



# Aggregation of thiol coated gold nanoparticles: A simulation study on the effect of polymer coverage density and solvent



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## ARTICLE INFO

### Article history:

Received 25 September 2013

Received in revised form 20 December 2013

Accepted 22 January 2014

Available online 18 February 2014

### Keywords:

Aggregation

Gold nanoparticles

Self-assembled monolayer

Thiol chains

Molecular dynamics simulation

## ABSTRACT

Molecular dynamics simulations have been carried out to investigate the effect of alkane thiol coverage density, terminal group and water solvent on the aggregation of thiol coated gold nanoparticles. The increase in polymer coverage density enhances the size of the aggregate as the van der Waals force of attraction dominates with the increase in the number of thiol chains. The change in the terminal group from methyl (hydrophobic) to hydroxy (hydrophilic) group modifies the size of the aggregate as the extent of interdigitation between thiol chains is reduced due to the hydrogen bond interactions between the hydroxy terminal groups. The water solvent does not much alter the aggregation of methyl terminated gold nanoparticles. It weakens the aggregation of hydroxy terminated gold nanoparticles due to the hydrophilic interaction between the water molecules and the hydroxy terminal groups.

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## 1. Introduction

The research activities are carried out in a tremendous amount in the field of gold nanoparticles since they have growing potential applications in the areas of chemistry, biology, medicine, optics, electronics, sensors, industry and technology [1–6]. The gold nanoparticles have become important in research and technology due to their characteristic features such as stability at ambient conditions, tunable optical properties, catalytic properties, bio-compatibility, biochemical and biomedical activities [7–9]. Generally gold nanoparticles are passivated by a monolayer of organic molecules to prevent agglomeration and to enhance their diverse functions and wide applications [1]. The strong affinity between the gold and sulfur atoms has been utilized to generate thiolated gold nanoparticles which can be tailored to produce the desirable functions by varying the chain length or terminal functional groups of thiol chains [10]. The alkane thiol self-assembled monolayers (SAM) on gold are studied most frequently as they can be easily prepared, organize themselves into ordered structures, and are useful in controlled wetting, lithography and sensors [10–12].

The aggregation or self-assembly is a fundamental process in which discrete components of a system organize themselves into an ordered or functional structure through direct interactions between components or indirect interactions via the environment. These interactions can be either electrostatic, van der Waals,

dipolar, hydrophobic or hydrogen bonding in nature [13]. The classical DLVO (Derjaguin–Landau–Verwey–Overbeek) theory [14] of colloidal systems, explains the aggregation process as the combined effect of van der Waals attraction and electrostatic repulsion and it has been employed to understand the experimental results of aggregation of gold nanoparticles [4,15]. The self-assembled gold nanoparticles can deaggregate, when the interaction force of repulsion exceeds the attractive forces between them. The aggregation of gold nanoparticles has been reported to be influenced by parameters such as size of nanoparticle, type of the passivating molecules, surfactants, pH value of the environment, solvent, and temperature [4,6,16] and can be modulated by UV light, external electric or magnetic field, or using templates [17,18].

The sensitivity and the dependence of the aggregation of nanoparticles to the external physical, chemical and biological environment and the significant changes induced in the inter-particle distance, size and morphology of the nanoparticles assembly as a result of aggregation alters their physicochemical properties. The distinctive dependent changes that follow from the aggregation of nanoparticles are harnessed for applications in spectroscopy, chemical and biomolecular sensing, catalysis, medicine, electronic and diagnostic devices [4,13,19]. Since the aggregation process is important in the frontier areas of research and in biological and technological applications, it is essential to have a better understanding and knowledge of the factors and parameters that drive and control aggregation and also on the morphology of aggregate in molecular and atomic detail. This will form the basis for the design and development of novel multifunctional nanomaterials

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and devices with improved tunable physical and chemical properties that can meet the demands and requirements of practical applications.

Computer simulations have played a significant role in understanding the properties of individual as well as aggregates of passivated nanoparticles [20–26]. From the molecular dynamics (MD) simulation studies, alkane thiol SAM on the gold nanoparticles surface has been shown to form an ordered molecular conformation with capping thiol chains tilted and grouped together as molecular bundles [21]. The structures of the aggregate have been reported to take an ordered spherical shape with the increase in the capping chain length from the results of coarse-grained molecular dynamics simulation of passivated gold nanoparticles in water [22]. The interactions between the capping chains and the packing of capping chains was reported to determine the equilibrium distance between alkylthiol capped gold nanocrystals in aggregates from the simulation studies [23].

