Recent Progress on the Preparation Methods and Properties of Nano-energetic Composites

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Abstract. Nano-energetic composites offer the potential of extremely high rates of heat release, substantial combustion efficiency, regulating energy release efficiency and pronounced decrease of sensitivity. In this paper, in order to explore recent progress in nano-energetic composites, a review on the preparation method including electrospray method, sol-gel method, spray drying method, solution method and some other methods were investigated and compared. What’s more, nano-energetic composites and their properties and sensitivity were summarized. Finally, based on research in recent five years, the development direction and problems that need attention of nano-energetic composites were proposed.

1. Introduction:
In the past few decades, there has been substantial progress in military science and technology. With the continuous changes in the form of international operations and the development of new weapons and equipment, the demands on energetic materials(EMs) is becoming increasingly greater, including higher energy density, higher reactivity, higher burning rate, smaller critical diameter and low sensitivity.

Energy materials can be divided into homogeneous and heterogeneous (composites) materials depending on how the fuel and oxidant are connected [1]. However, the energy density of homogeneous materials can only reach half of the composites. As the development of advanced assembly technology, the EMs composites which enjoy high level of energy density have tailored reactivity, sensitivity and reliability [2, 3]. Therefore, researchers devote to design and synthesis new nano-energetic composites to improve the energy output, reaction completeness and stability. Usually, nano-composites consist of a nano-matrix with energetic nanoparticles imbedding inside it. Because of the inert matrix, the nanocomposite presents very low sensitivities, although the energy performance was weakened.

This paper focus on the preparation method: electrospray method, sol-gel method, spray drying method, solution method and some other methods and properties end sensitivities of nano-energetic composites.
2. Preparation method of nano energetic compound

2.1. Electrospray method
This method can not only transform molecules in solution into gas phase ions, but also generate monodispersed aerosols and small particles with controllable particle size, which have been used a lot in the preparation of nanomaterials and showing strong advantages. By adjusting the voltage and flow rate, liquid streamlines of different diameters can be generated to generate particles of different particle sizes, with particle sizes ranging from tens of nanometers to hundreds of microns. And the generated particles present a good monodispersed state with narrow particle size distribution.

Yan et al.[4] have developed microspheres RDX integrated with nano-Al (nAl) particles and Viton through a two-solvent strategy. The morphology shows that the electrosprayed microspheres were hollow spheres containing well-dispersed RDX and RDX nano-crystals adhere tightly on both sides of the nAl@Viton skeletons. Experimental results showed that the laser ignition delay of the composites is shorter and the combustion flame is more vigorous than the physical mixture, which benefitted from the characteristic structure and synergistic effects of the components. The results show that the nAl@RDX@Viton(shown in figure 1) composites exhibits a shorter laser ignition delay with a violent combustion flame than that of the physically misixed nAl@RDX@Viton. It may be due to the characteristic structure and the synergistic effects of each component.

![Figure 1. Schematic diagram for the preparation of nAl@RDX@Viton composites.](image)

Si@AP/NC with content of Si (40%, 60%, and 80%) were designed and prepared by Zue et al.[5] successfully. The use of nano-Si improves the thermal conductivity of the system and improves the thermal performance of the fuel system.

2.2. Sol-gel method
Sol-gel method can also been called as sol–gel freezing–drying method. It is one of the methods for preparing materials under mild conditions. Since the prepared solid material have the high purity, good dispersibility, high specific surface area, rich pore structure and granular controllable degree, the sol-gel method are widely used in carrier and catalyst and has arose much attention in recent years, what’s more, this method has been used increasingly more in nano-energetics area.

For example, SiO₂ xerogel matrix has large specific surface area and superior impact resistance. Based on this, Cui et al.[6] taken SiO₂ as a template to synthesize HMX/SiO₂ nanocomposite by sol-gel method(shown in figure 1). The HMX was loaded up to 80.0 wt.% and the surface area value of HMX/SiO₂ can reach as high as 42.5 m²·g⁻¹. The results showed that the particle size of the ignition composition containing HMX/SiO₂ is smaller and more uniform than the normal type. The schematic diagram for the
preparation of HMX/SiO$_2$ are shown in figure 2.

