

Super-reactive Nanoenergetic Gas Generators Based on Periodate Salts**

Guoqiang Jian, Jingyu Feng, Rohit J. Jacob, Garth C. Egan, and Michael R. Zachariah*

Composite energetic materials are simple mixtures of the fuel and oxidizer (e.g., thermite). Although composite energetic materials usually have much higher energy density than monomolecular energetic materials such as 2,4,6-trinitrotoluene (TNT), nitrocellulose, cyclotrimethylenetrinitramine (RDX) etc., they suffer from slow rates of energy release, limited by the mass transfer rate between reactants. In large part, the idea of nanoenergetics is to promote intimate mixing between the fuel and oxidizer by decreasing the length scale.^[1] This relatively new class of energetic materials has been a topic of extensive research and has been investigated for applications involving gas generators, initiators, propellants, and explosives as well as propulsive power in micro-/nano-electromechanical systems (MEMS/NEMS).^[2] In the most widely studied nanoenergetic formulations, nanoaluminum (aluminum nanoparticles) is employed as the fuel because of its high reaction enthalpy and ready availability, and metal oxide nanoparticles serve as oxidizers (e.g. Fe_2O_3 , CuO , MoO_3).^[2,3] More recently, some other oxidizers, including KMnO_4 ,^[4a] I_2O_5 ,^[4b] NaClO_4 ,^[4c,d] have been introduced into nanoenergetic formulations for their high oxygen content and strong oxidizing nature. These strong oxidizers also display very promising gas-generating behavior, however, most of them have a reduced shelf life compared to metal oxide nanoparticles, for reasons of light sensitivity or hygroscopicity.^[5] Recently, efforts have been made to encapsulate perchlorate salt nanoparticles with less reactive metal oxide layers as a moisture barrier.^[4e] However, perchlorate salts, particularly potassium perchlorate (KClO_4), have raised environmental and public health concerns during manufacture, transport, and applications, and have been targeted for elimination from many traditional pyrotechnic formulations.^[6] In a recent report, Moretti et al. introduced periodate salts as an alternative to perchlorate salts as pyrotechnic oxidizers because of their low toxicity and hygroscopicities. Their results show that periodate salt based formulations have good performance in illumination applications.^[6d] The fabri-

cation of periodate salt nanoparticles and their applications as gas generators, however, remains a challenge.

Herein, we present an example of gas generators based on periodate salts as oxidizers in nanoenergetic formulations. A simple yet versatile aerosol spray drying approach was developed to produce periodate salt nanoparticles. The aerosol spray drying method is a promising method for the production of salt oxidizer nanoparticles with a high oxygen content and for the fabrication of salt nanoparticles that are not accessible by wet-chemistry methods.^[7] The prepared periodate salt nanoparticles were then tested as oxidizers in nanoenergetic formulations with nanoaluminum as the fuel. These periodate salt nanoparticles exhibit superior reactivity when evaluated as the oxidizers in nanoenergetic formulations, producing the highest reported gas pressure pulses. Fast heating scanning electron microscopy and temperature-jump mass spectrometry techniques were employed to probe the initiation/reaction mechanisms and provided direct evidence that gas phase oxygen release is responsible for the initiation of the periodate nanoenergetic formulations.

The general pathway of preparing periodate salt nanoparticles by using an aerosol spray drying method is illustrated in Figure 1a (for details see the Supporting Information).

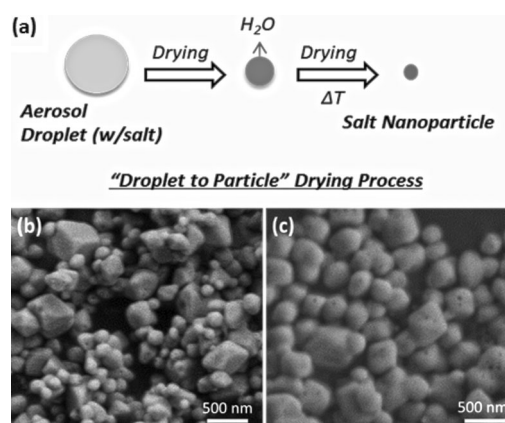


Figure 1. a) Illustration of preparing periodate salt nanoparticles by aerosol spray drying. w/ = with. b, c) SEM images of KIO_4 (b) and NaIO_4 (c) nanoparticles.

