Au nanoclusters in the plasmonic applications

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Abstract. One of the new applications of gold nanoparticles is the use of the plasmon effect, which occurs due to the interaction of an electromagnetic wave with free electrons in nanostructures. Particles of gold with a size smaller than the wavelength of a visible electromagnetic wave can strongly absorb light due to the collective oscillation of conduction electrons. Bulk gold has a high-symmetry fcc structure, but controlling the collection of metal atoms in solution can also lead to the growth of many anisotropic forms. The use of these different structures has a significant effect on the plasmonic properties, since defects at twin boundaries can serve as scattering centers of conduction electrons in a metal. Thus, on the basis of controlling the size, shape, and structure of Au nanoparticles, it is possible to control light with unprecedented accuracy, and therefore the determination of the morphology of individual gold nanoparticles is of great interest for studying their possible optical interaction.

1. Introduction

Silver and gold nanoparticles are currently two of the most studied nanostructured nanomaterials. Such studies involve the prediction of various physical properties of nanoparticles, novel methods of synthesis, sophisticated functionalizations and applications that motivate the scientific community to constantly improve these nanomaterials [1].

At present, gold nanoparticles are extensively studied due to their possible widespread use in microelectronics, sensors, catalysis, nonlinear optics, and biomedicine [1–3]. Moreover, gold nanoclusters serve as the basis for many synthesized molecular nanocrystalline materials. For example, when placed on a fullerene base, gold nanoclusters can form cluster composite superstructures. This information is sufficient for a comprehensive theoretical and experimental study of the structural, electronic, dynamic, and other physical and chemical properties of both isolated and passivated gold clusters.

It is well known that all metallic nanoparticles exhibit unusual optical, thermal, chemical, and physical properties mainly due to the high percentage of surface atoms and the free path of electrons on a nanometer scale (10–100 nm for many metals at room temperature). Critical parameters affecting these properties are the size and shape of nanoparticles; therefore, these parameters should be controlled by nanotechnologies.

The fact that the properties of many clusters depend, firstly, on the number of atoms in them and, secondly, on their structure, means that to determine the structure of nanoparticles, it is very important to identify the structure and properties relationship. Although bulk gold has a fcc structure, small atomic groups can form configurations that can violate standard crystallographic laws: when the size of the Au cluster reaches the nanometer scale, a number of highly symmetric structures become
energetically favorable for the system, which leads to the formation of icosahedral (Ih) and decahedral (Dh) modifications with a pentagonal symmetry [4].

The light interaction with nanostructures, especially those fabricated of noble metals, causes various fascinating optical phenomena. One of the current directions of research in the field of nanophotonics is the development of metal nanostructures that efficiently interconvert the propagating and localized optical fields and thereby facilitate the generation of strongly enhanced local electrical fields. Field enhancements (FEs) occur due to resonantly excited surface plasmons, which represent collective electron oscillations in metals coupled to electromagnetic fields in neighboring dielectrics. Strong FEs are extremely important for practical applications, for example, in sensing and catalysis, as well as in surface-enhanced Raman scattering (SERS). Noble metal nanostructures are also very promising for the formation of surface plasmon resonators, which have demonstrated enormous increase in the fluorescence of quantum emitters, thus facilitating the development of ultra-bright and stable single-photon sources. In addition, they can be used as real-time sensors, plasmonic solar cells, building blocks for light-energy guiding devices and metamaterials with unique optical properties, etc [2].

Gold exhibits excellent plasmonic properties and can be advantageously used in most of the above-mentioned applications. The frequency and intensity of plasmon resonance depend on the distribution of polarization charge across the nanostructure, which, in turn, is determined by its shape. Thus, to control the shape of the Au nanostructure means to control the wavelengths of light that it scatters and absorbs, as well as the extent to which it amplifies local electric fields [3].

2. Using of Au nanoparticles in plasmonics

Coinage metals, such as Au, Ag, and Cu, have been important materials throughout history. Although they were admired in ancient cultures primarily for their ability to reflect light, their applications became much more sophisticated with our deeper understanding and control of the atomic world. Today, these metals are widely used in electronics and catalysis, as well as structural materials, but when they are fashioned into structures with nanometer-sized dimensions, they also become tools for a completely different set of applications that involve light. These new applications go far beyond merely reflecting light and have renewed our interest in maneuvering the interactions between metals and light in a field known as plasmonics.