![Figure 2. Schematic diagram for the preparation of HMX/SiO$_2$ nanocomposite with sol-gel method.](image)

Jin et al. [7] prepared NC/RDX/AP nano-composite energetic material which has numerous pores with nanometer scale and the mean grain size of RDX in about 100 nm. Wang et al.[8] use sol-gel-supercritical method to fabricate a novel energetic HMX/NC (HMX/Nitrocellulose) nanocomposites in which nano-HMX imbedded in nano-NC matrix and studied the friction, impact, and thermal sensitivity properties. The NC nanoparticles was 30 nm cross-linked to form a network structure. The results show that HMX/NC nanocomposites have high reactivity and low sensitivity. Compared with raw HMX and NC, the decomposition temperature, activation energy and activation heat are lower. RDX/AP nano-composites are produced by Sajjadi[9]. Chen et al.[10] successfully prepared RDX/BAMO-THF (1,3,5-trinitro-1,3,5-triazine/3,3-bis (azidomethyl) oxetane-tetrahydrofuran copolymer) energetic nanocomposites by a sol–gel freezing–drying method(shown in figure 3). The RDX particles were successfully The results showed the RDX particles were embedded in the BAMO-THF gel and the BAMO-THF gel matrix could prevent the aggragation of RDX particles effectively. The results of impact sensitivity showed that the sensitivity of RDX/BAMO-THF nanocomposites decrease with increasing RDX content, but still more stable than raw RDX.

![Figure 3. SEM images of BAMO-THF (a), RDX0.20 (b), RDX0.30 (c) and RDX0.40 (d).](image)

Chen et al.[11] also use the same method to prepare CL-20/BAMO-THF(shown in figure 4) energetic nanocomposites. Compared with raw CL-20, the morphologies of CL-20 changed from prismatic to spherical and the average particle sizes of CL-20 in composites were decreased to nano scale. The impact
sensitivity results show that CL-20/BAMO-THF nanocomposites possess low sensitivity. What’s more, the thermolysis activity was lower. From the results of recent studies, the energetic nanocomposites can be a very promising ingredient for practical use, which may rich the application of nano-energetic composites.

**Figure 4.** SEM images (a) CL-200.20, (b) CL-200.60

The spray drying method is a facile, inexpensive and scalable method that has been adopted widely in the micro-sized and nano-sized spherical material, which have the advantages to prepare microspheres with smaller particle size and higher spheroidization. Meanwhile, the process parameters are easier to adjust and the solvent volatile quickly and the nucleation rate is high.

An et al. [12] used spray drying method to prepare cocrystals of HMX and CL-20 and studied the impact and friction sensitivity. Results show that, particles were spherical in shape and 0.5-5 μm in size and formed aggregates of numerous tiny plate-like cocrystals, whereas the thicknesses of CL-20/HMX cocrystals (shown in figure 5) were below 100 nm. Compared with HMX, after cocrystals formed, the impact and friction sensitivities decreased significantly. The drop height increased by 141% and friction probability reduced by about 20%.

**Figure 5.** SEM images of CL-20/HMX cocrystal explosive.

Song et al.[13] introduced the preparation of spherical shape phloroglucinol-Fe and CL-20 (Fe-Ph/Cl-by spray drying technology. By spray drying method, the decomposition temperature of CL-20 is advanced by 25℃. And the activation energy of the composite Fe-Ph/Cl-20 reduce by 25.7%. The stable composites which consist of Cu(en)₂NO₃ (ethylenediamine, en) have also been synthesized by song’s team[14], the results show that composite of Cu-en and CL-20, AP, RDX or HMX have benefit on the contact area between the catalyst and the materials thus increasing the reaction rate. The composite prepared by spray drying have good catalytic effect and can reduce the decomposition temperature of AP by 95℃.

Some scientists introducing nitrocellulose(NC) into the energetic compound, which can result in a three-dimensional network structure between the main explosive and the binder, thereby improving the energy output and mechanical characteristics of the system. Shi et al.[15] produced pure HMX/NC
nanocomposites (shown in figure 6.) by spray drying. The impact sensitivity of HMX/NC were lower than that of the HMX and the burning rate of the propellants (nano-composites-based) was higher than HMX, consequently, the HMX/NC nano-composites has great potential in the propellant and the fuel additives.

![Figure 6. HMX/NC nanocomposites at different magnifications.](image)

2.3. Solution method

Solution method can be divided into solvent/nonsolvent method and solution impregnation method. The solvent/non-solvent method is a method to mix other substances into solution, when the solution is allowed to reach a supersaturated state and crystals are precipitated. It does not require temperature operation or evaporation operation, and does not need to add the surface active agent. Therefore, this method are widely used. However, it also has disadvantages. When preparing energetic composites, the particle surface morphology and the particle size are relatively difficult to control, and it is not easy to achieve the design of energetic composites.

Using the solution impregnation method, Bian et.al [16] introduced a novel cellulose aerogel into RDX to get cellulose/RDX composite aerogel spheres (shown in figure 7). The diameter of the sphere is 1.5 mm with three-dimensional cross-linked network structure. Compared with the raw RDX, the impact sensitivity of the aerogel sphere composites were greatly reduced. The results obtained show that H50 was larger than 85 cm.

