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Flash-ignitable nanoenergetic materials with tunable underwater explosion reactivity: The role of sea urchin-like carbon nanotubes

Ji Hoon Kim [a], Sang Beom Kim [a], Min Goo Choi [b], Dae Hyun Kim [c], Kyung Tae Kim [d], Hae Moon Lee [d], Hyung Woo Lee [a], Jong Man Kim [a,b], Soo Hyung Kim [a,b,*]

[a] Department of Nano Fusion Technology, Pusan National University, San 30, Jangjeon-dong, Geumjung-gu, Busan 609-735, Republic of Korea
[b] Department of Nanomechatronics Engineering, Pusan National University, San 30, Jangjeon-dong, Geumjung-gu, Busan 609-735, Republic of Korea
[c] Institute of Material Technology, Poongsan Corporation, 266 Techno 2-ro, Yuseong-gu, Dae Jeon 305-510, Republic of Korea
[d] Powder & Ceramic Division, Korean Institute of Materials and Science, 797 Changwon-daero, Seongsan-gu, Changwon-si, Gyeongnam 642-731, Republic of Korea

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ABSTRACT

The underwater applications of nanoenergetic materials (nEMs) could be extended by developing more convenient and reliable ignition methods. However, the underwater ignition of nEMs is a significant challenge because water perturbs the reactants prior to ignition and also quenches the subsequent combustion reaction of nEMs upon ignition. In this study, we developed flash-ignitable nEMs for underwater explosion. This was achieved by adding sea urchin-like carbon nanotubes (SUCNTs) as the optical igniter into an nEM matrix, composed of Al/CuO nanoparticles. The SUCNTs absorb the irradiated flash energy and rapidly convert it into thermal energy, and then the thermal energy is concentrated to ignite the core catalysts and neighboring nEMs. The maximum burn rate was achieved by adding 1 wt% SUCNTs into the nEM matrix. The burn rate significantly decreased with increasing amount of SUCNTs ($\geqslant$2 wt%), indicating that the remote flash ignition and controlled-explosion reactivity of nEMs are possible by incorporating an appropriate amount of SUCNTs.

1. Introduction

Nanoenergetic materials (nEMs) composed of nano-sized metal fuel and metal oxide components can rapidly convert their internal chemical energy into thermal energy when they are ignited [1–3]. There are numerous applications of combustible nEMs in aqueous environments, including underwater propulsion, blasting and welding, torch and metal cutting, and alternative underwater power sources [4–9]. However, the underwater reaction applications of nEMs are extremely limited due to unpliable ignition methods and environmental constraints surrounding their explosive reactions.

The ignition of nEMs can be carried out with various external energy inputs, such as a hotwire igniter, electrical spark, or flame [1–3,10]. These traditional means of thermal ignition of nEMs are highly sensitive to surrounding environmental conditions, including temperature, pressure, space, and time. Successful ignition of nEMs can be achieved by providing a sufficiently high temperature at the surface of metal fuel components. However, the realization of the aforementioned traditional means of the underwater thermal ignition of nEMs requires complex mechanical and electrical auxiliary systems. Therefore, the development of an easy and reliable ignition method for the underwater explosion of nEMs is necessary to extend their underwater applications.

In general, nEMs cannot easily react in aqueous environments. This is because water perturbs the reactants prior to ignition, and it immediately quenches the combustion reaction of nEMs upon ignition. Several attempts have been made to use a hydrophobic binder in the formation of nEMs to prevent water permeation through the nEM-based matrix [4–6]. However, the hydrophobic binder-added nEM composites were observed to rapidly lose their heat to the aqueous surroundings prior to self-propagating the reaction, which quickly quenched the explosive reaction.

