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Nanostructured Energetic Materials Using Sol-Gel Methods

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The utilization of nanomaterials in the synthesis and processing of energetic materials (i.e., pyrotechnics, explosives, and propellants) is a relatively new area of science and technology. Previous energetic nanomaterials have displayed new and potentially beneficial properties, relative to their conventional analogs. Unfortunately some of the energetic nanomaterials are difficult and or expensive to produce. At LLNL we are studying the application of sol-gel chemical methodology to the synthesis of energetic nanomaterials components and their formulation into energetic nanocomposites. Here sol-gel synthesis and formulation techniques are used to prepare $\text{Fe}_2\text{O}_3/\text{Al}$ pyrotechnic nanocomposites. The preliminary characterization of their thermal properties and the degree of mixing between fuel and oxidizer phases is contrasted with that of a conventional pyrotechnic mixture.

Since the invention of black powder, one thousand years ago, the

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technology for making solid energetic materials has remained either the physical mixing of solid oxidizers and fuels (e.g. black powder), or the incorporation of oxidizing and fuel moieties into one molecule (e.g., trinitrotoluene (TNT)). The basic distinctions between these energetic composites and energetic materials made from monomolecular approaches are as follows.

In composite systems, desired energy properties can be attained through readily varied ratios of oxidizer and fuels. A complete balance between the oxidizer and fuel may be reached to maximize energy density. Table I is a summary of the some of the energy densities of composite and monomolecular energetic materials (1). Current composite energetic materials can store

Table I. Energy densities for several composite and monomolecular energetic materials (SOURCE: reproduced with permission from reference 1).

Energetic Material	Energy Density (kJ/cm³)
Ammonium dinitramide/ Aluminum	23
Compression moldable	19-22
Strategic propellants	14-16
CL-20(neat)	12.6
Tritonal	12.1
HMX(neat)	11.1
LX-14	10.0
TATB(neat)	8.5
Comp. C-4	8.0
LX-17	7.7
TNT(neat)	7.6

energy as densely as 23 kJ/cm³. However, due to the granular nature of composite energetic materials, reaction kinetics are typically controlled by the mass transport rates between reactants. Hence, although composites may have extreme energy densities, the release rate of that energy is below that which may be attained in a chemical kinetics controlled process.

In monomolecular energetic materials, the rate of energy release is primarily controlled by chemical kinetics, and not by mass transport. Therefore, monomolecular materials can have much greater power than composite energetic materials. A major limitation with these materials is the total energy density achievable. Currently, the highest energy density for monomolecular

materials is about half that achievable in composite systems. The reason for this is that the requirement for a chemically stable material and the available synthetic procedures limit both the oxidizer-fuel balance and the physical density of the material. Therefore, it is desirable to combine the excellent thermodynamics of composite energetic materials with the rapid kinetics of the monomolecular energetic materials. Thus, developing and or improving methods for the synthesis and processing of nanometer-sized oxidizers and fuels are needed for tailorable energy and power.

In composite energetic materials, decreasing reactant sizes to the tens of nanometers effectively increases the interfacial surface area contact between oxidizer and fuel phases. A remarkable increase in this contact area is possible with nanomaterials and should lead to energetic nanocomposites with new and potentially exceptional burn characteristics (e.g., burn rate, energy release mechanism). Both experimental and theoretical efforts by Brown *et al.* and Sukai *et al.* indicated that a decrease in particle size resulted in a qualitative increase in burn rates in solid-solid mixtures of oxidizers and fuels (2,3). In another example, Son and co-workers at Los Alamos National Laboratory (LANL) have recently shown that pyrotechnic nanocomposites of MoO₃ and Al burn at extremely rapid rates (>100m/s) and that the propagation mechanism is convective and not conductive, as is the mechanism of conventional pyrotechnics (4,5). These limited examples provide sufficient incentive for continued investigation of energetic nanomaterials.

