# Tuning the Reactivity of Energetic Nanoparticles by Creation of a Core–Shell Nanostructure

**A. Prakash,[†] A. V. McCormick,[‡] and M. R. Zachariah*,[†]**

*Department of Mechanical Engineering and Department of Chemistry and Biochemistry, University of Maryland, College Park, Maryland 20742, and Department of Chemical Engineering and Material Science, University of Minnesota, Minneapolis, Minnesota 55455*

## ABSTRACT

This article presents a novel method for tuning the reactivity of nanoenergetic materials by coating a strong oxidizer nanoparticle (potassium permanganate; ∼150 nm) with a layer of a relatively mild oxidizer (iron oxide). The measured reactivity for a nano-Al/composite oxidizer could be varied by more than a factor of 10, as measured by the pressurization rate in a closed vessel (psi/μs), by changing the coating thickness of the iron oxide. The composite oxidizer nanoparticles were synthesized by a new aerosol approach in which the nonwetting interaction between iron oxide and molten potassium permanganate aids the phase segregation of a nanocomposite droplet into a core–shell structure.

Thermite metastable intermolecular composites (MIC) are a fascinating class of energy-intensive materials and have been a subject of extensive research over the past decade.[1−3] Such materials are composed of an intimate mixture of nanoparticles of two components, fuel and oxidizer. Because the goal is to enhance the reactivity, the use of nanoscale material reduces the mass transport limitations between the fuel and oxidizer and the reaction becomes kinetically controlled.[4] Aluminum nanoparticles are invariably used as fuel, whereas there are a host of metal oxide nanoparticles that are used as oxidizers for the MIC. Thermodynamic calculations of adiabatic flame temperatures and reaction enthalpy help us choose the possible MIC components from a large number of possible nanothermite combinations. Of the numerous thermodynamically possible MIC formulations,[5] the most widely used are nano-Al (fuel) combined with $MoO_3$, $CuO$, and $Fe_2O_3$ oxidizers. We recently reported a new MIC formulation of nano-Al combined with $KMnO_4$ nanoparticles,[6] the reactivity of which is about 2 orders of magnitude higher than the traditional formulations.

Although there has been considerable success in formulating new composites with enhanced energy-release rates,[1−4,6−8] the subject of achieving a precise control over the reactivity of nanothermites is an opportunity for further research. There have been some studies done on the size-dependent reactivity[9,10] of nanoparticles as a means to control reactivity. In

one of our earlier works,[11] we reported a method of charge-enhanced particle assembly to realize enhanced energy-release rates.

An MIC mixture of $Al/KMnO_4$, although very reactive, has a very poor shelf life compared to the other traditional MIC combinations, the reason being the strong oxidizing nature of $KMnO_4$. In such an MIC, the oxidizer slowly converts all of the aluminum to its oxide, reducing the shelf life. In this contribution, we report a novel technique to moderate the reactivity of nanoenergetic materials. We describe the synthesis of composite oxidizer nanoparticles with a core containing the strong oxidizer (potassium permanganate) and the shell of variable thickness of a relatively mild oxidizer (iron oxide). Using a composite oxidizer (potassium permanganate coated with iron oxide) as described in this paper, we are able to tune the reactivity over a relatively large dynamic range by changing the thickness of the less-reactive oxidizer. An additional benefit is that the structure has an improved shelf life and also reduces the sensitivity of the nanoenergetic mixture to any unintended initiations.

The composite oxidizer nanoparticles were synthesized by a new single-step, two-temperature aerosol spray-pyrolysis method, the schematic of which is shown in Figure 1. A key to the synthesis of the desired microstructure is employing the difference in the characteristic temperatures of the two components. The difference between the thermal decomposition temperature of iron nitrate (<100 °C) and the melting point of potassium permanganate[12] (∼240 °C) in this

\* Corresponding author. E-mail: mrz@umd.edu.
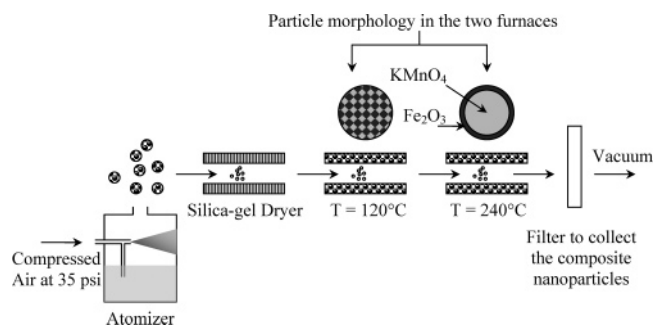† University of Maryland.
‡ University of Minnesota.

