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The role of gold atom concentration in the processes of formation of Cu-Au nanoparticles from the gas phase

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Abstract

Currently, bimetallic nanoparticles have been widely used in various fields of nanotechnology, but the main area of their application continues to be the catalysis of chemical reactions. However, it soon became clear that the catalytic activity of nanoalloys very much depends on their size, chemical composition, and shape. Therefore, the question of controlling the synthesis of bimetallic nanoparticles to obtain particles of the desired size, spatial structure, and chemical composition is very acute. In the synthesis of the Cu-Au studied by us, nanoparticles can occur either through chemical or physical methods, each of which has its own drawbacks. Though it is very difficult to achieve the required target chemical composition of nanoparticles during chemical synthesis, their size can be stabilized quite well. In turn, physical synthesis methods mainly allow you to withstand the required chemical composition, but the size of the resulting particles varies significantly. To solve this contradiction, we studied the formation of Cu-Au nanoparticles of different chemical compositions from a gaseous medium using computer Molecular Dynamics simulation to determine the effect of the concentration of gold atoms on the size and actual chemical composition of the formed bimetallic nanoparticles.

Keywords

binary nanoparticles; computer simulation; copper; gold; molecular dynamics

Introduction

Reactions of carbon-carbon compounds catalyzed by metal nanopowders (Cu, Pd, or Au), such as Ullmann or Songashira reactions lead to the formation of new carbon-carbon bonds are of primary importance in synthetic organic chemistry [1]. However, it is bimetallic nanoparticles that play a special role now in both homogeneous and heterogeneous catalysis due to the synergistic effect occurring between the atoms of different chemical elements. Moreover, it is often bimetallic nanoparticles that have the best catalytic activity when compared to their constituent monometallic components.

First of all, the catalytic properties of bimetallic nanocatalysts are determined by the influence of the atomic (quantitative) ratio of two metal components in such nanoclusters as well as their spatial distribution. For example, an ordinary nanoalloy, with core-shell or dumbbell structures, can behave differently in the same catalytic processes even despite the same percentage of chemical elements. It was thus determined that carbon-stabilized gold-based bimetallic nanoclusters (Au-Pt and Au-Pd) used as catalysts show very different selectivities in the aerobic oxidation of alcohols due to the different spatial structures observed in them [1].

The nanometer-sized Cu-Au compounds are now being studied quite actively [2-8] because of their potential application in the field of catalysis and optics. Thus, in heterogeneous catalysis, it has been shown that Cu-Au nanoalloys usually exhibit a synergistic effect in oxidative reactions and the selective oxidation of carbon monoxide (CO) to carbon dioxide at ambient temperature as well as in the selective oxidation of benzyl alcohol to benzaldehyde and in the epoxidation of propene with nitrous oxide. Moreover, in experimental and theoretical works [9], it was clearly shown that the partial substitution of copper with gold in many cases shows a change in the physicochemical properties, for example, there is an increase in catalytic activity when compared to the monometallic Au or Cu nanoparticles [3]. In addition to catalysis, Cu-Au nanoalloys are also of great interest in optics, where it was found that the doping of copper into gold nanoparticles causes

the appearance of strong surface plasmon resonances, with the energy and resonance line width depending on the percentage of copper.

A Cu-Au nanoalloy is often produced using standard chemical methods; however, usually, nanoparticles synthesized by such methods can vary greatly in size, the percentage of chemical elements in them, or structure formed during chemical reactions. Therefore, the relationship between the initial experimental conditions and the final result is far from explicit [2].

It is well known that in macroscopic samples, gold and copper mix in any proportion at high temperature. At low temperatures, Cu-Au alloys form an $L1_0$ tetragonal superstructure for the stoichiometry of CuAu and a cubic superstructure $L1_2$ for the stoichiometry of CuAu₃ or Cu₃Au [3]. However, a knowledge of the complete phase diagram of Cu-Au alloys is still missing at the nanoscale.

This fact limits the design of Cu-Au nanoparticles for various potential applications and, at the same time, contributes to their study as a model system. So in recent years, for the synthesis of Cu-Au nanosystems of various percentages, a wide range of chemical methods have been successfully implemented, the use of which led to the production of Cu-Au nanoparticles with spherical [4], pentagonal [5], rod-shaped [6, 7], and cubic [8] shapes. Nanocrystals of an alloy of gold and copper ranging from 45 to 200 nm in size with the presence of pronounced pentagonal structures were synthesized in [5] by the joint reduction of gold and copper salts. X-ray spectroscopy here confirms the formation of ordered nanosized alloys with a total gold content of 87.4%. In work [8], cubic Cu-Au nanoparticles with good control of the size of the resulting clusters were obtained through the polyol reduction method. The authors of [8] argue that in the case of the Cu₃Au and Au₃Cu compositions, they can stabilize the edge length of the synthesized nanoparticle with a value from 3.4 to 85 nm.

Although it is believed that a fairly good control of shape and sizes can be achieved through chemical methods, it is still unclear whether the chemical composition of the particles can also be finely tuned. This fact is explained by the lack of systematic studies to determine the composition of

chemically grown Cu-Au nanoparticles at the level of solitary particles to distinguish between real compositions and nominal ones obtained in a large ensemble of synthesized clusters. Ultimately, it was experimentally found in [10] that, during chemical synthesis, the preferred internal ordering and composition of the nanoparticles of the Cu-Au alloy even at room temperature is a very complex process that depends on the particle size and environmental properties.

Compared to chemical methods, physical methods offer better control over the composition of the synthesized bimetallic nanoparticles. As a typical example of such techniques, we noted the fabrication of Cu-Au bimetallic nanoparticles using ion implantation [11] or by thermal evaporation in ultrahigh vacuum [12, 13]. Also, in [14], the Cu-Au nanoalloys were deposited on amorphous carbon or substrates of magnesium oxide by laser evaporation of a bulk alloy with various stoichiometric compositions (Cu-Au, AuCu₃, and Au₃Cu). An analysis of individual clusters using electron diffraction and high-resolution transmission electron microscopy [14] showed that Cu-Au clusters form solid solutions in correspondence with their chemical composition to the composition of the vaporized material. In the case of cluster deposition on amorphous carbon, various cluster morphology was observed, such as cuboctahedral, decahedral, and more. For clusters supported on an MgO substrate, only particles with a truncated octahedral structure were observed. As can be seen from this work, a high control of the composition can be achieved with the help of physical methods but in the absence of dimensional and morphological homogeneity.

