



A Computational Study on Surface Chemistry of Silane-Coated Aluminum Nanoparticles by Reactive Molecular Dynamics Simulations

Hyung Sub Sim^{1,†}, Sungwook Hong^{2,†}, Chang-Min Yoon³

Abstract

The introduction of high-energetic metal nanoparticles into hydrocarbon-based liquid fuels presents benefits such as increased energy density and improved combustion efficiency. However, the inherent propensity of metal nanoparticles to aggregate poses significant challenges, including diminished energy density and instability in fuel dispersion. To address these issues, our study explores the use of silane coatings on the surface of aluminum nanoparticles (ANPs). Silane precursors are selected for their ability to prevent metal surface corrosion—akin to preventing oxidation on metal surfaces. We utilize molecular dynamics (MD) simulations based on the ReaxFF reactive force field to investigate the silane coating process and to examine the surface characteristics of silane-coated ANPs. The findings reveal that the silane precursor of octadecyltriethoxysilane (OTES) experiences C-O bond dissociation, leading to the formation of an unsaturated O-termination site. This site actively bonds with the surface of the ANPs, creating an Al-O-Si bond, consistent with the experimental observations. In addition, we introduce water molecules to both untreated and silane-coated ANPs to assess differences in surface reactivity. The results indicate that the silane coating layer effectively hinders a direct interaction between the surface of the ANPs and water molecules, potentially imparting hydrophobic characteristics to the metal nanoparticles.

Keywords: *Aluminum nanoparticles, Silane, Coating, ReaxFF, Molecular dynamics*

1. Introduction

Due to their high energy density and reactivity, aluminum nanoparticles (ANPs) have been chosen as additives in liquid-fueled propulsion systems to enhance combustion efficiency and energy density [1–8]. In order to gain the advantages of ANPs as fuel additives fully, preventing their aggregation is crucial. This ensures maximization of the surface area of individual particles and their uniform dispersion in liquid fuels over extended periods. Unfortunately, the inherent propensity of ANPs to rapidly aggregate in fuel—primarily due to Van der Waals forces—significantly reduces their surface area, adversely affecting their reactivity and dispersibility. To resolve this issue, surface coating of ANPs is proposed not only to prevent their aggregation [9–11] but also to enhance their dispersion stability within liquid propellants. In our recent study [12], we employed ReaxFF molecular dynamics (MD) simulations to investigate the application of hydrocarbon coatings on the surface of ANPs. These coatings were found to inhibit sintering and oxidation at low temperatures, while at high temperatures, both sintering and oxidation processes were observed to accelerate. Among various potential coating materials, silane is chosen in the present study for its proven effectiveness in corrosion protection on

¹ Assistant Professor, Aerospace Engineering, Sejong University, Seoul, Republic of Korea, hsim@sejong.ac.kr

² Assistant Professor, Physics and Engineering, California State University, Bakersfield, Bakersfield, CA, United States, shong10@csub.edu

³ Associate Professor, Chemical & Biological Engineering, Hanbat National University, Daejeon, Republic of Korea, cmyoon4321@hanbat.ac.kr

[†] Corresponding Authors

aluminum and other metals [13,14], a property that parallels the prevention of oxidation. This study, therefore, focuses on the use of silane coatings on ANPs with the goal of improving their dispersibility and reactivity in liquid fuels.

Silane coating is a widely adopted method for modifying the surfaces of nanoparticles (NPs). [14] This technique leverages the ability of silane groups to form covalent bonds with the hydroxyl groups on inorganic nanoparticles, while its organic functional groups can engage with various organic substances. [15] Aluminum nanoparticles (ANPs), characterized by their thin oxide layers and hydroxyl groups, readily form bonds with the $-SiX_3$ groups of silane coupling agents. [16] Similarly, the organic functional groups on boron nanoparticles (BNPs) facilitate the grafting of additional materials. The application of the silane coating layers prevents further growth of the oxide layers on BNPs when exposed to air, ensuring their compatibility and efficient combustion. In our recent experimental work [17], we used various silane precursors to modify the surface characteristics of the BNPs, which led to dual-silane capping. This resulted in improved dispersion stability and calorific value of liquid hydrocarbon fuels when used as a nanoadditive for enhancing the combustion properties. However, the silane coating process and the surface characteristics of silane-capped ANPs at the molecular level have not been fully understood yet. To develop an effective surface coating method, it is necessary to understand the coating processes and surface chemistry.

