Changes in the Shape and Optical Properties of Gold Nanoparticles Contained within Alumina Membranes Due to Low-Temperature Annealing

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The shape and optical properties of Au nanoparticles electrochemically deposited within the pores of porous alumina membranes have been studied as a function of the temperature to which the Au/alumina composite was heated. Low aspect ratio Au nanoparticles begin as thin skinned particles, essentially flakes of Au within the pores, but after heat treatment at low temperatures (<400 °C), they anneal to become dense, roughly spherical particles. Visually, the color of these membranes changes from blue to red after the thermal treatment. In contrast, the nanoparticles with an aspect ratio of *ca.* 3 exhibit essentially no change in either optical absorption characteristics or particle shape after exposure to the heating program. These membranes were initially red and did not change color with heating.

Introduction

We[1−6] and others[7−10] have been studying the properties of nanoscopic metal particles deposited within the pores of porous alumina template membranes. Special interest has been devoted to the optical properties of Au nanoparticle/alumina membrane composites.[2−6] The important feature of this template approach for preparing Au nanoparticles is that both the diameter and aspect ratio (length/diameter) of the particle can be varied at will. In previous work, we demonstrated that when the diameter of the Au nanoparticle was decreased, there was a blue shift in the wavelength of maximum absorption intensity of the plasmon resonance band, λ_{max}, of the Au nanoparticle/alumina composite. Also, when the aspect ratio of the nanoparticle was decreased, a red shift in the λ_{max} was observed. These effects have been modeled using Maxwell-Garnett (MG) effective medium theory.[3,4] More recently, we have developed a *dynamic* Maxwell−Garnett (DMG) effective medium theory for the prediction of optical properties of nanometal/alumina membrane composites.[2,6] This dynamic modification of the conventional MG theory allows for more accurate modeling of the nanoparticle plasmon resonance band when the diameter of the nanoparticle is not infinitely small (i.e., when the nanoparticle diameter is approximately between 20 and 100 nm).

While investigating the thermal stability of these composite membranes, we discovered that heating the Au nanoparticle/ alumina composite to temperatures well below the Au melting point sometimes resulted in dramatic changes in the optical properties (i.e., color) of the membranes. There has been a large number of studies investigating the effects of annealing on the structural and optical characteristics of nanosized metals,[11−15] semiconductors,[16] and inert gas crystalites[17] at temperatures significantly below their bulk melting point. Most of the prior work on the metal nanostructures has been carried out on island films.[11−14] Studies of these metal island films have shown diffusion and coalescence of the metal nanoparticles resulting in changes in nanoparticle shape, size, and optical properties. Such changes can occur at extremely low temperatures ranging from 400 °C down to room temperature. However, it is very difficult, if not impossible, to follow changes in the plasmon

resonance band solely as a function of particle shape for island films because the initial nanoparticles formed at room temperature coalesce into significantly larger nanoparticles after heat treatment.

In this paper, we will show low-temperature-induced Au nanoparticle size and shape changes and the effect of these changes on the optical properties without interference from nanoparticle coalescence. This is possible with the template-synthesized Au nanoparticle composite membranes because each Au nanoparticle is confined to its own pore. The temperature-induced changes in size and shape were determined using transmission electron microscopy. The corresponding change in optical properties were investigated using UV/Visible absorption spectroscopy.

