Short Communication

Propellants, Explosives, Pyrotechnics

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CL-20 Based Ultraviolet Curing Explosive Composite with High Performance

Hao Guo,[a] Shuai Xu,[b] Huihui Gao,[a] Xiaoheng Geng,[c] Chongwei An,*[a] Chuanhao Xu,[a] Qianbing Li,[a] Shuang Wang,[a] Baoyun Ye,[a] and Jingyu Wang[a]

Abstract: The integration of the Ultraviolet (UV) curable resin into energetic materials, has been a new direction in the field of explosive inks with high curing speed and high solid loading. In this ink formulation, polyurethane acrylate (PUA), 2,4,6-trimethylbenzoyl-diphenylphosphine oxide (TPO) and hexanitrohexaazaisowurtzitane (CL-20) were selected as binder, photoinitiator and main explosive, respectively. The CL-20 based UV-curing explosive composite was prepared by UV-curing and direct ink writing (DIW) technology. The rate of curing, micro-scale structure, morphology, crystal type, impact sensitivity, and detonation ability of the sample were characterized and analyzed. The results show that the curing process of CL-20 based UV-curing explosive ink could be completed within 7 minutes after UV-curing for 3 minutes, revealing rapid curing speed. In the preparation process of CL-20 based explosive composite, the crystal type of CL-20 do not change. Compared with raw CL-20, the explosive composite has a lower impact sensitivity. Moreover, the critical detonation size is around 1×0.078 mm, and the detonation velocity is 7357 $m\,s^{-1}$.

Keywords: UV-curing · CL-20 · explosive composite · detonation ability

1 Introduction

With the development of weapons informationization and various types of micro-weapons, new initiating explosive devices with the main features of informationization, structural miniaturization and sequence integration have emerged. Micro Electro-Mechanical Systems (MEMS) devices integrate micro-small, informatized and multi-functional into one, which greatly reduce the size of the detonation train and improve the safety and reliability of the weapon system. However, due to the smaller charge size of the MEMS devices, the traditional charge technology is no longer fit for MEMS[1–4]. Direct ink writing (DIW) which was first proposed by Cesarano can meet the charge process requirements of MEMS. In the field of energetic materials, B. Fuchs and A. Wilson successfully installed an explosive ink formulation (EDF-11) into the MEMS device by DIW in 2005. DIW has become the main explosive charge way of MEMS in the US Army now [5–7].

Explosive inks are multi-component systems consisting of explosives, binder systems (including binders and solvents) and other additives (other high energy explosives or additives, etc.). Explosive inks have two versions: all-liquid explosive inks and suspension explosive inks. The all-liquid explosive ink is made by dissolving explosives, binders and additives in organic solvents. However, the morphology of explosive (CL-20) crystal is not easy to control, resulting in some safety problems in application. Meanwhile, it takes a long time in the process of curing and DIW. The suspension explosive ink is cured by thermal initiation polymerization, which is difficult to cure in short time. And there are many materials waste generated in the preparation process [8–12]. They are not suitable to the practical application in MEMS devices. UV-curing technology is a kind of light processing technology that induces the photoinitiator to be excited by a certain wavelength of ultraviolet light to induce the liquid resin to be polymerized at a high speed. The UV-curing reaction is essentially a photoinitiated polymerization and crosslinking reaction. UV-curing has a fast curing speed, green, energy saving, excellent performance of the cured layer, and plays a significant role in the microstructure formation of energetic materials [13].

In this study, combining the UV curable resin (PUA) with the explosive (CL-20), a new UV-curing explosive ink with high curing rate and high solid loading was designed and developed and its curing rate, morphology, crystal type, detonation ability and impact sensitivity were characterized and analyzed.

