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The Completion of the Platonic Atomic Polyhedra: The Dodecahedron**

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The shape of metallic nanoparticles with diameters in the region of few nanometers is a topic of extreme importance in nanotechnology and catalysis. The atomic packing of a particle will define its surface orientation and, as a consequence, its catalytic activity, as well as many other properties.^[1–4] In addition, the shape of nanoparticles is strongly dependent on the preparation method^[5–7] and can be in a metastable or even in non-equilibrium state.^[8,9] Dramatic variations in their structure can be understood in terms of the “energy landscape” concept,^[10] whereby many structures, or isomers, are represented in a free-energy landscape by minima of similar energies and separated by relatively small energy barriers. This fact is clearly observed in the so-called quasi-melting states, where a nanoparticle changes its shape in a very dramatic way under an electron beam, an effect that has been extensively studied by several authors and is a direct proof of the energy landscape concept.^[8,9]

When metallic nanoparticles are synthesized, their three-dimensional (3D) shape or structure results in 2D projections in the transmission electron microscopy (TEM) image corresponding to different shapes such as squares, tri-

angles, hexagons, quasi-circles, and pentagons. These shapes can be associated in three dimensions to the cube, tetrahedron, cubo-octahedron, icosahedron, and decahedron, respectively,^[5] depending on the orientation of the particles on the substrate surface. When the particles are of 1–2 nm size, it is possible to observe the fivefold orientation more frequently, and this is probably due to truncations on the surface in contact with the substrate.^[11–14] Also, when bimetallic nanoparticles are synthesized, the frequency of the icosahedral particle increases, particularly for the smallest sizes.^[11,15]

Platonic solids^[16] are polyhedra formed by the faces made of a same regular polygon. In total there exist five Platonic solids, namely, the tetrahedron, cube, octahedron, dodecahedron, and icosahedron. Composed of regular triangles, there exists the tetrahedron, octahedron, and icosahedron with 4, 8, and 20 faces, respectively. The cube, with 6 faces, is the only Platonic solid composed of squares, and the dodecahedron, with 12 faces, is the only one composed of pentagons. No other solid can be constructed from regular polygons. This is the reason that ancient Greeks attributed five shapes of special significance to the five elements (fire, earth, water, air, and cosmos), believing they must constitute the basic building blocks of the universe.

Interestingly, today's modern technology has confirmed that many nanoparticles take on some Platonic-solid-related shapes. Each Platonic solid looks the same from any vertex, and intuitively they appear as good candidates for shapes found at atomic equilibrium. A very clear example is the icosahedral (I_h) particle, which only exhibits (111) facets that contribute to produce a more rounded structure. Indeed, many studies report the I_h form as the most stable particle at the size range $r \leq 20 \text{ \AA}$ for noble gases and for some metals.^[17–19] However, in Platonic-solid clusters of a particular shape, an internal strain builds up with size; at some point the surface tension is suppressed in expense of strain energy and a new shape is favored. In that limit two different faces appear and an Archimedean solid is generated. A very elegant analytical treatment of the transition between an icosahedron (Platonic) to a Wulff polyhedron (Archimedean) has been presented by Nagaev,^[20] and we refer the reader to that article for more details. This transition is size-dependent and for noble metals, $r \approx 20 \text{ \AA}$ corresponds to an optimum value for the transition.

The other Platonic solid structures such as tetrahedra, cubes, and octahedra have also been reported,^[5,21] but surprisingly dodecahedral structures have not been reported in this small size range. In this Communication we report the structure of small bimetallic nanoparticles of size $r \leq 2 \text{ nm}$. The profiles that these binary particles show in the microscope do not match with any of the known profiles in this size range. Therefore, we propose some very likely structures, based on the dodecahedron, with a close resemblance to the experimental profiles. We present some detailed models based on dodecahedral atomic growth packing, their corresponding HRTEM simulations, as well as their energetic stability through ab initio and embedded-atom method (EAM) calculations in order to discern/assign the structure for these binary AuPd nanoparticles.