In plasmonics, metal nanostructures can serve as antennas for converting light into localized electric fields (E-fields) or as waveguides for directing light to the desired locations with nanometer precision. These applications become possible due to a strong interaction between incident light and free electrons in the nanostructures. With a tight control over nanostructures in terms of size and shape, light can be effectively manipulated and controlled with unprecedented accuracy [5].

Although there are many varieties of plasmonic Au nanostructures, they can be differentiated based on the plasmonic modes they support: localized surface plasmons (LSPs) or propagating surface plasmons (PSPs). In LSPs, the time-varying electric field associated with light (E₀) exerts a force on the gas of negatively charged electrons in the conduction band of the metal and drives them to oscillate collectively. At a certain excitation frequency, this oscillation will be in resonance with the incident light, resulting in a strong oscillation of surface electrons, commonly known as the localized surface plasmon resonance (LSPR) mode. Structures that support LSPRs experience a uniform E₀ when excited by light as their dimensions are much smaller than the wavelength of light.

In contrast, PSPs are supported by Au structures that have at least one dimension that approaches the excitation wavelength. In this case, the E₀ is not uniform across the structure and other effects must be considered. For example, in a structure such as nanowires, SPs propagate back and forth between the ends of the structure. This can be described as a Fabry-Perot resonator with the resonance condition l = nλsp, where l is the nanowire length, n is an integer, and λsp is the wavelength of the PSP mode. One should also consider the reflection from the ends of the structure, which can change the phase and resonant length. The propagation lengths can be in the tens of micrometers (for nanowires), and the PSP waves can be manipulated by controlling the geometrical parameters of the structure.
It has now become clear that the size, shape, and structure of nanoparticles determine their optical properties, including resonance frequencies. Consequently, by adjusting the size, appearance of the Au nanostructure and environmental parameters, it is possible to control the light in various ways. Therefore, it is not surprising that the successes in the synthesis and assembly of Au nanostructures provided new opportunities for precise control of the interaction of Au nanoparticles with a light wave and, therefore, with discovered applications that were previously considered impossible. Thus, based on controlling the size, shape and structure of nanoparticles, light can be effectively controlled with unprecedented accuracy, and therefore the determination of the morphology of individual gold nanoparticles is of great interest for studying their possible optical interactions.

Gold have a highly symmetrical, face centered cubic crystal structure, but many anisotropic shapes can be grown by controlling the assembly of metal atoms in solution. Au nanostructures synthesized by chemical methods usually have one of four possible forms: an ideal nanoparticle; a nanoparticle with single twinning; a nanoparticle with multiple twinning (often with a symmetry axis of the fifth order); interconnected nanoparticles stacked with packaging defects. The use of these different structures has a significant effect on the properties of a plasmon, since defects at the boundaries of twins can serve as scattering centers for conduction electrons in a metal. But even in the case of the same type of synthesized nanostructure, the peak and shape of the plasmon resonance can vary greatly [5].

3. Results and discussion
Since the different internal structure of a metal nanoparticle means different physico-chemical properties, from the point of view of using gold nanoclusters in plasmon applications, it is very important to determine the boundaries of the thermal and dimensional stability of the initial crystal structure of nanoparticles. For this purpose, possible configuration changes in gold clusters when heated to the melting temperature were considered and an attempt was made to determine the dimensional boundaries of clusters in which a structural transition can occur. To analyze the clusters, the MDNTP computer program developed by Dr. Ralf Meyer from the University of Duisburg (Germany) will be used. The interatomic interaction forces were calculated using the modified tight-binding potential TB-SMA [6].

The simulation was performed in terms of the NVT ensemble; clusters with diameters D up to 3.5 nm were investigated. All clusters had the same initial internal structure, which corresponds to a perfect fcc lattice; to optimize their internal structure and shape, they were subjected to the procedure of thermal relaxation at 100 K.

