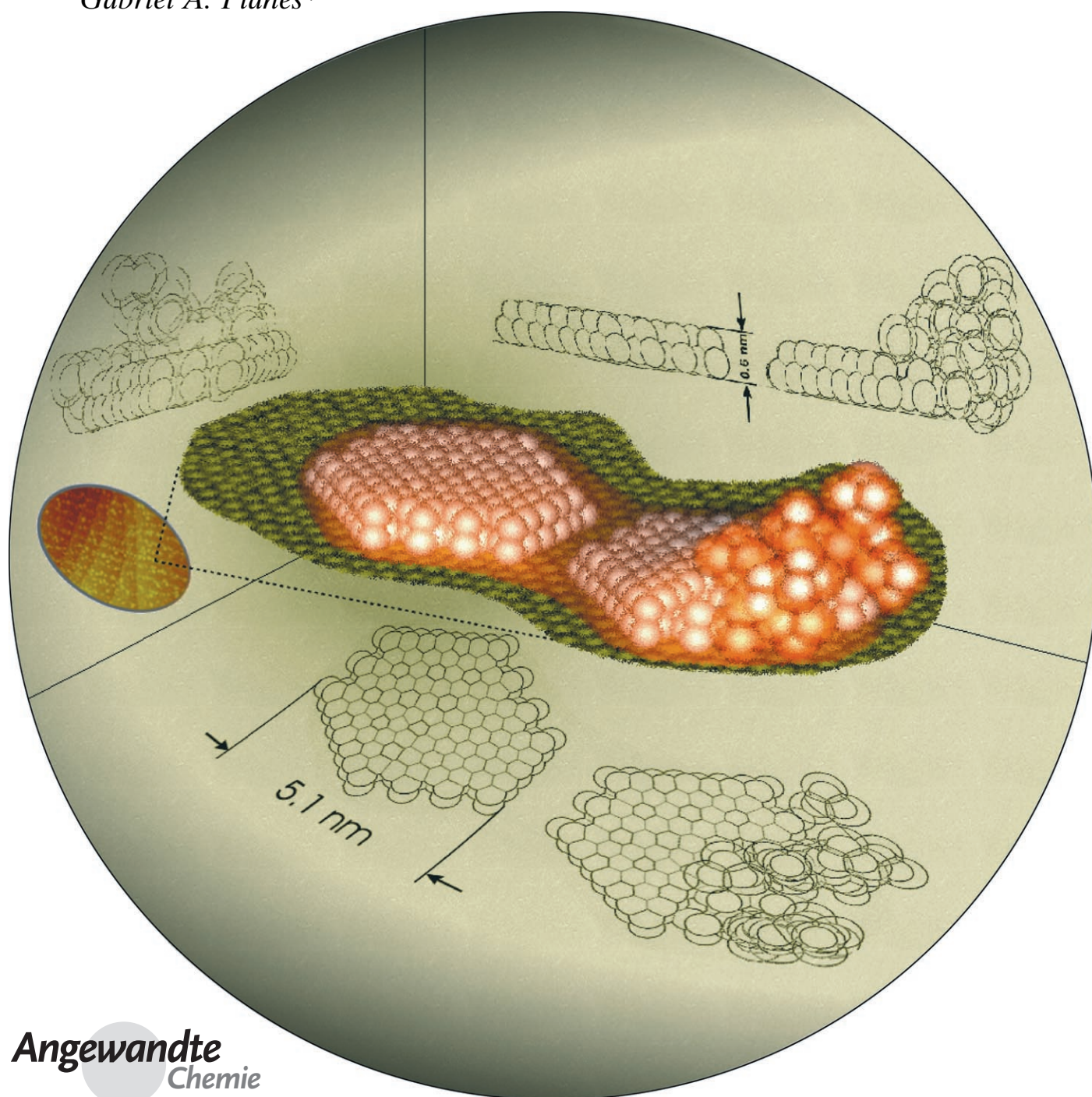# Assembly of Subnanometric 2D Pt Nanoislands in Parallel Rows onto Au(111) by Self-Organization of Pt Clusters**