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We have studied colloidal (stabilized in poly(*N*-vinyl-2-pyrrolidone) (PVP)) AuPd nanoparticles with Au to Pd atomic concentration ratios of 1:5, 1:1, and 5:1. The addition of a second metal introduces a new degree of freedom and helps the tetrahedral packing to be more efficient, as predicted by Doye and Wales^[22] and Leary and Doye.^[23] It has also been reported that polytetrahedral packing can generate exciting novel structures.^[24–26] The role of PVP as a stabilizer polymer is to avoid particle coalescence during the synthesis process. In order to produce particles of 1–2 nm size it is necessary to use a capping agent. The use of different capping agents does not alter the basic shapes reported in this paper. We have performed also a special experiment by irradiating the particles with the electron beam. Due to the size of the nanoparticles and the fact that the energy transmitted by the beam goes as $E \approx r^2$, the nanoparticles are not affected but the capping agent is removed; no change in the morphology was observed in every case.

It was possible to locate the particles at the edges of carbon films, which allowed their complete characterization since in those positions the particles are stuck to a particular structure, thus avoiding structural variations in a shallow energy landscape. In high-resolution electron microscopy (HREM) images, we could observe nanoparticles of 1–2 nm diameter, of which about 85% had a rounded shape. HREM images of such rounded particles were obtained at different orientations by tilting the samples inside the microscope and recording the images at optimum focus conditions. The shape of the particles did not match well with the shape of theoretically calculated images using an icosahedral particle model.

To identify the profiles revealed in experimental images (see Figures 2 and 3) we searched for some small and almost spherical structures by theoretical means. We considered five geometries with a central site: round-capped dodecahedron (RCD; Figure 1a); round TIC-based polyhedron, built using the regular Mackay icosahedron lattice but placing atoms in the triangular faces at interstitial positions (RTB; Figure 1b); modified round-capped dodecahedron (MRCD; Figure 1c); the triacontahedron (T_h ; Figure 1d); and the icosahedron (I_h ; Figure 1e) for comparison.

The study of the geometrical characteristics of these structures is based on the concepts of *equivalent sites* and on the *distance between sites in the cluster*. It is said that equivalent sites are those sites that keep the same distance from the central site and have similar environments. Equivalent sites are joined together in a shell, and various shells can form a layer that is considered to form onion-like clusters. On the other hand, d_{NN} is the nearest-neighbor distance, that is, the distance between nearest-neighbor atoms in a cluster.

An onion-like regular structure is formed by covering a minimum cluster (with a given geometry) with a layer formed by some shells preserving the original geometry. After that, the resulting cluster is covered by another layer, preserving the previous geometry, and so on. In contrast, another onion-like growth can be considered, where the cluster that is covered with a layer does not preserve the under-

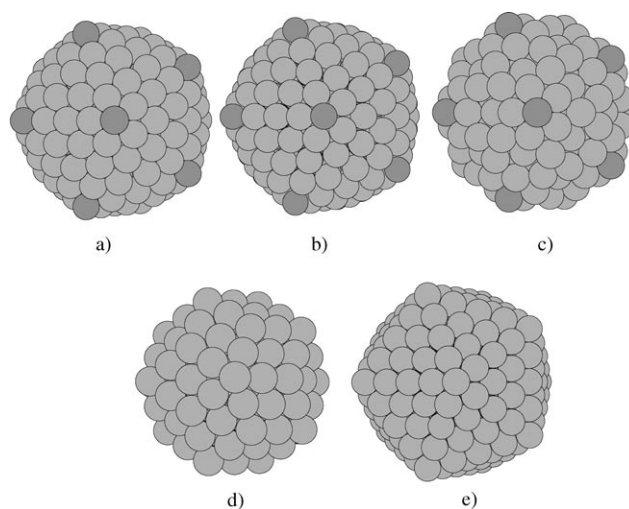


Figure 1. Five models proposed to represent the spherical particles in the experiment: a) round-capped dodecahedron (RCD) with 286 atoms; b) round TIC-based polyhedron (RTB) with 298 atoms; c) modified round-capped dodecahedron (MRCD) with 266 atoms; d) triacontahedron (T_h) with 309 atoms; e) icosahedron (I_h) with 309 atoms. Darker shades are used only to identify different atomic sites.

lying geometry. The icosahedron (I_h) and the triacontahedron (T_h) are onion-like regular structures, whereas RCD, RTB, and MRCD are onion-like structures that do not preserve the initial geometry of the clusters.

