Combustion and Flame 162 (2015) 1448–1454

Contents lists available at ScienceDirect

Combustion and Flame

journal homepage: www.elsevier.com/locate/combustflame

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

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ARTICLE INFO

Article history:
Received 6 July 2014
Received in revised form 11 November 2014
Accepted 11 November 2014
Available online 2 December 2014

Keywords:
Nanoenergetic materials
Al/CuO nanoparticles
Sea urchin-like carbon nanotubes
Optical igniters
Underwater explosion

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

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http://dx.doi.org/10.1016/j.combustflame.2014.11.011

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 ($H_2 = \sim 100$ 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 ($C_2H_2 = \sim 10$ sccm) and hydrogen ($H_2 = \sim 100$ 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.

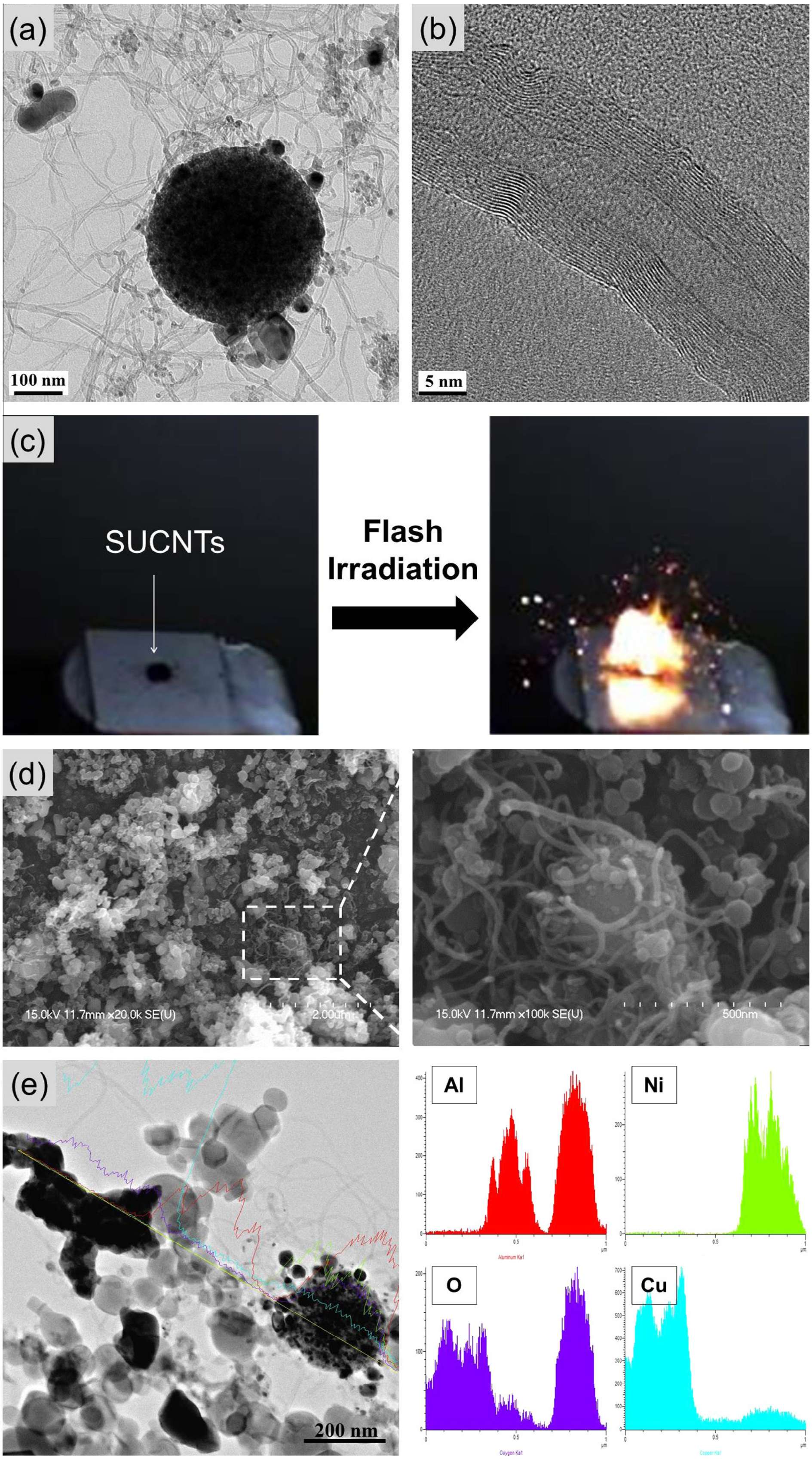

Fig. 2. (a) LRTEM and (b) HRTEM images of SUCNTs. (c) Photographs of a bundle of SUCNTs before and after flash irradiation. (d) SEM and (e) STEM images of SUCNT/nEM composite powders.

