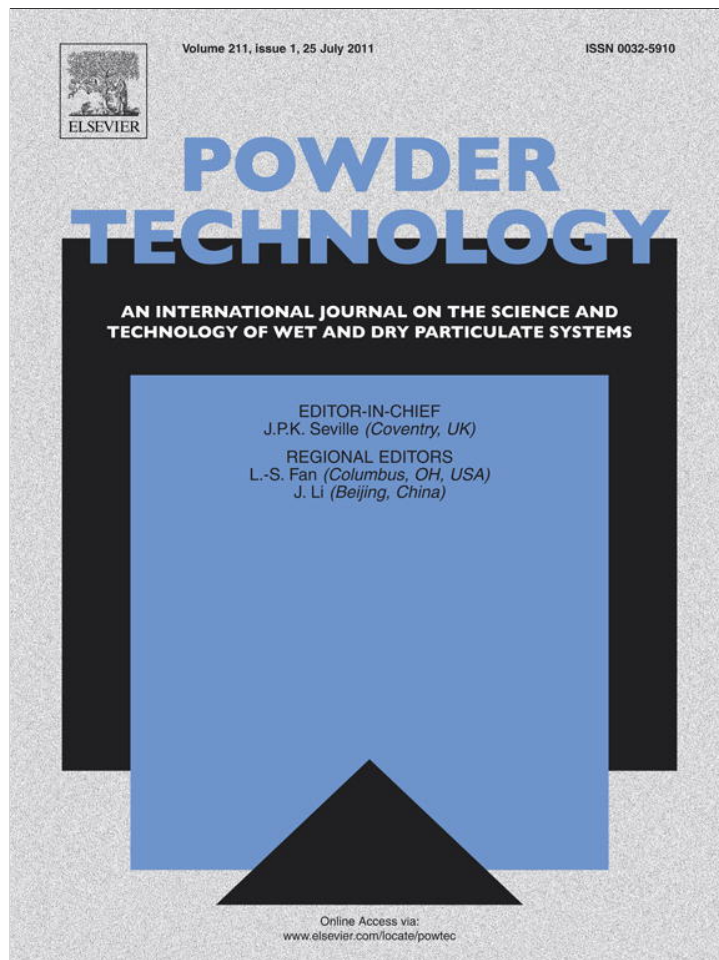


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Powder Technology

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Effect of metal oxide nanostructures on the explosive property of metastable intermolecular composite particles

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ARTICLE INFO

Article history:

Received 19 January 2011

Received in revised form 28 February 2011

Accepted 26 March 2011

Available online 5 April 2011

Keywords:

Electrospinning

Metastable intermolecular composites

Fuel

Oxidizer

Explosive property

ABSTRACT

The fineness of reactants, degree of intermixing and interfacial contact area between fuel and oxidizer comprising of metastable intermolecular composite (MIC) particles are important factors to determine their overall kinetics of burning process. Here, we demonstrate a viable method for enhancing the explosive property of MICs by tailoring the nanostructures of oxidizer located in close proximity to fuel nanoparticles. The measured pressurization rate for a specific sample of solid Al nanoparticle (fuel)–porous CuO nanowire (oxidizer) MICs exploded in a closed vessel was found to be increased by a factor of ~10 compared with that for solid Al nanoparticle–solid CuO nanoparticle MICs. In addition, with the assistance of intensive sonication energy, the fabricated porous oxidizer nanowires were disintegrated into oxidizer nanoparticles, which considerably reduced the pressurization rate when they were ignited with fuel nanoparticles. This suggests that the morphology of oxidizer nanostructures from solid nanoparticles (i.e. 0-D) to porous nanowires (i.e. 1-D) play a key role in significantly changing the interfacial contact area with fuel nanoparticles so that nascent oxygen can be produced effectively for promoting the explosive property of the fuel nanoparticles.

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1. Introduction

Generally, the rate of energy release from monomolecular energetic materials such as trinitrotoluene (TNT) is considerably higher than the rate of energy release from metastable intermolecular composites (MICs) composed of an intimate mixture of macro- or micro-scale fuel and oxidizer particles. This is because the rate of energy release is strongly dependent on the overall chemical kinetics of the reactants. For increasing the rate of energy release, it is necessary to prepare MICs comprising nanostructured particles (i.e., fuel and oxidizer particles) so that the overall kinetics of burning increases soon after the reaction between the fuel and the oxidizer is initiated [1–3].

MICs have prepared by various methods, including sonic-wave-assisted physical mixing [4,5], sol–gel chemistry [6], electrostatic assembly [7], and molecular self-assembly [8]. The key parameters that must be considered when preparing MIC assemblies are fineness of the reactants, uniformity of mixing, and degree of intermixing between the fuel and the oxidizer. The rate of energy release from MICs composed of uniformly interconnected fuel and oxidizer nanoparticles has been reported to be almost 1000 times higher

than the rate of energy release from reactants comprising macro- or micro-sized particles [9]. This is because the fuel nanoparticles rapidly react with the neighboring oxidizer nanoparticles so that the rate-limiting step due to mass transfer is suppressed. Here, we pose the following question: can one adjust the rate of energy release by changing the nanostructures of the reacting MICs, in which the area of interfacial contact between the reactants (fuel and oxidizer) can be altered?