Experimental Section

Preparation of Nanoporous Alumina Template Membranes. Nanoporous aluminum oxide template membranes were prepared in-house as described previously.[2−6] Briefly, 99.999% purity aluminum was electropolished to a mirror finish in 2:3 (v/v) phosphoric/sulfuric acid solution at 70 °C for 10 min at a current density of 75 mA cm⁻². The aluminum was then anodized at a constant potential (30 V) in 15% oxalic acid at a temperature between 0 and 5 °C at a current density between 1 and 2 mA cm⁻². This process results in the growth of a porous aluminum oxide film on the surface of the aluminum. Detachment of this alumina film from the aluminum substrate is accomplished via voltage reduction and subsequent immersion of the alumina/aluminum composite in 25% phosphoric acid.[3] The approximately 25 μm thick nanoporous alumina template was then washed thoroughly with ultrapure water (obtained by passing distilled water through a Millipore water purification system) and dried at room temperature in air. These alumina template membranes contained *ca.* 45 nm diameter pores, as determined using transmission electron microscopy.[2−6]

Gold Nanoparticle Electrodeposition. The Au nanoparticle/ alumina composites were fabricated via the electrodeposition of gold within the pores of the alumina template. This procedure is described in detail elsewhere.[2,3] Briefly, Ag is first thermally evaporated onto one face of the alumina template membrane. This silver layer functions as a cathode for the constant current electrodeposition of silver "nanoposts" which extend several

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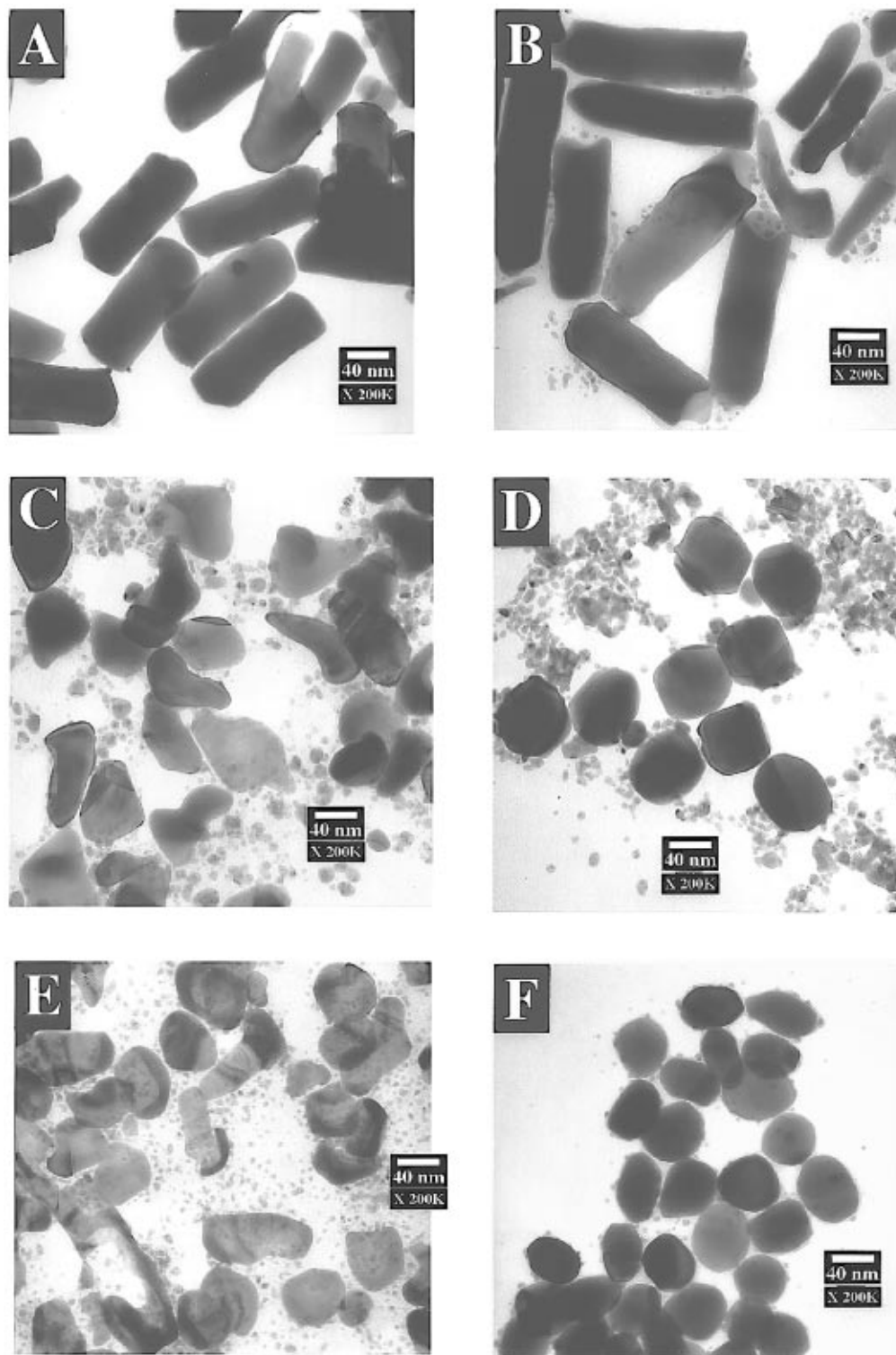
Figure 1. Transmission electron micrographs of Au nanoparticles before (A, C, E) and after heating (B, D, F) the membrane containing the particles to 400 °C. Particles having three different aspect ratios are shown. The aspect ratio was varied by varying the number of Coulombs used to electrochemically deposit the Au within the template membrane. The number of coulombs used was 0.40 C (A, B), 0.20 C (C, D) and 0.08 C (E, F).