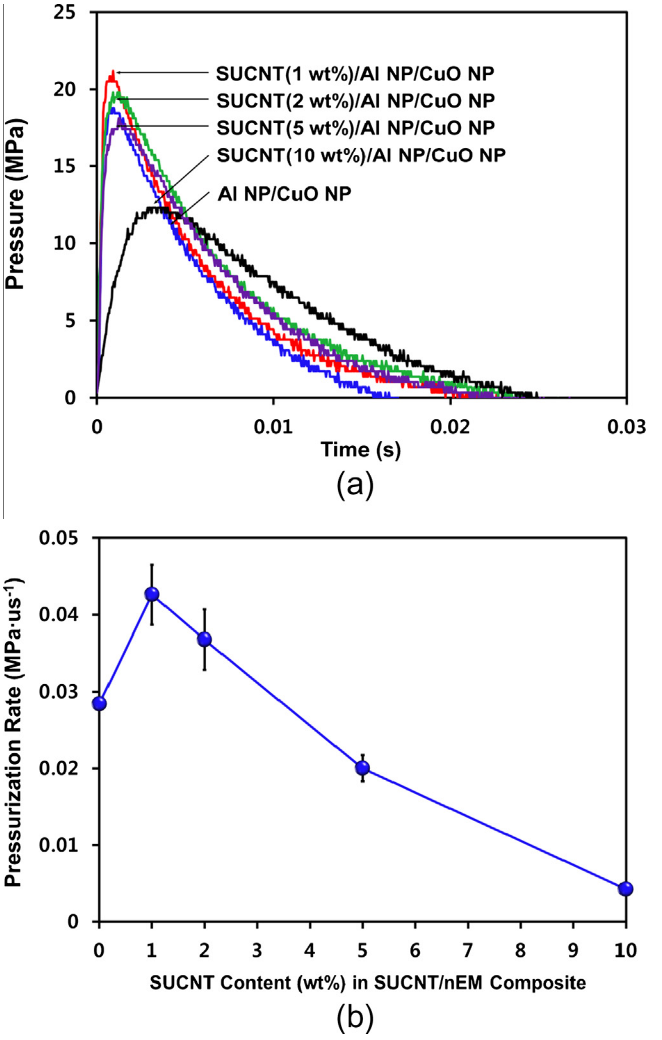

Fig. 3. Evolution of (a) the pressure of SUCNT/nEM composite powders with elapsed time and (b) the pressurization rate of SUCNT/nEM composite powders as a function of SUCNT content after the flash ignition and in-air explosion.

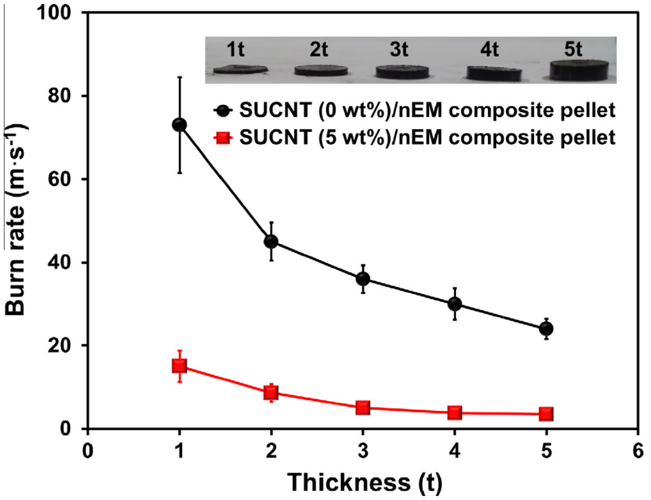

Fig. 4. The evolution of burn rates of SUCNT (0 wt%)/nEM and SUCNT (5 wt%)/nEM composite pellets as a function of pellet thickness (here, the unit thickness of 1t is approximately 0.3 mm).

