Research paper

Preparation and characterization of Al/Fe_2O_3/m-DNB nanothermites by electrospray

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Received: November 20, 2016 Accepted: May 28, 2018

Abstract

Aluminum (Al)/Ferric oxide (Fe_2O_3)/m-dinitrobenzene (m-DNB) composite energetic materials with different m-DNB concentration have been successfully prepared utilizing a typical electrospray process. m-DNB in the precursor solution plays an important role in morphology of composites. The peak temperature of exothermic reaction of Al/Fe_2O_3/m-DNB composites with 5 wt% m-DNB concentration prepared by electrospray is 41 °C lower than that of ultrasonic and magnetic stirring sample. The combustion test results show that the sample of Al/Fe_2O_3 prepared by electrospray significantly enhances combustion performance, thus leading to large flames. And the m-DNB addition can further increase combustion performance. The combustion intensity increases with increasing m-DNB addition when the m-DNB concentration is less than 10 wt%.

Keywords: m-DNB, energetic materials, electrospray, combustion performance

1. Introduction

Recently, a great deal of attention has been paid to nano-energetic materials because of their superior exothermic characteristics and high energy densities, which possess properties unattainable or greater to those of traditional organic-based energetics[1)-4)]. Nano-thermites are a class of energetic materials that are composed of nano-sized metal fuel and oxidizer particles[5),6)]. These materials are also termed metastable intermolecular composites (MICs). They have found numerous applications as gas generators[2)], in nanoscale welding[7)] and electric igniters[8)], as well as energetic additives in explosives and propellants[9)]. The performance of nano-thermites is dependent on the mass transport, diffusion distance, and stability of reactive components[10)-12)]. In recent times, in order to strongly improve the rate of energy release and properties of thermites, various ways have been used to fabricate nano-thermites[13)-21)]. On the other hand, the addition of energetic materials to nano-thermites is also a good method. C. Wu et al. incorporated high-oxygen-content strong oxidizer perchlorate salts into current nano-thermite composite formulations[22)]. The results showed that these composite systems significantly outperform the single metal oxide system in both pressurization rate and peak pressure. L. Shen et al. used a sol-gel synthetic approach combined with an ultrasonic method to prepare $Al/B/Fe_2O_3$ nano-thermites with high energy densities[23)]. Kun Gao et al. utilized sol-gel, wet impregnation and solvent anti-solvent process to prepare $AP/Al/Fe_2O_3$[20)].

m-DNB is a nitroaromatic compound used in the synthesis of dyes, plastics manufacturing industry and as explosives[24)]. To date, it has been widely adopted in the manufacture of intermediates in chemical synthesis industries[25)]. However, m-DNB is rarely used in energetic materials.

In this work, Al/Fe_2O_3/m-DNB (5 wt% nitrocellulose (NC) acts as a binder) composite materials with different m-DNB concentration were prepared by a typical electrospray process. m-DNB was used as catalyst to reduce the reaction temperature of Al/Fe_2O_3. At the same time, since the solubility of m-DNB in ether and ethanol is high, it is easy to control its content. The effect of m-DNB on the morphology of composites was studied by scanning electron microscope (SEM). Thermal characteristic was studied by the thermogravimetry-differential scanning calorimetry (TG-DSC). The combustion performances were recorded by camera in air environment.

2. Experiments

2.1 Materials

m-dinitrobenzene (m-DNB) was donated by China Academy of Engineering Physics. A sample of NC (1000 of polymerization degree, 11.9% of nitrogenous content) was kindly donated by Liaoning Qing Chemical Co., Ltd, China. Aluminum nano-powders (Al) were supplied by Nanjing Emperor Nano Material Co., Ltd (Nanjing, China) and tested by thermogravimetric method to determine the active Al content as ~70% by mass. Iron oxide nano-powders (Fe_2O_3) (99.5 wt%, ~30 nm) were purchased from Aladdin Reagent Industrial Corporation. Acetone used in this experiment was analytical grade and purchased from Shanghai Lingfeng Chemical Reagent Co., Ltd. Analytical grade ethanol was purchased from Sinopharm Chemical Reagent Co., Ltd. All of chemicals were directly used as received without further purification.

