Preparation, structure, and a coarse-grained molecular dynamics model for dodecanethiol-stabilized gold nanoparticles

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ABSTRACT

Thiol-stabilized metal nanoparticles possess unique properties in the comparison with larger-scale materials, which enable their use in many promising chemical and biological applications. We have synthesized thiol-coated colloidal gold nanoparticles (AuNP) soluble in non-polar organic solvents by a simplified procedure, in which $AuCl_4^-$ was initially reduced in aqueous phase and then coated with thiol residues and transferred to organic phase. Using the transmission electron micrograph (TEM) imaging, the average diameter of a dodecanethiol-stabilized AuNP was estimated to be 3.75 ± 0.06 nm. Based on the experimental TEM data, a new coarse-grained molecular dynamics model of AuNP was developed. The model was applied for studying self-assembly of AuNPs on a flat graphite surface, enabling further elucidating the structure and packing of the ligand shell around the spherical nanoparticle core.

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1. Introduction

Metal nanoparticles (NPs), capped with organic adsorbates and assembled into various nanostructures, have a strong potential for the development of new materials for nanotechnology [1–4]. Chemical control over nanoparticles size, shape, and composition presents one of the major challenges to this field, because these parameters govern many thermodynamic, optical, and chemical properties of such nanoassemblies [5–7]. Several approaches have been reported for manipulating the properties of metal nanoparticles, among which control over chemical properties of capping agent, such as modification of surface-stabilizing groups or alkyl chain length, were applied [8–10]. Recently, nanoparticle self-assembly (or aggregation) into larger structures, which properties depend on the size and shape of the constituent NPs, have also attracted considerable attention, enabling a wide tunable range for adjusting optical characteristics of such nanostructures [11,12].

In addition to continuously growing practical importance, the properties of novel nanomaterials became in focus of special interest in the theoretical modeling. Recently, there has been significant progress in using atomistic and coarse-grained molecular dynamics (MD) simulation for studying structure and dynamics of alkyl-

stabilized AuNPs [13–15]. The MD simulations have also been applied for examining ligand shell organization in self-assembled monolayers at nanoparticle surface [16]. The structural and thermal properties of the DNA-functionalized and DNA-linked particles have been modeled using both atomistic and coarse-grained MD simulations [17]. The coarse-grained methodology has also been applied to study penetration of alkyl-coated nanoparticles into cell membranes [18].

In this paper, we have synthesized gold nanoparticles using the recently reported simplified procedure [19], in which $AuCl_4^-$ was initially reduced in the aqueous phase and then have been transmitted to non-polar organic solvent with simultaneous coating by thiol residues to produce stable thiol-stabilized gold nanoparticles. Using the transmission electron micrograph (TEM) imaging, the nanoparticle size distribution was studied resulting in the average diameter of AuNPs of 3.75 ± 0.06 nm. We found that the dodecanethiol-stabilized AuNPs were quite stable and they could be preserved for a long period of time without any changes in their optical properties. Using the experimental data for the nanoparticle size and dodecanethiol organization around a spherical gold core, we developed a force field and a MD model, which reproduce a stable nanoparticle structure in good agreement with the experiment. A new MD model is based on the coarse-grained MARTINI force-field, because it is practically important to develop computational methods for studying not only individual AuNPs, but also self-organization of AuNPs into larger-scale assemblies.

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2. Materials and methods

2.1. Synthesis and purification

The thiol-stabilized AuNPs were prepared following the simplified method proposed by Eah and coworkers [19].

On the first step, starting solutions were prepared on the base of deionized water: 0.05 M of $HAuCl_4 \cdot 3H_2O$ in 1.0 M aqueous HCl (**A**), 0.05 M of $NaBH_4$ in 1.0 M aqueous NaOH (**B**) and 0.1 g of dodecanethiol in 5 g of *n*-hexane (**C**). One hundred microliters of solution **A** was added to 10 mL of deionized water under intensive stirring (with magnet stirrer) resulting in formation of brightly-yellowish transparent mixture. Then 100 μL of solution **B** was added slowly, during this step the solution color turns to the intensively-red. After this, 5 g of acetone was added and the mixture was shaken manually several seconds. Then solution **C** was added rapidly and the mixture was shaken manually during 30 s. Finally, the mixture was left quiet to allow the water and hexane layers to separate well one from another. The decolorization of the lower water phase was observed with the simultaneous dyeing of the upper organic phase. After that, the layer of *n*-hexane was removed. The procedure was repeated 10 times; all the collected *n*-hexane layers were combined together and concentrated in vacuum rotary evaporator under mild warming. The resulting concentrated solution was mixed with 5 mL of ethyl alcohol, from which the AuNPs were precipitated as dark amorphous solid. The precipitate was again dissolved in *n*-hexane and re-precipitated by ethanol to complete removing of dodecanethiol.

The synthesized AuNPs were stable in solid state and in solutions in the non-polar solvents. The prepared AuNPs were stored at 4–5 °C.

