

Surfactant-Coated Nanoparticle on a Stepped Surface

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Metal and semiconductor particles of nanometer (nm) size feature a large surface-to-volume ratio and quantum-scale dimensions. Due to the distinct energetics of surfaces atoms and the unique energy-level structures, these nanoparticles possess extraordinary thermodynamic, chemical, electric, optical, and magnetic properties unlike those of isolated atoms and bulk systems. Equally importantly, they can be utilized as building blocks, artificial analogs of atoms in a natural crystal, to manufacture an entirely new class of materials and devices with properties unparalleled by conventional approaches and tunable by particle size. They have thus been recognized as ideal foundations of next-generation technologies in a wide range of areas. Although the bottom-up approach with nanoparticles as building blocks was conceptualized decades ago, its realization had to wait until key developments were made recently in synthesizing nanoparticles that permit controllable fabrication.

Traditionally, fine metal or semiconductor particles are prepared as sols or electrically stabilized aqueous colloids, which tend to form fractal aggregates in solutions or when precipitated. Recently it was discovered that by capping nanoparticle surface with surfactant molecules during synthesis, the resultant surfactant-coated nanoparticles can remain well dispersed in solutions and tend to self-assemble into ordered arrays when deposited on solid substrates and on the free surface of water in a Langmuir trough. Although phenomenologically this change of behavior has been interpreted as an outcome of reduced interparticle interactions, the underlying molecular origin is still not completely understood. This is important because a slight change of the atomic-scale characteristics of the surfactant (e.g. surfactant chain length, terminal group, etc.) could lead to very different results. More importantly, the current fabrication methods of surfactant-coated nanoparticles are highly empirical in nature and produce only partially satisfactory results. These facts point out not only a direction for research of nanoparticle self-assembly, but also the value of fundamental studies that are capable of considering atomic-scale characteristics. We have performed molecular dynamics (MD) simulations with proper atomistic models to study the behavior of surfactant-coated nanoparticle on a stepped solid surface to understand its interaction with a solid surface and to assess the feasibility of using stepped surfaces as templates for controlled growth of one-dimensional nanoparticle arrays.

The model nanoparticles considered were Au_{140} coated with 62 thiol molecules ($-\text{SC}_n\text{H}_{2n+1}$), as shown in Fig. 1. The thiol molecules were bound to the nanoparticle surface via sulfur chemisorption represented by a Morse potential. Thiol alkyl tails and the solvent of choice, *n*-hexane (C_6H_{14}), were modeled using the anisotropic united atom (AUA) model. considered Au nanocrystal cores and Au surfaces are known to have face-centered-

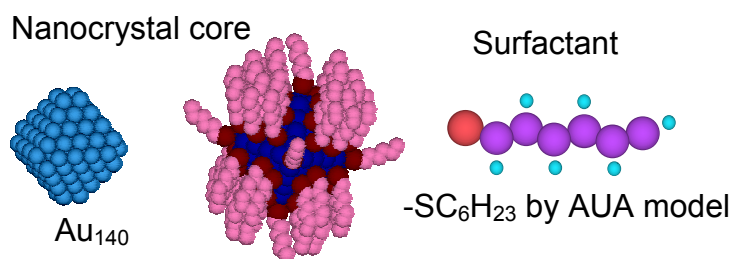


Fig. 1. Model surfactant-coated nanoparticle

cubic (fcc) structure. The former have truncated octahedron shapes with the larger facets corresponding to the fcc(111) surface. In this work, the model stepped surface is also chosen to be of fcc crystalline structure and the atoms in the solid surface were modeled the same as Au atoms using a Lennard-Jones potential whose parameters were fitted to reproduce Au lattice constant and cohesive energy. We tried and found that a terrace 29 atomic rows wide, that is the Au(14,13,13) surface, is appropriate to accommodate and study Au₁₄₀(SC₁₂)₆₂ nanoparticle on a stepped surface.