In this study, we demonstrate a viable method for producing MICs, in which the fuel nanoparticles are intermixed with oxidizer molecules that are in the form of low dimensional nanostructures [i.e., nanoparticles (hereafter referred to as NPs) or nanowires (hereafter referred to as NWs)]. We systematically investigate the effect of variations in the area of interfacial contact between the fuel NPs and the oxidizer nanostructures on the final energy release rate. We consider a thermite mixture of aluminum (Al; fuel) and copper oxide (CuO; oxidizer) as a specific example and show that the rate of energy release from MICs with a large interfacial contact area between the fuel NPs and the oxidizer NWs is much higher than that of MICs composed of fuel NPs and oxidizer NPs.

2. Experimental details

Passivated Al NPs (average primary particle size: ~80 nm, thickness of oxide layer: ~4 nm) purchased from NT base, Inc. were used as the

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fuel source. CuO samples with two different nanostructures (NPs or NWs) were used as the oxidizer sources. CuO NPs (average primary particle size: ~50 nm) were purchased from Sigma Aldrich and used as such without further purification. Briefly, the commercially available CuO NPs were produced as follows: 2 mmol of $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$ was dissolved in 25 ml of DMF followed by the addition of poly(vinyl pyrrolidone) (PVP) and NaBH_4 as a reducing agent. After stirring for several minutes, the mixture was heated at 85–95 °C and maintained for 2–6 min. The mixture was cooled to room temperature and washed by alcohol several times, which resulted in the formation of Cu_2O nanoparticles. CuO nanoparticles were then generated by annealing of spherical Cu_2O nanoparticles at 500 °C for 1–2 h [10]. Unlike commercially available CuO NPs, the CuO NWs were produced in-house by a combination of electrospinning and calcination as shown in Fig. 1 [11,12]. In this approach, a PVP/ $\text{Cu}(\text{NO}_3)_2$ precursor solution was prepared in the following manner by using $\text{Cu}(\text{NO}_3)_2$ (Sigma Aldrich) and PVP (Sigma Aldrich, Mw: 55,000). First, 4 g of PVP was dissolved in 6 g of EtOH, while 4 g of $\text{Cu}(\text{NO}_3)_2$ was dissolved in 4 g of deionized (DI) water. Then, the resulting PVP and $\text{Cu}(\text{NO}_3)_2$ solutions were mixed to obtain a final mixture in which the PVP: $\text{Cu}(\text{NO}_3)_2$ ratio was 1:1 (wt.%).

The aforementioned $\text{Cu}(\text{NO}_3)_2$ /PVP precursor solution was dispensed at the rate of 0.2 mL/h by using a precision syringe pump (KD Scientific, Model No.781100). When dispensing the precursor solution, a fixed positive voltage of approximately 35 kV was applied to the tip of the nozzle while simultaneously grounding the rotating plate. The

distance between the nozzle tip and the rotating plate was fixed at 15 cm. Subsequently, $\text{Cu}(\text{NO}_3)_2$ /PVP composite NWs were formed due to Coulombic explosion and were deposited on the surface of the iron mesh that covered the rotating plate. These composite NWs were then calcined at various temperatures (up to ~800 °C) for removal of the polymer templates and simultaneous thermal decomposition of the metal nitrate precursor into the corresponding metal oxide (CuO). The resulting CuO NWs were then mixed with Al NPs in an ultrasonication bath at 170 W and 40 kHz. The two types of MICs (Al NP/CuO NW and Al NP/CuO NP) were mixed in EtOH and sonicated for various times ranging from 1 min to 360 min. The resulting colloidal solutions were then dried at 80 °C in a convection oven for 30 min in order to remove excess EtOH. Finally, Al NP/CuO NP and Al NP/CuO NW composite powders were collected. The Al/CuO MICs formed were characterized by various techniques, including thermogravimetric analysis (TGA; TA Instruments, TGA Q50) at temperatures ranging from 25 °C to 900 °C, X-ray diffractometry (XRD; Philips, X'pert PRO MRD), scanning electron microscopy (SEM; Hitachi S4700) at 15 kV, and Cs-corrected scanning transmission electron microscopy (STEM; JEOL, JEM-2100) at 200 kV.