Olmedo Guillén-Villafuerte, Gonzalo García, Benito Anula, Elena Pastor, María C. Blanco, Manuel A. López-Quintela, Alberto Hernández-Creus, and Gabriel A. Planes*
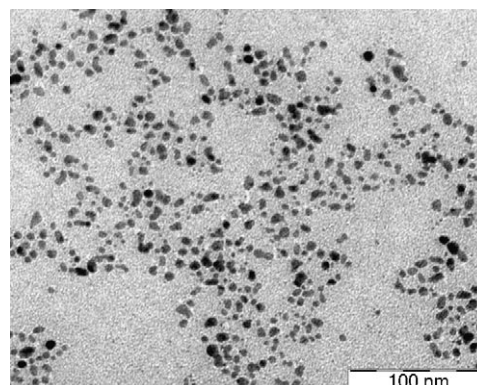
*T*he synthesis of ordered nanomaterials is one of the key points in the development of novel nanotechnologies. For this purpose, simple routes to prepare building nanoblocks and their self-assembly is of special importance in the bottom-up approach.[1] One of the most extensively studied ways to obtain nanoparticles is the microemulsion technique.[1–5] In this method, small quantities of water are added to a solution of surfactant/oil; the resulting mixture is known as a water-in-oil microemulsion. If a metal precursor is contained within the water droplets, the addition of a reducing agent can result in the formation of metal particles inside these aqueous nanoreactors.[6]

It has been recently demonstrated by in situ X-ray absorption spectroscopy studies that very small Pt clusters (diameters of less than 1 nm), with a coordination number per Pt atom as low as three, are the final product inside the micelle during the synthesis of Pt nanoparticles.[7] However, a posterior aggregation that produces larger nanoparticles occurs so frequently that it is difficult to find particles deposited on surfaces with sizes below 2–3 nm; in particular, TEM measurements in the same report showed contrasting results due to cluster aggregation during the drying process. On the other hand, metallic surfaces are frequently used to assemble stable nanometric or subnanometric structures by different techniques.[8] Nevertheless, this is usually a slow and expensive process. Herein, Pt clusters are assembled on two different hierarchical levels. The first level involves the formation of a 2D island over an Au(111) surface. At the same time, this island self-organizes to form patterns of parallel rows of several hundred of nanometers in length to give rise to a second hierarchical level.
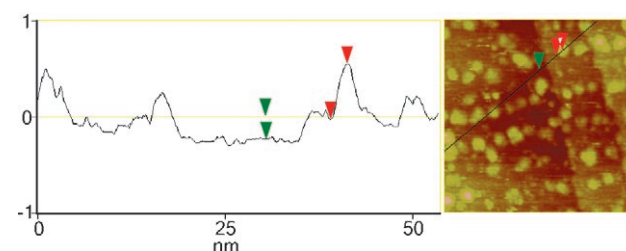
As a result of the high resolution at atomic scale, scanning tunneling microscopy (STM) was used to examine the morphology of the Pt nanoparticles deposited on the metal surface. These Pt nanoparticles were prepared by applying a modification of the method previously described by Rivadulla et al.[9] Pt clusters were formed following this synthesis using a low excess (25%) of reducing agent (microemulsion A). Transmission electron microscopy (TEM) analyses[9] were performed to measure the particle size. Thus, a few drops of

microemulsion A were deposited onto a TEM grid. Figure 1 confirms the existence of nanoparticles (dark spots) with a diameter range of 5.1 ± 0.8 nm. This value agrees with those previously reported.[9]

Figure 1. TEM image of Pt nanoparticles obtained from water-in-oil microemulsion A (using a PHILIPS CM-12 transmission electron microscope operating at 100 kV).

To obtain a more accurate idea of the spatial structure of these particles, 1 µL of microemulsion A was dropped on the Au (111) surface for STM studies. Then, the sample was washed copiously with acetone and finally with milli-Q water. Figure 2 shows a typical STM image (right) and the corre-

Figure 2. Cross-sectional analysis (left) and 52×52 nm^2 STM image (right) showing Pt nanoislands. The height of an island (red pointers) and that of a typical Au(111) monoatomic step (green pointers) are indicated for comparison.

sponding cross-section of the deposit (left). This result reveals that the gold surface is covered with circular structures. The dimensions obtained from the cross-sectional analysis show that these Pt deposits are 4–6 nm in diameter, in good agreement with data obtained from TEM. Surprisingly, the maximum in height reached by the Pt nanoparticles never exceeds 0.8 nm, with most of them around 0.6-nm high.[10] That is, the aspect ratio is more like that of flat disks than spheres. Thus, a single nanoisland is estimated to be composed of a total of about 500 Pt atoms.

