

Aerosol Synthesis of Energetic Materials

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Aerosols are facile and convenient methods for preparing many types of materials.¹ Ultrasonic spray pyrolysis² (USP) and chemical aerosol flow synthesis³ (CAFS) are two examples of aerosol synthesis techniques that have opened up new opportunities for nanostructured materials with diverse applications including electronics, spintronics, energy, and biology. USP and CAFS use ultrasound directed through liquid precursors to the surface where capillary wave action from the ultrasound results in the formation of fine droplets (diameters $< 5 \mu\text{m}$).^{4,5} A photograph of ultrasonic nebulization of water is shown in Figure 1a. As shown in Figure 1b and 1c, the droplets are carried into a heated furnace where they undergo various reactions, and the products are collected by bubblers or other particle collectors (e.g. cyclonic, electrostatic, etc). Using these techniques submicrometer particles and nanoparticles of metals,¹ metal nitrides,⁶ metal oxides,⁷ metal chalcogenides,^{8,9} and carbon^{10,11} with novel applications and morphologies have been produced.

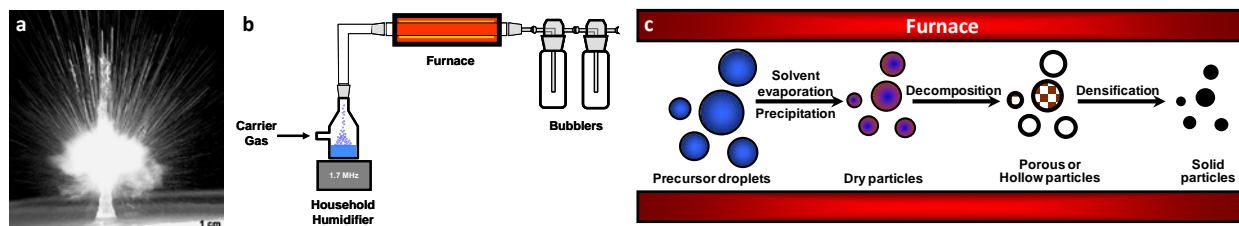


Figure 1. (a) Photograph of ultrasonic aerosol fountain generated by piezoelectric element submerged below the surface. (b) Schematic diagram of the laboratory ultrasonic spray pyrolysis setup. (c) Simplified diagram of processes that aerosol droplets undergo during pyrolysis.

Energetic materials such as finely divided aluminum have long been and continue to be of significant interest due the high heat of reaction to form aluminum oxide: 31 kJ/g. There has been an upsurge of interest in submicrometer morphologies of Al for use in high energy nanocomposites (i.e., nanothermite and other highly energetic mixtures for explosives or propellants) and for use in hydrogen storage. Using a modified CAFS process, hollow metallic aluminum particles were prepared (Figure 2). Numerous other metals have been prepared previously using aerosol processes¹, but this is the first time a metal with a reduction potential more negative than hydrogen has been produced without starting with the metal initially. Solutions of trimethylamine aluminum hydride (TMAH) in toluene were nebulized into a gas stream containing TiCl_4 , which catalyzes the decomposition of the TMAH into metallic

aluminum.¹² Characterization revealed the product to consist of hollow agglomerates of aluminum nanoparticles. Macroporous shells were created when the aerosol was heated to 100 °C, and transitioned to nonporous shells when heated to 200 °C. For the nonporous particles, traces of the TiCl_4 catalyst were trapped inside the particles. The prepared aluminum particles were found to be oxide passivated in spite of rigorous efforts to exclude oxygen from the system. The active aluminum content of the particles was measured using a previously reported redox titration method.¹³ The particles were found to consist of 72 wt% and 85 wt% active aluminum for particles prepared at 100 and 200 °C, respectively, even after storage at 22 °C and 30% RH for 5 months.

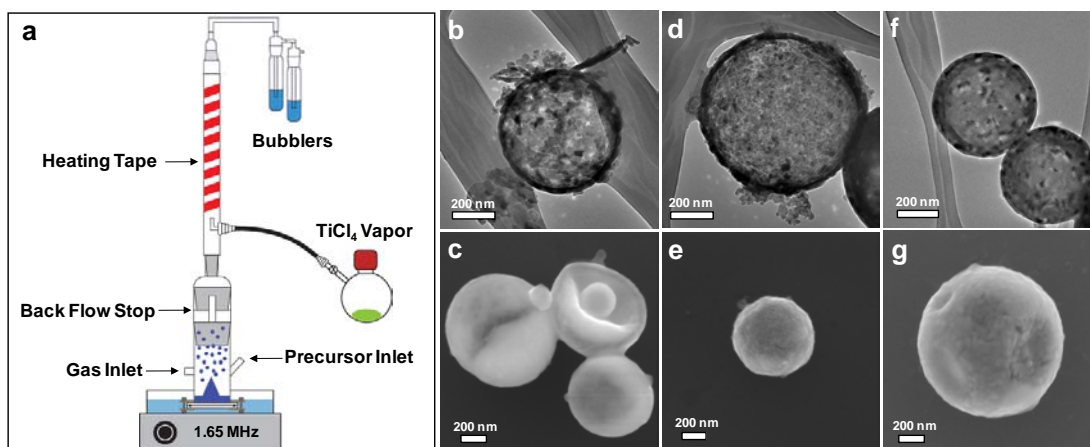


Figure 2. (a) Schematic diagram of the chemical aerosol flow synthesis set up. TEM and SEM micrographs of aluminum particles prepared from 1.0 M trimethylamine aluminum hydride at (b,c) 100, (d,e) 150, and (f,g) 200 °C.

A significant drawback to the use of metallic aluminum in energetic materials applications is that no significant amount of expansion gases is generated when reacted in nanothermites. Aluminum carbide, Al_4C_3 , is a hard ceramic material with few reports in the literature, and no applications to date.^{14,15} It was found that nanoparticles of Al_4C_3 could be synthesized by the pyrolysis of trialkyl aluminum precursors, and that these nanoparticles were passivated by a layer of amorphous carbon which protected the surface against oxidation unlike previous reports. The size of the nanoparticles could be increased from ~ 80 nm up to 250 nm by increasing the vapor pressure of the precursor, and the thickness of the amorphous carbon layer could be increased from 5 nm up to 15 nm by increasing the furnace temperature from 900 to 1100 °C. The Al_4C_3 nanoparticles were investigated in energetic materials applications by combining them with metal oxides to form metastable intermolecular composites (MICS). The nanoparticles show excellent brisance when reacted in a flame, and could be a useful energetic material due to the formation of permanent expansion gases (CO or CO_2) when reacted.

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