

Material Characterization of Plasma-Treated Aluminum Particles via Different Gases

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ABSTRACT

This work describes exploration of mitigating the parasitic amorphous alumina (Al2O3) shell of aluminum nanoparticles (n-Al) and modifying the surface using different plasmas, leading to n-Al with thinner shell and different coatings including carbons and oxidizing salt called aluminum iodate hexahydrate (AIH), respectively. The approach exploits a prototype atmospheric non-thermal plasma reactor with dielectric barrier discharge (DBD) configuration for nanoparticle surface modifications using n-Al of 80 nm average diameter as an example. Preliminary results indicate that the amorphous Al2O3 shell surrounding the active aluminum core can be mitigated with inert plasmas by as much as 40% using either helium (He) or argon (Ar). The particle surface becomes carbon-rich with carbon monoxide (CO) / He plasmas. By immersing the plasma-treated n-Al in an iodic acid (HIO3) solution, AIH crystals can be formed on the n-Al surface. Transmission electron microscopy (TEM) is used as a major tool to study the details of the modified surface morphologies, diffraction patterns, and chemical composition of the modified n-Al. The results demonstrate effective surface passivation of n-Al via atmospheric plasma techniques.

INTRODUCTION

Aluminum-based nanoparticles (n-Al) can hypothetically be excellent energetic additives due to their high energy content and potential rapid burning enabled by exceptionally large specific surface area to volume ratio. When incorporated into explosive formulations, n-Al can theoretically release two to three times more energy as conventional CHNO-based explosives [1]. However, the Al₂O₃ shell typically coating Al particles consumes a significant portion of the n-Al, lowering its energy content, and acts as a diffusion barrier for the unreacted Al core, leading to reduced energy release [2]. The higher surface energy of Al_2O_3 also causes the metal nanoclusters to aggregate and develop into Al₂O₃-covered large agglomerates that further exacerbate their inactivity [3]. Several attempts have been reported in recent years to mitigate the Al_2O_3 shell and control the surface properties of n-Al via different approaches. For example, n-Al passivated by an energetic oxidizer, aluminum iodate hexahydrate (AIH), has been successfully synthesized by Smith et al. via hand mixing commercial n-Al suspended in an iodic acid (HIO₃) solution [4]. The enhanced reactivity due to the presence of AIH was already demonstrated by Gottfried et al. via a lab-scale energetic test called laserinduced air shock from energetic materials (LASEM) [5]. On the other hand, Shahravan et al. [6] passivated the surface of n-Al via plasma-enhanced chemical vapor deposition (PECVD) and found that fluorinated coating on n-Al is more effective at reducing agglomerations when compared with n-Al suspended in aqueous environments.

Despite of the successful secondary passivation of n-Al, it is possible that the n-Al particle reaction mechanism can be altered and the performance of n-Al can be further enhanced if the Al₂O₃ shell is reduced or completely removed, prior to adding a chemical agent onto the n-Al particle surface. With alternative passivation chemistries or significantly reduced Al₂O₃ shell thickness, the active Al core in n-Al particles may react more effectively for different applications. The objective of this study is to explore how different plasmas would affect the Al₂O₃ shell and change the morphology and structure of n-Al surface via advanced material characterizations using transmission electron microscopy (TEM).