In this study, we demonstrate a viable method for the synthesis of sea urchin-like carbon nanotube (SUCNT)/nEM composite pellets coated with a hydrophobic polymer thin film that can achieve flash ignition and subsequent underwater explosion. The flash-induced combustion characteristics of nitrocellulose (NC)-coated SUCNT/nEM composite pellets were examined in terms of pressurization rates, total burning time, and burn rates. This provided evidence that the specially designed SUCNTs, which are composed of

* Corresponding author at: Department of Nano Fusion Technology, Pusan National University, San 30, Jangjeon-dong, Geumjung-gu, Busan 609-735, Republic of Korea.
E-mail address: sookim@pusan.ac.kr (S.H. Kim).

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radially grown multiple CNTs on the surface of a core Ni–Al bimetallic nanoparticle (NP), are essential for the flash ignition and underwater explosion of nanoenergetic formulations. Finally, reliable flash ignition and subsequent underwater explosion was successfully demonstrated with the NC-coated SUCNT/nEM composite pellets that were fabricated using this approach.

2. Experimental

2.1. Synthesis of sea urchin-like carbon nanotubes (SUCNTs)

A combination of conventional spray pyrolysis and thermal chemical vapor deposition (CVD) methods was used to synthesize SUCNTs [11–13]. Briefly, aluminum nitrate nonahydrate ($Al(NO_3)_3 \cdot 9H_2O$, Sigma Aldrich) and nickel nitrate hexahydrate ($Ni(NO_3)_3 \cdot 6H_2O$, Sigma Aldrich) were dissolved at a 1:1 molar ratio in deionized water at a total concentration of 3 wt%. This precursor solution was aerosolized using an ultrasonic nebulizer operated at 40 W and 60 kHz. Next, the metal nitrate aerosol droplets were transferred to a silica-gel dryer with N_2 flow of approximately 1 lpm. After passing through the silica-gel dryer, the solidified bimetallic nitrate aerosols were transformed into pure bimetallic NPs by thermal decomposition and hydrogen reduction (H_2 = ~100 sccm) processes in a quartz tube reactor (2.54 cm diameter, 30 cm heating length) heated to 1000 °C by a furnace. The resulting pure bimetallic NPs were then rapidly transported into a second quartz tube reactor (5.08 cm diameter, 30 cm heating length) enclosed by a second furnace heated to 750 °C. As they were reacted with acetylene (C_2H_2 = ~10 sccm) and hydrogen (H_2 = ~100 sccm) gases, SUCNTs were grown on the surface of Al–Ni bimetallic NPs during a residence time of approximately 50 s. The resulting aerosol SUCNTs were collected on a membrane filter with a pore size of 200 nm.

2.2. Fabrication of SUCNT/nEM composite powders and pellets

Commercially available Al NPs and CuO NPs (NT base Inc.) with average primary particle sizes of approximately 80 and 100 nm were used as the fuel and oxidizer, respectively. SUCNTs synthesized by thermal CVD with an average particle size of approximately 200 nm were used as an optical igniter. We prepared SUCNT/nEM composite powders to examine the SUCNTs as the optical igniter, as shown in Fig. 1. First, Al NPs (fuel) were mixed with CuO NPs (oxidizer) in an EtOH solution with a mixing ratio of fuel to oxidizer (Al:CuO) of 30:70 wt%. The SUCNTs were then added to the nEM precursor solution (Al NP/CuO NP/EtOH) in mixing ratios of 1, 2, 5, or 10 wt%. For homogeneous mixing of the Al NP/CuO NP/SUCNT in the EtOH solution, sonication was conducted at 200 W and 40 kHz for approximately 30 min. Next, the EtOH was evaporated in a convection oven at 80 °C for 30 min to obtain SUCNT/nEM composite powders. The resulting SUCNT/nEM composite powders were characterized by a SEM (Hitachi, Model No. S4700) operated at 15 kV and a STEM (JEOL, Model No. JEM-2100) operated at 200 kV. To investigate the underwater explosion of SUCNT/nEM composites, we prepared nitrocellulose (NC) thin-film-coated SUCNT/nEM composite pellets, as shown in Fig. 1. First, the SUCNT/nEM composite powders (~26 mg) were added to a disk-shaped metal mold and compressed at 300 MPa for 10 min using a mounting press machine [14]. The resulting SUCNT/nEM composite pellet was then encapsulated by a NC thin film through dipping in a collodion solution (Sigma Aldrich) and subsequently air drying for approximately 5 min. The collodion solution is highly volatile and leaves a thin NC film after the solvent is dried [15].