[a] *H. Guo, H. Gao, C. An, C. Xu, Q. Li, S. Wang, B. Ye, J. Wang*
School of Environment and Safety Engineering
North University of China
Taiyuan Shanxi, 030051, P. R. China
**e-mail: anchongwei@yeah.net*
[b] *S. Xu*
Sichuan HuaChuan Indistries Co., Ltd,
Chengdu Sichuan, 610106, P. R. China
[c] *X. Geng*
Urban and Environmental Science Department
BinZhou University
Binzhou, Shandong, 256600, P. R. China

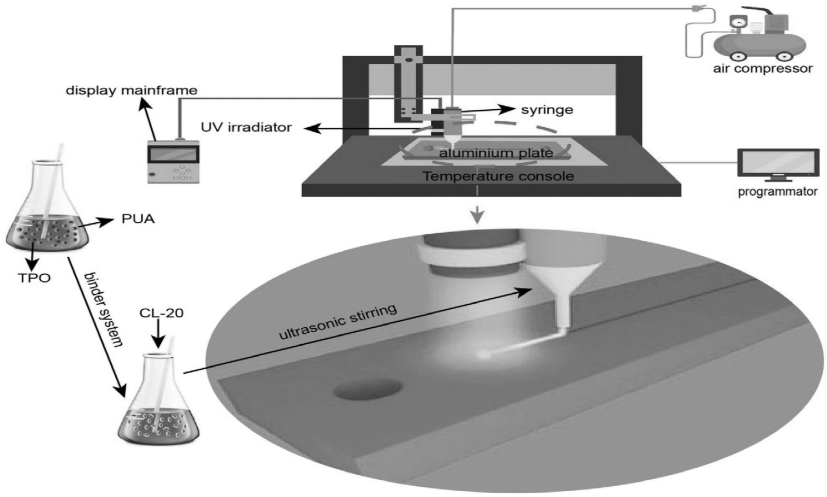

Figure 1. Diagram of preparation of binder system and CL-20 based UV-curing composite.

2 Experimental Section

2.1 Preparation of CL-20 Based Composite

The UV-curing explosive ink was prepared by adding 2.7 g of sub-micro CL-20 (self-made by North University of China), 0.3 g of PUA (produced by Guangzhou Tongyi Advanced Polymers Co.,Ltd), 0.02 g of TPO (produced by Nanjing Jiazhong Chemical Technology Co.,Ltd) into 1.2 g of ethanol (produced by Tianjin Fengchuan Chemical Technology Co., Ltd). Ultrasonic stirring was carried out at a temperature of 25 °C, and the uniformly mixed explosive composite was loaded into a syringe for pneumatic micro-direct-writing device (Self-made by North University of China). Then the composite was deposited in aluminum plate channels via DIW and UV-curing technology.

2.2 Characterization and Properties

According to the method of GBT 6739–2006, the hardness of the composite was determined by a pencil hardness tester at a temperature of 25°C, to determine the curing time of the explosive ink. The morphology of explosive samples including raw CL-20, sub-micro CL-20 and the CL-20 based composite was observed by a TESCAN Mira 3 Field Emission Scanning Electron Microscope (SEM). A DX-2700 X-ray diffraction (XRD) (produced by Dandong HaoYuan Instrument Co., Ltd.) was used to distinguish the crystal forms of raw CL-20, sub-micro CL-20 and the CL-20 based composite (light pipe voltage, 40 kV; current, 30 mA; scanning angle, 0°~50°). The impact sensitivity test was performed using a 601.3-12 type drop hammer apparatus (drop weight: 2.500±0.002 kg; sample mass: 35±1 mg; temperature: 25 °C; relative humidity < 80 %) [10].

The critical detonation test was performed using a wedge groove experiment [14]. The explosive ink was loaded into the wedge groove using DIW technology (groove length: 100 mm; groove width: 1 mm; the deepest of groove: 3 mm). After UV-curing, the prepared CL-20 based composite was ignited. The detonation velocity of the explosive ink was tested by an electrical signal probe method [15]. Using the same charge method, the CL-20 based explosive ink was loaded into an aluminum groove (groove length: 100 mm; groove width: 1.2 mm; groove depth: 1.0 mm) and was ignited.

The cornering ability of the detonation wave is also an important indicator to measure the detonation performance of explosive samples. Using the same charge method, the CL-20 based composite was loaded into a network channel of the explosion (section size: 1.0×1.0 mm) and was ignited.

3 Results and Discussions

3.1 Curing Rate and Curing Mechanism

It can be obtained from Table 1 that the hardness of the composite is gradually increased at 0 to 7 minutes. In these 7 minutes, the change of the hardness is essentially that the process of composites transforms to solid. The hardness is maintained at 2H from 7 minutes to 12 hours. According to the results, it indicates that the curing process of CL-20

Table 1. The change of hardness with time after UV-cuing for 3 minutes.

