

# Research Progress of Nano Copper Azide

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## Abstract

The development trend of miniaturization, chipization, integration, and intelligence of new energetic devices has put forward higher requirements for primary explosives, and the toxicity of lead-containing initiating explosives has also caused increasing concerns. Nano copper azide, due to its green and high-energy characteristics, has attracted increasing interest from researchers in recent years. The research progress of Nano copper azide energetic materials is summarized from the design and preparation of composite energetic materials, and the analysis of sensitivity changes. On this basis, the key points to realize its application prospects are discussed: Develop the preparation method of carbon material modification and the combination of processing and forming to prepare new composite materials to make up for their overly sensitive defects, while giving full play to their advantages of high energy density. By comparing the existing research progress of Nano copper azide, we can understand its performance parameters more systematically, and guide the further application of Nano copper azide.

## Keywords

Nano Copper Azide, Energetic Material, Primary Explosives

## 1. Introduction

With the development of weapons and equipment in the direction of miniaturization, intelligence, and integration, traditional initiating devices cannot meet the needs of micro-weapon devices due to their large volume, large charge, and large input energy required [1]. Therefore, in recent years, miniature-initiating devices have quickly become the main development direction. As the core component of the initiating device, primary explosives can explode and detonate the next level of charge under slight stimuli, such as impact, acupuncture, static electricity, flame, etc. [2]. The development of micro-detonating devices has put forward higher requirements on the detonation ability, safety performance, and

charging method of primary explosives [3]. Traditional primary explosives, such as the combination of lead azide and lead styphnate, cannot meet the needs of miniature detonators due to problems, such as environmental unfriendliness and weak detonating ability [4]. Researchers have also developed a large number of high-energy primary explosives, but they cannot be used in micro detonators due to their extremely high sensitivity and the production process cannot match the micro detonators [5]. Nano copper azide has attracted wide interest from researchers due to its excellent initiating ability, environmental friendliness, and the compatibility of the preparation process with micro-initiating devices [6]. However, the electrostatic sensitivity of Nano copper azide is extremely high, and it is difficult to process and shape, which has always restricted its application in miniature-initiating devices.

Based on the above problems, a lot of pioneering work has been reported. In order to improve the sensitivity of Nano copper azide, the researchers used porous carbon material as the skeleton and covered CA inside the skeleton, which effectively improved its electrostatic sensitivity [7] [8]. In the forming of Nano copper azide, a porous copper film prepared with hydrogen bubbles as a template was used as a precursor material, and the Nano copper azide film was prepared after an azidation reaction [9]. Furthermore, the researchers also developed a method for the electrochemical preparation of Nano copper azide, and the Nano copper azide film was prepared by the liquid-solid reaction [10]. However, each research method has its own advantages and disadvantages.

At this stage, the research on the modification of Nano copper azide is still a long way from practical application. In order to summarize the research progress of nanocrystalline copper azide energetic materials and promote the realization of its potential application prospects. In this paper, the preparation methods of Nano copper azide in recent years, the latest research progress in the modification methods of doped carbon materials, and the processing and forming methods of Nano copper azide are reviewed. The development direction and wide application prospects of modified Nano copper azide as a high-energy-density green and environmentally friendly primary explosive are prospected.

## 2. Preparation and Modification of Nano Copper Azide

### 2.1. Research on the Preparation of Nano Copper Azide

Nano copper azide has the advantages of simple preparation, economy, and excellent initiation performance, and becomes one of the suitable choices that are expected to replace lead azide. Compared with the serious environmental pollution caused by lead and mercury and the harm to human health, copper is relatively green and environmentally friendly. In recent years, in order to meet the needs of micro and small pyrotechnics, researchers have conducted a lot of research on the preparation and theoretical calculation of Nano copper azide.

In 2002, Ayazi's group used porous copper as the base material to prepare a micro-nano Nano copper azide initiating charge through *in-situ* azide reaction

and applied it to MEMS switches [11]. In 2005, Choi *et al.* used Nano copper azide as a precursor to slowly pyrolyze in a solvent environment and a relatively low temperature, and at the same time added a crystal form control agent to prepare copper nitride nanocrystals. It provides a new idea for the preparation and application of Nano copper azide [12]. Since 2007, Youngme *et al.* tried to apply Nano copper azide compounds as detonators to micro detonators so that the microcharge detonation sequence was regarded as an important research direction [13].

