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Major Goals: The scientific research objective of this proposal is to quantitatively determine the ignition temperature and minimum ignition energy of porous Si based energetic materials and to correlate those ignition properties with the physical microstructures of porous Si and the chemical compositions of the oxidizers. Leveraging the Zheng lab's extensive experience in synthesizing diverse Si nanostructures to prepare free-standing porous Si films with different microstructures, our project objectives will be to:

1. Synthesize a diverse range of hierarchically organized porous Si films as samples for ignition studies.
2. Measure the ignition onset temperature, heat release characteristics and any potentially evolved gas phase species using simultaneous thermo-gravimetric analysis, differential scanning calorimetry and mass spectrometry measurement.
3. Determine the minimum ignition energy of porous Si by non-intrusive optical Xe lamp flash ignition methods.
4. Characterize the morphology, crystal structure and chemical compositions of porous Si before and after the ignition experiments.

Accomplishments: 1. Silicon (Si) particles are widely utilized as high-capacity electrodes for Li-ion batteries, elements for thermoelectric devices, agents for bioimaging and therapy, and many other applications. However, Si particles can ignite and burn in air at elevated temperatures or under intense illumination. This poses potential safety hazards when handling, storing, and utilizing these particles for those applications. In order to avoid the problem of accidental ignition, it is critical to quantify the ignition properties of Si particles such as their sizes and porosities. To do so, we first used differential scanning calorimetry to experimentally determine the reaction onset temperature of Si particles under slow heating rates (~0.33 K/s). We found that the reaction onset temperature of Si particles increased with the particle diameter from 805 °C at 20–30 nm to 935 °C at 1–5 µm. Then, we used a xenon (Xe) flash lamp to ignite Si particles under fast heating rates (~103 to 106 K/s) and measured the minimum ignition radiant fluence (i.e., the radiant energy per unit surface area of Si particle beds required for ignition). We found that the measured minimum ignition radiant fluence decreased with decreasing Si particle size and was most sensitive to the porosity of the Si particle bed. These trends for the Xe flash ignition experiments were also confirmed by our one-dimensional unsteady simulation to model the heat transfer process. The quantitative information on Si particle ignition included in this Letter will guide the safe handling, storage, and utilization of Si particles for diverse applications and prevent unwanted fire hazards.

2. Silicon (Si) is another attractive fuel for thermites because of its high-energy content, thin native oxide layer, and facile surface functionality. Several studies showed that the combustion properties of Si-based thermites are comparable to those of Al-based thermites. However, little is known about the ignition properties of Si-based thermites. In this work, we determined the reaction onset temperatures of mechanically mixed (MM) Si/Fe₂O₃ nanothermites and Si/Fe₂O₃ core/shell (CS) nanothermites using differential scanning calorimetry. The Si/Fe₂O₃

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CS nanothermites were prepared by an electroless deposition method. We found that the Si/Fe₂O₃ CS nanoparticles (NPs) had a lower reaction onset temperature (~550 °C) than the MM Si/Fe₂O₃ nanothermites (>650 °C). The onset temperature of the Si/Fe₂O₃ CS nanothermites is also insensitive to the size of the Si core NP. These results indicate that the interfacial contact quality between Si and Fe₂O₃ is the dominant factor for determining the ignition properties of thermites. Finally, the reaction onset temperature of the Si/Fe₂O₃ CS NPs is comparable to that of the commonly used Al-based nanothermites, suggesting that Si is an attractive fuel for thermites.

3. Micron-sized aluminum (Al), due to its large volumetric energy density, is an important fuel additive for broad propulsion and energetic applications. However, micron-sized Al particles are difficult to ignite and react slowly, leading to problems such as incomplete combustion and product agglomeration. Many pioneering strategies have been investigated to overcome the above challenges, ranging from reducing Al particles to nanoscale, coating them with metallic or polymeric materials, to blending Al with other materials to form composites. On the other hand, porous Si has emerged as a promising energetic material with a volumetric energy density comparable to Al, high reactivity at low temperature, and ultrafast flame propagation speeds. To date, the potential of using porous Si as an additive to enhance ignition and combustion of micron-sized Al has not been explored. Herein, we experimentally investigated the effect of porous Si addition on the ignition and combustion characteristics of micron-sized Al with CuO nanoparticles. We consistently observed that the addition of porous Si facilitates both ignition and combustion of Al/CuO mixtures over a wide range of experimental conditions, ranging from slow heating rate conditions in differential scanning calorimetry, fast heating rate conditions in Xe flash ignition, flame propagation in microchannels, to constant-volume pressure vessel experiments. The enhancement effects are attributed to the easy ignition and fast burning properties of porous Si, which elevate the ambient temperature and/or pressure, and hence enhance the ignition, reaction rate, and combustion efficiency of micron-sized Al particles. This work demonstrates that adding porous Si is another viable strategy toward enhancing the ignition and combustion properties of micron-sized Al particles.

Training Opportunities: This grant is used to support one Ph.D student who is about to get his Ph.D. degree in a year and another postdoc who is going to start her assistant professor position at MIT early next year.