Thus, in all the experiments performed, different external and internal structures of Cu-Au nanoparticles were observed without a clear understanding of which structure, shape, and chemical composition could form as a result of one or another of the synthesis methods. Therefore, in the present work, we will concentrate on ascertaining through computer simulation the dependence of the atomic ordering of Cu-Au particles on the concentration of gold atoms in the initial gas medium.

Computer model

Synthesis from the gas phase is one of the main physical methods for producing nanopowders. This type of synthesis is a very promising method of environmentally friendly and, at the same time, economical production of nanoparticles created for a wide variety of technological purposes. Also, with this kind of synthesis, a fairly good control of the chemical composition of the resulting nanoparticles is possible. The method of gas-phase synthesis is attracting an increasing interest due to its versatility and independence from chemical precursors and surfactants. Now, after conducting a significant number of laboratory tests, this method has reached such a technological stage that its potential can already be realized for industrial use.

The real manifestation of the readiness of the gas-phase method for industrial use can be the design and development of complex multicomponent nanoparticles. The comparative advantage of multicomponent nanoparticles has two aspects: on the one hand, they provide new functional capabilities due to the combination of various chemical and physical properties characteristic of individual components [15]. On the other hand, due to the emergence of new types of bonds between the various components, multi-element nanoparticles can exhibit improved or even new properties that are usually not available for single-component nanoparticles. All these advantages make multicomponent nanoparticles especially attractive for a wide range of potential applications. As a result, in recent years, a large number of studies have been published that demonstrate a correlation between the composition, structure, and physical or chemical properties of a wide variety of multicomponent systems [10-16].

We also noted that the study of particle agglomeration processes occurring in a gaseous medium is much broader than a study on the simple production of nanoparticles, starting from the fundamental questions of the formation of gas-dust fragments in space as part of cosmological studies [17] to more prosaic, but no less important, issues in the extraction of gas-oil condensates [18-20] or chemical reactions of transformations [21].

However, because particle formation reactions occur, as a rule, in the nanosecond time interval and the sizes of the joining initial fragments lie in the nanometer range, experimental analysis of the processes occurring in this case is rather difficult. On the other hand, the theoretical description of the condensation process is also a difficult task since particles are formed under clear nonequilibrium conditions with a dependence on the physicochemical properties of the size of the nanoparticle.

In this paper, we present the results of a study by computer simulation of the process of condensation of gold and copper atoms. For modeling, we used the molecular dynamics (MD) method, which allows us to analyze the behavior of the simulated system over a wide time interval (from picoseconds to several nanoseconds) and with the required accuracy of considering small atomic groups.

Such modeling can be successful only if a sufficiently realistic potential of interatomic interaction is used. Since the simulation of the evolution of relatively large systems (several thousand atoms) in the nanosecond range by quantum mechanical methods is still very difficult, we used a simpler approach based on the modified TB-SMA tight-binding potential [22] with an interaction radius of up to the fifth coordination sphere inclusive. Based on this model, we focused on the question of determining the influence of several initial conditions on the initial stage of the synthesis of binary Cu-Au nanoparticles by condensation, in particular, the growth processes of these nanoparticles and the analysis of the chemical composition of the resulting nanoclusters.

The modeled region had a cubic shape with a face length of 1350 Bohr radii and contained a total of 91125 copper and gold atoms uniformly distributed in space. The initial temperature was set to $T_i = 1000$ K, which corresponds to the stage of transporting the atoms of the evaporated substances using the buffer gas to the synthesis chamber. The equations of atomic motion were solved based on the Verlet velocity scheme [23] with an integration step $h = 1$ femtosecond.

During nucleation and further growth of particles from the gaseous medium, the material undergoes dramatic changes in its chemical environment. Using direct inert gas pressure and its

effect on the cooling rate of the main gas mixture, that is, those parameters that are used in a real experiment, in a computer simulation is quite problematic. As a rule, even with a high density buffer (usually inert) gas, collisions between atoms of the synthesized material occur in the nanosecond range, which is the maximum possible time for MD simulation. Based on this, the analysis we represent is an attempt only at a qualitative level to understand the main features of the formation of Cu-Au nanoparticles under conditions similar to the process of real synthesis by condensation from the gas phase.

Typically, with this approach, bimetallic nanoparticles are made by evaporation of bulk targets from an alloy having the required percentage of both chemical elements. In this case, the stoichiometry of the target is reproduced quite well in the synthesized nanoparticles. You can also use another approach, in which gold and copper evaporate separately [3], which, in our opinion, makes it possible to study the processes of joining atoms of different metals into a single alloy in more detail.

In our model, all atoms were randomly distributed in a simple cubic lattice, with an average distance of 30 Bohr radii between them, in order to completely exclude their interaction at the very beginning of the simulation and to achieve a situation of random nature of placement in the synthesis zone. Inert gas atoms cooling the main simulated gas mixture were set using the Andersen thermostat [23] at a fixed temperature of 77 K, which simulated a fairly standard situation of cooling the system with liquid nitrogen. Computer program MDNTP developed by Dr. Ralf Meyer of University Duisburg (Germany), will be used for MD simulations.

Results and discussion

As is known, condensation from a gaseous medium occurs through two similar processes: homogeneous or heterogeneous nucleation. During homogeneous nucleation, small drops of the condensed phase spontaneously form in their vapor in the absence of impurities. Since very small particles of the condensed phase have low binding energies and are easily destroyed by thermal

mixing, they are unstable and disappear quickly. The formation of particles large enough to exist in equilibrium with the vapor that surrounds the particle occurs only due to statistical oscillations, and the thermodynamic and kinetic parameters of such stochastic processes are usually well modeled by the classical theory of nucleation (CNT). In heterogeneous nucleation, instead of spontaneous formation, condensate particles form on impurity particles already existing in the gas and are called condensation nuclei.

Since condensation is a kinetic process, according to the Ostwald rule, the condensate formed is not the most stable phase of the theoretically possible ones (for given values of temperature and pressure). Since the stable phase for the gas mixture at the used experimental parameters, in particular temperature, is not known in advance, nucleation from the gas medium, both into the liquid and solid phases, should be considered simultaneously. Also, any liquid droplets formed can crystallize later, and, therefore, the homogeneous nucleation of solid particles in supercooled liquid droplets should also be taken into account.

