

Size and concentration controlled growth of porous gold nanofilm

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At an air/water interface, diffusion-limited aggregation (DLA) of gold nanoparticles can form porous gold thin films. This porous film roughly consists of a network of irregular nanowires. For this air–water system, external parameters like temperature are well studied, while the influence of internal parameters, e.g., the size and concentration of the nanoparticles, have not been studied in detail. Here, we report on the growth of porous gold nanofilms for different nanoparticle sizes and concentrations to get a relationship between the morphology of the films and the internal parameters. The gold nanoparticles were synthesized by reducing HAuCl₄ using sodium citrate. Transmission electron microscopy (TEM) characterization

showed a linear relation between the formed gold nanowires and the concentration of $HAuCl_4$ if the concentration of sodium citrate is unchanged. A linear dependency was also found between the wire diameter and the gold nanoparticle concentration, and between the wire diameter and volume fraction of the nanoparticles. The electrical resistance of the films was measured, showing a linear relation between resistance and the inverse of the cross-sectional area of the nanowires. This study shows the relation between the morphology and resistance of the grown porous films and the controllable internal parameters that will be useful in further exploration of this thin-film growth method.

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1 Introduction Porous materials have attracted attention during the last decade and have been applied in several fields ranging from basic chemistry [1], biological sensor studies [2] to rocket materials [3]. The higher surface area of nanoporous materials is attractive, while other tailorable properties like surface plasmon resonances are also of interest [4]. The morphology of porous nanomaterials are zero-dimensional (0D) nanoparticles [5], 1D nanowires [6], 2D and 3D nanofilms [7, 8].

We have previously reported on the growth of singlelayer porous nanofilms using evaporation induced selfassembly of gold nanoparticles at the air/water and air/water/ glass interface [4, 7], showing the formation of gold films through the coalescence of gold nanoparticles. These films have different morphology, thickness, and electrical properties, depending on the growth temperature and the level of contamination. The growth of film at the air/water interface is a diffusion-limited aggregation process (DLA) [9]. The growth of DLA clusters is determined by the growth probability [10], that is how likely it is that the next nanoparticle will be attached to the cluster. This sticking probability can be influenced by several parameters, such as temperature, size of the nanoparticles, or concentration of the nanoparticles. The temperature influences the diffusion speed and the speed of coalescence of nanoparticles. The size of the nanoparticles also influences the coalescence into larger clusters, due to a size-dependent surface energy of the nanoparticles. Another important factor in the DLA process is the concentration of the nanoparticles that determines the particle-to-particle distances [11].

The growth, which is mainly at the air/water interface at low temperature, changes its behavior on increasing the temperature and instead occurs at the air/water/glass interface, causing deposition on the beaker walls [4]. As the interface changes, it is not easy to study how the temperature influences the size of the gold wires. However, in contrast to temperature, which is a external parameter, the size and concentration of gold nanoparticles are internal parameters, and can be used to study the growth mechanism.

In this paper, we report on the growth of gold films using gold nanoparticles of different sizes, while controlling two internal parameters: the size and concentration of the nanoparticles. Using transmission electron microscopy (TEM), we found that larger particles lead to a larger



diameter of the gold wires that forms the porous gold films. The influence of concentration of gold nanoparticles showed that higher concentrations gave thicker gold nanowires. The electric resistance was measured of the films, showing a nonlinear relation between resistance and wire diameters. These results showed relations between controllable internal parameters, the concentration and gold nanoparticle size, and the resulting morphology and resistance of the grown porous films. These relations could be useful in the applications of this air/water interface method for thin-film growth.

2 Experimental

2.1 Synthesis of gold nanoparticles All the reagents were purchased from Sigma without further purification. To synthesize gold nanoparticles, 3.0 ml sodium citrate (1.0 wt%) was added into 100 ml doubly distilled water and heated to boiling, followed by adding 0.1, 0.5, 1.0, and 2 ml HAuCl₄ (1.0 wt%) to synthesize gold nanoparticle with different sizes, where the concentrations of HAuCl₄ are 25.4, 127, 254, and 508 nM. The concentrations of gold nanoparticles were calculated using the expression $C=N_{\rm T}/(NVN_{\rm A})$ [12], where *C* is the molar concentration of gold nanoparticles, *N* is the number of atoms per nanoparticle, *V* is the volume of the solution, $N_{\rm A}$ is Avogadro's number, and $N_{\rm T}$ is the total number of gold atoms.

