

Growth of Gold Crystals under the Presence of Bubbles Trapped under the Surface of Gold – Poly(Vinyl Alcohol) Nanocomposite Films

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Abstract- Gold crystals of various morphologies have been produced by evaporating under controlled temperatures a solution of the gold-poly (vinyl alcohol) nanocomposite having entrapped hydrogen bubbles. Three-dimensional structures as well as two-dimensional dendritic gold nanostructures are formed on the different areas of the nanocomposite films. It is thought that the multitude of morphologies may be associated to the presence of bubbles of various shapes, entrapped under the surface of the polymer films and distorted by the confinement created by the drying films. The bubbles, through the intermediary of the over layer of poly (vinyl alcohol) film, may act as templates, providing preferential sites for nucleation of gold, confined in more and more reduced volumes, as the evaporation of the solvent advances. It is shown that the degree of super saturation of the solution, mediated by temperature, is one of the parameters determining the morphology of the growing crystals. The procedure holds promise as a new approach for the preparation of shaped gold nanoparticles.

Keywords- Bubbles; Gold Crystals; Shape Control; Templating Methods; Au-PVA Nanocomposite

I. INTRODUCTION

In addition to the control of the size, the ability to manipulate the shape or morphology of inorganic nanocrystals, provides a new strategy for tuning their optical properties for different applications. There are many literature reports focused on the preparation of non-spherical faceted nanoparticles, such as nanorods, plate-like structures (nanodisks), nanoprisms, etc. However, often, non-spherical nanoparticles have been found in mixtures and their yield appears to be low [1-10]. Planar structures such as triangular, hexagonal gold and silver plates were synthesized photochemically, by seed mediated [11,12] or seedless methods using PVP as a stabilizing agent [13]. A seedless method called ‘polyol’ process, carried out in the presence of ethylene glycol was used to synthesize nanocubes [14].

Generally, it was found that, by choosing a specific capping agent, a specific morphology can be favored, or at least, the enrichment in a specific shape can be expected. Gold nanoparticles can be easily prepared by solution-phase routes that consist of the reduction of gold ions in an aqueous solution, by employing a suitable reducing agent and stabilizing the gold nanoparticles against aggregation with a capping agent. The capping agent called also “directing” agent, selectively adsorbs on specific crystal planes, inhibiting the growth on these planes and controlling the growth rates along different crystal axes [14]. The capping agent can be a polymer and the new material is called a metal-polymer nanocomposite.

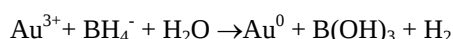
Poly (vinyl pyrrolidone) (PVP) has been used as a shape-directing polymer, for the formation of anisotropic polyhedral plates, rods and wires. The size of particles and plates, is generally, increasing with decreasing PVP/HAuCl₄ molar ratios [4, 15]. Due to the different absorption abilities of the different facets of the crystal, PVP would attach preferentially to the lowest energy [111] facet and suppress its growth rate.

Metal-polymer nanocomposite (or nanometal-polymer composite) films are hybrid materials with inorganic nanoparticles immobilized and integrated into a polymer matrix. Upon the combination of the properties of the two fundamentally different materials, novel functions can be generated, leading to a wide range of interesting applications. The polymer host provides process ability and transparency. By immobilizing the metal nanoparticles, the polymer protects them against aggregation or segregation.

Recently, we have reported on the synthesis of gold-gelatin nanocomposites by using sodium borohydride as a reducing agent [16]. We found that, under the conditions of the experiment, both, the nanocomposite solution as well as the film deposited on a glass substrate, had a large amount of entrapped hydrogen micro- and nanobubbles. The presence of bubbles in

the film engenders a number of interesting optical properties and morphological features that were thoroughly studied and future applications have been anticipated.

