

Polymerization Passivation Strategies for the Stabilization of Energetic Aluminum Nanomaterials

P. A. Jelliss^{*}, B. J. Thomas^{*}, A. Patel^{*}, E. Lloyd^{*}, E. A. Guliants^{**}, C. E. Bunker^{***}, and S. W. Buckner^{*}

^{*}Department of Chemistry, Saint Louis University, Saint Louis, MO 63103, USA, jellissp@slu.edu, buckners@slu.edu

^{**}Air Force Research Laboratory, Propulsion Directorate, Wright-Patterson AFB, OH 45433, USA

^{***}Department of Electrical & Computer Engineering, University of Dayton Research Institute, Dayton, OH 45469, USA

ABSTRACT

We have previously demonstrated that aluminum nanoparticles (Al NPs) can be synthesized by decomposition of molecular adducts of alane, AlH_3 , and passivated by assembling and polymerizing small organic precursor molecules on the nascent NP surface in the same solution. We are now developing further passivation strategies based on our established protocols with a view to fabricating air-stable Al NPs with long shelf-lives. Additionally we have discovered that our approaches have fortuitously yielded nanostructures with unprecedentedly high active Al^0 contents (typically >80%). The resulting nanomaterials could fulfill requirements in fuels technology for the production and use of additives with high energy content and improved combustion rates even after several months of storage under ambient atmospheric conditions. The use of monomers comprising alkene and alkyne bonds has afforded particularly stable nanomaterials and allowed us to design a passivation shell that incorporates a photosensitive poly(methylmethacrylate) component.

Keywords: aluminum, nanoparticles, passivation, polymerization

1 INTRODUCTION

The ability to passivate and kinetically stabilize reactive metal nanoparticles without compromising the active (usually elemental) metal content is a critical requirement for the development of synthetic protocols for energetic nanomaterials. We are particularly interested in addressing this problem with regard to fabrication of aluminum nanoparticles (Al NPs) with sub-100 nm diameters. Nanosized Al represents an attractive target for multiple high energy materials and fuels applications, but spatiotemporal passivation based on simple exposure to oxygen, O_2 , typically results in wasteful oxidation of a 2-6 nm surface layer. For Al NPs with a diameter of 20 nm or less, this leads to a loss of up to 70 % of the active Al content by mass and an undesirable attenuation of energetic value.¹ Nevertheless, size-dependency modeling studies have revealed to us the value of employing Al NPs for energetics applications: as Al NP size is reduced, the

enthalpy of oxidation to Al_2O_3 is increased.² But this requires that a significant proportion of the Al remain as active Al^0 upon NP surface passivation.

We have previously reported the passivation of Al NPs using 1,2-epoxyalkanes as capping agents (entry 1 in Table 1), with the nascent nanoparticle surface serving as a platform for ring-opening initiation and propagation of epoxide polymerization.³⁻⁶ Crystallite core sizes of 12-15 nm in diameter have been cloaked in a prophylactic barrier of organic polymer some 5-15 nm thick, as determined by a combination of transmission electron microscopy (TEM) and powder X-ray diffractometry (PXRD). Moreover, this passivation scheme has afforded nanostructured materials with active Al^0 contents in excess of 80 %. However, the capping shell proved to be somewhat easily compromised upon exposure to ambient air, leading to core metal oxidation and/or hydrolysis and degradation in a matter of hours or 1-2 days at best.

Thus we have endeavored to increase the kinetic stability of our Al NPs without sacrificing active Al content. To do this we have developed a dual integrative polymerization approach that incorporates more than one polymerizable functionality and in so doing, have discovered that long-chain hydrophobic alkenes and alkynes having proven to be remarkably effective capping agents in their own right.

2 EXPERIMENTAL OVERVIEW

2.1 Synthesis

While we are beginning to explore alternative top-down modes of Al NP generation, such as electrical explosion of wires (EEW), we currently synthesize all our nanostructured systems using Buhro's bottom-up method of molecular alane decomposition.⁷ Thus all syntheses begin with treatment of $\text{AlH}_3 \cdot \text{NEtMe}_2$ in toluene with $\text{Ti}(\text{iOPr})_4$ as an initiator. Without delay, a solution of capping agent is injected in to the reaction mixture, which may then be heated to 85 °C. The dark grey solids produced are dried by removal of solvent in vacuo at an elevated temperature.