Results Dissemination: Nothing to Report

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- Nano Letters Young Investigator Lectureship, 2015
- David Filo and Jerry Yang Scholar, 2015
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PARTICIPANTS:

Participant Type: PD/PI

Participant: Xiaolin Zheng

Person Months Worked: 12.00

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Other Collaborators:

Participant Type: Postdoctoral (scholar, fellow or other postdoctoral position)

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Other Collaborators:

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Other Collaborators:

Participant Type: Graduate Student (research assistant)

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Authors: Sidi Huang, Venkata Sharat Parimi, Sili Deng, Srilakshmi Lingamneni, Xiaolin Zheng

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Abstract: Silicon (Si) particles are widely utilized as high-capacity electrodes for Li-ion batteries, elements for thermoelectric devices, agents for bioimaging and therapy, and many other applications. However, Si particles can ignite and burn in air at elevated temperatures or under intense illumination. This poses potential safety hazards when handling, storing, and utilizing these particles for those applications. In order to avoid the problem of accidental ignition, it is critical to quantify the ignition properties of Si particles such as their sizes and porosities. To do so, we first used differential scanning calorimetry to experimentally determine the reaction onset temperature of Si particles under slow heating rates (0.33 K/s). We found that the reaction onset temperature of Si particles increased with the particle diameter from 805 °C at 20–30 nm to 935 °C at 1–5 μm. Then, we used a xenon (Xe) flash lamp to ignite Si particles under fast heating rates (103 to 106 K/s) and measured

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Quantification of Ignition Properties of Porous Si Based Energetics

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Project Summary

The *scientific research objective* of this proposal is to quantitatively determine the ignition temperature and minimum ignition energy of porous Si based energetic materials and to correlate those ignition properties with the physical microstructures of porous Si and the chemical compositions of the oxidizers.

We have made contributions in three frontiers of energetic materials: 1) demonstrated the first application of flash ignition of Si nanoparticles (NPs) and investigating the effect of NP size and packing porosity on the minimum ignition; 2) developed a new synthesis route to prepare Si/Fe₂O₃ core/shell NPs with shorter oxygen diffusion length and hence much enhanced ignition properties; and 3) demonstrated that the addition of porous Si can greatly improve the ignition and combustion performance of Al micron size particles..

Accomplish # I: Flash Ignition of Si Nanoparticles: Effects of Particle Size and Packing Porosity

Summary

In this work, the effects of size and packing porosity on the ignition of Si particles were investigated with both experimental and computational approaches. First, the effect of particle size on the onset temperature of Si ignition was elucidated with differential scanning calorimetry (DSC). Second, the minimum energy density E_{\min} (J/cm²) required to ignite such Si particle beds in air was quantified with a Xenon (Xe) flash ignition test. Third, the effects of particle size and packing porosity on the E_{\min} observed in the experiments were further elaborated with computations using the COMSOL software.

Experimental Methods and Results

Five sizes of Si particles were examined as received, which are 20-30 nm (U.S. Research Nanomaterial Inc), 50-70 nm (U.S. Research Nanomaterial Inc), 500 nm (Skyspring Nanomaterial Inc.), 1-3 μ m (U.S. Research Nanomaterial Inc), and 1-5 μ m (Alfa Aesar Inc.). In each DSC (Labsys Evo, Setaram) test, approximately 10 mg of the Si powder was placed in a 100 μ L alumina crucible and heated from 100 °C to 1200 °C under a constant heating rate of 20 °C/min. The carrier gas consisted of 80% Ar and 20% O₂ by volume was flowing at 40 ml/min. After the samples was cooled down to the room temperature, the same heating procedure was followed for the second time to provide a baseline, which accounts for the drifts caused by the change of specific heat with temperature [26]. All the DSC profiles reported in the current work have been corrected, as the raw data acquired during the first heating cycle has been subtracted by the baseline.

The specific heat flow profiles of Si oxidation are shown in Figure 1a. As Si particle size decreases, the heat release from the Si/O₂ reaction becomes more pronounced, and the largest heat release occurs at lower temperature, indicating an increase in the reactivity of Si particles. Such increase is due to the reduced diffusion distance between Si and O₂, as the size of Si particles decreases from microns to nanometers, similar to the oxidation of micro and nano aluminum particles [27, 28]. To quantify and illustrate the size dependence of the ignition of Si particles, the onset temperatures of the oxidation processes are shown in Figure 1b. The onset temperature is defined as the intersection of the tangent corresponding to the largest heat release rate and the extrapolated baseline, and an example corresponding

to the 1-5 μm Si is highlighted in Figure 1a. The onset temperature of oxidation decreases from 935°C for 1-5 μm Si to 805°C for 20-30 nm due to the increased specific surface area of Si particles [27].

Although DSC experiments elucidate the oxidation processes of Si particles in a quasi-steady state manner, in practical combustion applications, Si particles often undergo rapid heating. Consequently, the minimum ignition energy densities E_{\min} of Si particles were quantified with a xenon (Xe) flash. The experimental setup of the Xe flash ignition test is shown in Figure 2a. For each experiment, a pile of loosely packed Si particles, with fixed mass of 5 mg and cross sectional diameter of 6 mm, were placed on a 1 mm thick glass slide. The glass slide was placed directly on the Xe flash tube (AlienBeesTM B1600), as shown in Figure 2b. The typical diameter of Si particle beds (0.6 cm) is smaller than the diameter of flash tube (1.5cm), so the incident light on the entire sample could be assumed to be uniform. The areal impulse of the Xe flash tube was firstly calibrated by measuring the temperature rise of soot-covered silicon substrate exposed to the same flash intensity using a method discussed elsewhere [34,35]. E_{\min} of each sample was determined by gradually increasing the power of Xe flash until ignition occurred, and a fresh sample was utilized at each flash test to avoid partial oxidation from the previous flash. Upon flash triggering above E_{\min} , Si particles are ignited by the photo-thermal effect [30] and the subsequent combustion is self-sustained, as shown in Figure 2c.

Since both the particle size and packing porosity affect the optical absorption coefficient [30–36] and thermal conductivity [37,38] of Si, their effects on E_{\min} are investigated separately. The packing porosity of the Si particle bed is evaluated gravimetrically as:

$$P = 1 - \frac{m_{\text{Si}}}{\rho_{\text{Si}} V_t}, \quad (1)$$

where P is the packing porosity, m_{Si} is the mass of Si particle, ρ_{Si} is the density of Si (2.33 g/cm³), and V_t is the volume of the sample. Figure 3 illustrates the experimentally measured E_{\min} as a function of particle diameter and packing porosity, and the error bar represents the standard deviation of the E_{\min} measurements. E_{\min} reduces with decreasing particle diameter for the same packing porosity, and increases with decreasing packing porosity otherwise. These observations are further analyzed with the COMSOL Multiphysics software.

