there is easy access to change the
flow rates manually with a screw as required and also to easily read the displayed flow rate value. Figure 6 shows the mass flow controllers and mass flow meter mounted on cantilever plate.

Fig. 6. Mass flow controllers for methane, oxygen and acetylene and mass flow meter for air mounted on the cantilever plate.

The motor controller for the BISLIDE is also kept on the cantilever shelf behind the flow controllers. The gases from the methane and acetylene mass flow controllers are carried by tubing to a T-fitting and also similarly the gases from the oxygen mass flow controller and air mass flow meter to another T-fitting. In the T-fitting, the gases coming in from both the arms mix and leave through the third arm. The tube carries the fuel gases from the T-fitting to the fuel mixing chamber and the oxidizer gases from the T-fitting to the oxidizer mixing
chamber. The fuel mixing chamber is a brass tube attached vertically to the cabinet on the inside using hose clamp. The mixture enters from the top of the chamber and leaves from its bottom. Since the chamber is vertically mounted, there is wire gauze present at the bottom end of the chamber to prevent the glass beads from blocking the tubing at exit. The oxidizer mixing chamber is a stainless steel box that is placed at the base of the cabinet and held in position using strut channels and angle plates. The oxidizer mixture enters from the lower side and leaves from the top side of the oxidizer mixing chamber ensuring that the mixture fills the chamber evenly. Both the mixing chambers are filled with glass beads so that there is thorough mixing of the gases. The thoroughly mixed fuel and oxidizer mixtures now enter the top and bottom part of the burner respectively. The oxidizer mixture enters the bottom half of the burner by an elbow connection. Once again wire gauze is used on the end of the elbow inserted into the bottom half of the burner to prevent the glass beads from blocking the tubing. The fuel mixture enters the top half of the burner from the top. The tubing carrying nitrogen gas from the exit of the rotameter is connected to the side connection at the bottom half of the burner. The side connection is connected evenly in the 4 perpendicular directions in the horizontal plane to the outer concentric cylinder of the bottom half of the burner. This ensures that nitrogen gas evenly fills up the annular space.

2.3 Probe mount

The probe mounting assembly consists of the base mounting assembly and the probe holding assembly. The base mounting assembly consists of the strut channels, base plate, 4 posts and optical breadboard. Two strut channels are fitted near the side of the cabinet and are parallel to each other. The machined base plate is fitted over them. The lower ends of the 4 posts are
attached to the base plate holes using screws. Their upper ends are fixed to the optical breadboard. The posts thus support the optical breadboard at a fixed height above the base plate. This height is essential to ensure that the probe can be inserted into the flame at the desired axial position. Thus the posts are carefully selected according to the measured height difference between the base plate and the probe positioning.

The probe holding assembly consists of lab jack, probe holder block, 2 positioning studs, probe holding tube, probe holding cap, probe shield and Teflon screw as shown in Figure 7.

Fig. 7. Probe mount assembly viewed from the side.

The lab jack is fixed to the optical breadboard using screws and nuts. The probe holder block is a rectangular piece of aluminum which is machined so that the stainless steel probe holding tube can slide through it in the horizontal plane. The block also has 2 holes where the
positioning studs can be vertically inserted perpendicular to the probe holding tube. The studs lock the block in position on the lab jack. The probe holding tube is allowed to slide through the machined hole in the block and can be locked in position using the Teflon screw through another perpendicular machined hole in the horizontal plane on the side of the block. The probe holding cap is a stainless steel reducer whose smaller diameter end has a shot punched bead. When the smaller diameter end is inserted into the inner diameter of the tube, it fits into the probe holding tube and remains fixed so that it does not move relative to the probe holding tube. The larger diameter end has the same outer diameter as the outside diameter of the probe holding tube. The probe holding cap has a 1.1 mm diameter hole running through its entire length at its centre. The probe material wire is also of 1 mm diameter which protrudes out from this central hole in the probe holding cap. The probe shield is a stainless steel tube slightly larger in diameter than the outer diameter of the probe holding tube. This ensures that it slides freely over the probe holding tube. It is machined to appropriate length so that it can cover the probe entirely during its withdrawal and also facilitate the cutting of the withdrawn probe for analysis. The probe shield protects the synthesized nanostructures on the probe during the withdrawal from the non-uniform flame boundary envelope.

2.4 Experimental procedure

The experimental procedure consists of the startup, running and shutdown procedures. Eye glasses and gloves are worn at all times to ensure protection and minimize contamination. The experimental procedure is followed by examination of the sample under the Zeiss microscope and later under the scanning electron microscope.
### 2.4.1 Startup

The startup procedure involves setting up the probe in position and the preliminary steps required to turn the standard flame on. The probe is a coiled 1 m long vanadium wire which is 1 mm in diameter and of 99.99% purity from Goodfellow Corporation. Using latex gloves from Fisher Scientific at all times while handling the probe ensures that the probe material remains free from contamination. The probe shield is removed and by loosening the Teflon screw on the probe holding block, the probe holding tube is removed. The probe holding cap is held in a bench vice and the bench vice is tightened only slightly to ensure that the probe holding cap is not damaged. The probe holding cap is then separated from the probe holding tube. The vanadium wire is now passed through the probe holding tube until it comes out from the other end. This protruding part of the vanadium wire is now inserted into the central hole in the probe holding cap until sufficient length protrudes out from it. The probe holding cap is then fitted back into the probe holding tube. The protruding vanadium wire is pulled until about 4 to 5 mm protrudes out from the probe holding cap and is straightened manually. Now the probe holding tube fitted with the probe holding cap and containing the straightened vanadium wire is inserted into the hole in the probe holding block and the probe shield is placed over it. Using the motor controller for the BISLIDE, the BISLIDE is moved vertically until the probe holding tube can be inserted in the region between the exit nozzles of the fuel and oxidizer mixtures which is where the combustion occurs. The probe holding tube is now drawn out until the protruding vanadium wire touches the fuel exit nozzle tip. Now using a digital caliper placed on the lab jack, the position of the probe from the fuel nozzle end can be varied. Once positioned, the probe holding tube is pulled back away from the burner.
The flame composition for the strain rate of 20 s\(^{-1}\) is taken as the standard stable laminar air-methane diffusion flame condition irrespective of the actual flame composition and strain rate for which the experiment is to be run. Once this flame is achieved the flow rates and strain rates are varied as required for the particular experimental run. The outlet pressure for all the gases is fixed at 300 kPa absolute (30 psig). Initial check up is carried to ensure that all the valves on the experimental apparatus are closed. The cooling water supply and return are turned on. The cooling of the top half of the cylinder is manually felt to ensure that effective cooling of the top half of the burner carrying the hot exhaust continues normally. The carbon tape from SPI is cut and applied on the scanning electron microscope (SEM) cylinder specimen mount from Ted Pella, Inc. It is placed in the specimen storage box from SPI which is kept dry by inserting SPI desiccant capsules.

The air line is started and using the wall mounted air pressure regulator, the air pressure is set. The methane cylinder valve is opened and the valve MV01 on the Microline panel is turned on. This ensures that the high pressure gas in the cylinder enters the pressure regulator branch. Now methane pressure is set using the pressure regulator and valve MV03 is turned on so that the gas from the low pressure branch of the pressure regulator is available at the experimental apparatus. The oxygen cylinder and nitrogen cylinder valves are opened and the pressure regulators are used to set the pressure for these gases. Now methane, nitrogen and oxygen valves mounted on the exhaust panel are turned on. Using the air variable flow valve on the side panel, the flow rate for air which is displayed on the indicator of the air mass flow meter is set according to the standard flame condition. Now the methane valve on the side panel is turned on. Using the screw driver, the control screw in the side of the methane mass
flow controller is turned until the flow rate for the standard flame condition is achieved. The Microline custom pressure regulator panel for methane is shown in Figure 8.

Fig. 8. Microline custom made pressure regulator panel for methane.

Fig. 9. A photograph of counter flow diffusion flame used in the experiment.
Since combustible methane gas is dangerous if it spreads into the lab, it is essential that the standard flame condition is achieved without much delay. This is done very quickly in short steps with intervals, increasing the flow rate steadily in each step. At the end of each step, methane is given sufficient time to escape into the exhaust. The flame torch from Bernzomatic is tested for its operating condition away from the experimental apparatus. Once the standard flame condition is achieved, using the flame torch the mixture contained within the exit nozzles of fuel and oxidizer is lit. The rotameter is turned on so that the nitrogen shroud concentrically envelopes the flame and effectively contains it from spreading to the outside. The ignited stable flame photograph using a photo camera (30D, Canon Inc) is shown in Figure 9.