The main goal of this study is to replicate the coating process observed in experiments and to explore the surface chemistry of ANPs coated with silane precursors, utilizing the ReaxFF MD simulations. ReaxFF, a powerful computational tool for modeling reactive nanostructures, offers the distinct advantage of accurately representing chemical reactions [18], and it has been extensively applied across a wide range of applications [19]. This integrated approach significantly enhances our understanding of such processes at the molecular level. By combining experimental findings with theoretical knowledge of complex nanoscale coating process through ReaxFF MD simulations, we complement our molecular insights, enhancing the depth and extent of our study.

2. Computational Methods

ReaxFF is a bond-order based empirical force field designed to enable the simulation of chemical reactions within complex molecular systems. The efficacy of ReaxFF lies in its ability to model chemical reactions (i.e., bond forming and breaking in a dynamically changing environment), offering insights into the behavior of materials at the atomic level. The general expression for the total energy in the ReaxFF, which is typically shown as Eq. (1):

$$E_{system} = E_{bond} + E_{over} + E_{under} + E_{lp} + E_{val} + E_{tors} + E_{vdWaals} + E_{Coulomb} \quad \text{Eq. (1)}$$

The total energy term (E_{system}) contains the bond energy (E_{bond}), over-coordination (E_{over}), under-coordination (E_{under}), lone-pair (E_{lp}), valence angle (E_{val}), torsion angle (E_{tors}), van der Waals ($E_{vdWaals}$), and Coulomb ($E_{Coulomb}$) energy. The bond order is directly determined from the interatomic distances, which are recalculated at every iteration for all types of bonded interactions, including covalent bonds, valence angles, and torsion angles. Additionally, ReaxFF accounts for non-bonded interactions such as Van der Waals and Coulomb forces, calculated across all atom pairs without exceptions. Short-range interactions are dampened by using shielding terms to prevent unrealistic force magnitudes. Moreover, polarization effects are incorporated by adopting a geometry-dependent charge distribution, which is derived from the electronegativity equalization method. Comprehensive insights into the ReaxFF formalism could be found in the review paper. [19]

To perform ReaxFF MD simulations of the surface coating on ANPs with silane precursors and to observe their interactions with water molecules, we merged multiple ReaxFF force field parameters into a single force field file: Al-C-H-O [11], Si-O-H [20], Si-C [21] interactions. In addition, to better describe C-C interactions, we replaced C parameters with Ref. [22]. The modified force field has been shown to reasonably describe chemical reactions involving ANPs and silane precursors. MD simulations were executed using the Amsterdam Modeling Suite (AMS) [23] with the ReaxFF module [18]. To simulate the coating process with silane precursors, a single cluster of the ANPs was included in a cubic box (80 Å by 80 Å by 80 Å) while 100 octadecyltriethoxysilane (OTES), a chemical formula of $C_{24}H_{52}O_3Si$, molecules were randomly distributed in the surroundings. To control system temperatures, the canonical ensemble (NVT) with the Nose-Hoover thermostat was used for up to 200,000 iterations. The timestep was set to 0.25 fs with a damping constant of 100 fs. To ensure a uniform coverage of the

ANP surface by the OTES molecules, MD simulations were performed with the following coating/purging procedures: a) coating process: place raw/coated ANPs with intact silane precursors at 300 K; b) purging process: remove all gas phases molecules. These steps (a and b) were repeated until achieving a uniform coating of the ANPs with OTES molecules. The initial structure of the ANPs ($d=2.8$ nm) was derived from our earlier study [12], illustrated in Fig. 1 (a). Note that we chose to use OTES for the silane precursor as shown in Fig. 1 (b), because the recent study [9] shows that metal nanoparticles functionalized with OTES successfully enhance the dispersibility of the nanoparticles in liquid hydrocarbon fuels.