2.3. Flash ignition and explosion characterization of NC thin-film-coated SUCNT/nEM composites

A series of optical ignition and underwater explosion tests for the SUCNT/nEM composites were performed. To investigate the effect of the SUCNTs on the explosion characteristics of nEMs, we performed pressure-cell tests (PCTs) to measure the pressurization rates of the SUCNT/nEM composites. Briefly, 13 mg of SUCNT/nEM composite powder was placed in the pressure cell with a constant volume of ~13 mL. It was ignited by a heated tungsten wire that emits resistive heat, which was coupled to an external DC power supply operated at 2 A and 1.5 V. During the in-air explosion, the induced pressure was measured by a piezoelectric pressure sensor (PCB Piezotronics, Model No. 113A03) attached to the pressure cell. Simultaneously, the detected pressure signal was amplified and transformed into a voltage signal through a combination of an in-line charge amplifier (PCB Piezotronics, Model No. 422E11) and signal conditioner (PCB Piezotronics, Model No. 480C02). Finally, this signal was monitored and recorded using a digital

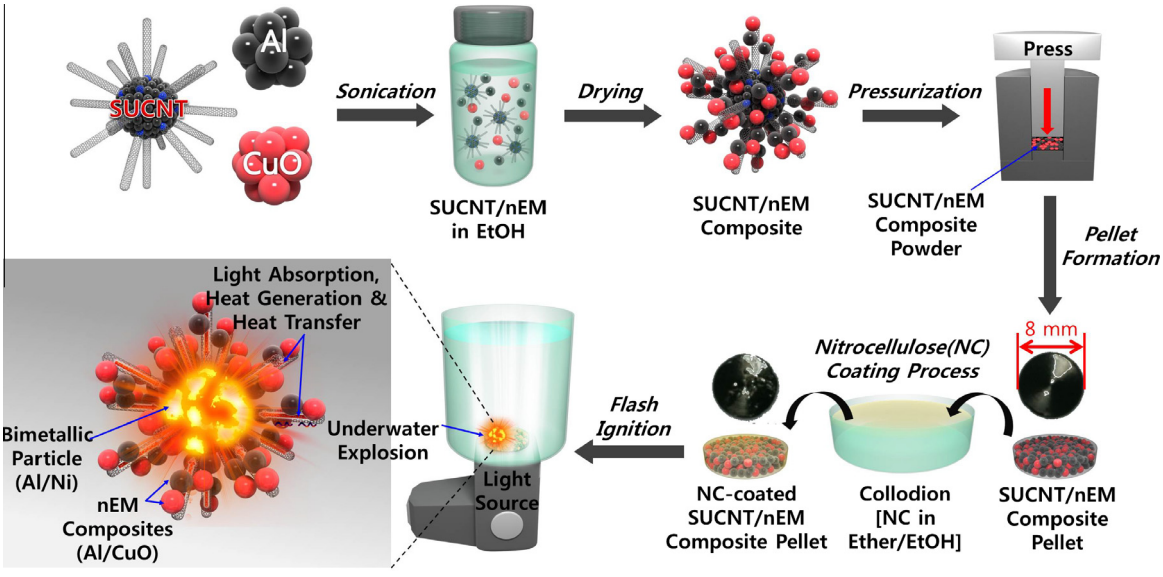

Fig. 1. Schematic of the fabrication and flash ignition of nitrocellulose-encapsulated SUCNT/nEM composite pellets for underwater explosion.