2.2 Fabrication of gold films The fabrication of gold films was done by placing the gold nanoparticle solution in a box at a temperature of 20 ± 1 °C and humidity of $30 \pm 2\%$ for 4 days. The gold nanoparticles for studying the influence of gold nanoparticle concentration to the morphology of the grown film were synthesized by adding 1.0 ml HAuCl_4 (1.0 wt%) as described above. Three concentrations were used; the original solution, and two or three times diluted solutions.

2.3 Characterization Transmission electron microscopy samples were prepared by dipping copper grids (without carbon film) under the gold films and then removing the grids. Standard TEM imaging procedures were performed on a JEOL 2000FX. Electrical characterizations were carried out on a 1800 wafer probe station (micromanipulator) using two stainless steel wires as electrodes.

3 Results and discussion

3.1 Influence of the concentration of gold nanoparticles The growth of nanofilms at the air/water interface is a DLA process, where an important parameter is the probability that a new particle will be added to a previously formed cluster [9, 10]. This sticking probability is determined by the distance between the particles [13]. This distance, the mean-free path between collisions, $l = (\sigma n)^{-1}$,



Figure 1 TEM images of gold nanofilms grown from nondiluted (A), and two (B) and three (C) times diluted gold nanoparticle solution.



Figure 2 (online color at: www.pss-a.com) Diameter distribution of gold nanowires in gold film grown from nondiluted, and two and three times diluted gold nanoparticle solution.

where σ is the total cross-section, *n* is the concentration of particles [14]. Thus, the growth rate should be higher for higher concentrations. The concentration of the nanoparticles should thus influence the diameters of the assembled gold nanowires in our experiments.

To study the effect of gold nanoparticle concentration, we selected three concentrations, the original synthesized colloidal gold, and two and three times diluted solutions. Figure 1 shows the TEM images of the obtained gold films with a porous structure. The distributions of the diameters were obtained by measuring 40 points on the gold nanowires (two TEM images are presented at www.pss-a.com as Supporting Information to show the cylindrical structure of the nanowires, cf. Fig. S1) randomly. As shown in Fig. 2, the diameters of the gold nanowires that grow from the original colloidal gold solution were 50-100 nm (average diameter 84 nm) while the two and three times diluted solutions had narrower ranges of 50-70 and 40-60 nm, with average diameters of 61 and 54 nm. The TEM images showed that the average diameters of gold nanowires decreased with decreasing gold nanoparticle concentration, showing that the concentration influenced the morphology of the resulting gold films. Figure 3 shows a linear relationship between the diameter of the gold nanowires and the concentration gold nanoparticles, using the same data as in Fig. 2.

3.2 Influence of the size of gold nanoparticles The size of gold nanoparticles is the other important internal parameter, besides the concentration of gold nanoparticles that influence the growth of gold nanofilms at the air/water interface. We selected four different sizes of gold nanoparticles by changing the amount of HAuCl₄ added to the reaction system. Figure 4 shows the TEM images of gold films that were grown from the original gold nanoparticle sizes of 10, 14, 35, and 74 nm. The size distribution of gold nanowires in the gold films is shown in Fig. 5, showing the average diameters of about 35, 60, 87, and 160 nm at the original gold nanoparticle sizes of 10, 14, 35, and 74 nm, respectively.

By plotting the diameters of gold nanowires the sizes of original of gold nanoparticles, and the concentration of the



Figure 3 (online color at: www.pss-a.com) Relation between the diameter of gold nanowires and the concentration of gold nanoparticles. The red line is a linear fitting.



Figure 4 TEM of gold films grown at the adding $HAuCl_4$ amount of 0.1 (A), 0.5 (B), 1.0 (C), and 2.0 (D) ml.

added HAuCl₄, we found that both the diameters and sizes were linearly dependent on the amount of added HAuCl₄ (Fig. 6).