Surface nanobubbles are emerging as a new class of quite stable structures that may alter many aqueous interfaces and affect phenomena such as biocompatibility, adhesion between hydrophobic surfaces in water. The most direct experimental evidence for the existence of nanobubbles at the liquid-hydrophobic surface comes from Atomic Force Microscopy (AFM) images [17]. It has to be noted that, contrary to the predictions of thermodynamic calculations, the lifetime of nanobubbles is very long (hours to months), depending on surface roughness, pH, concentration of electrolytes, temperature and pressure. Nanobubbles formed spontaneously on hydrophobic substrates have been used as templates to form hollow Au nanoparticles [18] as well as nanoporous conductive polymer films [19] and core-shell nanoparticles [20]. It has been shown that, next to the tremendous scientific interest attracted by nanobubbles, they also have a great potential for applications, for example in nanofluidics, ultrasound diagnostics, gaseous drug delivery. For a comprehensive review on nanobubbles, see ref. [21,22]. Under the conditions of our experiments, nano- and microbubbles are filled with hydrogen that results from the reduction reaction:



The amount of hydrogen bubbles depends on the molar ratio of the gold precursor and the reducing agent.

Until now, different morphologies have only been produced by solution-based synthesis [23, 24]. To the best of our knowledge, there are no reports on the formation of shaped gold nanoparticles in the presence of bubbles.

In this work, we are reporting on the synthesis and morphology of gold - poly (vinyl alcohol) nanocomposite films. The points of interest here are both, the characteristics of the entrapped micro- and nanobubbles, and, the shape and size of gold nanoparticles produced, under the same conditions of synthesis at different drying temperatures. Above all, we are interested to know, whether the presence of bubbles in the drying nanocomposite film, would affect the evolution of gold nanoparticles. This study originates from our observations of the SEM images of nanocomposite films dried under different conditions. Gold nanoparticles with different shapes and sizes as well as dendrimer-like fractal structures have been observed. The assumption at the base of this work is that the gold nanoparticles in supersaturated solutions are in a more confined space during the drying process, and the bubbles under the polymer film would act as templates for the growing gold crystals.

II. EXPERIMENTAL DETAILS

A. Material and Methods

PVA was purchased from Sigma-Aldrich, and the gold salt (hydrogen tetrachloroaurate trihydrate ($\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$)) from Alfa Aesar. All chemicals were used without any further purification. UV-Visible absorption spectra were measured by using Perkin-Elmer (Model Lambda 650) spectrophotometer. The morphology/topography analyses were carried out with both Scanning Electron Microscope (SEM) (Model JEOL JSM-7600 TFE) and Atomic Force Microscopy (AFM) Model NSCRIPTOTM DPN system DS006 (Nano INK). The AFM imaging was done by using a silicon cantilever of rectangular shape with a tip radius <10 nm and stiffness of 52-75 N/ m. The resonance frequency of the cantilever in air is 200-400 kHz.

B. Synthesis of Au-PVA Nanocomposite

An aqueous PVA solution was prepared by dissolving 0.15 g of PVA in 50 ml of DI water under stirring at 80°C. After dissolution, the PVA solution is cooled down to the room temperature 0.024 g of gold chloride is dissolved separately in water and added to the freshly prepared PVA solution under stirring. Finally, a solution of sodium borohydride is added drop by drop to the mixture, before bringing the final volume to 75 ml. The solution was then stirred for 15 min at room temperature and casted on a clean glass substrate. The volume of the casted solution was kept constant (150 μL). The film was left to dry at different temperatures (3, 23, 40 and 78°C).

III. RESULTS AND DISCUSSION

A. Micro- and Nanobubbles Entrapped in the Au-PVA Film

After the addition of the sodium borohydride solution to the Au-PVA solution (in a large excess compared to the stoichiometric requirement of the reaction), the color of the solution turned immediately to red, because of the formation of gold nanoparticles. A large excess of sodium borohydride was used in order to generate more bubbles through the decomposition of the reducing agent. At the same time, a large amount of hydrogen bubbles can be seen in the solution and above it. The reduction reaction was completed after approximately 15 min. It can be seen that the spectra (Figure 1) do not change over a very long time (6 months) proving the stabilizing effect of the bubbles trapped in the solution. The position of the band (526 nm) in the spectra of the solutions indicates the presence of spherical gold nanoparticles.

