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Major Goals: Funds are requested from the ARO Research Instrumentation (RI) Program for the upgrade of an ultrafast laser synthesis, ignition, and diagnostics system. Specifically, a femtosecond laser currently being acquired through an ARO DUIRP grant can have its output beam shifted into the visible with a second harmonic generator. A previously-acquired (from ARO funds) ICCD camera needs a new board for external triggering. These items would significantly augment the capabilities of the system.

Accomplishments: This Research Instrumentation grant (W911NF-21-1-0110) was used to upgrade an ultrafast laser with a second harmonic generator, fix the external trigger of an ICCD, and replace the digital oscilloscope. The ICCD serves as the detector for a Princeton Instruments Acton 0.5m imaging spectrometer. The oscilloscope monitors the system and takes data. Together, these instruments enable laser ablation synthesis of nanostructured materials and advanced laser-based spectroscopy to characterize the material-processing flow fields (as well as the materials themselves).

Training Opportunities: Nothing to Report

Results Dissemination: Nothing to Report

Honors and Awards: Nothing to Report

Protocol Activity Status:

Technology Transfer: Nothing to Report

RPPR Final Report
as of 28-Sep-2023

Partners

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I certify that the information in the report is complete and accurate:
Signature: Stephen Tse
Signature Date: 9/26/23 8:05PM

Final Report for RI: Upgrade of Equipment for Ultrafast Laser Synthesis, Ignition, and Diagnostics System for Energetics

(Grant W911NF-21-1-0110)

PI: Stephen D. Tse, Rutgers University

June 2023

Abstract

Funds from the ARO Research Instrumentation (RI) Program were used to upgrade an ultrafast laser with a second harmonic generator, fix the external trigger of an intensified CCD (ICCD), and replace the digital oscilloscope. Specifically, the ultrafast laser is a Spitfire ACE 1 kHz 7-Watt System (SPFIRE ACE-100F1K) with the following specifications: energy of 7 mJ at 1 kHz at 800 nm; pulse width of 100 fs; stability of <0.5% RMS over 24 hours; pointing stability of 5 uRad constant temperature, <20 urad variable temperature; and M-squared of </= 1.3. A second harmonic generator was purchased to double the output laser beam frequency. The external trigger for the ICCD camera, a PI-MAX3:1024 x 256 system featuring a 1024 x 256 spectroscopy CCD fiber coupled to a Gen III intensifier, which is sensitive from UV to NIR, has been fixed. The digital oscilloscope to monitor the laser system and take data was replaced.

The upgrade of the ultrafast laser, fixing of the external trigger of the ICCD camera, and replacement of the oscilloscope supports the ARO project, "Synthesis of Novel NanoEnergetics and Study of Their Reactant Interfaces" (Grant W911NF-17-1-0111). The studies involve the synthesis of novel nano-energetic composites involving thermite reactions with nano-Al. As described below, the improved instrumentation will establish new research capabilities to better examine the fundamental mechanisms of synthesis, machining/milling, and ignition, along with spectra diagnoses of the associated phenomena.

Acquired Equipment and Research Paradigm

This Research Instrumentation grant (W911NF-21-1-0110) was used to upgrade an ultrafast laser with a second harmonic generator, fix the external trigger of an ICCD, and replace the digital oscilloscope. The ICCD serves as the detector for a Princeton Instruments Acton 0.5m imaging spectrometer. The oscilloscope monitors the system and takes data. Together, these instruments enable laser ablation synthesis of nanostructured materials and advanced laser-based spectroscopy to characterize the material-processing flow fields (as well as the materials themselves).

The equipment supported the ARO research project, "Synthesis of Novel NanoEnergetics and Study of Their Reactant Interfaces," which involves the synthesis of novel nano-energetic composites involving thermite reactions with nano-Al. Additionally, interfaces where the nano-scale reactants are separated by graphene layer(s) and with their ignition and combustion behavior are investigated. Specifically, planar structures are examined based on materials that we can readily synthesize, e.g., intermetallic, such as Al/graphene/Ni, and metallic-polymer, such as Al/graphene/PVDF.

