

## Research Article

# Gas-Phase Synthesis of Bimetallic Oxide Nanoparticles with Designed Elemental Compositions for Controlling the Explosive Reactivity of Nanoenergetic Materials

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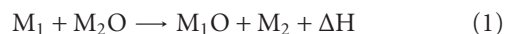
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We demonstrate a simple and viable method for controlling the energy release rate and pressurization rate of nanoenergetic materials by controlling the relative elemental compositions of oxidizers. First, bimetallic oxide nanoparticles (NPs) with a homogeneous distribution of two different oxidizer components (CuO and Fe<sub>2</sub>O<sub>3</sub>) were generated by a conventional spray pyrolysis method. Next, the Al NPs employed as a fuel were mixed with CuO-Fe<sub>2</sub>O<sub>3</sub> bimetallic oxide NPs by an ultrasonication process in ethanol solution. Finally, after the removal of ethanol by a drying process, the NPs were converted into energetic materials (EMs). The effects of the mass fraction of CuO in the CuO-Fe<sub>2</sub>O<sub>3</sub> bimetallic oxide NPs on the explosive reactivity of the resulting EMs were examined by using a differential scanning calorimeter and pressure cell tester (PCT) systems. The results clearly indicate that the energy release rate and pressurization rate of EMs increased linearly as the mass fraction of CuO in the CuO-Fe<sub>2</sub>O<sub>3</sub> bimetallic oxide NPs increased. This suggests that the precise control of the stoichiometric proportions of the strong oxidizer (CuO) and mild oxidizer (Fe<sub>2</sub>O<sub>3</sub>) components in the bimetallic oxide NPs is a key factor in tuning the explosive reactivity of EMs.

## 1. Introduction

Energetic material (EM) has chemical enthalpy, which can be rapidly turned into thermal energy when it is initiated by external energy input. An EM generally comprises two components: a fuel and an oxidizer. Once an EM begins to burn, a so-called self-sustaining exothermic reaction occurs as follows:



Here, M<sub>1</sub> is a fuel, M<sub>2</sub>O is an oxidizer, and ΔH is the heat of formation. The reaction enthalpies for the redox reactions of Al with CuO and Fe<sub>2</sub>O<sub>3</sub> as a specific example are given in Table 1 [1, 2]. EMs can be used in various fields of engineering; for example, they can be used as explosives or

propulsion fuels and can be used in pyrotechnics because of their strong exothermic characteristics.

Among numerous thermodynamically stable EM formulations, those comprising Al as a fuel that is mixed with various oxidizers, including Fe<sub>2</sub>O<sub>3</sub>, CuO, MoO<sub>3</sub>, and KMnO<sub>4</sub>, are widely used. In order to enhance the explosive reactivity of EMs, many research groups investigated the effect of the fineness of reactants, the degree of intermixing of the fuel and oxidizer, and the interfacial contact area between the fuel and oxidizer [3–9]. Since the use of nanoscale reactants reduces the limitations on the mass transport between the fuel and oxidizer and the reaction becomes kinetically controlled, nano-Al mixed with various nanostructures that act as oxidizers has been used in an attempt to increase the energy release rate of EMs. However,

TABLE 1: Adiabatic flame temperatures and heat of reaction of Al combustion with different oxidizers.

Reaction	Adiabatic flame temp. (K)	Heat of reaction (kJ/mole)
$\text{Fe}_2\text{O}_3 + 2\text{Al} \rightarrow 2\text{Fe} + \text{Al}_2\text{O}_3$	3132	-856.6 (-3.71 kJ/g)
$3\text{CuO} + 2\text{Al} \rightarrow 3\text{Cu} + \text{Al}_2\text{O}_3$	2846	-1212.5 (-4.14 kJ/g)

considerably complex chemical routes must be chosen to produce low-dimensional nanostructured oxidizers, including nanorods [10], nanowires (NWs) [11], and core-shell nanoparticles (NPs) [12]. Although numerous energetic composites with an enhanced energy release rate have successfully been formulated, precise and easy control of the explosive reactivity of EMs has not yet been achieved.

Unlike previous studies, the approach we adopted in this study was based on an investigation of the effect of the mixing ratio of the two components in oxidizer NPs on the final energy release rate of EMs. We employed a simple one-step spray pyrolysis method for generating bimetallic oxide NPs and precisely varied the stoichiometric ratios between two different metal oxide precursors, namely, CuO as a relatively strong oxidizer and  $\text{Fe}_2\text{O}_3$  as a relatively mild oxidizer. We demonstrated that the energy release rate and pressurization rate of EMs can be precisely controlled by simply changing the relative composition of the strong and mild oxidizers in the bimetallic oxide NPs mixed with Al-fuel NPs.