Numerical Methods and Results

The schematic setup of the computational domain is similar to the experimental configuration (Figure 1a) and is shown in Figure 4a. We assume that this is one-dimension (1-D) time dependent heat transfer problem in solids. The flash energy is assumed to be fully absorbed by Si particles according to Beer-Lambert Law, since the optical absorption coefficient of the glass slide is negligibly small. Heat transfer to the air by natural convection and conduction to the bottom glass slide is considered. Consequently, the temperature profile of Si bed is described by the 1-D unsteady heat transfer equation as

$$\rho C \frac{\partial T}{\partial t} = \frac{\partial}{\partial z} \left(k \frac{\partial T}{\partial z} \right) + \alpha(1 - R) \exp(-\alpha z) I_0(t) E_0, \quad (2)$$

where ρ , C , k , α , $I_0(t)$, E_0 , and R are the density(kg/m³), specific heat capacity(J/(kgK)), the effective thermal conductivity(W/(mK)), output power density(W/m²), flash energy intensity (J/cm²), and the reflectivity, respectively.

The initial and boundary conditions are:

$$T(z, t = 0) = 300 \text{ K}, \quad T(z = -1\text{mm}, t) = 300\text{K}$$

$$k \left. \frac{\partial T}{\partial t} \right|_{z=d} = h(300K - T(d, t)),$$

where d is the thickness of the Si bed, and h is the convective heat transfer coefficient of $10 \text{ W}/(\text{m}^2\text{K})$.

Key assumptions and approximations in the COMSOL model are summarized as follows.

1. The effective thermal conductivity of the particle bed is calculated using the effective medium theory [37], which can be written as

$$(1 - P) \frac{k_{si} - k_{eff}}{k_{si} + 2k_{eff}} + P \frac{k_{air} - k_{eff}}{k_{air} + 2k_{eff}} = 0, \quad (3)$$

where k_{eff} is the effective thermal conductivity of the Si bed (Si-air system), k_{si} is the size and temperature-dependent thermal conductivity of Si particles [38,39], and k_{air} is the temperature-dependent thermal conductivity of air [40,41]. The influence of both Si particle size and packing porosity is shown in Figure 4b.

2. The light emission from the flash tube is approximated to be monochromatic at 450 nm, where Xe flash peaks. Consequently, a linear fit of the reported absorption coefficients at 450 nm [30–36] was conducted, as shown in Figure 4c, to provide a correlation between the absorption coefficient and packing porosity. Similarly, the reflectivity of Si particles at 450 nm was adopted from Theiβ [35].

3. The effective heat capacity, ρC , is calculated as

$$\rho \rho C = (1 - P) \times \rho_{si} C_{si} + P \times \rho_{air} C_{air}, \quad (4)$$

where ρ_{si} , ρ_{air} , C_s , and C_{air} are the density of Si and air, specific heat capacity of Si and air, respectively [42,43].

4. The intensity of the light emission from the Xe flash tube, $I_0(t)$, is obtained experimentally using a photodiode (PDA36A, Thorslab). The recorded intensity time history is curve-fitted using MATLAB (Fig. S1) and used as an input parameter for COMSOL computations.

Representative temperature history profiles of 30 nm Si particles with different packing porosities (0.95 and 0.85) with an incident Xe flash energy density E_0 of $2.15 \text{ J}/\text{cm}^2$ are shown in Figure 5. Qualitatively, the temperature evolution trends for both porosities are similar. At $t=0 \text{ ms}$, the temperature of Si particle beds is at room temperature. Then, temperature of Si particle beds rapidly increases upon Xe flash discharge; The peak temperatures continue to drop after 0.5 ms due to the decline in energy supply from Xe flash discharge and heat losses to the glass slide. The temperature gradually drops along the Z-direction because the amount of light absorption drops exponentially with distance [30]. Once the flash pulse is terminated ($\sim 4 \text{ ms}$), the temperature of Si particle beds gradually returns to room temperature due to the heat losses to glass slide and ambient air.

As shown in Figure 5, the peak temperatures within the Si bed increase with increasing packing porosity. Furthermore, the calculated maximum temperature within the Si bed throughout the entire time history is

illustrated in Figure 6 for various particle sizes and packing porosities. Specifically, the size of Si particle varies between 30 nm and 6 μm , and packing porosity changes from 0.65 to 0.95. The incident flash energy density E_0 is fixed at 2.15 J/cm². First, for a fixed packing porosity of 0.65, the calculated maximum temperature decreases with increasing particle size due to the increase in effective thermal conductivity. However, such effect becomes less prominent at higher packing porosity because the effective thermal conductivity of Si particle beds remains very close to the thermal conductivity of air, due to the large volume fraction of air in the beds. Second, the calculated maximum temperature is strongly influenced by packing porosity. A higher packing porosity results in higher maximum temperature due to the combination effects of lower effective thermal conductivity, effective heat capacity, and reflectivity.

It has been noted that several parameters, namely packing porosity, flash energy intensity, size, reflectivity, absorption coefficient and effective thermal conductivity, affect the maximum temperature of Si particles, and it is interesting to further examine and identify the most important parameter through a sensitivity analysis using a sensitivity coefficient defined as

$$S = \frac{\partial \ln T_{max}}{\partial \ln \beta}$$

, where β is the parameter whose effect is being probed where T is the maximum temperature

The sensitivity analysis was performed for 30 nm silicon particles packed at 0.85 packing porosity with an initial energy intensity E_0 of 2.15 J/cm². The maximum temperature was computationally calculated by perturbing only one parameter at a time by 5%. Figure 7 illustrates the results of those sensitivity coefficients. Our sensitivity calculation reveals that the most significant parameter is packing porosity, which influences several parameters such as heat capacity, thermal conductivity, reflectivity, and absorption coefficient, all of which affect the temperature. The second most important parameter is the flash energy density.