During our simulation of the process of homogeneous condensation of copper and gold atoms, the temperature in the synthesis region was determined by two factors independent of each other, such as the cooling of the Cu-Au atomic vapor by a buffer gas and the release of thermal energy converted from the binding energy of atoms. The formation and growth of nanoclusters here occur in two stages. Initially, the nucleus is formed as a result of the collision of two atoms of the atomized metal and one atom of an inert gas, which removes the excess kinetic energy. Further, the cluster can grow either in collision with other clusters or through the process of atomic condensation (clusters grow due to atoms falling on their surface) [24, 25].

Initially, the union of atoms into dimers leads to a sharp increase in kinetic energy in the system, which results in a similarly sharp increase in temperature. That is because when two separate atoms collide with the formation of a bond between them, part of the binding energy is transformed into kinetic degrees of freedom, thereby causing an increase in temperature [2]. This

effect is rather difficult to observe in direct experimental studies, but this process makes a significant contribution to the further dynamics of nanoparticle growth.

The cooling rate of atomic vapor during the simulation was not directly controlled but was determined by the collision frequency and the difference in masses of the atoms of the cooling substance and the metal atoms. In our model, the buffer gas was the gas of virtual particles created by the Andersen thermostat. Using this technique allows you to quickly remove excess energy from the system through an elastic collision of virtual particles and metal atoms. The cooling rate of gold and copper vapor chosen by us was $U = 1 \cdot 10^{10}$ K/s, and cooling was carried out to $T_f = 77$ K.

The nucleation and growth of clusters are mainly controlled by the probability of collision of atoms and cluster fragments, which is determined by the pressure inside the synthesis chamber as well as the time spent by the clusters in it. When the inert gas flow increases, it quickly removes the clusters, thereby reducing their residence time in the synthesis chamber. Therefore, the interaction between an inert gas, clusters, and metal atoms decreases, contributing to a decrease in cluster size. Conversely, an increase in pressure decreases the mean free path of atoms of a vaporized metal, thereby increasing the probability of collision between metal atoms or clusters, which, accordingly, leads to an increase in cluster size [24]. Also, in [2], using MD modeling based on bond-order potential using SiC₂ nanoparticles as an example, it was shown that spherical clusters form, for the most part, at low cooling rates while cluster agglomerates form at high cooling rates.

In our model, the inert gas flow rate was set by the rate of removal of thermal energy. But since this effect is understandable enough, it was not considered in the present work, and the simulation took place with only one cooling rate. Therefore, the main objective of the study was to determine the possible effect of the initial chemical composition of the gas phase in the synthesis chamber on the distribution in size of the final particles and the chemical composition of gold and copper atoms. To analyze the processes occurring during condensation, four different compositions were taken: CuAu, Cu₆₀Au₄₀, Cu₃Au, and Cu₉₀Au₁₀ with a fairly uniform decrease in the percentage of gold atoms in them.

Initially, to determine the degree of reliability of the obtained results, a direct comparison was made of the data of our MD simulation and the data [3] on the size distribution of Cu₃Au clusters obtained by laser deposition. An analysis of the distribution of Cu₃Au clusters on the substrate and their shape [3] indicates that agglomeration processes were suppressed in this case. The reason may be the wide spatial distribution of the evaporated primary fragments of the cluster due to the high ambient temperature, which interferes with the combination of the resulting clusters as a result of the high kinetic energy of the atoms, and, possibly, the short approach time to the substrate. As a result, in the case of Cu₃Au, spherical nanoparticles, well separated in space, were obtained with an average size distribution of 1.9 ± 0.7 nm [3], which became zero at a particle diameter of 4.0 nm. The maximum possible cluster size was 5.5 nm. Nanoparticles were single crystals with the FCC structure displayed along the [110] axis and their lattice parameters were determined from 15 particles in HRTEM images.

From these measurements, the average lattice parameter of the synthesized Cu₃Au nanoparticles was estimated to be 3.74 ± 0.01 Å. The fact that this value lies between the lattice parameters of pure gold ($a_{\text{Au}} = 4.078$ Å) and pure copper ($a_{\text{Cu}} = 3.610$ Å) is evidence that the nanoparticles deposited on amorphous carbon were precisely a Cu-Au nanoalloy [3].

In our opinion, in this case, during the deposition, the substrate was bombarded with liquid droplets of a Cu₃Au nanoalloy. Once on the substrate, they spread out over it and took a round shape, as a result of which, after crystallization, the FCC structure that was formed there. The formation of the FCC structure with such a small cluster size in all synthesized Cu₃Au nanoparticles can only be explained by the fact that, at the moment of crystallization, the clusters were not in a state of free motion and therefore could not have a spherical 3D shape corresponding to a minimum of surface energy. As was shown in our work [26], under the condition of crystallization outside the substrate, spherical particles of a Cu-Au nanoalloy of this size in most cases have a pronounced five-particle structure (icosahedral or decahedral), but the FCC structure is quite rare. Therefore, we

can conclude that the Cu_3Au clusters hit the substrate precisely in the liquid state and precisely through collision, which proves the HRTEM image of a flat 2D nanoparticle [3].

All the above considerations were needed only to determine the possible temperature of the synthesized Cu_3Au nanoparticles at the moment of their collision with the substrate. Since particles with a maximum size of up to 5.5 nm (about 7000 atoms) were found in the spatial distribution shown in [3] and a pure copper cluster melts at 1100 K [27] even with a size of 2200 atoms, the temperature of the system should be the higher melting point ($T_m = 1358$ K for copper). Therefore, a comparative analysis of the spatial distribution [3] and our MD simulation was carried out at a simulation time of $t = 5.5$ ns when the temperature of the simulated space is still high ($T = 1380$ K) but active cluster formation in the liquid state has already been observed.