The positive pressurization rate of the ignited MICs was measured by using a pressure cell test unit (see Fig. 1). Since the rate of pressure rise strongly depends on the volume of reaction vessel, it comprised a constant volume of 13 mL reaction vessel was employed in this study for repeatable measurement of pressurization rate of MICs prepared. Also the pressure cell test unit comprised a pressure sensor (PCB

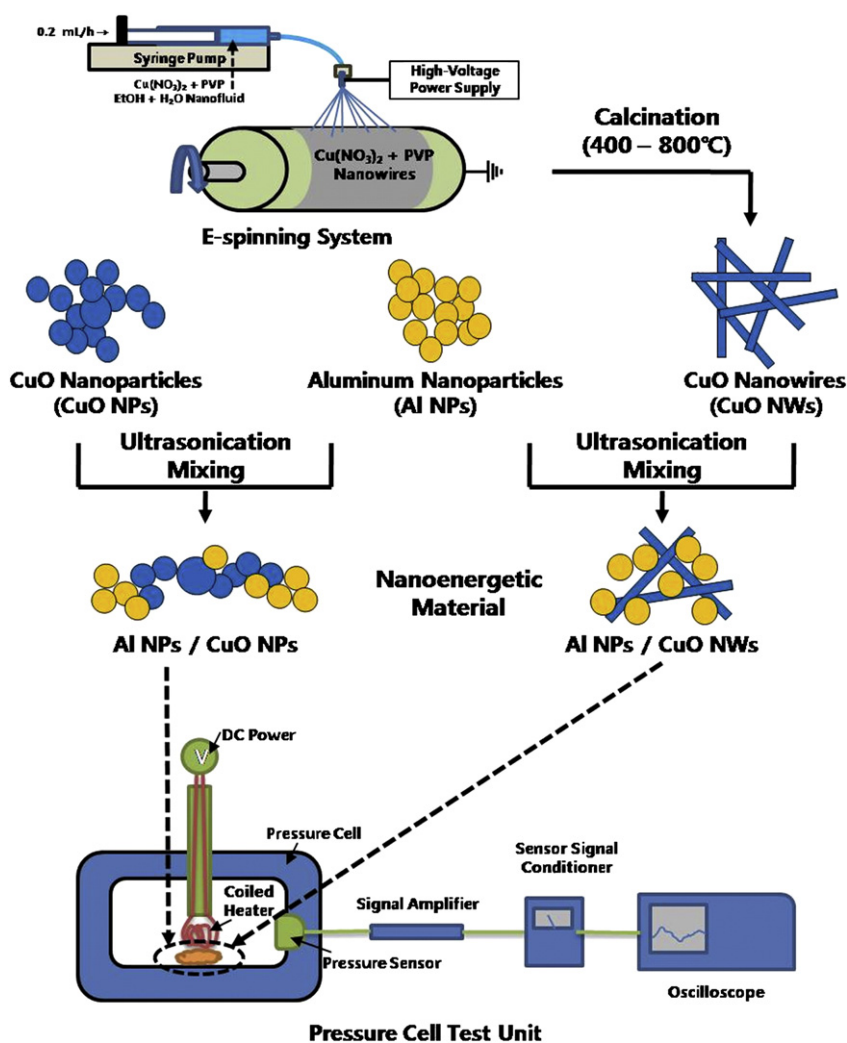


Fig. 1. Schematic of the experimental process.

Piezotronics, Model No. 113A03) with a maximum detection range of 120 psi, a signal amplifier (PCB Piezotronics, Model No. 422E11), a sensor signal conditioner (PCB Piezotronics, Model No. 480C02), and an oscilloscope (Tektronix, TDS 2012B). The MIC powder prepared in the reaction vessel was ignited with a tungsten wire that was heated by a direct current of approximately 2 A at 1.5 V. 13 mg of the MIC powder was exploded in the reaction vessel, and the explosion-induced pressurization rate was measured by the pressure sensor. The initial signal detected by the pressure sensor was amplified by an in-line charge amplifier and fed to the sensor signal conditioner, which transformed the signal into a voltage output. The output was then recorded by the digital oscilloscope. The pressure cell test unit was used for a quantitative

comparison of the pressurization rates of the different types of MIC powders prepared in this approach.

3. Results and discussion

In this approach, we employ a simple and easy electrospinning method that affords one-dimensional NWs of polymer-templated metal nitrates in very high yields. Initially, the composite polyvinylpyrrolidone (PVP)-templated $\text{Cu}(\text{NO}_3)_2$ NWs formed by electrospinning had uniform diameters of approximately 239 ± 5 nm, as shown in Fig. 2a. Calcining of the as-prepared PVP-templated $\text{Cu}(\text{NO}_3)_2$ NWs at moderate temperatures of 400 °C and 600 °C for 3 h resulted in the formation of