Surfactant chains have certain extent of structural flexibility and their interaction with the surface is significantly weaker than the interaction between a nanocrystal metallic core and a metallic surface. As a result, the surfactant chains are pressed and bent when a nanoparticle is adsorbed on a dry surface (cf. Fig. 2). However, such bent conformations also possess certain level of structural rigidity, giving rise to a metastable state, as indicated by Fig. 2. In our model system, the interaction between the nanocore and the surface is metallic and thus strong enough to overcome the metastable state to reach a final state where surfactant chains in between are squeezed out for the nanocore to make direct contact with the surface and the nanoparticle becomes immobilized. It can be understood that when nanoparticles are quickly immobilized on a surface, disordered structures form instead of self-assembly. Therefore, the result here can be thought to indicate the importance of the energetic characteristics of a surface in the behavior and self-assembly of nanoparticles on the surface.

The study presented above is on a dry surface without the presence of solvent. It is then interesting and important to know if solvent can play a role to alter the outcome of nanoparticle adsorption on a surface. For this reason, we study the behavior of surfactant-coated nanoparticle in a thin *n*-hexane film on the stepped Au(14,13,13) surface. The initial

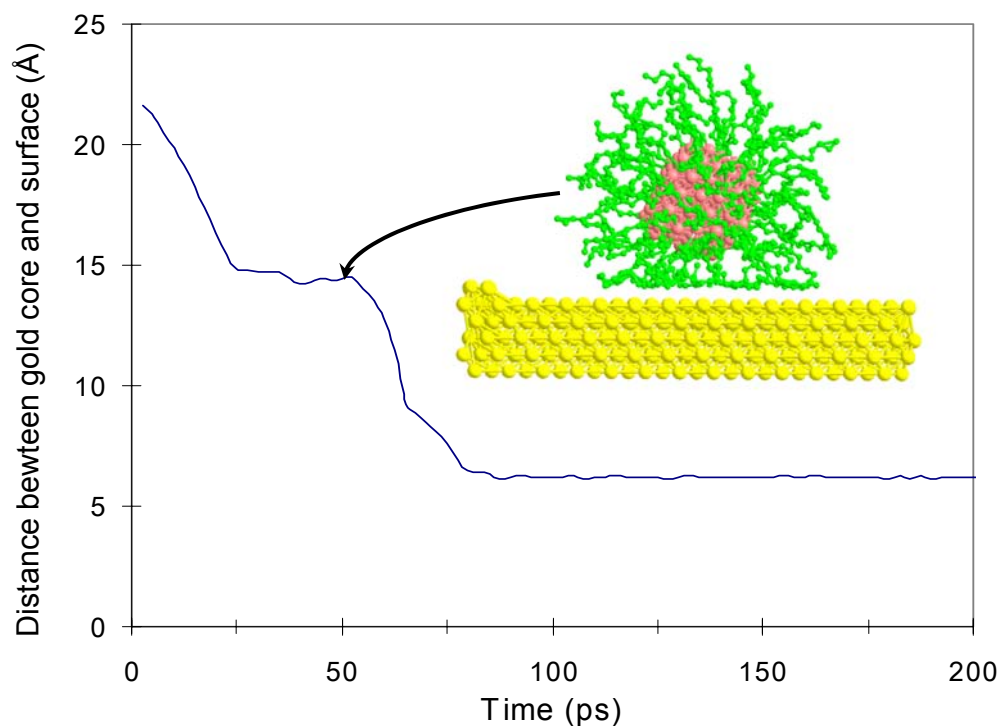


Fig. 2. Time evolution of the distance between the mass center of gold core and the surface.

condition of the simulation system was obtained by placing 1000 *n*-hexane molecules on the surface to form a thin film. A nanoparticle was then introduced from a location right above the film and given a small downward velocity. Gradually it submerged into the film and formed a simulation system whose configuration is shown Fig. 3. In this case, the nanoparticle was able to maintain its metastable state at a separation of about 15 Å from the surface till the end of simulation that lasts more than 1 ns. In other words, the presence of solvent molecules stabilizes the metastable state resulting from the bent conformations of surfactant chains and gives the nanoparticle certain surface mobility that is required for structural rearrangement on a surface. This finding is consistent with the fact that actual self-assembly process on a surface is relatively slow and requires the presence of solvent throughout the whole process.