In good agreement with previous findings,[7,11,12] the results described herein support the idea of a pool of isolated clusters, with each one formed from a few Pt atoms, in the aqueous medium of each droplet. Contrary to Ref. [7], in which Pt clusters probably collapse during the drying process

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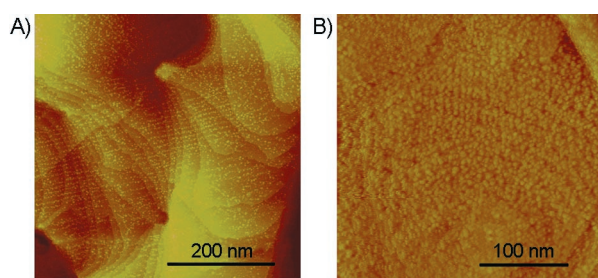Fax: (+34) 922-31-8033
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onto the carbon-coated grid, the interaction between an individual drop and Au (111) surface freezes the pool of clusters in a side-to-side configuration, thereby maximizing the Pt–Au contact surface and avoiding such agglomerations. This result then raises the question of the exact nature and structure of microemulsion-synthesized nanoparticles, and also confirms those reported in Ref. [7]. Under some experimental conditions, namely kinetics/concentration control, the formation of clusters from a few atoms is favored.

The second and more important finding is the trend of the islands to form straight, parallel lines in a long-range arrangement, as can be seen in the STM images given in Figure 3 A. Domains with rows of around 400 nm in length are

Figure 3. A) 500×500 nm² STM images of Au(111) surface showing the Pt nanoisland array. B) Surface after chemical reduction.

observed. Figure 3 A also reveals that rows of Pt islands are growing (approximately equally spaced, about 5 nm) in directions that are not those of the Au(111) steps. Moreover, the absence of Au reconstruction under such experimental conditions was verified, and the influence of the substrate as being directly responsible for this order was discarded.

To clarify the possible cause for spacing between the Pt rows, the same Pt-modified Au(111) plate was subsequently exposed to a dilute solution of aqueous hydrazine. STM analysis indicates that, after reduction, the surface is fully covered with a monolayer of Pt nanoislands of the same size as before. However, it is now difficult to appreciate the Au(111) substrate (see Figure 3 B). The same feature is achieved when reduced electrochemically (data not shown). This result points out that unreduced Pt ions, which are present initially in some micelles in microemulsion A, are filling the space between Pt rows. It has been shown that Pt ions can remain unreduced or partially reduced inside micelles.[7] These Pt ions are able to survive the hard cleaning process, probably by being stabilized inside the aqueous core of the attached micelle. A similar STM analysis was carried out with nanoparticles obtained by the microemulsion synthesis but using a higher excess of hydrazine during preparation of the particles (100% excess, microemulsion B). The corresponding image revealed that the surface is initially fully covered with such nanoislands (data not shown).

To check further if the Pt ions are really needed for the space between the rows, complementary experiments were carried out with a 1:3 w/w mixture of the microemulsion containing only Pt$_n$ clusters (microemulsion B) and a micro-

emulsion containing only perchloric acid (microemulsion C). The same results were obtained as in the case of using microemulsion A, that is, the formation of spaced Pt nanoislands rows over the Au(111) surface was observed. Therefore, it appears that these micelles have no special effect on ordering and that they are merely excluded during construction of the Pt island array and limited to form the interline gap.

The most surprising fact that we wish to comment on here is not the single rows of Pt nanoislands but the capability of the system to form them by selecting between micelles that contain Pt$_n$ clusters and those that are free of clusters. The trend of nanoparticles to connect and thereby form long nanowires has been found for other hybrid inorganic–organic structures.[13] The present system seems to obey the model of mesoscale transformation induced by crystallization, in which crystallization and surfactant reorganization are the driving force for the process.[14] In our case, the presence of surfactant molecules attached to Pt clusters avoids further crystallization while they are in a microemulsion. This idea is supported by the long-term stability of the microemulsion. At this first stage, permanent association of the micelle is impossible and all micelles in the microemulsion are isomorphs. However, during the deposition process, the micelles closely pack at the surface. Note that this theory is unable to explain the observed linear order.

The key point is that during deposition onto Au(111) (nanoisland formation), the isomorphic character of the micelles that contain clusters is significantly altered. The presence of a local crystalline order supplied by the Au(111) surface reinforces the trend of cluster aggregates to suffer an amorphous-to-crystalline transition when contacting with the surface. The formation of such an ordered array of clusters breaks the initial symmetry, and the anchored surfactant molecules are now reorganized according to the new situation. Hence, interparticle organizations, which probably involve association of surfactant molecules, unleash the mesoscale assembly. As cooperative particle interactions are energetically suitable for cluster-filled micelles only, the presence of cluster-empty micelles leads to a segregation process that produces the observed spaced linear arrays.