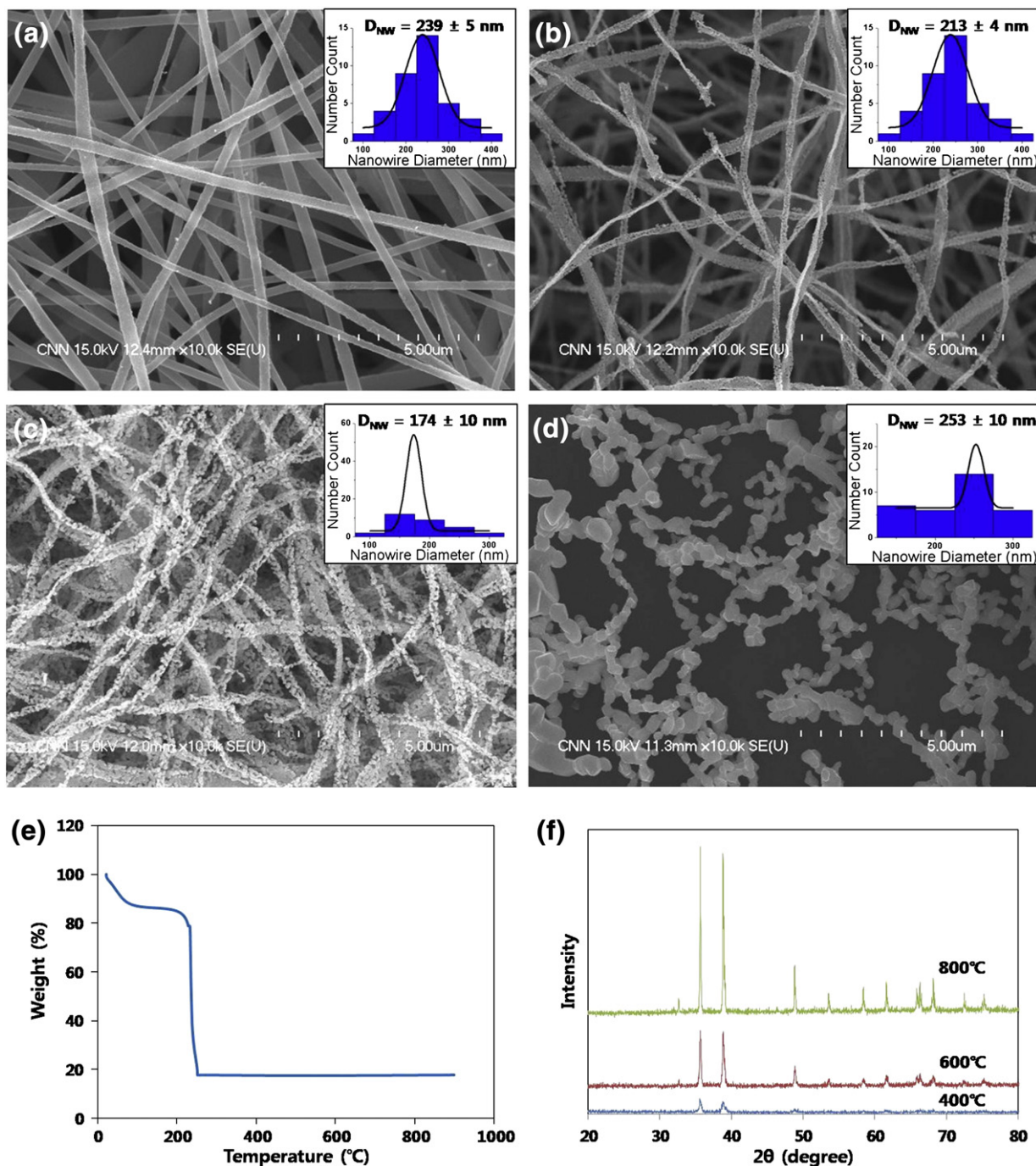


Fig. 2. SEM images of (a) as-prepared PVP-templated $\text{Cu}(\text{NO}_3)_2$ nanowires and CuO nanowires calcined at (b) 400 °C, (c) 600 °C, and (d) 800 °C (where, D_{NW} is the average diameter of nanowires). Results of (e) TGA analysis of PVP-templated $\text{Cu}(\text{NO}_3)_2$ nanowires at various temperatures and (f) XRD analysis of PVP-templated $\text{Cu}(\text{NO}_3)_2$ nanowires calcined at 400 °C, 600 °C, and 800 °C.

highly porous metal oxide NWs with final diameters of 213 ± 4 nm and 174 ± 10 nm, respectively (Fig. 2b and c), because of thermal evaporation of the polymer templates. We have stably reproduced porous CuO NWs by electrospinning method and subsequent calcination process at 400–600 °C, and the extensive SEM analysis for resulting nanostructured materials revealed that the porous CuO NWs were repeatedly formed. In contrast to calcination at moderate temperatures ($T_{\text{cal}} = 400\text{--}600$ °C), calcination at relatively high temperatures (800 °C) led to the formation of highly sintered metal oxide cluster particles, and consequently, the diameter of the resulting metal oxide NWs increased to 253 ± 10 nm. The thermal removal of the PVP templates and thermal decomposition of the metal nitrate ($\text{Cu}(\text{NO}_3)_2$) into the corresponding metal oxide (CuO) were corroborated by a combination of thermogravimetric analysis (TGA) and X-ray diffractometry (XRD), as shown in Fig. 2e and f, respectively. The mass ratio of CuO to PVP-templated $\text{Cu}(\text{NO}_3)_2$ ($M_{\text{CuO}}/M_{\text{PVP}+\text{Cu}(\text{NO}_3)_2}$) was estimated to be roughly 0.17 (here, $M_{\text{CuO}} = 79.5459 \text{ g}\cdot\text{mol}^{-1}$; $M_{\text{PVP}+\text{Cu}(\text{NO}_3)_2} = 483.2 \text{ g}\cdot\text{mol}^{-1}$). From this mass ratio, we expected the CuO content of the mixture obtained after calcination to be 17% by weight. From Fig. 2e, it could be clearly seen that the aforementioned $\text{Cu}(\text{NO}_3)_2$ -CuO conversion occurred at approximately 250 °C and that thermal removal of the polymer templates occurred at temperatures higher than 250 °C. The two strong major peaks in the XRD spectrum of the NWs calcined at 400 °C, 600 °C, and 800 °C (Fig. 2f) were identical to those obtained for pure CuO. The TGA and XRD results suggested that a moderate T_{cal} of 400–600 °C was sufficient for the thermal conversion of $\text{Cu}(\text{NO}_3)_2$ to CuO and complete removal of the PVP templates.