To determine the cluster structure, we considered an ensemble of clusters of the same size and gradually heated them to 1300 K, which significantly exceeded their melting point. During heating, the temperature was varied stepwise in steps of 10–20 K on average; at each fixed temperature, the clusters were kept for 0.4 ns. The results of this study showed that, with a particle diameter of more than 3.0 nm, the initial fcc structure was retained in all cases up to the melting temperature. This fact suggests the thermal stability of the fcc gold clusters with a diameter of more than 3.0 nm; however, with a smaller cluster size, the situation is not that simple.

As a typical example, let us consider a gold cluster consisting of 135 atoms (D = 1.6 nm), which is cut from a perfect fcc lattice. With an increase in temperature of about 400 K, a structural transition

![Figure 1](image-url)
from the initial fcc phase occurs, which is accompanied by a sharp change in the potential energy (figure 1). As the number of atoms in a cluster increases, the point of the polytypic transition shifts toward the melting temperature. It was shown that with an increase in cluster size, the structural transition occurs at a higher temperature. For example, in the case of a gold cluster with \( N = 201 \) atoms (\( D = 2.0 \) nm), substantial jumps in the potential energy are observed only near the melting point. This change in the potential energy corresponds to the transition of a cluster from a close-packed state (fcc lattice) to a state with an icosahedral structure. A similar picture of a stepwise change in the potential energy of the system before melting was also observed for a cluster consisting of 1157 atoms (\( D = 3.33 \) nm). However, the analysis showed that in this case there are no structural transformations, and energy jumps are associated with fluctuations near the phase transition.

Thus, with an increase in the number of atoms in a cluster, the following tendency is observed. At low temperatures, for a gold cluster with \( N = 55 \), a fcc–icosahedral structure transition occurs. However, with a further increase in temperature to 350–400 K, the icosahedral structure is destroyed with the formation of an amorphous-like state; for a cluster with the number of atoms \( N = 135 \), the structures alternate, and the amorphous phase is fixed in the medium temperature range for a short time. For a cluster with the number of atoms \( N = 201 \), the amorphous phase was not observed up to the melting point.

4. Conclusions
The facts that we have established have demonstrated that for small gold nanoclusters the process of structure formation is more complex than it follows from previous experiments. Until now, it was believed that with a decrease in the cluster diameter, the ratio of the cluster surface to its volume sharply increased, which was responsible for the most significant contribution of only the surface component to the total energy. As a result, the cluster tends to acquire the maximum spherical shape; for nanoparticles of fcc metals, this leads to the appearance of a cubooctahedral shape. In small clusters of metals, such as Au, Ag, Cu, Ni, and some others, with sizes below the critical size, the appearance of other crystal modifications with icosahedral or decahedral symmetry was observed.

However, in the case of gold nanoparticles, it cannot be definitely stated that the transition from the fcc configuration occurs only in the pentagonal phase and is always accompanied by a decrease in energy. Near this phase transition, the cluster is in a very unstable state, and the presence of structural defects in nanostructures leads to fluctuations of the potential energy near the point of the polytypic-transition. In all likelihood, it should be accepted that, for gold, especially for small particle sizes, even rather small defects can play a very important role in the formation of the equilibrium structure of particles. Thus, the mechanisms responsible for the formation of the structure in small gold particles require a more comprehensive study, since in many cases the observed picture remains quite unclear.

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References
[1] Horta-Fraijo P, Cortez-Valadez M, Hurtado R B, Vargas-Ortiz R A, Perez-Rodriguez A and Flores-Acosta M 2018 Physica E 97 111
[2] Novikov S M, Popok V N, Evlyukhin A B, Hanif M, Morgen P, Fiutowski J, Beermann J, Rubahn H-G and Bozhevolnyi S I 2017 Langmuir 33 6062
[3] Wiley B J, Chen Y, McLellan J M, Xiong Y, Li Z-Y, Ginger D and Xia Y 2007 Nanolett. 7 1032
[4] Gafner Yu Ya, Goloven’ko Zh V and Gafner S L 2013 J. Exp. Theor. Phys. 116 252
[5] Rycenga M, Cobley C M, Zeng J, Li W, Moran Ch H, Zhang Q, Qin D and Xia Y 2011 Chem. Rev. 111 3669
[6] Cleri F and Rosato V 1993 Phys. Rev. B 48 22