2.4.2 Running

The oxygen valve on the side panel is turned on. Now slowly using the screw driver to turn the control screw in the side of the mass flow controllers, the flow rates for methane and oxygen are changed to the required value while simultaneously the air variable flow valve is used to change air flow rate. Once the desired flame conditions are achieved, the vanadium probe is inserted at the fixed location into the flame. The residence time for the probe is monitored using a Timex digital wrist watch. Once the set time is reached, the probe is withdrawn while ensuring that the probe shield covers it completely during withdrawal. The flame is once again set back to the standard flame condition. The shield is now carefully taken off using tongs and the wire length that was inserted into the flame is cut. Using tongs, the wire is placed on the carbon taped SEM specimen mount and stored in the storage box. The wire is pushed until sufficient length protrudes from the probe holding cap. The position
of the probe can be changed by using the digital caliper with the lab jack. The standard flame is ignited and the procedure is repeated.

2.4.3 Shutdown

Once the experimental runs are completed and all the samples are collected, the shutdown procedure is followed. In this case, the oxygen cylinder valve is closed. The remaining oxygen is then drawn and consumed by the flame. Once the oxygen mass flow controller and both the high and low pressure dials of the pressure regulator read zero, the oxygen valves on the exhaust and side panels are turned off. Then the methane valve on the side panel is turned off and the flame extinguishes. The nitrogen cylinder valve is closed and the remaining nitrogen in the line is allowed to flow until the rotameter reads zero after which the rotameter and exhaust panel nitrogen valve are turned off. Now the methane cylinder valve is closed and MV01 valve is turned off. Now MV05 valve is turned on which bleeds the low pressure branch of the pressure regulator as well as the low pressure supply line into the exhaust. Once the low pressure regulator reads zero, the MV03 and MV05 valves are turned off. The MV02 valve is opened to release the high pressure in the cylinder pig tail to the exhaust. The MV01 valve is also opened to release the high pressure from the high pressure branch of the pressure regulator and its dial now reads zero. Both MV02 and MV01 valves are now closed. The air flow rate is now increased to the maximum and allowed to flow for additional 10 min after the end of the experimental run for cooling the hot top half of the burner. The air line is then turned off and once the air mass flow meter reads zero, the air variable flow valve is turned off. The cooling water is allowed to flow for additional 20 min
after the completion of the experimental run to ensure sufficient cooling of the burner. The cooling water supply and return valves are then closed.

### 2.5 Post experiment observation process

The initial observation of each probe sample after the experiment is carried out, is under the Zeiss Stemi 2000-C compound microscope where it is observed for any significant macroscopic effects that are visible to the naked eye. Any noticeable color change indicates the occurrence of chemical changes on the vanadium probe in the flame environment. Silvery shining coating with yellowish tinge on the vanadium probe starkly indicates typically the presence of vanadium oxide $\text{V}_2\text{O}_5$. If the synthesis has occurred on microscale level rather than nanoscale, then the coating and its peaks protruding out on the probe surface can be seen vaguely by the naked eye and very clearly under the compound microscope. It is then observed under the scanning electron microscope to account for the microscale and nanoscale effects of the flame gradient synthesis. In addition, energy dispersive X-ray spectroscopy (EDS) is carried out on the samples which show promising nanostructures to identify the chemical composition of the synthesized species. This is then compared against the EDS output of a standard 99.99% $\text{V}_2\text{O}_5$ powder sample from Sigma-Aldrich. The peaks for the chemical elements are compared to get an idea of the chemical composition of the synthesized material. The JEOL 6400F SEM is used for imaging and Hitachi S-3200N SEM is used for EDS.
3. OPPOSED FLOW DIFFUSION FLAME

3.1 Diffusion flames

In diffusion flames, the fuel and oxidizer are not initially mixed. The reaction occurs due to diffusion of fuel and oxidizer in proper proportions in the flame zone. A dimensionless number known as the Damköhler number (Da) is defined as the ratio of diffusion time to the chemical reaction time.

\[
Da = \frac{\text{diffusion time}}{\text{reaction time}}
\]  

(3.1)

Thus the Da number gives a measure of whether the combustion mechanism is diffusion controlled or reaction controlled. If the Da number $<< 1$, then the time required for diffusion is less as compared to the reaction time for chemistry. Thus the gas molecules diffuse in large magnitude building up their concentration while reaction occurs slowly. If the Da number $>> 1$, then the reaction time for chemistry is less as compared to the time required for diffusion. Thus the gas molecules react chemically very quickly to form products but diffuse slowly. It is assumed that the fuel and oxidizer burn completely when they diffuse into the flame zone. Thus the flame is assumed to exist at the stoichiometric condition plane. Several configurations exist for diffusion flames depending upon the relative orientation of the fuel and oxidizer exit nozzles. These are co-flow, inverse flow and counter flow diffusion flames configurations. In co-flow, the inner fuel jet is surrounded by an outer envelope of oxidizer while in the inverse flow as the name suggests, the inner oxidizer jet is shielded by an outer fuel envelope. In the counter flow configuration, the fuel and oxidizer jets flow in the opposite directions and impinge on each other generating the flame. The counter flow
diffusion flame is a strained flame and it is therefore convenient to use the strain rate to study these flames.

### 3.1.1 Counter flow diffusion flame

![Schematic of a counter flow diffusion flame.](image)

Fig. 10. Schematic of a counter flow diffusion flame.

The counter flow diffusion flame is modeled as two axisymmetric opposed jet flows shown in Figure 10. The flame is characterized by several parameters which include the strain rate, fuel and oxidizer flow rate and flame composition. We assume a very basic definition of strain rate $\varepsilon$ such that the stagnation plane for the opposed gas streams is assumed to lie at half the length between the fuel and oxidizer nozzle exits. Assuming the exit velocity profiles of both the oxidizer and fuel mixture gas streams to be radially uniform, the radial
component can be ignored. Thus the counter flow diffusion flame is treated as essentially one-dimensional in the axial direction. Thus the temperature, chemical species and velocity gradients vary axially. This simplifies the governing equations of the counter flow diffusion flame. Then the strain rate in its simplest form is given by,

\[ \varepsilon = \frac{v}{L/2} \]  \hspace{1cm} (3.2)

where \( L \) is the length between the fuel and oxidizer nozzle ends and \( v \) is the exit velocity of the fuel or oxidizer jets from their respective nozzles.

The assumptions made for the analysis of counter flow diffusion flame are:

1) Steady, laminar and axisymmetric boundary layer \( \left( \frac{\partial}{\partial x} \ll \frac{\partial}{\partial y} \text{ in transport} \right) \).

2) Radiation, kinetic energy, potential energy, viscous dissipation and body forces are neglected.

3) The ideal gas laws are applicable.

4) There is only Fickian diffusion \( (D_{ij} = D_{ji} = D) \).

5) There is global one-step chemistry.

6) Finite rate kinetics.

7) Constant pressure.

8) Lewis number \( L_e = 1 \).

9) \( u = \varepsilon x \), where \( u \) is the velocity in the horizontal \( x \)-direction and \( \varepsilon \) is the strain rate.

The approximate governing equations for conservation of mass, species and energy using order of magnitude analysis are given by Eq. (3.3), (3.4) and (3.5) respectively. The
conservation of momentum equation is neglected because it relates velocity to pressure, but pressure is already assumed to be constant.

\[
\frac{d}{dy}(\rho v) \approx -2\rho \varepsilon \tag{3.3}
\]

\[
\rho v \frac{dY_i}{dy} = \frac{d}{dy}\left(\rho D \frac{dY_i}{dy}\right) + \omega_i \quad \text{where } i = 1, 2, \ldots N \text{ species} \tag{3.4}
\]

\[
\rho C_p v \frac{dT}{dy} = \frac{d}{dy}\left(\lambda \frac{dT}{dy}\right) + \sum_{i=1}^{N} \omega_i h_i^o \quad \text{where } i = 1, 2, \ldots N \text{ species} \tag{3.5}
\]

where \(\rho\) is the density, \(v\) is the axial velocity, \(Y_i\) is the mass fraction of species \(i\), \(D\) is the diffusivity, \(\omega_i\) is the mass production rate of species \(i\) per unit volume, \(C_p\) is the specific heat at constant pressure, \(T\) is the temperature, \(\varepsilon\) is the strain rate, \(\lambda\) is thermal conductivity, \(h_i^o\) is the enthalpy of formation of species \(i\) and \(y\) is the axial direction co-ordinate. The Shvab-Zeldovich and Howarth-Dorodnitsyn transformations are performed simultaneously and a normalized conserved scalar \(\theta_i\) and stretched axial dimension \(\eta\) are introduced. This yields \(N\) linear convection-diffusion equations and a single non linear equation with Arrhenius rate kinetics as shown in Eq. (3.7) and (3.8) respectively. In this case \(D_1\) is Damköhler first number and is given by Eq. (3.6).

\[
D_1 = \frac{AY_i Y_o^{o_i}}{\varepsilon} \tag{3.6}
\]
\[
\begin{align*}
\frac{d^2 \theta_i}{d \eta^2} + 2\eta \frac{d \theta_i}{d \eta} &= 0 \\
\frac{d^2 \alpha_T}{d \eta^2} + 2\eta \frac{d \alpha_T}{d \eta} &= -D_T \tilde{Y}_f \tilde{Y}_o \exp \left( -\frac{\alpha_a}{\alpha_T} \right)
\end{align*}
\]  
(3.7)

(3.8)

where \( \tilde{Y}_f \equiv \frac{Y_f}{Y_f,\infty} \), \( \tilde{Y}_o \equiv \frac{Y_o}{Y_o,\infty} \), \( \alpha_a = \frac{C_p E_a}{q R_a} \), \( q = \frac{\text{heat of reaction}}{\text{kg of oxidizer}} \), \( R_a \) is the universal gas constant, \( E_a \) is activation energy and \( A \) is the pre-exponential constant in Arrhenius equation.