2.2 Precursor preparation

For a typical fabricating process, the required amount of m-DNB and 7.5 mg of NC were dissolved in 1.5 mL of cosolvent (0.75 mL of ether and 0.75 mL of ethanol) to form a clear solution with the m-DNB concentration range of 0 −20 wt% (based on the total weight of Al and Fe_2O_3, w/w). Finally, 30 mg of Al and 120 mg of Fe_2O_3 were added into the above NC/m-DNB solution. The mixture was ultrasonically mixed for 60 min to allow the nanoparticles to disperse homogeneously. This was followed by an additional 24 hours of magnetic stirring at room temperature.

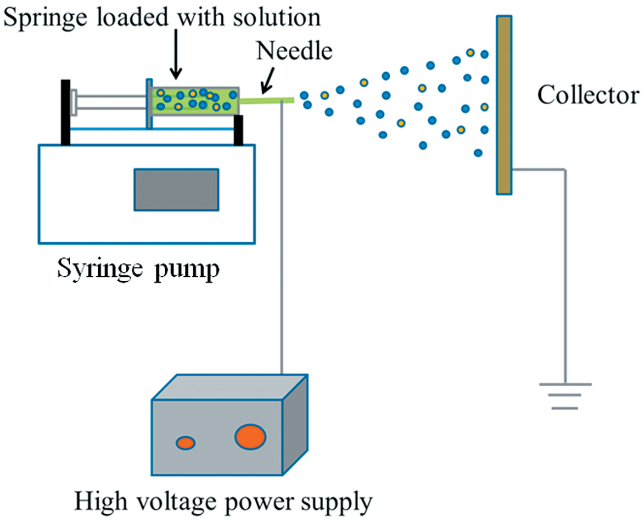

Figure 1 Schematic diagram of the experimental setup for producing Al/Fe_2O_3/m-DNB composite materials.

2.3 Electrospray deposition

As presented in Figure 1, the precursor solution was immediately loaded into a plastic syringe with a needle inner diameter of 0.8 mm. The syringe was fixed horizontally on a syringe pump. In the process of electrospray, a voltage of up to 18 kV potential was attached to the needle using a high-voltage power supply. The flow was set at 3 mL·h^{-1}. The composite materials were collected on the aluminum foil situated at 6 cm from the needle.

2.4 Morphology analysis

The morphologies of samples were observed by a cold field emission scanning electron microscopes (SEM) (FE-SEM, S-4800II, Hitachi High-Technologies Corp., Tokyo, Japan) with an acceleration voltage of 10.0 kV.

2.5 Thermal performance analysis

The thermal performances of the samples were investigated by means of TG—DSC (NETZSCH STA449 C). All samples were placed in alumina crucibles (85 μL), weighted at 1.50 ± 0.1 mg, heating rate at 10 K·min^{-1} from 40 °C to 800 °C in a high-purity argon gas purge with a flow rate of 20 mL·min^{-1}.

2.6 Combustion performances

Approximately 10.0 mg of the samples were ignited by a windproof igniter in static air. The high speed video was used to record the combustion process, and providing information on luminous flame development and combustion characteristics.

3. Results and discussion

3.1 Morphology characteristics of raw materials

In order to observe the morphology of the particle of Al and Fe_2O_3 before electrospray, SEM experiment was taken. Nano Measurer software was used to measure the diameter of Al from the SEM micrographs. Diameters were measured at 140 different points. The SEM images are shown in Figure 2 along with the size distribution of Al.

Compared the two images, it can be found that the sample of original Fe_2O_3 has a more uniform distribution of

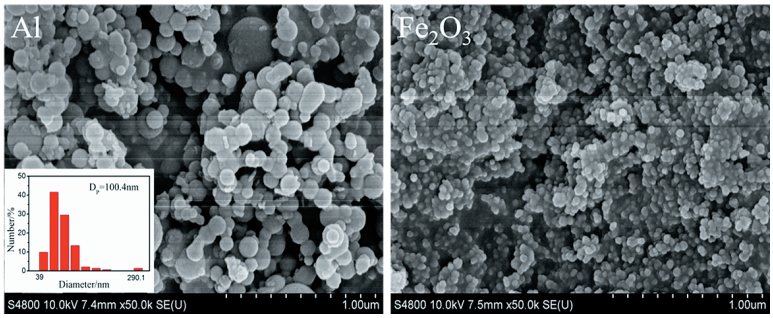

Figure 2 SEM images of raw Al and raw Fe_2O_3 before electrospray and the size distribution of original Al (where, D_P is the average diameter of aluminum nanopowders).