Briefly, periodate nanoparticles were formed through an aerosol “droplet-to-particle” process, whereby precursor aqueous solutions are continuously atomized to form micron-sized droplets, and subsequent solvent evaporation enables the formation of nanoparticles. The size of the nanoparticles ranges from 50 to 300 nm based on the scanning electron microscopy (SEM) images (Figure 1 b,c) and trans-

[*] G. Q. Jian, J. Y. Feng, R. J. Jacob, G. C. Egan, Prof. M. R. Zachariah
Department of Chemistry and Biochemistry, and
Department of Chemical and Biomolecular Engineering
University of Maryland
College Park, MD 20742 (USA)
E-mail: mrz@umd.edu

[**] This work was supported by the Defense Threat Reduction Agency and the Army Research Office. We acknowledge the support of the Maryland NanoCenter and its NispLab. The NispLab is supported in part by the NSF as a MRSEC Shared Experimental Facility.



Supporting information for this article is available on the WWW under <http://dx.doi.org/10.1002/anie.201303545>.

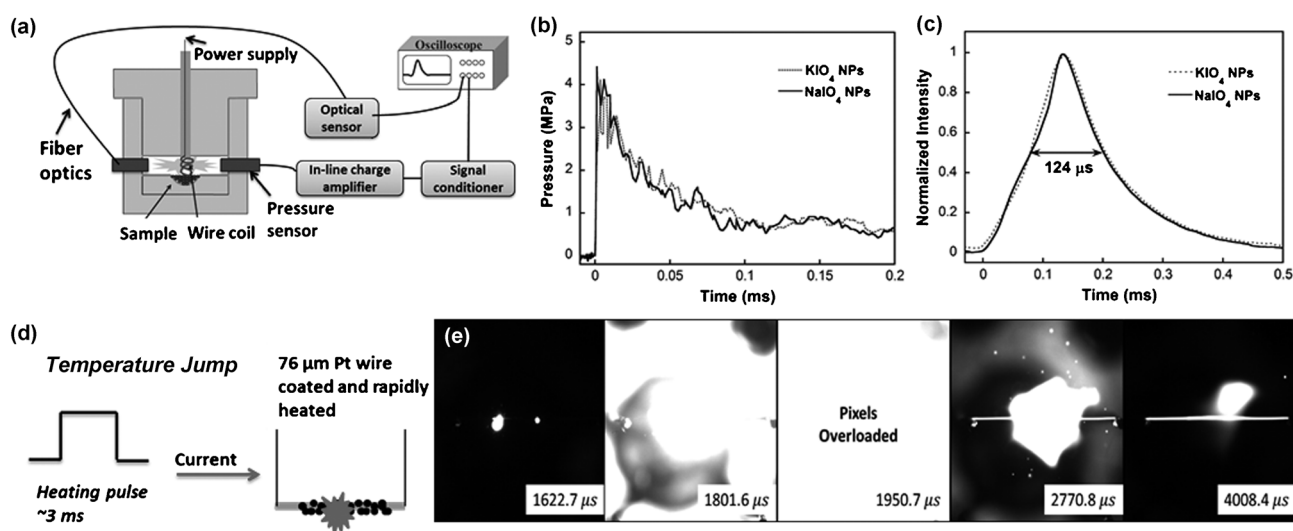
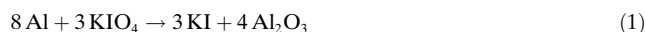


Figure 2. a) Illustration of the combustion cell. b,c) Pressure versus time (b) and normalized optical emission versus time (c) for nanoaluminum-based energetic formulations with KIO_4 and NaIO_4 nanoparticles as oxidizers. d) Schematic showing temperature-jump experiment. e) Sequential snapshots of Al/ KIO_4 nanothermite burning on a fast-heating wire in atmosphere (air).

mission electron microscopy (TEM) images (Figure S2 in the Supporting Information); the size of the nanoparticles is mainly dependent on the size distribution of the aerosol droplets. The prepared nanoparticles were further confirmed to be single crystal phase of KIO_4 and NaIO_4 by X-ray diffraction (XRD) analysis (Figure S3 in the Supporting Information).

Periodate nanoenergetic formulations were prepared by mixing oxidizer nanoparticles with nanoaluminum (< 50 nm) in a stoichiometric ratio shown in Equation (1).