oscilloscope (Tektronix, Model No. TDS 2012B). To examine the heat flow of SUCNT/nEM composites, DSC (Setaram, Model No. LABSYS evo) was performed at temperatures ranging from 30 °C to 1000 °C at a heating rate of 10 °C min^{-1} under N_2 flow. Underwater flash ignition tests were conducted to examine the underwater explosion of the SUCNT/nEM composite. Briefly, a NC thin-film-coated SUCNT/nEM composite pellet was placed in the bottom of a beaker filled with water. It was then ignited by flash irradiation from under the beaker. The entire burning process of the NC thin-film-coated SUCNT/nEM composite pellet was recorded with a high-speed camera (Photron, Model No. FASTCAM SA3 120 K) at a frame rate of 30 kHz.

3. Results and discussion

3.1. Synthesis, characterization, and in-air explosion of SUCNT/nEM composite materials

A schematic illustration of the preparation and flash ignition of SUCNT/nEM composite pellets for underwater explosion tests is presented in Fig. 1. We specifically considered NC thin-film-coated SUCNT/nEM composite pellets with a theoretical density of approximately 80%; the pellets are composed of aluminum nanoparticles (Al NPs) as the fuel, copper oxide nanoparticles (CuO NPs) as the oxidizer, and SUCNTs as the optical igniter.

The growth of SUCNTs in the gas phase has been described elsewhere and is described in detail in subsequent experimental section [11–13]. Figure 2a and b present the transmission electron microscopy (TEM) images of SUCNTs fabricated by this approach; clearly, multiwalled (~15 walls) CNTs with a diameter of approximately 15 nm and a hollow core were radially grown on the surface of Ni–Al bimetallic NPs. The flash ignition of a bundle of SUCNTs was qualitatively tested, as shown in Fig. 2c. As a result of flash irradiation, small fires were locally initiated and subsequently propagated throughout the bundle of SUCNTs, indicating that SUCNTs have potential for serving as optical igniters. The local ignition of SUCNTs can occur because multiple CNTs effectively absorb flash energy and rapidly heat up the surrounding air molecules. This process is known as the photoacoustic effect [16–20]. Then, the CNTs rapidly transfer and concentrate the heat into the core Ni–Al bimetallic NPs. This action sufficiently increases the temperature to a point at which the oxidation of both the carbon and catalysts in the SUCNT structure is initiated by flash irradiation. Scanning electron microscopy (SEM) and scanning transmission electron microscopy (STEM) analyses were performed to examine the degree of intermixing and the structure of the as-prepared SUCNT/nEM composite powder, as shown in Fig. 2d and e. The Al NPs (fuel) were closely connected to the CuO NPs (oxidizer) at the nanoscale level, and the SUCNTs (optical igniter) were homogeneously distributed throughout the Al NP- and CuO NP-based energetic matrix.

To examine the effects of SUCNT mass on the in-air explosion reactivity of nEMs, a fixed mass (~13 mg) of SUCNT/nEM composite powders was ignited in a confined cell with a constant volume of 13 mL. The pressurization rate was obtained by taking the ratio of the maximum pressure to the rise time. As shown in Fig. 3a and b, the most rapid increase in pressure with elapsed time and the highest pressurization rate were observed for the SUCNT (1 wt%)/nEM composite powder. The magnitude of the maximum pressure and rise time were considerably reduced with an increase in SUCNT mass to >2 wt%. In addition, we examined the effect of the presence of SUCNTs on the burn rate of nEM pellets with different thickness as shown in Fig. 4. The burn rate of a SUCNT/nEM composite pellet was experimentally determined by taking the ratio of pellet diameter to the total time from flame initiation to the flame reaching the furthest edge of the pellet. For the case of SUCNT (0 wt%)/nEM composite pellets (i.e., without adding

SUCNTs in the Al/CuO matrix), their burn rates were significantly decreased with increasing pellet thickness. This suggests that the increase of the number of boundary layer among Al/CuO NPs in a thicker pellet resulted in decreasing the flame propagation. For the case of SUCNT (5 wt%)/nEM composite pellets, we observed the similar trends that the burn rates of SUCNT (5 wt%)/nEM composite pellets were decreased with increasing pellet thickness. It was also clearly observed that the addition of SUCNTs in the nEM pellets (i.e., SUCNT (5 wt%)/Al/CuO pellets) resulted in considerably decreasing their burn rates over all pellet thickness from 1t (≅0.3 mm) to 5t (≅1.5 mm) compared to SUCNT (0 wt%)/nEM pellets. These results imply that heat dissipation was increased due to the presence of SUCNT agglomerations formed by large SUCNT mass contents in the nEM matrix, which served to quench the propagation of the explosion reaction.