The capabilities of the ultrafast laser and spectroscopy system will generate new nano-energetic geometries and provide knowledge about fundamental mechanisms. Ultimately, we will be able to optimize the structural details of the energetic nanocomposites, e.g., metal-oxide nanowire diameter, nanoplate thickness, array density, Al coating thickness, Al nanoparticle size and loading density, film component thicknesses, graphene disorder, polymer coating thickness, etc., to tailor the nanocomposite heat-release characteristics. Following are specific studies enabled by the purchased research instrumentation.

Synthesis of Al Nanoparticles by Ablation of Bulk Al in Liquids

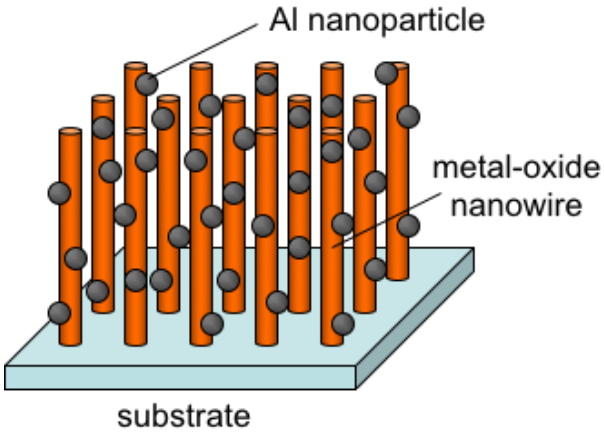

Figure 1. Schematic of Al-nanoparticle-decorated metal-oxide nanowire arrays.

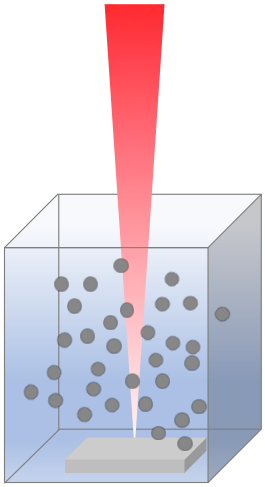

Figure 2. Schematic for the generation of nanoparticles during the laser ablation of a solid target in a liquid medium.

Al nanoparticle-decorated metal-oxide nanowires can also be studied and compared along with Al-coated metal-oxide nanowires (Fig. 1). High-purity Al nanoparticles can be produced via arc discharge, vapor deposition, electrochemical deposition, and ball milling. Still, the techniques often involve a high-vacuum system, pre-treatment, and complex gas delivery[1,2,3]. However, recent developments in laser ablation in confining liquids present a promising method to produce ultrafine active nanoparticles with high purity and crystallinity without extreme conditions (i.e., high pressure, ultra-low vacuum, high temperature), where the corresponding elements can be introduced into the liquid medium as a target[4] to be ablated, as shown in Fig. 2. The as-synthesized Al nanoparticles can then be drop deposited on the metal-oxide nanowires to from the energetic nanocomposite (Fig. 1).

This synthesis method is optimal for the University setting to produce lab-scale amounts of Al nanoparticles with very good size control[3]. The process typically takes a short period at the liquid-solid interface, i.e., a few microseconds[1], where the liquid medium is usually transparent to the laser-irradiated pulses[1]. The laser pulse interacts with the target, generating a plasma plume containing the vaporized target element. Subsequently, condensation or quenching of the plasma plume results in the formation of nanoparticles. The nanoparticle characteristics can be adjusted by selecting laser wavelength, pulse energy, pulse width, repetition rate, ablation liquid medium composition, and ablation duration[1]. Patil and co-workers[5] first demonstrated iron-oxide formation with metastable phase (FeO) on an iron surface in water using a Q-switched ruby laser (λ=0.694 μm) with 30-ns width at laser fluences of 10 and 15 J/cm^2. After the laser-pulse induced iron-water reactions at the solid-liquid interface, the rapid recombination of atoms in the plume (at high pressure and temperature) occurs, such that the high local concentration, pressure, and temperature gradients aid in forming the metastable phase of FeO[5]. As investigated by Grigoropoulos and co-workers with respect to the nucleation, growth, and collapse of bubbles, the

temperature can reach several thousand Kelvin; and the pressure can reach GPa inside the as-generated plasma plume upon laser irradiation at the solid-liquid interface[6,7,8,9,10].