## 2. Experimental

Al NPs that were commercially available from NT base, Inc., and had an average size of approximately 80 nm were used as a fuel without further treatment. In order to synthesize composite oxidizer NPs, an aerosol spray pyrolysis method was used, as shown in Figure 1. Briefly, copper nitrate ( $\text{Cu}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$ , Sigma Aldrich, 156 g of  $\text{Cu}(\text{NO}_3)_2/100$  g of  $\text{H}_2\text{O}$ ) and iron(III) nitrate ( $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ , Sigma Aldrich, 138 g of  $\text{Fe}(\text{NO}_3)_3/100$  g of  $\text{H}_2\text{O}$ ) were dissolved in deionized water at various mixing ratios of  $\text{Cu}(\text{NO}_3)_2$  and  $\text{Fe}(\text{NO}_3)_3$ , in particular,  $\text{Cu}(\text{NO}_3)_2 : \text{Fe}(\text{NO}_3)_3 = 1 : 0, 10 : 1, 5 : 1, 1 : 1, 1 : 5, 1 : 10$ , and  $0 : 1$ . Here, the total concentration of precursor solutions was fixed at 10 wt%. The metal-nitrate-containing solutions were then aerosolized by using an atomizer that was developed in-house and was operated by compressed air at 35 psi, and the moisture in the microsized evaporating droplets was removed by passing through a silica-gel drier. Metal nitrate particles were then continuously oxidized by passing through a quartz tube reactor enclosed in a tube furnace heated to  $500^\circ\text{C}$ ; the residence time in this process was approximately 1 s. The final CuO- $\text{Fe}_2\text{O}_3$  bimetallic oxide composite NPs were collected on a membrane filter with a pore size of 200 nm. The CuO- $\text{Fe}_2\text{O}_3$  composite NPs formed were characterized by various techniques, including thermogravimetric analysis (TGA; Perkin Elmer (USA), Pyris 1, Diamond) at temperatures ranging from  $50^\circ\text{C}$  to

$800^\circ\text{C}$ , 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 collected CuO- $\text{Fe}_2\text{O}_3$  bimetallic oxide NPs were then mixed with Al NPs in EtOH solution. The mixing ratio of the fuel and oxidizer was fixed at  $\text{Al} : \text{CuO-Fe}_2\text{O}_3 = 3 : 7$ . The solution comprising dispersed Al NPs and CuO- $\text{Fe}_2\text{O}_3$  NPs was sonicated at 200 W and 40 kHz for approximately 40 min and then dried in a convection oven operated at  $80^\circ\text{C}$  for approximately 30 min. Finally, the EM composed of Al NPs and CuO- $\text{Fe}_2\text{O}_3$  bimetallic oxide NPs was obtained. In order to observe the explosion characteristics of different types of EMs that were prepared, a pressure cell tester (PCT) system was designed and built. This system was designed to measure the pressurization rate of EMs during their confined combustion. The specifications of the PCT system are described elsewhere in detail [13]. Briefly, 13 mg samples of the EM were placed in the confined reaction cell ( $\sim 13$  mL) and ignited using a heated tungsten wire with a direct current of approximately 2 A at 1.5 V. The rate of explosion-induced pressurization was then measured in situ by the pressure sensor (PCB piezotronics, Model no. 113A03). The initial signal measured by the pressure sensor was then amplified by an in-line charge amplifier (PCB piezotronics, Model no. 422E11). The signal was transformed into a voltage output at the sensor signal conditioner (PCB Piezotronics, Model no. 480C02). The voltage output was then recorded by the digital oscilloscope (Tektronix, TDS 2012B).

## 3. Results and Discussion

The thermal decomposition of the metal nitrate into metal oxide was first verified by thermal gravimetric analysis, as shown in Figure 2(a). The formation of CuO and  $\text{Fe}_2\text{O}_3$  was clearly observed to occur at approximately  $300^\circ\text{C}$  and  $200^\circ\text{C}$ , respectively. This suggests that the CuO- $\text{Fe}_2\text{O}_3$  bimetallic oxide NPs can be completely formed by thermal decomposition of bimetallic nitrate NPs at  $500^\circ\text{C}$  during spray pyrolysis. The gas-phase formation of CuO,  $\text{Fe}_2\text{O}_3$ , and CuO- $\text{Fe}_2\text{O}_3$  bimetallic oxide NPs with a relatively short residence time of approximately 1 s was then corroborated by XRD analysis, as shown in Figure 2(b). The XRD spectra showed very strong diffractions from each metallic oxide NP and confirmed the formation of pure CuO NPs, pure  $\text{Fe}_2\text{O}_3$  NPs, and CuO- $\text{Fe}_2\text{O}_3$  bimetallic oxide NPs by spray pyrolysis.