DESCRIPTION OF EXPERIMENTS

Figure 1 shows a picture of the prototype DBD plasma reactor which is made of a standard glass test tube (1 inch diameter, 8 inch length) with a copper rod inserted at the center, shielded by an open-end quartz tube, and connected to an AC high voltage (HV) pulsed source (Amazing 1 PVM 500), copper tape wrapped around the tube exterior and connected to ground. The plasma conditions are 7-9 kV, 20-25 W, 25 kHz pulse frequency. For each experiment, approximately 150-175 mg n-Al particles (80 nm average size, Novacentrix Inc.) are weighed and loaded into the reactor prior to inserting the HV electrode. The reactor is then purged with either argon (Ar) or helium (He) through a gas tube into the reactor and just above the n-Al sample for more than 10 min. A relatively high flow rate of 1 standard liter per minute (SLPM) is used to facilitate the exposure of individual particles to the gas and interact with the active species in a plasma glow. After plasma treatment, the n-Al is then suspended in either acetonitrile (ACN) to prevent re-oxidation for subsequent characterizations with TEM, or in the iodic solution and hand-mix to allow AIH formation. For the latter, the relative ratio of $n-Al:H_2O:I_2O_5$ = 1:1:2.5 in wt.% pre-determined from an earlier work [4]. A different batch of pristine n-Al is also treated by plasma containing 100 standard cc per minute (SCCM) CO and 300 SCCM He for 10 min. All TEM specimens are prepared using ACN to suspend particles onto the holey carbon support film on TEM grids (Ted Pella, Inc). Microscopic experiments are conducted under a JEOL 2100FX TEM operated at 200 keV (JEOL USA, Inc.) by taking bright field (BF) images, and selected aperture diffraction (SAD) (25 cm camera length). The X-ray energy-dispersive spectrum (XEDS) are acquired using an Octane Elite T windowless detector with TEAM Analysis software (EDAX Inc) in the scanning mode (STEM).



Figure 1. A photo showing the prototype test-tube DBD reactor.

RESULTS AND DISCUSSION

Inert Plasma treatments

Figure 2 displays TEM images for the pristine n-Al particles used in this work. The sample has widely distributed particle sizes and pronounced coalesced particles, as shown in Figure 2a. The Al₂O₃ thickness is measured ~3 nm for smaller particles and ~4 nm for particles of larger sizes, as coarsely outlined in red in Figure 2b. In this image, the shell thickness for the ~23 nm diameter small particle on the bottom right is measured as 3 nm. In general, the average Al₂O₃ shell thickness is 4-5 nm. Therefore, the Al₂O₃ shell has a detrimental effect to lower the potential energetic performance of n-Al due to the dramatic reduction in the active Al content as the particle size shrinks (for example, ~65 wt.% for 80 nm particle size but only 30 wt.% for 20 nm particle size). Inert gas plasma treatments using either He or Ar for a 10 min duration result in a rough surface morphology (Figure 3a) and a reduced Al₂O₃ thickness to approximately 2.7 nm (Figure 3b and Figure 3c). Compared to pristine n-Al particles, it is more than 40% reduction. The results demonstrate the potential of reducing the Al₂O₃ shell with inert plasmas and the effectives are comparable between He and Ar.



Figure 2. TEM BF images showing (a) varying particle sizes of n-Al with pronounced particle coalescence indicated by small red arrows, and (b) an enlarged view of a few n-Al particles with the interface between the core and the shell outlined by red dotted lines. The shell thickness for the ~23 nm diameter small particle on the bottom right is measured as 3 nm.



Figure 3. TEM BF images showing the rough surface and reduced Al_2O_3 shell thickness after plasma treatment using (a and b) Ar and (c) He plasmas. The image in (a) is acquired in under-focus condition to meticulously exhibit the morphological features on the particle surface.

Oxidizer Coating on Plasma-treated n-Al

Figure 4 exhibits the resultant AIH containing Ar-plasma treated n-Al particles. The image in Figure 4a reveals the highly sporadically decorated AIH on the n-Al surface, shown as small darker particles. The non-uniform distribution of AIH formation on the particles can be attributed to the significantly non-homogeneous interfacial contact of n-Al with the iodic acid solution during mixing because of the limited amount of viscous iodic acid solution used in mixing. The SAD pattern shows several additional diffraction spots in addition to those corresponding perfectly to bulk Al which we suspect can be attributed to AIH crystals, as shown in Figure 4b. Figure 4c is a corresponding XEDS validating the presence of iodine peaks in the sample along with other major and background peaks. The small iodine peaks in XEDS are due to the volatile nature of iodine which continuously escapes from the sample leading to a diminishing content upon electron beam irradiation, as observed previously with other AIH-containing Al powders [4]. The thickness of amorphous Al_2O_3 shell is also found to be further reduced to only ~1 nm (not shown) after the particles are mixed with the iodic acid solution. The structures of AIH containing He-plasma treated n-Al particles are similar to those with Ar-plasma treated samples and therefore are not shown here.