One facet of nanoscience that has been under active investigation is the synthesis of materials with nanoscale dimensions. Both chemical and physical methods have been used in the preparation of nanomaterials. Chemical techniques include vapor condensation methods, micellar synthesis, chemical reduction, sonochemical synthesis, and the sol-gel methodology. Physical methods include sonication and ball milling of solids (6). All of these techniques have the advantages and disadvantages. For example, a major advantage of vapor phase condensation methods are small monodisperse particles of a variety of different materials. Both fuels (e.g., aluminum) and oxidizers (e.g., Fe₂O₃) can be made utilizing this technology (7-9). Drawbacks include its high operating costs, low production rates, and poor control of particle morphology. Sonochemical methods have also been used to prepare nanomaterials (10). As with dynamic vapor phase condensation, nanometer-sized oxidizers and some fuels can be prepared. However, the equipment is expensive and many of the precursors are volatile organometallic compounds which have health and safety issues. Chemical reduction of salts to nanometersized fuels can be done, but the reaction conditions can be harsh and some handling must be done under rigorous conditions (11).

For nanomaterials to have any noteworthy impact in the area of energetic materials processes for their synthesis must satisfy significant

production specifications such as cost, health and safety, and reproducibility. The sol-gel method may provide another approach to nanomaterials synthesis for energetic nanocomposites and, in some respects, it is a more suitable candidate method than those described previously.

The sol-gel method

Sol-gel chemical methodology has been investigated for approximately 150 years and has been employed in the disciplines of chemistry, materials science, and physics. Sol-gel chemistry is a solution phase synthetic route to highly pure organic or inorganic materials that have homogeneous particle and pore sizes as well as densities. The method is commonly used to prepare metal-oxide based materials (i.e., oxidizers from an energetic materials point of view). However, sol-gel methods do exist for the preparation of organic fuel based materials (e.g., resorcinol-formaldehyde sol-gel) so in that respect it can be used to prepare nanomaterials of both oxidizers and fuels (12-14). Its benefits include the convenience of low-temperature preparation using general and inexpensive laboratory equipment. From a chemical point of view, the method affords easy control over the stoichiometry and homogeneity that conventional methods lack. In addition, one of the integral features of the method is its ability to produce materials with special shapes such as monoliths, fibers, films, and powders of uniform and very small particle sizes. There are several excellent references on the sol-gel method, where more complete and additional information can be obtained (15-17).

The entire process is summarized in the scheme shown in Figure 1. A sol like that shown in the first beaker can be formed through the hydrolysis and condensation of dissolved molecular precursors. This produces nanometer-sized particles, which aggregate to form clusters, with very uniform size, morphology, and composition. The pH of the solution, the solvent, the temperature, and the concentrations of reactants used dictate the size of the clusters, which can be from 1 nm to 1000 nm in diameter. By controlling the aforementioned conditions in solution, the sol can be condensed into a robust gel. The linking together of the sol clusters into either aggregates or linear chains results in the formation of the stiff monolith. The gel can be dried by evaporation of the solvent to produce a monolithic xerogel or removed under the supercritical conditions of the pore liquid to produce an aerogel. Ambient condition drying results in the exertion of large capillary forces on the gel framework and causes in a significant amount of shrinkage of the material to produce a medium density material. Xerogel densities can be between 30-80% that of the bulk. With supercritical drying the capillary forces are effectively removed and aerogel densities are typically between 1-20% that of the bulk material.

Both aerogels and xerogels exhibit high surface areas and porosities. Typically the sol-gel materials are networks made up of nanometer-sized

particles that are linked together in a network that contains pores of slightly larger dimensions (mesoporous $\approx 2\text{-}20$ nm diameter). The sol-gel methodology allows the straightforward preparation of monoliths or powders of nanometer-sized particles of inorganic or organic constituents. The homogeneous distribution and small diameter of the pores provide a convenient location for a second distinct chemical component to reside. These are the properties of sol-gel derived materials that are of central interest to us. From an energetic materials perspective, we are interested in filling the pores with a phase (fuel or oxidizer) that will undergo rapid and highly energetic reactions with the skeletal gel component (fuel or oxidizer). Figure 2 is a schematic representation of such a sol-gel derived nanocomposite. In this case, the inorganic skeletal matrix is acting as the oxidizer, with the fuel particles embedded in the nanopores of this solid. Conversely, the skeletal component could be the fuel (e.g., organic sol-gel materials) with oxidizer in the pores. This figure illustrates the intimate mixing of oxidizers and fuels that are available with sol-gel methodology.

