

# Al/CuO Nanothermite Shell Assembled via Depositing Aluminum Nanoparticles onto CuO Nanowire Array on a Copper Wire

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## 1 Introduction

Nanothermites are composite energetic materials in which nanoscale active metal fuel (e.g. Al) and metal oxide (e.g. CuO, Fe<sub>2</sub>O<sub>3</sub>, MoO<sub>3</sub>, Bi<sub>2</sub>O<sub>3</sub>, etc.) are brought together in nanometer proximity. Reduction of the length scale leads to several advantages. Reaction rate can be increased due to the smaller diffusion distance between the nanoscale fuel and oxidizer particles. The enhanced surface-to-volume ratio of the smaller particles also results in enlarged interfacial contact such that ignition delay and potentially ignition temperature are decreased [1]. The highly exothermic and violent oxidation-reduction reactions of energetic materials have potential applications in propellants, welding, explosives, bicidal, drug delivery and pyrotechnics [2-7].

Nanothermites are usually assembled through physical mixing of fuel and oxidizer nanoparticles in solutions using ultrasonication. But it is a nontrivial task to control the mixing homogeneity and packing density of the nanothermite powders with the method. Various other approaches, including arrested reactive milling [8], so-gel [9], self-assembly [10,11], vapor deposition [12-14], electrophoretic deposition (EPD) [15,16], biosynthetic [17], and DNA strands complement [18], were nonetheless developed to address the challenges.

In this work, a novel nanothermite assembly approach is presented. The concept of the method as well as the assembly process are first introduced in the following section. Preparation of the oxidizer and fuel in the nanothermites, which are CuO nanowires (CuO NW) and aluminum nanoparticles (Al NP), respectively, were then discussed. Characterizations of the nanothermite reaction were performed using differential scanning calorimetry (DSC), and the influence of EPD electric field gradient on ignition temperatures and heat release of the assembled nanothermites were discussed.

## 2 The assembly process

The concept of assembling nanothermite via embedding aluminum nanoparticles in CuO NWs were schematically shown in Fig. 1(a). Aluminium nanoparticles (Al NP) are inserted into copper oxide nanowire (CuO NW) clusters on the surface of a copper wire through electrophoretic deposition. But unlike the EPD method demonstrated in the literature [15,16] in which both aluminum and CuO nanoparticles exist in the dispersion medium, only Al NP were dispersed in the solution in our approach. Only aluminum nanoparticles were dispersed in ethanol water solution. The particles carry positive surface charges in the solution, and are driven to the negative electrode when electric field is applied across the solution. By taking the copper wire covered with CuO nanowire as the negative electrode, aluminum nanoparticles can be embedded onto the nanowire array to form the binary energetic composite through EPD. Since the nanothermite exists as a shell layer directly formed on a copper wire of  $\sim 100 \mu\text{m}$  in diameter, problems associated with handling and filling nano powders are avoided. Furthermore, Reaction characteristics of the nanothermite can potentially be tuned through the manipulation of CuO nanowire number density and geometry, size of aluminum nanoparticles as well as EPD parameters.

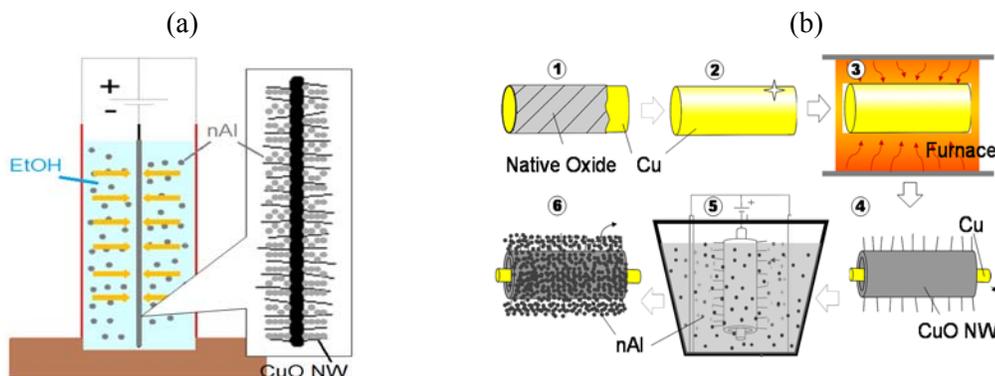


Figure 1. (a) Schematic of the assembly concept, and (b) the process flow of the assembly method.

Figure 1(b) schematically shows the process of the assembly method. The process begins with an ordinary copper wire of  $\sim 122 \mu\text{m}$  in diameter (40 SWG, purity  $> 99.95$ ). Native oxides of the copper wire should be removed with a pre-cleaning process prior to thermal oxidation. The wire was soaked in 35 % hydrochloric acid bath for 30 sec to remove the native oxide layer was rinsed by deionized water (Direct-Q Ultrapure Water Systems, Millipore) and immediately being ultrasonicated in acetone bath for one minute to get rid of remained impurities (DC300H, Delta).