Figure 4. The AIH-containing Ar-plasma treated n-Al particles: (a) TEM BF image showing distinct strain contrast, (b) the SAD pattern with additional diffraction spots, and (c) the corresponding XEDS.

CO Plasma-treated n-Al

Using CO as a precursor and mixing with He in the plasma, the resultant treated n-Al particles exhibit thinner shells surrounding the Al cores, as shown in Figure 5a. Compared to the Al_2O_3 shells for inert plasma treated n-Al particles, these shells appear to be relatively thinner. For CO plasmas, it has been proposed in the literature [7] that CO can be excited when colliding with electrons and the neutral and excited CO can interact with each other to form carbons (C) and CO₂. It is possible that some or all of these species can then react with Al_2O_3 based on the following equations.

$$CO + e \rightarrow CO * + e \rightarrow CO$$

$$CO + CO * \rightarrow C + CO_2$$
$$O + CO * + Al_2O_3 \rightarrow 2CO_2 + Al_2O_3$$

С

$$Al + Al_2O_3 + C \rightarrow CO_2 + Al + Al_2O$$

More in-depth materials characterizations are ongoing to study possible carbon and oxide structures. Nevertheless, we found that the rough surface on the particles shown as protruding nodules appear to have hexagonal geometries (Figure 5c). Figure 5d is a corresponding XEDS showing the presence of carbon in the CO/He plasma treated n-Al particles.



Figure 5. TEM BF images of CO/He plasma-treated n-Al particles showing (a) the reduced Al_2O_3 thickness, as specified with red arrows and measured values for several particles, (b) the rough surface exhibited as protruding nodules, (c) details of the surface morphological features of the rough surface and (d) the corresponding XEDS confirming the presence of carbon in the CO/He plasma treated n-Al sample.

CONCLUSIONS AND FUTURE WORK

This work presents the feasibility of mitigating the amorphous Al_2O_3 shell and the capability of modifying the surface of n-Al particles for energetic applications via atmospheric plasma surface treatments at a relatively short duration of only 10 min. Using inert gas plasmas, more than 40% of the Al_2O_3 shell thickness can be reduced by using either 1 SLPM Ar or He plasma and the effectiveness are comparable and appears to be independent on the gas type. By mixing the inert plasma-treated n-Al particles with iodic acid solution, the Al_2O_3 shell thickness is further reduced to ~1 nm and TEM studies demonstrate the presence of iodine content due to the formation of AIH on the n-Al surface. By adding 100 SCCM CO into a 300 SCCM He plasma, the resultant thinner shell exhibits nodules protruding from the rough surface having hexagonal geometries and XEDS show the pronounced presence of carbon. These preliminary results demonstrate the potential of altering the surface structure and chemistry of n-Al particles by changing plasma gas type, composition, and subsequent processing with chemicals after plasma treatment. Further optimization of plasma conditions and additional advanced material characterizations will be pursued in the future to elucidate possible reaction mechanisms in plasmas that alter the surface properties of n-Al particles.

ACKNOWLEDGMENTS

The collaboration between Texas Tech University (TTU) and US Army Research Laboratory is supported by the ARL Director's Research Award under the External Collaboration Initiative and Summer Journeyman Fellowship Program. The TTU authors are also grateful for the support from the Army Research Office under award W911NF-17-1-0387 and the Program Manager, Dr. Ralph Anthenien.

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