Samples are prepared with a variety of Al:capping agent ratios such as 1:1, 2:1, 5:1, 10:1, and 20:1. A detailed procedure based on the use of the monomer found in entry

2 of Table 1 has been recently reported.⁸ This protocol was slightly modified from that used to synthesize prior samples made with simple epoxyalkanes (entry 1, Table 1).⁴

2.2 Characterization

All products are routinely characterized by PXRD, electron microscopy, differential scanning calorimetry/thermogravimetric analysis (DSC/TGA), attenuated total reflectance fourier transform infrared (ATR-FTIR) spectroscopy, and Raman spectroscopy. Additionally we determine speciation of Al. Monitoring H₂ gas evolution through reaction of Al NPs with NaOH solution is used to evaluate active Al⁰, while total Al content is determined via a compleximetric Zn²⁺-EDTA back titration following alkali degradation. Active Al content may then be expressed as a percentage of total Al content.

3 RESULTS AND DISCUSSION

3.1 Epoxydecene-capped Al NPs

Following on the heels of our preliminary work with epoxyalkanes (entry 1, Table 1), we wished to reinforce the integrity of the Al NP capping material in order to further limit oxygen and moisture access to the underlying Al core and thus improve overall stability and shelf-life. It was critical to us, however, that we should build on the success of our epoxyalkane polymerization strategy in order to maintain high active Al content in our nanostructures.

The molecule 1,2-epoxy-9-decene (entry 2, Table 1) is commercially available. Structurally it features the terminal epoxide functionality at one end with a terminal alkene group at the opposite end of the molecule. Syntheses were carried out both with heating at 85 °C and without heating (stirring at ambient temperature). The most stable materials were produced using Al:capping ratios of 2:1, 5:1, and 10:1, though it could be clearly observed that long-term stability was only encountered when heat was applied to the reactions (vide infra).

The proposed scheme for Al NP passivation is outlined in Scheme 1. Initiation occurs via ring-opening activation of the epoxide functionality by the Al surface, resulting in the formation of a polyether loop. Propagation then occurs via insertion of additional epoxide monomer into the polyether loop. Polymerization is then terminated once the monomer supply at the core-shell interface has been depleted.⁴ With the addition of heat, the terminal alkene undergoes polymerization, resulting in Al NPs entrapped in an interconnected polymer matrix. An additional free-radical initiator is not required, suggesting thermally-supported Al activation is taking place.

Reaction of the alkene was confirmed by Raman spectroscopy. The characteristic alkene (C=C) stretching resonance at 1650 cm⁻¹ was observed in the monomer, but not in the epoxydecene-capped Al NPs, supporting the

notion of polymerization of the C=C group. Furthermore, diagnostic stretching resonances at 1300 cm⁻¹ and 1450 cm⁻¹ for the epoxide functionality were replaced by a resonance at 1000 cm⁻¹, attributed to polyether C-O stretches. A PXRD pattern confirmed the presence of crystalline face-centered cubic Al cores, with Scherrer analysis suggesting average core diameters of 19 nm.

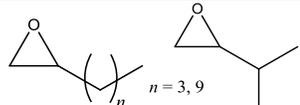
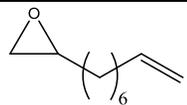
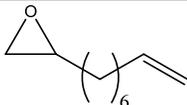
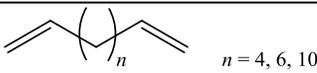
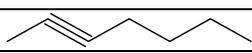
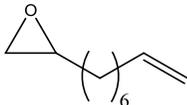
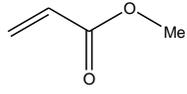
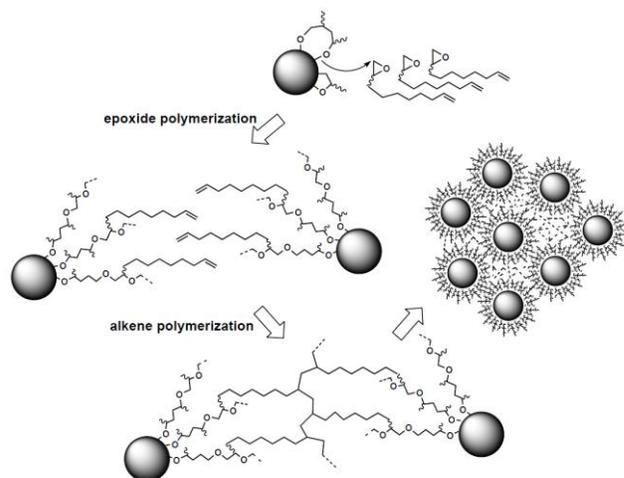
	Monomer 1	Monomer 2
1		
2		
3		
4		
5		
6		
7		
8		

Table 1: Various monomer substrates used for Al NP passivation.