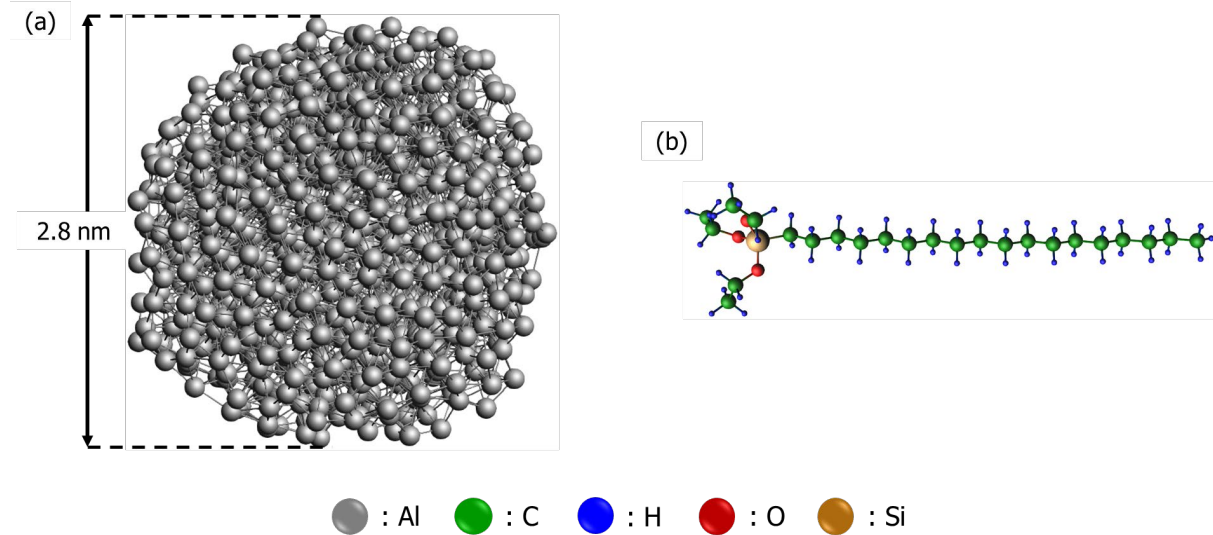


Fig 1. (a) 864 Al-atoms of the ANPs [12], (b) a single OTES ($C_{24}H_{52}O_3Si$) molecule

To investigate surface behaviors of the silane-coated ANPs with water molecules, specifically hydrophobicity and hydrophilicity, we conducted ReaxFF MD simulations for both uncoated and silane-coated ANPs. A single cluster of the uncoated/silane-coated ANPs was positioned at the center of the simulation box with 1,000 water molecules randomly placed around them. NVT-MD simulations were carried out at a room temperature of 300 K for a total of 500,000 steps, maintaining the same conditions as those used in the coating simulations.

3. Results and discussion

Fig. 2 shows the surface chemistry of silane coating on the ANPs, as obtained through our ReaxFF MD simulations at a relatively high temperature of 1,000 K. The results suggested that OTES precursors undergo dissociation with C-O bond breakage, resulting in an unsaturated O-termination site. This site then actively interacts with the ANP surface, forming an Al-O-Si connection. These observed reaction trends are in very good agreement with the experimental observations of silane coatings on boron particles. [17] In other words, the removal of methyl groups on OTES is key to the synthesis of silane-coated ANPs. As shown in Fig. 2(b), the connection between the surface of the ANPs and OTES through the Al-O-Si bond was clearly demonstrated. Given that the current focus of this study was not to capture or simulate the kinetics of the silane-ANPs reaction but rather to generate realistic atomic-scale models of silane-coated ANPs for further simulations (e.g., predicting surface reactivity), we deliberately eliminated three methyl groups in the silane precursors. Additionally, two O-termination sites were saturated by H atoms, leaving one active site available on each precursor. By doing this, we were able to accelerate the coating process at a reasonable amount of computational cost.

