Journal of Molecular Graphics and Modelling 74 (2017) 359–365

Contents lists available at ScienceDirect

Journal of Molecular Graphics and Modelling

journal homepage: www.elsevier.com/locate/JMGM

Simulation studies on structural and thermal properties of alkane thiol capped gold nanoparticles

J. Meena Devi

Centre for Nanotechnology & Advanced Biomaterials (CeNTAB) and School of Electrical & Electronics Engineering (SEEE), SASTRA University, Thanjavur 613401, Tamilnadu, India

ARTICLE INFO

Article history:
Received 20 December 2016
Received in revised form 28 March 2017
Accepted 29 March 2017
Available online 18 April 2017

Keywords:
Gold nanoparticles
Alkane thiol
Capping density
Specific heat capacity
Molecular dynamics simulation

ABSTRACT

The structural and thermal properties of the passivated gold nanoparticles were explored employing molecular dynamics simulation for the different surface coverage densities of the self-assembled monolayer (SAM) of alkane thiol. The structural properties of the monolayer protected gold nanoparticles such us overall shape, organization and conformation of the capping alkane thiol chains were found to be influenced by the capping density. The structural order of the thiol capped gold nanoparticles enhances with the increase in the surface coverage density. The specific heat capacity of the alkane thiol capped gold nanoparticles was found to increase linearly with the thiol coverage density. This may be attributed to the enhancement in the lattice vibrational energy. The present simulation results suggest, that the structural and thermal properties of the alkane thiol capped gold nanoparticles may be modified by the suitable selection of the SAM coverage density.

1. Introduction

The gold nanoparticles protected by self-assembled monolayer (SAM) of organic or bio-molecules offer improved, modified and tunable physical, chemical and biological properties and diverse functions [1–7]. The distinctive, extra-ordinary physical and chemical attributes and the advantageous synergistic properties of the surface functionalized gold nanoparticles make them a potential material for a broad range of growing applications such as molecular electronics, optics, catalysis, protective coating, chemical and biological sensors, targeted drug delivery, thermal therapeutic agent for cancer, cell attachment, molecular recognition, diagnostic tool, intracellular imaging agents, bio-materials, biological interface and so on [3–18]. The properties and the functions of the monolayer protected gold nanoparticles depend on their chemical composition as well as on their physical and structural parameters.

The coverage density of the capping chains on gold surface has been reported to influence their properties and applications [19–22]. Unsworth et al. [19] have identified the variation in the protein adsorption rate of gold surface modified with end tethered polyethylene oxide with respect to the surface chain density. Manson et al. [20] have demonstrated the influence of the capping density of polyethylene glycol coated gold nanoparticles on stability of various media like water, phosphate-buffered saline solution, phosphate-buffered saline solution containing bovine serum albumin and dichloromethane. Tournebize et al. [21] have revealed the role of capping density of the gold nanoparticles coated with dihydrolipoic acid to build a stable platform for the drug delivery systems. Biswas et al. [22] have determined the correlation between the capping density of the different alkanethiol coated gold nanoparticles and their catalytic property.

The characteristic part of the monolayer protected gold nanoparticles is its unique ability to interact with the different environment, external stimuli, and the target molecules in a specific, desired, controllable and predictable manner, which in turn can be harnessed for various sensing, biological and technological applications. The approach in the material designing of the core-shell nano-composite materials, constituting metal core and organic monolayer involves alteration either in the size, shape of the interior metal cores or in the chemical functional group, structure, length, concentration of the capping molecules. In order to employ the particular combination of chemical composition and molecular structure of the functionalized gold nanoparticles for the specific practical applications, it is essential to have the thorough knowledge on their overall structure at the molecular level and their fundamental properties. The study on the thermal properties of the functionalized gold nanoparticles plays an important role for designing the devices in the industrial, biological and engineering

E-mail address: jmeenadevi@sastra.ac.in

http://dx.doi.org/10.1016/j.jmgm.2017.03.023
1093-3263/

applications to activate, manipulate, control and maintain the heat transfer, thermal process, thermal stability and thermal load.

In the present simulation study, different thiol coverage densities are taken into account to explore the relation between the thiol coverage density and the structural and thermal properties of alkane thiol capped gold nanoparticles. The capping organic monolayer can induce the self-assembly of the passivated gold nanoparticles, and it plays a vital role in the interactions between the gold nanoparticles and the external chemical environment or target biological molecules. Hence it will be beneficial to study the different SAM coverage densities, so that the surface interactions of the gold nanoparticles may be controlled and tuned. In the present work, the gold nanoparticles with four different SAM coverage densities of alkane thiol are simulated at room temperature to investigate their structure and specific heat capacity. The results of this computational study, may enhance the molecular level understanding of the structure of the passivated gold nanoparticles and the influence of SAM coverage density on their structural and thermal properties. This simulation study may contribute to the understanding and the development of the monolayer protected gold nanoparticles for biological and technological applications.