Ultrasonication mixing was employed to prepare MICs composed of Al and CuO; a schematic representation of this process is shown in Fig. 1.

Two types of MICs were prepared by this method. (i) Al NP-CuO NW composites: Spherical Al NPs were mixed with CuO NWs prepared by a combination of electrospinning and calcination, as described earlier. (ii) Al NP-CuO NP composites: Commercially available spherical CuO NPs were mixed with Al NPs. The energy release rates of these two types of composites were compared in this study.

First, to ensure homogeneous intermixing between the Al NPs and CuO nanostructures (NWs or NPs) in the ultrasonication mixing process, scanning transmission electron microscopy (STEM) observations were carried out on the as-prepared MICs. As shown in Fig. 3a and b, in the case of the Al NP-CuO NW composite, the Al NPs (average primary size: ~80 nm) were strongly bound to the entire surface of the porous CuO NWs. Similarly, Al NP-CuO NP MICs shown in Fig. 3c and d comprised particles with the average primary sizes of ~80 and ~50 nm, respectively; moreover, the distribution of the NPs in these materials was relatively homogeneous. These observations suggested that ultrasonication mixing was effective for the formation of a relatively homogeneous mixture of the reactants (fuel and oxidizer) at the nanoscale level. Hence, the obtained Al NPs could be ignited easily and efficiently because of their proximity to the CuO nanostructures.

For an evaluation of the effect of MIC nanostructure on the explosive reactivity of the prepared MIC, 4 mg of the MIC samples was flame ignited at one end. Fig. 4a shows a series of snapshots of the burning test carried out on pure Al NPs. The flame propagation from one end of sample to the other with the total distance of 5 mm was finished in approximately 2.5 s, which experimentally determined the velocity of flame propagation of approximately 2×10^{-3} m/s. However, in the case of a homogeneous mixture of pure Al NPs and CuO NPs, ignition resulted in an instantaneous vigorous flame, and a brilliant flash of light could be

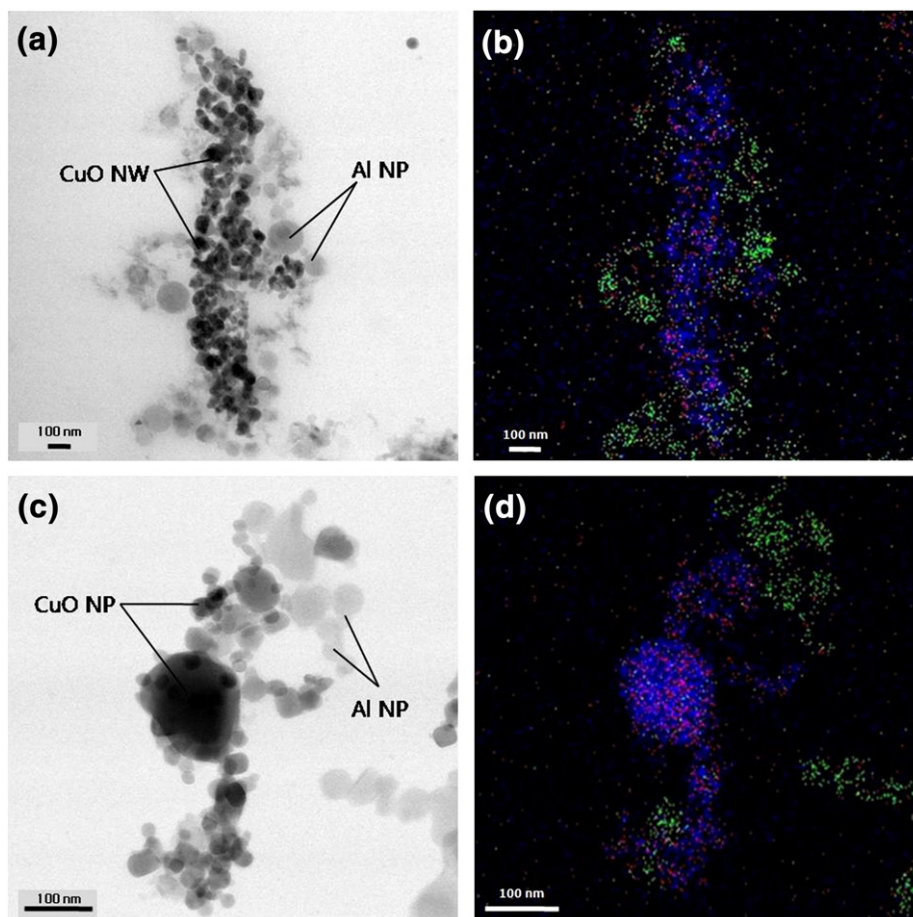


Fig. 3. (a) TEM image and (b) elemental mapping of Al NP/CuO NW composite. (c) TEM image and (d) elemental mapping of Al NP/CuO NP composite. (CuO nanowires were calcined at 400 °C. In the image showing the results of elemental mapping, blue, green, and red represent copper, aluminum, and oxygen, respectively).