2.2. Spectroscopy

The AuNPs electronic absorption spectra in *n*-hexane were recorded on HITACHI U-3210 spectrophotometer. Transmission electron micrograph (TEM) images were obtained on PEM-125K transmitting electron microscope with the accelerating voltage 100 kV (production of *JSC Selmi*, Ukraine). Samples for microscopic investigations were prepared by evaporation of AuNPs dilute hexane solution (of spectrophotometric concentration) on the surface of carbon films of approximate thickness near 100 nm. The TEM images were registered with CCD video camera and treated mathematically on the desktop computer.

2.3. Molecular dynamics modeling and simulation setup

The united atom model of gold-attached dodecanethiol is based on representing each of Au and S atoms and, CH_2 and CH_3 units of the alkyl chain by a single interaction center. In order to keep the model compatible with the popular MIRTINI coarse-grained (CG) force field [20,21], the S, CH_2 and CH_3 units were assigned to the corresponding nonbonded interaction sites of MIRTINI force-field version 2.1. The force field parameters of bonded interactions of gold-attached dodecanethiol were developed based on mapping of DFT(B3PW91 with LanL2DZ basis set for Au and cc-pVDZ for the other elements)-optimized geometry of all-atom gold-dodecanethiol ($Au–S–(CH_2)_{11}–CH_3$) into harmonic-type potentials which describe bond stretching and angle bending, and keeping bond lengths and angles at equilibrium values. The nonbonded parameters for gold–gold interactions were developed by reproducing experimental gold–gold nearest-neighbor distances of ~0.288 nm found in the face-centered cubic crystal structure [22]. The repulsion and dispersion terms of nonbonded interac-

tions were computed using the Lennard-Jones potential energy function.

$$V_{LJ}(r_{ij}) = 4\varepsilon_{ij} \left(\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^{6} \right) \qquad (1)$$

To model a gold nanoparticle, its gold core was initially constructed using 1500 Au atoms placed in a spherical, random close-packed configuration. The amorphous gold core was first annealed up to $T = 450$ K. After that the system was slowly relaxed to form the spherical crystalline gold core at $T = 298$ K. At the next step, the gold core was coated with 130 molecules of gold-attached dodecanethiol randomly distributed around the spherical gold surface. The dodecanethiol carbon chains were initialized in the all-trans orientation and placed perpendicular to the surface of the Au core. The assembled in such a way solvent-free gold nanoparticle was then equilibrated for 50 ns until the dodecanethiol chains adopt an equilibrium packing.

The coarse-grained model of the flat graphite surface was based on a four-to-one mapping, i.e., four carbon atoms of a graphite lattice were represented by a single CG interaction site. The graphite surface was modeled by one {1 1 1} graphite layer consisting of 14512 carbon atoms. The position of each CG graphite site in the crystalline lattice was kept rigid by the position restraint potential. With our newly developed coarse-grained model for a gold nanoparticle we have carried out solvent-free 200 ns-long molecular dynamics simulations of two-dimensional self-assembly of the thiol-capped gold nanoparticles on the graphite surface.

Two-dimensional *xy* periodic boundary conditions were applied with the *z* axis lying perpendicular to a graphite surface. MD simulations were carried out at the constant number of particles, constant pressure, $P = 1$ atm, and the constant temperature, $T = 298$ K (NPT ensemble). The cutoff distance of Lennard-Jones interactions was limited to 1.2 nm. The MD integration time step was 5 fs. The MD simulations were carried out using GROMACS set of programs, version 4.5.3 [23]. Molecular graphics and visualization were performed using VMD 1.8.7 software package [24].

3. Results and discussion

3.1. Structure of dodecanethiol-stabilized AuNP

The synthesis of dodecanethiol-stabilized gold nanoparticle was accompanied by changes in solution color from bright-yellowish to intensively red. Fig. 1 shows the UV–vis spectrum for solution of dodecanethiol-stabilized gold nanoparticles in *n*-hexane. The surface plasmon peak was observed around ~516 nm, which is consistent with the plasmons reported for alkanethiol-stabilized gold nanoparticles of low-intermediate size with diameters within the range of ~3–10 nm [5,19,25,26].

Haiss and coworkers have proposed the method for evaluation of the size of a nanoparticle from its UV–vis absorption spectra [25]. In this method, the nanoparticle diameter can be estimated from ratio of the absorbance at the surface plasmon resonance peak maximum to the absorbance at 450 nm. Using Eq. (11) from [25] we have estimated the ratio of $A_{516}/A_{450} = 1.14$, which resulted in the mean diameter of AuNP to be ~3.4 nm.

However, it has been reported that the peak position of the plasmon resonance is often affected not only by a nanoparticle diameter, but also by several other factors, such as, solvent dielectric constant, interparticle distance, and nanoparticle self-aggregation as well [27]. Therefore, in addition to the UV–vis spectra, the structure and size of AuNPs were studied with transmission electron microscopy (TEM). The TEM images for the synthesized AuNPs samples are shown in Fig. 2A. The statistic analysis of a series of the