The relative reactivity of the periodate nanoenergetic formulations was evaluated using a combustion cell (Figure 2a), from which temporal pressure rise and optical emission information can be obtained for the reaction in a small closed vessel. The pressure rise and optical emission of nanoenergetic reactions with synthesized periodate nanoparticles as oxidizers in the combustion cell are shown in Figure 2b,c, and peak pressure, pressurization rate and full width at half maximum (FWHM) burn time are summarized in Table 1, along with CuO nanoparticles (< 50 nm) as the reference material.^[4c] All pressure profiles show a rapid rise, which

Table 1: Results obtained in the combustion cell with nanoenergetic formulations with different oxidizer nanoparticles.^[a]

| Oxidizer (w/Al NPs, $\phi=1$) | P_{max} [MPa] | Pressurization rate [MPa μs^{-1}] | FWHM burn time [μs] |
|--------------------------------|------------------------|---|----------------------------------|
| KIO_4 NPs | 3.8 | 2.4 | ca. 124 |
| NaIO_4 NPs | 4.0 | 2.6 | ca. 124 |
| CuO NPs ^[4c] | 0.7 | 0.06 | ca. 170 |

[a] The pressurization rate (dP/dt) is defined as the initial slope of the pressure curve. FWHM burn time is defined as the full-width half-maximum of the optical emission curve obtained in the combustion cell tests. The results are the average values of three experiments.

occurs in a few microseconds, with peak pressures as high as approximately 4 MPa (Figure 2b), and average pressurization rates of 2.4 and 2.6 $\text{MPa}\mu\text{s}^{-1}$ for KIO_4 and NaIO_4 NPs (Table 1) respectively. Both the maximum pressure achieved and pressurization rate of Al/ KIO_4 and Al/ NaIO_4 significantly outperform CuO NPs (normally used as a standard; Table 1). We also compared the results with energetic formulations comprising aluminum nanoparticles and as-received KIO_4 and NaIO_4 (ca. 100 μm ; see Figure S7 in the Supporting Information); for the formulations with NPs we found a very significant increase in the maximum peak pressure (> 60x) and pressurization rate ($\geq 1000\times$), thus emphasizing the importance of employing nanosized oxidizers to improve the reactivity. In comparison to the reported values of pressurization rate for other nanoenergetic systems, for example, 1) 2.0 $\text{MPa}\mu\text{s}^{-1}$ for Al/ KMnO_4 ^[4a] and 2) 0.77–2.4 $\text{MPa}\mu\text{s}^{-1}$ for Al/ $\text{KClO}_4 + \text{CuO}$,^[4c] periodate nanoenergetic formulations deliver the highest values. Since we tested all the samples at a fixed mass of 25 mg, Al/ KIO_4 and Al/ NaIO_4 nanoenergetic formulations demonstrate the highest pressurization rates per mole of Al considering the relatively high molecular weight of periodate salts.

The normalized optical emission traces for periodate-based nanoenergetic formulations (Figure 2c) show that the burning time for both KIO_4 and NaIO_4 systems are roughly the same approximately 124 μs , which is much longer than the pressure-rise time, thus suggesting the burning behavior is rate limited by the aluminum, since the pressure rise is primarily due to oxygen release.^[8] The similar pressurization rates and burning time of KIO_4 and NaIO_4 imply, not surprisingly, that they have a similar reaction mechanism, which we will further explore later herein. Additionally, we found that the burning time of periodate salt based nanoenergetic formulations are shorter than of Al/CuO nanothermite (ca. 170 μs ; Table 1). In the periodate systems, the gas contributing to the pressurization is mainly formed through oxygen release from periodate salts decomposition,

which should enhance the burning rate of nanoaluminum. This point has been previously confirmed by Glumac and co-workers^[9] in the combustion of nanoaluminum in a pressurized oxygen environment. It has been found that the burning time of nanoaluminum can be significantly reduced, in some cases by 4 ×, in a pressurized environment.

High-speed imaging experiments of periodate nanoenergetic formulations in open air ignition (see Movie 2) and rapid wire ignition (Figure 2d,e, and details in Figure S8 in the Supporting Information) show that periodate salt nanoparticles demonstrate much more violent reactions and brighter emission than CuO nanoparticles, thereby indicating much faster energy release and pressurization rate for periodate nanoenergetic formulations. While we have not spectroscopically evaluated the emission, it is quite possible the enhanced brightness could in part be attributed to alkali atomic emission. Indeed the work of Moretti et al. has shown that incorporation NaIO₄ into pyrotechnics greatly enhances luminous efficiency and its potential application as the illuminant.^[6d] We should expect that with the more vigorous reaction expected using the nanomaterials, that this property would be significantly more enhanced and our combustion cell results do show a 15–30 × increase in optical emission (Figure S7a) as compare to the micron-sized material (Figure S7c).