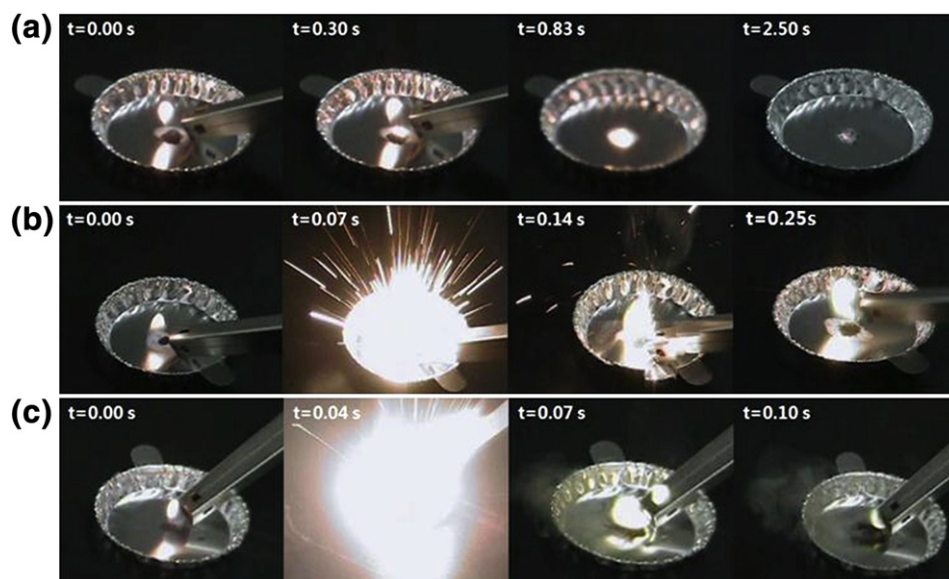


Fig. 4. Snapshots of thermally ignited (a) pure Al NPs, (b) Al NP/CuO NP composite, and (c) Al NP/CuO NW composite.

seen in the naked eye, and the velocity of the flame propagation was calculated to be approximately 2×10^{-2} m/s, which was 10 times higher than that of pure Al NPs, as shown in Fig. 4b. Interestingly, a brighter flash was observed in the case of the Al NP/CuO NW composite (Fig. 4c), and a loud explosion could be heard, and the resulting velocity of the flame propagation was found to be at least approximately 5×10^{-2} m/s, which was even 2.5 times higher than that of Al NP/CuO NP composite. This indicated that the CuO components present near the Al NPs afforded nascent oxygen, which reacted rapidly and vigorously with the fuel (Al NPs) to release energy (Fig. 4a vs. 4b). Further, it was apparent that by tailoring the metal oxide nanostructures to obtain highly porous NWs instead of solid NPs, we could effectively increase the interfacial contact area between the Al and CuO components; this in turn led to an increase in the explosive reactivity of the MICs (see Fig. 4b vs. 4c).

For further quantification of the effect of tailoring the oxidizer nanostructures on the explosive reactivity, the rate of pressurization during the confined combustion of the MICs was measured by using a pressure cell test unit (see Fig. 1). A fixed amount of the MICs (~ 13 mg) was electrically ignited in a confined-volume pressure cell, and the pressure increase in the cell was automatically recorded as a function of time. Here, the pressurization rate is defined as the initial slope of the line showing pressure increase and is expressed in $\text{psi} \cdot \mu\text{s}^{-1}$. A high pressurization rate indicates that the pressure increase occurs rapidly and that the MICs are highly reactive. Fig. 5a shows the pressurization rates at various fuel/oxidizer mixing ratios for Al/CuO mixtures sonicated for 5 min in EtOH. The pressurization rate of the Al NPs mixed with highly porous CuO NWs calcined at moderate temperatures of 400–600 °C (also see Fig. 2b and c) was higher than that of the Al NP/CuO NP MICs for different stoichiometric proportions. On the other hand, the pressurization rate of the Al NPs mixed with linearly clustered CuO NWs calcined at a relatively high temperature of 800 °C (also see Fig. 2d) was markedly lower than that of the Al NP/CuO NP MICs. This indicated that when using the highly porous CuO NWs, the interfacial contact area increased, and hence, nascent oxygen was effectively produced for promoting the explosive reaction of the Al NPs. In the case of the Al NP/CuO NP MICs, the maximum pressurization rate of $\sim 1.8 \text{ psi} \cdot \mu\text{s}^{-1}$ at 13 mg (i.e., $\sim 0.14 \text{ psi} \cdot \mu\text{s}^{-1} \cdot \text{mg}^{-1}$) was observed when the Al content of the Al/CuO mixture was approximately 30 wt.%, and this was found to be very similar with Anand et al.'s [5] results for Al NP/CuO NP MICs, which generated the maximum pressurization rate of $\sim 4.5 \text{ psi} \cdot \mu\text{s}^{-1}$ at 25 mg (i.e., $\sim 0.18 \text{ psi} \cdot \mu\text{s}^{-1} \cdot \text{mg}^{-1}$). It indicates that the maximum pressurization rate of Al NP/CuO NP MICs employed in this

