

PLASMONICS RESONANCE ENHANCED ACTIVE PHOTOTHERMAL EFFECTS IN
ALUMINUM NANOENERGETICS FOR PROPULSION APPLICATIONS

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TO MY PARENTS

ELIAS GEORGES ALEXI ABBOUD AND NOUHAD FARAH SALIBA EL SOURY

AND TO MY BROTHERS AND SISTER

GEORGES ABBOUD, JOWELLE ABBOUD YOUSSEF, AND JOHNNY ABBOUD

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ABSTRACT

In this dissertation, aluminum nanoparticles (Al NPs) are shown capable to on-demand enhance and control the local photothermal energy deposition, both spatially and temporally, via active photothermal effects initiated by the localized surface plasmon resonance (LSPR) phenomenon, and amplified by the Al exothermal oxidation reactions. Experiments in dry and wet environments along with computational modeling of the photothermal process are very desirable for gaining fundamental understanding, ignition optimization and parameter exploration.

Combined phenomena of motion and ignition of Al NPs are explored first in this study. Both resulting from exposing a pile of the nanoenergetics in hand to a single Xenon-tube flash in air, the movement extent is five orders of magnitude higher than that from femtosecond/nanosecond laser-induced photothermal ejection of gold nanodroplets and the ignition delay is two orders of magnitude faster compared to that from conductive heating.

Then experiments in wet conditions are conducted, mainly in propane-air flames, where flash-activated photothermal effect of the Al NPs is proved to ignite flows of those mixtures. In comparison with regular spark ignition, the ordeal of quenching distance is no more present and the opto-thermal minimum ignition energy (MIE) is at least 67 times less than that from conventional ignition tools.

In the last part of this thesis, organically coating the Al NPs in addition to modulating their geometry and configurations are shown to have significant effects on the absorption cross section of Al. Shift of the plasmon resonance affecting thermal ohmic losses, local electric field

enhancements leading to heat generation, and match of the spectra of the activation source and nanoenergetics can all be used to enhance the energy density of fuels in propulsion systems via active photothermal effects of Al NPs.

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INTRODUCTION

As the characteristic dimensions of a material approach the nanoscale, its properties and behavior can change drastically in comparison with those of its bulk form. For instance, it is hard to understand that the light from a simple flash tube could possibly have any significant effect on the physical structure of a bulk solid that is not normally opto-active. If we exclude the radiative energy dissipation, the absorption of light by a material leads to heat generation through photothermal processes that will be confined within the individual nanostructures, especially when heat transfer to the environment and to the neighboring nanostructures is slow.

Literature background

In all fuel aspects, the presence of nanoenergetics offers promising means of enhancing combustion power output with high efficiency and improved stability. Due to higher reactive interface areas as compared to micron-sized metals, nanoenergetics have significant reaction rate and energy deposition. Upon thermally igniting 100 nm or finer of aluminum nanoparticles (Al NPs) in a vapor phase oxygen, apparent flame speeds are several orders of magnitude greater than the speeds measured for the same micron-size material. Moreover, the majority of oxidation occurred at temperatures below the bulk aluminum melting point [1, 2]. Known to display increased catalytic activity [3] in addition to low sintering temperatures [4], Al NPs have proved to store energy in their surfaces, and their inclusion into solid and liquid fuels/propellants make them attractive for use in pyrotechnics and energetic composite materials with smart capability. This hence led some researchers to develop shock tubes and rapid compression machines for the purpose of investigating nanoparticles-enhanced combustion of fuels [5], such as with ethanol,

JP8, JP10, and n-decane, and to quantify oxidation characteristics and ignition delays through the use of Al NPs, boron, iron [6], etc.

After it was accidentally discovered that single-wall carbon nanotubes containing metal impurities can ignite in air when exposed to an ordinary camera flash [7], this ignition technique was further scrutinized and extended to other carbonaceous compounds synthesized on metal catalysts [8]. In a static combustion chamber, quiescent ethylene/air mixtures containing suspended carbon nanotubes were photo-ignited [9]; Okhura et al. [10] showed that the flash ignition is also applicable to flammable gaseous (methane), liquid (methane), and solid materials (CuO) by the addition of Al NPs. On the other hand, flash ignition has many benefits because of its lower power, lower material cost, and lower mass, in comparison with alternative sources such as spark ignition [1], laser ignition [11], plasma ignition [12], etc. Furthermore, photo-ignition can result in a distributed quasi-homogeneous ignition compared to a kernel spherical flame with the spark technique [13], and consumption of fuel/oxidizer mixture without the formation of an undesirable discernible combustion wave.

On a parallel line, optical properties of these metal nanoparticles were extensively explored for the need of a better understanding of the physical phenomena in play. It was shown that these materials strongly interact with visible and infrared photons due to the excitation of localized surface plasmons, a result of coherent oscillations of conduction electrons. Depending on the application of photothermal effects in plasmonic nanostructures [14-17], some nanoscaled metals are preferred over others since they exhibit higher scattering than absorption, once excited by a certain wavelength. For instance, compared to noble metal materials such as Au and Ag, Al is

considered to be a poor plasmonic material for sensing applications since it has larger dielectric constants in the visible spectra, leading to significantly more thermal ohmic losses in those regions [18, 19]. In an oxidizing environment, Al NPs are chemically unstable as well, and are passivated by a naturally occurring protecting oxide shell several nanometers thick, playing a key role in determining the reactivity. Consequently, elevated temperatures of 500-600 °C are required to trigger further oxidation of the remaining aluminum metal.

As a result, it is desirable to develop an alternative method to keep on the photothermal properties of pure Al NPs, i.e. good absorption and less scattering in the visible range making use of the phenomenon of Local Surface Plasmon Resonance (LSPR) on one hand, without having to face the ordeal of reduced energy content for this alumina-passivated Al NPs, on another hand.

Thesis outline

In the first chapter, the incorporation of local exothermal oxidation reactions of Al nanoenergetics to the LSPR phenomenon makes of them *active* photothermal media, opening new venues for innovations in combustion applications, propulsion, solar cells, etc. The overall process is similar to positive feedback that is much more efficient than “passive” laser-induced photothermal ejection. The photothermal activation source is a low power xenon flash lamp. LSPR triggered first, it confines and enhances the optical energy within the nanoparticles. Then the oxidation reactions amplify the local temperature increase and provide additional energy that is sufficient to accelerate the chemical reactions. Since the chemical energy from the

nanoenergetics is much higher and more efficient than the photothermal activation energy, the active photothermal approach is to control local energy deposition with a light trigger.

In chapter two, flash-activated ignition of the propane/air flames is exploited through the use of high-speed chemiluminescence images of OH and CH radicals. A comparison of flash and spark ignitions follows. Finally, the MIE from both types of ignition is discussed.

In chapter three, oleic acid coated aluminum nanoparticles (OA-Al NPs) are computationally and experimentally explored for plasmonics resonance enhanced photothermal ignitions. Being air-stable materials, they constitute an attractive substitute to the conventional alumina-passivated Al NPs due to the lower reaction temperatures ($\sim 150\text{-}400\text{ }^{\circ}\text{C}$ compared to $500\text{-}600\text{ }^{\circ}\text{C}$). Photo-ignition of OA-Al Nano is first conducted in air using a low-power xenon flash lamp, and then in lean gaseous fuels/air mixtures flows, namely in ethylene/air and methane/air. The electric field enhancement from LSPR among the aggregated nanoparticles is quantified using the Discrete Dipole Approximation technique (DDA), this enhancement leading to localized Joule heating and triggering subsequent oxidation reactions. The method developed here can be easily extended for the design and optimization of other core-shell nanoenergetic materials, serving in numerous and various applications.

Finally, we conclude with a summary and an outlook for future research.

CHAPTER I PHOTOTHERMALLY ACTIVATED MOTION AND IGNITION USING ALUMINUM NANOPARTICLES

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The supplementary material section of this article has been added as an appendix at the end of this chapter.

Abstract

The aluminum nanoparticles (Al NPs) are demonstrated to serve as active photothermal media, to enhance and control local photothermal energy deposition via the photothermal effect activated by localized surface plasmon resonance (LSPR) and amplified by Al NPs oxidation. The activation source is a 2-AA-battery-powered xenon flash lamp. The extent of the photothermally activated movement of Al NPs can be ~ 6 mm. Ignition delay can be ~ 0.1 ms. Both scanning electron microscopy and energy-dispersive X-ray spectroscopy measurements of motion-only and after ignition products confirm significant Al oxidation occurs through sintering and bursting after the flash exposure. Simulations suggest local heat generation is enhanced by LSPR. The positive-feedback effects from the local heat generation amplified by Al oxidation produce a large increase in local temperature and pressure, which enhances movement and accelerates ignition.

Introduction

Efficient control of local photothermal energy deposition at the nanoscale has numerous impacts on nanotechnology, including nanoscale detection, [14-16] photothermal tumor therapy, [15, 20, 21] nano-rotors, [22] and thermoelectric solar cells. [17, 23, 24] However, most of the current research can be categorized as “passive”, [25, 26] being focused on the unique nanostructures of the noble metals and specific light wavelength/duration/power to induce thermal effects. The underlying physics is localized surface plasmon resonance (LSPR), which utilizes resonant oscillation of free electrons in the metals under light illumination to confine, enhance, localize, or guide light radiations in the nanoscale structures. In searching better media for LSPR enhanced photothermal energy deposition, aluminum is less attractive compared to the noble metals. [16, 19, 27] Aluminum has significantly more thermal ohmic losses than the noble metals in the ultraviolet (UV) and visible ranges due to larger dielectric constants in those regions. [28] Additionally, pure aluminum is easily oxidized in the atmospheric environments.

In recent years, nanoenergetic materials have been extensively studied because of their high-energy densities and fast reaction rates. [29] Some research on flash ignition of single-wall carbon nanotubes (SWCNT) and aluminum nanoparticles (Al NPs) has been reported in the literature. [7, 10, 11] In comparison with alternative sources such as spark ignition, [30] laser ignition, [31] plasma ignition, [32] plasma-assisted combustion, [33] and combustion enhancement through the use of catalytic nanomaterials, [34] flash ignition has many benefits because of its lower power, lower material cost, lower mass, and no quenching from electrode-less configuration. SWCNT with metal impurities have been demonstrated to provide precise control over the time and location of a chemical reaction, [9] which may enable more rapid and

homogeneous ignition and combustion, enhance flame speed, and stabilize burning at extremely lean conditions (fuel/air ratio significantly less than stoichiometric, leading to ultralow emissions).

Here, we report an active approach for controlling the photothermal effect of the Al NPs by engaging local oxidation reactions, which has the potential to open another avenue for innovations in applications in combustion, propulsion, solar cells, and photothermal tumor therapy. The overall process is similar to positive feedback, which is much more efficient than “passive” laser-induced photothermal ejection. [35, 36] The photothermal effect is initiated and controlled by a xenon flash lamp that is powered by two AA batteries. LSPR effects confine and enhance the optical energy within the nanoenergetic particles. The oxidation reactions of the nanoenergetic particles are, thus, activated by the local temperature increase and provide additional energy that is sufficient to accelerate the chemical reactions. As a comparison, “passive” photothermal effect is to couple the light energy in the aluminum nanostructures and prevent the oxidation reactions. [37-39] Since the chemical energy from the nanoenergetics is much higher and more efficient than the photothermal activation energy; the active photothermal approach is to control local energy deposition with a light trigger.

Experimental setup

A commercial xenon flash was used as the photothermal source in our experiments. The average diameter of the Al NPs (NanoAmor Inc.) used was ~ 70 nm with a size distribution of 60 – 120 nm. To control the input energy from the flash, the NPs were placed on a glass slide at various distances from the end surface of the flash. The flash power was measured by a long-pulse-

thermopile power sensor. The power decreased roughly linear with respect to distance (See Fig. 5 in Appendix I). The maximum power used in the experiment was 1.9 J/cm^2 , which corresponded to a distance of 1 cm between the NPs and the end surface of the flash source. Sending the flash through a long-pass filter with a cutoff wavelength at 540 nm decreased the total power by $\sim 25\%$. Since UV light $< 350 \text{ nm}$ was blocked by the BK7/glass cover of the flash, the spectral profile of the flash covered from 350 nm to the deep-infrared range. The flash had a temporal profile including a spike of $\sim 50 \mu\text{s}$, a plateau of $\sim 6 \text{ ms}$, and a decay of 5 ms at full power. At different power levels, the duration of the plateau and decay portions changed, but the spike remained similar. The spectra of the flash remained similar for different portions of the spike, plateau, and decay at different power levels.

Results and discussion

Motion

The photothermally activated motion of Al NPs was observed with a fast camera (Photron Company FASTCAM SA5). Figure 1a shows the temporally resolved images of the motion activated by the flash, corresponding to different portions of the flash. The first image shows the non-impacted Al NP pile. The frames within the first 10 ms were saturated by the flash, which are not shown in Fig. 1a. The NPs began to move upward in the early stage of the flash pulse. A large portion of the nanoparticle pile was driven away from the surface. The highest point reached up to 6 mm from the surface without ignition is shown in the ninth image. The movement is $\sim 10^5$ times higher than that from femtosecond/nanosecond laser-induced photothermal ejection of gold nanodroplets. [35, 36]

Two important features for the photothermally activated motion have been identified. First, the delay between the incidence of the light and the motion is on the order of tens of microseconds. Additionally, the Al NP motion can be controlled by varying the magnitude of the energy input and/or UV light filtering, as shown in Fig. 1b. A decrease in the flash power can lead to a decrease in the height of the motion.