Sensitivities analysis on particle size, reflectivity, heat capacity, the absorption coefficient and effective thermal conductivity are also analyzed, but they have inverse effects to the temperature, and present as negative sensitivity coefficients. An increase in particle size will result in increment of thermal conductivity, hence thermal diffusivity, as a result of which more heat is lost to the glass slide or air. Increment of reflectivity will reflect more flash energy so that the total absorbed energy decreases. Similarly, the addition of heat capacity of Si beds will require more heat to raise its temperature. An increase in the effective thermal conductivity of the particle bed will result in an increased thermal diffusivity, so more heat is lost to the glass slide or air. Hence, the temperature will be lower. One sensitivity coefficient that shows an opposite trend than expected is the negative sensitivity of the absorption coefficient. An increase in the absorption coefficient means that more of the light absorption or more heat generation takes place over a smaller thickness of the bed, which results in a steeper thermal gradient. The steeper temperature gradient in the bed may result in more heat transfer to the glass slide compared to the layers of the particle bed farther away from the Si – glass interface, resulting in a negative sensitivity coefficient.

Conclusions and future work

In summary, the ignition behaviors of Si particles under slow and fast heating rates were investigated with DSC and Xe flash tests, respectively. Specifically, the effects of particle size and packing porosity on the onset temperature of oxidation and minimum ignition energy were quantified. At slow heating conditions, smaller Si particles have lower peak temperature and onset temperature, due to smaller diffusion distance and larger specific surface area. At fast heating conditions with Xe flash, the packing porosity of Si particles is the dominant factor for the minimum ignition energy. Both experiment and computation showed that the minimum ignition energy decreases with increasing packing porosity of the Si bed. Such trend was further explained with computations: higher temperature rise was achieved within the Si bed, even though the intensity of the Xe flash was constant. Also, through sensitivity analysis, packing porosity is determined to be the most important factor for Si ignitions. The fundamental understanding on Si ignition obtained in the current study is beneficial to designing silicon based energetic materials for combustion and more diverse applications.

Accomplish # II: Improved Ignition Properties with Si/Fe₂O₃ Core/Shell Structures

Summary

For thermite reactions, the solid diffusion of oxygen atoms towards fuel is the rate limiting step. Therefore, we hypothesized that by creating core/shell nanoparticles, the ignition properties of Si/Fe₂O₃ thermite can be improved through the enhanced interfacial contact and oxygen diffusion. To test our hypothesis, we first synthesized Si/Fe₂O₃ core/shell nanoparticles with electroless method. SEM and XPS characterizations confirmed the proposed morphology and composition. Furthermore, we investigated the ignition properties of Si/Fe₂O₃ core/shell nanoparticles at slow and rapid heating rates using DSC and Xe flash ignition, respectively, and compared with the mechanically mixed counterpart. It was found that forming the core/shell structure reduced the onset temperature in DSC experiments by as much as 150 °C and reduced the minimum ignition energy in flash ignition experiments by as much as 87%. We shall further characterize the core/shell structure with TEM and XRD analysis to provide evidence for the control and optimization of the synthesis procedure. In addition, we shall systematically investigate the size effects on the ignition properties, extrapolate the activation energy of Si/Fe₂O₃ core/shell nanoparticles, and benchmark with the mechanically mixed samples.

Synthesis and characterization of core/shell nanoparticles

Since the ignition of thermite composites is governed by the diffusion of oxygen atoms from oxidizer to fuel molecules, it is crucial to have good interfacial contact to facilitate such diffusion process and thus to improve the ignition behavior of thermite composites. Therefore, we hypothesize that the ignition properties of Si/Fe₂O₃ nanocomposites can be improved significantly by forming core/shell structures, which improve the interfacial contact between Si and Fe₂O₃, compared to the mechanically mixed counterpart. Such concept is illustrated in Fig. 1.

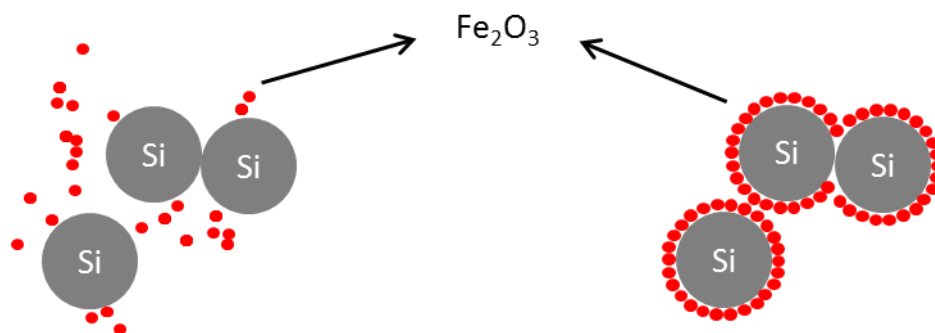


Figure 1. Schematics of the mechanically mixed (left) and the core/shell structure (right) of Si/Fe₂O₃ nanocomposites.

The synthesis procedure of Si/Fe₂O₃ core/shell nanoparticles (C/S NPs) are illustrated in Fig. 2. In brief, four major steps are taken to 1) make the surface of Si hydrophilic, 2) perform palladium coating on Si, 3) replace palladium coating with iron, and 4) anneal the Si/Fe C/S NPs to remove organic residues and form Si/Fe₂O₃ C/S NPs, respectively. In the first step, 100 mg of Si NPs is mixed with 100 mL of 2-propanol, 1 mL of (3-aminopropyl)triethoxysilane (APTES), 0.5 mL of Milli-Q water, and stirred for 1 h at 70 °C. In the second step, the APTES-coated Si NPs are washed with deionized water, dispersed in 40 mL of palladium precursor solution, which contains 0.5 g/L of PdCl₂ and 3.25 mL/L of HCl, and stirred for 20 mins in a Teflon cup with an overhead stirrer. In the third step, the Pd-coated Si NPs are washed with deionized water, dispersed in 100 mL of iron precursor solution, which contains 117.6 g/L of sodium citrate, 31.4 g/L of ammonium iron sulfate hexa-hydrate, 3.7 g/L of boric acid, 4.0 g/L of saccharin, and 1.0 g/L L-lysine, and stirred for 6 mins with an overhead stirrer. During stirring, 0.3 g of sodium borohydride is added to the solution to replace the Pd coating with Fe through electroless plating process. The result Fe-coated Si NPs are washed with 2-propanol and collected with a magnet. In the final step, the Fe-coated Si NPs are annealed in a furnace at 450 °C for 5 h to form iron oxide shell and thus the Si/Fe₂O₃ core/shell structures.