The average size and morphology of the fuel and oxidizer prepared in this study were then examined by SEM and TEM analyses, as shown in Figure 3. The average primary size of Al NPs (the fuel), as determined from Figures 3(a) and 3(b), was approximately  $81 \pm 4$  nm. The thickness of the passivation layer of Al NPs, as determined from the HRTEM image inserted in Figure 3(b), was approximately 5 nm. The average primary size of CuO- $\text{Fe}_2\text{O}_3$  bimetallic oxide NPs with a molar ratio of 1 : 1 was  $800 \pm 11$  nm; this value was determined from Figures 3(c) and 3(d). It should be noted that the variation in the mixing ratios of CuO and  $\text{Fe}_2\text{O}_3$  did not lead to any appreciable changes in the average

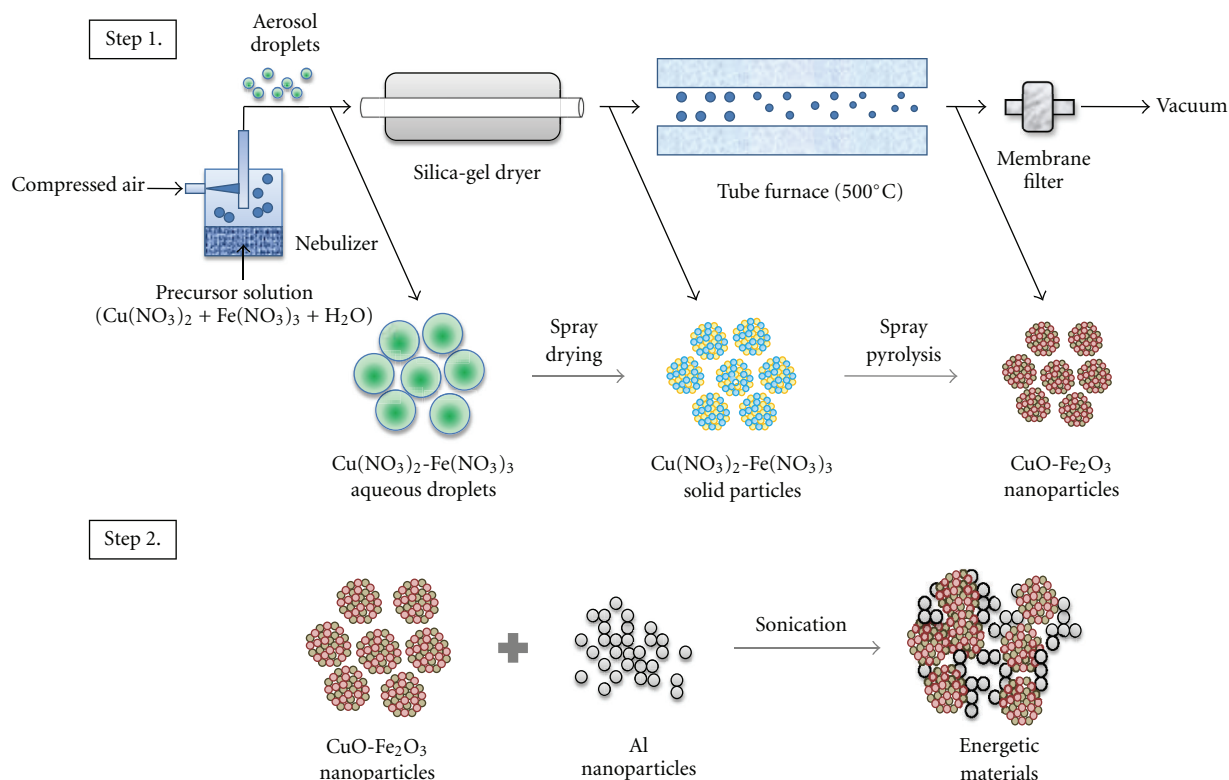


FIGURE 1: Schematic of the experimental setup for generating the energetic materials composed of Al nanoparticles (NPs) and  $\text{CuO-Fe}_2\text{O}_3$  bimetallic oxide NPs.

