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Full Length Article

Copper azide fabricated by nanoporous copper precursor with proper density

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ABSTRACT

Copper azide in-situ fabricated by nanoporous copper (NPC) precursor, as a replacement of lead-based primary explosives, have showed many promising advantages. In this work, NPC film with controllable density was prepared by electroless plating using polystyrene (PS) templates and copper azide with large density and enhanced initiation performance was subsequently in situ fabricated by NPC film with proper density. The tunability of NPC density or porosity was controlled by adjusting the loading amount and particle size of PS. For copper azide fabrication, the proper density of NPC should be slightly less than the ideal value of 1.12 $g{\cdot}cm^{-3}$. The density of copper azide prepared by NPC with density of 1.005 $g{\cdot}cm^{-3}$ was 2.014 $g{\cdot}cm^{-3}$, attaining 81.15% of theoretical density. The in-situ fabricated copper azide micro-charge has showed enhanced initiation performance compared to previous study.

1. Introduction

Primary explosive is one of the most sensitive explosive group that is widely used in various explosive systems such as percussion primers, detonators, and fuzes [1,2]. Once initiated, primary explosive transforms from deflagration to detonation within milliseconds or nanoseconds and thus initiates a less sensitive but higher energetic secondary explosive. Currently, the most prominent used primary explosives are lead azide and lead styphnate [3]. Lead azide possesses good initiation efficiency and lead stysphnate has high flame sensitivity [4,5]. However, long-term use of lead primary explosives has generated environmental contamination and poses a threat to human health [5,6]. Since primary explosive is highly sensitive to initiating stimuli, such as flame, impact, friction, and static electricity, the hazard caused by unwanted explosion during manufacturing and filling processes raises a major issue [7]. Moreover, with the miniaturization of explosive trains, the traditional lead-based primary explosives can hardly meet the limiting charge and assembly requirements [8]. Thus, an ideal primary explosive as replacement should be highly energetic but environmentally compatible and safe to handle.

In recent years, copper azide in-situ fabricated by porous copper precursor as a desirable replacement has been paid much attention [9,10]. Copper is less toxic than lead, meanwhile, copper azide is highly more sensitive and powerful than lead azide [11] and other primary explosives. However, due to the extremely high electrostatic sensitivity, copper azide has a limited application with the exception of primary explosive for detonators [12,13]. Nanoporous (NPC) could be incorporated into integrated chips and then reacts with azoimide gas to convert to copper azide explosive [14]. This in-situ method reduces risk of directly handling sensitive explosives, and more importantly, it can be integrated into standard circuits fabrication process and thus enables micro-detonators and micro-electromechanical (MEMS) fuzes to be mass-produced.

The key to affecting the properties of copper azide is NPC precursor. Despite considerable progress in the area of nanoporous materials fabrication, major challenges still remain in the preparation of bulk metals with controllable porosity as well as nanoscale walls. A common route to prepare nanoporous metals involves dealloying which generates pores by dissolving a base metal from an alloy [15,16]. Dealloying process has limited control over pore size and order [17]. In contrast, template-assisted synthesis, including anodic aluminum oxide (AAO) [18,19], colloidal crystals [20,21], block copolymer [22] and hydrogen bubble [23,24], provides access to highly ordered nanoporous metals but fails to prepare bulk solids with certain size. Up to now, some approaches have been exploited to synthesize NPC precursor, such as AAO [25] and metal-organic frameworks [26] template-assisted synthesis, decomposition and sintering of copper oxalate [27]. Unfortunately, those methods, which disregarded the importance of NPC density, were not suitable for copper azide fabrication. Since the volume of copper particles would expand after reacting with azoimide, the density and particle size of NPC have a significant influ-

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ence on copper reaction degree and charge density of copper azide. Additionally, copper azide could grow out of confinement due to insufficient porosity and thus raises the risk of undesired initiation.

The goal of this research is to synthesize NPC with desirable density for copper azide fabrication. In order to synthesize NPC with the density near the calculated ideal value, we intentionally selected electroless plating on polystyrene (PS) spheres as synthetic method for the reason that the density of NPC could be controlled with the loading amount and particle size of PS. According to the determination of copper shell and PS particle size on density of NPC, we successfully synthesized NPC with the density slightly less than the ideal value and thus desirable for copper azide fabrication. The subsequent in-situ synthesized copper azide micro-charge was assembled into a miniature device to test the initiation performance, and showed that the average flyer velocity increases compared to the value reported before.

2. Experimental section

The detailed experiment processes on synthesis of monodispersed PS microspheres and preprocessing procedure have been given in our recent report [28].

2.1. Materials

Copper sulfate pentahydrate (Xilong Chemical Co., Ltd, 99%), ethylene diamine tetraacetic acid disodium (Xilong Chemical Co., Ltd, 99%), sodium hydroxide (Xilong Chemical Co., Ltd, 96%), formaldehyde (Xilong Chemical Co., Ltd, 37–40%), stearic acid (Tianjin Fuchun Chemical Reagents Factory, 99%), sodium azide (MYM Biological Technology Co., Ltd, 99%) were used as received.