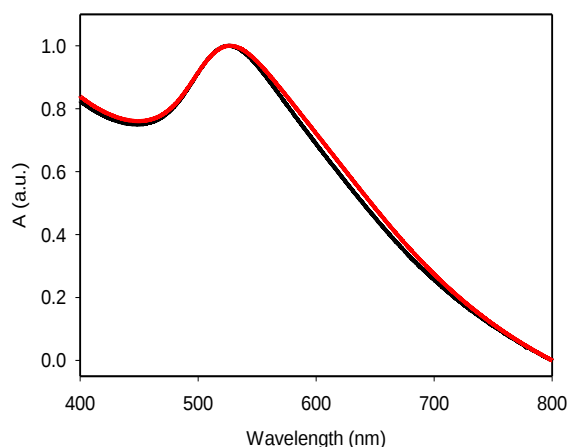


Figure 1 UV-Visible spectra of Au-PVA nanocomposite in solution.
No change of the Au-LSPR band is observed over a long period of time

The shape and the size of the bubbles entrapped in the Au-PVA film were studied for films dried at various temperatures. An attempt was made to connect them to the shape of the Au crystals grown on the surface of the film. A large part of the spherical gold nanoparticles are found entrapped in the film along with the bubbles.

Figure 2 shows the SEM images of the nanocomposite films obtained at different evaporation temperatures with a focus on the size distribution of micro- and nanobubbles. The bubbles are not spherical as it was found in the case of the Au-gelatin nanocomposite film [16]. The formation and the evolution of bubbles of different shapes are explained by the fusion and deformation of perfect spherical shapes during the drying process [25].