To further study the role of solvent, we examined the distributions of UA's in surfactant tails and in solvent molecules in the upper and lower hemispheres around the nanoparticle. Here it is important to point out that Au₁₄₀(SC₁₂)₆₂ surfactant-coated nanoparticle is dissolvable in a nonpolar solvent such as *n*-hexane considered in this work. Phenomenologically this has been explained by a change of effective nanoparticle surface characteristics (e.g. Hamaker force constant) from metal-like to alkane-like. As indicated by Fig. 4, it was observed in our MD simulation that the relevant mechanism on the molecular level is the interdigitation between solvent molecules and surfactant chains, that is, solvent molecules take part in the surfactant layer. Concerning the stabilization of the metastable state discussed above, it can be understood to be resulted from surfactant chains being totally surrounded by solvent molecules so that it is significantly more difficult for them to be squeezed out from between the nanoparticle and the surface.

We also examined the locations and trajectory of the surfactant-coated nanoparticle on the stepped surface. As shown in Fig. 5, the nanoparticle was found to prefer the terrace over the step sites and its center of mass tends to maintain an interestingly similar distance of about 15 Å relative to both the step and the surface. The surface diffusivity of the nanoparticle is

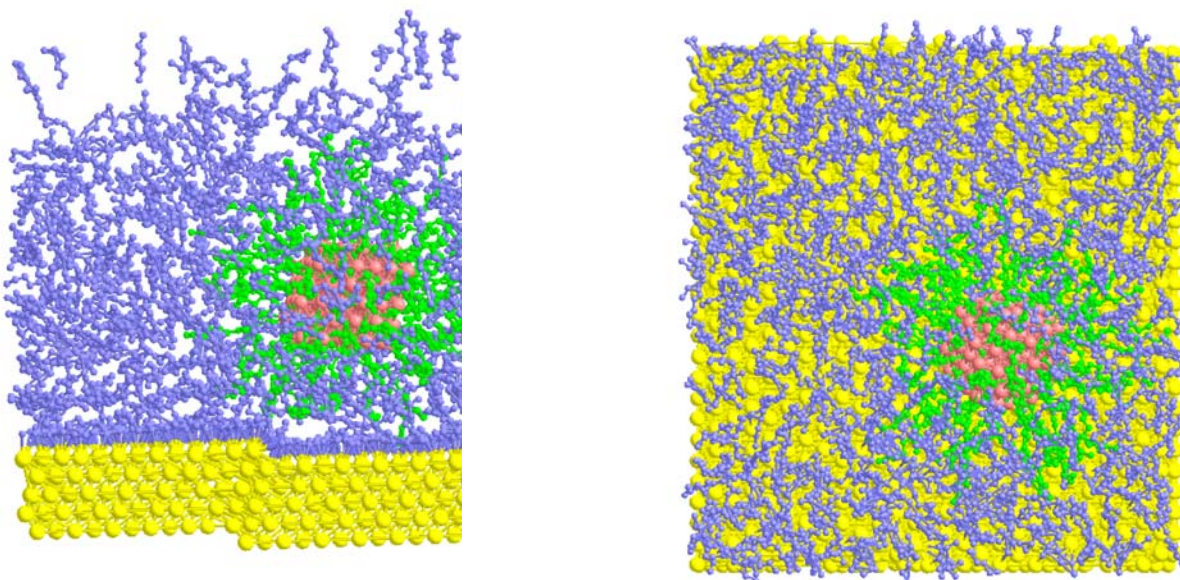


Fig. 3. Simulation snapshot of a Au₁₄₀(SC₁₂)₆₂ nanoparticle in a thin *n*-hexane film on the stepped Au(14,13,13) surface.