In 2009 [14], the U.S. naval research institute researched Nano copper azide from basic preparation to weapon application. For the first time, Nano copper azide was installed in a micro detonator and applied to an ammunition fuze. In 2012, Zhang Rui and others used anodic aluminum oxide as a template to successfully prepare copper elemental nanowires for the first time, and then prepared Nano copper azide nanowire arrays by gas-solid *in-situ* synthesis, and studied their thermodynamic properties. In the same year, Xie Ruizhen and others carried out technical research on the filling of Nano copper azide in micro-sizes and mounted Nano copper azide on silicon-based microdetonators for ignition sensitivity test and output power test. Research results show that the detonator requires low ignition energy and can successfully detonate CL-20.

In 2014, Zeng *et al.* designed an electro-acupuncture test device to determine the detonation velocity of Nano copper azide in the micro-flyer initiation system [15]. In 2015, Li *et al.* of Nanjing University of Science and Technology used the *in-situ* formation of a porous copper film on a titanium wafer, and then prepared a three-dimensional porous Nano copper azide by *in-situ* reaction, and studied the formation process of Nano copper azide. The results show that the gas-solid reaction between the copper element and azido acid preferentially produces  $\text{CuN}_3$ , and then  $\text{Cu}(\text{N}_3)_2$  [16]. In 2015, Zhang of the Shaanxi Institute of Applied Physical Chemistry used the same method to prepare three-dimensional porous Nano copper azide and used this Nano copper azide to detonate hexanitro heteroisowootzane (CL-20).

In 2018 [9], Yu *et al.* used PS as a template to control the density or porosity of the nanoporous copper film by adjusting the load and particle size of PS and prepared Nano copper azide and the density of Nano copper azide through the original azide. It is  $1.005 \text{ g}\cdot\text{cm}^{-3}$ .

In 2018 [17], Zhang *et al.* added the nano-copper powder to a binder of cetyltrimethylammonium bromide (CTAB) with a different blowing agent to obtain a three-dimensional porous precursor ink. After 24 hours of *in-situ* gas solidification, the copper precursor ink is completely converted to Nano copper azide after the azide reacts. An explosive device was designed to verify the explosive performance of Nano copper azide by direct writing, and the results show that it can reliably cause the CL-20 to completely explode.

In 2019 [10], Yu *et al.* developed a safe and effective (<40 min) liquid-solid strategy to manufacture CA membranes. Using CuO nanorods (NRs) arrays as

precursors, a nested CA film with excellent energy performance and excellent electrostatic stability can be generated *in-situ* in  $\text{NaN}_3$  solution by electrically assisted azide method. The resulting CA film electrostatic sensitivity (E50) value (0.81 mJ) is 16 times that of the original CA powder (0.05 mJ). This is not only due to the unique nest structure of the CA film, but also its uniform *in-situ* doping of CuO. Although the new synthesis method has greatly promoted the research of Nano copper azide, the preparation of Nano copper azide by liquid-solid reaction, on the one hand, has a large amount of unreacted copper oxide which affects its initiation performance, and on the other hand, the prepared azide the chemical copper film has high sensitivity, and how to install it in a miniature-initiating device is still a problem that needs to be solved.

It can be seen from the above literature that in recent years, the preparation of Nano copper azide has been prepared by using porous copper/copper mold as the precursor and using *in-situ* azidation reaction. This is because the sensitivity of Nano copper azide is extremely high. The preparation of sodium azide and copper nitrate under the condition of the solution will cause great safety hazards. Besides, the high sensitivity of Nano copper azide also makes it impossible to charge by conventional pressing. The use of porous copper for *in-situ* azide reaction can avoid the dangerous step of pressing. However, using porous copper as a raw material will produce a large number of by-products such as cuprous azide, copper oxide, copper, etc., which cannot guarantee the charge density and detonation ability, and there are potential safety hazards such as an electrostatic explosion. Therefore, it is necessary to develop a modification method of Nano copper azide and conduct research on modification of reducing sensitivity.

## 2.2. Study on the Modification of Nano Copper Azide

In order to improve the safety performance of primary explosives, researchers mainly used the following methods to modify primary explosives: adding anti-static agents and crystal shape control agents, physically doped carbon materials, and template carbonization doped carbon materials.