The boundary conditions applied to the Eq. (3.7) and (3.8) are given in Eq. (3.9).

\[
\begin{align*}
\eta \to -\infty, \theta_i &= 1, \alpha_T = \alpha_{T,\infty} \quad &\eta \to \infty, \theta_i &= 0, \alpha_T = \alpha_{T,\infty}
\end{align*}
\]  
(3.9)

There is no analytical solution to the non linear Eq. (3.8) and hence activation energy asymptotics are used to solve it numerically. The exact solution to the linear convection-diffusion equation is given by Eq. (3.10).

\[
\theta_i = \frac{1}{2} \text{erfc}(\eta)
\]  
(3.10)

The flame is always assumed to be at the stoichiometric condition and hence in terms of the stretched axial dimension \( \eta \), the flame is at the position \( \eta_{st} \). For hydrocarbon-air diffusion combustion, \( \theta_{st} < \frac{1}{2} \). Thus the flame sits on the oxidizer side below the stagnation plane during combustion. The opposed flow diffusion flame possesses strong chemical and thermal gradients that vary in the axial direction [45].
3.2 Flame structure for different flame conditions

By changing the composition of the reactants and strain rate, different flame conditions are achieved. The standard air-methane flame is always ignited initially during the experiment run. The specific changes in the flame condition are carried out after the standard flame has been established. During the shutdown, the flame is brought back to its standard flame condition and stabilized before shutdown.

The standard flame is always set for strain rate of \(20 \text{ s}^{-1}\). It is composed of 100% air by volume without any oxygen enrichment as its oxidizer composition and 100% methane by volume without any acetylene dilution as the fuel composition. Thus the methane and air flow rates are same since the fuel and oxidizer nozzle diameters are same. The simplest definition of strain rate is used in Eq. (3.2) which ignores the density difference between reacting components. The additional changes to the flame composition are then carried out carefully.

3.2.1 Effect of oxygen enrichment

The opposed flow diffusion flame typically shows two zones which are the fuel pyrolysis zone and the oxidation zone distinguished by the yellow and blue colors respectively. The yellow zone is rich in fuel pyrolysis species and soot while the blue zone denotes the flame front where oxidation of species occurs, triggering combustion. With increase in temperature, the sooting tendency of both co-flow as well as counter flow diffusion flames increases monotonically [46]. This occurs as there is no oxidative radical attack on the pyrolyzed products and increasing temperature increases the pyrolysis. The increase in oxygen content is found to have a complex effect on soot. In cases of propane-air counter flow diffusion
flame, slight increase in oxygen reduces soot as it acts as a diluent not contributing to the chemistry, significantly limiting soot production [47]. With further increase in oxygen, the oxidation and temperature rise to increase soot formation. Further oxygen enrichment increases the oxidation far more than the increase in temperature and soot production decreases [48]. In case of methane, increase in oxygen concentration in the oxidizer, increased the flame temperature [49]. This is attributed to the reduction in diluent action of nitrogen as oxygen is increased. The sooting tendency and temperature of oxy-methane counter flow diffusion flames are found to increase with increasing oxygen content [45]. The separation between the blue and yellow zones increases while the distance between the stagnation plane and flame front decreases. With increasing the oxygen content, the fuel consumption is increased. This enlarges and brightens the blue oxidation zone. There is some chemistry effect in play that appears counter intuitive which occurs such that the increased oxygen enrichment is coupled with increase in the yellow soot formation zone. The flame volume swells and both zones shine brightly. The flame images with varying oxidizer composition are shown in Figures 11 (a-c).
Fig. 11. Photographs of the flames with varying oxidizer composition are shown for a strain rate of 20 s\(^{-1}\): (a) 21%O\(_2\)+79%N\(_2\), (b) 30%O\(_2\)+70%N\(_2\), (c) 50%O\(_2\)+50%N\(_2\).
3.2.2 Effect of strain rate variation

The opposed flow diffusion flame shows the two blue oxidative and yellow soot zones distinctly. With changing the strain rate, the fuel and oxidizer nozzle exit velocities increase. The overall heat release rate increases [50]. However with the increased velocities of the opposed jets, the reaction zone of the flame gets squeezed and flattens the oxidative flame front. This causes the peak flame temperature to drop as the reaction zone shrinks. This is observed in Figures 12 (a, b) where the blue reactive oxidation zone is found to become thinner. The explanation for this seemingly contradictory result involves overall and specific heat release rates. The heat release rate is an extensive property and hence it increases with increasing the gas velocities by increasing the strain rate. However the intensive property to characterize the reactivity of the flame is the specific heat release rate which decreases with increasing strain rate [51]. Thus increasing strain rate causes the specific heat release rate and hence reactivity of the flame to decrease, due to which the flame loses heat and eventually extinguishes when heat loss cannot be sustained. The soot production decreases with increasing strain rate as the flame temperature decreases [45]. This is observed as the yellow zone diminishes and shines less brightly. Figures 12 (a, b) show the varying flame images with different strain rates of 20 s$^{-1}$ and 40 s$^{-1}$ respectively, for 50%O$_2$+50%N$_2$ volume composition of the oxidizer. An excel sheet is used for the determination of flow rates and velocities of the reactants for a given strain rate and given reactant composition by volume. Different flame conditions are achieved by varying the volume composition of the reactants along with the strain rate. Appendix B shows the excel sheet used for the flame composed of 50%O$_2$+50%N$_2$ as the oxidizer composition and 96%CH$_4$+4%C$_2$H$_2$ as the fuel composition for a strain rate of 20 s$^{-1}$. 


Fig. 12. Photographs of the flames with varying strain rates for $50\%$O$_2$+$50\%$N$_2$ oxidizer composition are shown: (a) 20 s$^{-1}$, (b) 40 s$^{-1}$. 
4. RESULTS FOR SYNTHESIS OF VANADIUM OXIDE NANOSTRUCTURES

4.1 Flame parameters affecting the synthesis

The probe flame interaction producing nanomaterials of metal oxide is achieved by utilizing the axial gradients of chemical species and temperature in the opposed flow diffusion flame [27]. The flame possesses distinct blue oxidation and yellow soot and pyrolysis zones as seen in Figures 11 (a-c) and 12 (a, b). The flame environment thus changes form a hydrocarbon rich zone near the fuel nozzle end to oxygen rich zone at the oxidizer nozzle end [27]. The flame synthesis is affected by the variation of probe position, residence time, reactant composition and strain rate. The variation in these parameters affects the synthesis in the following ways:

- By changing the probe position axially within the flame, the effect of the variation in chemical and thermal gradients on the synthesis is taken into account.
- The change in the residence time incorporates the available time for crystal growth.
- The variation in the reactant composition and strain rate affects the axial gradients of temperature and chemical species.

Another important parameter that is found to affect the flame gradient synthesis is the probe diameter [27]. However the probe diameter effect is ignored in this research as the probe selected is 1 mm diameter 99.99% purity obtained from Goodfellow Corporation and is kept fixed throughout all the experiments. The effect of variation of axial distance, oxidizer composition, residence time, acetylene addition and strain rate are discussed in Sections 4.3, 4.4, 4.5, 4.6 and 4.7 respectively. The numerical predictions on temperature profile and the distribution of chemical species for counter flow diffusion flame composed of 50%N₂+50%O₂ and 96%CH₄+4%C₂H₂ is shown in Figure 13.
Fig. 13. Numerical profiles of temperature and major chemical species in opposed flow diffusion flame composed of 50%N₂+50%O₂ and 96%CH₄+4%C₂H₂ [27].