![Figure 7. Appearance and SEM image of cellulose/RDX composite aerogel.](image)

Coating method can also be divided into solution method. In CL-20-based composites, polymer coating plays an efficient role in enhancing the thermal resistance and mechanical and of explosive crystals, and graphite is a helpful ingredient used in composites. Wang et al. [17] adopted the graphene (rGO) and carbon nanotube (CNT) as conductive fillers to improve the thermal performance of CL-20-based composites. The impact sensitivity of samples are shown in the figure. After coated with rGO and CNT, the sensitivity decreased significantly. The SEM images are shown in figure 8.
The result show that CL-20 embedded nano composite exhibits a good burning propertiy with a steady and stability while reducing mechanical sensitivity. Zhu et al.[21] prepared CuO/Al/CL-20 nano-energetic nano-composites. This method can greatly reduce the agglomeration between nanoparticles, and has high graphite materials (GIMs) off into graphene materials (GEMs) get nanoscale grain size CL-20/GEMs nano-composites. Besides, there are some other method that can produce nano-composites. For example, in aqueous suspension of CL-20, Ye et al.[20] used a scalable ball milling technique which involves exfoliating graphite materials (GIMs) off into graphene materials (GEMs) get nanoscale grain size CL-20/GEMs nano-composites. This method can greatly reduce the agglomeration between nanoparticles, and has high stability while reducing mechanical sensitivity. Zhu et al.[21] prepared CuO/Al/CL-20 nano-energetic composite by combination of magnetron sputtering and recrystallization method. Firstly, the CuO/Al nanowire arrays were produced by magnetron sputtering method, then the CL-20 recrystallize on the top. The result show that CL-20 embedded nano composite exhibits a good burning property with a steady and violent combustion flame. The SEM images of samples of CL-20/rGOs and the abrication process are shown in figure 10 and figure 11.

![Figure 8. SEM image CL-20/CNT; and f CL-20/rGO + CNT.](image8)

![Figure 9. SEM images of RDX/PMMA nano-composites.](image9)

2.4. Other methods

Besides, there are some other method that can produce nano-composites. For example, in aqueous suspension of CL-20, Ye et al.[20] used a scalable ball milling technique which involves exfoliating graphite materials (GIMs) off into graphene materials (GEMs) get nanoscale grain size CL-20/GEMs nano-composites. This method can greatly reduce the agglomeration between nanoparticles, and has high stability while reducing mechanical sensitivity. Zhu et al.[21] prepared CuO/Al/CL-20 nano-energetic composite by combination of magnetron sputtering and recrystallization method. Firstly, the CuO/Al nanowire arrays were produced by magnetron sputtering method, then the CL-20 recrystallize on the top. The result show that CL-20 embedded nano composite exhibits a good burning property with a steady and violent combustion flame. The SEM images of samples of CL-20/rGOs and the abrication process are shown in figure 10 and figure 11.

![Figure 10. SEM images of samples of CL-20/rGO5.](image10)
3. Properties of nano-energetic composites

At present, researchers are devoting to reduce the sensitivity of energetic materials by common methods such as ultrafine processing, spheroidization, and composite technology. However, only one or two of the above ways have been reported, and the obtained sensitivity was unsatisfactory.

Zhu et al. [22] tried to further reduce the sensitivity of CL-20 by combining the three method above. The composite CL-20/PNCB (P-nitrochlorobenzene) was precipitated from the interface between the interface of the ethyl acetate and water and the $H_{50}$ was improved to 63 cm, which can greatly improve the sensitivity of CL-20.

In order to show the sensitivities of nano-composite clearly, the shock sensitivities characterized by $H_{50}$ was summarize in figure 13.

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**Figure 11.** (a) Fabrication process of hybrid CuO/Al/CL-20 nanoenergetic composite arrays (b) SEM of CuO/Al/CL-20 composite.

**Figure 12.** Micro-sized spherical CL-20/PNCB composite and EDX maps of the C, N, Cl distribution.

**Figure 13.** $H_{50}$ of the nano-energy composites summarized.
As is shown in the graph, nano-energetic compounds can reduce the sensitivity of energetic materials to varying degrees, and have a significant desensitizing effect.

4. Conclusions
This paper briefly classifies and summarizes the preparation methods and properties of nano-energetic composites in the past five years and briefly discuss the preparation method including electrospray method, sol-gel method, spray drying method, solution method and some other methods. Nano-energetic composites have been more and more studied by researchers in recent years. We hope that the research of nano-energetic composites should pay more attention to problems in the three following aspects.

1. Strengthen the research on the basic characteristics of nano-energy composite materials, pay attention to the improvement of the safety performance of materials and design materials with higher energy and maintaining the safety at the same time.

2. At the micro and nano scale, attach importance to the surface interface and reaction mechanism of materials and explosive components. Use simulation methods to design optimal parameters suitable for nano-energetic composite materials to improve the overall performance of the system.

3. Through the method of material modification and material combination, the reaction energy and safety of the material system are further improved. While focusing on scientific research, it also of great significance on the material's scale-up production capacity, so that nano-energy composite materials can be used in explosives and propellants systems.

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