As can be seen from Figure 1, at this temperature, most clusters around the size of about 250-600 atoms (diameter $D = 1.8 - 2.5$ nm) with a maximum at $D = 2.3$ nm, which practically coincides with the data [3] ($D = 1.9 \pm 0.7$ nm) indicated in the inset in Figure 1. The only difference was that we still observed quite a few single atoms ($N = 44$), dimers ($N = 219$), trimers ($N = 71$), and cluster fragments of very small size, i.e., consisting of 4-10 atoms ($N = 134$), which were simply impossible to see on HRTEM images [3]. Therefore, for the convenience of information perception, small cluster fragments with sizes up to 15 atoms were not shown in Figure 1. The value of the maximum cluster recorded during MD modeling was slightly lower (≈ 4.76 nm).

Consequently, we can conclude that with the chosen simulation parameters, the size of the system and the number of atoms in it, it was already technically possible to repeat the results of direct experiments on the synthesis of Cu-Au nanoparticles with a fairly good degree of reliability.

Next, we proceed to a detailed analysis of the results obtained during MD modeling. For a more accurate understanding of all the processes occurring during this process, we first give data on copper condensation, since gold atoms were considered as an impurity in this case. In part, we performed such an analysis in [28], where it was shown that under similar conditions of simulation synthesis at the final stage of simulation ($T = 77$ K), most of the particles obtained were in the size

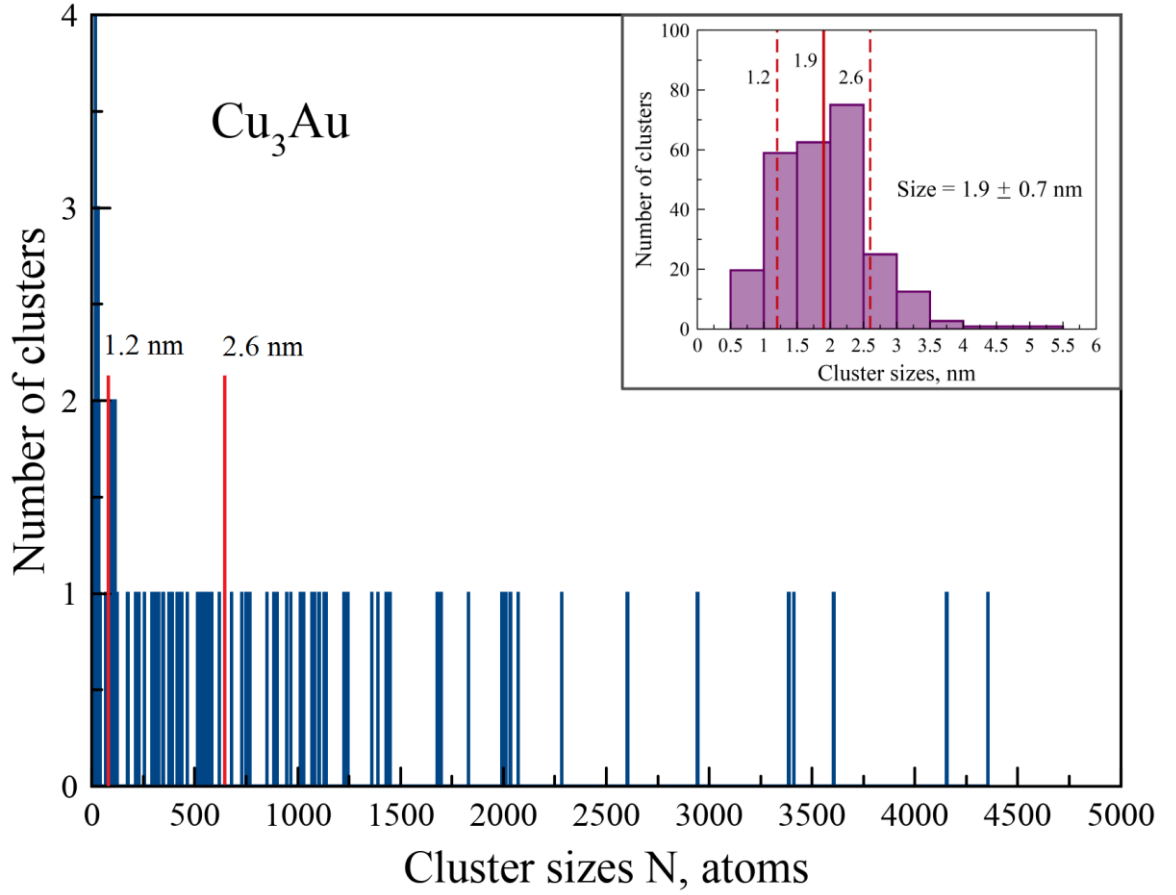


Figure 1. Size distribution of binary nanoparticles with the target composition of Cu_3Au at a temperature of $T = 1380$ K. MD simulation time $t = 5.5$ ns. The inset shows the experimental size distribution based on the data presented in [3] for Cu_3Au nanoparticles obtained by laser deposition.

region of up to 5.0 nm. In addition to this basic group, another five particles with a diameter of up to 6.5 nm were discovered, formed by agglomeration at sufficiently low temperatures. A similar pattern was observed by us at all used rates of heat energy removal, so this distribution can be considered basic, taking into account the fact that with an increase in the cooling rate, the maximum cluster size was expected to decrease in the simulated system in full accordance with experimental data [24].

As a check, we compared these results with the data on the performed MD simulation in the case of $\text{Cu}_{90}\text{Au}_{10}$. The very similar size distribution of the binary Cu-Au particles obtained by such a chemical composition of the initial gas medium is visible with the results from a simulation of the

process of synthesis of Cu nanoparticles. The main group of clusters with a diameter of up to 5.0 nm and five larger particles was also recorded [28].

However, with an increase in the percentage of gold atoms in the initial binary vapor, the situation changes significantly (Figure 2). It is noticeable that, in this case, there is a decrease in the maximum cluster size as well as in the number of clusters of a relatively large size. This means that there is a clear tendency to suppress the intensity of the agglomeration of nanoparticles with an increase in the content of gold atoms in them. Let's try to explain our results.

It is known that in the bulk state, the melting points of copper and gold are practically equal ($T_m = 1358$ K and $T_m = 1337$ K, respectively), but this is no longer true in the case of nanoscale.