### 2.2.1. Add Antistatic Agent and Crystal Shape Control Agent for Modification

In 2005, Choi *et al.* [12] used Nano copper azide as a precursor, slowly pyrolyzed it in a solvent environment and a relatively low temperature, and added a crystal form control agent to prepare Nano copper azide nanocrystals. The preparation and application of copper nitride provide new ideas. In 2006, Talawar *et al.* studied the effect of polyvinylpyrrolidone (PVP) coated detonator on its electrostatic spark sensitivity. After coating, the electrostatic spark sensitivity of lead azide is significantly reduced, and the change of silver azide is not large. PVP coating makes 5-nitrotetrazolium mercury more sensitive to electrostatic stimulation. Therefore, it is resistant to different agents. The effects of electrostatic agents are very different [18].

In 2013 [19], Zhou *et al.* used four surfactants to improve the antistatic ability

of lead phenate and lead azide. The results show that lauryl dimethylamine betaine (BS-12) can significantly reduce the static accumulation of LS and LA. The electrostatic sensitivity, 5 s delayed explosion temperature, and the thermal decomposition curve of the compound was measured, and the selected products were studied by scanning electron microscope (SEM). The results show that for LS, the performance of the product with additives is less affected, while for LA, the sensitivity of the product in the presence of surfactants is significantly reduced.

It can be seen from the literature that many researchers have added dextrin, carboxymethyl cellulose, etc. to develop many new types of explosives during the preparation process of explosives. This is because the preparation methods of lead azide/lead styphnate are mainly liquid-liquid reactions (reaction of lead nitrate and sodium azide solution). Many crystal shape control agents are added in the preparation process to control the crystal shape of the detonator and adjust its sensitivity and flowability.

### 2.2.2. Physically Doped Carbon Materials for Modification

In 2010 [20], Li prepared graphene nanosheets/lead azide composites by adding graphene nanosheets to the reaction solution. Similarly, he also doped graphene during the preparation of lead styphnate to prepare graphene nanosheets/lead styphnate composites [21] [22]. Graphene is an excellent conductive material [58 - 68]. In the case of uneven physical mixing, graphene effectively reduces the electrostatic sensitivity of primary explosives.

In 2010 [23], Pelletier *et al.* used an anodized aluminum oxide template to prepare multi-walled carbon nanotubes (MWCNTs) with large diameters (200 nm) by chemical vapor deposition and used CuO sol by vacuum impregnation method. Pouring into it, after hydrogen thermal reduction and azide, the carbon nanotube-coated Nano copper azide nanocomposite material was prepared. It is confirmed by the characterization that only part of the Cu filled in MWCNTs has undergone azide reaction. Due to the selected vacuum immersion sol method and the limitations of MWCNTs, such as limited loading and insufficient specific surface area, the tube is not filled with CuO, and there is still CuO remaining in MWCNTs after hydrogen thermal reduction. It was confirmed that the sample can be successfully ignited.

In 2014 [24], Liu *et al.* of Nanjing University of Science and Technology used the experimental method of Pelletier *et al.* to suction and filter the nano CuO prepared by the direct precipitation method into the AAO template and use the chemical vapor deposition method to prepare aligned carbon nanotubes to obtain Cu@CNTs nanomaterials, and then generate  $\text{Cu}(\text{N}_3)_2$ @CNTs through azide reaction. The obtained samples are characterized. The results show that: due to insufficient specific surface area and porosity, only a small amount of Cu nanotubes filled in CNTs has azide. However, the research results have laid a certain experimental foundation for further research and development of new nano-energetic materials.

It can be seen from comprehensive literature that carbon nanotubes and graphene have excellent electrical conductivity and can be used as a conductive agent for explosives to reduce the impact of static electricity on them. However, the preparation of the initial medicament by the physical mixing method has problems such as poor sample uniformity, high cost, and high risk in the preparation process. Some unreacted detonator particles will also reduce the detonator performance of the overall detonator. Therefore, a method of using carbon-containing templates for carbonization to obtain a metal-porous carbon composite material, and then preparing a detonator through *in-situ* azide reaction has emerged.

### 2.2.3. Template Carbonization of Doped Carbon Materials for Modification

In 2015, copper phthalate was used as the precursor to prepare a carbon-based Nano copper azide interspersed composite with suitable sensitivity and good energy output after carbonization and azidation for the first time, with uniform element distribution. The electrostatic sensitivity of carbon-based NANO copper azide is 1.6 mJ, the flame sensitivity is 42 cm, and the limit charge of detonating hexogen is 10 mg [25].