Of the five structures considered, the RTB and the I_h are polyhedra based on a 13-atom icosahedron, whereas RCD, MRCD, and T_h are polyhedra based on a 20-atom dodecahedron at the core (12 pentagonal faces formed with 20 atoms without a central atom). By adding atoms at each one of the central sites of the pentagonal faces of the 20-atom dodecahedron, we obtain the 32-atom triacontahedron (30 rhombohedral faces formed with 32 atoms).

For a systematic comparison of the calculated images of the models with the experiment, we obtain several images at different tilting angles of the particles in the microscope and compared them with the images of the model using multislice dynamical diffraction theory. From the five models tested here, it is clear that the icosahedral structures do not explain the observed profile of the particles with sizes < 2 nm. Only for larger particles ≈ 3 –5 nm were the HREM images consistent with the well-known contrast from I_h particles. A much better agreement was found with both, the RCD and the MRCD, as shown in Figure 2. Both structures have fivefold axis with a round profile in the (001) direction, and also appear with a spherical profile in the (010) direction and are somewhat faceted in the (100) direction, in agreement with the experimental data.

Moreover, two critical experiments revealed that the round-shaped particles are only consistent with the dodecahedral structures initially seen with an elongated (ellipsoidal) shape (Figure 3a). The other shapes observed in that Figure could be obtained by tilting away from the fivefold axis in the x and the y directions by 15° . Finally (in Figure 3b), starting with the fivefold axis and tilting away by

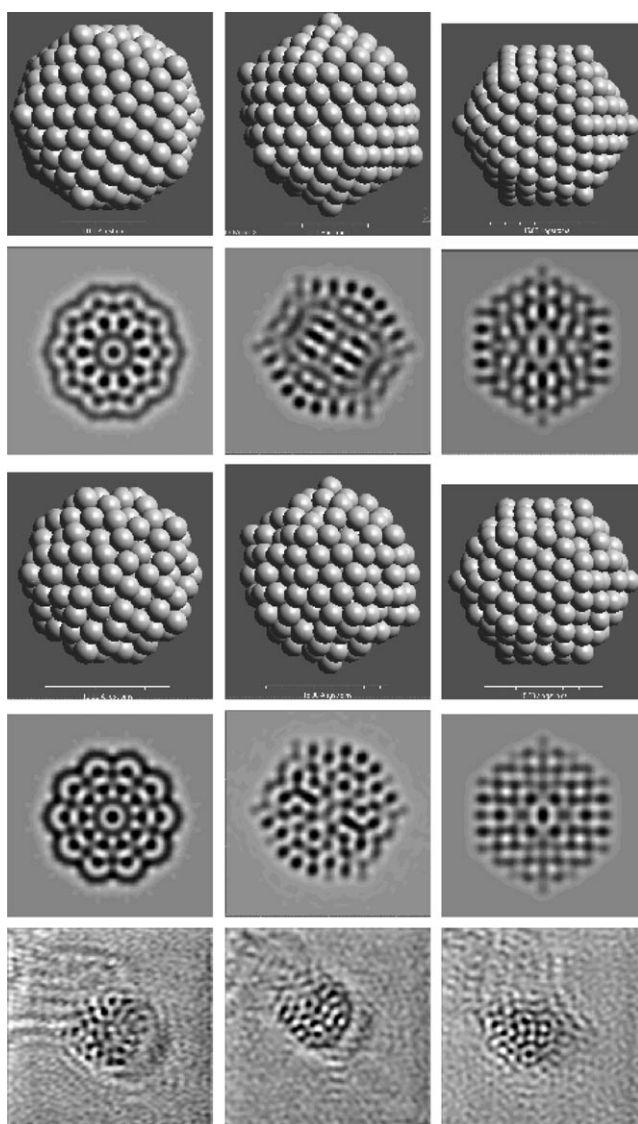


Figure 2. Different orientations (left: (001), center: (010); right: (100)) for the model of the round-capped dodecahedron (RCD) with 287 atoms, shown in a hard-ball style (first row) and as the calculated HRTEM (second row). The third and fourth rows contains the same details for the modified round-capped dodecahedron (MRCD) model with the following TEM conditions: $E=200$ kV and $C_s=0.5$ mm at the Scherzer defocus. The last row shows experimental HRTEM images.