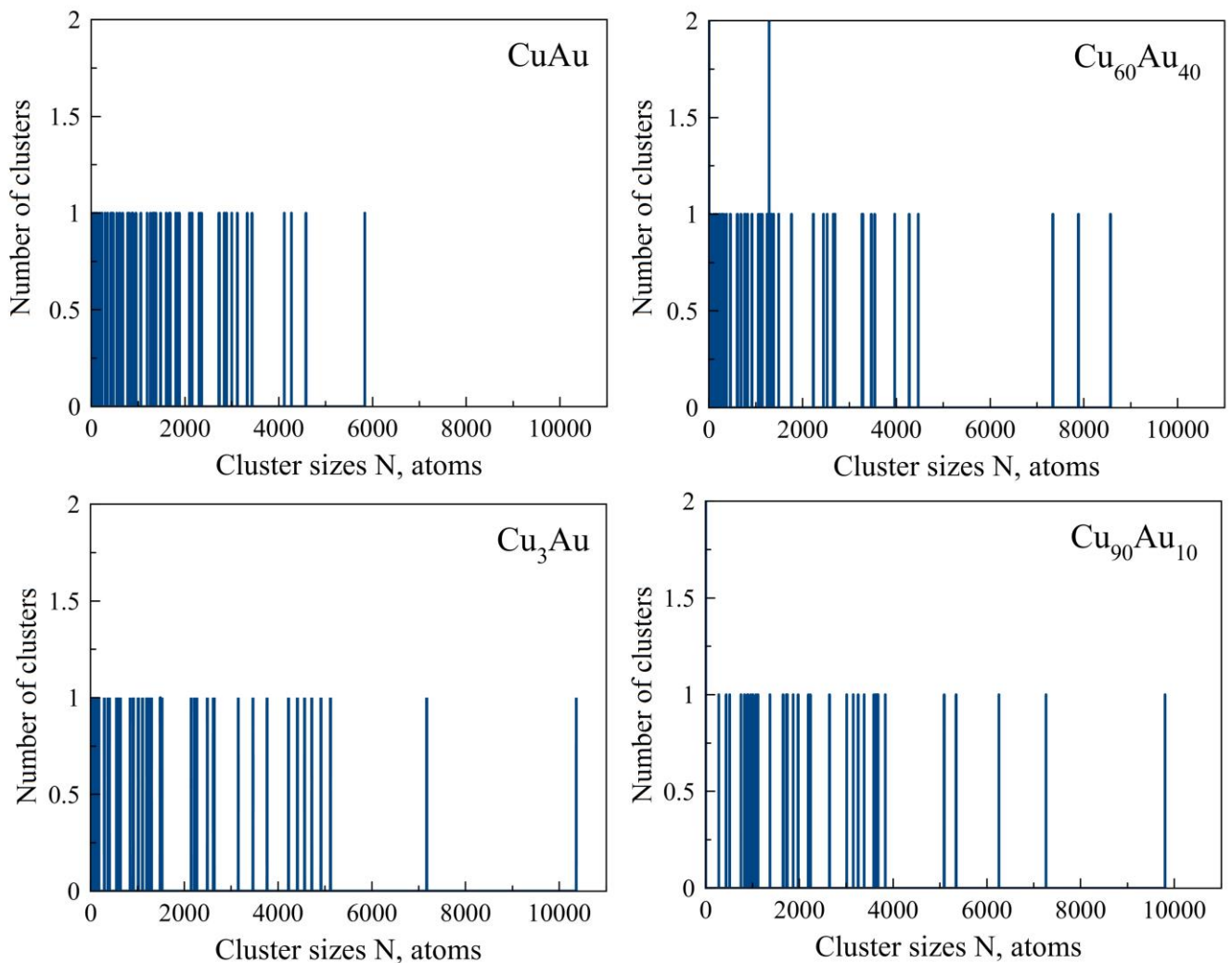


Figure 2: Distribution of binary Cu-Au nanoparticles of different chemical compositions at $T = 77$ K.

MD modeling [27, 29] showed that at an equal size ($D < 10$ nm), the melting temperature of copper nanoclusters is 30-40% higher than that of gold clusters, which signifies lower binding energy between gold atoms in such small clusters.

The effect we found in computer MD modeling based on the tight-binding potential has direct experimental confirmation. In [3], a comparative synthesis of Au_3Cu and AuCu_3 nanoparticles was performed using the chemical method and method of laser evaporation. Let us dwell on the features of the second experiment noted in [3]. In [3], the laser energy and the number of necessary laser shots for the evaporation of each metal sample were presented. After analyzing these data, one can notice that the laser energy required for the evaporation of gold is lower by about 100 mJ than what is required for copper. Also, despite the lower laser energy used, the level of evaporation was much higher for gold than for copper. As a result, the number of laser shots in a gold sample was much lower than that of a copper one.

This fact, most likely, is decisive of the formation of binary Cu-Au nanoparticles. In the initial stages of formation, due to the high temperature available in the simulated system, Cu-Au clusters are small drops of highly heated liquid. To reduce the surface energy of such liquid droplets when combined, it is often energetically advantageous to again separate them into several parts. It is clear that the lower the binding energy between the atoms, the more intensely these processes will occur, as observed in the case of a higher percentage of gold atoms in Cu-Au nanoparticles.

Besides, it was found in [9] that during the heating of Cu_3Au nanoclusters, typical changes called the “order-disorder” transition occur in its structure, leading to the decomposition of the initial $L1_2$ crystal structure with its transfer to the FCC structure with a destroyed atomic distribution in the long-range coordination spheres. In the case of bulk, copper and gold atoms are distributed arbitrarily at the sites of the face-centered cubic lattice. However, it was shown in [9] that with an increase in temperature, the initially homogeneous chemical composition of Cu-Au nanoparticles begin to change due to the displacement of Au atoms into the surface layer.

Moreover, the rate of segregation increases with temperature, which is confirmed experimentally [30].

This effect is a direct consequence of the different binding energies of gold and copper atoms, i.e., with such sizes of nanoparticles, the binding energy of copper atoms is greater than that of gold atoms. Consequently, the more copper atoms there are in a binary Cu-Au nanoparticle, the greater the probability of the preservation of primary clusters joined in a random motion in a single nanoparticle, as seen in Figure 2.

An analysis of the Au_3Cu and AuCu_3 chemical compositions performed in [3] shows that the average nanoparticle size was 4.8 ± 1.3 nm in the sample of the Au_3Cu composition, while AuCu_3 nanoparticles had an average size of 22.9 ± 1.5 nm. This experimental result confirms our conclusion that an increase in the content of gold atoms in Cu-Au nanoparticles leads to a suppression of the intensity of their agglomeration processes.