The approach of Stratakis et al.[3] can synthesize Al nanoparticles free of both surface-active substances and counter-ions using a femtosecond laser to ablate an Al target immersed in a liquid (e.g., ethanol). They[3] found that while quenching of the hot plasma from the laser-target interaction by the surrounding liquid can also result in reactions with the liquid and air/oxygen dissolved in it, the high reactivity of Al with oxygen can partially be compensated by ablating using ultrashort laser pulses because faster quenching can minimize either oxide or hydroxide formation on the particle surface. Since the time scales for femtosecond (fs) laser pulses are considerably shorter than nanosecond (ns) or picosecond (ps) laser pulses[2] traditionally used in ablation processes, responses of the solid targets (e.g., expansion and decomposition) upon rapid heating can differ dramatically[2]. The fs laser pulses may have minimal interaction/affect with/on the ejected materials in the plasma plume because the pulse ends before the solid expands. The fs pulse can be absorbed before any significant heat conduction so that the local target spot can be heated to a much higher temperature and pressure than a longer pulse[2].

As mentioned above, the ablation liquid medium can either be reactive or non-reactive depending on the formation process and type of the desired nanoparticles. For the synthesis of Al nanoparticles, a relatively non-reactive liquid medium (e.g., ethanol, acetone, ethylene glycol[4]) would be best utilized. As shown by E. Stratakis et al.[3], the fs laser ablation of bulk aluminum in pure ethanol was done by using a Ti:sapphire laser beam (wavelength λ=800 nm, pulse width of 200 fs, repetition rate of 1 kHz) with the spot size on the solid target at ~500 μm (corresponding to laser fluence of 0.2 J/cm^2) for the exposure time of ~10 minutes, where the ethanol layer is about 1-2 mm above the Al target. Their[3] average nanoparticle size was ~20 nm for fs cases and ~60 nm for ps cases, with narrower distribution and better crystallization using fs pulses. Notwithstanding, Kumar and Thareja[11] reported the synthesis of the Al nanoparticles using deionized water as the liquid medium. With the second harmonic generator, laser ablation with wavelength λ=400 nm can be examined, which is expected to yield different nanoparticle characteristics.

Machine/Mill Energetic Nanocomposites into Specific Micro/Meso/Bulk-Structures

Our energetic nanocomposites can be machined/milled into specific micro/meso/bulk-scale structures. For example, holes and channels can be milled into the planar energetic nanocomposites described above to give porosity, where the holes can be left open or filled with other material, thereby adjusting the heat-release rate characteristics. Additionally, our energetic nanowire arrays can be trimmed to set lengths or 'mowed' to certain patterns, e.g., swiss roll, to examine propagation speeds.

Laser machining (i.e., ablating, drilling, cutting, welding, etc.) has been successfully used to modify materials utilizing CO_2, Nd:YAG, and excimer lasers[12,13,14]. Ultrashort-pulse laser machining can provide high laser intensity and precise breakdown threshold with reduced laser fluence, such that the ablation of materials is in a very limited heat-affected volume, leading to high precision ablation[12,15]. Absorption (wavelength dependent) of ultrashort pulses occurs on a time scale where material can be ablated with virtually no heat transfer to the surrounding material. For example, a 100 fs laser pulse with a pulse energy of 0.33 mJ can reach a peak intensity of 1015 W/cm^2 when irradiated on a 20 μm spot, while 100 J/pulse is needed for a 10 ns laser pulse to create the same intensity[12]. The energy absorption happens at the solid phase for the ultrashort pulses, while the absorption mainly takes place at the plasma layer for longer pulses. For ultrashort pulses, electrons are of much higher temperature than the ions during the high non-equilibrium

interaction, so the laser-matter interaction time is much shorter than the electron-ion energy relaxation time (matter heating up)[15,16]. During material breakdown and ablation under laser irradiation, the ablated materials can become either a liquid phase (using a long pulse) or a vapor phase (using an ultrashort pulse). For long laser pulses, a larger volume around the beam is melted with limited material vaporization. For ultrashort pulses, a larger volume of the materials is directly vaporized. Figure 3 shows the calculated melt and evaporation layer thickness for Si for both 7 ns and 100 fs pulses irradiations. The melt layer is more than 10 times the evaporation layer in the 7 ns case, and the melt thickness is an order of magnitude less[12].