study can be a comparable baseline for determining the enhancement of explosive reactivity made by various Al NP/CuO NW MICs. In the case of the Al NPs mixed with CuO NWs prepared in this study, the maximum pressurization rates were approximately 4.2, 3.2, and 0.8 $\text{psi} \cdot \mu\text{s}^{-1}$ when

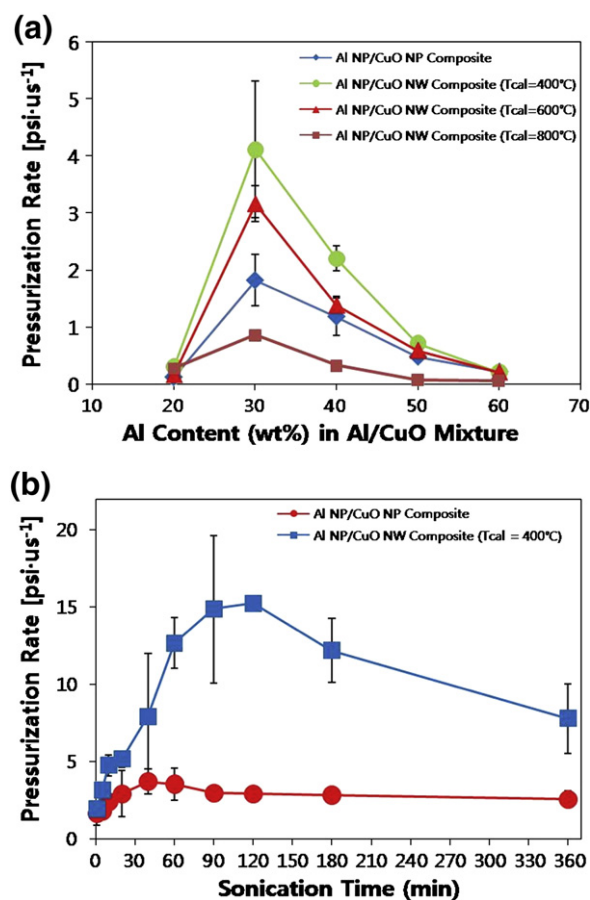


Fig. 5. (a) Pressurization rates of MICs comprising Al NPs and CuO nanostructures as a function of Al content in the Al/CuO mixture (all MICs were mixed in an ultrasonicator for 5 min). (b) Pressurization rates of Al NP/CuO NP composites and Al NP/CuO NW composites as a function of sonication time (the Al content of the Al/CuO mixture was fixed at 30 wt.%, and the CuO NWs were calcined at 400 °C).

the calcination temperatures were 400 °C, 600 °C, and 800 °C, respectively. This result further confirmed the fact that we could tune the explosive reactivity of our MICs by simply tailoring the oxidizer nanostructures.

In our approach, we found that the degree of intermixing between the reactants was strongly dependent on the sonication time. We believed that the low pressurization rate of the MICs was partially due to incomplete homogeneous mixing of the reactants. Therefore, it was necessary to verify the effect of sonication time on the reactivity of the MICs. The pressurization rates of the two types of MICs prepared in this study (Al NP/CuO NP and Al NP/CuO NW composites ($T_{cal}=400\text{ °C}$)) were measured as a function of sonication time, as shown in Fig. 5b. In the case of the Al NP/CuO NP composite, the pressurization rate steadily

increased up to 60 min of sonication and then remained constant, indicating that the degree of intermixing was slightly enhanced during the early stages of the sonication process (<60 min). However, in the case of the Al NP/CuO NW composite, the degree of intermixing between the Al NPs and the CuO NWs was considerably enhanced with an increase in the sonication time. Hence, after sonication for 120 min, the pressurization rate increased to a maximum of approximately $15\text{ psi}\cdot\mu\text{s}^{-1}$, which was 10 times that observed for the Al NP/CuO NP composite. This suggested that the pressurization rate of the Al NP/CuO NW composite could be significantly altered by simply adjusting the sonication conditions. After 120 min of sonication, the pressurization rate of the Al NP/CuO NW composite decreased significantly. This was presumably because of the following two reasons: (i) the disintegration