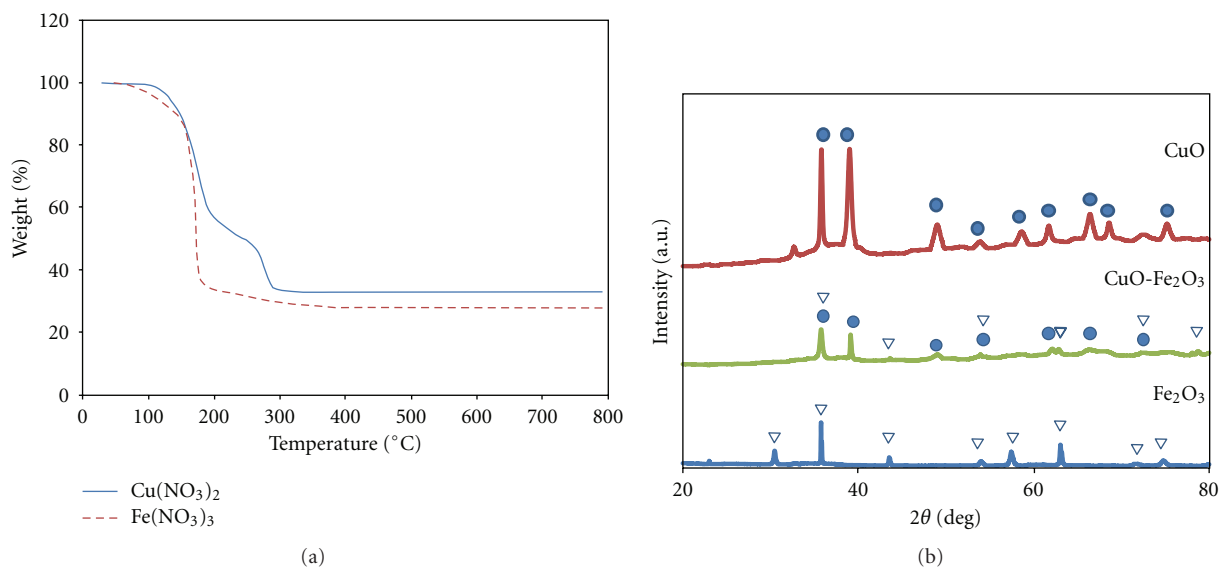


FIGURE 2: (a) TGA analysis of metal nitrates and (b) XRD analysis of the  $\text{CuO}$ ,  $\text{Fe}_2\text{O}_3$ , and  $\text{CuO-Fe}_2\text{O}_3$  nanoparticles prepared by spray pyrolysis.

size of the resulting bimetallic oxide NPs, because the total concentration of the initial bimetallic nitrate precursors was fixed at approximately 10 wt%.

When the fuel NPs begin to burn, their explosive reactivity can be altered by the amount of oxygen supply from various types of oxidizers. One of the key factors

in tuning the explosive reactivity of EMs composed of a fuel and an oxidizer is to simply change the elemental composition of the oxidizer. In this approach, bimetallic oxide NPs composed of  $\text{CuO}$ , a relatively strong oxidizer, and  $\text{Fe}_2\text{O}_3$ , a relatively mild oxidizer, were synthesized by using a conventional spray pyrolysis method, in which the initial