Time	1 min	3 min	5 min	7 min	1 h	5 h	12 h
Hardness	2B	2B	HB	2H	2H	2H	2H

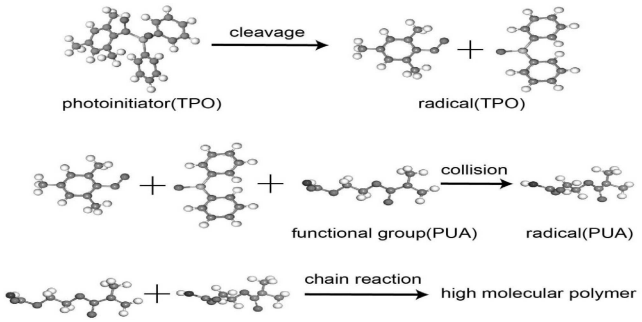

Figure 2. Diagram of UV-curing mechanism.

based UV-curing explosive ink could be completed within 7 minutes after UV-curing for 3 minutes. Compared with a functional sub-micro CL-20/GAP energetic composite ink developed by Wang et al [1] which were cured at a temperature of 40°C for 120 hours and compared with a new CL-20 explosive composite created by Daniel Stec et al [16] which dried within about 12–24 hours at ambient temperature, the curing productiveness of CL-20 based UV-curing explosive ink has qualitative improvement.

This is because under the ultraviolet light, the molecule of TPO transforms from the ground state to the excited triplet state, and rapidly cleaves to generate radicals in the excited triplet state. The radical (TPO) and the prepolymer (PUA) collide with each other, transferring energy to break the double bond of the molecule (PUA) to form a new radical, triggering the chain reaction. The radicals (PUA) and the large amount of C=C unsaturated double bonds in the prepolymer (PUA) rapidly polymerize to form an irregular, three-dimensional crosslinked polymer. The UV curable resin rapidly change from a liquid state to a solid state, thereby greatly reducing the curing time of the explosive ink [17].

3.2 Morphology Characterizations

It can be seen from Figure 3 (a) that the particle size of the raw CL-20 material is about 30 μm. Research shows that sub-micro CL-20 is more suitable for the preparation of explosive inks[18]. The particle size of CL-20 crystal is greatly reduced by a mechanochemical process. As shown in Figure 3 (b), for sub-micro CL-20, the particles have a good uniformity with the size ranging from 100 nm to 300 nm. Meanwhile, the sub-micro CL-20 particles are spherical in shape, and the roughness of the surface is also greatly reduced.

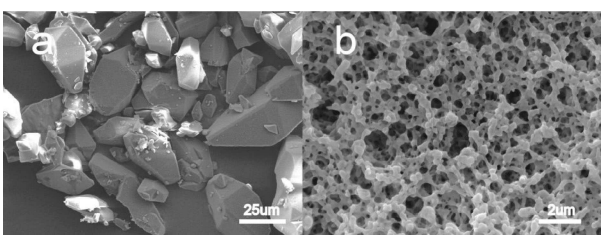

Figure 3. SEM photos of raw CL-20 (a) and sub-micro CL-20 (b).

As shown in Figure 4 (a, b), after UV-curing, the surface of the CL-20 based explosive composite is smooth and flat. But at higher magnification, there are still some small pores on the surface of the composite. The possible reason is that the air is filled after the ethanol volatilized. Observed from the cross section of the composite (Shown in Figure 4 (c) and 4 (d)), PUA undergoes a crosslinking reaction, and the CL-20 crystal particles are connected together by a binder to form a honeycomb structure. And the CL-20 particles are uniformly dispersed after the composites cured, and the agglomeration of explosive particles is not obvious.

3.3 XRD Characterization

The XRD test results of the raw CL-20, the sub-micro CL-20 and the CL-20 based composite are shown in Figure 5. The results show that the CL-20 based composite has corre-

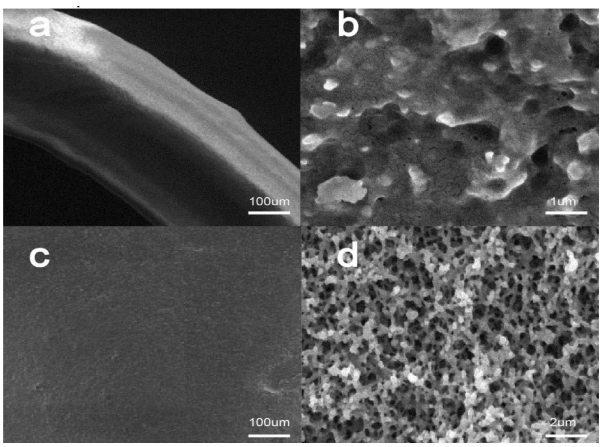

Figure 4. SEM images of surface (a, b) and cross section (c, d) of CL-20 based composite.