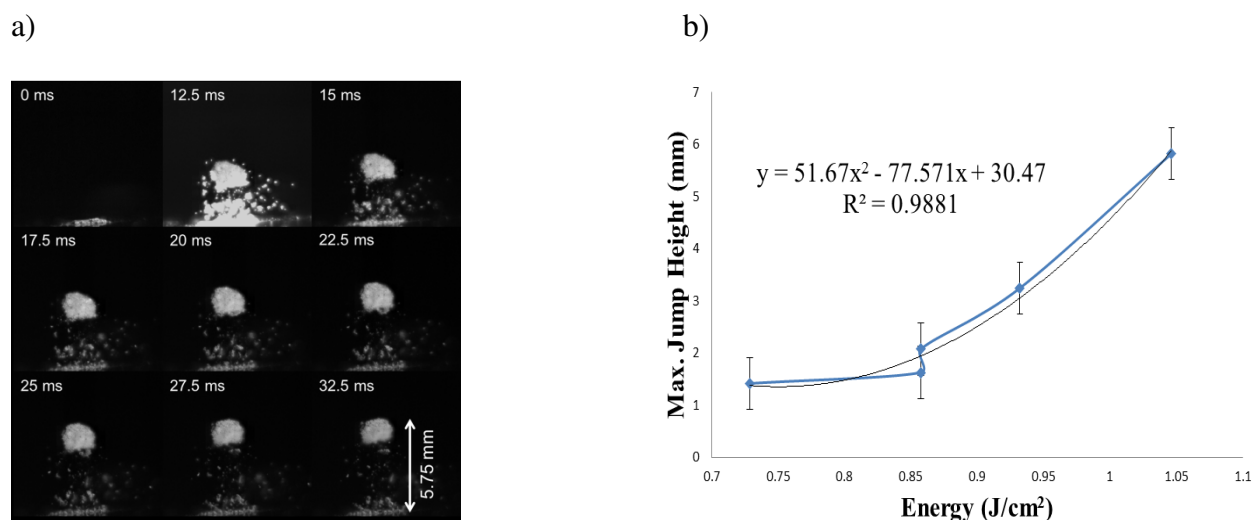


Figure 1. Photothermally activated motion of 1 mg of Al NPs with a single xenon flash pulse. (a) Photothermally activated motion of NPs observed by a fast camera at a frame rate of 10 KHz. Each frame size is 8.6 mm in height x 8.9 mm in width. (b) Height of photothermally activated motion is approximately quadratically dependent of flash power.

When a long-pass filter with the cutoff wavelength at 540 nm was placed between the NPs and the flash, a decrease in the height of the motion was also observed.

Second, the NPs can be moved up by the flash activation oxidation without ignition, which has been confirmed by scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDS) analyses. The original Al NPs are uniform in size, with ellipsoidal and irregular shapes (See Fig. 6). Aggregation of multiple NPs can be observed. After the flash exposure, two types of products - larger particles with diameters of several microns and smaller NPs with diameters of ~ 50 nm - have been found in the Al NP residues. Large particles were formed through sintering multiple Al NPs. Smaller NPs were formed through bursting. EDS analyses show that the original Al NPs are slightly and non-uniformly oxidized. The mole ratio of Al to oxygen is about 4:1, varying slightly for different locations inside the NP pile because of local oxidation. After a single exposure of the flash, the Al NPs become more uniformly oxidized. The mole ratios decrease to $\sim 2.5:1$ for the melted Al NPs and to 1.4:1 for the burst ones. A significant amount of the oxidation occurs after the flash exposure, even without ignition.

Ignition

When the flash power was increased, flash activated ignition of Al NPs was experimentally observed shown in Fig. 2. Al NPs at the periphery of the pile were ignited first. The combustion propagated toward the center and the bottom of the sample. A sample of 10 mg of Al NPs ignited in air has an average combustion time of ~ 10 s. Al NPs can be consecutively ignited up to four times, with average combustion duration of ~ 7 s for each ignition. The total combustion process

can last more than 30 s. The ignition delay was recorded by a high-speed camera operated at 100 KHz.

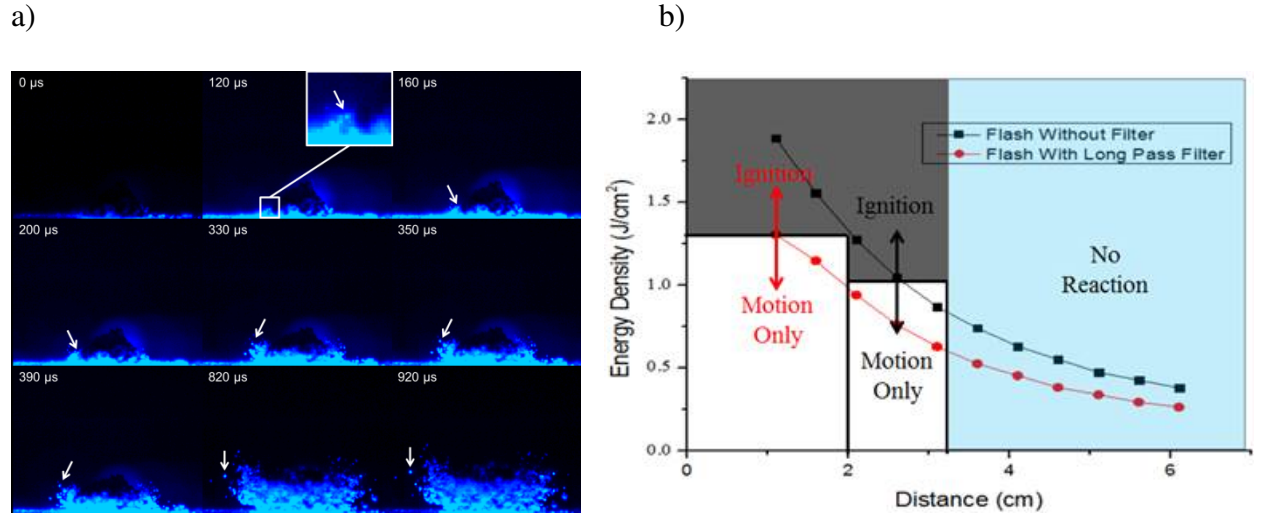


Figure 2. (a) Photothermally driven ignition of Al NPs by a single xenon flash pulse at a frame rate of 100 KHz, at incident power of $1.6 \text{ J}/\text{cm}^2$. Ignition was identified in the second image, which was acquired $\sim 0.12 \text{ ms}$ after the flash incidence. Ignition is spatially localized. Each frame size is 3.8 mm in height x 4.9 mm in width. (b) Flash power dependence for transition of ignition and motion only with and without the long pass filter cutoff at 540 nm. It shows that UV is more efficient for motion and ignition.

For Al NPs with an average diameter of ~ 70 nm, the ignition delay was ~ 0.12 ms with the flash, as shown in Fig. 2, which is about 100 times faster than that by conductive heating. [3] The ignition process is highly localized. Similarly, the entire Al NP pile has been lifted about 1mm above the surface by the photothermal activation.

UV light filtering has been used to control the ignition of the Al NPs. Long-pass filtering with the cutoff wavelength at 540 nm leads to a decrease in height, and ignition may not be triggered under the illumination of the flash at certain powers with filtering. For a flash power of 1.1 J/cm^2 with filtering, which corresponds to 1.6 cm from the flash end surface, ignition is not induced.

At a similar power level without filtering, i.e., power without filtering at 2.5 cm, the Al NPs can be ignited. Further increase of the flash power with filtering to $\sim 1.3 \text{ J/cm}^2$ can induce ignition, as shown in Fig. 2b. This indicates higher efficiency of UV light for ignition. Ignition can be achieved for a pile of < 0.5 mg. SEM images of Al NPs after the flash ignition and burning are shown in Fig. 7. Similar to the movement without ignition, the Al NPs either melt into larger particles or burst into smaller NPs. As a comparison, EDS analyses of the product at the burning regions show that the mole ratio of Al to oxygen is $\sim 1:2$, indicating that more than 80% of the Al has been oxidized to alumina.

Simulations and suggested mechanisms

The effect of the direct absorption-induced global heating has been determined. Light absorption using the discrete dipole approximation (DDA) [40] for alumina-coated NPs with various shapes, sizes, coating thicknesses, and aggregation configurations was computed. In DDA, each particle is represented by an array of point dipoles (Appendix I).

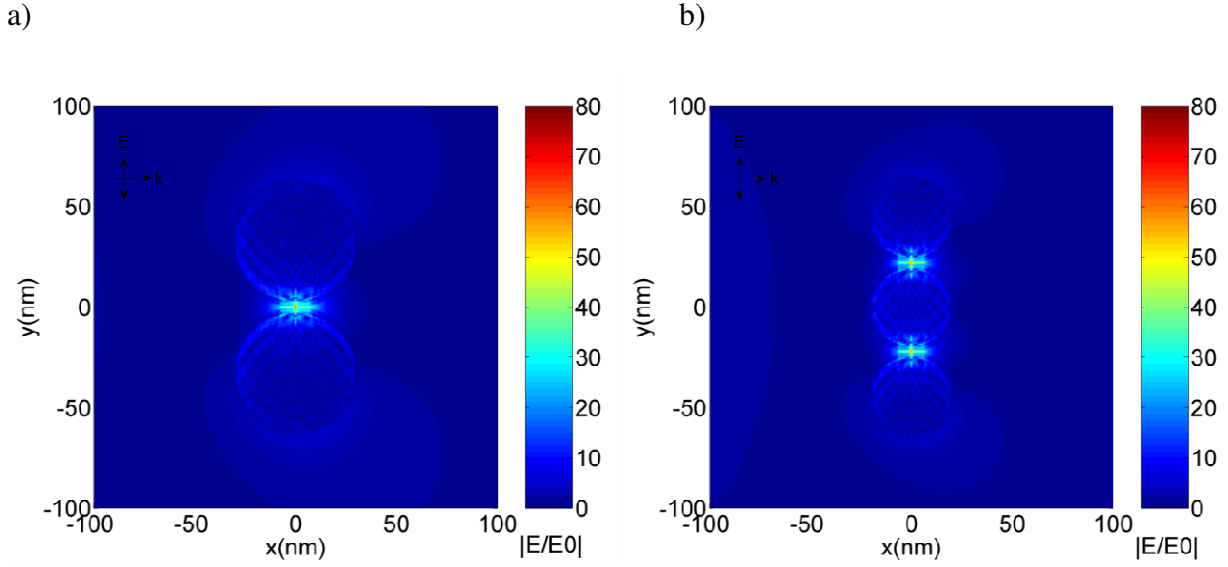


Figure 3. Electric-field distributions under the flash illumination for NPs with 2-nm alumina shell and aluminum core at their plasmon resonance. (a) Two contacting spheres with radii of 35 nm. The plasmon resonance is at 381 nm. (b) Three contacting spheres with radii of 20 nm. The plasmon resonance is at 354 nm. For both cases, the local electric-field enhancement can reach as much as 80 times, leading to local heat enhancement up to 6400 times as compared to the global heating.

The absorption behavior of the target was calculated, based on the interactions between the incident light and the dipoles. The absorption spectra for several configurations of the experiment are given in Fig. 8. The peak wavelengths of the plasmon resonance of the Al NPs shift from ~ 200 nm for spherical particles to the visible and near-infrared regions for prolonged spheres. To take into account the aggregation effects, absorption by multiple Al NPs was

calculated. Similar red shifts were observed. The plasmon resonance and absorption occurred mainly within the near UV and visible range for these configurations.

It has been confirmed through simulation that the global heating of Al NPs by absorption of the flash light is not the main contributor for the ignition of a single Al NP. It should be noted that there is no consensus in the open literature on thermal ignition of metal nanoenergetic materials. For Al NPs, the reported ignition temperature ranges from 900 K (below the Al melting point) to 2300 K (close to the melting point of alumina). [3, 29, 41] The global-temperature increase of a single Al NP due to light absorption was calculated using the standard heat-transfer equation. [26, 42-44] The heat generated by the light absorption was obtained by integration of the flash spectrum over the theoretical absorption curve. The total temperature increase for a single Al NP is < 1 K for the input power of 2 J/cm^2 . This result suggests that certain kinetic or local heating effects in addition to global heating have contributed to the flash-activated motion and ignition of the Al NPs.

Positive feedback, initiated by plasmon-resonance enhanced local heating and further amplified by the Al oxidation reaction, is suggested to be responsible for sintering the Al NPs [3, 4] and rupture of the alumina shell. [41, 45] Figure 3 shows the distribution of the local electric field near the Al NPs with 2-nm-thick alumina coating at various wavelengths. In the calculation, the electromagnetic wave was propagating from left to right. The local fields were clearly enhanced near the interface between the alumina shell and the Al core. The location of the enhancement depends on the wavelength of the incident light and the relative positions of multiple NPs. In the near UV-region, the electric-field enhancement inside a single spherical Al NP is less than five times that of the original incident electric field, while the maximum enhancement in the two

contacting spherical NPs at the plasmonic resonance is ~ 80 , as shown in Fig. 3. Since the local heat flux is $\Delta Q = 1/2 \epsilon_0 \omega \text{Im}(\epsilon_r) |E|^2$, where ϵ_0 is the permittivity of the vacuum, ϵ_r is the relative permittivity of Al or alumina (frequency dependent), ω is the frequency of the light, and E is the electric field, the local heat generation can be enhanced up to 6400 times, leading to a large increase in the local temperature and thus pressure. For a 5-nm region near the largest enhancement in the Al NPs, the local temperature can reach ~ 1070 K, which is sufficiently high to activate the local oxidation process. This is consistent with the results of EDS analyses of Al NPs after the pure movement and ignition. Positive-feedback processes of local heating generation and Al oxidation also move and/or ignite the Al NPs. For the small gaps in the Al NPs pile, the pressure may increase four to eight times as a result of the rapid temperature rise. Thus, the force applied to the Al NPs pushes them upward.

Figure 4 shows the overall suggested mechanism of the photothermally activated process. The plasmon resonance among Al NPs generates a significant amount of local heat. The oxidation reactions of Al are, thus, activated.