The probe is heated by convection from the flame and cools by radiation. The energy balance is shown in Eq. (4.1). The conductive heat transfer through the probe material is neglected due to the small diameter of the probe.

\[ hA_p(T_f - T_p) - \sigma\varepsilon A_p T_p^4 = 0 \]  

(4.1)

The temperature of the probe can be evaluated from the relation in Eq. (4.2)

\[ T_p = T_f - \frac{\sigma\varepsilon T_p^4}{h} \]  

(4.2)

where \( h \) is the heat transfer coefficient, \( A_p \) is the surface area of the probe, \( \sigma \) is the Stefan-Boltzmann constant, \( T_p \) and \( T_f \) are the probe and flame temperatures, respectively.
The heat transfer coefficient is evaluated from the Eq. (4.3).

\[ h = \frac{k}{d} \frac{\text{Nu}}{\text{d}} \]  \hspace{1cm} (4.3)

where Nu is the Nusselt number, \( k \) is the thermal conductivity of the fluid and \( d \) is the diameter of the probe. This shows that the temperature of the probe is always lower than the flame temperature. It begins approaching the flame temperature only in the limit of the infinitely small diameter. The probe temperature decreases with increasing diameter. Assuming the flame temperature of 2400 °C, the temperature difference is \( \sim 1000 \) K for probes which are 1 mm in diameter which is clearly observed in Figure 14.

Fig. 14. Plot of variation in the temperature of the probe with change in diameter.
4.2 General mechanism of material transport in flame environment

The lower surface of the inserted metal probe shows a slightly worn out pattern indicating loss of material from this region which undergoes oxidation. The synthesized V$_2$O$_5$ structures are observed to cover the entire upper surface of the probe. The outer part of the probe shows abnormal peak like structures. Figure 15 provides a schematic of probe, showing the position of abnormal peak like structures.

![Fig. 15. Schematic of the probe showing the position of abnormal V$_2$O$_5$ peak like structure formation in relation to the flame position.](image)

The highly oxidative environment of the flame results in the oxidation of vanadium to form V$_2$O$_5$. The high temperature at the lower surface of the probe vaporizes V$_2$O$_5$. It is transported from the high temperature oxidation zone at the bottom to the slightly cooler temperature zone downstream. In this process the material gets transported axially not only through gradients of temperature but also of chemical species. Since this transport occurs from the oxidation zone, chemical species with oxygen content are predominant in chemically affecting the transported species. The probe cross-section showing deposits of V$_2$O$_5$ which are observed under SEM for understanding their morphology and also areas of formation of abnormal oblate and sharp peak like structures of V$_2$O$_5$ are shown in Figure 16.
Fig. 16. Schematic of probe cross-section showing the material ablated from the bottom of the probe and the region of $V_2O_5$ deposition and also abnormal peak formation on the exterior as compared to the interior surface of the probe.

These $V_2O_5$ vapors crystallize on the upper cooler surface of the probe. Thus $V_2O_5$ nanostructures and microstructures get formed. The mild discoloration of the outer end of the oxidized probe could be seen with the naked eye along with abnormal peaks projecting outward on the probe surface at its outer end when viewed under the Zeiss compound microscope in certain experiments where the oxidative environment was intense. This happens at the outer part of the probe since this part is subjected to the outer curving of the flame. The peaks are prominent at the exterior of the surface of the probe and they progressively become shorter in the interior of the probe surface. Their formation is dependent on the interaction between the probe surface and the outer curved part of the flame. The $V_2O_5$ deposits occurring in the interior region of the probe are viewed under SEM for observing their morphology.
4.3 Influence of axial position of probe on the morphology of synthesized structures

4.3.1 Morphology observed under SEM

The initial test condition selected is using low strain rate $20 \text{s}^{-1}$ and oxidizer composition by volume $50\%\text{O}_2+50\%\text{N}_2$. These parameters are selected based on the previous results for solid support synthesis of tungsten oxide and molybdenum oxide nanorods which were performed at this strain rate and oxidizer composition [52]. The fuel composition selected is $100\%\text{CH}_4$ initially. The addition of acetylene in the proportion $96\%\text{CH}_4+4\%\text{C}_2\text{H}_2$ is carried out in the later experiments which did not yield similar results with vanadium as have been previously observed with tungsten and molybdenum [52]. The length between the fuel and oxidizer nozzle exits is kept fixed at 2.54 cm (1 inch). The axial position of the probe selected is 12 mm from the fuel nozzle end and residence time selected is 60 seconds.

Deposits of nanomaterials could be seen with naked eyes projecting out on the surface of the probe. Channel like structures and striations of slight yellowish tinge indicating predominantly $\text{V}_2\text{O}_5$ are observed under the Zeiss compound microscope. Under the SEM, thick network of channels is observed. These are long rectangular channels usually 10-20 $\mu\text{m}$ in thickness and about 100-400 $\mu\text{m}$ long as seen in Figures 17 (a, b). The synthesized structures appear to cover both the top as well as the bottom surface of the probe over its entire length due to the intense combustion environment. However, the structures at the top part of the surface appear more densely packed as compared to the bottom part which is mildly oxidized and shows etching which confirms the material transport explained in Section 4.2.
Fig. 17. SEM images of highly oxidized probe: (a, b) Dense overlapping and interconnected network of V$_2$O$_5$ microchannels.

Almost the entire probe surface is covered with these dense networks of channels. In most cases they appear to have fused into each other partially or completely. The direction of their
growth is random such that the channels appear to be star shaped spreading about in all directions in their growth from the centre. Several such star like structures are observed scattered over the probe surface. Most of these channels are solid channels filled with material throughout when viewed in their cross-section plane. However in very few places, small hair like nanowires of about 30-80 nm in thickness and about 1.5-5 μm in length could be seen growing on the surface of the microchannels, as shown in Figure 18. The dense network of channels is due to the intense synthesis in the combustion environment resulting in the synthesized structural dimensions being of microscale than nanoscale. A small percentage of channels are internally hollow channels, as shown in Figure 19 (a). Some of the other hollow structures observed are due to the gaps about 8-10 μm in dimensions existing in between the overlapped microchannels and microplates seen in Figure 19 (b).

Fig. 18. SEM image of nanowires seen growing on surface and tips of microchannel for axial position 12 mm.
Fig. 19. SEM images of hollow structures: (a) microchannel with hollow internal centre, (b) hollow gaps between overlapped microchannels.
Thus the axial position of the probe is shifted away from the high temperature oxidation zone of the flame toward the fuel nozzle end by 1 mm making the new axial position of the inserted vanadium probe at 11 mm from the fuel nozzle end. The other flame parameters are kept constant.

Under the SEM, a dense overlapping layer of rectangular chips about 300-400 nm in thickness and about 1 μm in length could be seen predominantly near the outer end of the probe as shown in Figure 20. Similar crystallite structures of slightly larger microscale dimensions are also observed in hydrothermal synthesis [53], [54] and by using the spin coating and annealing procedure [55]. The experimental result obtained by the flame gradient technique has been able to replicate these results at a nanoscale which is unique. This once again demonstrates the advantage of flame gradient technique where careful manipulation of parameters results in fine tune control of the morphological aspects to the order of nanoscale.

Fig. 20. SEM image of the chip like structures observed.
Over the remaining surface of the probe, oblong structures made of about 2-4 bead like components could be seen scattered randomly. The beads are about 500-700 nm in length and about 150-300 nm in diameter. 2-4 of these beads are linked end to end or are piled and appear like oblong structures dispersed over the probe surface as seen in Figures 21 (a, b).

Fig. 21. SEM images of nanobeads of $\text{V}_2\text{O}_5$ which show their end to end linking forming small linear chains which are randomly dispersed over the probe surface: (a) Low magnification image, (b) High magnification image showing bead structures with clarity.
Spherical nanoparticles of V$_2$O$_5$ about 50 nm in diameter attached to each other in branches have been synthesized [30]. These bead like structures bear no resemblance to the clusters of spherical nanoparticles but rather appear to be primordial building blocks for the formation of the chip like structures. These beads get linked to each other or even merge into each other producing the nanochips. Near few of the rectangular chip like structures, channels about 1-3 μm in thickness and about 20-40 μm long are observed as shown in Figure 22. Over these channels, nanowires about 3μm long and 50-70 nm in diameter could be seen projecting outwards as observed in Figure 23. However these structures do not dominate the probe surface.

Fig. 22. SEM image of the microchannel seen in very few regions for the axial probe distance 11 mm.
Due to the reduction of the synthesized structures to the order of nanoscale with the axial position of the inserted probe at a distance of 11 mm from the fuel nozzle end, the position of the probe is further axially shifted to 10 mm from the fuel nozzle end. At 10 mm axial distance, the probe is subjected to lower thermal and chemical effects. The synthesized structures now appear to grow vertically to give rise to nanowalls. These nanowalls are randomly scattered all over the top surface of the probe and are randomly oriented as seen in Figure 24. They are more clearly seen under higher magnification in Figure 25.
Fig. 24. SEM image of nanowalls scattered over probe surface.