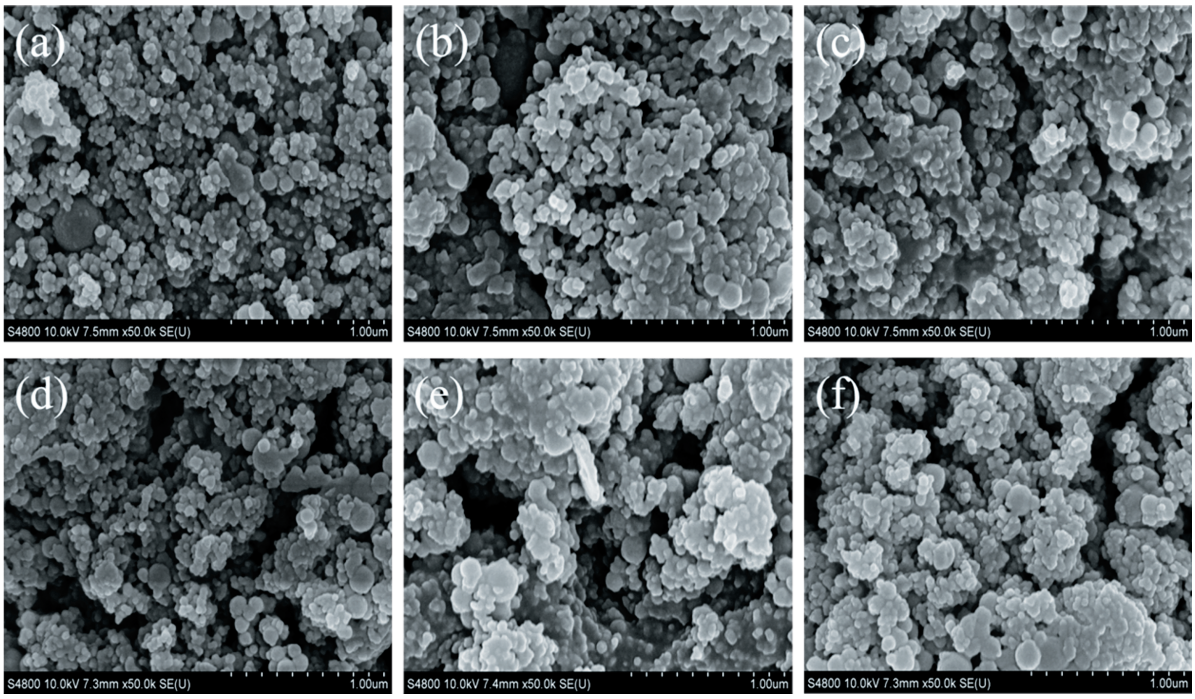

Figure 3 SEM images of (a) $(Al/Fe_2O_3)_0$ prepared by ultrasonic and magnetic stirring, (b–f) Al/Fe_2O_3/m-DNB (5 wt% NC acts as a binder) composite materials with different m-DNB concentration prepared by a typical electrospray process, (b) 0 wt%, (c) 5 wt%, (d) 10 wt%, (e) 15 wt%, (f) 20 wt%.

particles than that of Al. The distribution of Al is from 39 nm to 320 nm. However, over 50% of particle, are smaller than 100 nm. Moreover, the form of Al and Fe_2O_3 is soft aggregates, especially Fe_2O_3. Substantially no adhesion phenomenon, the emergence of soft reunion is due to the electrostatic attraction between the particles and the role of the van der Waals force makes the particles together.

3.2 Morphology analysis of composite materials

As shown in Figure 1, the electrospray process is a one-step process, in which all materials within droplets aggregate during solvent evaporation, to generate composite materials. In order to know the nominal advantage of electrospray over other methods, Al/Fe_2O_3 composite material without a binder was prepared by ultrasonic and magnetic stirring. 30 mg of Al and 120 mg of Fe_2O_3 were added into 1.5 mL of cosolvent (0.75 mL of ether and 0.75 mL of ethanol). The mixture was ultrasonically mixed for 60 min to allow the nanoparticles to disperse homogeneously. This was followed by an additional 24 hours of magnetic stirring at room temperature. Finally, the sample was air-dried in fume hood at room temperature and abbreviated as $(Al/Fe_2O_3)_0$.

