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14. ABSTRACT

Funds from the ARO Research Instrumentation (RI) Program were used to upgrade the CCD-fiber-optic assembly of an intensified-CCD (ICCD) detector. The detector is coupled with an imaging spectrometer for use in the on-going ARO project, “Novel Flame-Based Synthesis of Nanowires for Multifunctional Application,” (Grant W911NF-08-1-0417) on the synthesis of nanowires of MoO3, CuO, WO3, Fe2O3, Bi2O3, and MnO2 for nano-energetic applications involving thermite reactions with nano-Al. Specifically, the CCD-FO component of

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Report Title

Final Report for RI: CCD-FO Assembly for Spectroscopic Characterization of Flame Synthesis Processes

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Funds from the ARO Research Instrumentation (RI) Program were used to upgrade the CCD-fiber-optic assembly of an intensified-CCD (ICCD) detector. The detector is coupled with an imaging spectrometer for use in the on-going ARO project, "Novel Flame-Based Synthesis of Nanowires for Multifunctional Application," (Grant W911NF-08-1-0417) on the synthesis of nanowires of MoO3, CuO, WO3, Fe2O3, Bi2O3, and MnO2 for nano-energetic applications involving thermite reactions with nano-Al. Specifically, the CCD-FO component of the detector is used as part of a laser-based spectroscopy setup to determine local gas-phase temperatures and major species concentrations, along with nanomaterial characteristics, during synthesis. The instrumentation can also be used as an imaging camera for planar laser-induced florescence (PLIF) and molecular filtered Rayleigh scattering (FRS).

The metal-oxide nanowires, which can be exploited for tailored heat release, are synthesized using strategic flame-based configurations that can be easily probed for conditions conducive to nanowire growth that can be translated to other geometries and even perhaps other gas-phase synthesis methods for large-scale production. To optimize processing, fundamental understanding of the mechanisms involved in the gas-phase processing flow field is crucial. By measuring the major fields in the synthesis process, the full aero-thermo-chemical nature of the process can be characterized. As such, the upgraded instrumentation readily enhances the quality of current ARO research.

Enter List of papers submitted or published that acknowledge ARO support from the start of the project to the date of this printing. List the papers, including journal references, in the following categories:

(a) Papers published in peer-reviewed journals (N/A for none)

Received Paper

TOTAL:

Number of Papers published in peer-reviewed journals:

(b) Papers published in non-peer-reviewed journals (N/A for none)

Received Paper

TOTAL:

Number of Papers published in non peer-reviewed journals:

(c) Presentations

Number of Presentations: 0.00

Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Received Paper

TOTAL:

Number of Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Peer-Reviewed Conference Proceeding publications (other than abstracts):

Received Paper

TOTAL:

Number of Peer-Reviewed Conference Proceeding publications (other than abstracts):

(d) Manuscripts

Received Paper

TOTAL:

Number of Manuscripts:

Books

Received Paper

TOTAL:

Patents Submitted

Patents Awarded

Awards

Graduate Students

NAME	PERCENT_SUPPORTED
FTE Equivalent:	
Total Number:	

Names of Post Doctorates

NAME	PERCENT_SUPPORTED
FTE Equivalent:	
Total Number:	

Names of Faculty Supported

NAME	PERCENT_SUPPORTED
FTE Equivalent:	
Total Number:	

Names of Under Graduate students supported

NAME PERCENT_SUPPORTED

FTE Equivalent:

Total Number:

Student Metrics

This section only applies to graduating undergraduates supported by this agreement in this reporting period

The number of undergraduates funded by this agreement who graduated during this period:	0.00
The number of undergraduates funded by this agreement who graduated during this period with a degree in science, mathematics, engineering, or technology fields:......	0.00
The number of undergraduates funded by your agreement who graduated during this period and will continue to pursue a graduate or Ph.D. degree in science, mathematics, engineering, or technology fields:......	0.00
Number of graduating undergraduates who achieved a 3.5 GPA to 4.0 (4.0 max scale):......	0.00
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The number of undergraduates funded by your agreement who graduated during this period and intend to work for the Department of Defense	0.00
The number of undergraduates funded by your agreement who graduated during this period and will receive scholarships or fellowships for further studies in science, mathematics, engineering or technology fields:......	0.00

Names of Personnel receiving masters degrees

NAME

Total Number:

Names of personnel receiving PHDs

NAME

Total Number:

Names of other research staff

NAME PERCENT_SUPPORTED

FTE Equivalent:

Total Number:

Sub Contractors (DD882)

Inventions (DD882)

Scientific Progress

See Attachment.