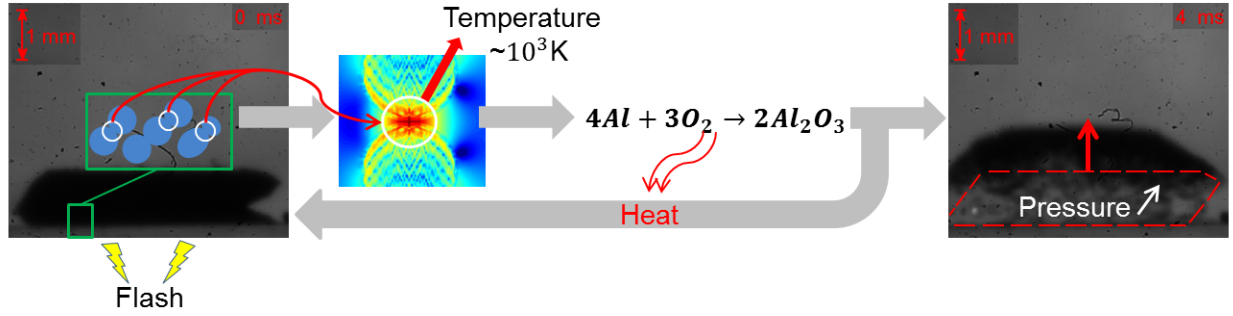


Figure 4. Suggested positive feedback mechanism for the flash-induced photothermally activated motion and ignition of Al NPs.

Through positive feedback, a significant increase in the local temperature and pressure is produced, which results in the motion and ignition of Al NPs. Since the Al NPs used in the experiments are spherical and slightly oblate, as shown in the SEM images, the plasmon resonance occurs mainly at the near-UV and visible ranges. Thus, light in the near-UV range is more efficient for ignition, in agreement with our experimental observations.

Conclusions

We reported the properties of Al NPs as an active photothermal media to enhance and control local heat generation, particle motion, and ignition via LSPR and Al oxidation. The photothermally activated movement of NPs under a single 10 ms pulse from a xenon flash can be as high as 6 mm from the surface without ignition, which is $\sim 10^5$ times higher than that from

femtosecond/nanosecond laser-induced photothermal ejection of gold nanodroplets. Depending on the flash power and spectrum, ignition delay by the flash can be on the order of 0.1 ms, which is ~ 100 times faster than ignition by conductive heating. Active control by varying the flash power or UV filtering of the low power xenon flash has been achieved for both motion and ignition. Both SEM and EDS measurements of motion-only and after-ignition products indicate significant oxidation of Al NPs occurs through sintering and bursting after a single flash exposure. Electromagnetic simulations indicate that the local heat generation is significantly enhanced by the local electric field inside and among the alumina-coated Al NPs. The positive feedback effects from the local heat generation are amplified by Al oxidation. The local heat-induced pressure pulse in the NPs is responsible for the large movement. The local heating inside and among the NPs generates and accelerates the ignition.

Appendix I

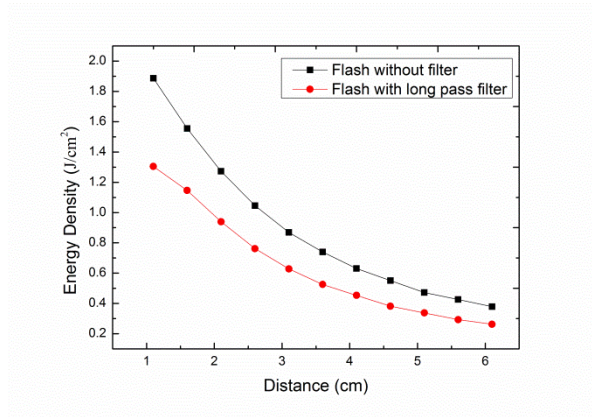
Discrete Dipole Approximation Code DDSCAT 7.1

DDSCAT 7.1 is a Fortran-90 software package that applies the “discrete dipole approximation” (DDA) to calculate scattering and absorption of electromagnetic waves by targets with arbitrary geometries and complex refractive index. The targets may be isolated entities such as nanoparticles, but may also be 1-d or 2-d periodic arrays of target unit cells, which can be used to study absorption, scattering, and electric fields around arrays of nanostructures.

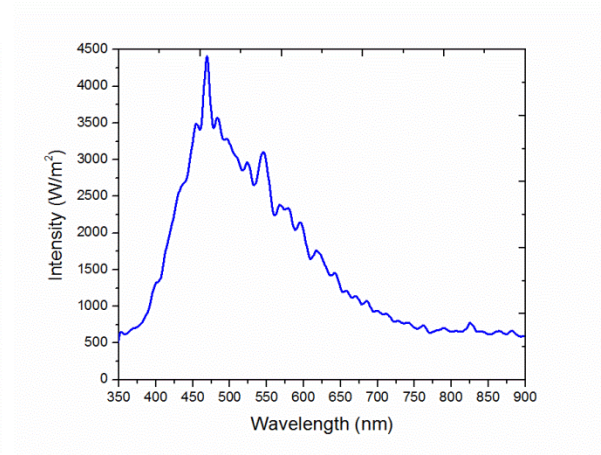
The DDA approximates the target by an array of polarizable points, and DDSCAT 7.1 allows accurate calculations of electromagnetic scattering from targets with “size parameters” $2\pi a_{eff}/\lambda \lesssim 25$ provided the refractive index m is not large compared to unity ($|m-1| \lesssim 2$).

DDSCAT supports calculation for a variety of target geometries such as ellipsoids, regular tetrahedral, rectangular solids, finite cylinders, etc. Target materials may be both inhomogeneous and anisotropic. The software automatically calculates total cross sections for absorption and scattering and selected elements of the Mueller scattering intensity matrix for specified orientation of the target relative to the incident wave, and for specified scattering directions. It can also calculate scattering and absorption by targets that are periodic in one or two dimensions. It supports post-processing to calculate the electric and magnetic fields at user-selected locations in or near the target.

a)



b)



c)

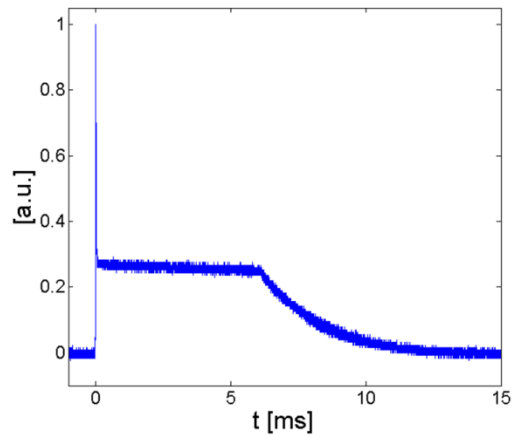


Figure 5. Characteristics of the photothermal activation source. (a) The flash power dependence on the distance between the flash end surface and the target. (b) Spectral profile of the flash. The spectra at different locations of spike, plateau, and decay at different power levels are the same; (c) Flash temporal profile.

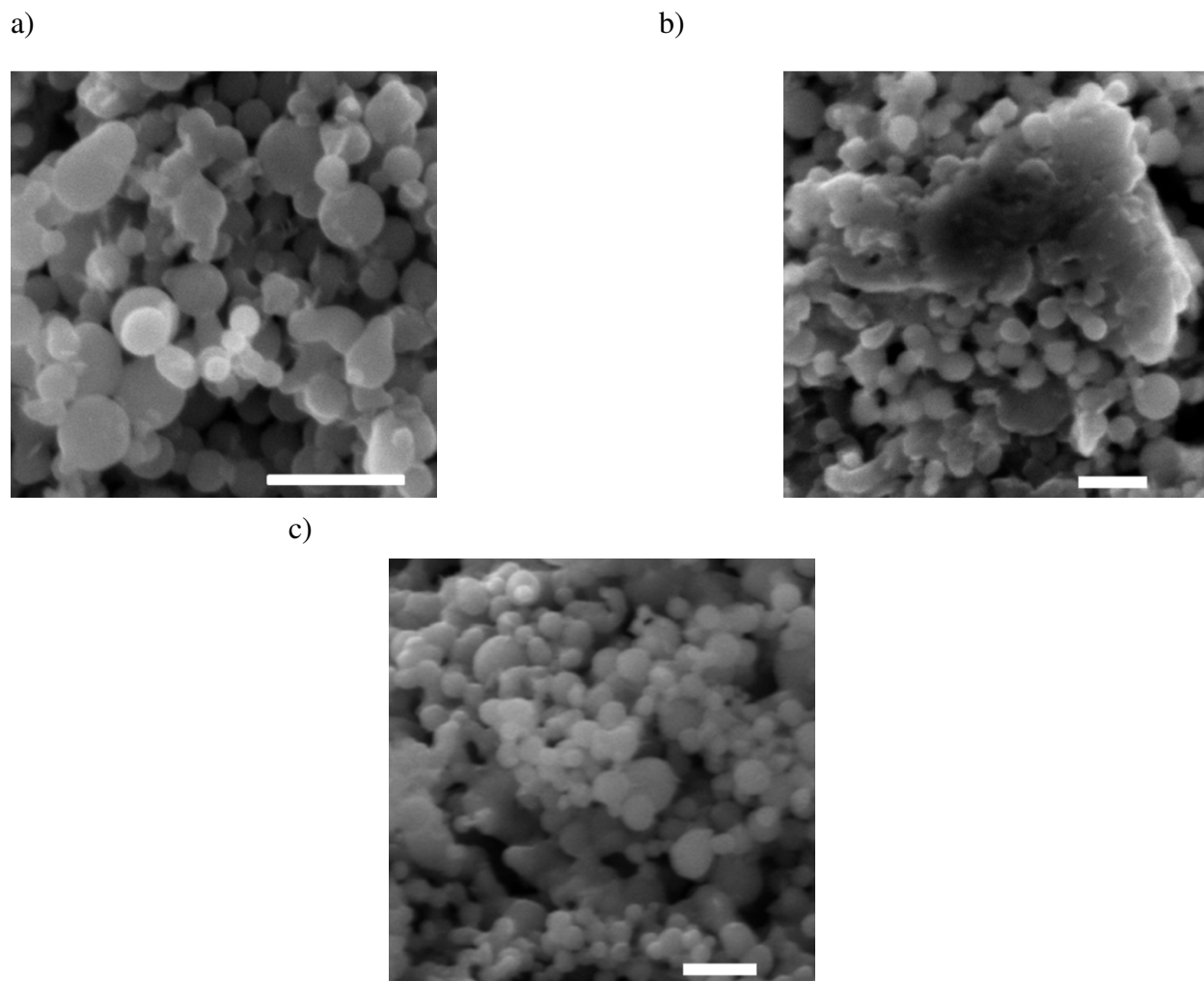
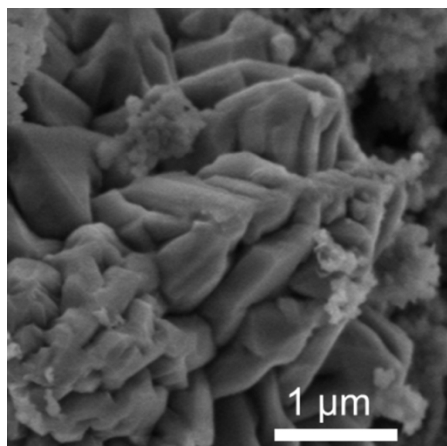


Figure 6. SEM images of the Al NP residues after a single flash exposure for the photothermally activated movement. (a) Original NPs with an average diameter of ~ 70 nm, with ellipsoids and irregular shapes present. Aggregation of multiple NPs can be observed. Sharper contrast on the edges indicates the alumina coating. (b) Sintering into a large particle after the flash; (c) Bursting into smaller NPs after the flash, with an average diameter of ~ 50 nm. Scale bars represent 200 nm.

a)



b)

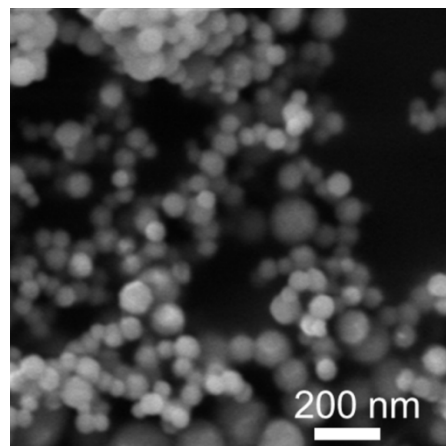


Figure 7. SEM images of the product after ignition. (a) Large particles with sizes of several microns formed by sintering small NPs. (b) Smaller NPs with an average diameter of 50 nm formed by bursting.

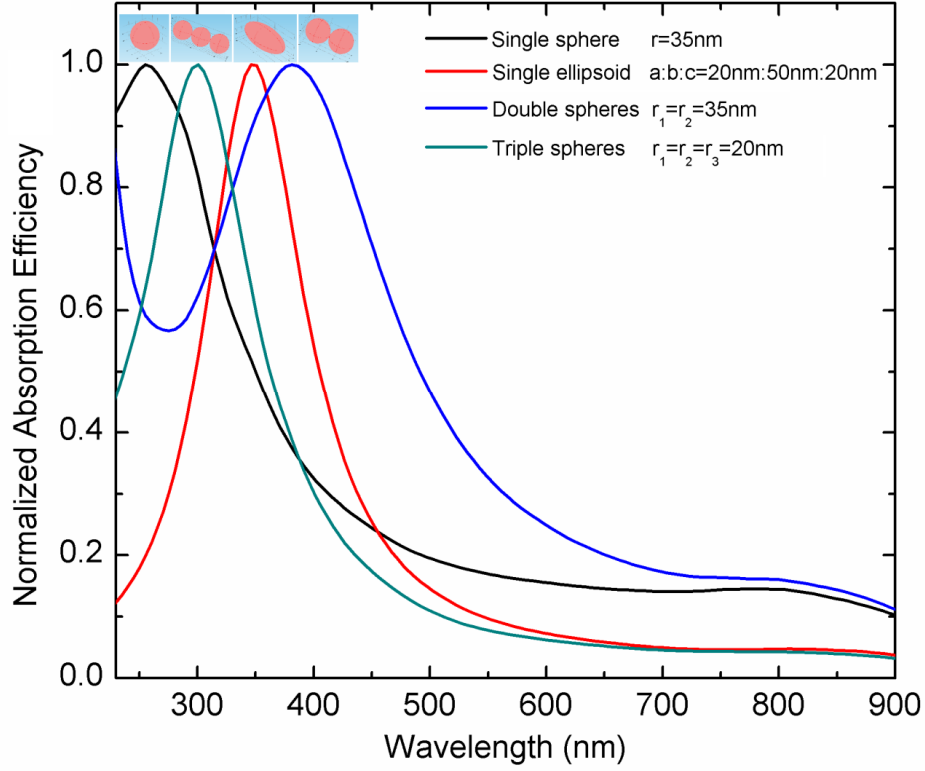


Figure 8. Calculated absorption spectra for an alumina-coated Al NP with various shapes, coating thicknesses and aggregation. All nanoparticles are made of Al cores and alumina coating of 2 nm. All dimensions are in nanometers. The figure shows that the major absorption is observed in the ultraviolet and visual regions. Although the coating thickness has little effect on the overall absorption coefficient, it is evident that the thicker the alumina coating, the lower the absorption.

