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Effect of gamma radiation on alkanethiolate-capped gold nanoparticles: Theoretical studies

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HIGHLIGHTS

- Gamma radiation effects on alkanethiolate-capped Gold nanoparticles were simulated.
- Effects of gamma radiation depend on the Gold nanoparticle structure.
- Icosahedral nanoparticles were the most stable to gamma radiation.
- At the studied gamma irradiation doses, the metallic cores were stable up to 10 kGy.
- Major modifications can occur on the alkyl chains of the capping agent.

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ABSTRACT

Theoretical studies of the effect of gamma irradiation on alkanethiolate-capped gold nanoparticles are presented. Icosahedral, decahedral and fcc nanoparticles protected with 1-dodecanethiolate (SC12) were obtained by molecular mechanics simulations, analyzing the effect of gamma irradiation through MonteCarlo. The studied doses were 1, 10 and 20 kGy. It was observed that slight structural modifications of the metallic core might occur and these are dependent on the shape of the nanoparticle. However, the most significant effect was observed on the organic passivating layer, where torsions, bending and scission of the alkyl chains were detected.

1. Introduction

Since the great potential of nanoscale materials was exhibited, different scientific and technological fields have focused on the possibility of using their novel properties to fabricate new or improved materials on a number of applications. With no doubt, nanomaterials have occupied an important place in the development of systems or devices either for medicine, catalysis, electronics and aerospace. In some of these applications it is required that the nanomaterials withstand (Mariscal et al., 2010; Nara et al., 2004; Yourdshahyan and Rappe, 2002; Yuan et al., 2014; Askerka et al., 2012) harsh conditions as radiation fields, which have sufficient energy to induce changes in matter. For example, the new nanomaterials for the nuclear and thermonuclear power engineering (Andrievski, 2011), or nanodevices to be used in the space exploration (Dharani et al., 2013). On the other hand, radiation in combination with nanomaterials may be used to improve the function of the material in areas such as redox catalysis, environmental remediation, electronics and radiotherapy (Meisel, 2005). For example, for radiation therapy high-Z materials, such as Au nanoparticles, can be used to amplify the dose of delivered ionizing radiation (Cooper et al., 2014) or in electronics for the manufacturing of silicon solar cells in which Au nanoparticles are used to enhance their efficiency (Abdullah, 2013).

Whatever the case, the information about the nanomaterials behavior under irradiation is very important especially when they will be exposed to an intense radiation field. For metallic nanoparticles specifically, there are many reports focused in the application of radiation to synthesize them, however, little information is available on the stability of nanoparticles when they are exposed to radiation of any kind, such as gamma rays. Furthermore, up to now, to our knowledge, there are no reports about the radiation effects on surface protectors over metallic nanoparticles. It should be mentioned that surface protector is very important in the dimensional stabilization of the nanoparticle, then, if the protector suffers any modification, the nanoparticle can destabilize and change its properties.

In order to gain knowledge on the advantages or limitations of

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the application of nanoscale materials in a radiation field, in this paper we present a theoretical simulation analysis of the effects of gamma radiation on alkanethiolate-capped gold nanoparticles. The study was based on three of the most commonly found shapes of nanoparticles in the size range of 1–4 nm, icosahedron, decahedron and fcc. For this theoretical analysis, we simulated the behavior of gold nanoparticles exposed to ionizing radiation at a deposited energy per mass unit of 1, 10 and 20 kGy (Dose), considering that gamma radiation is widely used in medicine, industry and investigation. The theoretical analysis was performed using the PENELOPE (http://www.oecd-nea.org/lists/penelope.html) code of the Monte Carlo Method (Metropolis and Ulam, 1945).

2. Experimental

Minimum energy configuration models were obtained through geometrical optimization. The minimum energy configuration models were determined using a universal potential, with a maximum number of iterations of 5000 steps and a convergence criterion of 0.000 1 kcal/mol.

Models of icosahedral, cuboctahedral and decahedral gold nanoparticles of 55 atoms respectively, were constructed and geometrically optimized to refine the geometry of their atomic structure. This process was performed through an iterative sequence, which adjusts the atomic coordinates to bring the system to a minimum energy structure. The algorithm SMART (Ermer, 1976) was used to perform these calculations, which is a combination of steps descent methods, conjugate gradient and Newton-Raphson. A Universal (Rappé et al., 1992) potential was used. Once these gold nanostructures models Au55ico, Au55dec Au55cub were obtained, they were capped by 20 molecules of SC12 each, and the system was again optimized to a minimum of energy. The energy of the systems was calculated through density functional theory (DFT), based on the Kohn and Sham theory, by applying a local density approximation (LDA) (Kohn and Sham, 1965; Barnard and Curtiss, 2006; Carr et al., 2012; Zhang et al., 2009).