Wire ignition experiments were employed to determine the ignition temperature of the nanoenergetic formulations at high heating rates (ca. $5 \times 10^5 \text{ K s}^{-1}$) by applying a rapid heating pulse, as illustrated in Figure 2d. The measured ignition temperature of Al/KIO₄ and Al/NaIO₄ nanoenergetic formulations are 950 K and 880 K (Figure S8 in the Supporting Information), respectively, which are lower than the ignition temperature of Al/CuO nanothermite (ca. 1040 K).^[10a] We note that for Al/NaIO₄ nanoenergetic formulations, the ignition temperature is even lower than the melting point of aluminum (933 K).

Naturally, we would expect that the superior gas-generating behavior and relative low ignition temperatures should be related to the properties of periodate oxidizer nanoparticles upon heating. Since KIO₄ and NaIO₄ nanoparticles behave similarly, we only present KIO₄ results in the following (NaIO₄ results are in the Supporting Information). Temperature-jump time-of-flight mass spectrometry^[10] was used to measure the species that formed at different stages during the decomposition of KIO₄ nanoparticles under rapid heating (ca. 3 ms, heating rate ca. $5 \times 10^5 \text{ K s}^{-1}$; Figure 3a,b). The background spectrum in Figure S10b in the Supporting Information shows H₂O, N₂, and a small amount of O₂. Unlike the decomposition of KClO₄, which proceeds in a single step (Figure S11b in the Supporting Information), KIO₄ appears to decompose in two stages. In the first stage at relatively low temperature < 800 K (Figure 3a), O₂ is the only species detected, while O₂, K, and small amount of I are seen at higher temperatures > 900 K (Figure 3b). The temporal oxygen release profile in Figure 3c shows two regimes as demarked in the figure, which are highly reproducible in repeated experiments. We observed an onset temperature for oxygen release of ca. 740 K, which is also the onset decomposition temperature of KIO₄ nanoparticles. The second stage

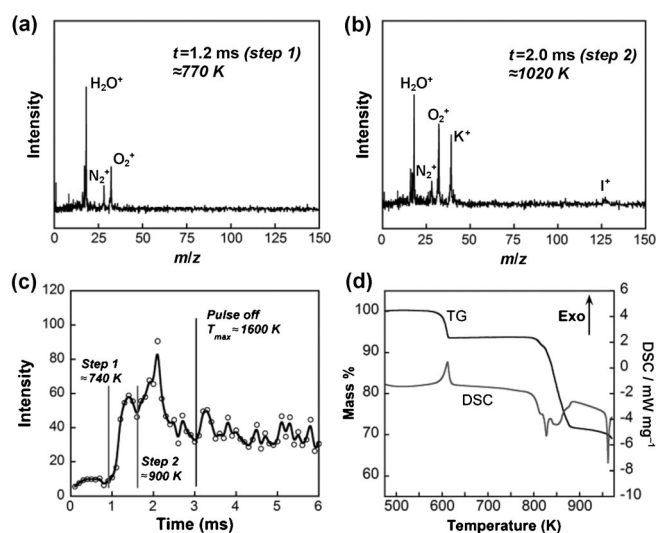


Figure 3. a, b) Selected mass spectra obtained from rapid heating of KIO₄ nanoparticles. c) Temporal profile of oxygen release upon heating KIO₄ nanoparticles. Measured data points (○) and a curve fitted to these data points (—) are shown. d) Thermogravimetric/differential scanning calorimetry (TG/DSC) curves of KIO₄ nanoparticles.

of decomposition shows an increase in oxygen starting at ca. 900 K, which also corresponds to the first appearance of potassium.

The decomposition of KIO₄ nanoparticles at low heating rate was studied by thermogravimetric analysis (TGA) with simultaneous heat flux by differential scanning calorimetry (DSC; Figure 3d). KIO₄ decomposes in two steps in Figure 3d, which is in agreement with the temperature-jump measurements at a high heating rate in Figure 3a–c, and previous thermoanalytical studies at a slow heating rate.^[11] As seen from Figure 3d, KIO₄ begins to decompose to KIO₃ and O₂ (ca. 7% weight loss) exothermically at 570 K, while a second endothermic decomposition step begins at 780 K, to form KI and O₂ (ca. 20% weight loss). Different from most metal oxide decompositions, which are endothermic, periodate decomposition is exothermic, which presumably is responsible for the relatively low ignition temperature. Indeed we find that perchlorate nanoparticle decomposition is also exothermic, but through a single-step decomposition (Figure S11 b,c).