Scientists at LLNL have been actively investigating the application of sol-gel chemistry and nanoscience to the field of energetic materials for several years (18-20). The appeal of the sol-gel approach to energetic materials is that it offers the possibility to precisely control the composition, density, morphology, and particle size of the target material at the nanometer scale. These are important variables for both safety and performance considerations. The fine control of these parameters allows the chemist the convenience of making energetic materials with tailored properties. In addition, ambient temperature gelation and low temperature drying schemes prevent degradation of the energetic molecules, and the water-like viscosity of the sol before gelation, allows easy casting to near net shapes, which is preferred over the hazardous machining alternative.

Energetic Nanocomposites

Energetic nanocomposites are a class of material that has a fuel component and an oxidizer component intimately mixed on the nanometer scale. A portion of our work, in this area, has focused on the development sol-gel methods to synthesize porous monoliths and powders nano-sized transition metal oxides (i.e., Fe_2O_3 , Cr_2O_3 , and NiO). When combined with oxophillic metals such as aluminum, magnesium, or zirconium ensuing mixtures can undergo the thermite reaction (a scheme of the reaction is given below in **(1)**). In the thermite reaction the metal oxide ($\text{M}_{(1)}\text{O}(s)$) and oxophillic



metal ($M_{(2)}O(s)$) undergo a solid state reduction/oxidation reaction, which is rapid and very exothermic (21). Some thermite reaction temperatures exceed 3000K. Such reactions are examples of oxide/metal reactions that provide their own oxygen supply and, as such, are difficult to stop once initiated. The energy densities for some thermite reactions are in the upper range of those in Table 1 (16-19 kJ/cc) (22). Thermite compositions have found use in a variety of processes and products. They are used as hardware destruction devices, for welding of railroad track, as torches in underwater cutting, additives to propellants and high explosives, free standing heat sources, airbag ignition materials, and in many other applications. Traditionally, thermites are prepared by mixing fine component powders, such as ferric oxide and aluminum. Mixing fine metal powders by conventional means can be an extreme fire hazard; sol-gel methods reduce that hazard while achieving ultrafine particle dispersions that are not possible with normal processing methods. In conventional mixing, domains rich in either fuel or oxidizer exist, which limit the mass transport and therefore decrease the efficiency of the burn. However, sol-gel derived nanocomposites should be more uniformly mixed, thus reducing the magnitude of this problem.

Preparation of nanosized metal oxide component by sol-gel methods

We have developed a sol-gel procedure for synthesizing monolithic and powdered aerogels and xerogels of nanostructured metal oxides from common inorganic salts (23-25). This is significant as historically, the sol-gel method has employed the use of metal alkoxide precursors. This synthetic route has proven to be an efficient, easy, and successful approach to the production of predominantly SiO_2 , Al_2O_3 , and ZrO_2 -based porous materials. However, it is much less well developed for oxides of interest as pyrotechnics (i.e., Fe_2O_3 , MoO_3 , NiO , CuO). This is largely because many of their metal alkoxides are expensive and still others are sensitive to moisture, heat, and light making their use and long-term storage difficult. In addition, some metal alkoxides are not commercially available or are difficult to obtain, thus precluding detailed studies on the preparation, characterization, and potential applications of their resulting porous metal oxides. The epoxide addition method has been successfully used at LLNL to prepare many different metal-oxide skeletons, of thermodynamically relevant oxides (i.e., Fe_2O_3 , NiO) for nanocomposite thermites. The addition of any one of several different epoxides to a solution containing the dissolved transition metal salt results in the formation of monolithic metal oxide gels. The as formed gel can be dried to either a xerogel or an aerogel. Characterization of resulting materials by nitrogen adsorption and desorption analyses, and transmission electron microscopy (TEM) indicate that the materials have high

surface areas, pore sizes with mesoporic dimensions (2–23 nm) and have a microstructure made up of nanometersized particles like that shown in Figure 2.

