Engineering Aluminum-Silica Nanoparticles via Nonthermal Plasma: Synthesis and Characterization

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Abstract: Aluminum nanoparticles (Al NPs) exhibit desirable size-dependent energetic properties, but they form a problematic native oxide layer. Passivating the surface of these particles is the key to unlocking their potential. This work showcases an Ar/H_2 capacitively coupled plasma for the in-flight synthesis of surface-modified Al NPs using silane (SiH_4). Al-SiO_2 core-shell and Janus particles were characterized over a range of plasma parameters.

1. Introduction

Al NP research has recently focused on improving the performance of nano-thermite mixtures and developing synthetic techniques to precisely control particle size distribution and surface composition. Ignition temperature and reaction rate are critical to the successful application of this material. These are hindered by the formation of a native oxide layer (Al_2O_3) which takes up a significant mass fraction of each nanoparticle. Here, a flow-through nonthermal plasma reactor is used to synthesize Al NPs with varying surface properties including Al NPs with a shell containing amorphous silicon (Al-SiO_2). This surface modification partially or completely passivated the surface of the Al NPs and limited the formation of a native oxide layer. This work presents the materials characterization results of parametric studies designed to control the sample composition.

2. Methods

An RF capacitively coupled Ar/H_2 containing plasma at intermediate pressure is used to produce Al NPs from sublimated $AlCl_3$. Dilute silane (5% SiH_4 in Ar) is added to the afterglow of the plasma to passivate the surface of the Al NPs continuously in flight. The input power ranged from 20-60 W and the dilute SiH_4 flow rate was varied from 2-8 sccm to explore the parameters that form surface-modified Al NPs. Nanoparticle samples were collected via impaction and characterized using the suite of instruments at the University of Minnesota Characterization Facility. X-ray diffraction (XRD) indicated the evolving crystalline phases as parameters were adjusted. X-ray photoelectron spectroscopy (XPS) and Fourier transform infrared spectroscopy (FTIR) indicated the changing surface composition. Transmission electron microscopy (TEM) and scanning TEM with energy dispersive X-ray spectroscopy (STEM-EDS) elemental maps showed the morphology and NP structure. These data yield an understanding of how changing plasma parameters impact the formation of complexly structured Al-SiO_2 particles.

3. Results and Discussion

Figures 1a and 1b show two net-intensity STEM-EDS elemental maps with line profiles. These samples were deposited at an input power and dilute SiH_4 flow rate of (a) 50W and 4 sccm and (b) 20W and 8 sccm. The line profiles show the signal from each element with position. In Figure 1a, an Al-SiO_2 core-shell particle is shown, Si and O signals are localized to the shell with Al at the particle's core. Figure 1b, shows Al-Si Janus particles deposited at an input power of 20W and a dilute SiH_4 flow rate of 8 sccm. The line profile shows a clear phase separation of Al and Si comprising a single ellipsoidal particle with the O signal localized to the periphery in a 3-5 nm thick layer.

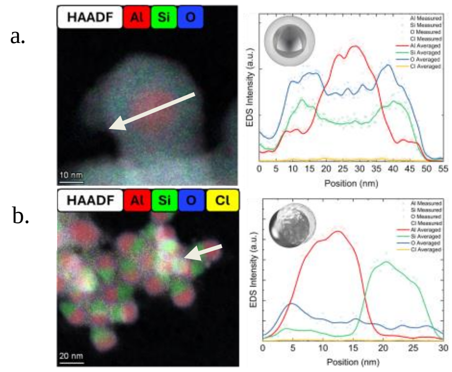

Fig. 1a. and 1b. STEM-EDS elemental maps and line profiles showing (a) an Al-SiO_2 core-shell and (b) an Al-Si Janus particle. Results from input power and dilute SiH_4 of (a) 50W and 4 sccm and (b) 20W and 8 sccm.

The particle composition is shown to strongly depend on the input power and dilute SiH_4 flow rate by XRD, XPS and FTIR. A narrow tunable range to control the shell thickness in Al-SiO_2 particles was found to exist. Within this tunable range, samples of Al-SiO_2 were shown to exhibit limited energetic characteristics by TGA/DSC characterization. The behavior of the Al-SiO_2 sample was compared to neat plasma synthesized Al and commercially available Al NPs.

4. Conclusion

Al-SiO_2 NP synthesis strongly depends on the plasma power and dilute SiH_4 flow rate. A range to control the morphology, structure, material composition, and shell thickness in Al-SiO_2 particles is reported. Future work will seek to improve the energetic characteristics of this material and extend the in-flight nonthermal plasma synthesis technique to form Al-based core-shells with other shell materials.

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