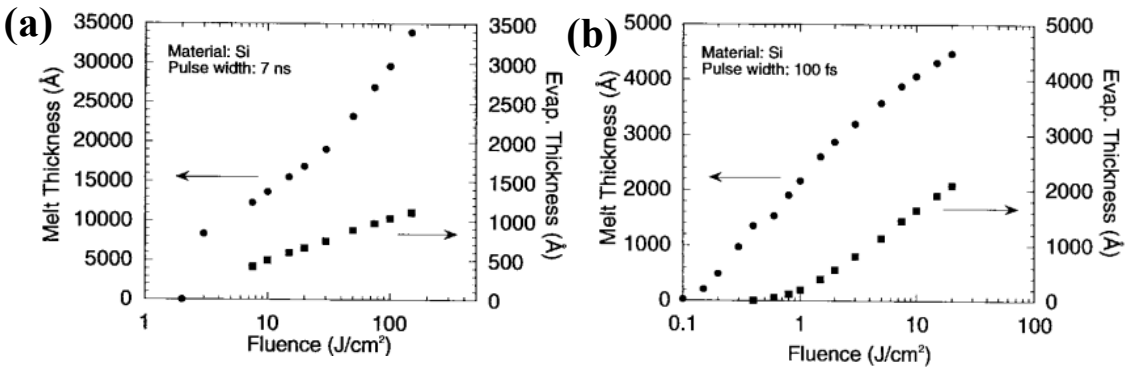

Figure 3. Calculated melt and evaporation thickness of Si under (a) 7 ns pulses and (b) 100 fs pulses. (Adapted and reproduced from Ref. 12.)

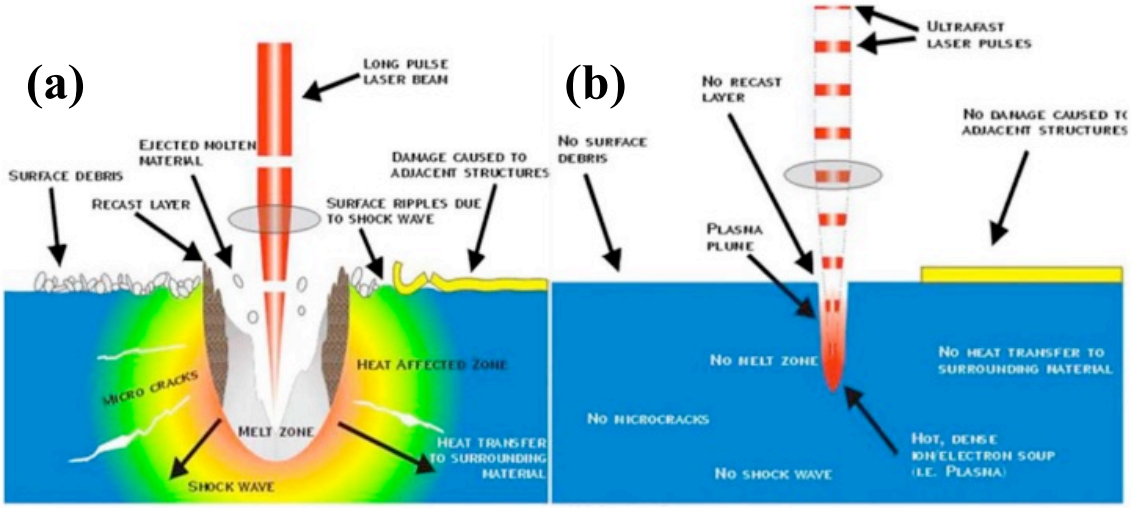

Figure 4. Schematic of (a) ns ablation (b) fs ablation. (Adapted and reproduced from Ref. 15.)