**Figure 1.** Aerosol experimental system for the synthesis of core−shell composite oxidizer nanoparticles.

case is the key to obtaining coated particles. An aqueous solution of iron (III) nitrate nonahydrate ($Fe(NO_3)_3 \cdot 9H_2O$) and potassium permanganate ($KMnO_4$) is sprayed into droplets using a collision-type nebulizer. The total salt precursor concentration is kept constant at about 2 wt %. The initial droplet size is about 1 $\mu$m in diameter (measured by a high-sensitivity laser aerosol spectrometer). The moisture from the aerosol is absorbed in a silica gel diffusion dryer. The aerosol is then passed through two tube furnaces, the first one maintained at about 120°C (above decomposition temperature of iron nitrate) and the second at about 240°C (∼melting point of permanganate). The composite particles are then collected on a 0.6-$\mu$m DTTP filter manufactured by Millipore.

In the first furnace, iron nitrate decomposes to form iron oxide while the permanganate remains a solid. Under these conditions, an intimate mixture of the two components exists.

In the second furnace, as the permanganate melts, the solid iron oxide particles become more mobile in the presence of a liquidlike matrix. This increased mobility of the iron oxide particles enables the phase separation and aggregation at the exterior of the particle. The final core−shell morphology reflects a minimization of the free energy of solvation of the two components. This results in the formation of a composite nanoparticle of $KMnO_4$ coated with $Fe_2O_3$.

A TEM image along with the STEM elemental map of the composite nanoparticles is shown in Figure 2. The TEM image shows core−shell structure particles clearly. The nature of the core−shell structure is confirmed with the STEM elemental map, which shows high iron intensity on the perimeter of the particles and high Mn content in the interior. Our experiments indicate that a certain minimum amount of iron nitrate precursor was necessary to coat the permanganate particles successfully. We find that an iron nitrate to potassium permanganate ratio of at least 3:1 (by weight in the precursor) was necessary to coat the particles and corresponds to a particle of 86 vol % $KMnO_4$ (for a 150-nm composite particle with a ∼4 nm iron oxide coating). The STEM elemental map shown in Figure 2 is in agreement with our estimation of coating thickness. Using a smaller amount of nitrate in the precursor resulted in the formation of the particles that were uncoated or partially coated, as evaluated by dispersing the particles in water, followed by sonication and centrifugation. A photograph of three different centrifuged samples is shown in Figure 3. The first vial contains nanoparticles of pure $KMnO_4$, which dissolve completely in water, showing a pink color with no settled
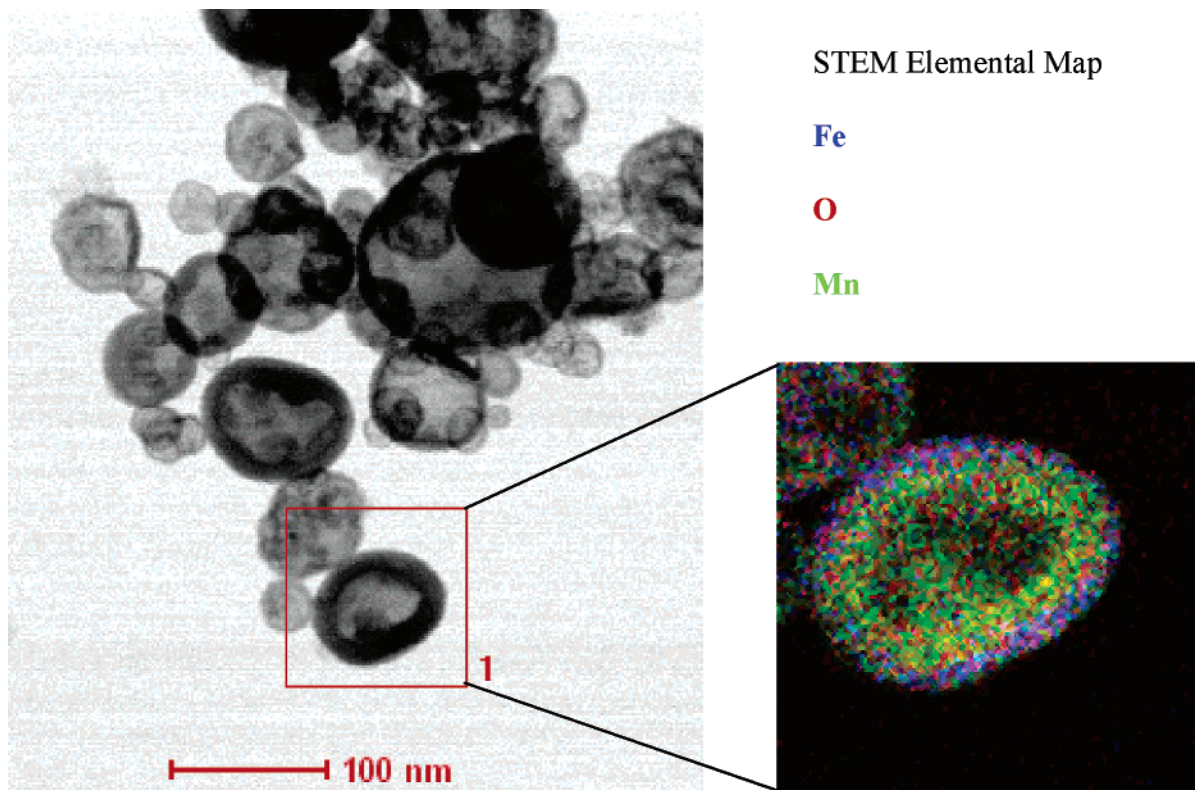