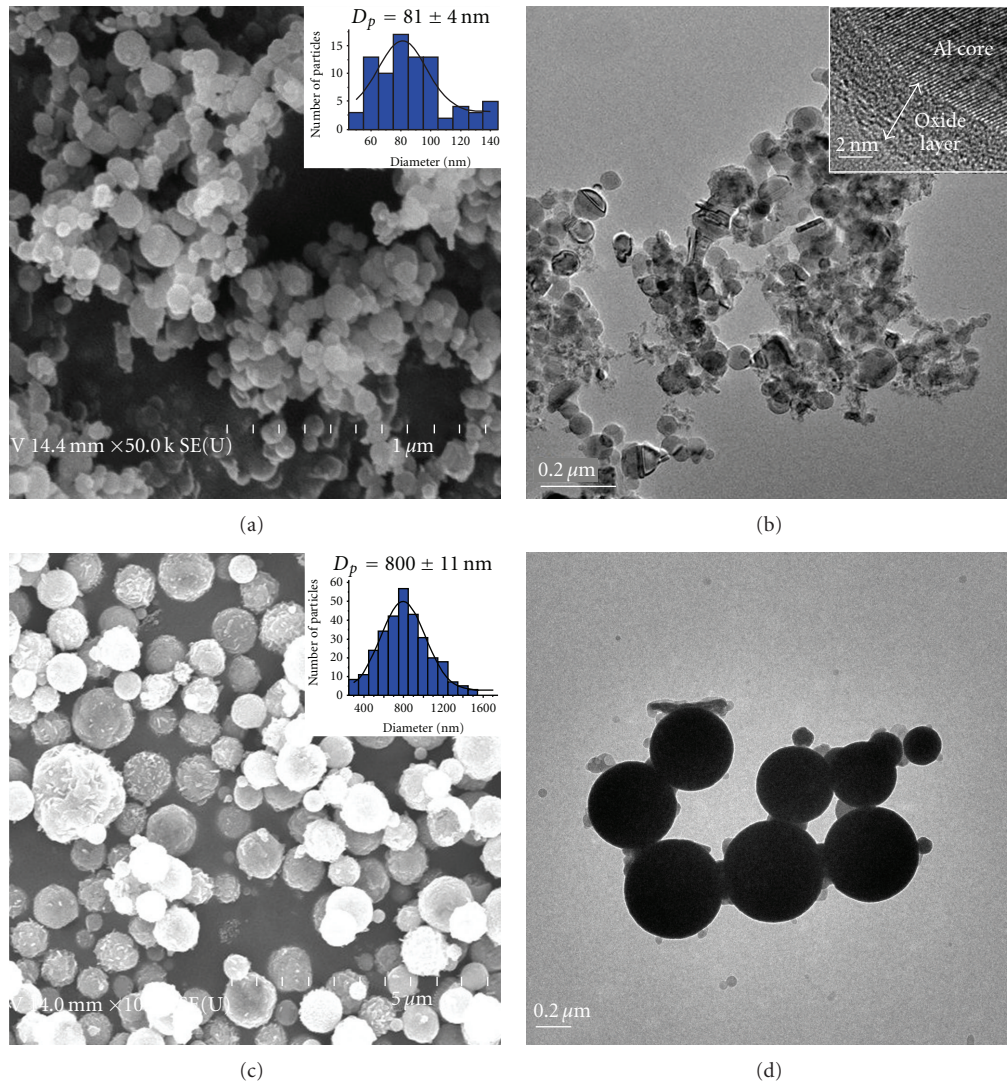


FIGURE 3: SEM and TEM images of Al NPs ((a) and (b)) and CuO-Fe<sub>2</sub>O<sub>3</sub> bimetallic oxide NPs ((c) and (d)) (the insets are the particle size distributions and  $D_p$  is the average particle size).

stoichiometric mixing ratios of the Cu(NO<sub>3</sub>)<sub>2</sub> and Fe(NO<sub>3</sub>)<sub>2</sub> precursors dissolved in an aqueous solution were precisely controlled. In order to verify the homogeneous distribution of the two metal oxide components in the aerosol bimetallic oxide NPs formed by the spray pyrolysis route, a series of STEM analyses were performed. Figure 4 shows STEM images and the elemental mapping of the prepared CuO-Fe<sub>2</sub>O<sub>3</sub> bimetallic oxide NPs with various mixing ratios of CuO and Fe<sub>2</sub>O<sub>3</sub>. In the elemental mapping, Cu, Fe, and O were found to be homogeneously distributed in the resulting bimetallic oxide NPs, and the magnitudes of the signals due to Cu and Fe increased when the initial proportion of Cu and Fe was increased. This suggests that the conventional spray pyrolysis method employed in this approach is a very simple and viable method for producing oxidizer NPs with various desired chemical compositions.

A fixed amount (~13 mg) of the EM (in the form of a loose powder) composed of 30 wt% Al NPs and

70 wt% CuO-Fe<sub>2</sub>O<sub>3</sub> bimetallic oxide NPs with different stoichiometric proportions of CuO and Fe<sub>2</sub>O<sub>3</sub> was ignited in the PCT system, and the pressurization rate of the confined reaction cell corresponding to the ignition of EMs was measured in situ [11]. Figure 5(a) presents the typical pressure traces of Al NP/CuO NP, Al NP/CuO-Fe<sub>2</sub>O<sub>3</sub> NP (CuO:Fe<sub>2</sub>O<sub>3</sub> = 1:1), Al NP/CuO-Fe<sub>2</sub>O<sub>3</sub> NP (CuO:Fe<sub>2</sub>O<sub>3</sub> = 1:5), and Al NP/Fe<sub>2</sub>O<sub>3</sub> NP, respectively. One can easily see that Al NP/CuO NP nanocomposites show the highest pressurization rate. With decreasing the mass fraction of CuO in CuO-Fe<sub>2</sub>O<sub>3</sub> bimetallic oxide nanoparticles, the magnitude of maximum pressure was decreased, and the rise time was slower. The maximum pressurization rates measured for different stoichiometric proportions of CuO and Fe<sub>2</sub>O<sub>3</sub> are plotted as a function of the mass fraction of CuO in the CuO-Fe<sub>2</sub>O<sub>3</sub> NPs in Figure 5(b). Here, the maximum pressurization rate was calculated by obtaining the ratio of the maximum pressure to the rise time. The