CuO NWs were grown on the surface of the copper wire via thermal oxidation method [19]. The oxidation temperature and duration should be appropriately selected to avoid full oxidation of the copper wire into copper oxides, because the existence of the copper core is essential for the subsequent electrophoretic deposition (EPD) process. For the study of temperature effects, copper wire was heated in furnace from  $30 \text{ }^\circ\text{C}$  to various temperatures between  $400$  and  $900 \text{ }^\circ\text{C}$ . It has been found that the oxidation temperature affected both the length and density of copper oxides nanowires formed on the copper wire surface. The cross-sectional SEM image of the copper wire (Fig. 2) shows that an oxide shell was formed and was detached from the copper core after thermal oxidation. A two-layered structure was further found in the oxide shell shows. EDS measurements showed that the finer outer layer and the NWs consist of CuO, while the coarse inner layer was made of  $\text{Cu}_2\text{O}$ . CuO NWs were found on the surface of the copper wire

between 400 °C and 600 °C. The CuO NWs are unidirectional and almost perpendicular to surface of Cu wire. At 700 and 800 °C, the surface of the copper wire becomes porous. It was found that oxidizing the wire at 550°C for 3 hours gave the best results. In the process, pre-cleaned 170 mm long wires were placed on an alumina plate in a box furnace for oxidation.

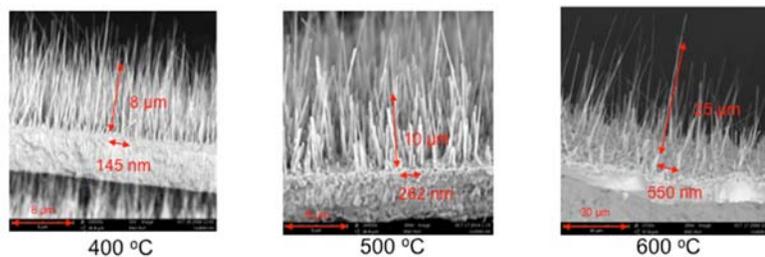


Fig. 2 Effects of oxidation temperature on CuO NW growth.

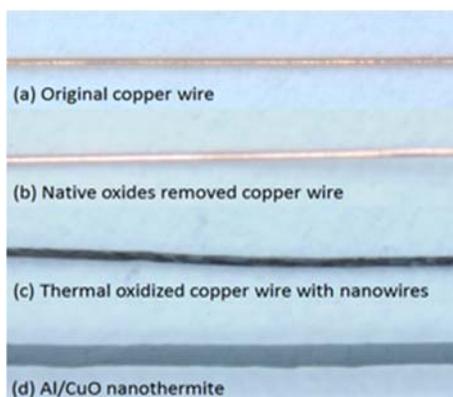


Figure 3. The copper wire (a) before pre-cleaning, (b) after pre-cleaning, (c) after thermal oxidation, and (d) after EPD.

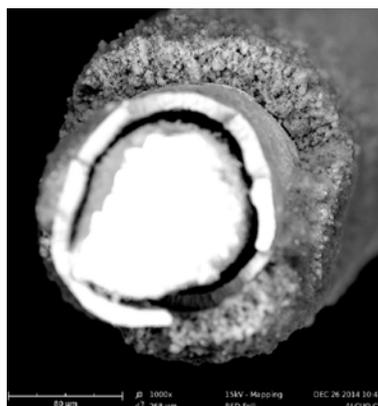


Figure 4. SEM image of the copper wire after EPD.

Electrophoretic deposition of the aluminum nanoparticles begins with dispersing the particles in a 3:1 ethanol/water solution. Ethanol was utilized to minimize water electrolysis during the electrolytic deposition process. The size of the nanoparticles was  $\sim 90$  nm in diameter (Yon-Zhen Technomaterial). The aluminum particle loading of the solution was 0.2 vol.%. The solution was ultrasonicated with a 500W ultrasonic processor (BB03, E-Chrom Tech) under cyclic of 20 sec pulses of 50% duty cycle for 2.5 minutes to disperse nanoparticles. Zeta potential and hydrodiameter of nanoparticles were measured with zeta potential analyzer equipped with particle size analyzing module (ZetaPALS, Brookhaven). The dispersion was diluted to 0.02% for the measurements. The average zeta potential was  $\sim +26$  mV, and the diameter was 250 nm, indicating agglomeration of 2 to 3 nanoparticles.

To assemble the Al/CuO nanothermite using EPD, a copper tube of 15 cm was placed on a plastic base as the positive electrode and solution container. The copper wire with CuO NW on the surface was suspended in the middle of the tube, in which circumferentially uniform and radially inward electric field would be generated in the annulus between the inner surface of the tube and the wire surface during EPD. The tube was filled with the dispersion to a level slightly lower than the depth of the tube. Tube and wire were connected to the positive and negative outputs of a high voltage power supply (GPR-30H10D, Good Will Instrument Co., Ltd), respectively.