Technology Transfer

Final Report for RI: CCD-FO Assembly for Spectroscopic Characterization of Flame Synthesis Processes

(Grant W911NF-10-1-0018)

PI: Stephen D. Tse, Rutgers University

Abstract

Funds from the ARO Research Instrumentation (RI) Program were used to upgrade the CCD-fiber-optic assembly of an intensified-CCD (ICCD) detector. The detector is coupled with an imaging spectrometer for use in the on-going ARO project, “Novel Flame-Based Synthesis of Nanowires for Multifunctional Application,” (Grant W911NF-08-1-0417) on the synthesis of nanowires of MoO_3, CuO, WO_3, Fe_2O_3, Bi_2O_3, and MnO_2 for nano-energetic applications involving thermite reactions with nano-Al. Specifically, the CCD-FO component of the detector is used as part of a laser-based spectroscopy setup to determine local gas-phase temperatures and major species concentrations, along with nanomaterial characteristics, during synthesis. The instrumentation can also be used as an imaging camera for planar laser-induced florescence (PLIF) and molecular filtered Rayleigh scattering (FRS).

The metal-oxide nanowires, which can be exploited for tailored heat release, are synthesized using strategic flame-based configurations that can be easily probed for conditions conducive to nanowire growth that can be translated to other geometries and even perhaps other gas-phase synthesis methods for large-scale production. To optimize processing, fundamental understanding of the mechanisms involved in the gas-phase processing flow field is crucial. By measuring the major fields in the synthesis process, the full aero-thermo-chemical nature of the process can be characterized. Thus, the controlling mechanisms can then be unambiguously identified, analyzed, modeled, and compared with detailed computational simulation for quantitative realism, fundamental understanding, and predictive capability. As such, the upgraded instrumentation readily enhances the quality of current ARO research.

Acquired Equipment and Research Paradigm

This Research Instrumentation grant (W911NF-10-1-0018) was used to upgrade the CCD-fiber-optic assembly of a Princeton Instruments (Roper) PI-MAX:1300HQ Digital ICCD detector. Specifically, the instrumentation is characterized by an exclusive scientific grade 1, front-illuminated CCD, 1340x1300 pixels; 1:1 fiber-optic bonded 25mm Grade 1, Gen III image intensifier, fiber optic input; 20 x 20 mm pixels (25.0 mm image area); and <10ns gating capability. The intensifier offers high sensitivity from UV to NIR. The ICCD serves as the detector for a Princeton Instruments Acton 0.5m imaging spectrometer. Together, these instruments enable advanced laser-based spectroscopy to characterize the material-processing flow fields (as well as the materials themselves) during synthesis of nanostructured materials.

The equipment supports the ARO research project, “Novel Flame-Based Synthesis of Nanowires for Multifunctional Application,” which investigates flame synthesis of metal-oxide/carbide nanowires in aerodynamically simple flow fields, i.e. flat-flame stagnation-point (premixed) and flat-flame counterflow (non-premixed), along with utilization of external electric fields. Such well-defined combustion configurations allow for the probing of the fundamental growth mechanisms. As a result, the utilization of ***advanced spectroscopic diagnostics***, which enables the mapping of species concentrations and the quantitative determination of thermodynamic properties to properly characterize the material processing flow fields, becomes requisite in order to gain fundamental understanding of the mechanisms of nanowire formation and growth. This knowledge in turn allows for the ability to define process conditions that enable high purity and high rate yields of various nanostructured materials.

The equipment allows for an integrated effort incorporating a novel and robust flame-based processing technique, non-intrusive ***in-situ spectroscopic diagnostics***, state-of-the-art materials characterization, and computational modeling, as depicted in Fig. 1. Specifically, we investigate synthesis of metal-oxide nanowires such as Al_2O_3, SnO_2, ZnO, MoO_3, CuO, WO_3, Fe_2O_3, Bi_2O_3, and MnO_2. Metal-carbide nanowires synthesized include Al_4C_3, WC_x, and Fe_3C.