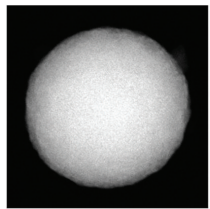
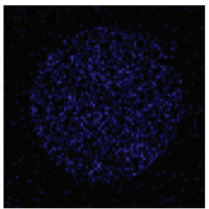
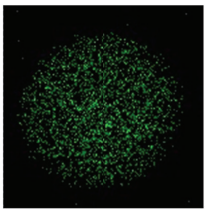
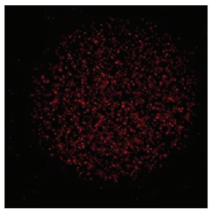
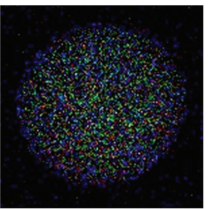
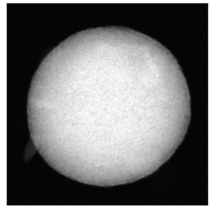
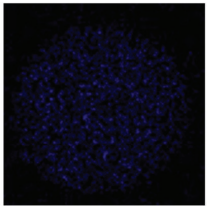
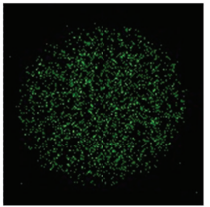
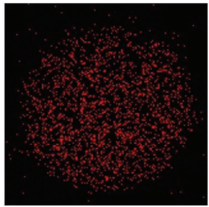
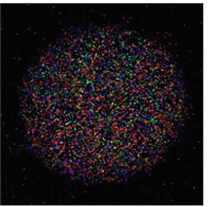
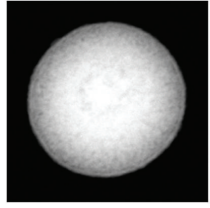
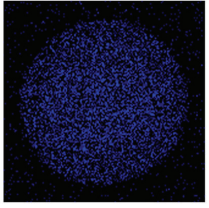
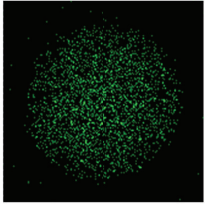
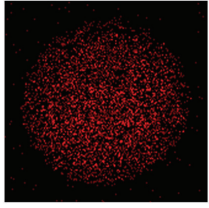
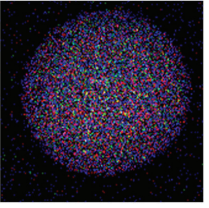
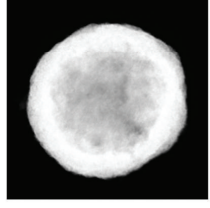
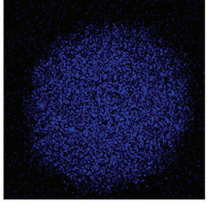
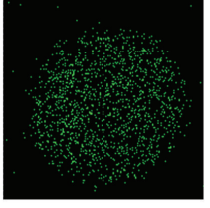
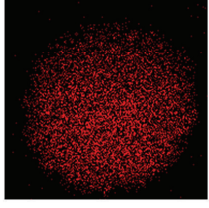
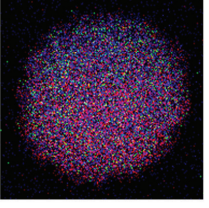
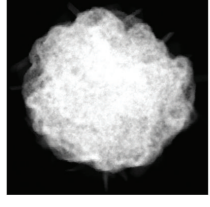
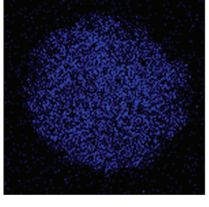
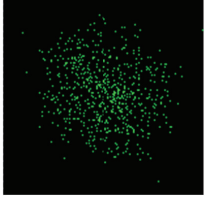
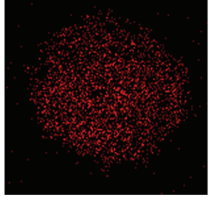
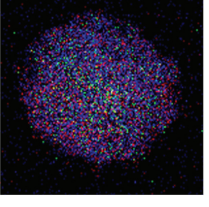
CuO : Fe <sub>2</sub> O <sub>3</sub>	STEM image	Cu	Fe	O	Overlay
1:10					
1:5					
1:1					
5:1					
10:1					