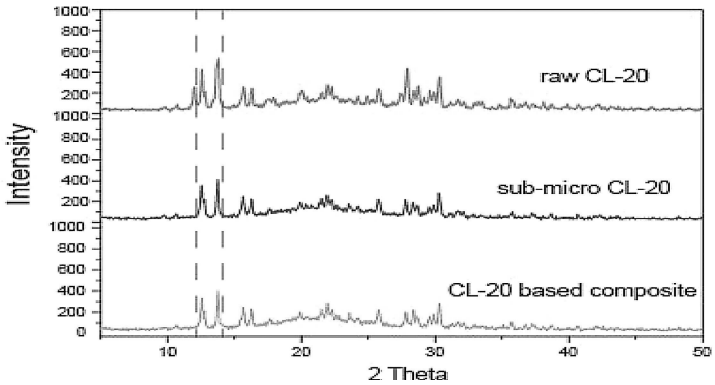

Figure 5. X-ray diffraction spectra of raw CL-20, sub-micro CL-20 and CL-20 based composite.

sponding characteristic peaks at diffraction angles (12.55°, 13.75° and 30.3°), which is in agreement with the raw CL-20 and sub-micro CL-20. These three diffraction angles correspond to the three crystal faces ((1 1 −1), (2 0 0) (2 0 −3)) of ε-CL-20. Therefore, DIW and UV-curing will not affect the crystal morphology of CL-20.

Meanwhile, it can be seen from Figure 5 that the intensity of the diffraction peaks for the three samples was different at the same diffraction angle. The intensity of the diffraction peak for the raw CL-20 is much greater than that of the sub-micro CL-20 and explosive composites. The intensity of the diffraction peaks for sub-micro CL-20 is also slightly stronger than the ink sample. This is because the intensity of the diffraction peaks decreases as the CL-20 particle size decreases. The agglomeration of sub-micro CL-20 may be the main reason why the diffraction peak of sub-micro CL-20 is slightly stronger than the composite.

3.4 Detonation Velocity and Critical Detonation Size

The critical detonation size was tested by the linear critical explosion thickness method. Figure 6 indicates that the value of explosion track is 97.4 mm. According reference [19], the critical size of the detonation is calculated to 0.078 mm. It means that the CL-20 based explosive composite can stably detonate more than 1×0.078 mm. It indicates that the formulation has a good application prospect in the initiating explosive devices. As shown in Figure 6, the detonation wave is detonated from deep to shallow along the groove after ignition and is extinguished at a certain distance from the end of the groove. As the charge depth decreasing, the trace of explosion gradually narrows. It indicates that the detonation energy is gradually weakened. There is no steep increase or steep decrease in energy, which further indicates that the composite can be reliably detonated under small-sized charging conditions.

It can be seen from Figure 7 and Table 2, the CL-20 based composite can be reliably and stably detonated in the micro-channel. The charge groove has obviously trace of explosion and deformation. And the average detonation velocity is

7357 $m\,s^{-1}$, when the average density of samples is 1.67 $g\,cm^{-3}$. The result show that the composite has higher molding density effect and less internal defects, and the explosion in the channel is stable.

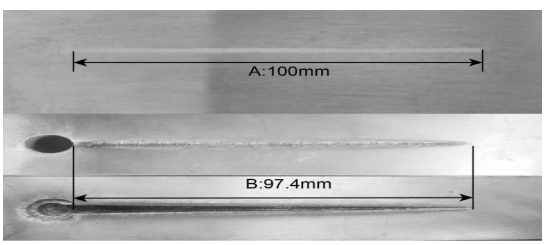

Figure 6. Comparison chart of CL-20 based composite before and after detonation.

Figure 7. Optical photograph of CL-20 based composite before and after detonation in the detonation velocity test.

Table 2. Propagation time and velocity of detonation between each pair of probe.