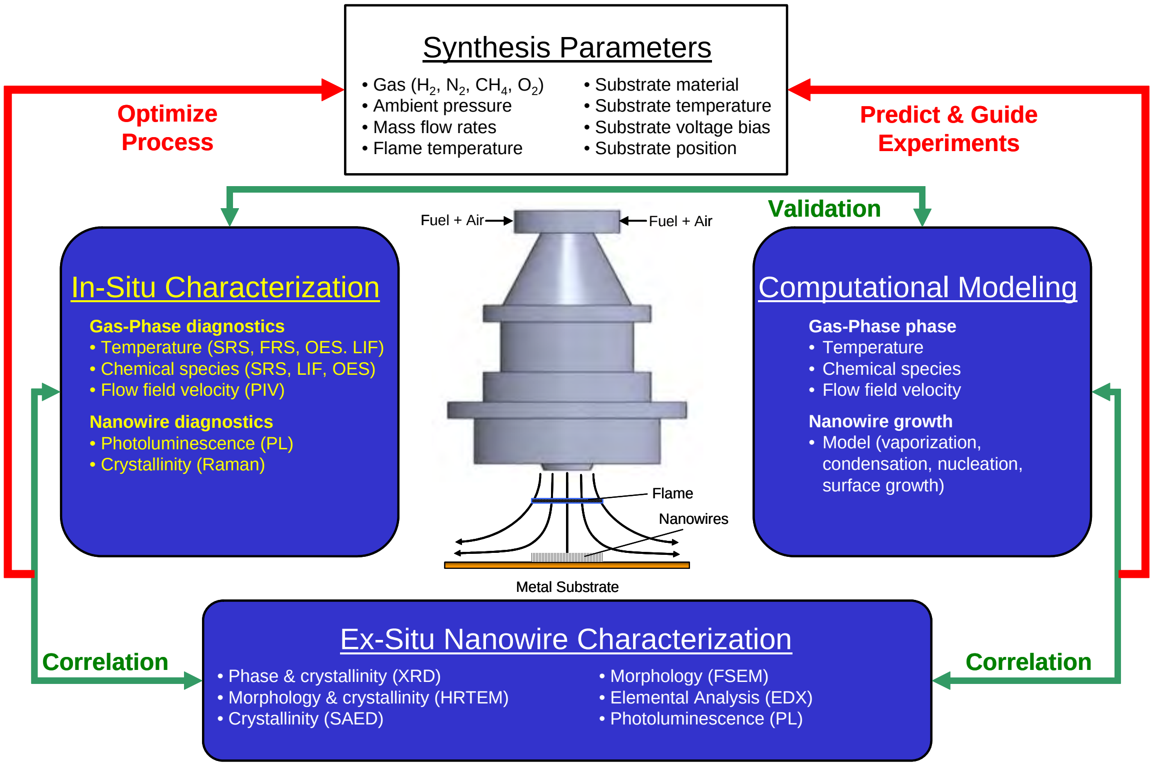

Figure 1. Concept diagram showing the key role of ***in-situ spectroscopic characterization*** in the optimized flame synthesis of metal oxide/carbide nanowires.

Diagnostics

The upgraded CCD-fiber-optic assembly within the ICCD camera serves as the detector for an imaging spectrometer, forming a multipurpose equipment, with high flexibility of configuration. As such, the research instrument allows for diagnostics such as Raman spectroscopy (SRS), laser-induced fluorescence (LIF), laser-induced incandescence (LII), and optical emission spectroscopy (OES). Specifically, Raman spectroscopy is used to measure the temperature and concentrations of major species (e.g. N_2, O_2, H_2O, CO_2, CH_4, H_2, C_2H_2, etc.); LIF measures the relative concentrations of important radical species (e.g. H, OH), as well as, gas-phase precursors (e.g. PAHs and C_2 leading to carbide formation); and LII measures the relative concentrations of particles. Chemiluminescence imaging provides an overall view of the combustion zones as well as spatial distribution information. Existing PIV equipment is used to obtain the velocity field in a plane. Raman spectroscopy and photoluminescence (PL) characterizes the nanowires in-situ. Such unambiguous information is essential for the modeling of governing mechanisms, along with detailed computational simulation for quantitative realism, fundamental understanding, and predictive capability.