SEM images for all composite materials are shown in Figure 3. Figure 3(a) shows the SEM image of $(Al/Fe_2O_3)_0$. The sample after ultrasonic and magnetic stirring seems to produce a more uniform distribution of particles. The samples (Figure 3(b)–3(f)) prepared by a typical electrospray process show that the composition aggregates together. It appears that NC acts as a binder to hold the jammed aggregates into a structure that upon deposition retains their physical shape to prevent disintegration. Moreover, the NC also serves the function of a gas generator within the particles during combustion

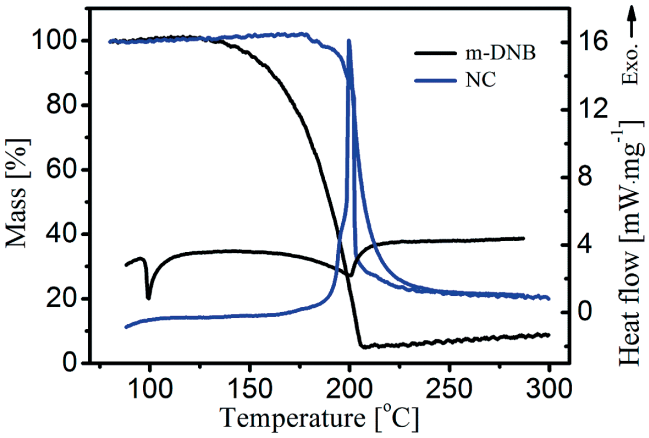

Figure 4 TG/DSC curves of NC and m-DNB.

of thermite[26]. The composition with m-DNB show no severely aggregates compared to samples without m-DNB. This is because NC concentration plays an important role in the entanglement regime which dictates composition formation. After adding m-DNB to composition, the ratio of NC in composite materials (w/w) decreased. This concentration is no sufficient to generate a significant degree of entanglement. m-DNB was formed between molecule chains during solvent evaporation to limit chain entanglements. As a result, with the addition of m-DNB, a loose structure was formed.

3.3 Thermal performances analysis

Thermogravimetry-differential scanning calorimetry (TG-DSC) measurements were used to examine the thermal characteristics of samples. Figure 4 shows the TG -DSC curves of NC and m-DNB. The curves of sample NC first show a relatively slow decomposition process, followed by a sharp exothermic behavior with a maximum

at 203.1 °C, accompanied by a sharp weight loss. Previous studied[27] showed that, the decomposition of NC at this temperature produces H_2O, CO, NO and CO_2 as evolved gases and CO is the major decomposition product of NC. m-DNB exhibits an endothermic peak at 92.2 °C caused by m-DNB melting, followed by an endothermic peak at 203.9 °C caused by volatilization of m-DNB, corresponding to a weight loss process. The decomposition process was invisible in the DSC curve of m-DNB.

In order to know how the m-DNB concentration influences thermal performances of Al/Fe_2O_3/m-DNB composite materials. The DSC measurement of Al/Fe_2O_3/m-DNB composite materials with different m-DNB concentration was performed. Figure 5 shows the DSC curves of all samples in temperature range of 400 ~ 700 °C.

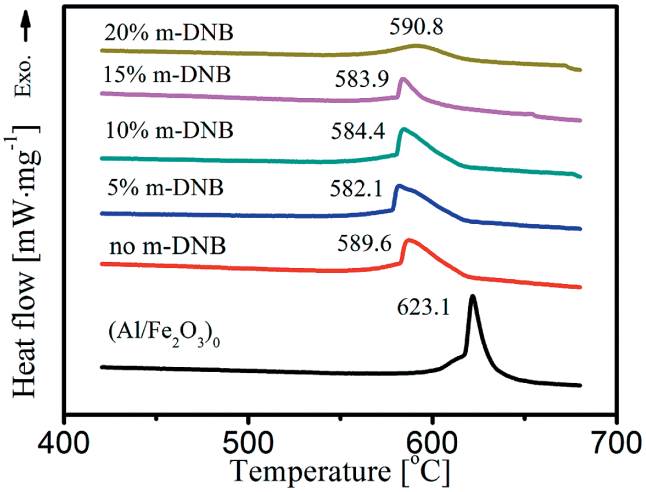

Figure 5 DSC curves of Al/Fe_2O_3/m-DNB (5 wt% NC acts as a binder) composite materials with different m-DNB concentration prepared by a typical electrospray process, and $(Al/Fe_2O_3)_0$ prepared by ultrasonic and magnetic stirring.