Iron oxide/aluminum nanocomposites

One transition metal oxide material of particular interest to this study is ferric oxide (Fe_2O_3). When ferric oxide powder is combined with powdered aluminum metal it forms the classic thermite reaction as described by Goldschmidt (21). The energy density for a stoichiometric mix of Fe_2O_3 and aluminum is 16.5 kJ/cc (22). Although this reaction is not as energetic as other thermite reactions, we believe that the low cost, low toxicity, and abundance of iron (III) precursors available makes nano-sized Fe_2O_3 an interesting as well as practical oxide component for energetic nanocomposites.

We have reported previously on the formulation of $\text{Fe}_2\text{O}_3/\text{Al}$ energetic nanocomposites via the *insitu* sol-gel synthesis of Fe_2O_3 in a suspension of ultra fine grain (UFG) Al nanoparticles, whose particle sizes range from 20-60 nm in diameter (18,20). The sol-gel Fe_2O_3 phase grows around and encapsulates the solid suspended Al particles to form an energetic nanocomposite like that shown in Figure 2. This process takes advantage of the non-linear viscosity increase of the sol-gel solution as it approaches its gel point. Once the gel forms the matrix is rigid and has effectively “frozen” the finely dispersed Al into place within the gel network. The UFG Al used in this study was obtained from the Indian Head Division of the Naval Surface Warfare Center and from LANL, and was prepared via dynamic vapor phase condensation. The gel nanocomposites have been dried to both aerogel and xerogel monoliths. Figure 3 is the photo of one such sol-gel $\text{Fe}_2\text{O}_3/\text{UFG Al}$ aerogel monolith. Ambient and inert atmospheric drying of xerogels was done under ambient and elevated ($\sim 100^\circ\text{C}$) conditions. (**CAUTION:** In our hands, the wet pyrotechnic nanocomposites cannot be ignited until the drying process is complete. However, once dry, the materials will burn rapidly and vigorously if exposed to extreme thermal conditions. In addition, the autoignition of energetic nanocomposites has been observed upon rapid exposure of hot $\sim 100^\circ\text{C}$ material to ambient atmosphere.)

Qualitatively, the $\text{Fe}_2\text{O}_3(s)/\text{UFG Al}(s)$ energetic nanocomposites appear to burn much more rapidly and are more sensitive to thermal ignition than conventional thermite powders. This is not unexpected as the ignition threshold of UFG aluminum powders depends upon its physical particle morphology (7). We are currently in the process of performing detailed burn rate measurements to more thoroughly quantify these observations.

The intimacy of mixing between oxidizer and fuel is very likely an important factor in the behavior of these materials. One problem, that all nanomaterials suffer from, is the tendency for agglomeration into larger

aggregates. In such a case the properties of the resulting composite may be influenced by the size of the aggregate and not the size of the individual nanoparticles, thus defeating the potential benefit of the nanomaterial. Even though nanosized components are used, there is no guarantee that the sol-gel composite will have such mixing. To characterize this degree of mixing we have analyzed our composite material using energy filtered transmission electron microscopy (EFTEM) at LLNL.

EFTEM can be used to construct an elemental specific map of a given TEM image. The EFTEM technique is performed using a conventional TEM microscopy in conjunction with very precise magnetic filters (26). Plate 1 contains a TEM image of a Fe_2O_3 /UFG Al aerogel and the EFTEM maps for aluminum and iron respectively. The areas of the image representative of sol-gel Fe_2O_3 are colored green and those of Al nanoparticles are red. The EFTEM images in Plate 1 reveal the superb mixing that the sol-gel Fe_2O_3 and UFG Al in the composite. The two component phases are intimately mixed on this length scale with no evidence of agglomeration. This characterization technique indicates that sol gel processing is an effective route to imbedding UFG Al particles into a sol-gel Fe_2O_3 matrix with excellent mixing of the components.