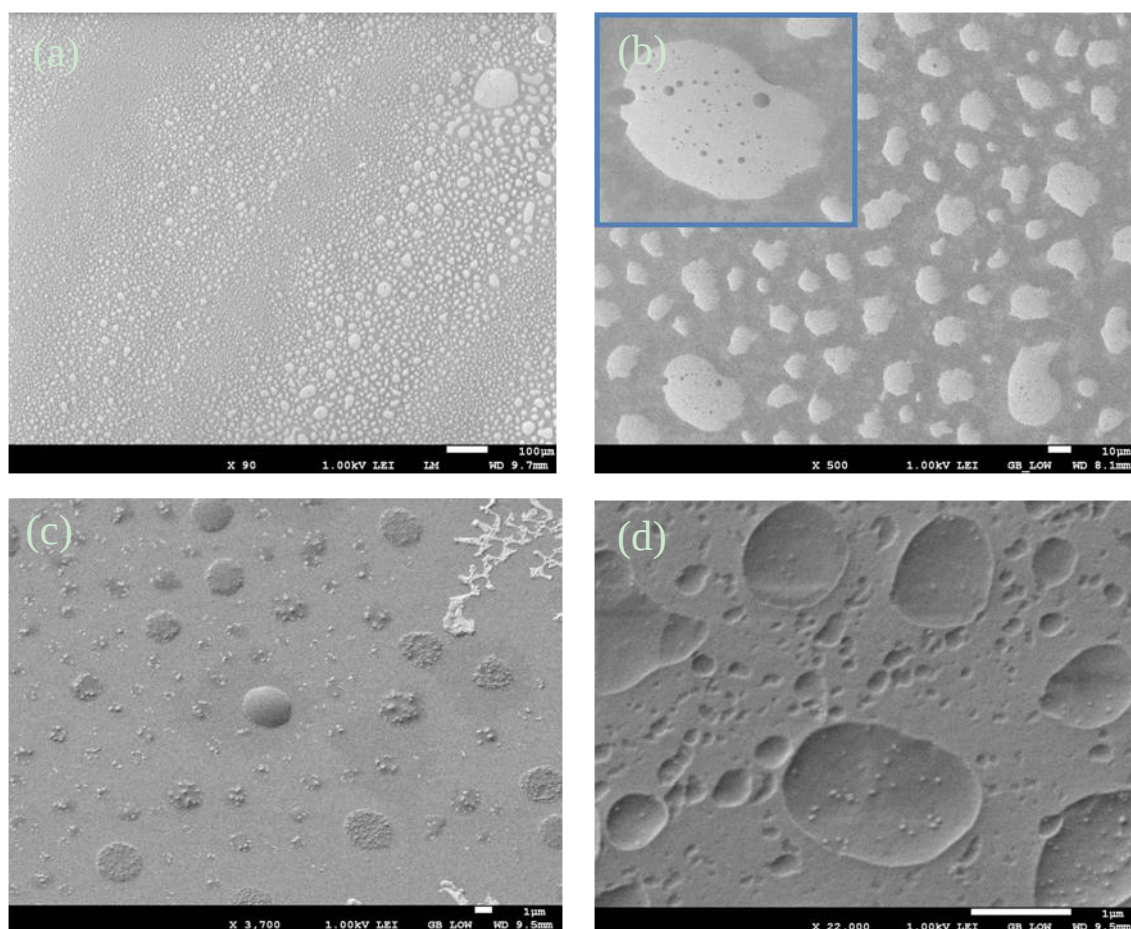


Figure 2 Size and distribution of micro- and nanobubbles in films dried at different temperatures: (a) SEM image corresponding to the separation process of bubbles during low- temperature drying (3°C , ~ 20 h), (b) SEM image corresponding to an area with a high density of polymer-coated bubbles

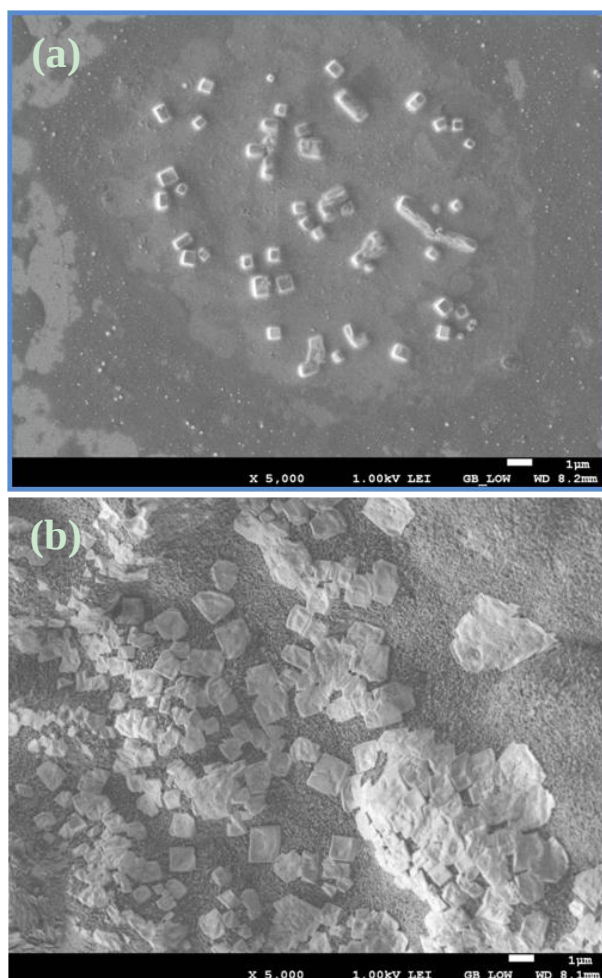
The inset shows the enlarged image of the largest bubble at the bottom (left) ; (c) SEM image of gold nanoparticles (and bubbles) formed by drying at room temperature (23°C , ~ 10 h) ; (d) SEM image of the traces left by the exploded bubbles

(solution dried at RT) ; (e) SEM image of bubbles and large Au crystals grown by drying the nanocomposite solution at around 40-45°C (~ 60 min) ; (f) SEM image of bubbles and gold nanoparticle aggregates bridging them (78°C).

It becomes clear that the rate of drying is an important factor that controls, not only the characteristics of the bubbles, but the size and shape of the gold crystals as well. It can be seen that a very slow drying allows an almost complete separation of bubbles and gold particles as shown in Figures 2a and b. Under these conditions, it appears that the bubbles themselves undergo a process of separation, resulting in the pattern shown in Figure 2a. The separation is by size, the bubbles arrange themselves in rows, and large bubble rows alternate with small bubbles in a repeating pattern. The figure also shows that a large area of the film (more than 1 mm²) is completely covered by the compactly packed bubbles. By focusing inside one of the rows of large bubbles, it can be seen that even the large bubbles are not uniform in size. The inset in Figure 2b shows the enlarged view of one of the largest bubbles and it can be seen that its surface is covered (black spots in the image) by the traces left by small bubbles that exploded during drying. When the diffusion rate becomes higher, the bubbles and nanoparticles do not segregate anymore (Figure 2 c). The bubbles, which are now smaller (1.0-2.5 µm), are surrounded by nanoparticles, accommodated by the surface of bubbles and traces (Figure 2 d). By further increasing the rate of drying, it appears that the size of the bubbles is decreasing even more (100-300 nm compared to the 5-20 µm bubbles seen in Figure 2a) while that of the crystals is increasing (Figure 2e).