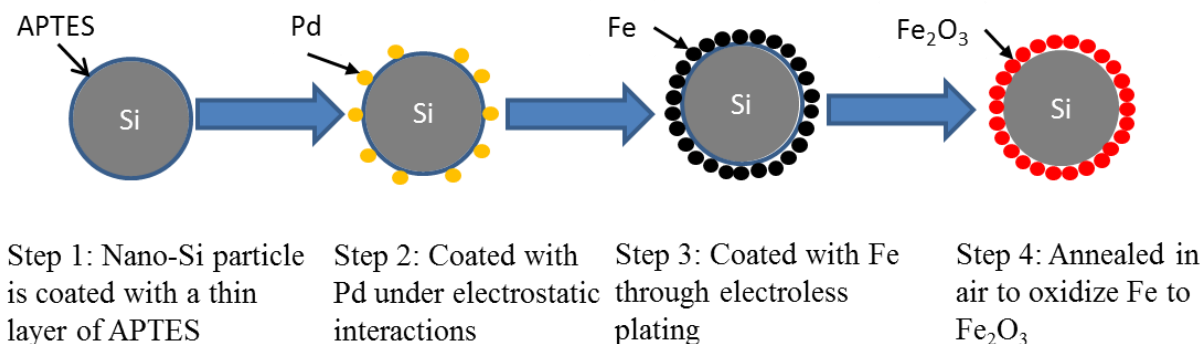


Figure 2. Schematic of the synthesis procedure of Si/Fe₂O₃ core/shell nanoparticles.

The morphology of the Si/Fe₂O₃ core/shell structure is demonstrated with scanning electron microscopy (SEM) in Fig. 3. It can be seen that the coverage of Fe₂O₃ on the surface of Si NPs is very uniform and compact, indicating good interfacial contact. Although the transition from Fe to Fe₂O₃ after annealing is

visually confirmed with the color changing from black to red, X-ray photoelectron spectroscopy (XPS) further demonstrate the oxidation state of iron oxide, shown in Fig. 3.

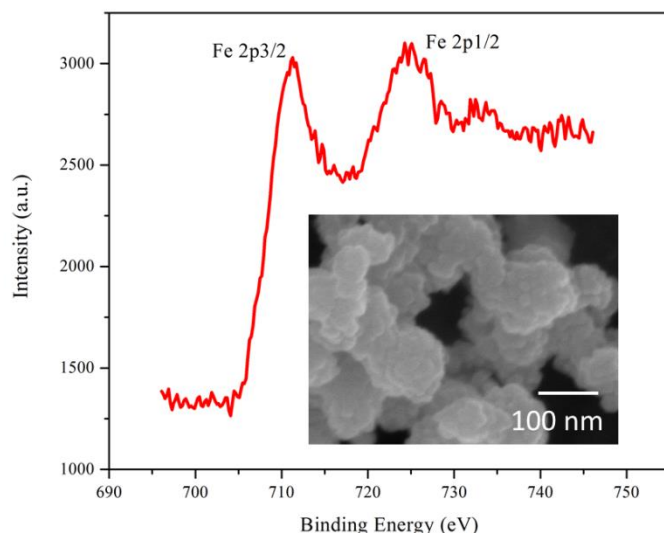


Figure 3. XPS and SEM analysis of 20 nm Si/Fe₂O₃ core/shell NPs annealed at 450 °C for 5 h.

DSC analysis of core/shell and mechanically mixed Si/Fe₂O₃ nanoparticles

The hypothesized enhanced ignition properties of Si/Fe₂O₃ core/shell NPs were quantified with differential scanning calorimetry (DSC) and benchmarked with mechanically mixed (MM) stoichiometric Si and Fe₂O₃ (20-40 nm Skyspring Nanomaterial Inc.) NPs. In each DSC (LabSys Evo, Setaram) test, approximately 5 mg of the C/S or MM sample was placed in a 100 μ L alumina crucible and heated from 100 °C to 1000 °C under a constant heating rate of 10 °C/min. The inert carrier gas Ar was flowing at 40 mL/min. After the samples cooled down to the room temperature, the same heating procedure was followed for the second time to provide a baseline, which accounts for the drifts caused by the change of specific heat with temperature. All the DSC profiles reported in the current work have been corrected, as the raw data acquired during the first heating cycle has been subtracted by the baseline.

The specific heat flow profiles of Si/Fe₂O₃ C/S or MM NPs are shown in Fig. 4. The ignition property is quantified with the onset temperature of the exothermic Si/Fe₂O₃ thermite reaction, which is defined as the intersection of the tangent corresponding to the largest heat release rate and the extrapolated baseline. Such onset temperatures of both samples are also specified in Fig. 4. Clearly, forming core/shell structures significantly reduces the onset temperature of Si/Fe₂O₃ reaction, as we hypothesized.