60° in the x direction, we recover the initial fivefold axis. This result is totally inconsistent with the icosahedron structure and consistent with the proposed dodecahedron structures.

Since we selected the model structures while being guided by geometrical considerations to fit the observed structures of the images, we calculated the stability of these models by first-principles density functional theory (DFT) calculations.^[27] We use SIESTA^[28] for gold monometallic clusters with the generalized gradient approximation (GGA).^[29] Core electrons were replaced by scalar-relativistic norm-conserving pseudopotentials^[30] and valence electrons were described with a basis set of double- ξ , s , p , and d numerical

pseudo-atomic orbitals. In each case, the geometries were relaxed until the maximum forces were smaller than 0.01 eV \AA^{-1} . The calculated icosahedron (ICO) is the most stable structure ($E_{\text{ICO}}^{147} = -2.3451$ eV atom⁻¹), followed by the cuboctahedron (CO; $E_{\text{CO}}^{147} = -2.3218$ eV atom⁻¹), the RTB ($E_{\text{RTB}}^{137} = -2.3162$ eV atom⁻¹), the RCD ($E_{\text{RCD}}^{124} = -2.3036$ eV atom⁻¹), and the MRCD ($E_{\text{MRCD}}^{104} = -2.2184$ eV atom⁻¹).^[31] Additionally, this calculation was repeated using the EAM^[32] fitted for monometallic Pd and the main trends above described for DFT calculations still remain. The results are presented in Figure 4. We compare the cohesive energies but for families of icosahedra and cuboctahedra for reference, and families of the models proposed in this study. It can be seen that ICO is the most stable structure in the range up to 310 atoms; T_h is the least-stable structure. In the range between 100 and 150 atoms, the RTB competes with the stability of ICO. As a general trend, the RTB and RCD are more stable than MRCD and the TRIA structures; compared with the ICO and CO stability curves in the range between 250 and 310 atoms, RCD, RTB, and MRCD are all energetically favorable structures.

In conclusion, we have explored for the first time the structure of 1–2 nm bimetallic AuPd nanoparticles using HREM at a series of tilting angles from an electron beam. From the experiment, we observe that the addition of a second metal allows the nanoparticles to reach a quasi-spherical shape. That shape can be explained in terms of a dodecahedron, which is very close to a spherical shape along its fivefold axis. The majority of the particles in the experiment correspond to a dodecahedral shape. Also, monometallic DFT (Au) and EAM (Pd) calculations demonstrate that the structure is stable. Therefore the missing regular solid has been found. The shape for very small particles corresponds to a Platonic solid and larger particles correspond to Archimedean solids. We conclude that in the very small size range of both mono- and bimetallic nanoparticles, the complete sequence of structures that is formed corresponds to the following sequence: atoms \rightarrow clusters \rightarrow Platonic solids \rightarrow Archimedean solids, defected structures (twins, stacking faults, etc.), and finally bulk-like structures.

Experimental Section

The colloidal nanoparticles were prepared by the simultaneous reduction of the corresponding metal ions, as described elsewhere.^[26,33] An ethanol solution of palladium(II) chloride (0.033 mmol in 25 mL of ethanol) was prepared by dissolving PdCl₂ powder in ethanol while stirring for 48 h. Similarly, a solution of tetrachloroauric acid (0.033 mmol in 25 mL of water) was prepared by dissolving HAuCl₄ crystals in deionized water. For the synthesis of bimetallic clusters, a previously prepared aqueous solution of HAuCl₄ was mixed with the ethanol solution of PdCl₂ in desired volume ratios to prepare a 50-mL metal-ion mixture. Then 50 mL of a pure ethanol/water mixture containing 150 mg of PVP (K-30, $M_w = 10\,000$) was added. The proportion of water and ethanol in the final mixture was maintained at 1:1 with a total metal-ion content of 6.6×10^{-5} mol. The mixture was stirred and refluxed at about 100°C for 2 h. The colloidal sam-