3.2. Underwater explosion of NC thin-film-coated SUCNT/nEM composite pellets

To use SUCNT/nEM composites for underwater explosions, they must be prepared in the form of pellets with a hydrophobic thin-film for easy handling in water and diverse underwater applications. In this approach, we employed nitrocellulose (NC) as a hydrophobic coating material for SUCNT/nEM composite pellets. To examine the water permeability, the contact angle was measured on SUCNT/nEM composite pellets with and without the NC thin-film coating. Figure 5 shows that the average contact angle was found to be approximately 40° and 88° for the SUCNT/nEM composite pellets with and without a NC thin-film coating, respectively. Furthermore, the SUCNT/nEM composite pellets without NC thin-film coatings were not ignited by flash irradiation. This observation suggests that the presence of NC thin films on the surface of SUCNT/nEM composite pellets avoids water permeation by maintaining hydrophobicity, which enables the pellets to ignite even after approximately 10 days of aqueous submersion.

To corroborate the role of SUCNTs, underwater flash ignition tests were carried out on NC thin-film-coated nEM pellets without added SUCNTs. No flash ignition or underwater explosion of NC thin-film-coated nEM pellets was observed, suggesting that the presence of a critical amount of SUCNTs is essential for the flash ignition and subsequent underwater explosion of nEM pellets. Table 1 summarizes the burning characteristics of SUCNT/nEM composite pellets in water. Both the ignition delay time and total burning time increased considerably with increasing the amount of SUCNTs in the nEM matrix. This result suggests that the presence of a large amount of SUCNTs in the given nEM matrix increased heat dissipation, thereby hindering the rapid ignition and subsequent burning of nEMs.

Differential scanning calorimetry (DSC) analysis was performed to examine the effect of SUCNT embedment on the total heat energy of nEMs, as shown in Fig. 6. Clearly, all the samples exhibited exothermic reactions and similar ignition temperatures of 450–500 °C. The integration of the exotherm quantifies the total heat of the exothermic reaction as approximately 0.902 kJ g^{-1} over the tested temperature range for the SUCNT (0 wt%)/nEM composite pellets. The total heat is gradually decreased by increasing the amount of SUCNTs in the nEM matrix, suggesting that the presence of SUCNTs in the nEM matrix hinders the complete combustion reaction to some extent. Therefore, SUCNTs could potentially play

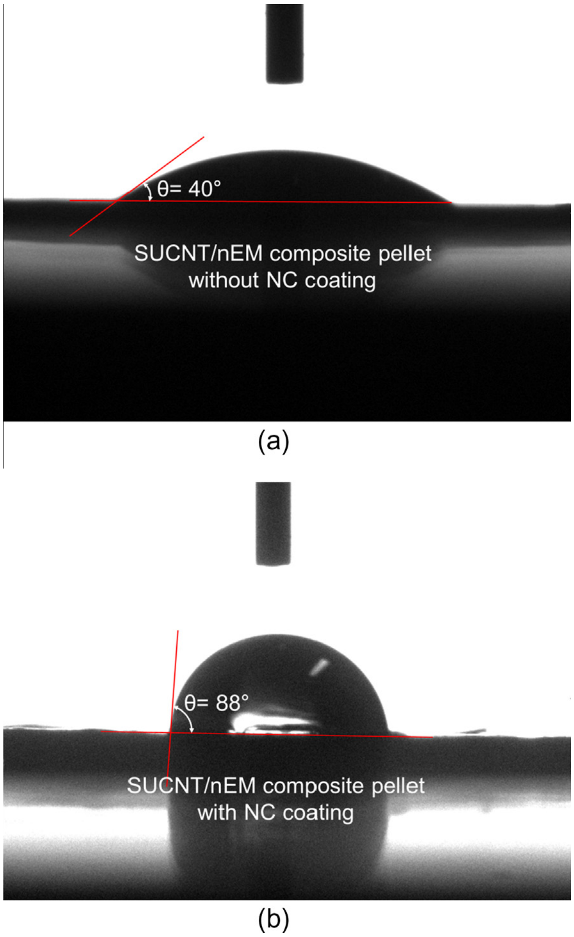

Fig. 5. Photographs of contact angle measurements for the SUCNT/nEM composite pellets (a) without and (b) with a nitrocellulose (NC) thin-film coating.