**Figure 2.** TEM micrograph of potassium permanganate nanoparticles coated with iron oxide. The STEM elemental map of a single particle shows the presence of iron oxide on the periphery and manganese in the core of the particle.
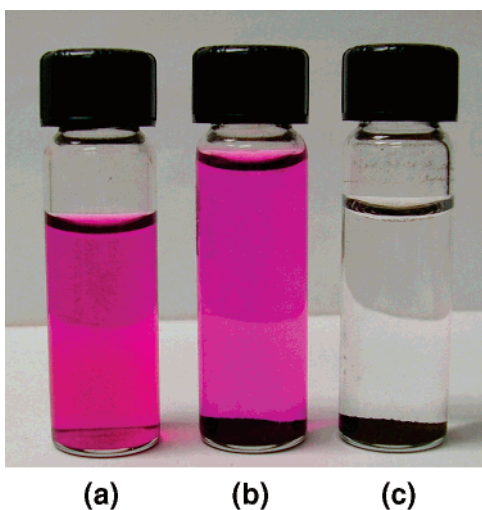
**Figure 3.** Photograph of composite nanoparticles dispersed in water and sonicated. (a) Pure KMnO$_4$ particles dissolve completely in water with no residue. (b) KMnO$_4$ nanoparticles partially coated with iron oxide. (c) KMnO$_4$ nanoparticles completely coated with iron oxide.

particles. The second vial contains particles synthesized with a nitrate to permanganate precursor ratio of less than 3:1. The pink coloration of the solution suggests that the permanganate particles are not coated completely, and hence dissolve in water, whereas the coated particles and the iron nitrate from the partially coated particles settle at the bottom of the vial. The third vial contains particles that are estimated to have a ∼4-nm iron oxide coating and show a colorless dispersion, suggesting that the permanganate particles are coated completely. Our current synthesis experiments are focused toward assessing the generic nature of the approach for creation of a variety of core−shell structures.

Having coated a very strong oxidizer (KMnO$_4$) with a very mild oxidizer (iron oxide), we measured the reactivity of these composite oxidizer particles with aluminum to see if we could modulate the reactivity by changing the coating thickness. One approach to estimate the reactivity of MICs is to measure the pressurization rate during confined combustion. A fixed amount of MIC (25 mg) is ignited in a small-volume (∼13 cm$^3$) pressure vessel, and the pressure of the vessel is monitored as a function of time. The initial slope of the pressure rise is defined as the pressurization rate and is reported in units of psi/$\mu$s. The more reactive the MIC is, the faster the pressure in the vessel rises and the higher the pressurization rate is. The details of the pressure-vessel apparatus and measurement protocol can be found in a prior work.[6]

Figure 4 shows the pressurization rate measured as a function of different stoichiometric proportions of fuel and oxidizer. The three different curves show measurements for three oxidizers of different compositions. We notice that increasing the coating thickness of a weaker oxidizer moderates the reactivity of the MIC steadily. The maximum pressurization rate measured for Al/KMnO$_4$ MIC is about 290 psi/$\mu$s, whereas that for Al/Fe$_2$O$_3$ is ∼0.017 psi/$\mu$s. In principle, we should be able to tune the reactivity between these two limits by modifying the composition of the
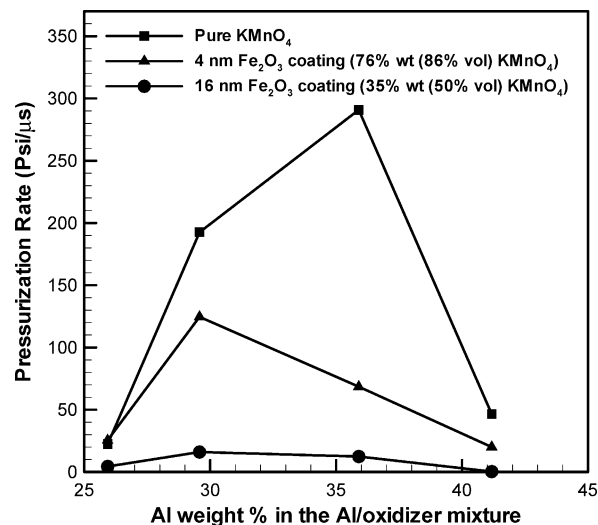