Fig. 25. Magnified SEM image of nanowalls densely packed
The walls appear to have rough curves as well as rough edges while in some cases they appear to be pointed as needles. These nanowalls are typically 60-120 nm in thickness and about 1-2 μm in length and height as seen in Figures 26 (a, b).

Fig. 26. Magnified SEM images of few nanowalls showing clear morphology: (a) Morphology shows rough edges, (b) Morphology shows rough curves.
The synthesized nanowalls may also contain soot or may be composed of hydrocarbons entirely. In order to identify the chemical composition of the synthesized nanowalls, energy dispersive X-ray spectroscopy (EDS) is carried out. These results are then compared with the X-ray spectrum obtained from a standard V₂O₅ powder sample of 99.99% purity from Sigma Aldrich. The setting of the standard is explained in the next Section.

4.3.2 Setting a standard for EDS

The EDS is carried out at various locations within the V₂O₅ powder to minimize the error due to peculiarities at some locations. Also at each location, EDS is carried out multiple times with longer real time capture of X-rays to ensure that large number of counts of the X-rays are detected. Usually the real time employed for capture of X-rays is around 300-400 seconds to ensure X-ray count to be around 20,000. This minimizes the error due to lower count of detected X-rays. The SEM image of the sample used as the standard is provided in Figure 27. EDS is carried out at various energies from 5, 10, 20 to 30 keV and the results are shown in Figures 28-31.

Fig. 27. SEM image of the V₂O₅ powder.
Fig. 28. EDS carried out on standard V$_2$O$_5$ powder sample at 5 keV.

Fig. 29. EDS carried out on standard V$_2$O$_5$ powder sample at 10 keV.

Lower energy X-ray for vanadium overlapped with oxygen.
Fig. 30. EDS carried out on standard V$_2$O$_5$ powder sample at 20 keV.

Fig. 31. EDS carried out on standard V$_2$O$_5$ powder sample at 30 keV.

Higher energy X-ray for vanadium
The effect of increasing voltages is clearly seen in Figures 28-31. The lower energies of 5 and 10 keV are not able to penetrate deep into the sample but can scan more area of the sample. As a result they are only able to better pick up the lower energy X-rays for vanadium specifically the one occurring at La1. However the higher energy X-rays occurring at Ka1 and Kb1 for vanadium are not detected with the use of 5 keV and are not smoothly detected by 10 keV energies. Once the energy is increased to 30 keV, only the higher energy X-ray is detected while the lower energy X-ray for vanadium is barely picked up in comparison. Therefore it is decided to select 20 keV for EDS for it resolves both these high and low energy X-rays problems for vanadium. Figure 32 shows the EDS with 20 keV where both the low energy and high energy X-rays for vanadium are detected clearly.

Fig. 32. EDS for 20 keV repeated and compared with the previous result at the same location for reducing any error.
The overlap of X-rays for oxygen and low energy X-ray for vanadium poses a difficulty in determining the definitive presence of either vanadium or oxygen or both. However since this sample is 99.99% purity $V_2O_5$, it can be reasonably assumed that the low energy X-ray detected corresponds to both vanadium as well as oxygen. This assumption can only be made safely if the composition of the standard sample is known with certainty.

Now at the same location on the powder, for 20 keV, another reading for EDS is taken to check for any drastic variations in the detected X-ray spectrum as shown in Figure 32. The X-ray spectrum observed shows the characteristic spikes observed at the locations where X-rays are detected for vanadium and oxygen. The earlier spike occurs at lower energy X-ray within 0.0 to 1.0 keV, while the other spike is close to 5.0 keV at higher energy X-ray. The lower energy spikes are difficult to observe due to the large difference in the number of counts detected at lower and higher energy X-rays. The atomic percentage for both the cases is also very similar within the standard deviation. Thus X-ray spectrum shown in Figure 32 is set as the standard.

### 4.3.3 EDS characterization of the synthesized nanowalls

EDS is carried out on the samples showing nanowall growth. These results are shown in Figures 33 and 34. These results are then compared with a standard X-ray spectrum for $V_2O_5$ powder sample of 99.99% purity from Sigma Aldrich shown earlier in Figure 32. Several locations on the probe surface which show nanowall formation are selected for EDS so that error is minimized.
Fig. 33. EDS for the nanowalls showing characteristic peaks for vanadium and oxygen in regions lightly covered by nanowalls.

Fig. 34. EDS for the nanowalls showing characteristic peaks for vanadium and oxygen over densely packed nanowall regions.
As seen in Figure 34, there is a slight impurity detected of iron and aluminum. This occurs because the sample is mounted on to an aluminum stud before being inserted in the Hitachi S-3200N SEM. The probe holding tube, cap and shield are all made up of stainless steel which is in contact with the probe. These are considered to contribute to these impurities. However in spite of these impurities, the EDS spectrum closely agrees with the standard spectrum shown in Figure 32.

The atomic percentages for vanadium and oxygen seen in Figures 33 and 34 match closely with those in Figure 32. The slight discrepancy observed in Figure 34 is due to the impurities and such slight changes without a drastic change in the atomic percentages are considered reasonable. Thus the nanowalls structures are confirmed to be $V_2O_5$. Similar nanowalls of $V_2O_5$ are synthesized using hydrothermal method [39]. These unique structures have been synthesized using the flame gradient in the experiments perhaps for the first time.

4.3.4 Analysis of effect of variation in axial position of the probe in the flame

From the results, it is clear that for shorter residence time in regions close to the flame front, the formation of microchannels is influenced. The formation of nanochips and nanobeads occurs at position slightly away from the flame front at relatively lower temperature and chemical species concentration. When the probe is inserted further away from the flame front, there is a greater tendency to form nanowalls.

The lower temperature and chemical species concentration favors the growth of nanoscale and well defined $V_2O_5$ nanostructures. Positioning the probe close to the flame increases the temperature to which the probe is exposed and this leads to the formation of microchannels. The effect of reduction of the axial distance of the probe from the fuel nozzle end is shown in
Table 2. The change in thickness is drastic for the axial distance variation from 12 mm to 11 mm but is rather mild for further reduction in axial distance to 10 mm.

Table 2. Effect of reduction of axial distance of probe from fuel nozzle end on morphology of synthesized structures.

<table>
<thead>
<tr>
<th>Axial distance of probe from the fuel nozzle end</th>
<th>Dominant structures synthesized</th>
<th>Thickness/Diameter</th>
<th>Length</th>
</tr>
</thead>
<tbody>
<tr>
<td>12 mm</td>
<td>Channels</td>
<td>10-20 μm</td>
<td>100-400 μm</td>
</tr>
<tr>
<td>11 mm</td>
<td>Chips/Beads</td>
<td>300-400 nm/150-300 nm</td>
<td>1 μm/600 nm</td>
</tr>
<tr>
<td>10 mm</td>
<td>Walls</td>
<td>60-120 nm</td>
<td>1-2 μm</td>
</tr>
</tbody>
</table>

The reduction of the axial distance to 9 mm yields no synthesis of oxides but rather the probe gets inserted in the yellow soot zone of the flame. This axial distance is therefore not selected in the experiment as the probe surface will show more soot deposition and not oxides of vanadium. Since 12 mm axial distance only shows microscale structures predominantly, it is excluded from being used in further experiments. Thus 10 mm and 11 mm are selected as the effective variations in the axial position of the probe from the fuel nozzle end.

4.4 Influence of oxidizer composition on the morphology of synthesized structures

4.4.1 Morphology observed under SEM

The effect of oxidizer composition is considered by holding the other parameters constant. The strain rate is 20 s⁻¹, axial position of the probe from the fuel nozzle end is 10 mm and the residence time is 90 seconds. Since the residence time is now increased to 90 seconds, the axial distance is correspondingly lowered to 10 mm to facilitate nanoscale growth.
The axial position of the probe at a distance of 10 mm from the fuel nozzle exit places the probe further away from the flame front. The lowered temperature and altered species concentration environment facilitates growth of structures that are predominantly of the order of nanoscale as seen in Figures 35 and 36.

Fig. 35. SEM image of nanochips densely covering the probe surface.
The oxidizer composition is changed to 70%N₂+30%O₂ so that oxidizer enrichment decreases. This lowered oxidative combustion environment reduces the temperature and amount of oxygen available for oxidation. This is expected to facilitate the growth of
structures of nanoscale order rather than microscale order resulting from excessive oxidation.

The SEM images for 10 mm axial distance are shown in Figures 37-39.

Fig. 37. SEM image showing fluffy structure.