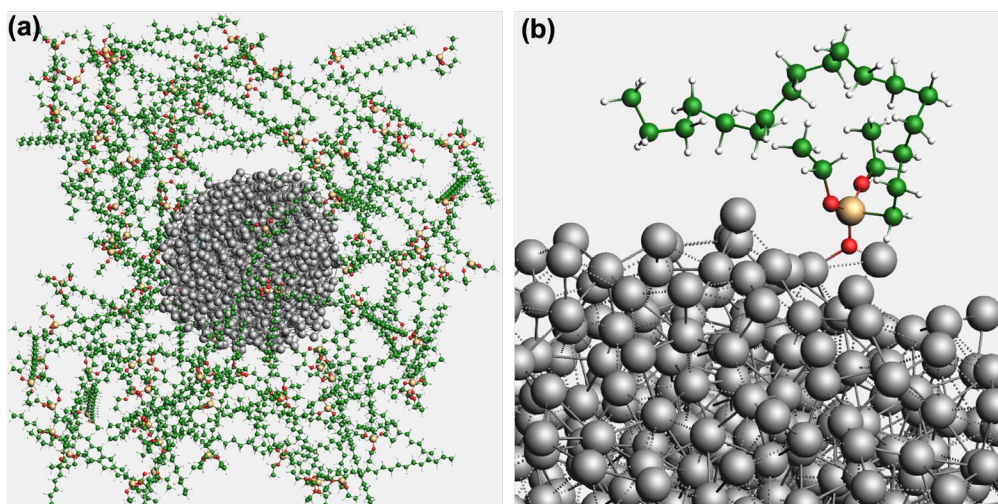


Fig 2. (a) ANPs with 100 OTES silane precursors (at 0 ps); (b) the silane precursor bound to the surface of ANPs via Al-O-Si bond connection (at 125 ps)

Subsequently, coating simulations were conducted for up to three cycles, which followed similar modeling steps previously published in Ref. [11]. Fig. 3 presents snapshots of the coating sequences after three successive cycles. After the 1st cycle, it was found that a few of the silane precursors attached to the ANP surface, while a significant amount of silane precursors remained intact in the system. Following the 2nd cycle, most of the silane molecules had bonded to the surface of the ANPs, but there were still areas of the ANP surface not covered by the silane precursors. Finally, after the 3rd cycle, the surface of the ANPs was fully covered with the silane precursors, indicating the completion of the coating procedure. It was found that the surface coverage by the modified silane precursors increased with additional coating cycles. For further simulations, the silane-capped ANPs after the last cycle were used as the initial configuration. Interestingly, the long-hydrocarbon chains bent and encapsulated the ANP surface, which measures approximately 1.0 nm in size. This encapsulation might prevent water molecules from diffusing into the ANP surface.

Additional ReaxFF MD simulations were conducted to investigate the differences in surface reactivities between uncoated and silane-coated ANPs, focusing on hydrophobicity and hydrophilicity. This investigation was prompted by our recent experimental findings [17], which demonstrated that silane precursor capping on the ANPs significantly improved their dispersibility in liquid fuel by altering the surface from hydrophilic to hydrophobic. Given that the surface of silane-coated ANPs was nearly