B. Formation of Gold Crystals of Various Morphologies on the Drying Film

In addition to bubbles, the shape and size of gold crystals have to be considered as well. Figure 3 shows the presence of gold nanocrystals of different shapes, formed under low-temperature drying conditions. It can be seen that fairly uniform nanocubes and rectangular plates are formed on the different areas of the film (Figure 3a and b). The crystals grow at low temperature, on the areas of the film where no bubbles can be seen underneath. The size of cubes appears to be smaller than that of the plates, their side lengths range between 50 and 500 nm and they are better separated than the plates that appear self-assembled, due to the capillary force established by the evaporating water. Figure 3a shows small clusters of nanocubes, each containing three or four closely spaced cubes. The separation between the cubes, inside a cluster is in the range of 800-1000 nm. Figure 3a shows the presence of many small nanocubes, distributed around the large cubes. It has been shown that the surface free-energy of a cubic crystal decreases in the order $\gamma[110] > \gamma[100] > \gamma[111]$ and, thus, anisotropic growth will give the most stable [111] face on the top surface [14].



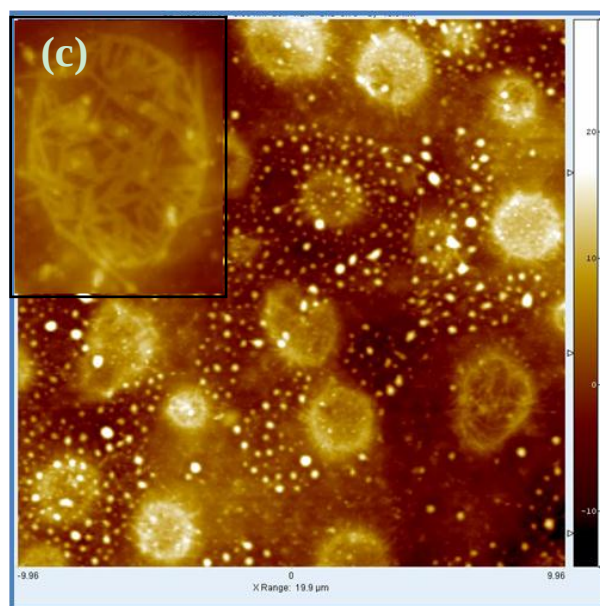


Figure 3 Crystallization of gold under low-temperature drying conditions on different areas of the film
(a) SEM image of nanocubes and nanorods ; (b) SEM image of rectangular plates ; (c) AFM image of needle-like gold structures

Au nanocubes and plates can readily assemble together due to their flat faces (26, 27). Figure 3c shows the presence of needle-like gold particles, or more precisely, gold nanowires that grow on top of the exploded bubbles. An enlarged image of the nanostructure is shown in the inset of Figure 3c. We suppose that, in this case, the particles grow on the top of ellipsoidal templates that originate from the bubbles diffused and exploded during the drying process. The traces of the exploded bubbles act as receptacles for the nanoparticles as we have shown previously [16]. The size of the ellipsoidal receptacle is approximately $2.2\ \mu\text{m}$ (short axis) and $2.7\ \mu\text{m}$ (the long axis) and they are surrounded by small bubbles underneath as seen in the figure.

Both Figure 4(a) and (b), show the presence of dendrites. In Figure 4(a), the dendritic structures are formed in an area containing a large number of bubbles of different sizes and the whole area is delimited by a row of bubbles with an almost uniform size. In Figure 4(b), two of the branched structures are formed around large hexagonal gold crystals and other leaf-like structures can be seen which lack the hexagonal center. The side length of the hexagon is found to be around $1.5\ \mu\text{m}$ and the length of the branches is around $7\text{--}8\ \mu\text{m}$. The formation of dendritic structures has, generally, been observed in a non-equilibrium growth process [28, 29]. The formation of the dendrites with a fractal nature has been explained as a continuous process of reduction-nucleation-adsorption-growth-branching-growth, where the rate of the nucleation and growth of the crystal control the formation of dendrites.