Some of the thermal properties of these materials have been investigated. Figure 4 contains the differential thermal analysis (DTA) traces for two energetic nanocomposites: sol-gel Fe_2O_3 /UFG Al (top) and a dry powder mix of Fe_2O_3 /Al (bottom), prepared from commercially available micron-sized powders. It is clear from these DTA traces that the thermal behavior of these materials is quite different. In the sol-gel Fe_2O_3 /UFG Al nanocomposite there are thermal events at ~ 260 , ~ 290 , and $\sim 590^\circ\text{C}$. We have determined that the two lower temperature events are related to a phase transition and crystallization of the amorphous Fe_2O_3 phase. The exotherm at $\sim 590^\circ\text{C}$ is the most interesting as it corresponds to the thermite reaction (confirmed by powder X-ray diffraction of reaction products). This exotherm is very narrow and sharp, possibly indicating a very rapid reaction. Another fascinating point to be made here is that the thermite reaction takes place at a temperature markedly below the melt phase of bulk Al ($T_m = 660^\circ\text{C}$). This is very significant as in conventional thermite mixtures it is commonly thought that thermite reactions are initiated by the melting or decomposition of one of the constituent phases (5).

Alternatively, the DTA trace of the dry powder mix of Fe_2O_3 /Al commercial micron-sized powders is significantly different than that of the nanocomposite. There are no low temperature events in this DTA. This is not surprising, as the oxidizer in this mixture is crystalline Fe_2O_3 and not amorphous hydrous sol-gel Fe_2O_3 . The main features of the trace occur at $\sim 660^\circ\text{C}$ and $\sim 915^\circ\text{C}$. The 660°C endotherm corresponds to the melting of the micron-sized Al and the $\sim 915^\circ\text{C}$ exotherm is from the thermite reaction. In this case the

thermite reaction takes place after the melting of Al. The ignition point of the traditional thermite material is $\sim 325^{\circ}\text{C}$ higher than that for the nanocomposite. This peak is also broader than that seen in the nanocomposite DTA and likely indicates a less rapid reaction. Although somewhat qualitative, the DTA analyses indicate that the thermal behavior of the sol-gel $\text{Fe}_2\text{O}_3/\text{UFG Al}$ and the conventional Fe_2O_3 composite are quite different. The grounds for these differences are still under active investigation in our laboratory. Regardless, the composites made by this method with these materials are readily ignited, using a thermal source, and burn very vigorously as is demonstrated in the photo in Figure 5.

Additional Materials:

As one can surmise, this sol-gel method allows for the addition of insoluble materials (e.g., metals or polymers) to the viscous sol, just before gelation, to produce a uniformly distributed energetic nanocomposite upon gelation. This process can be used for added materials with particle sizes from nanometers to millimeters and particle densities from low to high. In addition, to preparing $\text{Fe}_2\text{O}_3(s)/\text{UFG Al}(s)$ nanocomposites we have prepared composites using micron-sized aluminum powders also. These materials also are readily ignited using thermal sources. They too seem to burn more rapidly and are more sensitive to ignition than conventional thermites. However, they burn more slowly and are less sensitive to ignition than the $\text{Fe}_2\text{O}_3(s)/\text{UFG Al}(s)$ nanocomposites. The integration of polymers into the thermitic nanocomposites results in a new material with gas generating properties. This material may have potential use as a high temperature stable gas generator. It is important to note that under ambient conditions these materials are insensitive to standard impact, spark, and friction small-scale safety tests.