**CHAPTER II SPATIAL AND TEMPORAL CONTROL OF ON-DEMAND
PROPANE-AIR FLAME IGNITION BY ACTIVE PHOTOTHERMAL
EFFECT OF ALUMINUM NANOPARTICLES**

A version of this chapter was originally published in Combustion and Flame by Jacques E. Abboud, Naibo Jiang, Zhili Zhang, Sukesh Roy, and James R. Gord:

Abboud, J., et al., *Spatial and temporal control of on-demand propane-air flame ignition by active photothermal effect of aluminum nanoenergetics*. Combustion and Flame, 2013.

Abstract

Active photothermal effects of aluminum nanoenergetics are demonstrated to control spatially and temporally the ignition of propane/air flames. High-speed chemiluminescence images of hydroxyl (OH*) and methylidyne (CH*) radicals and aluminum oxide (AlO) are employed to confirm the local flame ignition and propagation by activation of the nanoenergetics through the use of a single exposure from a xenon flash lamp. The photothermal effects of the nanoenergetics can efficiently activate the localized exothermal aluminum oxidation reactions, leading to sequential flame ignition. Most of the energy required for ignition is provided by the oxidation reaction of the aluminum nanoparticles such that the photothermal MIE (Minimum Ignition Energy) is at least 67 times less than that from regular spark ignition.

Introduction

Forced flame ignition is among the most important phenomena involved in combustion, which is one of the most irreplaceable techniques in the modern society [46-48]. Fundamental combustion research for the development of low-emission engines and fire-safety control inevitably involves the flame ignition processes. Spark ignition is the most widely used method for many propulsion and automotive combustion engines. It usually involves two circular electrodes with flanges at

the tips, producing an arc discharge with various durations ranging from tens of nanoseconds to hundreds of milliseconds. As a point heat source, the spark generates a localized high-temperature spot to dissociate partially and ionize most of the fuel and oxidant molecules, leading to a thermochemical runaway followed by a rapid transition to a self-sustained intense burning [48]. The advantages of this method include low cost, small size, and minimum weight. However, spark discharges require the presence of adjacent electrodes, which act as heat sinks and tend to quench the flame. The spark-discharge size is usually limited because of the high voltage required to break down the air. The low “wall-plug” efficiency (defined as the ratio of the energy deposited in the gas to the electrical energy consumed in producing the discharge) is also a limiting factor for power-contingent applications. Additionally, a rather large amount of energy (~ 0.3 mJ for most gaseous fuels at stoichiometric conditions and even higher at fuel-lean and fuel-rich conditions) must be deposited into the flow to overcome flame self-extinction and blowout due to large flame stretch and other significant conductive and radiative heat losses during the initial phase of ignition. Other forced-ignition methods, including pilot-flame ignition [49], laser ignition [31], plasma ignition [32, 50, 51], and catalytic ignition [52, 53], have been investigated. However, various difficulties associated with those methods prevent broad applications. For example, pilot-flame ignition requires an additional flame ignition along with a flame-holding system. Laser ignition requires optical access and extremely high optical intensities to induce gas breakdown.

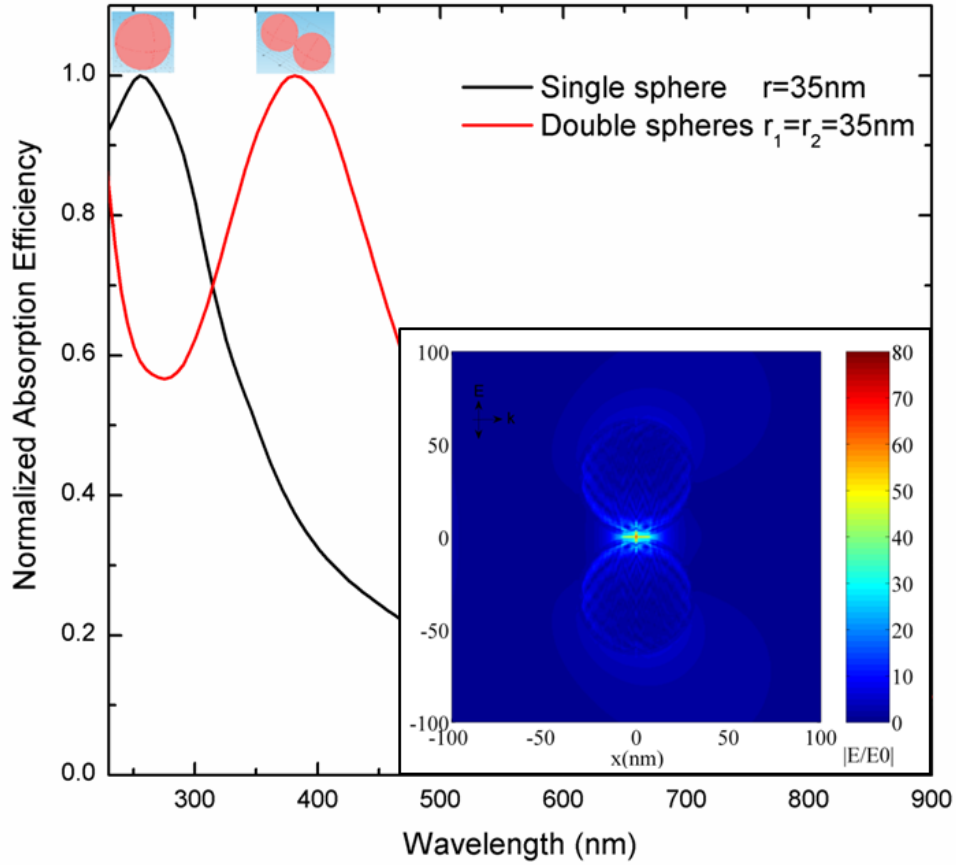


Figure 9. Calculated absorption spectra for 70 nm-diameter Al particles. Single isolated sphere and an aggregation of two contacting spheres were considered. The major absorption was observed in the UV and visible regions. Inset is the electric field distribution under flash illumination of double spheres at plasmon resonance (381 nm). The local electric field reads 80 times enhancement at the interface, leading to a local heat enhancement up to 6400 times as compared to the global heating. Plasma ignition has similar shortcomings as a regular spark-ignition technique, and catalytic ignition suffers from relatively slow reaction time.

The present study demonstrates spatial and temporal control of on-demand ignition of gaseous fuels through the use of Localized Surface Plasmon Resonance (LSPR)-enhanced active photothermal effects of aluminum nanoenergetics. In stark comparison, flash ignition [54] overcomes many shortcomings of the existing methods through the use of low-power active photothermal effects. Similar to laser ignition, flash ignition is a remote process whereby the heat loss to the electrodes and their quenching effects are inherently avoided. Moreover, similar to spark ignition, spatially focusing and temporally gating the flash pulse can lead to on-demand ignition. Multi-point and near-homogeneous ignition can be achieved through utilization of multiple and/or high-power light sources. Additionally, the flash is only an activation source for the active photothermal effects of the nanoenergetics. Most of the ignition energy is provided by the exothermal oxidation reaction of the nanoenergetics. The photothermal MIE can be several orders of magnitude lower than that of spark ignition, which is an advantage for power-contingent applications.

Compared to “passive” photothermal effects [15, 25], the active effect incorporates both the Localized Surface Plasmon Resonance (LSPR)-enhanced photothermal effect and exothermal oxidation reactions of the nanoenergetics. The photothermally activated movement of NPs under a single 10 ms pulse from a xenon flash can be as high as 6 mm from the surface without ignition, which is $\sim 10^5$ times higher than that from femtosecond/nanosecond laser-induced photothermal ejection of gold nanodroplets. Depending on the flash power and spectrum, ignition delay by the flash can be on the order of 0.1 ms, which is ~ 100 times faster than ignition by conductive heating. Active control by varying the flash power or UV filtering of the low power xenon flash has been achieved for both motion and ignition.

The LSPR effect confines the optical energy within and near the nanoenergetic particles. Figure 9 shows the absorption spectra of 70 nm-Al particles: an individual isolated sphere and two spheres aggregated together. As shown, the plasmon resonance and absorption occurred within the near UV and visible range for these configurations. The local electric-fields were clearly enhanced near the interface of the two-contacting spheres (see the inset of Fig. 9). Since the local heat flux is proportional to the square of local electric field, the localized Joule heating can be enhanced up to 6400 times, leading to a large increase in the local pressure and temperature, the latter estimated to be on the order of 1070 K [54]. The oxidation reactions of the nanoenergetic particles are, thus, activated by the local temperature increase and provide additional energy that is sufficient to accelerate the chemical reactions. The effect is similar to positive feedback, referred here as the “active photothermal effect”. Since the chemical energy from the nanoenergetics is much higher and more efficient than the photothermal activation energy, the optical energy can be regarded as a trigger. Here, the active photothermal effect is initiated and controlled by a xenon flash lamp that is powered by two AA batteries.

In this paper, the experimental setup is first described. Flash-activated ignition of the propane/air flame is then discussed. A comparison of flash and spark ignitions follows. Finally, the MIE from both types of ignition is discussed.

Experimental setup

The experimental setup shown in Fig. 10 consisted of three major components: (1) a burner that produces a premixed, evenly distributed conical flame either with or without nanoenergetics seeding, (2) a flash igniter, and (3) a high-speed camera equipped with an intensifier for

luminosity measurements. The burner [55] has a cylindrical (44-mm diameter x 50-mm long) stainless-steel head. The premixed gas inlet orifices were formed by five concentric rings of 84 closely spaced, 1.0-mm-diameter holes, the largest ring having a diameter of 16 mm. The propane and air were premixed before entering a straight burner section. About 5 mg of aluminum nanoenergetics (nominal diameters of 50 nm, purchased from NanoAmor Inc. without further treatment) were placed along the flow path inside the straight section to ensure approximately uniform seeding of nanoenergetics in the flow. The equivalence ratio and flow speeds were held constant with a pair of flow meters for the fuel and air, with accuracy within 0.8% of the reading. The air and propane were flowing at 10 slpm (standard liters per minute) and 0.5 slpm, respectively, at an equivalence ratio of $\phi = 0.875$. The flames had combined fuel and air flow rates of around 2.0 m/s in this experiment, which was measured by Particle Image Velocimetry (PIV) in the previous study [55]. Experiments were performed in the lab fume hood. The overall turbulence level is low in the flow.

A commercial flash powered by two AA batteries was used as an igniter. The flash consisting of a xenon lamp that is 4 cm in length and 0.5 cm in diameter was placed beside the flow exiting the burner. The flash energy density was $\sim 1.9 \text{ J/cm}^2$ at 1 cm distance from the xenon lamp surface, as measured by a long-pulse thermopile power sensor. The power decreased roughly linearly with respect to distance.

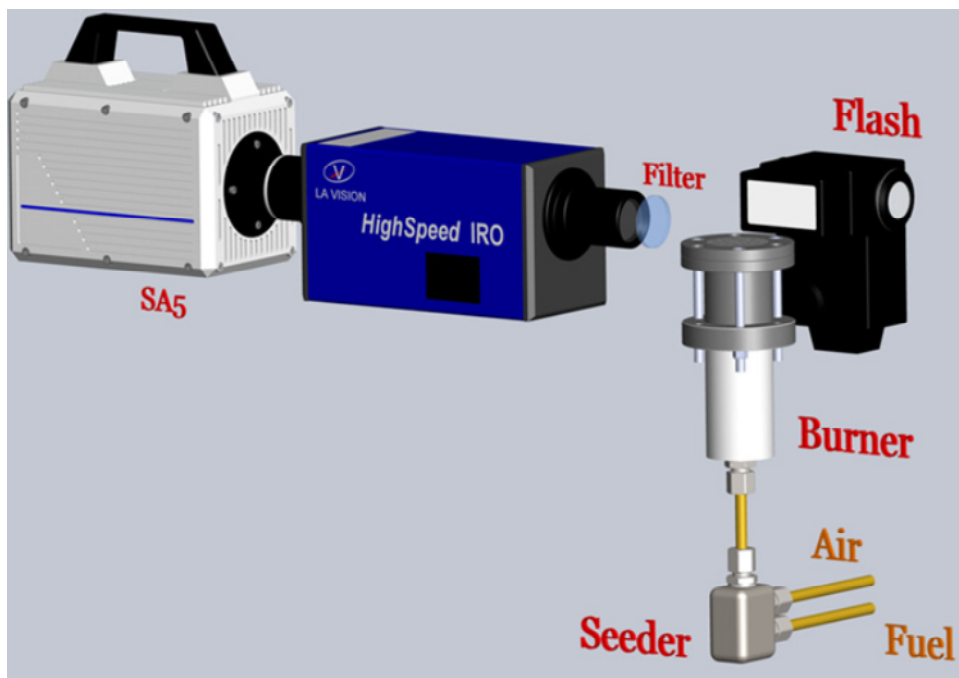


Figure 10. Experimental setup of flash-activated active photothermal effects of aluminum nanoenergetics for on-demand flame ignition.