FIGURE 4: STEM images and elemental maps of CuO-Fe<sub>2</sub>O<sub>3</sub> bimetallic oxide NPs.

maximum pressurization rate of 13 mg samples of the EMs composed of 30 wt% Al and 70 wt% pure Fe<sub>2</sub>O<sub>3</sub> (the mild oxidizer) was observed to be approximately  $0.4 \text{ psi} \cdot \mu\text{s}^{-1}$  (i.e.,  $\sim 31 \text{ psi} \cdot \mu\text{s}^{-1} \cdot \text{g}^{-1}$ ). The maximum pressurization rate of the EMs increased linearly with the proportion of the CuO component in the CuO-Fe<sub>2</sub>O<sub>3</sub> NPs. The maximum pressurization rate of 13 mg samples of the EMs composed of 30 wt% Al and 70 wt% pure CuO (the strong oxidizer) was approximately  $1.6 \text{ psi} \cdot \mu\text{s}^{-1}$  (i.e.,  $\sim 123 \text{ psi} \cdot \mu\text{s}^{-1} \cdot \text{g}^{-1}$ ). This suggests that the concentration of oxygen generated from

the decomposition of CuO was significantly increased with increasing the reaction temperature of Al/CuO nanocomposites [12] so that the increase of CuO proportion in the CuO/Fe<sub>2</sub>O<sub>3</sub> bimetallic oxide NPs results in promoting the explosive reactivity of the resulting energetic materials. As such, the precise control of the explosive reactivity of EMs can be achieved by controlling the relative mixing ratios of the two oxidizer components in the bimetallic oxide NPs.

We performed XRD analysis for Al/CuO and Al/Fe<sub>2</sub>O<sub>3</sub> nanocomposites before and after ignition test in order to

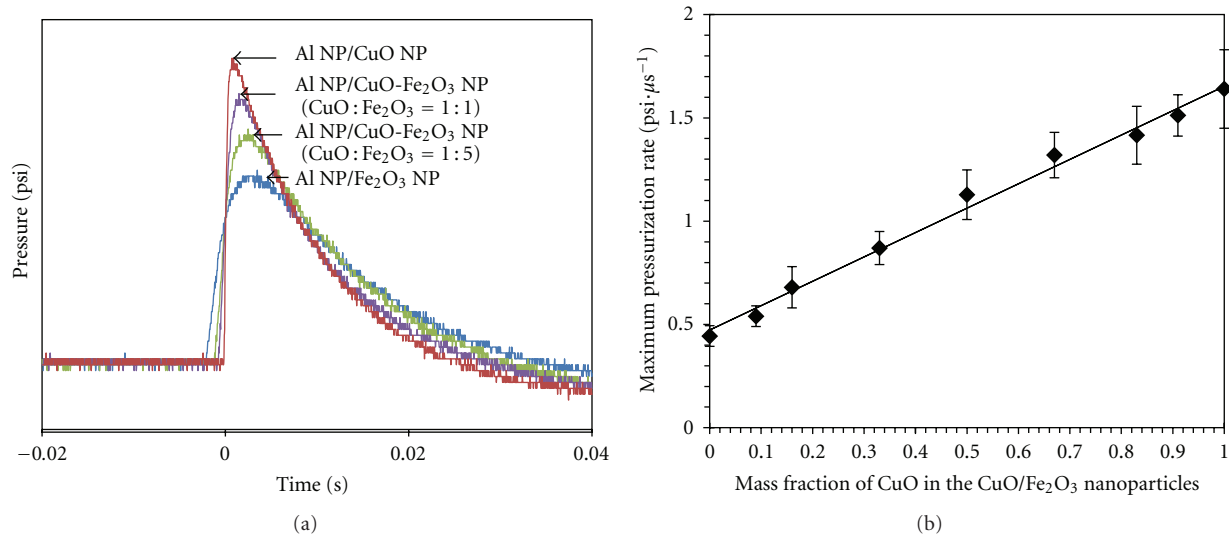


FIGURE 5: (a) Pressure traces of various EMs ignited in the PCT system, (b) maximum pressurization rates for EMs composed of Al nanoparticles (NPs) and CuO-Fe<sub>2</sub>O<sub>3</sub> bimetallic oxide NPs as a function of the mass fraction of CuO in the CuO-Fe<sub>2</sub>O<sub>3</sub> composite NPs.