Low-Intensity Laser- Induced Breakdown Spectroscopy

Recently, using the acquired instrumentation, a novel low-intensity laser-induced breakdown spectroscopy (LIBS) method has been used to examine nano-aerosols in-situ during flame synthesis of TiO_2 nanoparticles. Collected emissions (Fig. 2) agree well with Ti atomic spectra from the NIST database. In contrast to traditional application of LIBS on particles, the power used here is much lower (~20mJ/p or 50J/cm^2 at 532nm); and no spark is visually observed. Nevertheless, the low-intensity LIBS shows interesting selectivity, only exciting Ti atoms in particle phase, with no breakdown emission occurring for gas molecules (e.g. TTIP precursor). The emission intensity increases as the nanoparticles grow in the synthesis flow field, flattening out as the particles become larger than 6nm, indicating the absorption efficiency to be size-dependent for small particles. The signals saturate at a fluence of ~40J/cm^2. When the precursor concentration is larger than 150ppm (corresponding to particle sizes of 6-8nm), the emission intensity increases linearly with precursor concentration. The selectivity of the low-intensity LIBS for such application could be advantageous for tracking nanoparticle formation and for measuring particle volume fraction during gas-phase synthesis. The size-dependent absorption efficiency could be used to measure nanoparticle size in-situ.

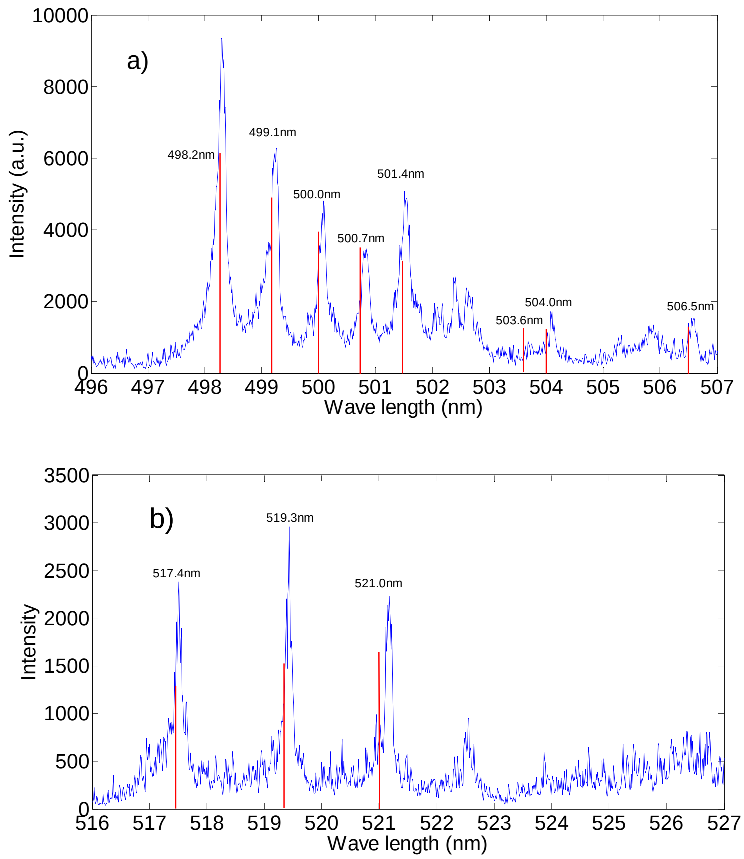

Figure 2. Emission spectra acquired from a laser excitation of 532nm (35mJ/p). Ti atomic spectra from NIST database is marked by red lines.