The flash had a temporal profile, including a spike of $\sim 50 \mu\text{s}$, a plateau of $\sim 6 \text{ ms}$, and a decay of 5 ms , as measured by a photodiode with the resolution of 1 ns rise time. The spectral profile of the flash covered from 350 nm to the deep-infrared range, as measured by a fiber spectrometer. Deep-UV emission was blocked by the BK7 glass cover on the flash.

A high-speed camera (Photron SA5, at 90 K frames per second, fps) and a high-speed image intensifier (LaVision IRO) were used to track the chemiluminescence from the flame-ignition and propagation events. In addition to the direct luminescence, spectrally resolved interference

filters for OH* (A–X) and CH* (A–X) chemiluminescence were utilized to identify the flame reaction zone and capture the flame front and propagation. Both filters were interchangeable. The OH* filter was centered at 308 nm, with a 10-nm bandwidth. The CH* filter was centered at 430 nm, with a 10-nm bandwidth. It should be noted that the AlO ($v = 3$, B–X, 430–446 nm) emission band lies within the passing band of the CH* filter [56]. Thus, the burning aluminum particles were also captured in the CH* filtered images. The 2-D chemiluminescence images were acquired with a $\sim 10 \mu\text{s}$ exposure time. Because of the nature of the volume-averaged chemiluminescence images, the measurements can be regarded as an average over the line of sight across the flame.

Results and discussions

Flash ignition

The photothermally activated localized ignition was observed by the high-speed chemiluminescence images. Figure 11 shows the temporally resolved images of OH* chemiluminescence after the flash activation. Since OH* only exists in the flame reaction zone and after-burn region, OH* chemiluminescence can be regarded as an indicator of the flame front for accurate tracking of flame ignition and propagation. The first frame shows the entire flow field, partly saturated by the flash. After ~ 6 ms of flash incidence, localized ignition of aluminum nanoparticles was evident, as shown in the second image, along with flame formation. Beginning with the third image, the flame front propagated rapidly outward from the ignition location. A classical evolution from an outwardly propagating spherical flame to a planar flame is shown in the fourth to the seventh image. The premixed flame finally stabilized on the burner

surface in the ninth image. It should be noted that the OH* notch filter can efficiently block the emissions from Al and AlO; thus no particle burning was identified in Fig. 11. This clearly demonstrates that the flame ignition can be achieved spatially and temporally on-demand, from a single flash pulse powered by two AA batteries, for the mixture of propane/air flowing through the burner.

Figure 12 shows the temporally resolved images of CH* chemiluminescence and AlO emissions after flash activation. In comparison with Fig. 11, a notch filter centered at 430 nm with a 10-nm bandwidth was used, which covers both CH* (A–X) chemiluminescence and AlO ($v = 3$, B–X) emission. Since the CH* radical only exists in the reaction zone of the flame and CH* chemiluminescence is also a good indicator of the time-averaged heat release distribution, it is clear that the flame ignition was highly localized. Figures 11 and 12 show consistency in the fact that the flame was observed after around 5 ms from the flash exposure. Also, the evolution from the outwardly propagating spherical flame to the planar flame was shown from the third to the sixth frame.

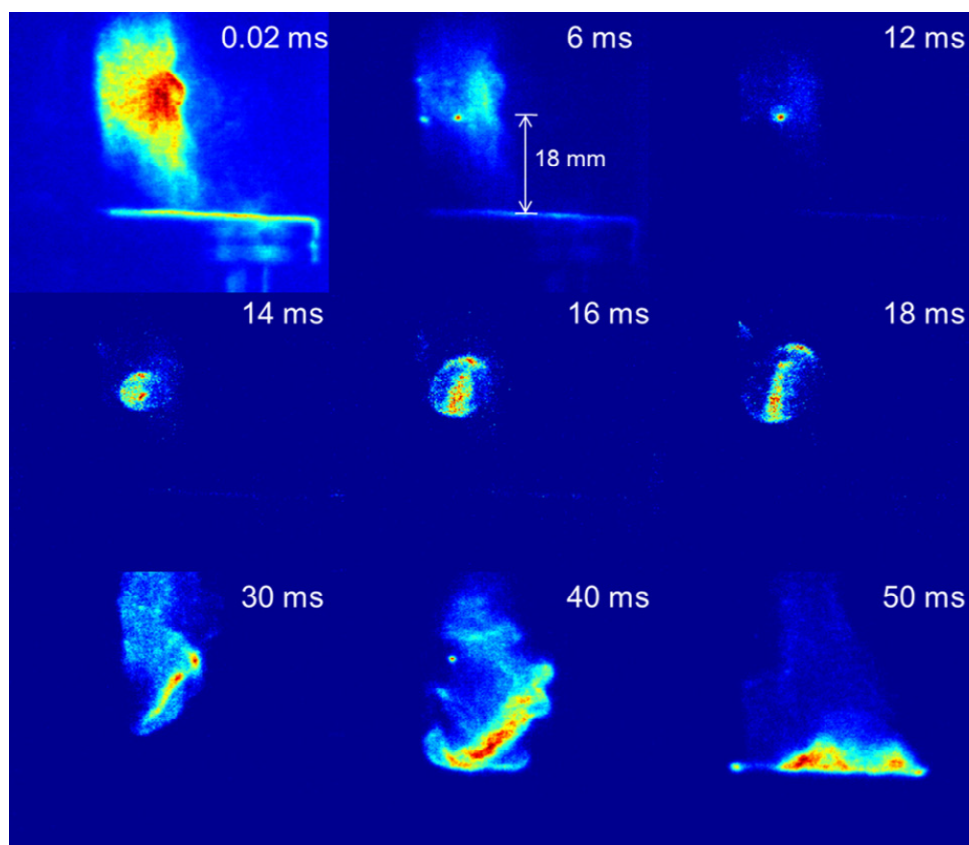


Figure 11. High-speed OH* chemiluminescence from flash-activated aluminum-nanoenergetics-assisted ignition of the propane/air flame. The frames were taken at elapsed times of 0.02, 6, 12, 14, 16, 18, 30, 40, and 50 ms after the flash activation, respectively. Localized ignition of a single aluminum nanoparticle is evident in the second image. The flame front propagated rapidly outward from the ignition location and stabilized on the burner surface.

Depending on the power of the flash lamp, ignition at single (Fig. 11) or multiple (Fig. 12) points can be achieved. AIO emission from aluminum burning was shown before initiation of the spherical flame. This indicates that aluminum nanoenergetics were ignited before the hydrocarbon mixtures. Additional AIO emission began within the flame front during the propagation, which shows that the aluminum nanoparticles were very easily ignited when the temperature was high in the flame front. This places them in a sharp contrast with micron-size particles, where the photo-ignition process was not observed under any conditions [10]. Neither the photo-ignition of 800 nm-size Al NPs was successful in our lab. A few-micron size particle cannot replace an agglomeration of nanoparticles in terms of photo-ignition. Two main reasons are responsible for the phenomena [54]. First, due to Localized Surface Plasmonic Resonance (LSPR) effect, the local electric field in the nanoparticles is orders of magnitude higher than that in micron sized ones. It is even higher in the aggregated nanoparticles due to interactions among the heat within the aggregation. Second, the surface exposure to the oxidizer in the latter case is orders of magnitude higher than the former micro-particle, where the air can penetrate within the gaps of the aggregation, and the convection is high in the flow mixture situation. The positive feedback from the aluminum oxidation is accelerating the process. Finally, the burning of aluminum nano-particles can extend far downstream of the flow, as shown in the last two images. Because of the high energy density and the high combustion temperature of the nanoenergetics, it should be anticipated that significant changes of the overall flame temperature and structure may occur.

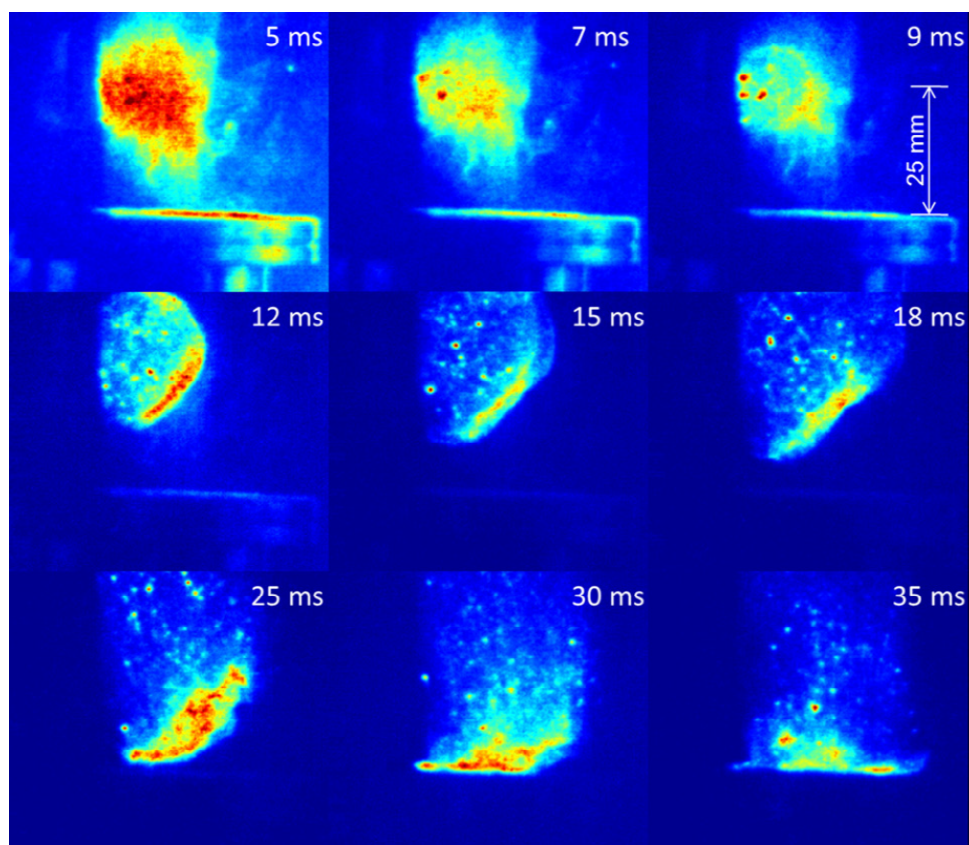


Figure 12. High-speed CH^* chemiluminescence and AlO emission from flash-activated aluminum nanoenergetics-assisted ignition of propane/air flame.

It should be noted that two ignition processes are involved in this photothermal-effect-activated flame ignition. First, the ignition of the aluminum nanoparticles is very fast, and was reported to be on the order of 0.01 ms by the broadband low-power flash lamp at ambient atmospheric conditions [54]. Unfortunately, frame saturation provoked by the flash prevented the investigation of the ignition time delay of Al nanoparticles as a function of their work involving

photo-ignition time scales of particles has been reported in the literature. Second, the flash-activated ignition of the flow of propane/air mixture was shown to be around 4 ms by the same flash in this study. This concludes that Al NPs ignition delay is at most that amount of time, making it consistent with the 5 ms photo-ignition time delay of single walled carbon nanotubes (SWCNTs) suspended in quiescent ethylene/air mixtures, and equal half the time taken by the 105 mJ spark (10 ms) to ignite the same mixtures, at an equivalence ratio of 0.9 and a pressure of 1 bar [9].

Spark ignition

To provide a comparison with the flash ignition, regular spark ignition was conducted and imaged by the high-speed camera. Figure 13 shows the time-resolved OH* chemiluminescence from spark ignition of the propane/air flow without aluminum nanoenergetics seeding. As expected, the spark served as a high-temperature point source. An outwardly propagating spherical flame quickly transited into a planar flame, resulting in self-sustained intense burning on the burner surface. During the ignition process, the spark electrodes were clearly visible near the flame front.

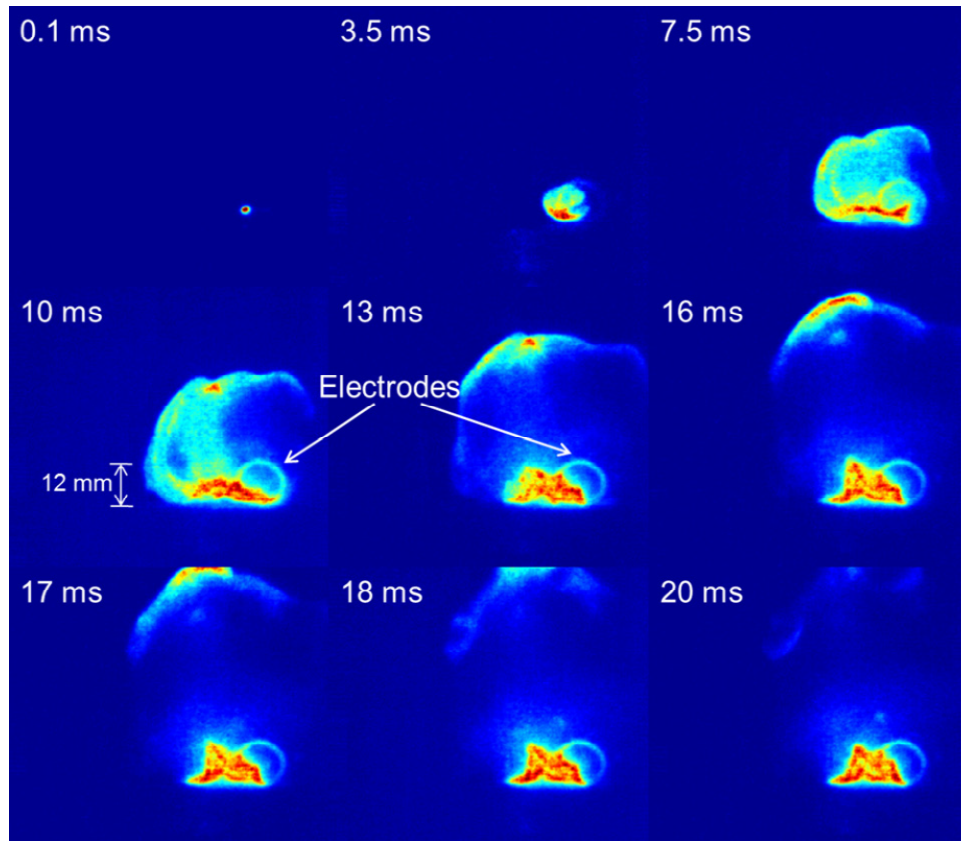


Figure 13. High-speed OH* imaging of spark ignition of the propane/air flame. The spherical electrodes of the spark were clearly visible, starting with the third image.