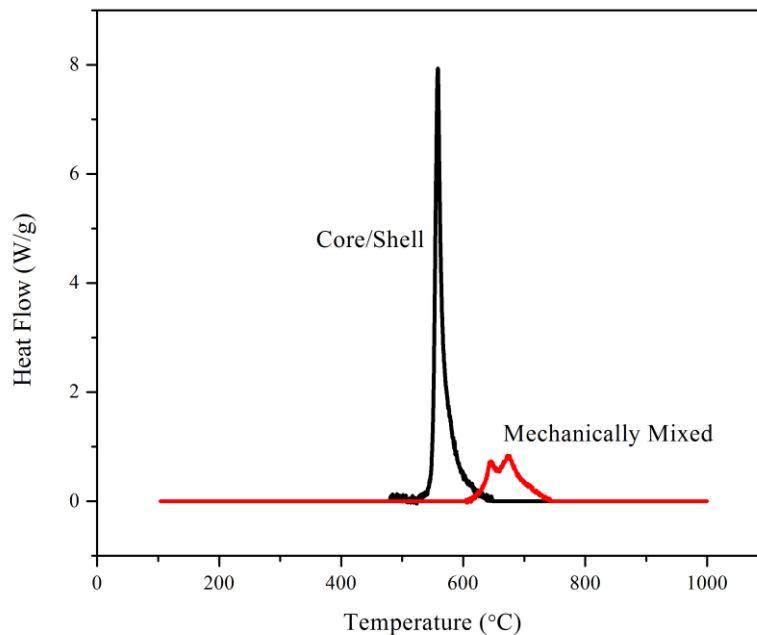


Figure 4. DSC analysis of 20 nm Si/Fe₂O₃ core/shell and mechanically mixed NPs with the same heating rate of 10 °C/min.

We further investigated size effects on the ignition of Si/Fe₂O₃ C/S and MM NPs. For both mixing mode, three sizes of Si NPs, which are 20-30 nm (U.S. Research Nanomaterial Inc), 100 nm (U.S. Research Nanomaterial Inc), and 500 nm (Skyspring Nanomaterial Inc.), were utilized to illustrate the effect of particle size on the onset temperature. As shown in Fig. 5, increasing the size of Si NPs increases the onset temperature of MM samples. This observation agrees with the general argument that the characteristic diffusion distance increases with decreasing particle size. It is noted that the size effect is less prominent for the 500 nm case. This might be due to the fact that the size of Fe₂O₃ powder is the same (20-40 nm) in all three cases and is comparable to the 20-30 and 100 nm Si. When the size of the Si particle is one order of magnitude larger than Fe₂O₃, the size dependence is limited by the Fe₂O₃, and therefore, we do not see further increase in the onset temperature.

However, size effect is not as prominent in the C/S case for all three cases investigated. This is due to the fact that with the core/shell structure the contact between Si and Fe₂O₃ is already at atomic level. This further implies that forming core/shell structures is more effective than utilizing smaller NPs to reduce the onset temperature of nanothermites.

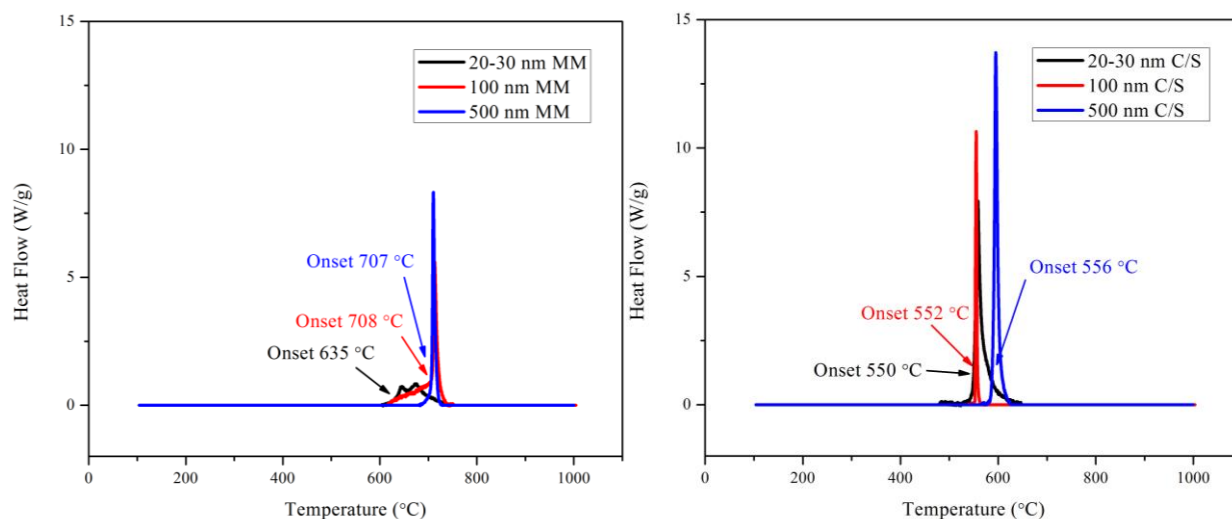


Figure 5. DSC profiles of Si/Fe₂O₃ mechanically mixed (MM) and core/shell (C/S) NPs with the same heating rate of 10 °C/min but with different sizes of Si.

Flash ignition of core/shell and mechanically mixed Si/Fe₂O₃ nanoparticles

DSC experiments elucidate the oxidation processes of Si/Fe₂O₃ NPs in a quasi-steady state manner, however, in practical combustion applications, thermites often undergo rapid heating. To demonstrate the improved ignition property of the Si/Fe₂O₃ core/shell NPs compared to the mechanically mixed counterpart, xenon (Xe) flash ignition tests were performed to quantify the minimum ignition energy density E_{\min} .