Because of the stochastic nature of radiation interaction, Monte-Carlo simulations techniques are very convenient to know the ionizing radiation effects in a specific material. Consequently, the theoretical simulation analysis of the irradiation process on gold nanoparticles-SC12 with radiation such as gamma rays, as those of ^{60}Co, were performed using the Monte-Carlo Method. When radiation passes through matter, it interacts with atoms (electrons and nucleus) that conform this matter. Depending on the ionizing radiation energy, different interactions mechanisms can take place: coherent scattering (Rayleigh), incoherent scattering (Compton), photoelectric effect and pair production. For ionizing radiation, energies such as those associated to ^{60}Co, Compton scattering is the dominant interaction. In this process, a radiation beam transfers a fraction of its energy to an atomic electron, which is ejected. With its smaller energy, the radiation beam can undergo a photoelectronic effect by an atom: in this process, the atom emits an electron. These multiple interaction process can be simulated by the PENELOPE code of the Monte-Carlo method. This simulation algorithm is based on a scattering model that combines numerical databases with analytical cross section models for the different interaction mechanism and is applicable to energies from a few hundred eV to ~1 GeV PENELOPE-2008; Arqueros and Montesinos, 2003; Tajik et al., 2015).

3. Results and discussion

On the first stage of this study the minimum energy models of the gold nanostructures capped by SC12, shown in Fig. 1, have been calculated. These are labeled as Au55ico, Au55dec Au55cub. The model of an icosahedron capped with SC12 was built, placing each SC12 over the exposed planes on the surface, at hollow sites on the face (111), with a distance S–Au of 2.4 Å (Majumder et al., 2002; Mazzarello et al., 2007). SC12 in a cuboctahedron structure, were placed in hollow sites over (100) and (111) facets with an average distance of S–Au of 2.4 Å. For the decahedron structure, the SC12 were placed on the hollow sites on the surface planes (111) and (100), with an S–Au distance 2.4 Å average. The capping molecules were attached on three-coordinated hollow sites for (111) planes and tetra-coordinated hollow sites for (100) planes, as it has been reported for similar systems (Ching Shih et al., 2007; Sheppard et al., 2011; Luedtke and Landman, 1996; Wilson and Johnston, 2002).

The beam direction of the radiation was applied to interact with planes (111) and (100) for each system, having finally two different results for the cuboctahedral and decahedral models and one for the icosahedron.

3.1. Icosahedron

The calculated energy of a 55 atoms-icosahedron with 20 molecules of SC12 is originally of −418970.70 eV. The model of this system is shown in Fig. 2a. Studies for this system were based on the interaction of the radiation beam with the (111) plane, as indicated by the arrow in Fig. 2b. It was observed that the energy of the system increases as the radiation dose rises. At 1, 10 and 20 kGy, the energy obtained for each system is −418964.46 eV, −418961.44 eV and −418945.86 eV respectively. The resulting structures obtained after an irradiation at 20 kGy are presented, showing the type of modifications that could be expected. Fig. 2b

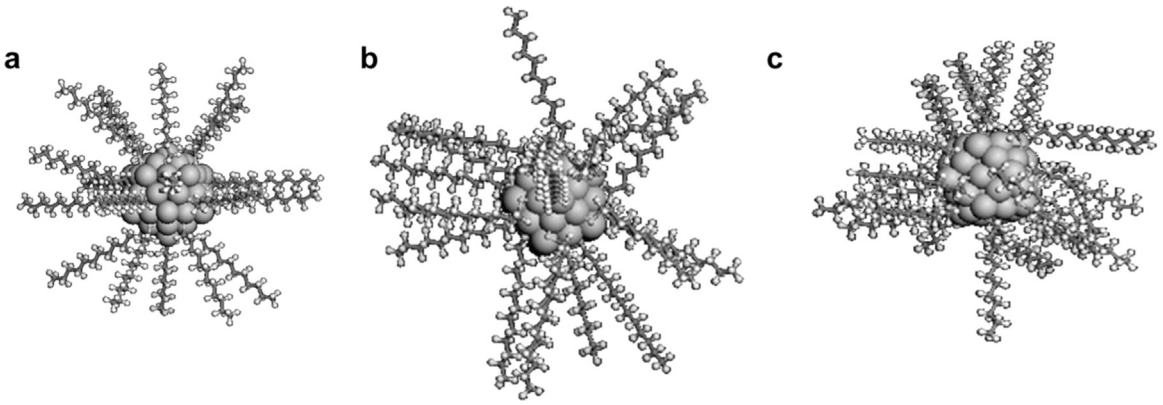

Fig. 1. Models of 1-dodecanothiolate-capped gold nanoparticles. (a) icosahedron, (b) decahedron and (c) cuboctahedron.