As discussed earlier, this might cause significant heat loss to the electrodes as well as quenching effects that lead to flame self-extinction and blowout, especially in the early stage of the ignition processes.

MIE and quenching distance

MIE is a standard measure of the least energy deposition required for successful flame initiation/ignition. For spark ignition, if the MIE is not met, an unsuccessful initiation results through a stationary flame ball, a propagating self-extinction flame, or a decaying ignition kernel [57]. For the equivalence ratio of $\phi = 0.875$ that was used in the current experiments, the MIE of $E_{\min}$ for spark ignition is ~ 1 mJ for the quiescent propane/air mixture [48]. The minimum energy in the flow system therein is even greater because of the lengthening of the spark path, causing the energy input to be distributed over a much larger volume.

In comparison, flash-induced ignition is delivered through the active photothermal effects of the nanoenergetics. The flash lamp serves only as the activation source. Most of the ignition energy is provided by the exothermal oxidation reaction of the nanoenergetics. Complete oxidation of one spherical aluminum nanoparticle of diameter of 50 nm generates a thermal energy of ~ 11 nJ [48]. If the ignition were due to the pure thermal effect, around 90 million fully oxidized aluminum nanoparticles would be needed to achieve an energy of 1 mJ, the spark MIE, with an estimate surface temperature of ~ 1070 K due to Joule heating [54]. Because of the large tendency of aggregation for the Al nanoparticles shown in Fig. 14 and the sparse AlO emission points shown in Fig. 12, a large micron-sized particle thus formed is believed to be the major contributor of flame ignition.

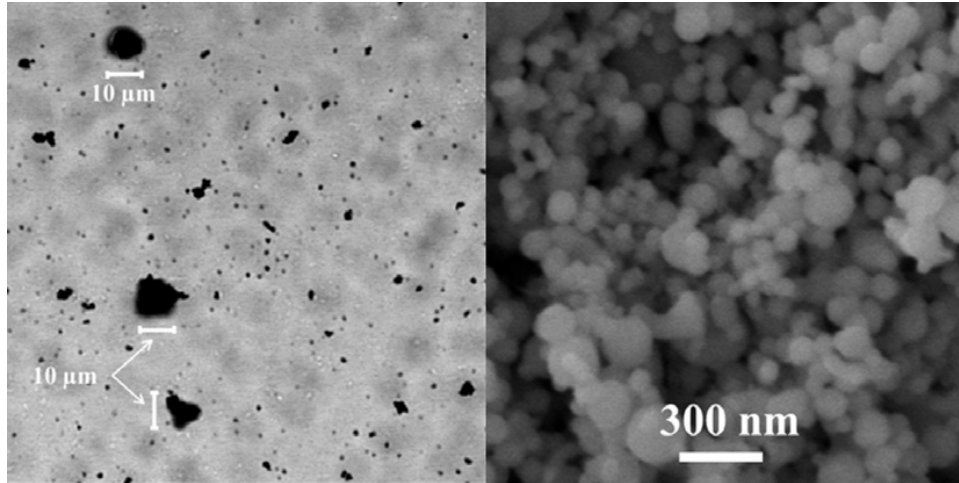


Figure 14. Optical and SEM images of the aluminum nanoparticles before ignition. The samples were collected on a glass slide after blowing through the burner system. A large tendency toward aggregating to form large particles is evident. The sparse seeding density is also shown.

From a rough estimation, the aggregation could be a cube of $450 \times 450 \times 450$ aluminum nanoparticles, with a typical size of 23 nm or less, based on our measurement. The total amount of light illuminating those nanoparticles (or illuminating one face from that cube) was then $\sim 15.11 \text{ } \mu\text{J}$, which is ~ 67 times less than that delivered by the spark.

Additionally, as compared to spark ignition, no quenching-distance requirement exists for flash ignition. For spark ignition, the MIE is E_{min} that is proportional to the (quenching distance)³. The quenching distance is $\sim 3 \text{ mm}$ for spark ignition of propane/air at $\phi = 0.875$. For more fuel-

lean conditions, the MIE and quenching distance become even larger. Because of its remote nature, flash ignition can occur without the limitation of the electrodes.

Conclusions

In this study, the flash-activated photothermal effect of aluminum nanoenergetics was demonstrated to ignite the propane/air flame. Both spatial and temporal control of on-demand ignition was achieved. OH^* and CH^* chemiluminescence and AlO emission were captured by a high-speed camera. Compared to regular spark ignition, flash ignition of aluminum nanoenergetics can efficiently reduce the MIE and remove the restriction of quenching distance. Most of the energy for ignition was released from the oxidation reaction of aluminum nanoenergetics, the light being used as an activation source only. Thus, the MIE of flash ignition is at least 67 times less than that of spark ignition.

CHAPTER III CORE SHELL ALUMINUM NANOENERGETICS FOR PLASMON RESONANCE ENHANCED PHOTOTHERMAL IGNITION

A version of this chapter was originally submitted for revision by Jacques E. Abboud, Xinyuan Chong, Naibo Jiang, Zhili Zhang, Sukesh Roy, Christopher E. Bunker, and James R. Gord:

Abboud, J., et al., *Core Shell Aluminum Nanoenergetics for Plasmon Resonance Enhanced Photothermal Ignition*. Advanced Energy Materials, 2013.

Abstract

Core-shell nanoenergetics of oleic acid coated aluminum nanoparticles (OA-Al NPs) are computationally and experimentally examined for Localized Surface Plasmon Resonance (LSPR) enhanced photothermal ignition. Effects of various core/shell materials, geometry, and configurations are evaluated for resonant enhancement of local energy deposition and triggering subsequent oxidation reactions. Compared to noble metal materials, aluminum has significantly more ohmic losses in the visible region and higher reactivity in the oxidizing environment. Thin OA coating has little effect on overall photothermal heating while keeping minimum dead weight. Multiple contacting nanoparticles generate more local heating than an isolated one. Match of the spectra of the activation source and nanoenergetics at certain configurations can significantly increase the efficiency. Lower sintering temperature leads to more than 30 % decrease on the ignition threshold. Methane and ethylene are ignited at ultralean conditions by photothermally activated OA-Al NPs.

Introduction

Rapid advancements in the field of nanoenergetics call for their incorporation into pure fuel/oxidizer mixtures for enhanced propulsion applications. The presence of energetic nanoparticles in all fuel aspects – solid, liquid, and gas – sets forth promising means of enhancing combustion power output with high efficiency and improved stability for the next generation of propulsion systems. [1, 3] Compared to micron-sized metals, nanopowders are characterized by larger combustion enthalpy, lower melting temperature, lower ignition temperature, greater flame speed ($d^{-0.3}$ or d^{-1} laws where d is the diameter of the nanoparticle), and larger reaction rates due to their higher specific surface areas. However due to the natural oxidation in air, the “dead weight” of alumina (Al_2O_3) could account up to 70 % of total weight for nanoparticles with diameters less than 20 nm, which is a severe limiting factor for total enthalpy and reactivity. Various approaches of core-shell nanoenergetics materials have been synthesized to replace the nonreactive Al_2O_3 with air-stable and reactive shells. [58, 59] It is usually unclear how the combustion performance is affected by utilizing the new core-shell materials.

Compared to spark ignition [30], laser ignition [31], and plasma ignition [32], plasmonics resonance enhanced photothermal ignition has many advantages because of its lower power, lower material cost, and lower mass. [60, 61] The method is spatially and temporally on-demand, quenching free from the electrodes, and has ~ 100 times smaller Minimum Ignition Energy (MIE) than that of spark ignition. [60, 61] It was accidentally discovered that single-wall carbon nanotubes containing metal impurities can be ignited in air when exposed to an ordinary camera

flash [12]. Further scrutinization showed that the ignition technique can be extended to other carbonaceous compounds containing metal impurities [8], silicon nanowires and nanoparticles [62, 63], and aluminum nanoparticles. It has also been shown that photothermally ignited nanoparticles can be used for ignition of gaseous, liquid, and solid fuels. [9-11]

The plasmonics resonance enhanced photothermal ignition of nanoenergetics materials was based on the local surface plasmonics resonance (LSPR) and subsequent oxidation reactions of the nanomaterials. Localized surface plasmons (LSPs) are a result of coherent oscillations of conduction electrons. Depending on the applications of photothermal effects in plasmonic nanostructures [23, 24, 64-66], some metal nanostructures are preferred over others since they may exhibit higher scattering than absorption for instance, once excited by a certain wavelength. Compared to noble metal materials such as Au and Ag, Al is considered to be a poor plasmonic material for sensing applications since it has larger dielectric constants in the visible spectrum, leading to significantly more thermal ohmic losses in those regions [19, 67]. In an oxidizing environment, aluminum is chemically unstable as well, and is passivated by a naturally occurring protecting oxide shell several nanometers thick, playing a key role in determining the reactivity. Consequently, elevated temperatures of 500-600 °C are required to trigger further oxidation of the remaining aluminum metal. As a result, it is desirable to develop an alternative method to hold over the photothermal properties of pure Al NPs, i.e. good absorption and less scattering in the visible range making use of the phenomenon of Localized Surface Plasmon Resonance (LSPR) on one hand, without having to face the ordeal of a reduced energy content for this oxide-passivated Al NP, on the other hand [58].

Here the core shell nanoenergetics materials, OA-Al NPs are computationally and experimentally investigated for plasmonics resonance enhanced photothermal ignitions. The air-stable nanomaterials are an attractive alternative to conventional oxide-passivated materials due to the lower reaction temperatures ($\sim 150\text{-}400\text{ }^{\circ}\text{C}$ compared to $500\text{-}600\text{ }^{\circ}\text{C}$), and the possibility of tuning the reaction onset temperature by varying the choice of the capping agent. In the present work, we photo-ignite OA-Al NP in air, as well as in the flow of gaseous fuels/air mixtures, namely in ethylene/air and methane/air at lean conditions, using a low-power xenon flash lamp. We also fathom the electric field enhancement from LSPR among the aggregated nanoparticles using the Discrete Dipole Approximation technique (DDA) [40], this enhancement leading to localized Joule heating and triggering subsequent oxidation reactions. The method developed here can be easily extended to design and evaluate other core shell nanoenergetics materials.

Results and Discussions

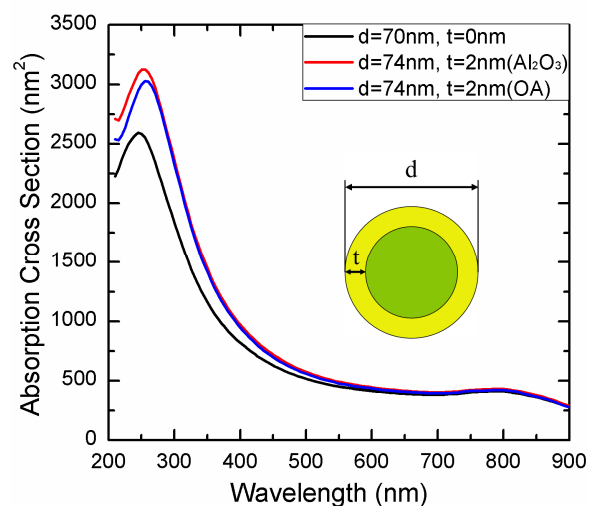
Effects of Coating on Light Absorption

Impact of various coatings on the efficiency of photothermal effects has been evaluated. First, the effect of oleic acid coating on the Al NPs' absorption cross section was calculated. Light absorption and scattering using the Discrete Dipole Approximation [40] from pure, oxide-passivated, and organically capped aluminum nanoparticles with core diameters at 70 nm were computed, shown in Fig. 15a. For the coated nanoparticles, shells of Al_2O_3 and OA at 2 nm were added to the core, respectively. It showed a small discrepancy for the three configurations in both the absorption cross sections, and the peak absorption wavelengths ($\sim 250\text{ nm}$). The main reason

was due to the fact that the refractive indexes of Al_2O_3 and OA are small compared to aluminum at ultraviolet and visible ranges. This implies that there is no wastage in the functional Joule heating or thermal ohmic losses in the aluminum at the expense of the OA coating.