The results show noticeable differences in the position and shape of the reaction peaks. The DSC curve of $(Al/Fe_2O_3)_0$ indicates that an exothermic peak is formed at about 623.1 °C, which belongs to the redox reaction of Al and Fe_2O_3. The redox reaction has a relatively slow reaction process, followed by a sharp reaction. The exothermic reaction of Al/Fe_2O_3 (5 wt% NC acts as a binder) composite materials prepared by electrospray has a peak temperature of 589.6 °C, which is 33.5 °C lower than that of 623.1 °C of simply mixed sample ($(Al/Fe_2O_3)_0$). The peak temperature of 582.1 °C for Al/Fe_2O_3/m-DNB with 5 wt% m-DNB concentration is 41 °C lower than $(Al/Fe_2O_3)_0$.

3.4 Combustion analysis

Combustion analysis can provide important clues used to evaluate the reactivity of a thermite. To further evaluate the reactivity of nanothermites prepared by electrospray. The high speed video test was performed. Figure 6 shows the flame images that represent the burning process of all samples.

The sample $(Al/Fe_2O_3)_0$ prepared by ultrasonic and magnetic stirring exhibits a low-intensity flame. The sample Al/Fe_2O_3 (5 wt% NC acts as a binder) prepared by electrospray increases combustion performance, thus leads to large flames. The m-DNB addition can further increase combustion performance. The combustion intensity increases with increasing m-DNB addition. However, the intensity of flame decreases when the m-DNB concentration is over 10 wt%. A comparison of the flames of all samples shows that electrospray technology clearly enhances the combustion of the Al/Fe_2O_3 sample. On the other hand, less than 10 wt% of m-DNB addition can further increase combustion performance of the Al/Fe_2O_3 sample.

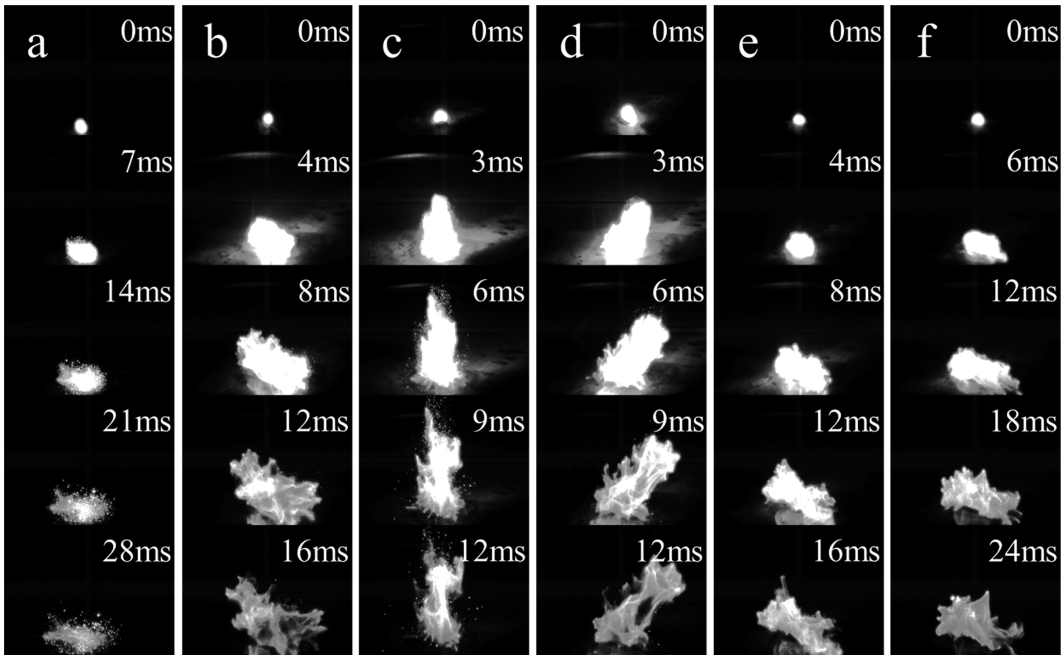

Figure 6 High speed video images: (a) $(Al/Fe_2O_3)_0$ prepared by ultrasonic and magnetic stirring; (b–f) Al/Fe_2O_3/m-DNB (5 wt% NC acts as a binder) with different m-DNB concentration prepared by a typical electrospray process, (b) 0 wt%, (c) 5 wt%, (d) 10 wt%, (e) 15 wt%, (f) 20 wt%.