The sol-gel approach also allows for the relatively simple incorporation of other metal oxides into the metal-oxide matrix to make a mixed-metal-oxide material (16,17). Different metal-oxide precursors can be easily mixed into the solution, before the addition of the epoxide. Dilution of the thermitic material with inert oxides such as Al_2O_3 (from dissolved AlCl_3 salt) or SiO_2 (from added alkoxide) leads to a pyrotechnic material that is not as energetic as a pure iron (III)-oxide-aluminum mixture. Energetic materials of this type have been prepared. Qualitatively, the resulting pyrotechnics have noticeably slower burn rates and are less energetic. Alternatively, one could add metal-oxide components that are more reactive with $\text{Al}(s)$ to increase the energy released. Finally, this would also permit the addition of metal-oxide constituent(s) that provide a desired spectral emission to the energetic nanocomposite. This type of

synthetic control should allow the chemist to tailor the pyrotechnic's burn and spectral properties to fit a desired application.

SUMMARY

Here we have described the synthesis and partial characterization of energetic nanocomposites using sol-gel chemical methodology. Thermite composites were prepared using this approach to produce nanostructured metal oxidizer network along with UFG Al fuel. The resulting nanocomposites were found to have superb mixing of both metal oxide and fuel phases at the Quantitative thermal analyses revealed that all of these nanocomposites underwent the thermite reaction at much lower temperatures than a thermite mixture prepared with micron-sized Fe_2O_3 and Al. Phenomenological burn observations indicate that the nanocomposites also burn much more rapidly than their conventional analogs. We are currently investigating the role that both the oxidizer and fuel particle sizes play individually on the thermal properties of the material and obtaining quantitative burn rate data for sol-gel $\text{Fe}_2\text{O}_3/\text{Al}$ nanocomposites.

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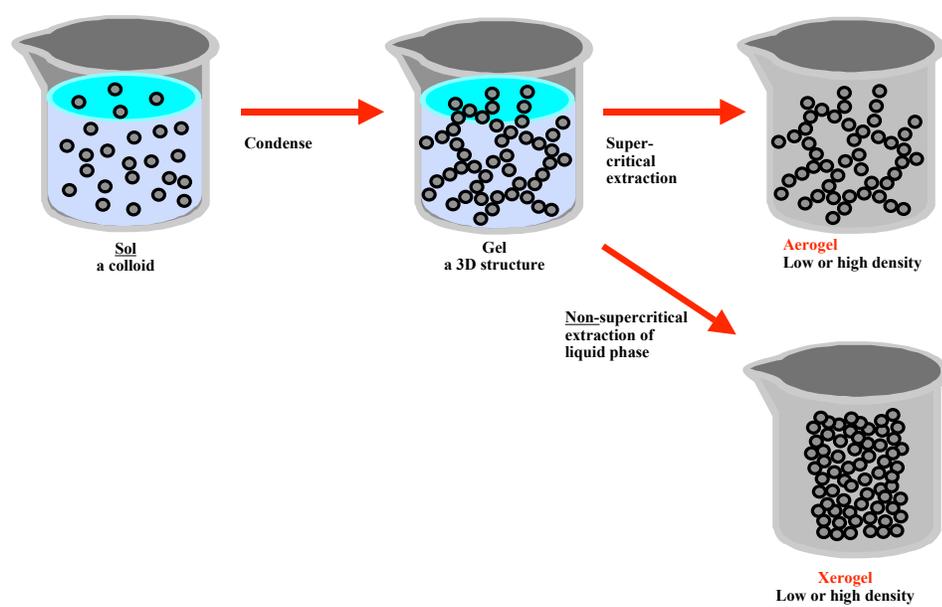


Figure 1.