Figures 3(a), (b), (c) and (d) show the original copper wire, the wire after pre-cleaning, the wire after oxidation, and the wire after EPD, respectively. Shiny surface was found in Fig. 3(b) after native oxide of the copper wire was removed. The wire turned into black in Fig. 3(c) after the surface was covered with CuO NW. The wire shown in Fig. 3(d) clearly demonstrates the effectiveness of depositing aluminum nanoparticles on the copper wire through EPD. Considerable increase in diameter due to the formation of aluminum layer was found after treating the wire with 20 seconds EPD in the 0.2% aluminum dispersion. Microscopic image of the wire after EPD is shown in Fig. 4. Three layer were observed in the cross-sectional view. The outer surface of the shell was fully blanketed by Al NP deposition, and a tubular oxide shell was found to be enclosing the inner copper core. Thickness of the deposition was  $\sim 30$   $\mu\text{m}$ , and the deposition looks highly porous. Packing density of the Al NP layer was approximately  $1.05 - 1.35$   $\text{g}/\text{cm}^3$ , depending on the electric field gradient applied during EPD. The CuO NW array on the copper oxide tube formed after the oxidation step were completely covered by the Al NP layer.

### 3 Reaction characterization

Differential scanning calorimetry (DSC) measurements were performed to characterize the ignition temperature and heat release curve of nanothermites. The temperature in the furnace of the simultaneous TGA/DSC analyzer (SDT Q600, TA Instruments) was ramped from  $30$   $^{\circ}\text{C}$  to  $800$   $^{\circ}\text{C}$  at  $10$   $^{\circ}\text{C}/\text{min}$ , and the furnace was purged with nitrogen to eliminate the potential of Al NP reacting with air in the tests.

Figure 5 shows the heat flow curves of nanothermites assembled under three different electric field gradients. Upward peaks on the DSC curve are exotherm. At least two exothermic peaks and one endothermic peak were found on each curve between  $400$  and  $800$   $^{\circ}\text{C}$ . Exothermic peaks corresponding to solid-solid reaction between aluminium and copper oxides were observed starting from  $575$   $^{\circ}\text{C}$  and peaking at  $630$   $^{\circ}\text{C}$  in all curves. But the peaks were more pronounced for nanothermites fabricated with higher field gradient. The endothermic peaks at  $660$   $^{\circ}\text{C}$  on DSC curves further show that not all aluminum particles were reacted during the first stage. This endothermic peak was less significant for the nanothermites fabricated with the lowest electric field gradient ( $40$   $\text{V}/\text{cm}$ ) since the smaller amount of Al NP was deposited. The

second heat release appeared after melting point of aluminum, and could be resulting from the reaction between liquid aluminum and the underlying copper oxide shell.

Integrations were performed on the the exothermic peaks, and the heating values ranged from 300 to 1000 J/g, which were significantly lower than the theoretical value of Al/CuO thermite reaction. The heating value obtained was the highest with 80 V/cm EPD for 20 sec. However, the values could not represent the real heating value of the nanothermite since not all the mass of the copper wire was reactive for the current nanothermite wire. In conventional powder thermite, all the mass in the material is reactive and should be counted when calculating heating values through DSC measurements. SEM images of the copper wire cross-section showed that the penetration depth of the copper oxide layer was approximately 20  $\mu\text{m}$ , the proportion of the reactive mass was therefore only around 1/3 of the total mass of copper wire. Consequently, the actual heating value per unit mass of the assemble thermite should be much higher.

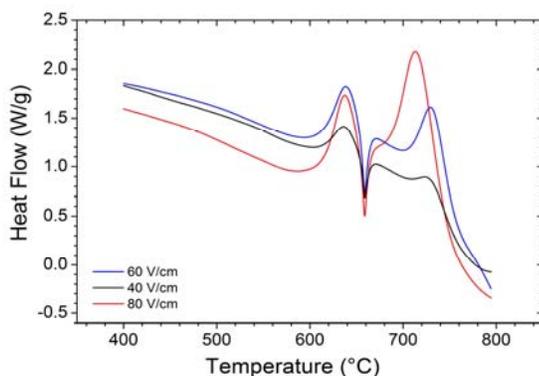


Figure 6. DSC curves of Al/CuO nanothermites assembled under different electric field gradients.

## 4 Conclusions

A novel method for assembling Al/CuO thermite on a copper wire has been successfully developed. The method is based on electrophoretic deposition of aluminum nanoparticles into CuO nanowire array on the surface of a copper wire. The copper wire act as both the base material for growing CuO NWs through thermal oxidation, and as the carrier of the nanothermite shell. It has been found that the density and length of CuO NW array obtained by oxidizing copper wires in a box furnace at 550 °C for 3 hours was suitable for the assembly with 90 nm Al NP. Aluminium nanoparticles were first dispersed in 3:1 ethanol water solution, and then driven into the gaps of CuO NWs under the influence of electric field between the tube and the copper wire itself. Various EPD electric field gradients have been applied for the assembly. Ignition temperature of the nanothermite shell formed through the electrophoretic deposition process was found to be around 575 °C. The first stage of the thermite reaction peaked at ~ 630 °C. The ignition temperature was lower than the melting temperature of aluminum indicating that the reaction was solid-solid reactions between aluminum and copper oxide. After the melting temperature of aluminum, a second stage heat release, which may be due to the reaction between melt aluminum and the remaining copper oxides layer, occurred between 680 and 750 °C.

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