The experimental setup of the Xe flash ignition test is shown in Fig. 6a. For each experiment, a pile of loosely packed Si/Fe₂O₃ NPs, either with the core/shell structure or mechanically mixed, with fixed mass of 5 mg and cross sectional diameter of 6 mm, were placed on a 1 mm thick glass slide. The glass slide was placed directly on the Xe flash tube (AlienBees™ B1600), as shown in Fig. 6b. The typical diameter of sample beds (0.6 cm) is smaller than the diameter of flash tube (1.5cm), so the incident light on the entire sample could be assumed to be uniform. The areal impulse of the Xe flash tube was firstly calibrated by measuring the temperature rise of soot-covered silicon substrate exposed to the same flash intensity. E_{\min} of each sample was determined by gradually increasing the power of Xe flash until ignition occurred, and a fresh sample was utilized at each flash test to avoid partial oxidation from the previous flash. Upon flash triggering above E_{\min} , Si/Fe₂O₃ particles are ignited by the photo-thermal effect and the subsequent combustion is self-sustained, as shown in Fig. 2c.

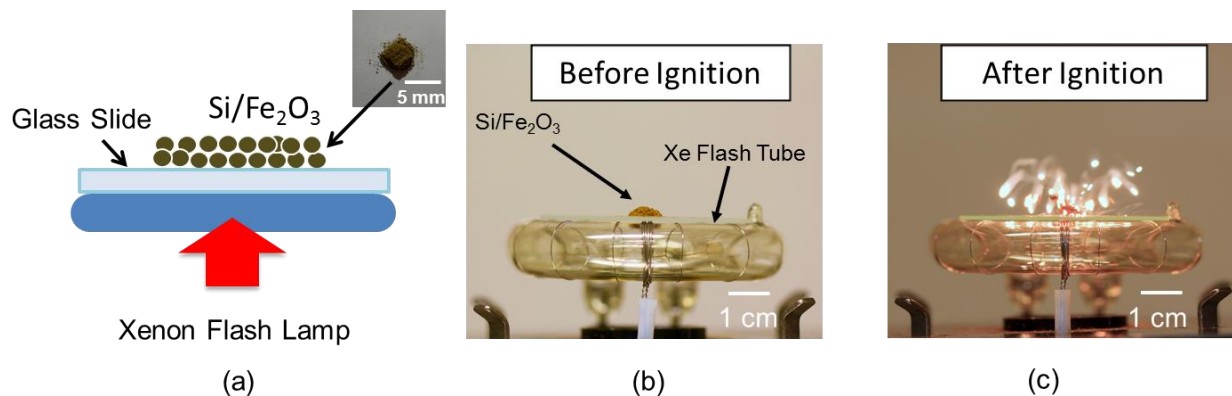


Figure 6. (a) Schematic of the experimental setup for flash ignition with a representative image of test samples shown in the inset. (b) Optical image of the experimental setup. (c) Optical image of the self-sustained combustion of 100 nm Si/Fe₂O₃ core/shell NPs after flash ignition.

The improved ignition behavior with forming core/shell structure is demonstrated in Fig. 7, where 100 nm Si/Fe₂O₃ MM and C/S NPs were flash ignited at their corresponding E_{\min} . For better benchmarking, a normalized ignition energy (NIE) is reported, which is defined as the E_{\min} normalized by that of the MM case. As shown in Fig. 7, the C/S NPs can be ignited at significantly reduced flash energy, i.e. 12.5% of the MM counterpart, demonstrating the improved ignition property of the core/shell structure at rapid heating rate.

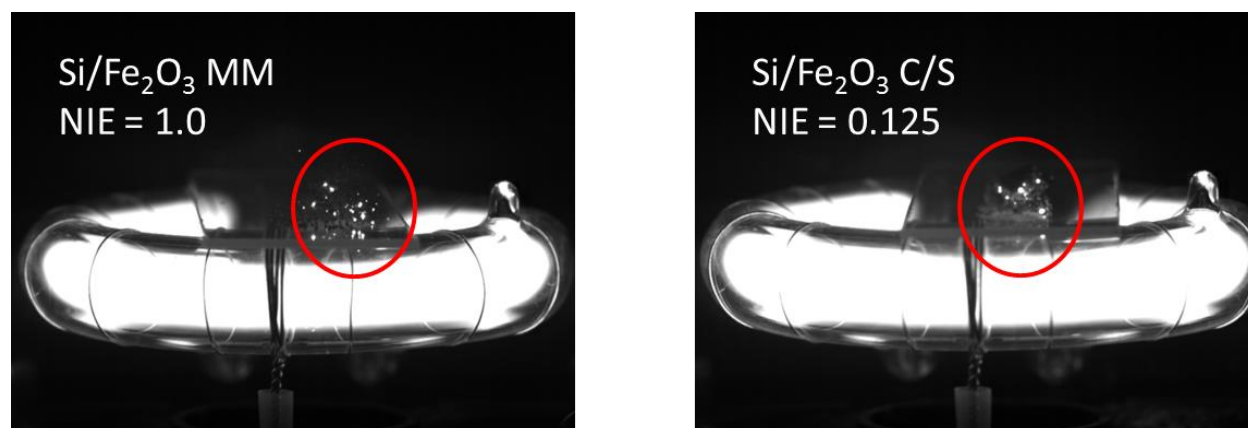


Figure 7. High speed camera images of Xe flash ignited 100 nm Si/Fe₂O₃ MM and C/S NPs at corresponding E_{\min} . The normalized ignition energy (NIE) is defined as the E_{\min} normalized by that of the MM case.

Conclusions and future work

We synthesized Si/Fe₂O₃ core/shell NPs with electroless plating method. SEM and XPS analyses were carried out to characterize the morphology and composition of the C/S structure. DSC and Xe flash ignition experiments were carried out to and investigated the ignition properties. We have verified our hypothesis that the ignition properties of Si/Fe₂O₃ core/shell NPs are significantly improved compared to the mechanically mixed Si/Fe₂O₃ NPs, due to better interfacial contact.

Specifically, at slow heating rate during DSC experiments, with the same particle size, the onset temperature of the C/S NPs is significantly lower than that of the MM NPs. The decrease in the onset temperature can be as much as 150 °C for 500 nm Si particle cases. Although decreasing the particle size reduces the onset temperature of the MM NPs, forming core/shell structures is found to be a more effective way. Moreover, the onset temperature of Si/Fe₂O₃ C/S NPs is not sensitive to the variation in the size of Si nanoparticles in the current study. Furthermore, at rapid heating rate during Xe flash ignition experiments, the minimum ignition energy for the C/S NPs are almost an order of magnitude lower than that of the MM sample with the same particle size.