Table 1
Combustion characteristics of SUCNT/nEM composite pellets ignited by flash irradiation in water.

SUCNT content in the nEM matrix (wt%)	Ignition delay time (ms)	Total burning time (ms)	Burn rate (m s^{-1})
0	No ignition	No burning	~0
1	~0.4	~13.3	~34
2	~0.6	~15.2	~28
5	~1.3	~16.6	~14
10	~3.0	~74.7	~3

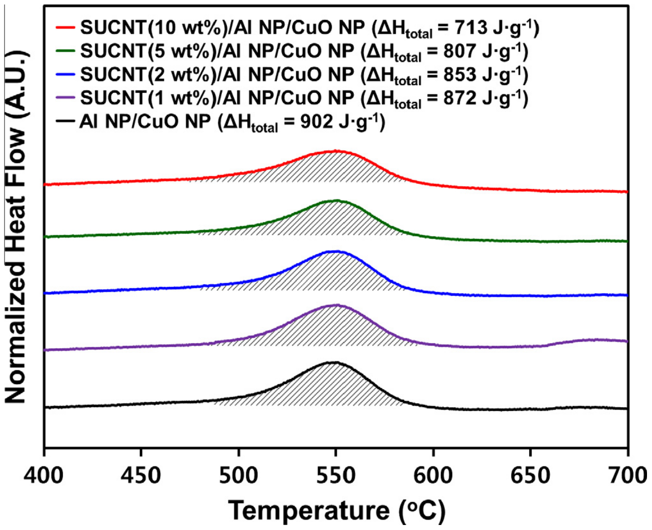

Fig. 6. Differential scanning calorimetry (DSC) results of various SUCNT (0, 1, 2, 5 and 10 wt%)/nEM composite powders.