Scheme 1: Integrated polymerization scheme for epoxydecene.

While samples made using epoxydecene were stable for several weeks, incorporation of an equimolar amount of the diene species tetradecadiene (entry **3**, Table 1) afforded yet more stable materials. PXRD patterns measured multiple times for a single sample over the span of 7 weeks (Figure 1) showed no appreciable attenuation of peak intensities.

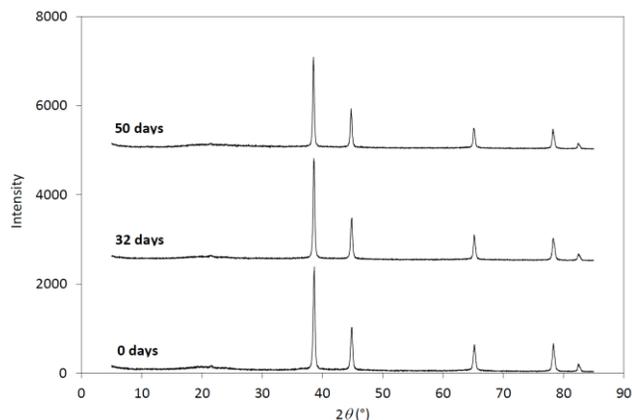


Figure 1: PXRD patterns of Al NPs capped with a 10:1:1 molar ratio of Al:epoxydecene:tetradecadiene following exposure to ambient air.

Furthermore, Al speciation measurements revealed that exceptionally high active Al content values (> 80 %) dropped to no less than 50 % over this timeframe for epoxydecene-capped systems **2**, while comonomer materials **3** retained 78 % active Al after 6 months exposure to ambient air.

3.2 Alkene- and alkyne-capped Al NPs

The observed stability incurred by incorporation of alkene moieties into the oligoether passivation protocols alerted us to the possibility that alkenes may lend themselves to effective Al NP core passivation. This led us to attempt syntheses using both dialkene and even monoalkene species (entries **4** and **5**, respectively, Table 1). In all cases, dark grey powders with high active Al contents were isolated (Table 2). A representative PXRD pattern for octadiene-capped confirmed crystalline Al formation and Scherrer analysis revealed Al NP core diameters of ca. 25 nm, similar to epoxydecene-capped systems.

Thermal properties of the new materials were investigated by combined DSC/TGA analysis. Shown in Figure 2 are the measurements for octadiene-capped systems (as an example of a type **4** material) along with those for epoxydecene/tetradecadiene-capped type **3** materials for comparative purposes. In both cases, a gradual mass decrease is observed upon heating to ca. 450 °C. A broad, ill-defined exotherm accompanies this mass loss and is strongly indicative of combustion of involatile polymer material. While some 40 % of the mass loss may be attributed to the polymer coating combustion in the case of material **3**, the corresponding TGA for nanomaterial **4**

suggests that less than 10 % of the total mass is organic capping agent, i.e. ca. 90 % of the total mass is attributable to Al and of that >80 % is active Al metal. The DSC trace shows a clear Al ignition exotherm at 550 °C for the comonomer species **3**, though is less well-defined for the octadiene-capped nanomaterial **4**. The mass gain (corresponding to formation of Al₂O₃) is approximately the same.

Capping agent	Structure	Active Al (%)
1,7-octadiene		83±6
1,9-decadiene		80±6
1,13-tetradecadiene		78±5
1-octene		90±10
1-decene		89±3

Table 2: Active Al contents for dialkene- and monoalkene-capped Al NPs.

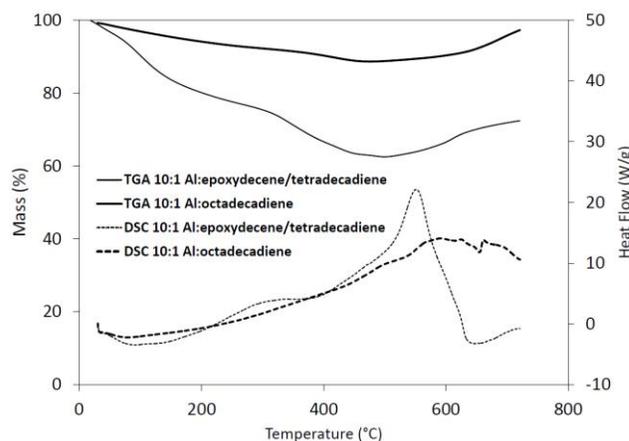


Figure 2: DSC/TGA of Al NPs capped with 10:1 Al:epoxydecene and also with 10:1:1 Al:epoxydecene:tetradecadiene.