Furthermore, multiphoton absorption processes exist during ultrashort pulse irradiation with high peak intensity, where the bonds between electrons are directly broken with minimal heating effects[15]. As a result, the target is in non-equilibrium with electron gas of several thousand Kelvin inside a lattice of room temperature[15,17]. Figure 4 shows the difference between ns pulses ablation and fs pulses ablation. Therefore, femtosecond laser machining can be employed as a "***cold and safe***" cutting/milling process, as demonstrated by Roos et al.[18], to modify energetic materials (e.g. high explosives, detonators, and propellants) into desired shapes without coupling

energy into the energetic materials under precisely controlled ablation threshold, in conjunction with limited thermal and mechanical changes to the rest of the material.

Pulsed Laser Ignition of Novel Nano-energetic Samples

Previously, our $WO_{2.9}$/Al coaxial nanowire arrays were ignited via joule heating by passing current through the tungsten substrate (wire). Our energetic samples can also be ignited through local energy deposition using pulsed laser ignition. Total energy and power thresholds will be determined for different designs of our energetic nanocomposites. Since femtosecond pulses will have minimal conduction to the surrounding energy deposition area, as described in the 'machining' session (see Fig. 4b), comparisons between results for femtosecond and nanosecond pulses can shed light on the pulsed laser-material interactions, along with chemical and thermal-diffusive rate balances involved in ignition. For example, ns pulsed laser ignition thresholds should be much less than fs[19]. Characterization of temperature and/or chemical species, as described in the 'diagnostic' section above, will be conducted both spatially and temporally. Ignition in inert versus oxidative environments will be compared. Additionally, with the second harmonic generator, we can examine laser ignition at wavelength λ=400 nm and the fundamental at λ=800 nm.

Diagnose Chemical Species and Temperatures during Ignition and Burning

To understand fundamental mechanisms, chemical species and temperatures need to be characterized during the ignition and burning of energetic nanocomposites. For decades, traditional continuous-wave and nanosecond-pulsed lasers (e.g., Q-switched Nd:YAG laser, excimer laser) have been successfully applied to study combustion phenomena, using laser-induced fluorescence (LIF), particle image velocimetry (PIV), laser-induced incandescence (LII), coherent anti-Stokes Raman scattering (CARS), and resonant four-wave mixing (RFWM)[20]. Recently, the rapid development of ultrafast pulsed lasers, e.g., picosecond (ps) and femtosecond (fs), has enhanced diagnostic techniques and provided new measurement methods[21,22,23,24]. For example, the ultrashort pulses with high repetition rates make conducting detailed and high-resolution temporal studies possible. Ultimately, ultrafast laser diagnostics will be key to understanding the chemical kinetics and combustion dynamics of advanced energetics. The mode-locked Ti:sapphire ultrafast laser is a workhorse of laser-based combustion diagnostics. First, the ultrashort pulse duration makes a single collection achievable for some measurements because of the avoidance of collisional and pressure effects, such as temperature measurement in high-pressure, turbulent flames. Second, the spectral coverage is expanded to obtain higher-order signals because of its nonlinearities, where extreme UV and X-rays can be generated for various applications. Third, the high pulse repetition rates (1-300 kHz) can be applied to study fluctuation phenomena (e.g., timescale of 1-100 μs for high-pressure turbulent combustion) with more time-correlated details.

Diagnostics with high temporal resolution are needed to characterize combustion of energetic nanocomposites. Techniques such as ultrafast PLIF and CARS can measure gas-phase radicals and major species concentrations, especially if the energetics react in an oxidative ambient environment, augmenting heat release. Moreover, for ignition using femtosecond laser pulses, significant vaporization will occur, as described in the 'machining' section above, such that gas-phase phase diagnostics are needed to characterize the process. Finally, it is also possible to measure temperatures of the solid energetic material using femtosecond stimulated Raman scattering.

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