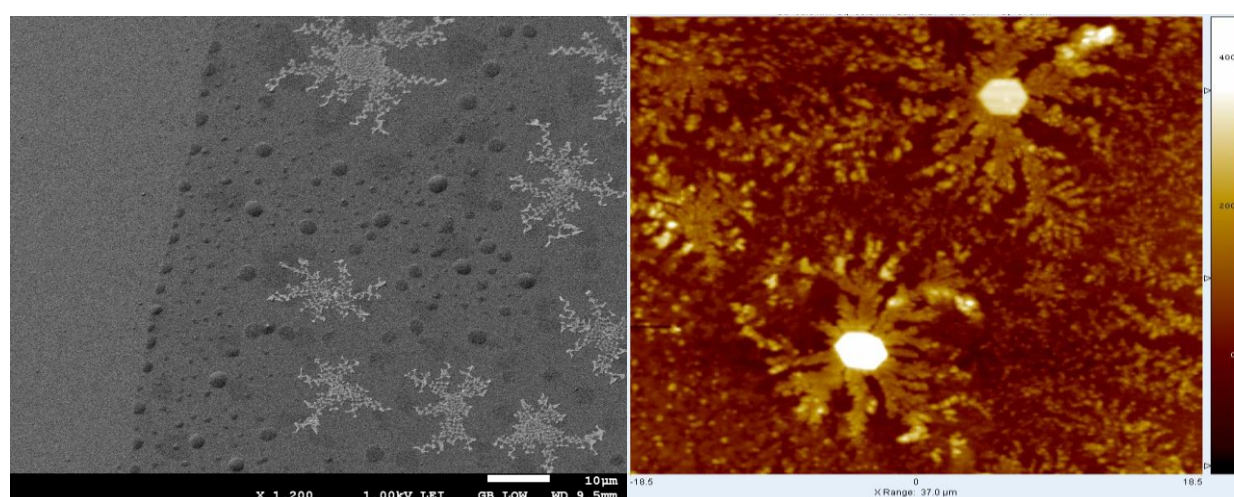


Figure 4 SEM and AFM image of gold particles and aggregates formed by drying at room temperature:
(a) dendritic structures surrounded by the traces of exploded bubbles, and (b) large hexagon in the center of dendritic structures

It can be observed visually that some of the dried films have cracks as shown in Figure 5. Figure 5 shows that, this particular film (or area), is broken, probably, due to the strain exerted during the drying process. Both the AFM image in the inset and the SEM image reveal clearly the irregular surface of the film that may act as a template for the growth of some of

the shaped gold crystals.

C. Growth of Au Crystals in the Presence of Bubbles

At room and high temperatures, the bubbles and the particles are not segregated, that is, they are found in the same area. At higher temperatures, crystals are smaller (less than a micron), due to the high rate of evaporation, and their density in some areas of the film is very high.

In order to make an efficient use of these in applications, it is necessary to be able to control and predict the outcome of a given experiment. In order to account for the formation of gold nanocrystals, it is necessary to understand rigorously the fundamental physical mechanisms by which the control of crystal nucleation and growth can be achieved. However, that crystallization in the nanoscale regime cannot be entirely predicted by using the existing theories.

In our experiments, the initial concentration of gold nanoparticles is the same ($6.2 \mu\text{g/mL}$) for all the solutions used for the deposition of films, therefore, the crystallization is controlled only by the temperature of evaporation of water during the drying process. Under low-temperature drying, at 3°C , the evaporation is slow and the critical value of supersaturation allowing nucleation, will be achieved only after several hours. During this interval, most of the bubbles have the time to diffuse through the solution and to undergo the separation and ordering process shown in Figure 2a. Nucleation, at a low rate and growing is happening on the PVA film, on an area which is almost bubble-free as shown in Figure 3a. Gold, like most of noble metals crystallize in a face-centered cubic (fcc) lattice, is in isotropic shapes. The polymer (PVA) chains would attach preferentially to the lowest energy [111] facet (cubes and rectangular plates) and suppress its growth rate. The growth of the other facets continues as long as the concentration of growth species in the ambient phase is high enough to supersaturate the particle. The needle-like structures shown in Figure 3c grow on the ellipsoidal templates provided in certain areas, by the traces left by the exploded bubbles. The supersaturation degree is increasing not only with the temperature, but along the evaporation front of the solvent as well. This change in the supersaturation degree, irrespective of the temperature, could explain the formation of particles with different morphologies on the different areas of the film. At room temperature, the evaporation is considerably faster (the film is dried after 10 hours, compared to approximately 20 hours at 3°C), and the critical value of supersaturation is reached sooner. Under these conditions, many micro- and nanobubbles will explode and their traces will become receptacles for the gold nanoparticles as shown in Figure 2d. However, in the area where the crystals grow (especially dendrites), a high concentration of bubbles can be seen. Nanoparticles are likely to aggregate in a diffusion-controlled manner when the concentration of particles is low [30]. This would mean that the area of the film showing the presence of dendritic nanostructures, is the one corresponding to the last stage of drying where it is logical to assume a low concentration of nanoparticles. At this point, it is difficult to understand, how the flower-like exquisite branched structures grow around a perfect hexagon plate. At higher temperatures, when the critical supersaturation degree is reached much faster, singly twinned structures such as triangular bipyramids are formed [31].