We now turn to the consideration of the effect of the initial content of gold atoms in a gaseous medium of Cu-Au composition on the chemical composition of the synthesized nanoparticles. As is known, a characteristic feature of chemical synthesis techniques is the heterogeneity of the resulting nanoparticles in composition. Thus, the experiments in [3] on the chemical preparation of nanoparticles with the target composition of Au_3Cu and AuCu_3 showed the following results. For nanoparticles with a nominal composition of Au_3Cu , a random change in the content of copper atoms was found, without any explicit size dependence. The Cu content ranged from 6 to 23 at.% in binary particle sizes up to 8 nm with an average composition of 11 ± 3 at.% Cu.

A similar analysis undertaken for nanoparticles with the target composition of AuCu_3 again showed the absence of clear relationships between their size and composition, but unexpectedly, the nanoparticles were much more enriched in gold than could be expected from the assumed nominal composition of the precursors. Here, the chemical composition was between 8 and 19 at.% Cu with an average composition of 12 ± 2 at.% Cu for nanoparticles with sizes up to 26 nm. From an

analysis of these experiments in [3], it was concluded that the copper content in the Cu-Au nanoparticles was limited to approximately 11-12 at.% Cu and, therefore, regardless of the primary composition of the precursors, the real composition of the nanoparticles is always close to Au₈Cu [3], which was experimentally observed in earlier studies [31,32] on the synthesis of Cu-Au nanosized alloys using chemical methods.

Also, in [3], the formation of small spherical particles with an average size of about 2 nm that seemed to surround a much larger nanoparticle with a nominal composition of AuCu₃ was noticed. An experimental study of the ensemble of these nuclei demonstrated that they are nanostructures of pure copper.

The obtained results clearly illustrate the fact that the spectral analysis, often used to determine the chemical composition of sufficiently large samples, can take into account not only the actual composition of Cu-Au nanoparticles but also include the composition of all very small copper particles, which leads to a reassessment of the real content copper in particles. Therefore, it is very important to measure the composition of the synthesized nanoparticles point wise to exclude the contribution of the resulting side-by-side small Cu clusters. The experimental observations indicate that it is difficult to obtain Cu-Au nanoparticles with a well-controlled composition using the chemical method used in work made in [3].

Incomplete doping of gold in Cu-Au nanoparticles can be explained based on the kinetics of reactions associated with the chemical synthesis of these nanosystems. The synthesis of the Cu-Au compound according to the method [3] includes the following reactions: $\text{Au(aq)}^{3+} + 3\text{e}^- \rightarrow \text{Au(s)}^0$ and $\text{Cu(aq)}^{2+} + 2\text{e}^- \rightarrow \text{Cu(s)}^0$. The redox potential (Au³⁺/Au) associated with the first reaction is +1.50 V [33]. For the reduction reaction of Cu ions, the corresponding potential (Cu²⁺/Cu) is +0.34 V [33]. The redox potential of the reduction of Au(III) ions is higher than that of Cu(II) ions; therefore, gold ions are more readily reduced in metallic Au(0) than copper ions in metallic Cu(0). Consequently, gold nuclei can be formed and grown before all copper ions are reduced, which explains the difficulties in the formation of an alloy of gold and copper under the conditions used

for chemical synthesis with these reagents. The copper atoms remaining after the chemical reaction then form small Cu nanoparticles observed in the experiment [3].

In the case of physical methods for producing Cu-Au nanoparticles, it still appears possible to create particles with the desired chemical composition. So, in [2], MD modeling based on bond-order potential synthesized from a gaseous medium using the example of SiC₂ nanoparticles. The formation of SiC₂ clusters was studied at different initial concentrations of atoms and the particles obtained at the final stage (simulation time 5 ns) mainly had a stoichiometric composition. In [3], the Cu-Au nanoparticles obtained by laser deposition on a graphite substrate were analyzed using TEM-EDS. From the analysis of the spectra, the average Cu content was 20 ± 1 at.% in the sample with the target composition of Au₃Cu and 73 ± 3 at.% in the sample with the target composition of AuCu₃. Moreover, due to the very small dispersion of the average lattice parameters of the Cu-Au alloy, it was concluded that a high uniformity of composition was achieved in each synthesis process.

Figure 3 shows the data on the percentage of copper atoms in all clusters with the target compositions Cu₅₀Au₅₀, Cu₆₀Au₄₀, Cu₇₅Au₂₅, and Cu₉₀Au₁₀ obtained by us in MD modeling. At first glance, the average content of copper atoms was quite close to the required values: 46.50 at.% for the target composition of 50% (deviation of 3.50%), 57.87 at.% for the target composition of 60% (deviation of 2.13%), 71.59 at.% for the target composition of 75% (deviation of 3.41%), and 89.81 at.% for the target composition of 90% (deviation of 0.19%). Besides, our results from a computer experiment on the synthesis of binary Cu-Au nanoparticles from a gaseous medium are in good agreement with the experimental work [3] in the case of Cu₃Au (73 ± 3 at.%) considered there.

On the other hand, a clear relationship between the percentage of copper atoms in the primary gas medium and the final binary clusters is still absent. But here, the following unexpected regularity is traced - the largest deviations from the target chemical composition were obtained in the cases of Cu-Au clusters with stoichiometric compositions of CuAu and Cu₃Au. In our opinion, a possible cause should be sought in the crystal structure of the synthesized nanoparticles. As already