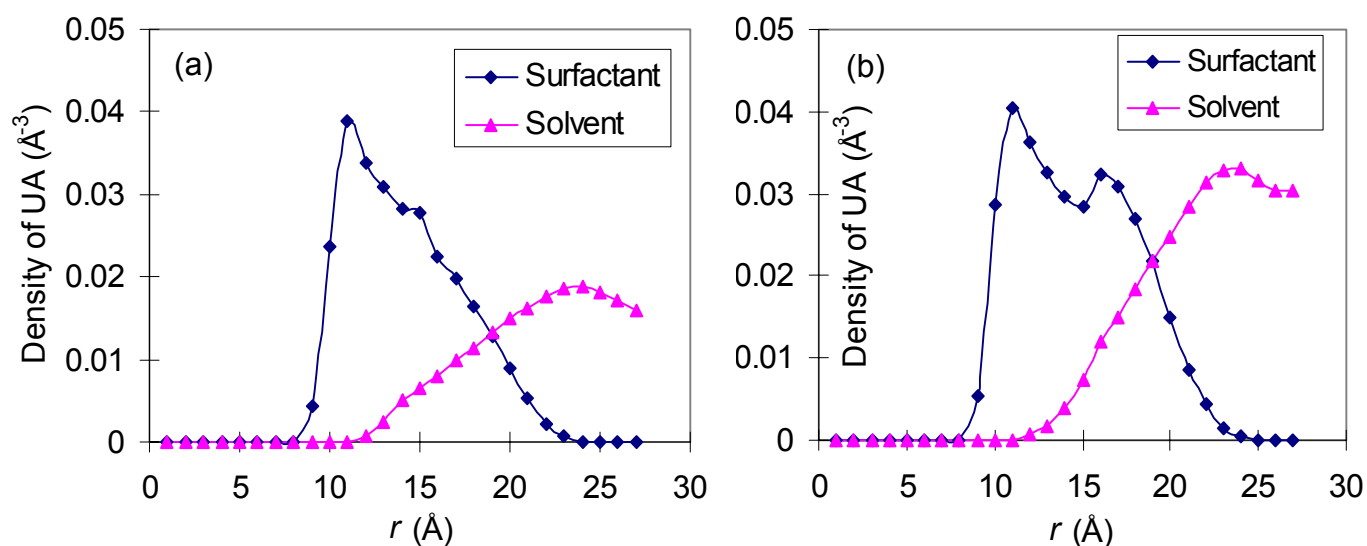


Fig. 4. Distribution of UA's in the (a) upper and (b) lower hemispheres around a $\text{Au}_{140}(\text{SC}_{12})_{62}$ nanoparticle in a thin n -hexane film on the stepped $\text{Au}(14,13,13)$ surface

estimated to be about $5 \times 10^{-9} \text{ m}^2/\text{s}$ in the thin solvent film environment. Perhaps more importantly, the surface mobility and trajectory of the nanoparticle are seen to be not isotropic but substantially prefer the direction along the step edge. Such anisotropy implies that surface steps could be considered to be used as “canals” to transport nanoparticles on a surface and as “templates” to promote one-dimensional nanoparticle arrays.

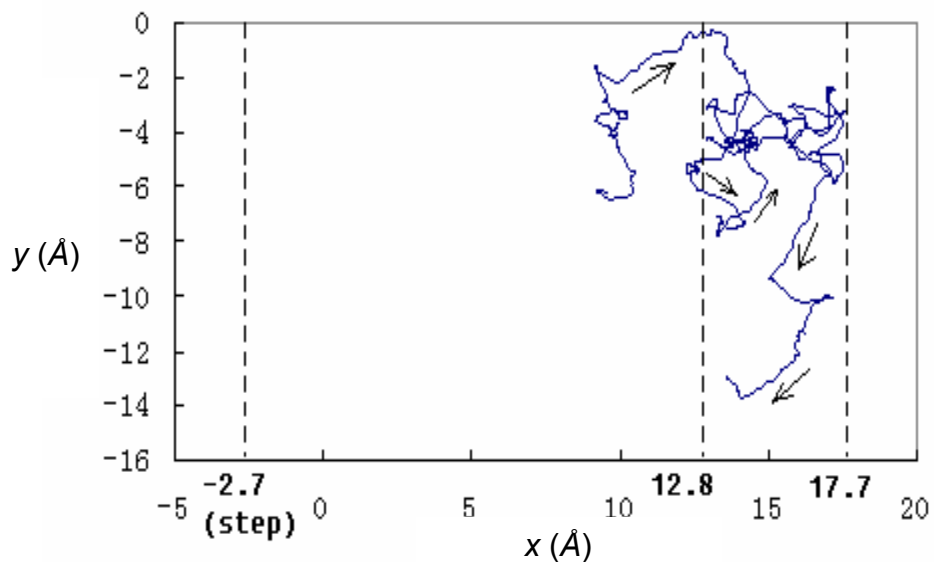


Fig. 5. Trajectory of a $\text{Au}_{140}(\text{SC}_{12})_{62}$ nanoparticle in a thin n -hexane film on the stepped $\text{Au}(14,13,13)$ surface