Samples	t_1-t_0	t_2-t_1	t_3-t_2	Average
Time	2638 ns	4222 ns	4161 ns	
Detonation velocity		7305 $m\,s^{-1}$	7409 $m\,s^{-1}$	7357 $m\,s^{-1}$

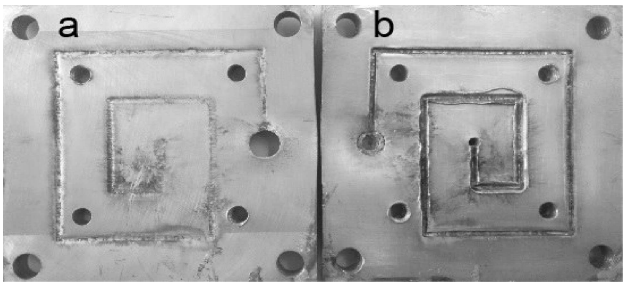

Figure 8. Picture of CL-20 based composite after detonation in the detonation performance test for Continuous corner of 90°.

3.5 Detonation Performance Test for Continuous Corner of 90°

As can be seen from Figure 8, CL-20 based UV-curing composite can be reliably detonated in a network channel of the explosion. The results show that the detonation wave formed by the detonation of CL-20 based composite can successfully pass through continuous corner of 90°. Meanwhile, after the explosion, the closer the network channel of the explosion is to the center of the substrate, the more obvious the widening of the explosion trace (shown in Figure 8 (b)). The reason of this phenomenon may be that the constraints of the explosion network channel in the center of substrate are greater than the constraints of the periphery. During the detonation wave propagation, the external detonation wave loses much more energy than the center.

3.6 Impact Sensitivity Analysis

It can be seen from the Table 3 that the H_{50} value of the sub-micro CL-20 is 21.2 cm higher than the value of the raw CL-20, indicating that the impact sensitivity of the sub-micro CL-20 is greatly reduced. By comparing the raw CL-20 with the CL-20 based composite, it is found that the H_{50} value is increased from 13.2 cm to 40.6 cm, which increases 3.07 times. This is because that CL-20 particles in the composite has a smaller particle size, a larger specific surface area, a smoother surface, less edge angle, which are more difficult to form hot spots [20]. Therefore, the sensitivity of composites is lowered. In addition, the binder wrapped on the surface of the CL-20 particles, reduces the friction between the particles, and plays a certain buffering effect on the external impact, then greatly reduces the probability of hot spots formation.

Table 3. Impact sensitivity of raw CL-20, sub-micro CL-20 and CL-20 based composites.

Sample	Impact Sensitivity[H_{50} ($\pm$S)] cm^{-1}		
	Experiment 1	Experiment 2	Average
Raw CL-20	13.2 $\pm$ (1.0)	12.8 $\pm$ (0.9)	13.0
Sub-micro CL-20	33.2 $\pm$ (0.8)	35.2 $\pm$ (0.9)	34.2
CL-20 base composite	40.3 $\pm$ (1.0)	40.9 $\pm$ (0.9)	40.6

4 Conclusions

In this work, a UV curable resin (PUA) and an explosive (CL-20) were engineered to prepare the CL-20 based UV-curing explosive ink. The explosive ink was loaded under micro-size devices using UV-curing and DIW technology, which can greatly improves the curing efficiency. The results show that the composite has a rapid curing speed, less internal defects, low impact sensitivity, a critical detonation size of 0.078 mm, and a detonation velocity of 7357 $m\,s^{-1}$. This study may further expand the preparation of energetic composites. What's more, the excellent properties of the composite make it possible to be applied in the micro-detonation train.

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References

[1] D. Wang, B. Zheng, C. Guo, B. Gao, J. Wang, G. Yang, H. Huang, F. Nie, Formulation and Performance of Functional Sub-Micro CL-20-based Energetic Polymer Composite Ink for Direct-Write Assembly, *RSC Adv.* **2016**, *6*, 112325–112331.

[2] Q. Zeng, B. Li, M. Li, X. Wu, A Miniature Device for Shock Initiation of Hexanitrostilbene by High-Speed Flyer, *Propellants Explos. Pyrotech.* **2016**, *41*, 864–869.