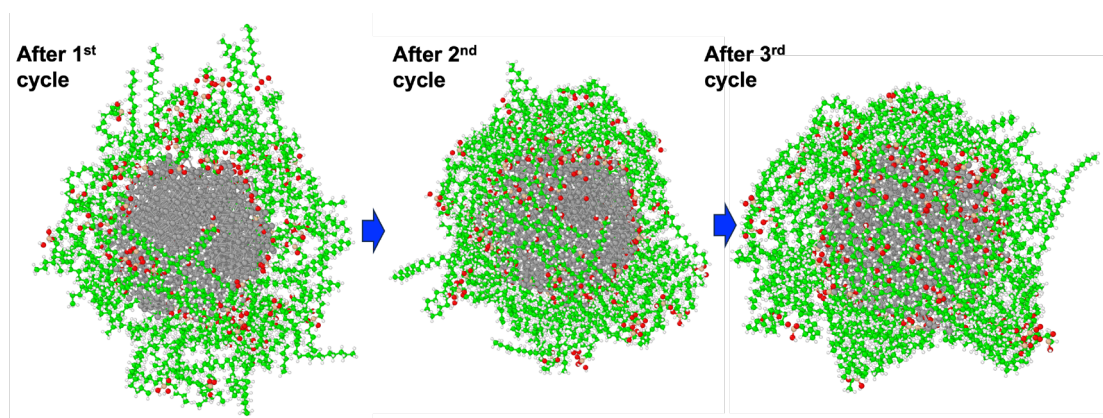


Fig 3. Surface coverage of the ANPs by silane precursors as a function of the coating cycle, showing that the surface achieves reasonable coverage after the 3rd cycle

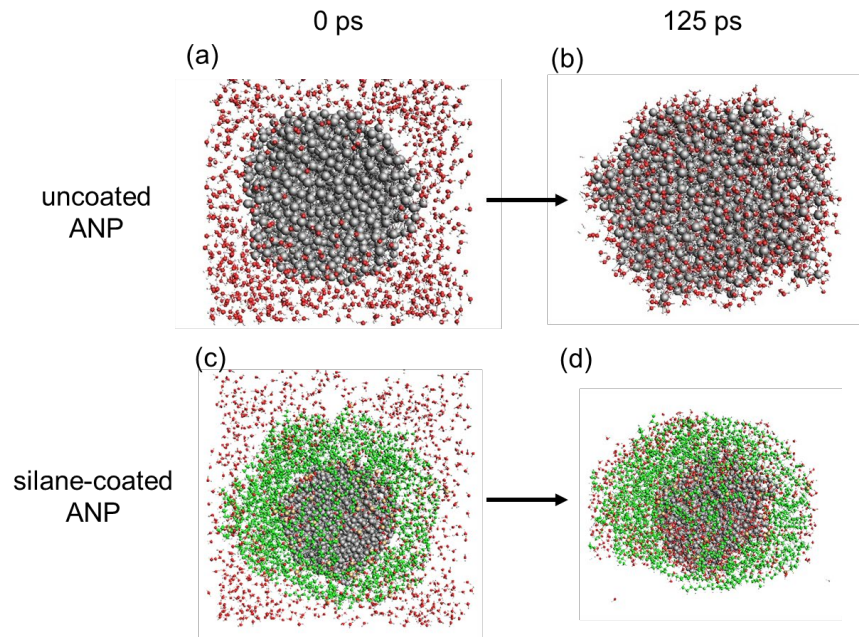


Fig 4. Interaction and adsorption of water molecules on uncoated ANPs (upper figures) and silane-coated ANPs (lower figure), observed through ReaxFF MD simulations at 300 K, illustrating the dynamics of water molecules interacting with the ANPs and highlighting differences in chemical and physical adsorption on uncoated versus silane-coated surfaces