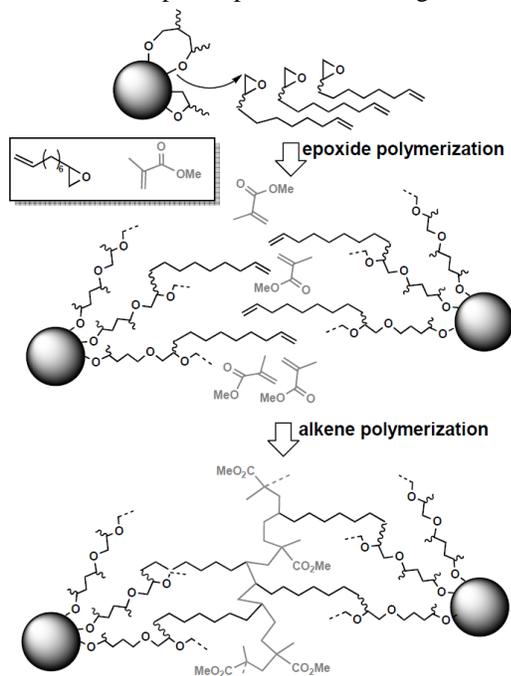
We have extended this methodology to use alkyne species, both terminal and internal (entries **6** and **7**, respectively, Table 1). Preliminary data suggests formation of materials that are as stable as their alkene congeners (entry **5**, Table 1), though the exact nature of the capping material structure is currently under investigation.

3.3 Epoxydecene/methyl methacrylate-capped Al NPs

The successful sequestration of Al nanoparticles by polymerization passivation with retention of high active Al

content has yielded some unintended consequences. The resulting nanomaterials are so well protected that access to the energy-rich Al core is limited and they are only slowly reactive toward oxidation or hydrolysis. Thus while these nanomaterials can be stored under ambient conditions for long periods, the ability to tap into their energy reserves expeditiously is compromised.

To combat this problem, we have sought to modify our methodology to create polymer caps, which may be subjected to some specific degradative trigger, such as photolysis. A number of options are being considered, one of which includes incorporating methyl methacrylate (MMA) into the passivation scheme (entry 8, Table 1). A simplified rationale is depicted in Scheme 2. If the interconnecting polymer matrix that forms around the Al NP cores incorporates elements of poly(MMA), which is photodegradable under UV light, then the polymer shell may be broken down upon exposure to a UV light source.



Scheme 2: Integrated polymerization scheme for epoxydecene with MMA.

An ATR-FTIR spectrum of the dried solid nanomaterial recently synthesized clearly revealed a strong $\nu_{\max}(\text{C}=\text{O})$ resonance at 1740 cm^{-1} with no corresponding $\nu_{\max}(\text{C}=\text{C})$ resonance. PXRD patterns revealed crystalline Al cores (diameter ca. 18 nm), which remained intact after 4 weeks exposure to ambient air (Figure 3). Preliminary post-photolysis testing has indicated a substantial enhancement in oxidation/hydrolysis as evidence of photodegradation.

4 CONCLUSIONS

We have successfully fabricated Al NPs and passivated them by polymerizing simple epoxides and/or alkenes to

afford energetic nanomaterials with very high active metal contents and unprecedented kinetic stabilities.

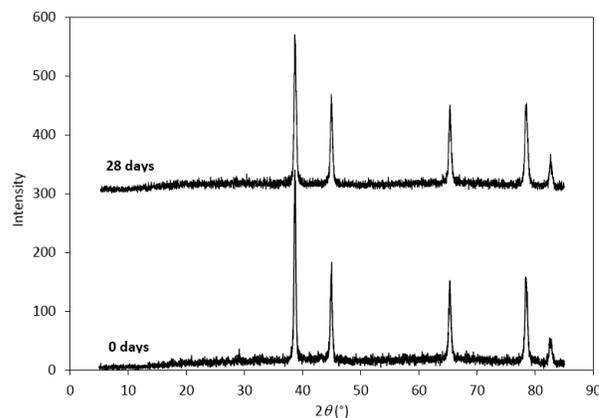


Figure 3: PXRD patterns for Al NPs capped with 10:1:1 Al:epoxydecene:MMA with 0 and 28 days air exposure.

ACKNOWLEDGEMENTS

We thank the US Air Force Nanoenergetics Program for funding. Acknowledgement is made to the National Science Foundation for support under grant CHE-0963363 for renovations to the research laboratories in Monsanto Hall.

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