To further explore initiation mechanisms of periodate nanoenergetic formulations, we rapidly heated them to 1173 K at 10^6 K s^{-1} in a hot-stage SEM; images before and after heating are shown in Figure 4a,b for Al/KIO₄. Quite surprising, and unlike our prior SEM studies with thermite mixtures (Al/CuO, Al/WO₃),^[12] we found that no obvious fuel-oxidizer reaction is apparent, with only the nanoaluminum left on the sample holder after rapid heating (more evidence shown in Figure S14 in the Supporting Information). Considering the fact that the microscope experiments performed with high heating rates were carried out in high vacuum, we employed the temperature-jump wire heating experiments for Al/KIO₄ with in situ high-speed imaging and mass spectrometry. These results showed that there was very little if any burning on the wire in contrast to the very violent

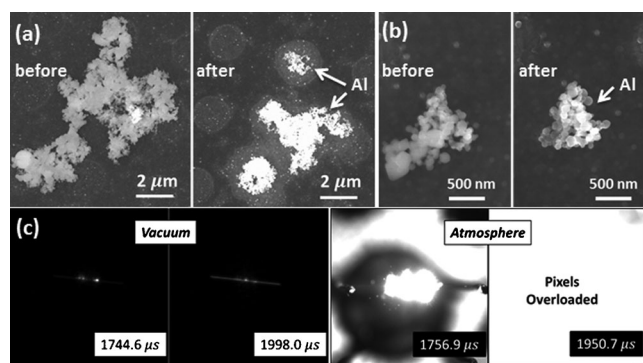


Figure 4. a, b) SEM images of Al/KIO₄ nanoenergetic formulations before and after rapid heating to 1173 K at 10⁶ K s⁻¹ and holding for 1 ms. c) High-speed imaging of Al/KIO₄ nanoenergetic reaction in vacuum (T-Jump/MS) and at atmospheric pressure (air).

burning at atmospheric pressure in air (Figure 4d) and argon (Figure S9a in the Supporting Information) environments. Further mass spectrometry results (Figure S15 in the Supporting Information) showed spectra similar to the neat periodate nanoparticles. Since the decomposition of KIO₄ nanoparticles, i.e., oxygen release, commences at 740 K (Figure 3c), it is reasonable to conclude that oxygen released from the oxidizers in vacuum escapes from the composite energetic sample before reaching its ignition temperature. The results imply that the reaction mechanism of periodate salt based nanoenergetic formulations differ from those of metal oxide nanothermites,^[10] and gas phase oxygen is critical to the ignition and burning of periodate nanoenergetic formulations. We must emphasize this is the first direct evidence of the contribution of gas-phase oxygen on the ignition and combustion of nanoenergetic formulations.

In summary, periodate salt nanoparticles were prepared through an aerosol spray drying process; these nanoparticles demonstrate highly reactive properties when formulated into an aluminum-based nanoenergetic material. Several in situ techniques at high heating rates suggest that exothermic decomposition of periodate salts contributes to the low ignition temperature of their nanoenergetic formulations. We also show direct evidence to support that direct gas phase oxygen release from the oxidizer decomposition is critical in the ignition and combustion of periodate nanoenergetic formulations.

Received: April 25, 2013

Revised: June 6, 2013

Published online: ■■■■■, ■■■■■

Keywords: energetic materials · nanoparticles · periodate · reaction mechanisms · thermite