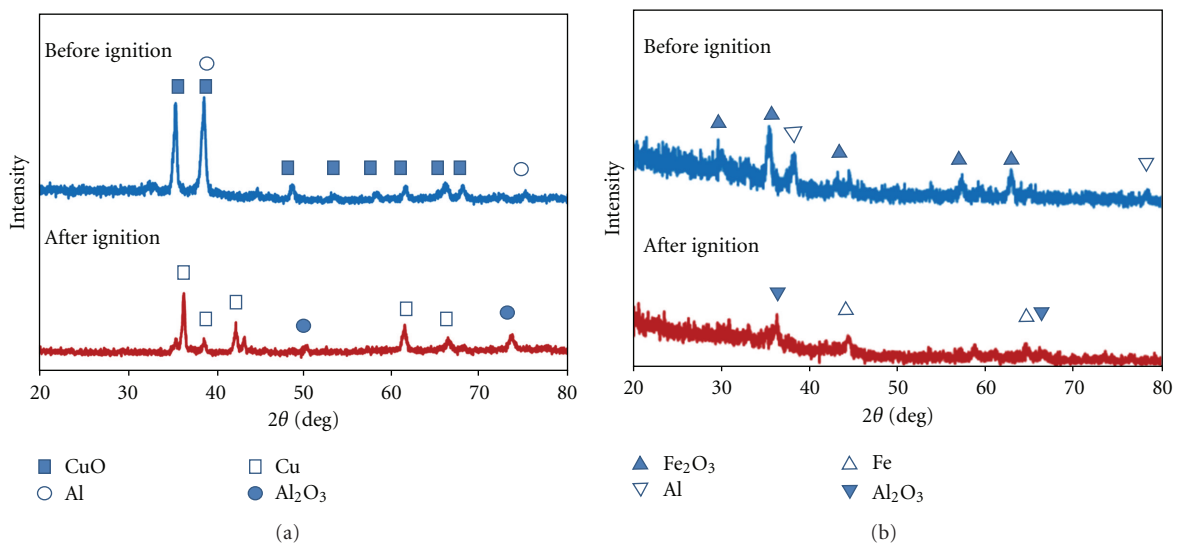


FIGURE 6: (a) XRD signals for Al/CuO nanocomposites before and after ignition test, and (b) XRD signals for Al/Fe<sub>2</sub>O<sub>3</sub> nanocomposites before and after ignition test.

examine the completeness of the exothermic reactions as shown in Figure 6. Figure 6(a) presents the XRD signals for Al/CuO nanocomposites before and after ignition test. The presence of both CuO and Al was identified before ignition. However, after ignition, the signals of Al and CuO disappeared, and then the strong signals of Cu and Al<sub>2</sub>O<sub>3</sub> appeared. Figure 6(b) also presents the XRD signals for Al/Fe<sub>2</sub>O<sub>3</sub> nanocomposites before and after ignition test. Similarly, the presence of Fe<sub>2</sub>O<sub>3</sub> and Al was identified before ignition test. However, the signals of Fe<sub>2</sub>O<sub>3</sub> and Al disappeared after ignition, and then the signals of Fe and Al<sub>2</sub>O<sub>3</sub> appeared. Those confirmed that the redox reaction between Al/CuO or Al/Fe<sub>2</sub>O<sub>3</sub> was completed in this approach.

## 4. Conclusions

In summary, we have demonstrated the formation of bimetallic oxide composite particles by spray pyrolysis, in which the initial mixing ratios of two different metal nitrate precursors in aqueous solution were varied and metal nitrate particles were simultaneously converted into bimetallic oxide particles by thermal decomposition. The resulting bimetallic oxide NPs were found to have a homogeneous distribution of strong oxidizer (CuO) and mild oxidizer (Fe<sub>2</sub>O<sub>3</sub>) components. By subsequent ultrasonication, Al NPs were mixed with the CuO-Fe<sub>2</sub>O<sub>3</sub> bimetallic oxide NPs, and, finally, EMs were formed. The energy release rate and pressurization rate of the synthesized EMs composed of Al NPs and CuO-Fe<sub>2</sub>O<sub>3</sub>

bimetallic oxide NPs were found to increase linearly with the mass fraction of CuO in the CuO-Fe<sub>2</sub>O<sub>3</sub> NPs. This suggests that the precise control of the stoichiometric proportions of strong and mild oxidizer components in the bimetallic oxidizers is a key factor in tuning the explosive reactivity of the resulting EMs. By employing the combination of spray pyrolysis and ultrasonication mixing process, one can reproducibly obtain materials that may act as EMs with the desired explosive reactivity by controlling the relative elemental compositions in the oxidizer.

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