In 2018, a novel, green and simple strategy was developed: using low-cost cellulose derivatives as raw materials, through carbonization and azide synthesis of Nano copper azide-composite, in which nano-scale azide the copper oxide is evenly distributed in the porous carbon framework. Detailed characterization and control experiments show that this excellent performance originates from the excellent conductivity of the nano-scale porous carbon cage. Due to the advantageous unique structure, the prepared mixture exhibits a low electrostatic sensitivity of 1.06 mJ. Also, the ignition ability is high, and the flame sensitivity can reach 47 cm.

In the same year, Yu *et al.* [9] prepared a copper nanowire/reduced graphene oxide composite material by a simple one-pot hydrothermal method. The prepared copper nanowire/reduced graphene oxide composite material is then subjected to a gas-solid phase azidation reaction to obtain a Nano copper azide/reduced graphene oxide composite energetic material. The exothermic reaction peak temperature of this new type of composite energetic material is 189.7°C, and the exothermic amount is about 1521.5 J·g<sup>-1</sup>. When the content of reduced graphene oxide is 15%, its 50% electrostatic ignition energy is 0.92 mJ.

In 2020 [6], new copper thiolate cluster-assembled material (Cu<sub>12</sub>bpy) functions as a precursor to prepare Nano copper azide hybrids (CA-HPCH), which outperform other reported counterparts with high CA contents (89.43%), remarkable flame ignition ability ( $H_{50} \geq 60$  cm) and good electrostatic safety ( $E_{50} = 1.1$  mJ). The micro-initiating device fabricated by CA-HPCH exhibited an ultrafast energy-release rate (7.0 μs) and extremely low input ignition energy (0.106 mJ).

### 2.2.4. Template Carbonization of Doped Carbon Materials for Modification

The processing and shaping of Nano copper azide during the modification process

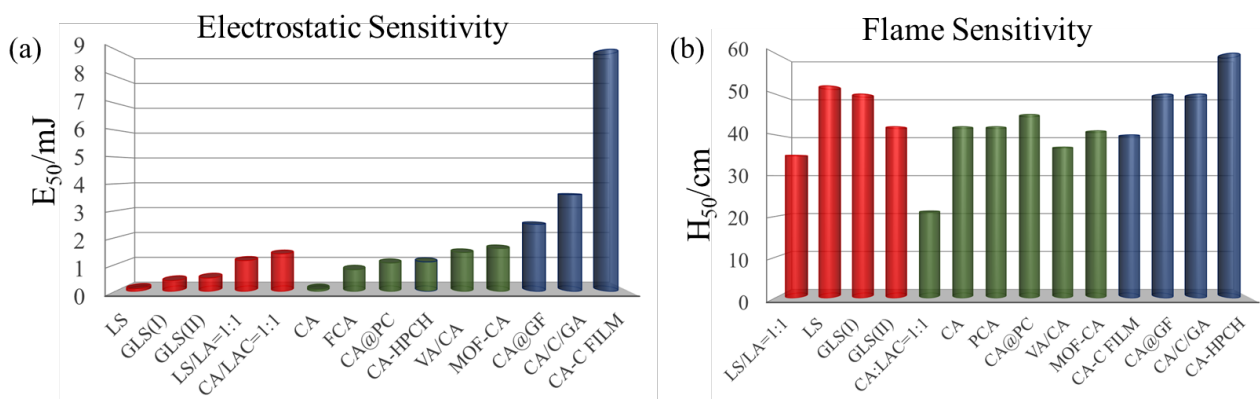
to match the charging mode of the micro-initiator is of great significance to promote its practical application. In 2019, Electrospinning technology was innovatively used for the first time, using copper-containing MOF as raw material, through spinning, carbonization, and *in-situ* azide reactions to prepare a thin-film carbon-based Nano copper azide composite. The precursor material can be cut and prepared into any shape, which is well-matched with the charging mode of the micro-initiating device or even the special-shaped initiating device. Furthermore, the electrostatic sensitivity of the prepared Nano copper azide film is increased to 9 mJ, and CL-20 can be successfully detonated in a micro-detonating device. This work provides new ideas for the processing and shaping of primary explosives and promotes the practical application of Nano copper azide in miniature-initiating devices.