In future, we plan to carry out more detailed characterization of the core/shell structures. For example, we will utilize transmission electron microscopy analysis to characterize the thickness of the iron oxide shell, which could provide us information to compute the overall equivalence ratio of the sample. Although the equivalence ratio is not expected to influence the ignition behavior significantly, it might influence the combustion properties, such as heat release rate. Such information will be beneficial to further modify the synthesis procedure to produce Si/Fe₂O₃ C/S NPs with desired ignition and combustion properties. Moreover, we plan to utilize X-ray diffraction analysis to future characterize the composition of the iron oxide. For DSC analysis, we plan to carry out Kissinger analysis to extract the activation energy of the C/S and MM NPs. It is hypothesized that the C/S NPs also have lower activation energy than their counterpart, due to enhanced solid diffusion through improved interfacial contact.

Accomplish # III: Enhancing Ignition and Combustion of Micron-sized Aluminum by Adding Porous Silicon

Summary

Micron-sized aluminum (Al), due to its large volumetric energy density, is an important fuel additive for broad propulsion and energetic applications. However, micron-sized Al particles are difficult to ignite and react slowly, leading to problems such as incomplete combustion and product agglomeration. Many pioneering strategies have been investigated to overcome the above challenges, ranging from reducing Al particles to nanoscale, coating them with metallic or polymeric materials, to blending Al with other materials to form composites. On the other hand, porous Si has emerged as a promising energetic material with a comparable volumetric energy density as Al, high reactivity at low temperature, and ultrafast flame propagation speeds. To date, the potential of using porous Si as an additive to enhance ignition and combustion of micron-sized Al has not been explored. Herein, we experimentally investigated the effect of porous Si addition on the ignition and combustion characteristics of micron-sized Al with CuO nanoparticles. We consistently observed that the addition of porous Si facilitates both ignition and combustion of Al/CuO mixtures over a wide range of experimental conditions, ranging from slow heating rate conditions in differential scanning calorimetry, fast heating rate conditions in Xe flash ignition, flame propagation in microchannels, to constant-volume pressure vessel experiments. The enhancement effects are attributed to the easy ignition and fast burning properties of porous Si, which elevates the ambient temperature and/or pressure, and hence enhances the ignition, reaction rate, and combustion efficiency of micron-sized Al particles. This work demonstrates that adding porous Si is another viable strategy towards enhancing the ignition and combustion properties of micron-sized Al particles.

Details

Please refer to the attached paper in the following pages

Other Accomplishments

1. Awards received and nominations

- 2016, Resonate Awards that honor outstanding achievement in renewable energy and sustainability-focused science and technology.
- 2015, Nano Letters Young Investigator Lectureship
- 2014, David Filo and Jerry Yang Scholar
- 2014, National Geographic Emerging Explorer Award
- 2014, 3M Nontenured Faculty Grant Award

2. ALL Dissemination with ARO Support: papers, articles, journals, and books.

Journal Papers

- (1) "Ignition Properties of Nano- and Micron-Sized Silicon Particles", S. D. Huang, V.S. Parimi, S.L. Deng, S. Lingamneni and X. L. Zheng, *Nano Letters*, DOI: 10.1021/acs.nanolett.7b01754, (2017).
- (2) "Stabilizing Silicon Photocathodes by Solution-Deposited Ni-Fe Layered Double Hydroxide for Efficient H₂ Evolution in Alkaline Media", J. H. Zhao, L.L. Cai, L. Hong and X. L. Zheng, *ACS Energy Lett.*, 2 (9), 1939–1946 (2017).
- (3) "Electroless Deposition and Ignition Properties of Si/Fe₂O₃ Core/Shell Nanothermite", S. D. Huang, S.L. Deng, Y. Jiang and X. L. Zheng, *ACS Omega*, 2 (7), 3596–3600 (2017).
- (4) "Enhancing Ignition and Combustion of Micron-sized Aluminum by Adding Porous Silicon", V. S. Parimi, S.D. Huang and X. L. Zheng, *Proc. Combust. Inst.* 36, DOI:10.1016/j.proci.2016.06.185 (2016).
- (5) "Flash Ignition of Freestanding Porous Silicon Films: Effects of Film Thickness and Porosity", Y. Ohkura, J. M. Weisse and X. L. Zheng, *Nano Letters*, 13(11), 5528-5533 (2013).

Conference Presentations

- (1) "Enhancing Ignition and Combustion of Micron-sized Aluminum by Adding Porous Silicon", 36th *Int. Sym. on Combustion*, Warsaw, Poland, 2016.
- (2) "Engineering Nanomaterials for Energy Conversion: From Flame Synthesis to Water Splitting", the Resnick Young Investigators Symposium, Caltech, Sep. 12, 2016
- (3) "Activating and Optimizing MoS₂ Basal Planes for Hydrogen Evolution through Formation of Strained Sulphur Vacancies", Fusion Conference on Molecules and Materials for Artificial Photosynthesis Conference, Cancun, Mexico, Feb. 25-28, 2016
- (4) "Bridging combustion and nanotechnology", University of Houston, Mechanical Engineering, Oct. 1, 2015
- (5) "Bridging combustion and nanotechnology", 2015 ACS Nano Letter Young Investigator Lecture, Boston, MA, August 18, 2015

3. Names of all supported students and post docs.

- Sidi Huang, 4th year graduate student, expected to finish on June, 2019

- Jiheng Zhao, graduate student, expected to finish on June, 2018
- Dr. Venkata Sharat Parimi, Engineer, Applied Materials
- Dr. Sili Deng, accepted an assistant professor position at MIT