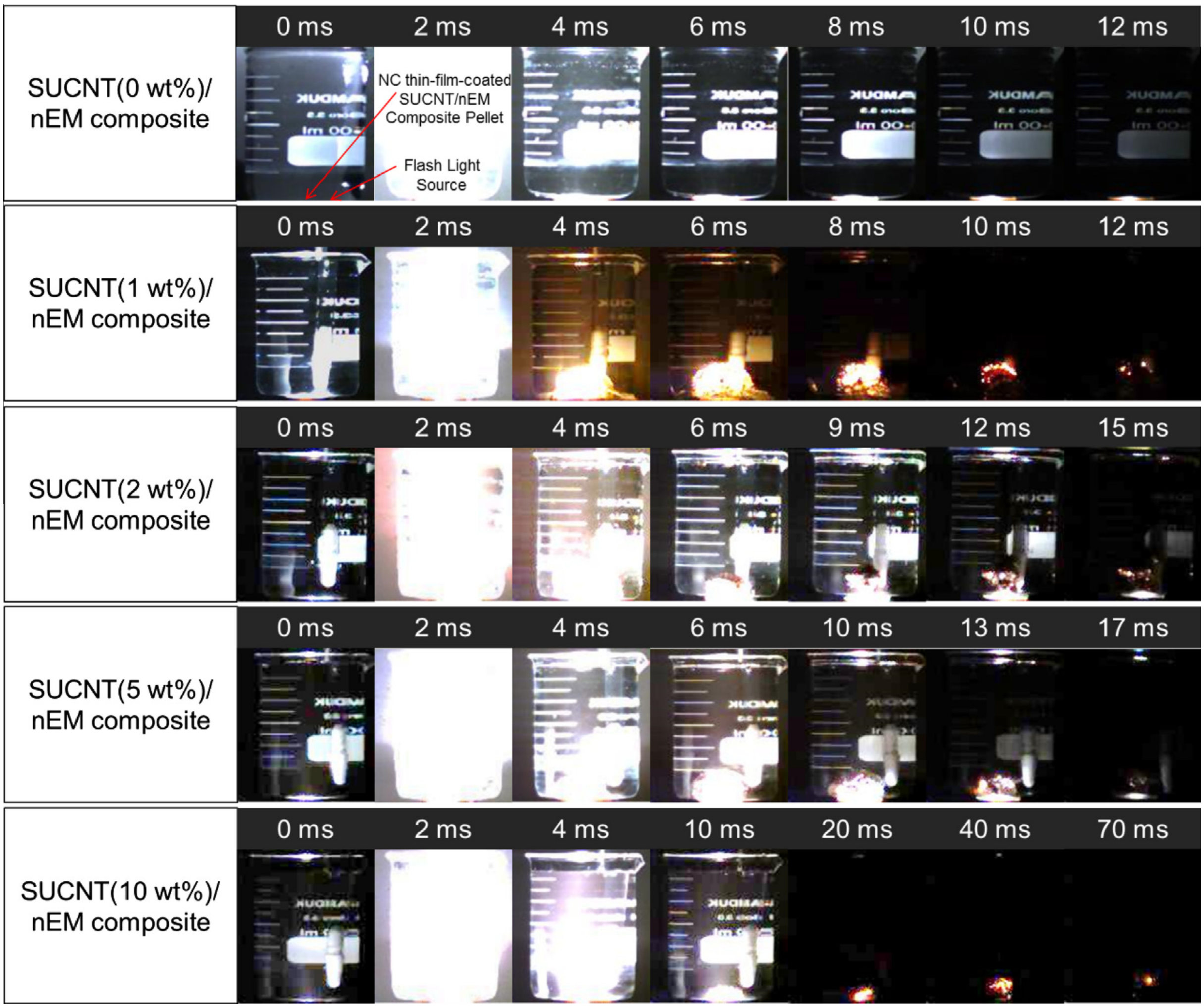

Fig. 7. Sequential snapshots of the flash ignition and subsequent underwater explosion of nEM-based matrix pellets embedded with various amounts of SUCNTs (0–10 wt%). [The pixels of still images in 2 ms are commonly overloaded due to flash irradiation.]

an important role in controlling explosion reactions by intervening in the thermal interactions of nEM reactants.

Figure 7 presents a series of photographs of the gas-bubble formation and flame propagation of various flash-ignited SUCNTs (0, 1, 2, 5, and 10 wt%)/nEM composite pellets in water. Based on these high-speed video stills, the SUCNT (0 wt%)/nEM composite pellet was not ignited by flash irradiation. However, after the flash irradiation, SUCNT (1, 2, 5, and 10 wt%)/nEM composite pellets instantly exploded and generated a single bubble, which quickly grew and divided into smaller bubbles and then floated to the top of the beaker filled with water. The resulting underwater burn rates were approximately 34 m s^{-1} for the SUCNT (1 wt%)/nEM composite pellet, 28 m s^{-1} for the SUCNT (2 wt%)/nEM composite pellet, 14 m s^{-1} for the SUCNT (5 wt%)/nEM composite pellet, and 3 m s^{-1} for the SUCNT (10 wt%)/nEM composite pellet. These results suggest that the embedment of SUCNTs is essential for the reliable ignition and underwater explosion of nEM matrices. An increase in the amount of SUCNTs in the nEM matrix can retard the explosion reaction by rapid heat dissipation to the environment and by the physicochemical intervention with reacting fuel metal and oxidizer materials.

4. Conclusions

In this work, we have successfully demonstrated the flash ignition and underwater explosion of nEM pellets with embedded SUCNTs as the optical igniter. We have shown that the specially designed structure of SUCNTs allows the absorption of the irradiated flash energy to rapidly convert it into thermal energy. This thermal energy is then sufficiently concentrated to ignite the core catalysts and neighboring nEMs at the nanoscale. Flash-induced burning tests indicated that the presence of SUCNTs in the nEM matrix is essential for reliable flash ignition and subsequent underwater explosion. However, both pressure-cell tests and DSC analysis confirmed that the embedment of excess SUCNTs in the nEM matrix could significantly suppress the heat energy generation and burn rate of SUCNT/nEM composites due to rapid heat dissipation to the surrounding environment and physicochemical intervention in the reactants. By embedding the specially designed SUCNTs into nEM pellets, nEM composite powders and pellets can be obtained with the ability to flash ignite as well as the desired underwater explosion reactivity.

Acknowledgments

This research was supported by the Civil & Military Technology Cooperation Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Science, ICT & Future Planning (No. 2013M3C1A9055407). This research was also partially supported by the Fundamental Research Program funded by the Agency for Defence Development of Korea (No. UD130033GD).

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