Fig. 38. SEM image showing nanofiber growth.
Fig. 39. SEM image of nanofiber formation alongside fluffy structure.

Fluffy structure growth is observed in certain regions on the probe surface as shown in Figure 37. The nanofibers seen in Figure 36 are about 150-250 nm wide and grow to about 1.5-3.5 μm in length. These fluffy structures and nanofibers are observed in Figures 37 and 38 to grow individually at certain spots over the entire probe length while in some regions they appear to grow alongside as seen in Figure 39. The tips of the nanofibers show hair like fluffy growth. This suggests that the fluffy structures grow onto nanofibers in some regions while in others they remain unaffected.

The oxygen enrichment is decreased further so that only air-methane flame is established. The oxidizer composition is now 79%N₂+21%O₂. However, no significant structures are synthesized during the experiment and the SEM image shows an unaffected probe surface
with slight cracks. Thus oxygen enrichment is crucial for oxidation of vanadium to give rise to vanadium oxide.

4.4.2 EDS characterization of the soot and carbon nanofiber structures

The synthesized structures in Figures 37-39 resemble soot and carbon nanofiber formation and hence it is crucial to investigate the chemical composition of these structures using EDS. The Figures 40 and 41 show the EDS results carried out on the nanofibers and fluffy structures respectively.

**Fig. 40. EDS result for the synthesized nanofibers.**
The EDS characterization proceeds by comparison of the X-ray spectrum of this sample with the standard shown in Figure 32. The sharp carbon peaks observed in both the Figures 40 and 41 indicate the presence of carbon nanofibers and soot respectively. These figures also indicate the higher atomic percentage of carbon present. This confirms that the nanofibers and the fluffy structures are carbon nanofibers and soot respectively. The formation of these structures occurs due to the fact that at 10 mm distance from the fuel nozzle end, the probe is further away from the oxidative flame front and very much affected by its proximity to the yellow pyrolysis zone. This causes the formation of these structures on the vanadium probe surface.
4.4.3 Analysis of effect of variation in oxidizer composition

The effect of decreasing oxygen enrichment in the oxidizer mixture did not yield well organized nanostructures. The decreasing oxygen content in oxidizer reduces the flame temperature [45]; however it also reduces oxygen content which plays a primary role in oxidation. On the contrary, the nanochips formation is seen for oxidizer composition 50%N₂+50%O₂, while for pure air-methane flame; no significant structures are synthesized. The effect of oxidizer composition on the morphology of the synthesized structures is shown in Table 3.

Table 3. Effect of variation of oxidizer composition on the morphology of synthesized structures.

<table>
<thead>
<tr>
<th>Oxidizer composition</th>
<th>Dominant structures synthesized</th>
<th>Thickness</th>
<th>Length</th>
</tr>
</thead>
<tbody>
<tr>
<td>50%N₂+50%O₂</td>
<td>Chips</td>
<td>300-500 nm</td>
<td>1 μm</td>
</tr>
<tr>
<td>70%N₂+30%O₂</td>
<td>Soot + Carbon nanofibers</td>
<td></td>
<td></td>
</tr>
<tr>
<td>79%N₂+21%O₂</td>
<td>No structures</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

This strongly suggests that oxygen enrichment is necessary for oxidation of vanadium. Thus oxidizer composition 50%N₂+50%O₂ is considered a standard oxidizer composition for generating oxides of vanadium. Further reduction in oxidizer composition is excluded from the experimental procedure.
4.5 Influence of residence time on the morphology of the synthesized structures

4.5.1 Morphology observed under SEM

The residence time is a crucial parameter governing the synthesis of nanostructures. Longer residence time increases the coalescence of the growing structures giving rise to larger microscale structures while shorter residence time influences nanostructure formation. The residence time is varied from 90 seconds down to 30 seconds for the axial probe position of 11 mm, in order to reduce the dimensions of the synthesized structures from microscale to nanoscale. The SEM image of the probe inserted in the flame for a residence time of 90 seconds is shown in Figures 42-44.

Under the SEM, sharp edged channels about 4-25 μm in thickness and 100-500 μm in length are observed over the probe surface as seen in Figure 42 which are the dominant synthesized structures.

Fig. 42. SEM image of microchannels for residence time 90 seconds.
In fewer regions slightly smaller curved bounded mounds and peaks about 5-12 μm in diameter and about 20-50 μm in length are observed as shown in Figure 43 while nanowire growth along the edges of microchannels is shown in Figure 44.

Fig. 43. SEM image showing micron sized mounds for residence time 90 seconds.

Fig. 44. SEM image of nanowire growth on microchannel for residence time 90 seconds.
These mounds appear to be the preliminary structures that later grow to give microchannels. The channels have a dense network over almost the entire probe surface. Nanorods about 100-300 nm in thickness and about 10-15 μm in length appear in some cases to be smeared over the microscale structures. In some other cases nanowires appear to be growing on the edges of microscale structures and also wrapping them, being about 25-50 nm in thickness and 1-4 μm in length as seen in Figure 44.

The dense network of microchannels is attributed to the excessive growth of structures due to increased residence time. Thus synthesized structures have dimensions predominantly in microscale than nanoscale. In order to reduce this effect, the probe was kept in the flame for a shorter residence time of 60 seconds. The SEM images of the synthesized structures for a residence time of 60 seconds are shown in Figures 45 and 46. The synthesized structures show a mixture of nanobeads and nanochips.

![SEM image of nanobeads covering the probe surface for a residence time 60 seconds.](image)

Fig. 45. SEM image of nanobeads covering the probe surface for a residence time 60 seconds.
These nanobeads are about 150-300 nm in thickness and about 2-2.5 μm in length while the nanochips are about 400-600 nm in their length, width and height. The nanobeads and nanochips appear scattered over the surface of the probe without any particular orientation of growth. The structures are densely packed suggesting intense crystallization.

The lowering of the residence time reduces the microscale growth to nanoscale. Therefore the residence time is now further reduced to 30 seconds to observe nanoscale synthesis in further detail. However, the reduction in residence time to 30 seconds results in no significant synthesized structures. The probe surface appears slightly cracked without any other significant change.
4.5.2 Analysis of effect of residence time variation

The lowering of the residence time brings down the dimensions of the synthesized structures from microscale to nanoscale. Higher residence time of 90 seconds increases the coalescence and growth of structures to form micron sized structures. The tendency decreases with reduction in residence time as the crystal growth occurs for a limited time. Nanoscale structures are predominantly observed for residence time of 60 seconds. Extremely low residence time of 30 seconds is insufficient for the formation of any significant structures from the crystallization of flame transported vanadium oxide vapor. The effect of variation in residence time on the morphology of the synthesized structures is shown in Table 4.

Table 4. Effect of variation of residence time of probe inserted in the flame on the morphology of synthesized structures.

<table>
<thead>
<tr>
<th>Residence time</th>
<th>Dominant structures synthesized</th>
<th>Thickness</th>
<th>Length</th>
</tr>
</thead>
<tbody>
<tr>
<td>90 seconds</td>
<td>Channels/Mounds</td>
<td>4-25 μm/5-12 μm</td>
<td>100-500 μm/20-50 μm</td>
</tr>
<tr>
<td>60 seconds</td>
<td>Beads/Chips</td>
<td>150-300 nm/400-600 nm</td>
<td>2-2.5 μm/500 nm</td>
</tr>
<tr>
<td>30 seconds</td>
<td>No structures</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

From Table 4, it can be seen that there exists a limiting condition on the residence time where exceedingly low residence time of 30 seconds yields no significant synthesized structures. Such a low residence time is avoided during the experiments. A residence time exceeding 90 seconds will facilitate the growth of microstructures and hence residence time above 90 seconds is also avoided.
4.6 Influence of acetylene addition on the morphology of the synthesized structures

4.6.1 Morphology observed under SEM

The fuel composition used in the experiments whose results are described in Sections 4.3-4.5 consists of 100%CH₄. The effect of addition of acetylene is explained in this Section. The fuel composition used is 96%CH₄+4%C₂H₂ [52]. The axial position of 11 mm is initially selected while residence time is set to 60 seconds. The SEM images of synthesized structures with acetylene addition are shown in Figure 47.

Fig. 47. SEM image showing microchannel formation with acetylene addition and axial position 11 mm.
The acetylene addition contributes to the synthesis of metal oxides [52]. Microchannels of about 7-22 μm thick and about several hundred micrometers long are observed in a dense network. These structures appear in star shaped groups scattered over the probe surface when observed under low magnification. These structures appear to be originating from a common centre within this star shaped group and the channels tend to radiate outwards. Acetylene is stopped and fuel composition is restored to 100%CH₄. The SEM images with acetylene removal at the same axial position of 11 mm are shown in Figure 48.