microns into the pores of the template. Gold nanoparticles are subsequently electrodeposited on top of these silver posts using a commercial Au plating solution (Orotemp 24, Technic, Inc.). The silver posts ensure that the gold particles are formed well into the template pores where pore diameter is more uniform. The silver is then dissolved away by immersion in concentrated nitric acid, leaving an Au nanoparticle within each pore of the alumina membrane.

The aspect ratio of the Au nanoparticles is determined by the number of coulombs of charge used during the electrodepo-

sition.[2,6] In this work, Au nanoparticles were prepared by electrodepositing 0.40, 0.20, and 0.08 Coulombs of Au over a geometrical template surface area of 3.54 cm². An EG&G Princeton Applied Research Model 173 potentiostat equipped with a PAR Model 176 digital coulometer was used for the electrodeposition.

Spectral Characterization. UV/visible absorption spectra were acquired using a Hitachi U-3501 spectrophotometer. The template membranes were oriented perpendicular to the incident beam such that the diameter of the Au nanoparticles was aligned

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parallel with the electric field vector of the light. To study the effects of temperature on the optical properties of the Au/alumina composites, the membranes were heated to the desired temperature, held at this temperature for 1 h, and then cooled to room temperature. An absorption spectrum of each Au nanoparticle/alumina composite was measured before and after each heat treatment. The heating temperatures used ranged from 40 to 400 °C.

Transmission Electron Microscopy (TEM). The dimensions of the Au nanoparticles were characterized using a JEOL 2000 transmission electron microscope. This was accomplished by dissolving the alumina template and collecting the Au nanoparticles on a carbon-coated copper TEM grid (Ted Pella, Inc.). This procedure involved placing a section of composite on the grid in a 1 mL plastic container. The container was filled with 1 M NaOH. After a 2 h immersion period, the NaOH was removed carefully so as not to disturb the gold particles. The container was then refilled with ultrapure water and drained again. After two additional rinse cycles, the grid was dried in air at room temperature and imaged with the TEM.

Results and Discussion

All of the Au nanoparticles investigated here were obtained by electrodepositing Au within a nanoporous alumina membrane with 45 nm diameter pores. Au nanoparticles with varying aspect ratios were obtained by electroplating three different amounts of Au within the pores of the template membrane. TEM images of these Au nanoparticles before and after heating the Au/alumina composite to a temperature of 400 °C are shown in Figure 1.