The setup for the laser-based diagnostics is illustrated in Fig. 3. The second harmonic (532nm) of an Nd:YAG laser operating at 10Hz serves as excitation source. The beam is focused by a 500mm focal-length plano-convex fused silica lens (Thorlabs, LA4782) to a waist diameter of ~200µm. As seen from Fig. 3, the collection optics consists of two 300mm focal-length achromat (Thorlabs, AC508-300-A), a holographic notch filter (Kaiser Optics, SuperNotch-Plus, 532nm), an image rotator, and a depolarizer (Thorlabs, DPU-25-A). Thus, the scattered light from a 200µm diameter by 1mm length measurement volume at the beam focus is collected at 90º into a 0.5m spectrometer (Acton SpectraPro 2500i, f/6.5) with 2400 groove/mm holographic grating (Richardson,68×84 mm, VIS) and 200µm slit width. The wavelength resolution is ~0.1nm. The detector is the upgraded ICCD camera acquired by this grant. Signals are gated to minimize the interference from flame emissions and other sources. The typical gate width is 200ns, and the typical collection time is 20s (200 shots) for laser induced emissions.

Gas-phase temperatures are determined using spontaneous Raman spectroscopy (SRS). The vibrational band of N_2 (centered ~2330cm^{-1} shift) is used to obtain the gas-phase temperature by least-square fitting the shape of the Q-branch spectrum to a library of theoretical spectra. The uncertainty of the measurement is ±50K. Elastic laser-light scattering (ELS) is employed to assess particle coagulation. For example, the local Rayleigh signals from a “clean” flame without precursor loading are acquired first. Then, the Rayleigh signals from a “synthesis” flame with precursor loading and nanoparticles are acquired. Comparisons of the two signals give insight into net scattering intensity from nanoparticles in the flow field. Note that the Raman notch filter is removed during ELS measurements. Currently, an iodine cell is being fabricated to do filtered Rayleigh scattering, using the upgraded ICCD.

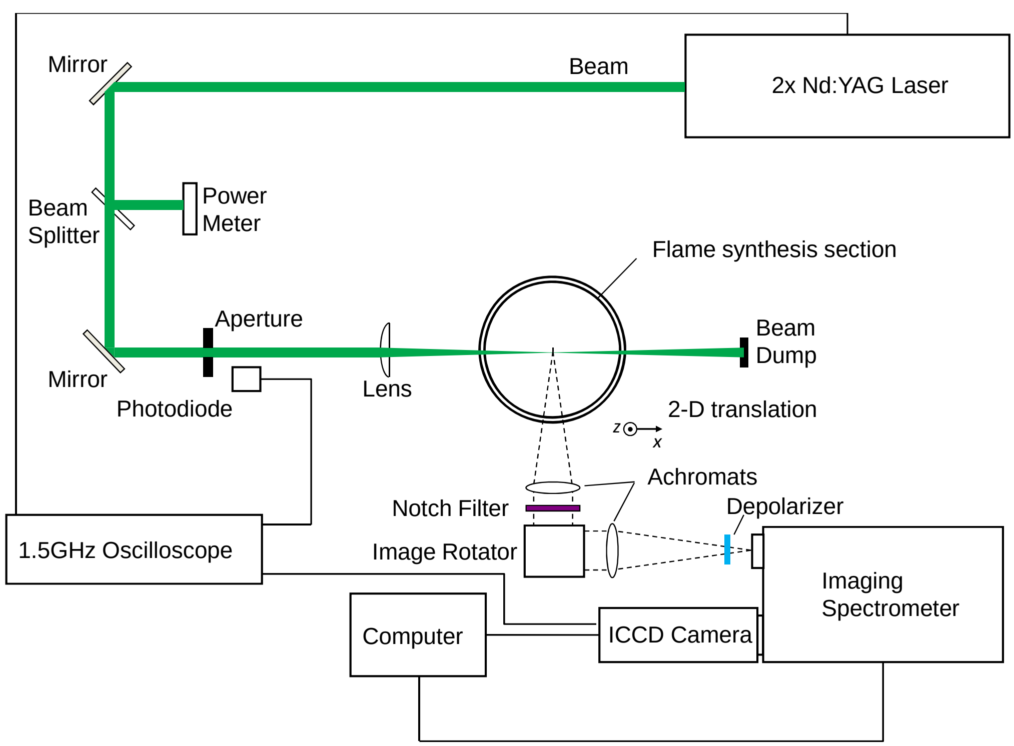

Figure 3. Schematic of the *in-situ* laser-based diagnostics for flame synthesis.