[3] L. Liu, Y. Xue, R. Xie, X. Ren, K. Li, Study on Performance of Silicon Ignitiors based on Energetic Chip of Porous Silicon. MATEC Web of Conferences, EDP Sciences. **2017**.

[4] B. Bao, N. Yan, W. Geng, C. Li, Simulation and Experiment Investi-gation on Structural Design and Reinforcement of Pyrotechnical Sliding micro-actuators, *Analog Integr Circ Sig Process.* **2016**, *88*, 431–441.

[5] CESARANO III J, SEGALMAN R, CALVERT P, Robocasting Provides Moldless Fabrication from Slurry Deposition. *Ceram. Ind.*, **1998**, *148*, 94–102.

[6] B. E. Fuchs, A. Wilson, P. Cook, D. Stec III, Development, Performance and Use of Direct Write Explosive Inks. Proc. 14th Int. Det. Symp, Idaho, **2010**.

[7] A. Ihen, W. Lee, B. Fuchs, A. Petrock, P. Samuels, V. Stepanov, A. D. Stasio, Inkjet-Printing of Nanocomposite High-Explosive Materials for Direct Write Fuzing. 54th Fuze Conf., Kansas City, MO, May. **2010**, 11–13.

[8] Y. Yao, L. Wu, Y. Tang, B. Cheng, R. Shen, Y. Ye, Y. Hu, P. Zhu, Direct Writing Rule of Nano CL-20 Explosive Energetic Ink. *Chin. J. Explos. Propellants* **2016**, *39*, 39–42.

[9] J. Wang, C. Xu, C. An, C. Song, B. Liu, B. Wu. X. Geng, Preparation and Properties of CL-20 Based Composite by Direct Ink Writing. *Propellants Explos. Pyrotech.* **2017**, *42*, 1139–1142.

[10] Q. Li, C. An, X. Han, C. Xu, C. Song, B. Ye, B. Wu, J. Wang, CL-20 Based Explosive Ink of Emulsion Binder System for Direct Ink Writing. *Propellants Explos. Pyrotech.* **2018**, *43*, 1–6.
[11] C. Xu, C. An, Y. He, Y. Zhang, Q. Li, J. Wang, Direct Ink Writing of DNTF Based Composite with High Performance. *Propellants Explos. Pyrotech.* **2018**, *43*, 754–758.
[12] C. Xu, C. An, Q. Li, S. Xu, S. Wang, H. Guo, J. Wang, Preparation and Performance of Pentaerythrite Tetranitrate-Based Composites by Direct Ink Writing. *Propellants Explos. Pyrotech.* **2018**, *43*, 1149–1156.
[13] Christian Decker, Kinetic Study and New Applications of UV Radiation Curing. *Macromol. Rapid Commun.* **2002**. *23*, 1067–1093.
[14] C. Kong, Y. Wei, Z. Zhou, Application of Detonation Physics. Vol. 4, National Defense Industry Press, Beijing, **2000**, pp. 224–237.
[15] S. Jin, Q. Song, Explosive Theory. Vol. 6, Northwestern Polytechnical University Press, Xian, **2010**, pp.260–278.
[16] D. Stec III, A. Wilson, B. E. Fuchs, N. Mehta, P. Cook, High Explosive Fills for MEMS Devices. US patent, 8636861 B1, The United States of America as represented by the Secretary of the Army, Washington, DC, USA . **2014**.
[17] Xiao. P, J. Lalevée, Allonas. X, Fouassier. J. P, Ley. C, El-Roz. M, Shi. S. Q, Nie. J, Photoinitiation Mechanism of Free Radical Photopolymerization in the Presence of Cyclic Acetals and Related Compounds. *J. Polym. Sci. Part A* **2010**, *48*, 5758–5766.
[18] C. Song, C. An, B. Ye, Q. Li, S. Wang, J. Wang, Influence of Particle Size on Critical Detonation Performance of CL-20 Explosives Ink. *Chin. J. Energet. Mater.* **2018**, *26*, 1014–1018.
[19] C. Xu, C. An, Y. Long, Q. Li, H. Guo, S. Wang, J. Wang, Inkjet Printing of Energetic Composites With High Density. *RSC Adv.* **2018**, *8*, 35863–35869.
[20] A. M. Mellor, D. A. Wiegand, K. B. Isom, Hot Spot Histories in Energetic Materials, *Combust. Flame* **1995**, *101*, 26.

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