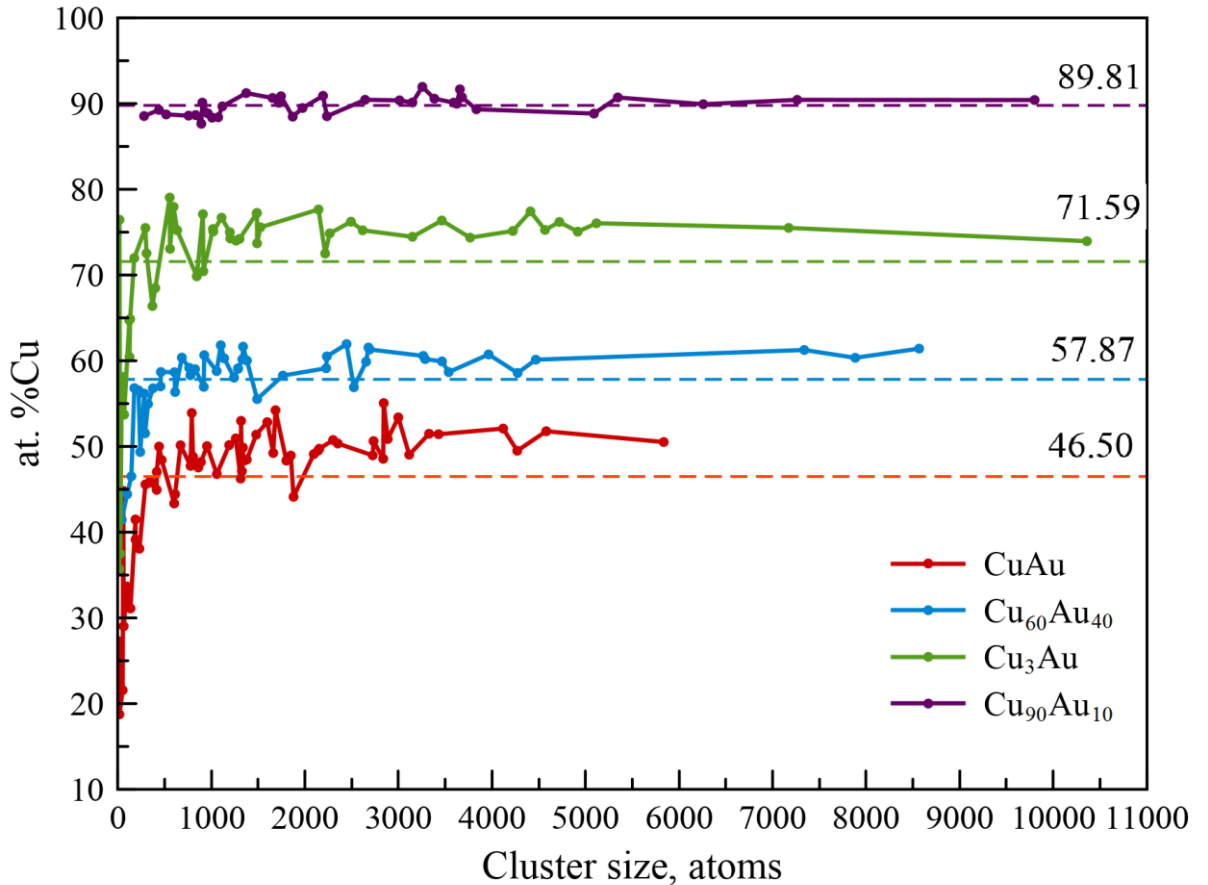


Figure 3: The percentage of copper atoms in binary Cu-Au nanoparticles with different chemical compositions of the initial gas mixture. The analysis was carried out at the final stage of the simulation ($T = 77$ K, $t = 25$ ns). Dashed lines show the average content of copper atoms in binary Cu-Au nanoparticles at various target compositions.

mentioned, at low temperatures, macroscopic Cu-Au alloys form an $L1_0$ tetragonal superstructure in CuAu stoichiometry and an $L1_2$ cubic superstructure in Cu_3Au stoichiometry. Alloys with the chemical compositions $Cu_{60}Au_{40}$ and $Cu_{90}Au_{10}$ do not possess such a structure. It is this fact that plays a key role in explaining the results.

Even though Cu-Au nanoclusters with five-particle symmetry were nevertheless chemically synthesized [5], it is possible to obtain Cu-Au nanoclusters with the usual FCC structure using these methods. However, as shown by the results of our MD simulation, the arrangement of atoms in many Cu-Au nanoparticles corresponded precisely to a five-particle symmetry (Figure 4). Thus, we

can conclude that the physical synthesis of binary Cu-Au particles contributes to the formation of icosahedral clusters in contrast to the chemical methods where these processes are difficult.

The appearance of the particle in Figure 4 indicates that its formation occurred at low temperatures. This assumption is confirmed by the fact that at such temperatures, the process of coalescence (fusion) of the clusters among themselves is almost completed due to the lack of the high kinetic energy necessary for this and the agglomeration processes, or simple particle sticking together begins to prevail, as can be seen in Figure 2. Therefore, the formation of an icosahedral structure had a different nature, different from coalescence. In [34], we suggested and verified the assumption that a lower density of a nanocompacted material in comparison with ordinary bulk samples leads to an increase in the probability of formation of an atomic structure with five-particle symmetry due to the greater diffusion mobility of atoms of a nanocompacted material. A similar effect can be observed in this case.

It is well known that in bimetallic alloys the lattice parameter varies linearly depending on the composition according to the Vegards law, varying between the parameters of pure components.