In 2020, two synthetic paths of CA based on a porous graphene skeleton are proposed. First, a viscous homogeneous mixed solution is rapidly frozen in liquid nitrogen to form a spherical copper-containing precursor material. The Nano copper azide/carbon/graphene composite (CA/C/GA) was fabricated by freeze-drying, high-temperature thermal decomposition, and *in situ* azidation. Second, a cylindrical copper/graphene gel formed by high-temperature hydrothermal self-assembly is served as a precursor material. Also, hydrogen reduction and *in situ* azidation procedures were utilized to synthesize Nano copper azide@graphene foam (CA@GF). Detailed characterization indicates that the excellent performance of composite materials is ascribed to the excellent electrical and thermal conductivity of graphene material. The electrostatic sensitivities of CA/C/GA and CA@GF were 3.6 mJ and 2.5 mJ, respectively, and the flame sensitivity was 50 cm. The course of fabrication is environmentally friendly and easy to perform and it may be well-matched with the charge of the micro-detonation system.

It can be seen from the literature that the electrostatic sensitivity of CA is higher after being modified while being shaped. Therefore, it is very meaningful to develop a CA composite preparation method that combines CA modification and molding methods.

### 3. Analysis of Electrostatic Sensitivity of Modified Nano Copper Azide Materials

The sensitivity performance of the primary explosive takes effects on its practical application. Therefore, we have summarized the electrostatic sensitivity and flame sensitivity of the modified CA material as shown in **Figure 1**. It can be seen from **Figure 1** that the pure CA electrostatic sensitivity is only 0.08 mJ. Furthermore, the CA material synthesized with porous copper as a template has by-products such as CuO, and the electrostatic sensitivity is reduced to 0.81 mJ (FCA). When the CA material is covered by the porous activated carbon skeleton, the electrostatic sensitivity of CA is further reduced to 1.6 mJ (MOF-CA). When graphene is used as the frame material, the electrostatic sensitivity of CA



**Figure 1.** Comparison chart of electrostatic sensitivity and flame sensitivity of CA modified materials.

is further reduced to 3.6 mJ (CA/C/GO). When CA is coated with carbon material and processed into a thin film at the same time, the electrostatic sensitivity of CA is reduced to 9 mJ (CA-C film). Therefore, it can be seen that the electrostatic sensitivity of CA has a great relationship with the content of CA and the types of carbon materials. After the CA is processed into shape, the static charge generated by the friction of the CA particles is further reduced, so the electrostatic sensitivity is lower. Also, the flame sensitivity of CA is maintained at about 40, and the modified materials of CA have high ignition ability. Therefore, when preparing CA-modified materials, it is necessary to pursue a high content of CA in the composite material and lower electrostatic sensitivity.

#### 4. Conclusions

This paper combs and summarizes the research progress of energetic materials based on Nano copper azide at home and abroad, and draws the following conclusions:

1) As far as the preparation method of Nano copper azide is concerned, the gas-solid phase azide reaction between azide acid gas and copper element is still the main method. Such reactions require the solid phase precursor to have a larger specific surface area. The electrochemical-assisted synthesis method shows an optimistic application prospect due to its extremely high efficiency and excellent safety.

2) The excellent conductivity of carbon materials can significantly improve the electrostatic safety of composite energetic materials based on Nano copper azide. Further development of the preparation method of doped carbon materials while processing and shaping Nano copper azide is beneficial to the practical application of Nano copper azide as an explosive in weapon systems and engineering practice.

The environmental friendliness, high energy density and other characteristics of azide copper meet the requirements of low-energy ignition and high-energy output of micro-charges of pyrotechnic devices by miniature-initiating devices. Based on the current research status of Nano copper azide, it is suggested that



future research on Nano copper azide should focus on the following aspects:

1) Through the structural design and performance optimization of nanostructured composite energetic materials, the safety of energetic materials based on Nano copper azide is improved, while achieving high energy and insensitivity. Further, develop a preparation method combining Nano copper azide modification and molding to obtain an insensitive and high-energy Nano copper azide composite material that matches with a micro-initiating device.

2) Through experimental study or simulation of azides, the energy release characteristics of copper nanoparticles are further elucidated. It provides a theoretical and experimental basis for the mature application of Nano copper azide as a primary explosive in micro-initiating devices and further expands the potential application fields of Nano copper azide energetic materials.

### Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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