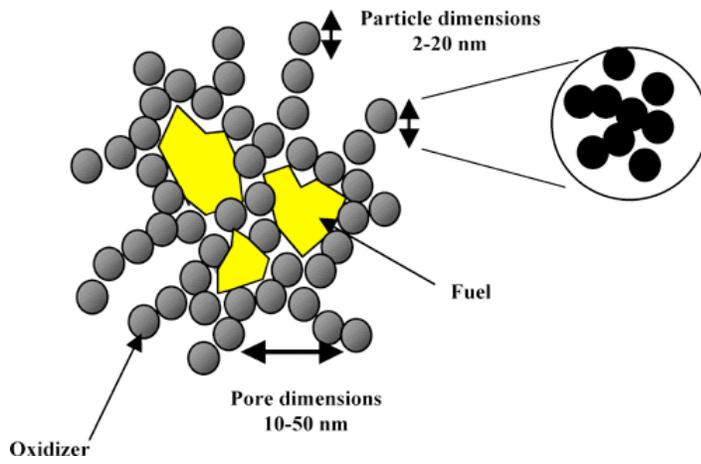


Figure 2.

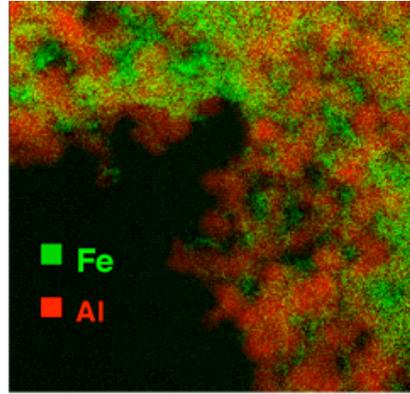
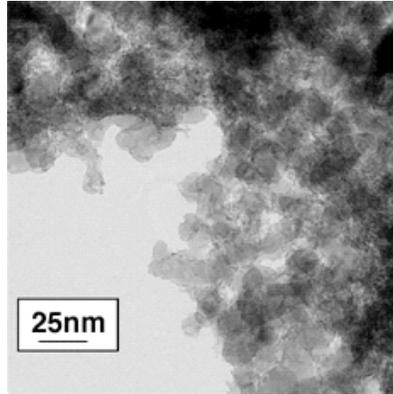


Plate 1.



Figure 3.

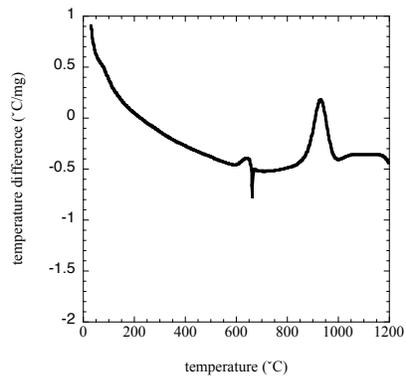
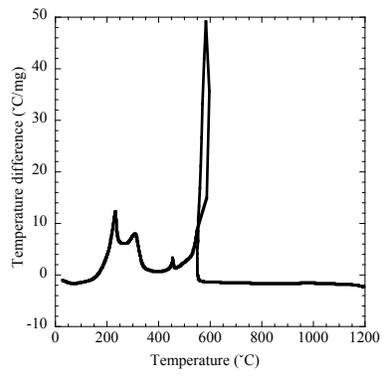


Figure 4.



Figure 5.

Figure 1. Steps in the sol-gel process.

Figure 2. Schematic representation of sol-gel derived energetic nanocomposite, where the sol-gel skeleton is the oxidizer and the fuel particles are residing in the pores.

Plate 1. Transmission electron micrograph (TEM; left image) and energy filtered TEM (EFTEM; right) of a sol-gel derived $\text{Fe}_2\text{O}_3/\text{UFG Al}$ aerogel. The EFTEM image is a color-coded map of the elemental distribution of iron oxide (green) and aluminum (red) in the energetic nanocomposite.

Figure 3. Sol-gel $\text{Fe}_2\text{O}_3/\text{UFG Al}$ aerogel monolith.

Figure 4. Differential thermal analysis traces of sol-gel $\text{Fe}_2\text{O}_3/\text{UFG Al}$ nanocomposite (top) and conventional $\text{Fe}_2\text{O}_3/\text{Al}$ thermite (mixture of μm -sized powders)(bottom).

Figure 5. Photo of the thermal ignition of a $\text{Fe}_2\text{O}_3/\text{UFG Al}$ nanocomposite.