4. Conclusionn

In summary, Al/Fe_2O_3/m-DNB (5 wt% NC acts as a binder) composite energetic materials with different m-DNB concentration have been successfully prepared utilizing a typical electrospray process. m-DNB in the precursor solution plays an important role in morphology of composites. The peak temperature of exothermic reaction of Al/Fe_2O_3 (5 wt% NC acts as a binder) composites prepared by electrospray is 33.5 °C lower than that of ultrasonic and magnetic stirring sample. With the addition of m-DNB, the peak temperature further decreases to 582.1 °C which is 41 °C lower than that of ultrasonic and magnetic stirring sample. The combustion test results show that the sample of Al/Fe_2O_3 prepared by electrospray significantly enhances combustion performance, thus leading to large flames. And the m-DNB addition can further increase combustion performance. The combustion intensity increases with increasing m-DNB addition when the m-DNB concentration is less than 10 wt%.

Acknowledgements

This work was supported by the Fundamental Research Funds for the National Natural Science Foundation of China (NSFC51202113).

References

1) Y. F. Ivanov, M. N. Osmonoliev, and V. S. Sedoi, Prop. Explos. Pyrotech., 28, 319−333 (2003).
2) K. S. Martirosyan, J. Mater. Chem., 21, 9400−9405 (2011).
3) R. A. Williams, J. V. Patel, and A. Ermoline, Combust. Flame, 160, 734−741 (2013).
4) S. Singh, G. Singh, and N. Kulkarni, J. Therm. Anal. Calorim., 119, 309−317 (2015).
5) S. Yan, G. Jian, and M. R. Zachariah, ACS Appl. Mater. Interfaces, 4, 6432−6435 (2012).
6) X. Li, P. Guerieri, W. Zhou, C. Huang, and M. R. Zachariah, ACS Appl. Mater. Interfaces, 7, 9103−9109 (2015).
7) C. Rossi, A. Estéve, and P. Vashishta, J. Phys. Chem. Solids, 71, 57−58 (2010).
8) E. L. Dreizin, Prog. Energy Combust. Sci., 35, 141−167 (2009).
9) V. E. Sanders, B. W. Asay, T. J. Foley, B. C. Tappan, A. N. Pacheco, and S. F. Son, J. Propul. Power, 23, 707−714 (2007).
10) C. Farley and M. L. Pantoya, J. Therm. Anal. Calorim., 102, 609−613 (2010).
11) M. L. Pantoya and J. J. Granier, J. Therm. Anal. Calorim., 85, 37−43 (2006).
12) J. Sun, M. L. Pantoya, and S. L. Simon, Thermochim. Acta., 444, 117−127 (2006).
13) K. J. Blobaum, M. E. Reiss, J. M. Plitzko, and T. P. Weihs, J. Appl. Phys., 94, 2915−2922 (2003).
14) K. J. Blobaum, M. E. Reiss, J. M. Plitzko, and T. P. Weihs, J. Appl. Phys., 94, 2923−2929 (2003).
15) M. Schoenitz, T. S. Ward, and E. L. Dreizin, Proc. Combust. Inst., 30, 2071−2078 (2005).
16) S. M. Umbrajkar, S. Seshadri, M. Schoenitz, V. K. Hoffmann, and E. L. Dreizin, J. Propul. Power, 24, 192−198 (2008).
17) S. H. Kim and M. R. Zachariah, Adv. Mater., 16, 1821−1825 (2004).
18) K. T. Sullivan and M. A. Worsley, Combust. Flame, 159, 2210−2218 (2012).
19) T. M. Tillotson, A. E. Gash, R. L. Simpson, L. W. Hrubesh, J. H. Satcher, and J. F. Poco, J. Non-Cryst. Solids, 285, 338−345 (2001).
20) K. Gao, G. Li, and Y. Luo, J. Therm. Anal. Calorim., 118, 43−49 (2014).
21) L. Shen, G. Li, Y. Luo, K. Gao, and Z. Ge, Sci. China Chem., 57, 797−802 (2014).
22) C. Wu, K. Sullivan, and M. R. Zachariah, Adv. Funct. Mater., 22, 78−85 (2012).
23) L. Shen and G. Li, Sci. China Chem., 57, 797−802 (2014).
24) J. Oh, S. H. Heo, and S. Yoon, Reprod. Toxicol., 43, 45−55 (2014).
25) S. Ludwiga and H. Tinwell, Toxicol. Lett., 213, 275−284 (2012).
26) H. Wang, G. Jian, G. C. Egan, and M. R. Zachariah, Combust. Flame, 161, 2203−2208 (2014).
27) L. Huwei and F. Ruonong, J. Anal. Pyrol., 14, 163−167 (1988).