Fig. 48. SEM image of lung like synthesized structure without acetylene for axial position 11 mm.
The lung like structures are even clearly seen at another location upon high magnification as shown in Figure 49.

Fig. 49. SEM image of lung like structure with higher magnification for axial position 11 mm.

Nanobranches about 300 nm in thickness and about 20 μm in length are observed while nanoblocks about 300-500 nm in their dimensions of random shapes are found interspersed between them. From Figures 48 and 49, the structures appear to have the appearance of lungs where the nanobranches appear as the branches of the bronchioles while the nanoblocks appear as the alveoli. Nanobranches appear to have folds at their edges which are slightly curled. This is perhaps an initial stage in the tendency to form nanoscrolls by tending to fold upon itself. Experiments with same values of governing parameters such as oxidizer composition 50%N₂+50%O₂, residence time 60 seconds, axial position of probe 11 mm, fuel
composition 100%CH\textsubscript{4} and strain rate 20 s\textsuperscript{-1} have been carried out and results reported in Section 4.3. The nanoblocks like structures have also been observed in Section 4.3, however the nanobranches are only observed in this experiment even though the governing parameters remain the same. The reason for this is not well understood. It is likely that such structures also existed in earlier case in Section 4.3, but they were covered with nanochips completely so that they were not visible easily. The results obtained do not show any influence of addition of acetylene as has been previously observed [52].

In order to better understand the effect of acetylene addition, the axial position is now changed to 10 mm from the fuel nozzle end and all other parameters are kept same. The SEM images of the synthesized structures with addition of acetylene are shown in Figures 50 and 51.

![SEM image of carbon nanotrees synthesized with acetylene addition for axial distance 10 mm.](image)

Fig. 50. SEM image of carbon nanotrees synthesized with acetylene addition for axial distance 10 mm.
The curled structures resemble carbon nanotrees. In this case both carbon nanotrees and $\text{V}_2\text{O}_5$ nanowalls about 80-130 nm thick and about 1-2 $\mu$m long are observed as shown in Figures 50 and 51 respectively. The carbon nanotree formation occurs predominantly in the region of the probe deep into the flame while the nanowall formation occurs in the region that is slightly on the outer side of the probe. The contribution of acetylene has a very different effect when the axial distance of the probe is changed to 11 mm as compared to axial distance of 10 mm. Now acetylene is stopped so that 100%CH$_4$ constitutes the fuel composition. The SEM results of the synthesized structures with removal of acetylene while keeping all other parameters constant are shown in Figure 52.
Fig. 52. SEM image of the synthesized nanowalls without acetylene for an axial position 10 mm.

Figure 52 shows the nanowalls which appear sloping down due to the tilt introduced in the SEM. This was required for proper observation of the structures. These nanowalls are about 100 nm thick and about 2 µm long. These structures have also been previously observed in Section 4.3 with same governing parameters. Thus acetylene addition did not yield any significant structures. Instead when the probe was positioned closer to the flame, microscale synthesis occurred while the positioning of the probe further away from the flame front resulted in carbon nanotree formation along with V$_2$O$_5$ nanowalls. Nanobranches along with nanoblocks and nanowalls without any carbon presence are synthesized with same values of governing parameters when acetylene is completely removed.
4.6.2 Analysis of the effect of acetylene addition

In the case of vanadium, acetylene addition did not yield the expected results observed previously with other metals. This occurs because the increase in acetylene raises the heat release and flame temperature. The increase in temperature facilitates the formation of microstructures and acetylene contributes to form carbon nanotrees. The effect of acetylene addition on the morphology of the synthesized structures is shown in Table 5.

Table 5. Effect of addition of acetylene in the fuel composition on the morphology of synthesized structures.

<table>
<thead>
<tr>
<th>Fuel composition</th>
<th>Axial probe distance</th>
<th>Dominant structures synthesized</th>
<th>Thickness</th>
<th>Length</th>
</tr>
</thead>
<tbody>
<tr>
<td>4%C$_2$H$_2$+96%CH$_4$</td>
<td>11 mm</td>
<td>Channels</td>
<td>7-22 μm thick</td>
<td>100s μm</td>
</tr>
<tr>
<td>100%CH$_4$</td>
<td>11 mm</td>
<td>Nanobranches/Nanoblocks</td>
<td>300 nm/300-500 nm</td>
<td>20 μm/400 nm</td>
</tr>
<tr>
<td>4%C$_2$H$_2$+96%CH$_4$</td>
<td>10 mm</td>
<td>Nanowalls/Carbon nanotrees</td>
<td>80-130 nm</td>
<td>1-2 μm</td>
</tr>
<tr>
<td>100%CH$_4$</td>
<td>10 mm</td>
<td>Nanowalls</td>
<td>100 nm</td>
<td>2 μm</td>
</tr>
</tbody>
</table>

The particular catalytic chemical effect of acetylene in synthesizing nanorods of other metal oxides is starkly absent with vanadium [52]. The primary reason for this is the low melting point temperatures of both vanadium and V$_2$O$_5$ which easily permits the formation of microstructures. Hence acetylene addition is avoided in the experiments.
4.7 Influence of variation of strain rate on morphology of the synthesized structures

4.7.1 Morphology observed under SEM

The strain rate plays an important role in regulating the temperature of the flame. The increase in the strain rate reduces the thickness of the reactive zone of the flame and decreases the flame temperature. In order to prevent the flame temperature from dropping too low to result in significant synthesis, oxygen enriched air which is 50%O$_2$+50%N$_2$ is supplied as the oxidizer to burn 100%CH$_4$. The strain rate is 40 s$^{-1}$ while the residence time is 90 seconds and axial distance is 11 mm.

The SEM images shown in Figures 53 and 54 (a, b) reveal the morphology of the synthesized structures. The entire probe is covered with microchannel like structures as seen in Figure 53.

Fig. 53. SEM images showing microchannels and microbelts for strain rate 40 s$^{-1}$. 
Fig. 54. SEM images showing synthesized microchannels and microbelts with (a) nanohair and (b) nanorod growth at their edges and tips for strain rate $40 \text{ s}^{-1}$.
With increasing strain rate, the flame temperature decreases however the flow rates of the reactants increase. Under the SEM, the probe shows the formation of microchannels and microbelts about 5-10 μm thick and 100 μm long as seen in Figure 53. In the tip regions of the microbelts and along the edges of the microchannels, wire like structures having a diameter about 40-80 nm and a length of about 1-2 μm are seen in Figure 54 (a). Along the edges and tips of some other microstructures, small nanorod bundles are observed. These nanorods appear to be fused together with very little separation between them as seen in Figure 54 (b). Such bundled nanorods are also observed in hydrolysis synthesis method [53]. The strain rate is now reduced to 20 s⁻¹ while keeping the other parameters constant. The SEM image of the synthesized structures is shown in Figure 55.

Fig. 55. SEM image of microchannel synthesis for strain rate 20 s⁻¹.
The synthesis for lower strain yields microscale structures which appear about 8-12 μm thick and about 100 μm long. These microchannels predominantly do not show nanowire or nanorod growth at their tips or along their edges. These features appear upon increasing the strain rate to 40 s⁻¹.

4.7.2 Analysis of effect of strain rate variation

The increase in strain rate leads to reduction in the flame temperature as the reactive zone in the flame gets squeezed. Higher strain rate also increases the reactant flow velocities ensuring that more of the reactants are available at the flame for combustion. This effect coupled with oxidizer composition 50%N₂+50%O₂ supplies the oxygen ensuring the microscale synthesis of the structures. This reduction in temperature however has a trimming effect at the tips and along the edges of these structures which show nanowire and nanorod growth. The effect of strain rate variation on the morphology of the synthesized structures is shown in Table 6.

Table 6. Effect of strain rate variation on the morphology of synthesized structures.