2. Materials and methods

The functionalized gold nanoparticles with the four different alkane thiol coverage densities were chosen in this study. The gold core was cut from a face-centered cubic gold lattice. The gold core is approximately spherical with the rough surface. The gold core contains 249 gold atoms and its size calculated using radius of gyration is 7.8 Å. The gold atoms of the gold core were kept free. Four different thiol coverage densities 25%, 50%, 75% and 100% were considered in this study and they correspond to 29, 57, 86 and 114 number of capping alkane thiol chains respectively. The capping monolayer has the chemical composition S-$[CH_2]_{12}$-CH3. The united atom model has been applied for the methylene and methyl groups. The sulphur atoms of the thiol chains were covalently bonded to the surface gold atoms of the gold core. The sulphur head groups were randomly distributed on the gold surface. The alkane thiol chains were set in trans configuration with their sulphur head groups perpendicular to the gold surface and attached in atop position.

The force field parameters for gold [23] and alkane thiol chains [24] were taken from the literature and they are listed in Table 1. The Lennard-Jones (LJ) interaction parameters for the gold atoms have been reported to yield significant results in the literature [25–28] for gold systems. Lee and Schatz [25] have used LJ potential to describe the interactions between the gold atoms to investigate the structural features of DNA functionalized gold nanoparticles. Kalia et al. [26] have employed LJ potential to model the interaction for gold to study the supercrystals of DNA functionalized gold nanoparticles. Gopalakrishnan et al. [27] have used LJ potential for the gold atoms to study the complexation of small interfering RNA with gold clusters. Mudedla et al. [28] have employed LJ potential for the gold atoms to study the interaction between collagen like peptides with a gold nanosurface. Hence the approach of modeling the interactions between gold atoms using LJ potential in the present investigation can yield correct description for the structural and thermal properties of the alkane thiol capped gold nanoparticles.

In the present work, all the molecular dynamics simulations have been performed with NAMD2.9 package [29]. The systems were simulated under canonical (NVT) ensemble. Langevin dynamics has been used with a damping coefficient of 5/ps for temperature control. Periodic boundary conditions were imposed. Energy minimizations were performed using conjugate gradient energy minimization method and the number of steps taken for minimization was 3000. A time step of 2 fs was used for integrating equations of motion and all the systems were run for 30 ns at room temperature. All the analysis were carried out for the last 10 ns.

Table 1
Force Field Parameters.

Lennard–Jones potential

Atoms	$R_{min}/2$ (Å)	ϵ (kcal/mol)
Au	1.4418	10.540
S	1.9940	0.2500
C (CH_2)	2.2055	0.0930
C (CH_3)	2.2055	0.2266

Bond stretching

Bond	r_o (degree)	K_r (kcal/(mol/Å^2))
Au—S	2.40	1000
S—C	1.82	1000
C—C	1.54	900.58

Angle bending

Angle	θ_o (degree)	K_θ (kcal/(mol/rad^2))
Au—S—C	100.0	124.28
S—C—C	114.0	124.28
C—C—C	114.0	124.28

Torsion

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

R_{min} – Distance at which the potential reaches its minimum.
ϵ – Depth of the potential well.
r_o – Equilibrium bond length.
K_r – Bond stretching constant.
θ_o – Equilibrium bond angle.
K_θ – Angle bending constant.
a_n – Dihedral force constant.
n – multiplicity of the dihedral potential.

3. Results and discussions

3.1. Structural analysis

Molecular Dynamics simulations of the alkane thiol capped gold nanoparticles were carried out under canonical ensemble for a period of 30 ns at room temperature for four different SAM coverage densities (25%, 50%, 75% and 100%). The gold core remained intact in all simulations during 30 ns. This suggests the validity of using Lennard-Jones potential to model the interactions between the gold atoms. The snapshots of all the four thiol capped gold nanoparticles at the end of the simulation are shown in Fig. 1. The overall shape of the passivated gold nanoparticles may influence their biological and technological applications. The spatial arrangement, pattern of organization and conformation of the thiol chains on the surface of the gold core will determine the overall shape of the thiol capped gold nanoparticles.

The overall structure of the thiol capped gold nanoparticles in relation to the spherical structure, can be roughly estimated by calculating the shape factor. The shape factor is defined as the ratio between the length along the x axis and y axis of the system. The shape factor is unity for a sphere. The deviation of the structures from the sphericity is determined by the difference between the shape factor and unity and it is given in Table 2 for all the four