2.2. Methods

2.2.1. Synthesis of NPC film

Copper sulfate ($0.1\ \mathrm{mol \cdot L^{-1}}$) pentahydrate and ethylene diamine tetraacetic ($0.12\ \mathrm{mol \cdot L^{-1}}$) acid were dissolved in deionized water. The sodium hydroxide solution was added slowly at high stirring speed to pH of 12.85. The preprocessed PS ($0.2\ \mathrm{g \cdot L^{-1}}$) was dispersed into the alkaline bath, followed by adding formaldehyde ($15\ \mathrm{ml \cdot L^{-1}}$) to induce depositing reaction. The plating process was conducted at 40 °C for 15 min under ultrasonic. PS/Cu core-shell microspheres were collected by centrifuging the mixed solution at 4000 rpm for 4 min, washed by deionized water for three times and dried in a vacuum at 50 °C for 24 h to yield PS/Cu powders. 0.1 g powders were pressed by a powder pressing machine to form round film. NPC film was produced by sintering PS/Cu film with heating rate of 5 °C/min in N_2 atmosphere at 400 °C for 1 h to remove PS templates.

2.2.2. Fabrication of copper azide confined in polycarbonate shell

The NPC film was pressed into the pores in polycarbonate confinements which was custom-made for fabrication of copper azide micro-charge. 2 g sodium azide and 10 g stearic acid were mixed in a three-neck round-bottom flask. The left neck was equipped with a gas inlet valve and a thermometer was placed on the right neck of the flask. The middle neck was connected to a custom glass-made sand core filter to place NPC filled polycarbonate confinements separately for maximum exposure to HN_3. The top of the filter was connected to buffer absorption equipment with saturated KOH to filtrate unreacted HN_3. Before reaction, the left neck was introduced to N_2 for 10 min to exclude O_2 from the system and then the flask was heated by simethicone to 135 °C. After reaction, N_2 was also introduced for 10 min to absorb residual HN_3. After every 12 h, 2 g sodium azide and 10 g stearic acid were added into the flask to confirm a steady stream of HN_3 gas.

2.3. Initiation

A copper wire was located at the bottom side of barrel to determine the initial electrical signal and the final signal was captured by PVDF piezoelectric film. Both electrical signals were acquired by an oscilloscope. The thickness of titanium flyer and barrel were 0.028 mm and 0.67 mm, respectively, and the barrel had the same diameter with copper azide micro-charge. The time difference between the initial and final triggering signals is the time that flyer takes in the barrel. The copper azides confined in polycarbonate were initiated by applying voltage of 60 V to the Ni-Cr bridge-wire which was placed under polycarbonate confinement.

2.4. Characterization

Particle size distributions of the three kinds of PS were measured by laser particle size analyzer (Mastersizer 2000, UK) using deionized water as disperser. X-ray diffraction (XRD) analysis of copper azide was performed on a diffractometer (Rigaku, Japan) in the range from 10° to 80° with Cu Kα radiation. The microstructures of those samples were characterized by scanning electron microscopy (SEM, S4800, Japan). The IR spectra of copper azides were collected by infrared spectrometer (TENSOR 27, Germany).

3. Results and discussion

Fig. 1 demonstrates the synthetic procedure of NPC film. Monodisperse PS microspheres were prepared by dispersion polymerization and PS diameter was controlled by dispersant (polyvinyl pyrrolidone, PVP) content. Before depositing copper nanoparticles, the PS templates were preprocessed, including roughening, sensitization and activation, to decorate catalytic center on surface. PS/Cu core-shell structures were produced by electroless copper plating on PS templates. Since the synthesized composites were incompact after drying, the powders were preformed by a powder pressing machine to obtain films with PS/Cu microspheres in parallel compaction. The obtained films were sintered in N_2 at 400 °C for 1 h to remove PS templates and to strengthen the connection between copper nanoparticles. For security reasons, copper azide was synthesized after NPC was pressed in a polycarbonate confinement, to avoid direct handling of primary explosive. The confinement filling with NPC reacted with HN_3 and sufficient time for complete conversion ensured efficient reaction of the inside copper hollow microspheres.

Copper reacts with azoimide and forms various copper azides, such as cuprous CuN_3, cupric $Cu(N_3)_2$ and $Cu(N_3)_2{\cdot}nCu(OH)_2$ (n = 1, 2, 3), depending on synthesis condition. Cuprous azide forms as an intermediate product when copper reacts with azoimide, the reaction could be expressed as [12,13]:

$$2Cu + 3HN_3 \rightarrow 2CuN_3 + NH_3 + N_2$$

When exposed to atmosphere oxygen, CuN_3 is further oxidized to $Cu(N_3)_2$ or $Cu(N_3)_2{\cdot}Cu(OH)_2$ [12]. A different reaction was reported when copper is in contact with moist azoimide [29],

$$Cu + 4HN_3 \rightarrow Cu(N_3)_2 + NH_4N_3 + N_2$$

Azoimide gas is obtained from the following reaction at high temperature [30]:

$$CH_3(CH_2)_{16}COOH + NaN_3 \rightarrow CH_3(CH_2)_{16}COONa + HN_3$$

Further investigations reveal that the products of the above reaction between copper and azoimide are the mixture of copper azides ($Cu(N_3)_2$ or $Cu(N_3)_2$) [25,27]. Since the precursor is bulk