The findings here can be used to produce gold networks of nanowires with a certain diameter. If the synthesis of the gold nanoparticles is performed in the same lab, Fig. 6 should be a guide to predict the nanowire diameters. However, if the particles are off the shelf with a fixed size, then one can use Fig. 3, but only if the nanoparticle diameter is 35 nm. For other nanoparticles sizes, Fig. 7 will be useful, which shows the relation between nanowire diameter and the volume fraction of gold nanoparticles, regardless of the sizes of the



Figure 5 (online color at: www.pss-a.com) Diameter distribution of gold nanowires in gold films at the adding $HAuCl_4$ amount of 0.1 (A), 0.5 (B), 1.0 (C), and 2.0 (D) ml.





Figure 6 (online color at: www.pss-a.com) Relation between the diameter of gold nanowires in gold films, the diameter of the nano-particles, and the concentration of the added HAuCl₄.



Figure 7 (online color at: www.pss-a.com) The relation between the diameter of gold nanowires and the original volume fraction of gold nanoparticles. The volume fraction here is calculated from the gold nanoparticles with an average diameter of 10, 14, 35, 74 nm and concentration of 1.025, 1.875, 0.24, and 0.051 nM, respectively.

nanoparticles. We can explain the linear relationship through a simple expression, $V_f \Delta V = V_w = L(D^2/4)$, where V_f is the volume fraction, ΔV is the evaporated volume of gold nanoparticle solution that is the same for all the samples, $V_{\rm w}$ is the volume of gold wires, L is the total length of gold nanowires, and D is the diameter of the gold nanowires. The total volume of gold nanoparticles that coalesced equals the total volume of gold nanowires. The length (L) can be estimated from the TEM image, L = (Ap/D), where A is the total projected area, p is the percentage of gold nanowire in the area (we assume a simple rectangular geometry here). This gives the relation $V_f \Delta V = (ApD/4)$. From the TEM images, we obtained the percentage of gold nanowire projected area for the studied samples as 59, 57, 57, and 60%, which shows no significant difference in the area (A) among these samples. With A constant, there will thus be a linear relationship between the diameter of gold nanowires and the volume fraction of gold nanoparticles.

3.3 Electrical properties of the gold films The electrical properties of the obtained porous gold films are of interest in some applications. Figure 8A shows the current–



Figure 8 (online color at: www.pss-a.com) *I–V* measurements of the gold films grown at nondiluted, two and three times diluted gold nanoparticle solution (A), and the relationship between resistance and the diameter of gold nanowires in the gold films (B). (C) *I–V* measurements of the gold films at different gold nanoparticle sizes grown at the HAuCl₄ concentration of 127, 254, and 508 nM, and the relationship between resistance and the diameter of gold nanowires in the gold films (D).

voltage (I-V) curves of gold films grown at different concentrations of gold nanoparticles, with a typical ohmic linear characteristic. Figure 8B shows the resistance of gold films for different diameters of gold wires, showing a nonlinear relationship. The same behavior was found on the films that were grown for different sizes of the gold nanoparticles, as shown in Fig. 8C and D. The obtained porous gold films were networks of gold nanowires, thus the resistance of the gold films is related to the diameter of the gold nanowires, regardless of how the films were made. The data from both Fig. 8B and D are shown in Fig. 9 with a linear relation between resistance and r^{-2} , where r is the



Figure 9 (online color at: www.pss-a.com) Relationship between measured resistance of the films and r^{-2} , where *r* is the nanowire radius. The line is a linear fit to the experimental data.

523

radius of the gold nanowires. The resistance of any wire is inversely proportional to the cross-sectional area. Our porous gold films consisted of gold nanowires, which can be considered as a network circuit. The total conductance of such a network film is proportional to each conductance in the network, provided that we are well away from the percolation threshold [15], which was the case in our lowohmic films. The total resistance should thus be inversely proportional to the cross-sectional area of each nanowire in the network film.

4 Conclusions In summary, we investigated the relationship between the morphology of porous gold films and two internal parameters: (1) the concentration and (2) the size of the gold nanoparticles. We measured the diameter of the resulting gold nanowires in the porous films as a function of the internal parameters. These results showed that the diameter of gold nanowires in the grown gold films were proportional to the concentration of gold nanoparticles if the size of the particles are the same. For the size parameter, the conclusion is that the diameter of the gold nanowires is proportional to the volume fraction of the gold nanoparticles. Electrical characterization shows that the resistance of gold films was proportional to r^{-2} , where r is the radius of gold nanowires. These relations between the controllable internal parameters and the morphology and resistance of the grown porous films will be beneficial to the applications of this air/water interface method for growing porous thin films.

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