Figure 1A,B shows images of the Au nanoparticles obtained after passing the largest amount of charge (0.40 C) during the Au electrodeposition. As would be expected, these nanoparticles have the highest aspect ratio (*ca.* 3) of any of the nanoparticles investigated in this study. A comparison of the images in parts A and B of Figures 1A and 1B shows that neither the size nor the shape of these Au nanoparticles changes upon heating to 400 °C. Electron diffraction patterns before and after heating showed no discernible changes, indicating that there are no major changes in crystallinity of these Au nanoparticles.

This lack of temperature-induced change in the size and shape of these aspect ratio = 3 Au nanoparticles is reflected in the optical absorption spectra. Membranes containing these Au nanoparticles were heated at various temperatures up to 400 °C, and the optical absorption spectra were obtained after each heat treatment, Figure 2. Note that the position of the plasma resonance band does not change with temperature. This is further illustrated in Figure 3 (curve A), which shows a plot of the λ_{max} for the plasmon resonance band versus the temperature at which the membrane was heated. These data clearly show that the λ_{max} is insensitive to applied temperature for the membranes containing these highest aspect ratio particles.

The Au nanoparticles in Figure 1C,D were obtained by depositing 0.20 C of Au within the pores of the alumina membrane. Looking first at the TEM image obtained after heating to 400 °C, Figure 1D, these Au nanoparticles have, as expected, a lower aspect ratio than the 0.40 C nanoparticles discussed previously. More interesting, however, there is now a change in the shape of the Au nanoparticles before versus after heating to 400 °C. After heating, the Au nanoparticles have a uniform, almost spherical shape with the expected *ca.* 45 nm diameter. In contrast, before heating, the Au nanoparticles have very irregular shapes and sizes, Figure 1C. Some of the particles appear like thin skins, as if some of the Au deposited preferentially along the pore wall. This skin-like
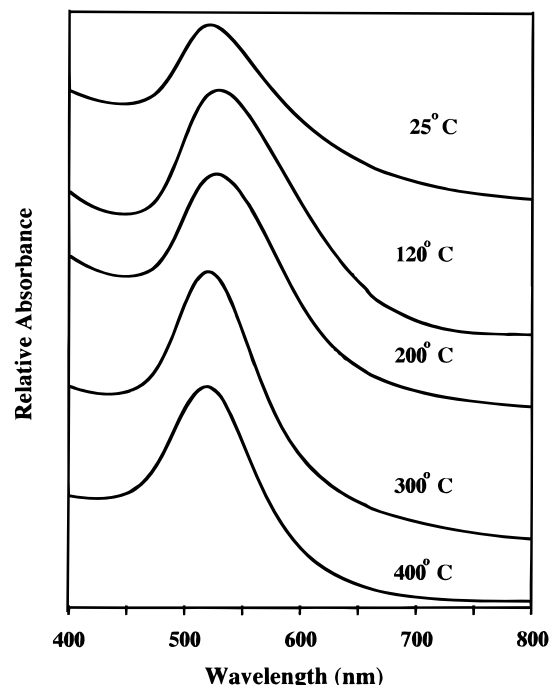
Figure 2. Absorption spectra obtained before and after heating the 0.40 C Au nanoparticle/alumina composite. The temperatures used are as indicated.
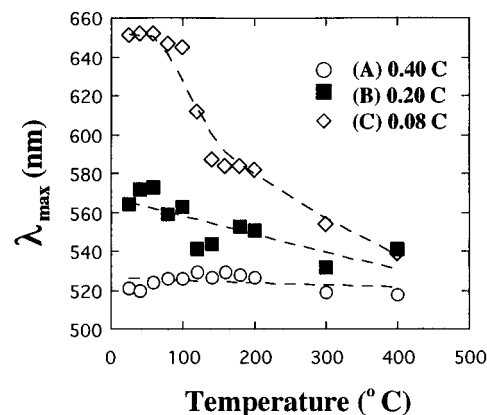

Figure 3. Plot of λ_{max} for the plasmon resonance band of the three different Au/alumina composites versus the temperature at which the Au nanoparticle/alumina composite was heated: (A) 0.40 C, (B) 0.20 C, and (C) 0.08 C.

interpretation is reinforced by the electron transparency of some of the particles in this image. However, after heating, the nanoparticles are electron opaque.