<table>
<thead>
<tr>
<th>Strain rate</th>
<th>Dominant structures synthesized</th>
<th>Thickness</th>
<th>Length</th>
</tr>
</thead>
<tbody>
<tr>
<td>40 s⁻¹</td>
<td>Channels with nanowires and nanorods at tips</td>
<td>5-10 μm, 40-80 nm</td>
<td>100 μm, 1-2 μm</td>
</tr>
<tr>
<td>20 s⁻¹</td>
<td>Channels</td>
<td>8-12 μm</td>
<td>100 μm</td>
</tr>
</tbody>
</table>
4.8 Presence of hydroxides in combination with vanadium pentoxide

It is essential to investigate the presence of water in the synthesized V$_2$O$_5$ structures. Using water-electrolysis induced precipitation, hydrous manganese oxide MnO$_2$.0.5H$_2$O nanowall arrays have also been synthesized [56]. The presence of water molecules in the MnO$_2$ nanowall structure occurred due to the effect of electrolysis of water. Such an effect has occurred when V$_2$O$_5$ in solid and liquid state was placed in a reaction cell and subjected to oxygen enriched saturated steam [57]. The reaction occurring between 639°C and 899°C is given by Eq. (4.4).

$$ V_2 O_5_{(s\ or\ l)} + 3H_2 O_{(g)} \xrightarrow{O_2} 2VO(OH)_3_{(g)} $$  \hspace{1cm} (4.4)

The synthesized vanadium oxide trihydroxide exists in the gas phase. The formation of such structures would be occurring in the flame gradient synthesis as air supplied in the oxidizer contains some moisture traces. Since flame temperature is much higher than temperature for this substance to exist in the solid phase, it is not possible to observe them in crystalline form over the probe surface. Such structures can be analyzed by using a TEM grid and analyzed on transmission electron microscope. This supports the need to extend the solid support synthesis to volume synthesis within the flame. The presence of such V$_2$O$_5$-H$_2$O combinations may occur in solution based synthesis processes such as the one observed with hydrous manganese oxide. Such V$_2$O$_{5-x}$H$_2$O bundle-like nanostructures were synthesized by hydrothermal process [58] while in hydrothermal synthesis of V$_2$O$_5$ nanowires, it is categorically mentioned that pure V$_2$O$_5$ nanowires depicting orthorhombic structure were observed without any impurities in the X-ray diffraction technique XRD pattern [43].
4.9 Crystal growth mechanism

The growth mechanism for the crystals follows the vapor-solid (VS) mechanism. In such a mechanism, the crystal structure assumes the thermodynamically more favorable structure and thus equilibrium thermodynamics plays a crucial role [6]. The crystal growth occurs under the influence of several parameters; important among these are the driving force, temperature, dislocations, and impurities. The driving force for crystals growing from vapor phase growth is given by the ratio of equilibrium vapor pressure to the pressure at growth. The driving force is given by Eq. (4.5),

\[
\text{Driving force} = \ln \frac{p}{p_\infty} = \frac{\Delta \mu}{kT} \quad (4.5)
\]

\[
\mu_g = f(N,T) \quad (4.6)
\]

Where \( \Delta \mu \) is the difference in chemical potential in the two phases = \( \mu_{(g)} - \mu_{(s)} \), \( T \) is absolute temperature, \( k \) is Boltzmann constant, \( P \) is the growth pressure, \( P_\infty \) is equilibrium vapor pressure, and \( N \) is the number of vapor particles [59]. Thus the ratio \( \Delta \mu/kT \) gives the generalized driving force. The lower the driving force, the smoother is the interface of growth and the crystal grows by a spiral or layer-by-layer mechanism. The higher the driving force, greater is the interface roughness and growth proceeds to an adhesive type [59]. The incoming vapor phase atoms possess kinetic energy while the probe surface possesses nucleation sites and dislocations. If the chemical potential difference between the two phases exceeds the kinetic energy of the vapor phase particles which means the driving force is higher, then the vapor phase is able to bond with any nucleation site and grow. Thus the
interface formed is rough and growth is of adhesive type. On the other hand, if the kinetic energy of the vapor phase particles is higher, then it is unable to bond with most of the nucleation sites and only selective sites favor the bonding. Thus growth is highly selective, smooth interfaces are formed and growth proceeds either spirally or by layer-by-layer mechanism. Crystals growing from vapor phase generally have a smooth interface while those growing from a condensed melt phase usually have a rough interface.

Polyhedral crystals are bounded by smooth flat surfaces. In order for a crystal to grow, the driving force must be above a certain critical value. If the driving force is below this critical value, then the growth occurs by spiral mechanism employing a screw dislocation. Thus the polyhedral crystal appears smooth and flat. If the driving force is above this critical value then the layer-by-layer growth takes place. There is a transition between smooth and rough interfaces. Further increase in the driving force produces needle like or dendritic growth [59].

Microchannels bounded by flat, smooth faces are synthesized when the synthesis temperature is high. The chemical potential is a function of both temperature and number of particles. The growth from vapor phase to solid phase involves higher $\Delta \mu$. However if the temperature is sufficiently higher, then the overall driving force decreases. The lowered driving force facilitates the synthesized channels to be smooth and have flat faces. The growth mechanism is expected to be the spiral growth mechanism involving smooth interface [59]. This typically occurs when the probe is placed very close to the flame front, residence time is increased with a low strain rate.

The reduction in temperature by changing the axial position away from the flame front or the reduction in the residence time increases the driving force. This facilitates the growth of rough interfaces into chips and walls. In some cases where the nanowires are observed at the
edges of microstructures, the driving force is typically higher at edges than at the faces [59]. Thus high driving force facilitates the growth of structures formed by rough interface growth such as nanowires, nanorods, nanowalls and nanochips. This occurs when the probe position is decreased, residence time is reduced and strain rate is increased. The driving force alone cannot be considered for complete characterization of crystal structures. The driving force explains the growth of a single crystal. For polycrystalline aggregates, other effects such as twinning, banding and intergrowth need to be accounted. Several other factors such as impurities and dislocations play an important role along with driving factor.
CONCLUSIONS

Solid support synthesis of one-dimensional V$_2$O$_5$ nanostructures is carried out in an oxy-methane counter flow diffusion flame. The variation in parameters which include axial probe position, oxidizer composition, residence time, acetylene addition and strain rate are found to affect the morphology of the synthesized structures. Nanowalls, nanochips, nanobeads and nanobranches are the one-dimensional nanostructures observed with the variation of these parameters. The effect of various parameters on the morphology is summarized as:

- Reduction in axial position from 12 mm to 10 mm is observed to change microchannel synthesis to give nanowalls.
- Reduction in oxidizer composition from 50%N$_2$+50%O$_2$ does not facilitate the nanostructure synthesis. Rather oxygen enrichment is crucial for oxide formation and reduction in oxygen content has an adverse effect on synthesis.
- The decrease in residence time shows the change from microchannel synthesis to nanochips.
- The addition of acetylene did not yield the expected results. The increase in heat released due to acetylene addition, increases the temperature. This is observed to result in the formation of microchannels.
- The increase in strain rate facilitates the synthesis of nanowires along tips and edges of microchannels.

Lower temperature increases the driving force for an oxygen enriched flame. This facilitates the growth of nanostructures. Molybdenum oxide structures synthesized on solid support using an oxy-fuel counter flow diffusion flame show hollow channels of micron size [52]. The relatively low melting points of both molybdenum oxide and vanadium pentoxide
suggests the tendency of these structures to readily form microchannels while for similar conditions nanorods are obtained for tungsten oxide and iron oxide which have higher melting point. However by the manipulation of the parameters which control growth within the flame, it is possible to synthesize V$_2$O$_5$ nanowalls, nanochips, nanoblocks and also nanobranches. However nanorods and nanowire formation do not occur in bulk but rather on the tips and along edges of micron sized structures. The lower axial probe position, higher oxygen enrichment, low residence time, acetylene absence and high strain rate are observed to facilitate synthesis of one-dimensional nanostructures.


**FUTURE WORK**

The flame gradient method has been applied for solid support synthesis of one-dimensional V$_2$O$_5$ nanostructures. The predominant structures synthesized are nanowalls, nanobeads and nanochips instead of structures such as nanorods and nanotubes in excess. The higher temperature facilitates the growth of channels which are one-dimensional but the excessive material transport from the lower part of the probe to its upper part results in the synthesis of micron sized structures. It is therefore essential to use another material as the substrate for the synthesis. The height of the material from the probe may be varied to understand its effect on synthesis.

When the probe is inserted into the flame, there is a distinct glow in the flame. Also some glowing particles are seen travelling through the flame volume. This clearly suggests the presence of particles in the gas phase within the flame volume. It is therefore crucial to carry out TEM analysis of these to account for the gas phase synthesis. The implementation of another material substrate and TEM analysis will help in better understanding the synthesis and also allow for synthesis of one-dimensional V$_2$O$_5$ nanorods and nanotubes in bulk. Incorporating numerical model of the flame synthesis on solid support and laser diagnostics will provide greater insight into the flame chemistry and better understanding of the factors governing the structural morphology.
REFERENCES


APPENDIX A

The molecular crystalline structure of V$_2$O$_5$ is shown in Figure A1 [60]. The Figure shows the bulk V$_2$O$_5$ crystal structure with unit cell.

Fig. A1. The crystal structure of V$_2$O$_5$ is shown with atoms of vanadium and oxygen depicted along with unit cell [60].
APPENDIX B

Fig. B1. The excel sheet used for flame with oxidizer composition of 50%O₂+50%N₂ and fuel composition 96%CH₄+4%C₂H₂ for strain rate 20 s⁻¹.