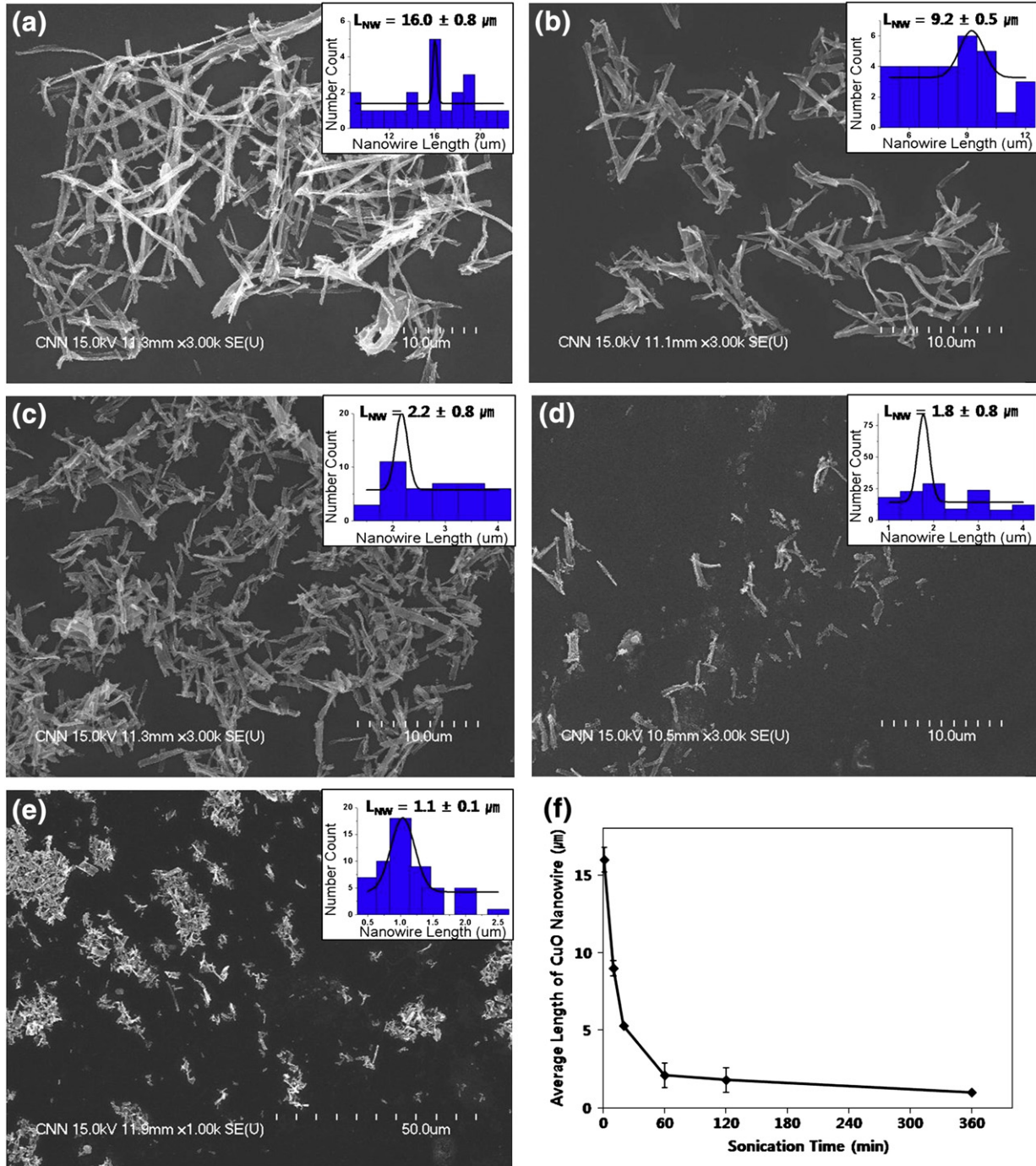


Fig. 6. SEM images of CuO NWs after sonication for (a) 1 min, (b) 10 min, (c) 60 min, (d) 120 min, and (e) 360 min (L_{NW} is the average length of nanowires). (f) Average length of CuO NWs as a function of sonication time.

of the porous structure of the CuO NWs by the intensive sonication energy and (ii) decrease in the length of the CuO NWs during prolonged sonication. The latter possibility was confirmed by measuring the length distribution of the CuO NWs as a function of sonication time, as presented in Fig. 6. It was apparent that the average length of the CuO NWs decreased significantly after intensive sonication. This suggested that the initial interfacial contact area afforded by the highly porous CuO NWs was significantly reduced by the sonication-energy-induced destruction of the porous structure of the NWs and the shortening of the NWs after sonication.

4. Conclusions

In conclusion, we have demonstrated the formation of highly porous metal oxide NWs by using a combination of electrospinning and calcination. The ultrasonication process carried out after electrospinning and calcination is a viable method that enables homogeneous mixing of the low-dimensional nanostructured reactants in the MICs. The MIC reactivity and the kinetics of burning of the MICs can be tuned by simply tailoring the oxidizer nanostructures, which play a key role in varying the interfacial contact area between the fuel and the oxidizer.

Acknowledgement

This work was supported by the National Research Foundation of Korea Grant funded by the Korean Government (2009-0070665).

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