This change in shape of the 0.20 C Au nanoparticles upon heating is reflected in the optical absorption spectra, Figure 4. Note that in contrast to the higher aspect ratio particles, there is now a small blue shift in the λ_{max} of the plasmon band with increasing temperature. This is illustrated in Figure 3 (curve B), which shows a plot of λ_{max} for the plasmon resonance band versus temperature at which the membrane was heated. This change in λ_{max} is more easily seen with the eye as the membranes go from blue before heating to pink after heating.

In addition to the shift in λ_{max} for the plasmon resonance band, the band also becomes significantly more narrow after heating, Figure 4. This narrowing reflects the uniformity in nanoparticle size and shape after thermal treatment, as indicated in the TEM images. The unheated 0.20 C particles begin as an ensemble of irregular sizes, shapes, and aspect ratios, and as a result, the plasmon absorption is very broad. However, after
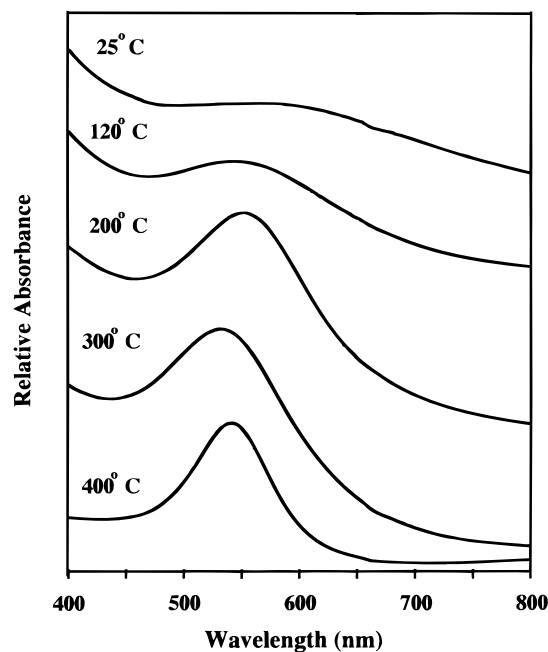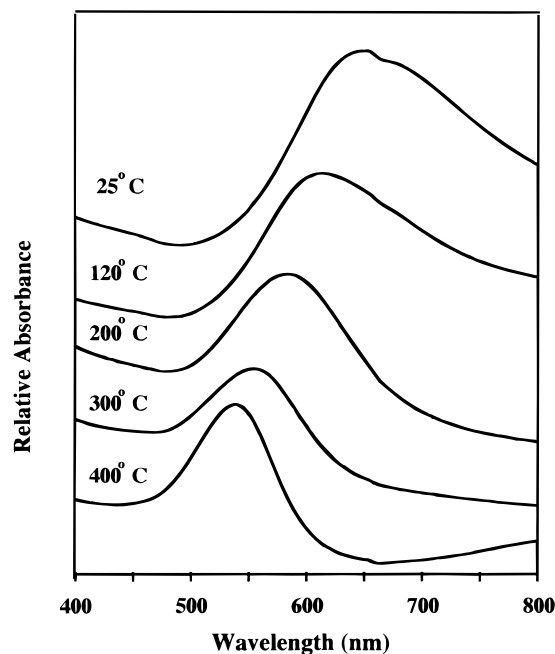
Figure 4. Absorption spectra obtained before and after heating the 0.20 C Au nanoparticle/alumina composite. The temperatures used are as indicated.