**Figure 4.** Pressurization rate measured as a function of fuel wt % in the MIC mixture for different oxidizers.
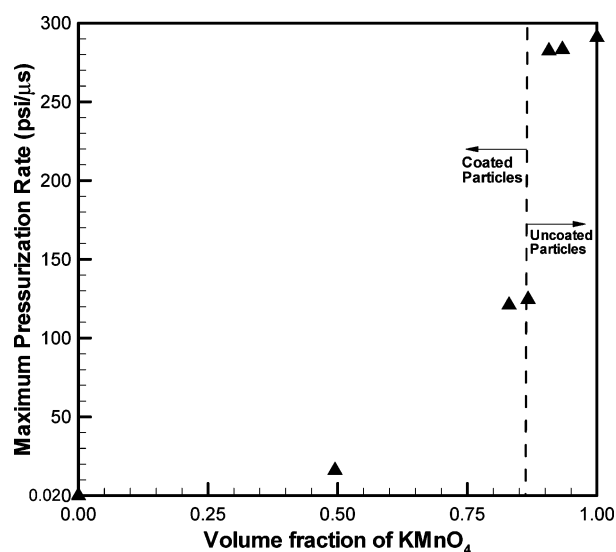


**Figure 5.** Maximum recorded pressurization rate as a function of volume fraction of KMnO$_4$ (coating thickness of iron oxide).

oxidizer. The maximum pressurization rates measured for different coating thicknesses have been plotted in Figure 5 and indicate that we are in fact able to moderate the reactivity of a strong oxidizer by varying the passivating thickness of the weak oxidizer. In the region to the right of the dashed line, the amount of iron oxide is not sufficient to coat the permanganate particles completely, and such partially coated particles trace the pressurization rate curve for pure KMnO$_4$ particles very closely. The data points to the right of the dashed line are suggestive of the fact that by merely mixing the two oxides we may not be able to tune the reactivity. However, by encapsulating the strong oxidizer inside a shell of the weak oxidizer, we could moderate the reactivity over a large dynamic range (points to the left of the dashed line).

In conclusion, we have been able to create core−shell-type composite oxidizer nanoparticles by taking advantage of the temperature difference between the decomposition temperature of the shell material (iron nitrate) and the melting point of the core (potassium permanganate). We have shown

that we could tune the reactivity of the nanoparticles by varying the coating thickness of the weaker oxidizer.

## References

(1) Prakash, A.; McCormick, A. V.; Zachariah, M. R. *Chem. Mater.* **2004**, *16*, 1466.
(2) Granier, J. J.; Pantoya, M. L. *Combust. Flame* **2004**, *138*, 373.
(3) Tillotson, T. M.; Gash, A. E.; Simpson, R. L.; Hrubesh, L. W.; Satcher, J. H.; Poco, J. F. *J. Non-Cryst. Solids* **2001**, *285*, 338.
(4) Aumann, C. E.; Skofronik, G. L.; Martin, J. A. *J. Vac. Sci. Technol., B: Microelectron. Nanometer Struct.—Process., Meas., Phenom.* **1995**, *13*, 1178.
(5) Fischer, S. H.; Grubelich, M. C. Presented at the 24th Int. Pyrotechnics Seminar, Monterey, CA, July 1988.
(6) Prakash, A.; McCormick, A. V.; Zachariah, M. R. *Adv. Mater.* **2005**, *17*, 900.
(7) Dreizin, E. L.; Shoshin, Y. L.; Mudryy, R. S.; Hoffmann, V. K. *Combust. Flame* **2002**, *130*, 381.
(8) Hunt, E. M.; Plantier, K. B.; Pantoya, M. L. *J. Mater. Res.* **2004**, *19*, 1.
(9) Granier, J. J.; Pantoya, M. L. *Combust. Theory Modell.* **2004**, *8*, 555.
(10) Tomasi, R.; Munir, Z. A. *J. Am. Ceram. Soc.* **1999**, *82*, 1985.
(11) Kim, S. H.; Zachariah, M. R. *Adv. Mater.* **2004**, *16*, 1821.
(12) Moghaddam, A. Z.; Rees, G. J. *Fuel* **1984**, *63*, 653.

NL0506251