

Investigation of gold and silver clusters using reactive force fields and machine learning potential

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Gold and silver nanoparticles (NPs) have attracted significant attention in various scientific fields due to their remarkable optical, electrical, thermal, and biological properties. Capping these nanoparticles with alkylthiolates gives protective capabilities, allowing for the precise tuning of their characteristics and the formation of Self-Assembled Monolayers (SAMs) with specific architectures, as defined by Wood's notation. For silver NPs, experimental investigations have revealed the formation of a $\sqrt{(7 \times 7)}$ R19.1° assembly, occasionally accompanied by the creation of an Ag₂S shell through sulfidation, resulting in substantial system restructuring. For gold NPs, two distinct assemblies: $\sqrt{(3 \times 3)}$ R30° and c(4×2) have been found, with the latter characterized by the unique phenomenon of staple formation.

This theoretical study employs molecular dynamics simulations to assess the consistency of the current force field parametrization for these complex systems. Given the impracticality of employing quantum calculations due to their computational costs, we utilize a reactive force field, specifically ReaxFF, which gives a balance between computational cost and accuracy. Furthermore, our chosen parametrization is expected to provide precise descriptions of adsorption sites compared to Density Functional Theory (DFT). Our research initially focuses on silver surfaces and NPs up to 10 nm in size, comparing the stability of different assemblies within SAMs. Additionally, we investigate various properties to validate their agreement with prior experimental findings and to uncover any potential surface restructuring phenomena.

In the case of gold NPs, as the existing force field parametrization proves inadequate for these systems, we introduce an innovative approach using machine learning potential. We present our model and demonstrate its effectiveness in describing gold NPs.

This comprehensive theoretical study advances our understanding of the behavior of gold and silver nanoparticles capped with alkylthiolates, providing insights into their stability, reactivity, and surface restructuring phenomena. Our findings contribute valuable insights that bridge the gap between theoretical predictions and experimental observations, furthering our ability to control and harness the potential of these nanoparticles in various applications.

Keywords: nanomaterials, molecular dynamics, machine Learning