Figure 5. Absorption spectra obtained before and after heating the 0.08 C Au nanoparticle/alumina composite. The temperatures used are as indicated.

thermal treatment, the particles adopt a uniform size and shape, and the plasmon band narrows.

Finally, the Au nanoparticles in Figure 1E,F were obtained from membranes that were plated with a much lower amount of Au, 0.08 C. Even more evident than with the 0.20 C particles, the unheated form of these 0.08 C particles is irregularly shaped and is apparently quite thin, as indicated by the electron transparency of the particles, Figure 1E. After heating, these particles appear to have a uniform, mostly spherical shape with a diameter of *ca.* 35 nm, Figure 1F. With less Au electrodeposited within the pores, the final annealed nanoparticles are definitely smaller than the previously discussed particles.

This change in shape of the 0.08 C Au nanoparticles upon heating is reflected in the optical absorption spectra, Figure 5. There is now a dramatic blue shift in the position of the plasmon band with increasing temperature. This is clearly illustrated in the plot of λ_{max} versus membrane annealing temperature, Figure 3 (curve C). Once again, the plasmon resonance band of the 0.08 C particles becomes significantly more narrow after heating, Figure 5. As before, this narrowing reflects the uniformity in nanoparticle size and shape after thermal treatment, as indicated in the TEM images.

As previously mentioned, studies of metal island films have shown diffusion and coalescence of metal nanoparticles resulting in changes in nanoparticle shape, size, and optical properties at low temperatures ranging from 400 °C down to room temperature.[11−14] In addition, it has been well established that the activation energy for diffusion of Au surface atoms (versus bulk Au) is sufficiently low that these Au atoms have high mobilities at temperatures well below the bulk melting point.[18−21] Such surface diffusion processes are most likely responsible for the shape changes of the low aspect ratio Au nanoparticles investigated here. It is of interest to note, however, that the aspect ratio = 3 nanoparticles did not change shape upon heating. This is undoubtedly due to the lower surface area of these particles relative to the flake-like particles obtained from the 0.20 and 0.08 C depositions. Furthermore, since these aspect ratio = 3 nanoparticles fill the entire diameter of the pore, there is no free space within the pore for rearrangement of the particle shape.

With respect to the changes in the optical properties of these membranes, we have recently reported on the optical properties of Au nanoparticles with aspect ratios less than unity (i.e., oblate or pancake-like particles).[6] We found that as the aspect ratio went from below unity (pancake-like) to unity (sphere-like), there was a blue shift in the λ_{max}. These experimental observations were found to be in agreement with the predictions made via the DMG effective medium theory.[6] These results provide an explanation for the spectral changes observed in this report for the 0.20 and 0.08 C Au nanoparticles. As shown in the TEM images, the as-deposited particles are thin skins and flakes (pancake-like). Our prior studies[6] indicate that such particles with aspect ratios from 0.7 to 0.3 would have a λ_{max} between 560 and 670 nm (i.e., the membrane would be blue in appearance). The observed absorption maxima for these as-deposited 0.20 and 0.08 C nanoparticles fall within this range, Figure 3. After heating, all these irregularly shaped, flat particles become significantly more spherical, resulting in the aspect ratio of the nanoparticles increasing to *ca.* unity. Our previous studies[2,6] show that these annealed nanoparticles should have a λ_{max} of *ca.* 540 nm (i.e, the membrane would appear red), which is observed, Figure 3.

Conclusions

We have found that low aspect ratio Au nanoparticles (0.08 and 0.2 C used in the electrodeposition) start out as irregularly shaped skins or flakes of Au within the pores, but after heat treatment at surprisingly low temperatures, they anneal to become dense, roughly spherical particles. The visual color of these membranes started out blue but turned pink after this thermal treatment. In contrast, the 0.4 C nanoparticles (aspect ratio = 3) exhibited no change in optical absorption characteristics, gold particle shape, or electron opacity after exposure to the prescribed heating treatment. This membrane was initially red and did not change color with heating.

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