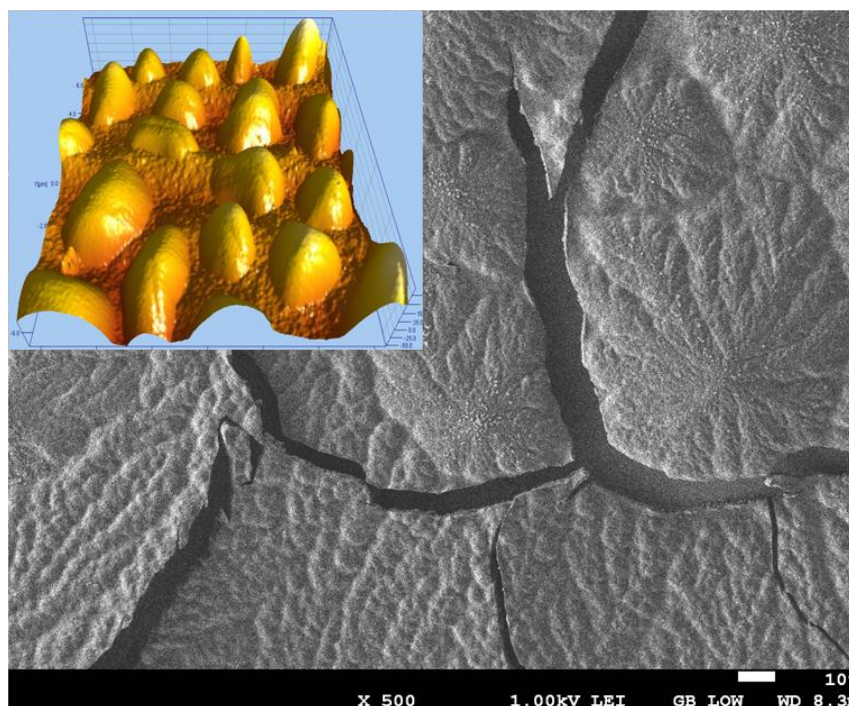


Figure 5 SEM of a large area of a film dried at 40°C . The inset shows surface bubbles of elliptical shape

It is difficult to control the formation of gold nano- and microcrystals with different morphologies. The only explanation for the presence of such a morphological diversity, is the effect the bubbles may have on the shape of the polymer films. Under

different temperatures of drying, the interaction between the bubbles and the film over them, imposes a particular shape (or shapes) to the gold crystallizing on the surface of the film. Further improvement of this method, may provide additional ways to synthesize gold crystals with multiple shapes.

IV. CONCLUSION

Gold-poly (vinyl alcohol) nanocomposites have been prepared by reducing the gold ions by using sodium borohydride as a reducing agent. The reaction takes place with the formation of gold nanoparticles and hydrogen gas which are entrapped in both the solution and dried nanocomposite films. A multitude of morphologies such as cubes, triangular, rectangular plates, and dendritic structures are found in films dried at controlled temperatures. It is found that the size of bubbles decreases with increasing temperature, while that of the gold crystals increases. As the temperature of evaporation increases, the morphologies of nanocrystals are changing from cubes to twined crystals. The formation of the different morphologies is accounted for by the templating of the bubbles entrapped underneath the polymer films. This method could be used for the templated growth of gold crystals with controlled shapes.

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