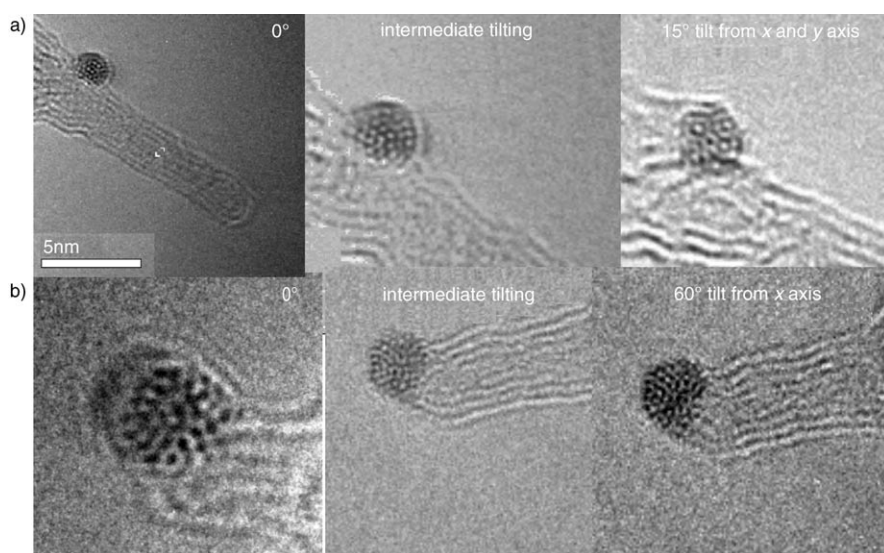


Figure 3. a) HREM images of a 1.7 nm AuPd nanoparticle (supported on an extremely thin carbon film) showing a nearly spherical shape but with a pointed end (image at the center), which is consistent with the dodecahedral structure. The second-particle contrast was obtained on tilting by 15° in x and y directions, respectively; b) HREM images of a 2 nm AuPd particle showing the typical contrast in fivefold symmetry. After tilting 60° along the x axis, the fivefold symmetry is recovered. The intermediate contrast is shown. The latter behavior of the particle is not consistent with I_h symmetry and can only be explained by a dodecahedral particle.

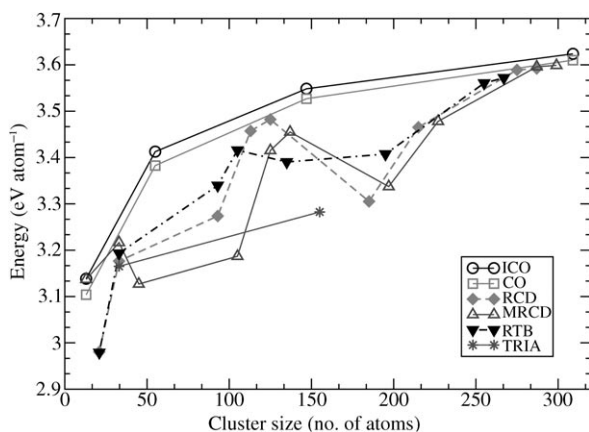


Figure 4. Energy stability EAM calculations for the five different family models in the small size range (1–2 nm) that were studied: the round-capped dodecahedron (RCD), the modified round-capped dodecahedron (MRCD), the round TIC-based polyhedron (RTB), the tricontahedron (TRIA), and the icosahedron (ICO). For comparison, we have also calculated the curve for the cubo-octahedral family (CO).

ples were dispersed on a carbon-coated TEM grid and observed by a Jeol 2010 FEG and Tecnai 20 FEG at optimum focus conditions. Images were obtained at different tilting angles using a single tilt holder. For the simulation of HRTEM images we used a software developed for nonperiodic structures such as nanoparticles.^[34]

Keywords:

atomic structure • density functional theory • modeling • nanoparticles • template synthesis

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