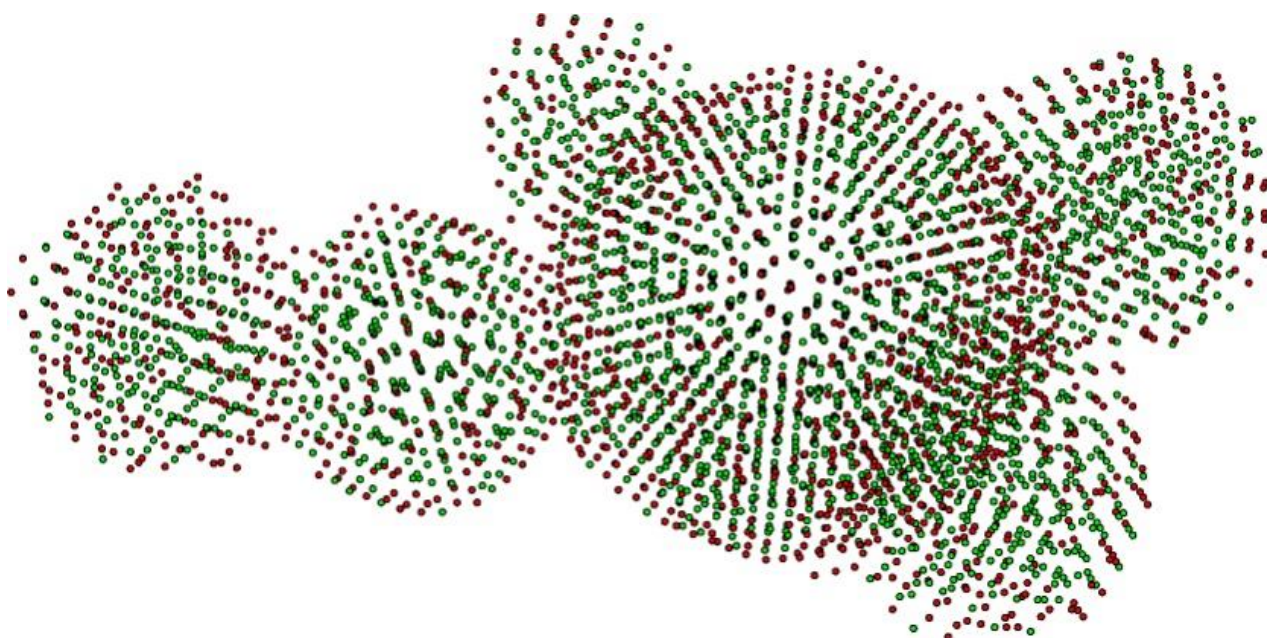


Figure 4: Image of $\text{Cu}_{60}\text{Au}_{40}$ nanoparticle obtained by MD modeling. Copper atoms are shown in green; gold atoms are shown in red.

In the framework of this experiment [3], its validity was also confirmed for the Cu-Au bimetallic nanoalloy. The sample consisting of 20 ± 1 at.% Cu had an average lattice parameter of 3.99 ± 0.01 Å, and for a sample consisting of 73 ± 3 at.% Cu, the average lattice parameter was 3.74 ± 0.01 Å. Recall that the lattice parameter of pure copper is 3.610 Å and that of pure gold is 4.078 Å. Thus, the introduction of gold atoms into a copper lattice leads to its loosening, which, in the case of nanoclusters, allows copper atoms to diffuse more easily. In the presence of sufficiently large time, and in our case, the real-time of the MD simulation was 25 ns; this circumstance can make the formation of an icosahedral structure possible [28].

However, in the case of stoichiometric compositions of CuAu and Cu₃Au, these processes are supplemented by the influence of crystallographic laws requiring the rearrangement of atoms into a superstructure L1₀ or L1₂. In addition, the processes of displacement of gold atoms to the cluster surface, which we noted in [9], also play a role. A cluster begins to form with a copper core and a gold shell (core-shell clusters). Surface atoms, which already have lower binding energy due to a decrease in their coordination number, and surface gold atoms will all the more have a very low binding energy when compared to the atoms of the copper center.

At high temperatures in the synthesis chamber, the influence of all these factors prove the fact that the discharge of the smallest droplets of gold from the surface of a binary cluster can be energetically favorable. Therefore, as can be seen from Figure 3, it was precisely for the stoichiometric compositions of CuAu and Cu₃Au that very small cluster fragments were observed, which were significantly enriched in gold atoms. Note that the copper content in such very small clusters obtained in the case of synthesis with the target composition of Cu₃Au ($\approx 18\%$) is comparable with [3] but only in comparison with the chemical production method (11–12 at.% Cu). This gives us reason to believe that a different mechanism for the formation of a binary compound was involved here when compared to clusters of larger size ($N > 400$ -500 atoms) that were formed conditionally according to the “physical” scenario. Apparently, at such small sizes, the incomplete

content of copper in Cu_3Au nanoparticles can be explained only based on the kinetics of chemical reactions.

As already mentioned, the reduction potential of Au(III) ions is greater than that of Cu(II) ions; therefore, gold ions are more readily reduced in metallic Au(0) than copper ions in metallic Cu(0), which leads to a predominant growth of gold nuclei. Such a “chemical” method for the formation of the Cu-Au compound was also observed in the case of synthesis with the target composition of $\text{Cu}_{60}\text{Au}_{40}$, although not in such an explicit form. In the synthesis with the target composition of $\text{Cu}_{90}\text{Au}_{10}$, the observed effect was completely absent, as were the small cluster fragments themselves.

Thus, according to the results of the MD simulation, several important conclusions can be drawn. First, an increase in the percentage of gold atoms in a binary vapor of the chemical composition of Cu-Au leads to a decrease in the size of the synthesized nanoparticles. Secondly, in cases of stoichiometric chemical composition of the initial gas mixture (CuAu or Cu_3Au), very small clusters with an overwhelming content of gold atoms in them are observed. With an increase in the cluster size, this effect decreased and then completely disappeared, which indicates that at the initial stage of synthesis, the gold and copper atoms are in the ionized state. Thirdly, clusters with a size of more than 400-500 atoms, regardless of the chemical composition of the initial vapor, mainly adhere to the specified target composition, and the largest deviations from it ($\approx 3.5\%$) are observed in the atomic vapor of a stoichiometric composition. In other cases, with a decrease in the percentage of gold atoms in the initial steam, there was a decrease in the deviations of the cluster chemical composition from a given target composition.

Conclusion

Undoubtedly, in recent years, the study of nanomaterials is one of the fastest growing areas of scientific knowledge. In scientific and technological fields, a special place of interest among the widest range of nanosystems studied is held by metal binary nanoparticles. Such particles usually

exhibit new chemical and physical properties, in particular, than conventional bulk materials because of the much higher surface to volume ratio.

It turned out later that even these unusual properties of metal nanoparticles can be changed and fine-tuned by adjusting their size, shape, and chemical composition. Thus, several studies on composition-dependent control of properties showed that the combination of even two metals into a single nanoparticle, i.e., the formation of a bimetallic nanoparticle or the so-called nanoalloy can lead to very important synergistic effects in areas such as catalysis of industrial reactions, optics, optoelectronics, and medical applications.

We also noted that predicting the structure of nanoparticles consisting of different chemical elements is not a trivial task because of its dependence on both size and complex energy landscape - to achieve equilibrium, bimetallic nanoparticles must optimize both the geometric shape and chemical ordering. However, nanoparticles grown by gas-phase synthesis often fall into metastable configurations due to nonequilibrium growth conditions; therefore, their configuration is determined not only by energy effects but also by kinetic effects. Using molecular dynamics (MD) methods, we tried to determine the chemical ordering of Cu-Au particles in this synthesis and to elucidate some of the mechanisms of their formation.

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