In summary, our results clearly show a hierarchical organization of Pt clusters at two different levels. The process starts with a pool of clusters inside the droplets of the microemulsion. On depositing the solution over the surface, two organization levels appear: The first, related to the interaction between microemulsion droplets and the surface (in this particular case Au) promotes the formation of a monolayer composed of circular arrays of those clusters. The diameters of the islands correspond approximately to the observed nanoislands by TEM, but they are only 0.6 nm in height. The next and more complex level implies the spontaneous formation of alternated lines, of hundred of nanometers long, composed of empty and cluster-filled micelles. Moreover, this atypical level of order can not be understood in classical terms, such as surface structure of the substrate or simple arrangement of undistinguishable objects, and it is a property governed (at least partially) by the nature of the micellar contents.

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Finally, our results also agree with recently reported findings,[7,11,15] thus showing that the formation of nanoparticles proceeds through special stable clusters that can be identified and, in some cases, also conveniently stabilized and isolated in appreciable amounts.[11] Owing to the key importance for future developments in the bottom-up building concept of materials science, studies devoted to understand more accurately the effect of parameters on the mechanism for patterning are specially interesting. Studies focused on clarifying the properties of Pt clusters and nanoislands, as well as the structural characterization of the clusters, are now in progress.

Experimental Section

Platinum nanoparticles were obtained by reduction of H_2PtCl_6 (8% wt; Aldrich) with hydrazine monohydrate (99.0% Fluka) using a water/oil microemulsion of water/polyethyleneglycol-dodecylether (BRIJ 30)/n-heptane.[9] The size of the microemulsion droplet is determined by the molar ratio (R) of water to surfactant.[2] In this work, R was fixed to six. The concentration of the surfactant was 16.54% w/w and that of the H_2PtCl_6 solution employed in the synthesis was 0.2 M (in the aqueous phase).

Briefly, synthesis of the nanoparticles proceeded as follows. First, two microemulsions were prepared, one of them containing hexachloroplatinic acid in the aqueous phase, and the second one containing hydrazine. Both microemulsions were left stirring during several hours until a clear homogeneous solution was obtained (this is a key point in the synthesis: shorter times promoted the appearance of a dark precipitate during synthesis). After that, they were combined under stirring to form a single microemulsion. The final solution has a clear red color. Solid deposits were never detected, even for aged microemulsions of Pt nanoparticles. UV/Vis spectra did not reveal a peak at 300 nm, which was attributed to agglomeration of the particles in Ref. [9], and did not change over time (several months) thus suggesting an especially stable cluster system.

Two different microemulsions containing Pt nanoparticles were prepared. Microemulsion A contained a low excess (25%) of the reducing agent, whereas microemulsion B contained a 100% excess of hydrazine. During the reduction process, the color of the microemulsion changed from yellow-orange to red-brown. A third microemulsion without Pt (microemulsion C), containing an aqueous solution of perchloric acid (0.2 M), was prepared for comparison purposes.

The electrochemical reduction was carried out in a thermostated three-electrode cell using a computer-controlled Heka PG 310 potentiostat/galvanostat, with 0.1 M perchloric acid as electrolyte. A potential of 0.20 V (vs RHE) was applied until complete reduction of Pt ions occurred.

STM images (constant current mode) were taken with a Nanoscope IIE (Digital Instrument, Santa Barbara, CA) using commercial and electrochemically etched Pt-Ir tips. All images were acquired in air. Typical tunneling currents and applied voltages to obtain good-quality images were 0.6–0.8 nA and 0.3–0.6 V, respectively, at scan rates ranging from 0.5 to 2 Hz. Au plates (1×0.5 cm^2; arrandee) were used as the substrate. After flame annealing, these plates consisted of micrometer-sized Au(111) preferred oriented crystals with atomically smooth terraces separated by monoatomic steps in height. The height of these steps (0.24 ± 0.02 nm) was used to calibrate the piezotube of the STM in the z direction. Several STM samples were prepared and investigated, and different sites over each modified surface were analyzed. The STM and electrochemical experiments as well as the microemulsion synthesis were carried out at room temperature. For micelle deposition over Au(111), the Au plate was maintained at 60 °C.

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