Furthermore, normalized absorption spectra of single and double spherical aluminum nanoparticles were shown in Fig. 15b, to evaluate the impacts of aggregation on the plasmonic resonance. The major reason is to reflect the reality of aggregation effects as shown in SEM images. (Fig. 18) Besides the single aluminum nanoparticles in Fig. 15a, double contacting spherical aluminum nanoparticles with Al_2O_3 and OA at thickness of 2 nm were calculated. The peak wavelengths of the nanoparticles' LSPR shift from the deep ultraviolet range ~ 250 nm for standalone single nanoparticles, to the violet range ~ 400 nm for the case of two contacting spheres, a needful and substantial shift to the visible light region as we will explore in the forthcoming section, where the aluminum ohmic losses are much higher than those from noble metal materials. The impacts of Al_2O_3 and OA coatings are small on the LSPR peak wavelengths for both single and double aggregated aluminum nanoparticles. Figure 15 essentially states that OA coating on aluminum nanoparticles can remove the dead weight in the alumina-aluminum nanoparticles without sacrificing the photothermal efficiency and dramatically shifting the photothermal resonance of the nanoparticles.

a)



b)

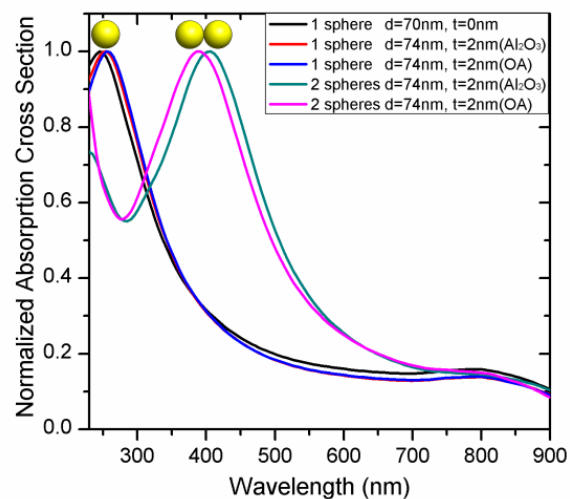


Figure 15. (a) Effect of coating on the absorption cross sections of pure, alumina coated, and OA coated aluminum nanoparticles at diameters of 70 nm. (b) Effects of coating and aggregation on the surface plasmonics resonance. Plasmonic resonance shifts toward the visible range. Real and imaginary parts of the permittivity of OA were extrapolated from [68]. The data for Al and Al_2O_3 are taken from [69].

Matching of Nanoenergetics with Activation Source

To achieve the maximum efficiency of plasmonics resonance enhanced photothermal ignition, the photothermal properties of nanoenergetics should match the activation source. The maximum heat generation inside the nanoenergetics should coincide with the peak of the activation source.

Since a xenon flash tube was used in the experiments, parameters for nanoenergetics are explored here.

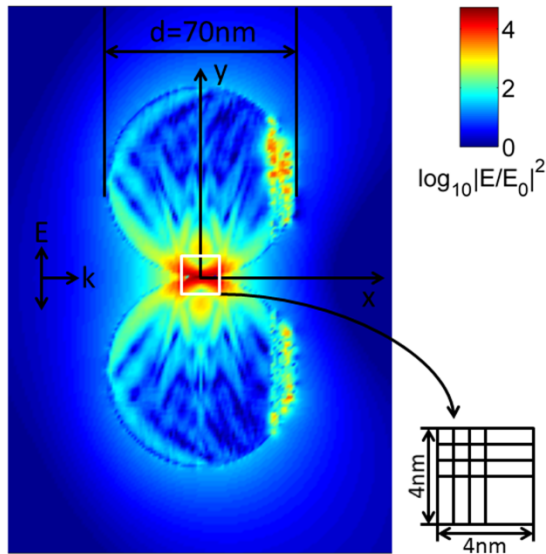
In order to estimate and compare the plasmonic resonance enhanced photothermal heat generation inside the nanoparticles for the aluminum, gold, and silver, the electric field enhancement from two 70 nm-diameter contacting spheres was examined. They were continuously illuminated by an electromagnetic planar wave propagating from left to right, in Fig. 16a. The XY plane framed by $z = 0$ constituted the plane of interest. Since the location of the maximum electric enhancement was found corresponding to the dipoles at the interface of the two NPs at all wavelengths, therefore this area exhibited the most heat generation and served as the nano-source of heat. For a dipole position $\mathbf{X}(x,y)$, the heat power density q reads

$$q(X, \omega) = \frac{\omega}{2} \varepsilon_0 \varepsilon''(\omega) |E(X, \omega)|^2 = \pi c \varepsilon_0 \frac{\varepsilon''(\lambda)}{\lambda} |E_{max}(\lambda)|^2$$

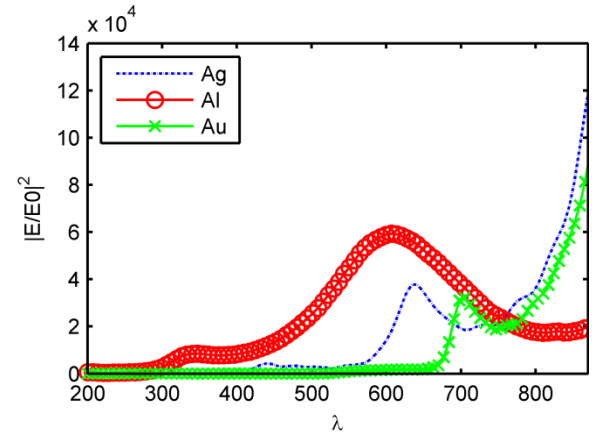
where ε_0 is the vacuum permittivity, ω is the angular frequency of the light, ε'' is the relative permittivity of Al, Au, or Ag, and $\mathbf{E}(\mathbf{X}, \omega)$ is the resulted electric field. For a fixed 16 nm^2 area of interest in Fig. 16a composed by 21×21 dipoles at the contact region, maximum heat power density corresponds to the peak electric field enhancement according to the above equation. For each metal under study, the wavelength was varied from 200 nm to 900 nm. The $\mathbf{E}$ field was evaluated at the 441 dipoles. Only the maximum was represented in the heat generation equation, and plotted in Fig. 16b. Even though the square of local electric field can be enhanced up to 4 orders of magnitude shown in Fig. 16a when computed at the plasmonic Al resonance of 642 nm declared by the peak in Fig. 16b, it is not necessarily the summit of heat that could be achieved.

As clearly seen from the last equation, the comparison among the heat power density for the different metals is limited to defining the maximum of $\varepsilon''(\lambda)|E_{max}(\lambda)|^2/\lambda$. Figure 16c plots the imaginary part of the permittivity values for Al, Au, and Ag [69], in the wavelength range of focus. This enabled us to calculate the maximum heat generation as a function of wavelength, as shown in Fig. 16d. Since the heat originates from Joule effects, aluminum has significantly more thermal ohmic losses in the visible spectral region compared to gold and silver; at 642 nm, the maximum heat generation amongst all was found for Al. Around this wavelength, and for an input intensity of 2 J/cm^2 , the photothermal heat production in Al is 30 times and 638 times higher than that from Ag and Au, respectively. The maximum heat generation in Ag and Au lies in the infrared region.

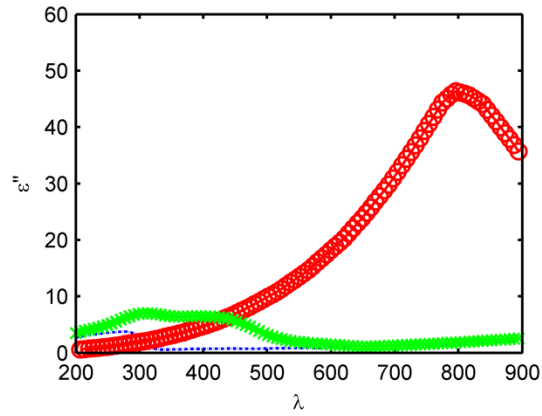
a)



b)



c)



d)

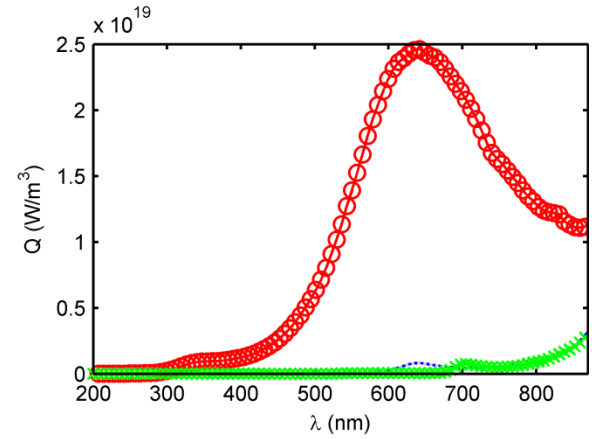


Figure 16. Search for the highest heat generated in the visible range among Al, Au, and Ag. (a) Two 70 nm-contacting spheres of Al continuously illuminated by an electromagnetic planar wave at its plasmonic resonance 607 nm. The region of contact experiences the highest electric field enhancement which is ~ 2 orders of magnitude greater than the input E field. The area of interest is 4 nm x 4 nm comprised of 441 dipoles. (b) The square of the maximum enhanced

electric field in the contact region plotted as a function of wavelength for various materials. (c) Imaginary part of the permittivity of Al, Au, and Ag, taken from [69]. (d) Plot of the heat generation, defining the thermal ohmic losses for the metals in hand as a function of wavelength.

Photothermal Ignition of Dry OA Al Nanoenergetics in Air

The effect of oleic acid coating on the oxidation characteristics and combustion phenomena of the 70 nm Al NPs was experimentally investigated. Figure 17 shows time resolved images of light emission from OA-Al NPs photothermal ignition in atmospheric air obtained at a frame rate of 1 KHz. The OA-Al NPs were placed on the glass slide at a distance of 14 mm away from the xenon flash tube, corresponding to an energy density of 1.1 J/cm^2 . In these time-resolved images, the flash started at $t=0$ ms. The flash lasted for ~ 10 ms, leading to frames' light saturation along with the hot glowing ignition points of the NPs until around 15 ms. A separate experiment shows that ignition occurs within less than 1 ms [3]. The photothermally induced motion continued upward for another 15 ms (frame 4), and the jump height indicated a maximum of ~ 7 mm before the particles returned to the glass slide after approximately 80 ms. By varying the distance between flash tube and the nanoparticles, both photothermal motion and ignition can be controlled through the change in magnitude of the photothermal energy density. The farther the nanoparticles are from the xenon flash tube, the lower the nanoparticles jump height is. Throughout all dry experiments, and in addition to the particles movement detected by the fast shutter camera [35, 36, 70], ignition was a persistent companion until neither of the two

phenomena was detected, i.e. when the pile was placed at a distance exceeding 2 cm (energy density $\sim 0.8 \text{ J/cm}^2$) from the photothermal activation source. As a comparison, alumina coated aluminum nanoparticles have a threshold of $\sim 1.1 \text{ J/cm}^2$, which is about 38% higher than that for OA-Al NPs.

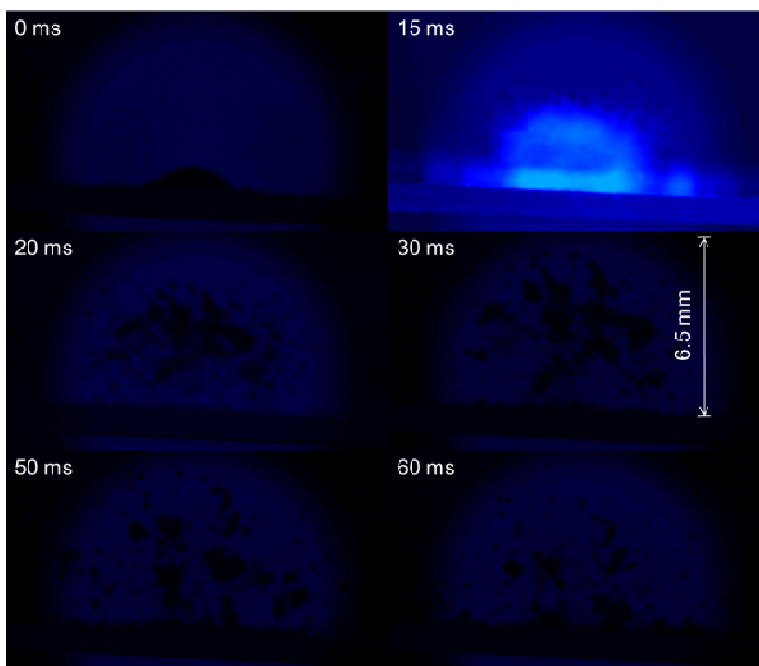
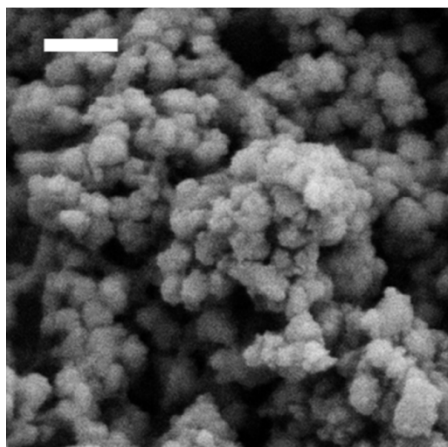


Figure 17. Photothermal induced motion and ignition of dry OA Al NPs in atmospheric air. The flash tube is 14 mm from the NPs pile, corresponding to an energy density of 1.1 J/cm^2 .

The SEM images of intact and ignited OA-Al NPs are shown in Fig. 18 to determine their size and morphology. The burnt particles are mostly uniform in size, tens of nanometers larger than

the originals. Each particle seems to be resultant from some sintered original ones melted together after the heat-induced thin oleic acid film desorption. It was shown recently that reactive sintering occurs on a fast timescale and helps improve the reactivity of the nanoenergetic material. [4] It should be noted that no bursting effect was detected in OA-Al NPs burnt product. As a sharp comparison, the flash ignition of alumina coated Al NPs were oxidized into much smaller NPs (5-50 nm), as reported in [10, 60]. Flash-activation oxidation has also been confirmed by Energy-dispersive spectroscopy (EDS) analyses. Material composition from more than 10 locations in the burnt products sample were reported, showing on average a 5 % increase in the oxygen element (in weight), faced by the same percentage decrease in the carbon element, in comparison with EDS analyses recorded from original OA-Al NPs. It demonstrates that OA-Al NPs are an attractive alternative to conventional oxide-passivated materials due to the lower reaction temperatures (~150-400 °C compared to 500-600 °C), establishing the possibility of tuning the reaction onset temperature by varying the choice of the capping agent, and the faster reaction rates due to easy sintering processes.

a)



b)

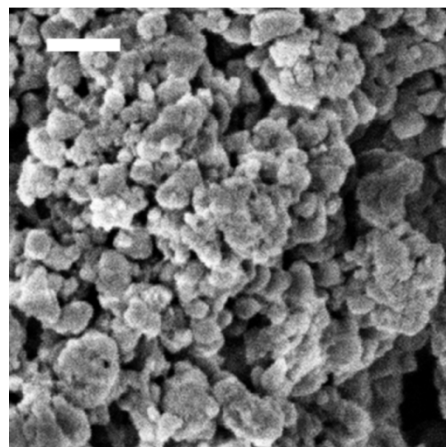


Figure 18. SEM images of (a) intact oleic acid coated aluminum nanoparticles with an average size of 70 nm and (b) the ignited OA Al NPs in air. The white bar in the figure stands for 300 nm. Sintering can be identified, but not the bursting as opposed to the case of Al_2O_3 -coated Al ignited in air [60].