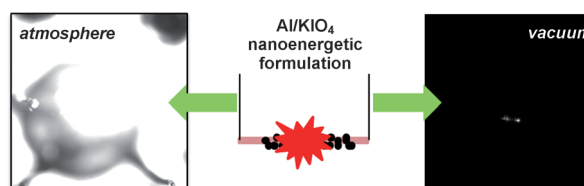
- [1] a) C. E. Aumann, G. L. Skofronick, J. A. Martin, *J. Vac. Sci. Technol. B* **1995**, *13*, 1178–1183; b) C. Rossi, A. Estéve, P. Vashishta, *J. Phys. Chem. Solids* **2010**, *71*, 57–58; c) M. R. Zachariah, *Propellants Explos. Pyrotech.* **2013**, *38*, 7.
- [2] a) D. G. Piercey, T. M. Klapötke, *Cent. Eur. J. Energ. Mater.* **2010**, *7*, 115–129; b) C. Rossi, K. Zhang, D. Estéve, P. Alphonse, P. Thailhades, C. Vahlas, *J. Microelectromech. Syst.* **2007**, *16*, 919–931; c) E. L. Dreizin, *Prog. Energy Combust. Sci.* **2009**, *35*, 141–167; d) K. S. Martirosyan, *J. Mater. Chem.* **2011**, *21*, 9400–9405.
- [3] a) R. A. Yetter, G. A. Risha, S. F. Son, *Proc. Combust. Inst.* **2009**, *32*, 1819–1838; b) N. H. Yen, L. Y. Wang, *Propellants Explos. Pyrotech.* **2012**, *37*, 143–155.
- [4] a) A. Prakash, A. V. McCormick, M. R. Zachariah, *Adv. Mater.* **2005**, *17*, 900–903; b) K. S. Martirosyan, L. Wang, D. Luss, *Chem. Phys. Lett.* **2009**, *483*, 107–110; c) C. R. Becker, S. Apperson, C. J. Morris, S. Gangopadhyay, L. J. Currano, W. A. Churaman, C. R. Stoldt, *Nano Lett.* **2011**, *11*, 803–807; d) A. Plummer, V. Kuznetsov, T. Joyner, J. Shapter, N. H. Voelcker, *Small* **2011**, *7*, 3392–3398; e) C. W. Wu, K. Sullivan, S. Chowdhury, G. Q. Jian, L. Zhou, M. R. Zachariah, *Adv. Funct. Mater.* **2012**, *22*, 78–85.
- [5] a) D. R. Lide, *CRC Handbook of Chemistry and Physics, 85th ed.*, CRC, Boca Raton, **2004**; b) A. F. Holleman, E. Wibler, N. Wibler, *Inorganic Chemistry*, Academic Press, New York, **2001**, p. 465.
- [6] a) J. Giles, *Nature* **2004**, *427*, 580–581; b) E. W. Fournier, B. B. Brady, *J. Propul. Power* **2005**, *21*, 937–941; c) G. Steinhäuser, T. M. Klapötke, *Angew. Chem.* **2008**, *120*, 3376–3394; *Angew. Chem. Int. Ed.* **2008**, *47*, 3330–3347; d) J. D. Moretti, J. J. Sabatini, G. Chen, *Angew. Chem.* **2012**, *124*, 7087–7089; *Angew. Chem. Int. Ed.* **2012**, *51*, 6981–6983.
- [7] a) C. Boissiere, D. Grosso, A. Chaumonnot, L. Nicole, C. Sanchez, *Adv. Mater.* **2011**, *23*, 599–623; b) A. Carné-Sánchez, I. Imaz, M. Cano-Sarabia, D. MasPOCH, *Nat. Chem.* **2013**, *5*, 203–211.
- [8] a) K. Sullivan, M. R. Zachariah, *J. Propul. Power* **2010**, *26*, 467–472; b) G. Q. Jian, L. Liu, M. R. Zachariah, *Adv. Funct. Mater.* **2013**, *23*, 1341–1346.
- [9] T. Bazyn, H. Krier, N. Glumac, *Combust. Flame* **2006**, *145*, 703–713.
- [10] a) G. Q. Jian, S. Chowdhury, K. Sullivan, M. R. Zachariah, *Combust. Flame* **2013**, *160*, 432–437; b) L. Zhou, N. Piekielek, S. Chowdhury, M. R. Zachariah, *Rapid Commun. Mass Spectrom.* **2009**, *23*, 194–202.
- [11] K. Muraleedharan, M. P. Kannan, T. Gangadevi, *J. Therm. Anal. Calorim.* **2010**, *100*, 177–181.
- [12] K. T. Sullivan, N. W. Piekielek, C. Wu, S. Chowdhury, S. T. Kelly, T. C. Hufnagel, K. Fezzaa, M. R. Zachariah, *Combust. Flame* **2012**, *159*, 2–15.

Communications

Energetic Materials

G. Q. Jian, J. Y. Feng, R. J. Jacob,
G. C. Egan,
M. R. Zachariah* ———— ■■■■-■■■■

Super-reactive Nanoenergetic Gas
Generators Based on Periodate Salts



Nanoenergetic formulations under flash heating: Periodate salt nanoparticles are synthesized by a facile aerosol spray drying process and demonstrate highly reactive properties as oxidizers in an

aluminum-based nanoenergetic formulation. Direct evidence supports that gas phase oxygen release from the oxidizer decomposition is critical in the ignition and combustion of these formulations.