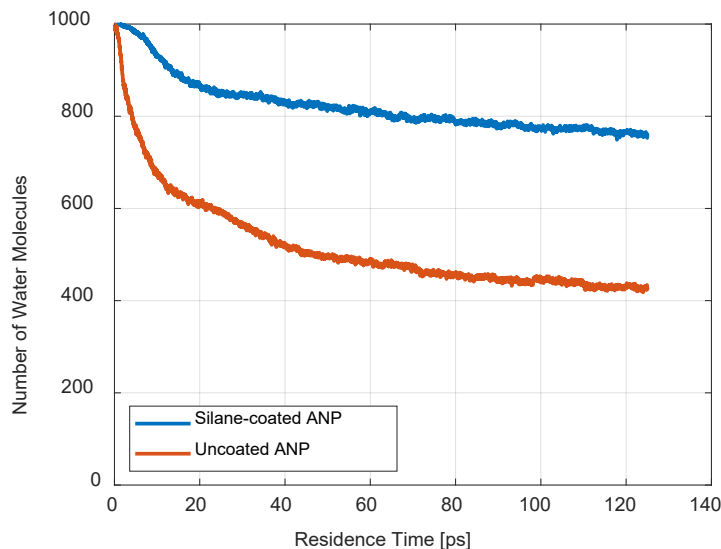


Fig 5. Temporal profiles of water molecule interactions with uncoated and silane-coated ANPs as a function of residence time

enveloped by silane precursors after the 3rd coating cycle (Fig. 3), we hypothesized that the ANPs capped with silane precursors underwent a similar transition in surface characteristics as observed in the experimental work. Fig. 4 directly compares the initial and final interactions of water molecules with both uncoated (upper figures) and silane-coated ANPs (lower figures). It was observed that water molecules chemically bonded to the surface of uncoated ANPs, indicating hydrophilic behavior. In contrast, water molecules exhibited weak interactions with the silane coating layers on the ANPs, indicative of hydrophobic characteristics. This alteration in the surface of the ANPs, conferred by the silane coatings, supports our hypothesis that silane-capped ANPs transition from hydrophilic to hydrophobic properties, aligning with the experimental observations. The results of our MD simulations

corroborate that silane coating layer effectively prevents direct interaction and chemical bonds between the surface of the ANPs and water molecules, leading to the observed hydrophobicity.

Fig. 5 illustrates the changes in the number of water molecules interacting with the surface of the ANPs as a function of residence time, reflecting the extent of chemical reactions of the ANPs and water molecules. For uncoated ANPs, there's a rapid decrease in the number of water molecules, indicating that water molecules were preferably bound to the surface of uncoated ANPs. Conversely, the interaction with silane-coated ANPs shows a much slower rate of decrease, confirming that a fewer number of water molecules reacted with the surface of the ANPs and silane coating layers.

4. Conclusions

In this study, we refined the existing ReaxFF force field parameters to enhance the description of hydrophobic and hydrophilic characteristics in silane-coated ANPs. ReaxFF MD simulations of the silane coating process on the ANPs suggested that OTES precursors undergo dissociation with C-O bond breakage, resulting in the termination of methyl groups and thus formation of an unsaturated O-termination site. This site actively interacts with the ANP surface, forming an Al-O-Si bond. These mechanisms predicted by ReaxFF MD simulations are in very good agreement with the experimental observations of the silane coatings on boron particles. Subsequent ReaxFF MD simulations involving water molecules, and comparing uncoated and silane-coated ANPs, revealed that the silane coating alters the surface characteristics of ANPs from hydrophilic to hydrophobic, thereby preventing interactions with water molecules. This alteration offers a viable approach for achieving well-dispersed ANPs in liquid propellant systems and mitigating further aggregation, highlighting that significant potential for the use of metal-based nanoparticles in liquid propellant fuels for advanced high-speed vehicles. As a future work, we will extend this research using different types of metal nanoparticles, in collaboration with experimental works. We believe our research efforts will substantially contribute to the field of fuel technology for high-speed flight vehicles. To the best of the authors' knowledge, this study is the first of its kind to achieve the length and time scales required to investigate the various properties of such systems.

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