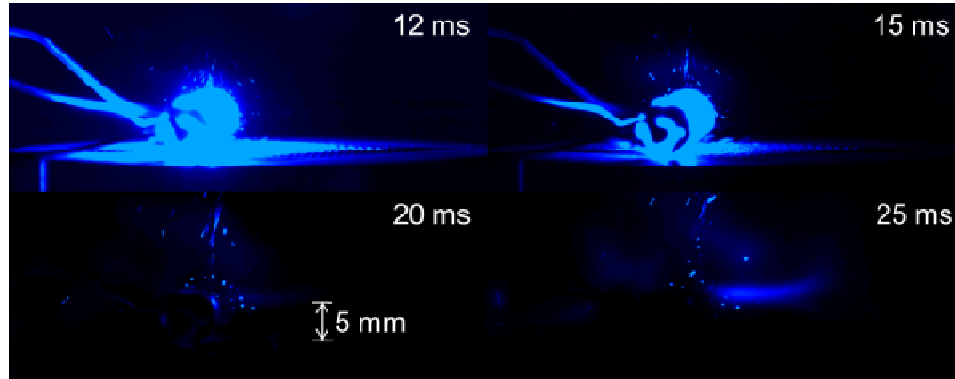
Ignition of Ultralean Combustion Mixtures

Camera images of unfiltered light emission were also obtained at 1 KHz repetition rate for OA Al NPs photothermal ignition of lean ethylene/air or methane/air mixtures, shown in Fig. 19. From the aforementioned critical distance for NPs ignition in air, nanopowders were sprinkled around the xenon tube at a distance not exceeding 20 mm. Mixture flowing stably, triggering the flash induced the instantaneous NPs ignition, which in turn prompted the reaction and ignition of

the gaseous fuel/air mixture flow. Experiments with equivalence ratios of 1 down to 0.8 were all successful in flow ignition in the case of ethylene (flows of 0.56 slpm and 10 slpm for ethylene and air respectively), and down to 0.6 when using methane (0.315 slpm and 5 slpm for methane and air respectively). Figures 19a and 19b show the ignition of fuel/air mixture induced by the OA Al NPs photothermal ignition, at their leanest conditions at atmospheric pressure and temperature.

These observations unravel the potential of nanoparticles photo-ignition-induced controlled and enhanced combustion of, not only quiescent gaseous fuels/air mixtures containing suspended nano-composites [9, 10], but more importantly of *flows* of these mixtures. In particular, they suggest that, having a flow of fuel/air mixture, an on demand spatiotemporal (in any location and at any time) energy deposition can drive the mélange ignition through the use of energetic nanoparticles such as OA-Al NPs. Moreover, while this technique can be a standalone ignition tool by itself after it has been proved that photothermal ignition delay is two orders of magnitude smaller than that from spark ignition, it can serve as an assistant to traditional means as well, for instance in automotive industry, where the flame front can hardly reach the hidden weak spots in the combustion chamber at very high rpms.

a)



b)

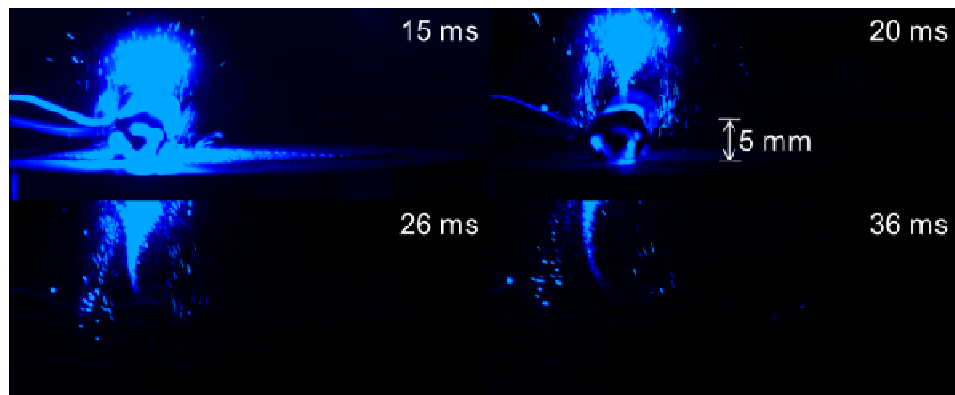


Figure 19. Energy deposition from OA-Al NPs photo-ignition in the flow of gaseous fuel/air mixture at lean conditions, at ambient temperature (293 K) and pressure (1 atm). (a) In ethylene/air mixture at $\phi = 0.8$. (b) In methane/air mixture at $\phi = 0.6$.

Conclusions

In conclusion, photothermally induced motion and ignition in air and in the flows of lean methane/air and ethylene/air mixtures were demonstrated.

Dry experiments showed, in addition to particles ignition in air, a companion jump of the order of 7 mm. More importantly, wet nanoenergetics were also successfully ignited at very lean conditions of gaseous fuels/air *flow* mixtures.

By exploiting the effect of coating the nanoparticles using oleic acid on the absorption cross section of Al, the organic capping showed a weak influence on the photothermal properties of the metal under study. Noticeably, a shift of the plasmon resonance from the UV for a single sphere, to the visible range for two contacting spheres, was reported using DDA. Moreover, local electric field measurement at the interface of two contacting 70 nm Al NPs recorded 100 times enhancement from LSPR effect, leading to 4 orders of magnitude increase in thermal ohmic losses, following the heat generation equation.

Depending on the application (sensing applications, combustion and energy deposition applications), the heat generation determines the suitability and appropriateness of the material, independently from the plasmonic resonance value. Substantial for boosting oxidation, the heat production from Al is 30 times and 638 times larger than that from Ag and Au in the visible range, respectively. On the basis of our observations, we provide a consistent explanation of the on demand spatiotemporal energy deposition for gaseous fuels/air flow mixtures. Radiative energy from the flash tube is absorbed and confined in the nanoenergetics structure causing

build-up in thermal ohmic losses, providing high temperatures which in turn provoke oxidation of the metal catalyst nanoparticle. For instance, photothermal properties of these nanoenergetic particles could be used to enhance the energy density of fuels in propulsion systems.

In summary, and depending on the application, the right material is chosen, correctly illuminated, and suitably capped to give the required results. The metal type and wavelength modulation define the functional region of spectrum turning it into an ideal nano-source of heat, remotely controllable using light; and the right capping is needed to determine the onset reactive temperature on one hand, without affecting the light properties of the metal and replacing the dead weight from oxide passivation, on the other hand.

Experimental Section

Discrete Dipole Approximation Analyses

The computational approach known as Discrete Dipole Approximation (DDA) [40] was used to calculate the absorption coefficients and near-field electric field distributions of the Al NPs with various alumina-coating thicknesses, sizes, shapes, and aggregations. Local energy depositions were thus obtained by remote activation of Al NPs with low-power light.

Synthesis of Oleic Acid coated Aluminum Nanoparticles

The procedures used to synthesize oleic acid-capped aluminum nanoparticles have been described in detail elsewhere. [59] Briefly, aluminum nanoparticles were synthesized using an initial solution of 11.4 mM oleic acid dissolved in dodecane. The solution was subjected to several freeze–pump–thaw cycles in order to reduce the dissolved oxygen concentration and

then placed inside a dry nitrogen glovebox, where N,N-dimethylethylamine and a titanium(IV) isopropoxide catalyst were added to the solution. The concentrations of the alane complex and titanium catalyst in this solution were 50 and 0.55 mM, respectively. This solution was then transferred into a sonication flask (Sonics Inc., Suslick flask) and sonicated. The sonication instrument (Sonics Inc. Vibra Cell) was operated at 20 KHz and, the solution was sonicated at 37% power (~ 22 W) for 7.5 min active time, using a 1-s-on, 1-s-off duty cycle. During sonication, the bulk solution temperature reached approximately 70 °C. These conditions produced a black solution that gradually precipitated a grayish-black powder. The powder was recovered by evaporation of the solvent under vacuum, followed by repeated washings with hexane. The aluminum nanoparticles produced by this process were spherical, with an average size of ~ 5 nm and a size distribution of 2–15 nm.

Organically coated aluminum oxide particles were synthesized via a refluxing procedure. A 10.5 mg sample of the nanoaluminum oxide was heated to ~ 120 °C for several minutes to drive off any adsorbed water. These particles were placed in a flask, and 8 mL of dodecane and 18 μ L of oleic acid were added. The mixture was then refluxed at 130 °C for 24 h. A white powder was recovered by evaporation of the solvent under vacuum, followed by repeated washings with hexane.

Photothermal Activation Source Characterization

Flash ignition of these nanoparticles is achieved using a xenon-flash tube having a maximum energy density of 1.9 J/cm^2 , measured by a long-pulse-thermopile power sensor. The flash radiant exposure decreases roughly linearly with distance to reach at 25 mm a value of ~ 0.72

J/cm^2 . An $\sim 50 \mu\text{s}$ spike, followed by a 5 ms plateau and another 5 ms decay constitute the temporal profile of the photothermal activation source in hand, that was covered by a BK7 glass cover, and which intensity peaks at 470 nm. Time-resolved images were obtained using a TSI high speed camera and associated software with 1 ms exposure time. These aluminum particles were coated with a thin layer of oleic acid about 2-3 nm thick to prevent oxidation. Some of the nanoparticles are spherical and uniform; others experience ovalness and tend to agglomerate. The size distribution ranges from 50-250 nm.

Ignition experiments

In the case of dry OA-Al NPs, a manually poured pile of hundreds of micrograms was placed on top of a 1/16" glass slide located at a variable distance above the xenon flash tube. The pile was ignited by a single exposure to the flash tube.

For wet nanoparticles ignition, i.e. in the flow of gaseous fuels/air mixture, two fuels were considered, methane and ethylene. Experiments were carried out at the exit of a Hencken burner to investigate the potential of nanopowders photo-ignition-induced mixture ignition. The Xe flash tube was first sat on the top surface of the burner with its axis parallel to the burner surface, to be removed quickly once the ignition is initiated. In this case, an approximate amount of 0.05 mg of nanoparticles was sprinkled on the tube and in its vicinity at a distance not exceeding couple of centimeters. Afterwards, compressed gaseous fuel and air flows were let premix inside the burner at equivalence ratios ranging from 1 down to 0.6 for methane/air mixture and to 0.8 in the ethylene case, and then flow to the atmosphere where the ambient temperature was 293 K and the pressure atmospheric.

CONCLUSION AND OUTLOOK

In this dissertation, we worked on the design, development and implementation of a novel flame ignition technique by active photothermal effect of Al NPs, to enhance and control the combustion process in solid, liquid, and gaseous fuel/air mixtures. In addition to its lower mass and cost compared to traditional ignition tools, this new method led to two orders of magnitude faster ignition (~ 100) and lower power requirement (~ 70).

Scanning electron microscopy (SEM), Energy dispersive X-Ray spectroscopy, high speed imaging of OH* and CH* radicals' chemiluminescence, in addition to other investigation tools, have all served to fathom and understand the experiments that were held in dry (air) and in wet environments (propane, methane, and ethylene/air mixtures). As for the computational part, a discrete dipole approximation approach was used to compute the electric field enhancements, and to identify the plasmon resonance for different nanoparticles configurations (isolated particles or aggregated together), sizes, and coatings, illuminated at various wavelengths.

The photothermally activated movement of NPs under a single 10 ms pulse from a xenon flash was shown to be as high as 6 mm from the surface without ignition in the first chapter, which is $\sim 10^5$ times higher than that from femtosecond/nanosecond laser-induced photothermal ejection of gold nanodroplets. Also, active control for both motion and ignition can be achieved by varying the flash power or UV filtering of the low power xenon flash. Both SEM and EDS measurements of motion-only and after-ignition products indicate significant oxidation of Al NPs occurs through sintering and bursting after a single flash exposure. The positive feedback effects from the local heat generation are amplified by Al oxidation. The local heat-induced

pressure pulse in the NPs is responsible for the large movement and the local heating inside and among the NPs generates and accelerates the ignition.

In the second chapter, we conducted a spatiotemporal on-demand ignition of propane/air flames. OH* and CH* chemiluminescence and AlO emission were captured by a high-speed camera. Compared to regular spark ignition, photo-igniting the aluminum nanoenergetics can significantly reduce the MIE. Most of the energy for ignition was released from the oxidation reaction of aluminum nanoenergetics, the light being used as an activation source only.

In the third chapter, photothermally induced motion and ignition in air and in the flows of lean methane/air and ethylene/air mixtures were demonstrated. Though the effect of organically coating the nanoparticles proved weak on the absorption cross section of Al, a drastic shift of the plasmon resonance from the UV for a single sphere, to the visible range for two contacting spheres has been reported using DDA. Moreover, local electric field measurement at the interface of two contacting 70 nm Al NPs recorded 100 times enhancement from LSPR effect, leading to 4 orders of magnitude increase in thermal ohmic losses, following the heat generation equation. Depending on the application, we also showed that the maximum heat needed is independent of the plasmonic resonance value. The right material has to be chosen first, correctly illuminated, and suitably capped to give the required results. The metal type and wavelength modulation define the functional region of the electromagnetic spectrum, turning it into an ideal nano-source of heat, remotely controllable using light; a right capping is always needed to replace the considerable dead weight at the nanoscale, without bringing any harm to the absorption cross section of the metal.

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VITA

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