To achieve direction and control of self-assembly of nanoparticles for applications, thermodynamic forces driving the self-assembly of gold nanoparticles may be modulated by the rational use of chemistry or by templating or by means of an external field [18]. The aggregation of nanoparticles can be regulated by tailoring the intrinsic characteristics of nanoparticles such as their shape, size, and chemical composition, concentration of the capping molecules and length of the passivating chains. So far, less attention has been given to the effect of polymer coverage density on the aggregation of gold nanoparticles. The manipulation of the surface of the nanoparticles by modifying the concentration of chemical functionalities, changing the terminal group and medium may affect aggregation. Moreover the aggregation of thiol coated gold nanoparticles with hydrophobic/hydrophilic terminal group in the water environment is of prime importance in the fields of chemistry, biology, medicine, and biotechnology. Hence in the present work, a series of MD simulations are performed to investigate the dependence of SAM coverage density, terminal group and water solvent on the aggregation of four thiol coated gold nanoparticles. This study focuses on the morphology of the aggregate including interdigitation, orientation and conformation order of the thiol chains, the size of the aggregate and the behavior of water molecules near the nanoparticles.

## 2. Computational details

The systems contain four replicas of passivated gold nanoparticles, each with a gold core coated with alkane thiol chains of chemical composition  $S-[CH_2]_{12}-X$ , where X is the terminal group. In this study, two different terminal groups namely methyl (hydrophobic) and hydroxy (hydrophilic) are considered. Each gold core contains 249 atoms. The size of a bare gold nanoparticle calculated using radius of gyration is 7.8 Å. The alkane thiol chains are set in trans configuration with their sulfur head group perpendicular to the gold surface and attached in atop position. The four different SAM coverage densities 25%, 50%, 75% and 100% are taken into account to investigate the effect of SAM coverage density on aggregation. The 100% SAM coverage density system is taken as a standard system for observing the effects of terminal group and water solvent. The united atom model is applied for methylene and methyl groups. In the initial configuration, center of mass distance between the two bare gold nanoparticles or gold cores of the two thiol coated nanoparticles is  $\sim 54$  Å. The same interparticle separation was maintained in the initial configuration both in the absence and presence of water.

The force field parameters for gold and alkane thiol chain are adapted from the literature [27–29] and they are given in Table 1. All the MD simulations have been performed with NAMD2.7

package [30]. The systems with solvent are simulated under isobaric-isothermal (NPT) ensemble while the systems without solvent are simulated in canonical ensemble (NVT). The TIP3 water model [31] is used and pressure is held at a constant value of 1.013125 bar. The Langevin dynamics is used with a damping coefficient of 5/ps for temperature control. The periodic boundary conditions are imposed corresponding to a box of dimensions  $125 \times 130 \times 73$  Å<sup>3</sup>. The particle mesh Ewald method is employed for long-range electrostatics. A time step of 2 fs is used for integrating equations of motion and all the systems are run for 100 ns. The summary of the systems prepared and other simulation details are given in the [Supplementary information](#).

## 3. Results and discussions

### 3.1. Single thiol coated gold nanoparticle

Prior to the investigation of aggregation of thiol coated gold nanoparticles, MD simulations are also performed on the single thiol coated gold nanoparticles for the time period of 30 ns to understand the individual molecular structure. The final structure obtained for a single thiol coated gold nanoparticle of 100% SAM coverage density with methyl terminal group at room temperature is shown in Fig. 1. The alkane thiol chains on gold nanoparticle surface organize themselves as an ordered structure of molecular bundles in agreement with the results reported in the literature [21]. The packing of capping thiol chains can also be seen from the tilt

**Table 1**  
Force field parameters.

<i>Lennard-Jones potential</i>			
Atoms	$R_{\min}/2$ (Å)	$\epsilon$ (kcal/mol)	
Au	1.4418	10.540	
S	1.9940	0.2500	
C (CH <sub>2</sub> )	2.2055	0.0930	
C (CH <sub>3</sub> )	2.2055	0.2266	
O	1.6000	0.1591	
H	0.8000	0.0498	
$R_{\min}$ – Distance at which the potential reaches its minimum $\epsilon$ – Depth of the potential well			
<i>Bond stretching</i>			
Bond	$r_0$ (Å)	$K_r$ (kcal/(mol/Å <sup>2</sup> ))	
Au–S	2.40	1000	
S–C	1.82	1000	
C–C	1.54	900.58	
C–O	1.42	200	
O–H	0.96	225	
$r_0$ – Equilibrium bond length $K_r$ – Bond stretching constant			
<i>Angle bending</i>			
Angle	$\theta_0$ (°)	$K_\theta$ (kcal/(mol/rad <sup>2</sup> ))	
Au–S–C	100.0	124.28	
S–C–C	114.0	124.28	
C–C–C	114.0	124.28	
C–C–O	111.0	22.5	
C–O–H	109.5	17.5	
$\theta_0$ – Equilibrium bond angle $K_\theta$ – Angle bending constant			
<i>Torsion</i>			
Dihedral	$a_1$ (kcal/mol)	$a_2$ (kcal/mol)	$a_3$ (kcal/mol)
Au–S–C–C	0	0	0
S–C–C–C	2.8239	–0.5424	6.2941
C–C–C–C	2.8239	–0.5424	6.2941
C–C–C–O	0	0	1.6000
C–C–O–H	0	0	0.5000
$a_n$ – Dihedral force constant $n$ – multiplicity of the dihedral potential			

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