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Stability and Morphology of Gold Nanoisland Arrays Generated from Layer-by-Layer Assembled Nanoparticle Multilayer Films: Effects of Heating Temperature and Particle Size

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Abstract

This article reports the effects of heating temperature and composition of nanoparticle multilayer films on the morphology, stability, and optical property of gold nanoisland films prepared by nanoparticle self-assembly/heating method. First, nanoparticle-polymer multilayer films are prepared by the layer-by-layer assembly. Nanoparticle multilayer films are then heated at temperature ranging from 500 °C to 625 °C in air to induce an evaporation of organic matters from the films. During the heating process, the nanoparticles on the solid surface undergo coalescence, resulting in the formation of nanostructured gold island arrays. Characterization of nanoisland films using atomic force microscopy and UV-vis spectroscopy suggests that the morphology and stability of gold island films change when different heating temperatures are applied. Stable gold nanoisland thin film arrays can only be obtained after heat treatments at or above 575 °C. In addition, the results show that the use of nanoparticles with different sizes produces nanoisland films with different morphologies. Multilayer films containing smaller gold nanoparticles tend to produce more monodisperse and smaller island nanostructures. Other variables such as capping ligands around nanoparticles and molecular weight of polymer linkers are found to have only minimal effects on the structure of island films. The adsorption of streptavidin on the biotin-functionalized nanoisland films is studied for examining the biosensing capability of nanoisland arrays.

Keywords

Nanoislands; Nanoparticles; Self-Assembly; Plasmonics; Au

INTRODUCTION

Previous studies have revealed that the metal nanoisland structures show localized surface plasmon extinction peaks in the visible to near-infrared range, making them suitable materials for optical biosensing.¹⁻⁵ The basis that allows to measure the adsorption of

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Supporting Information Available: More AFM images and T-LSPR sensing results are included in the supporting information. The material is available free of charge via the internet at <http://pubs.acs.org>.

material onto the surface of gold nanostructures is the excitation of surface plasmon and the propagation of the produced polariton. Since the propagating wave is on the boundary of the gold and the external medium, these oscillations are very sensitive to any change of the boundary. Recently, the localized surface plasmon resonance (LSPR) nanosensor arrays based on small gold (or silver) nanostructures have extensively been studied by several research groups.⁶⁻²⁰

This article describes in-depth studies on our nanoisland preparation method that can complement the previously reported process of thermal vacuum evaporation technique.⁹⁻¹¹ Since the morphology and optical properties of nanostructured films have a direct impact on the sensitivity of LSPR measurement, other research groups have tried to control the size and shape of films using various methods including the nanosphere lithography with polystyrene masks⁶⁻⁸ and the deposition of thin metal films with different thicknesses (5 – 15 nm).⁹ However, these preceding methods of building nanoisland arrays on glass substrates required elaborate and expensive procedures including the use of special equipments such as vacuum evaporation chamber.⁶⁻¹¹ In comparison, our method is based on a facile nanoparticle self-assembly/heating method, which utilizes only common laboratory supplies.

The instability of the gold nanoisland films on the glass substrates, generated by the vacuum evaporation method, has been well documented.^{9,21} The substantial mobility of metal islands on glass substrates caused changes in morphology of the films and altered the shape and intensity of gold SP bands. Recently, there have been several reports related to the efforts on enhancing stability of gold nanoisland films prepared by vacuum evaporation method. For example, the use of thin organic or inorganic films to coat and stabilize nanoisland film arrays was introduced.⁹ Rubinstein's group also reported the stabilization of the gold nanoisland films by high temperature post-annealing of vacuum evaporated thin gold films.²¹ They have shown that the higher temperature annealing caused a slight embedding of nanoisland arrays on the glass surface, so it could prevent the morphological changes of the films when the films are in contact with other chemical reagents or solvents.

Inspired by this result, we attempted to prepare nanoisland films directly from nanoparticle multilayer films at high temperature. The scope of this study is to see how different heating temperatures ranging from 500°C to 625°C affect the stability of nanoisland structures generated from layered nanoparticle films. In addition, the effect of heating temperature on the morphology of nanoisland films is also investigated to examine the coalescence behavior of nanoparticle multilayer films. Since our method applies an easy-to-control layer-by-layer self-assembly approach which allows us to readily alter the structure and composition of nanoparticle multilayer films, the systematic studies will be able to offer an opportunity to further understand the surface coalescence behavior of gold nanoparticles during heat treatments.

EXPERIMENTAL SECTION

Materials

The following materials were purchased from the indicated suppliers and used as received: Hydrogen tetrachloroaurate ($\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$), tetraoctylammonium bromide, toluene, sodium borohydride (NaBH_4), ethanol, methanol, acetone, acetonitrile, tetrahydrofuran (THF), glass microscope slides, sulfuric acid, 30% hydrogen peroxide, *N,N'*-dicyclohexylcarbodiimide (DCC), ethylenediamine, biotin, streptavidin, phosphate buffered saline 10X Solution (PBS), and 3-mercaptopropyl trimethoxysilane (MPTS) were purchased from Fisher Scientific. 1-Hexanethiol, 11-mercapto-1-undecanoic acid (MUA), thioctic acid, trisodium citrate, sodium hydroxide, and poly(allylamine hydrochloride) (PAH; MW *ca.*

70,000 or MW *ca.* 15,000) were purchased from Aldrich. Water was purified by Barnstead NANOpure Diamond ion exchange resins purification unit.

Synthesis of COOH-Functionalized Gold Nanoparticles

The COOH-functionalized gold nanoparticles (MUA NPs: average molecular formula of $\text{Au}_{314}\text{L}_{91}$) used for the film preparation were synthesized by the following methods. Hexanethiolate-protected gold nanoparticles were first synthesized using a convenient two-phase synthesis known as the Schiffrin reaction. Briefly, AuCl_4^- was transferred to toluene using tetraoctylammonium bromide as the phase-transfer reagent. The addition of hexanethiol (2/1 mole ratio to HAuCl_4) to organic-phase AuCl_4^- followed by the reduction with NaBH_4 generated hexanethiolate-protected gold nanoparticles with average core size of ~ 2.2 nm.^{22,23} The incorporation of COOH-functional groups to the monolayer involved a modification of the hexanethiolate-protected gold nanoparticles by ligand-replacement.^{22,23} In the exchange reaction, the incoming 11-mercaptoundecanoic acid (MUA) ligands replaced the hexanethiolate ligands on nanoparticles in THF by an associative reaction. The relative concentration of incoming ligands was carefully controlled for the synthesis of nanoparticles to have ~ 20 % of COOH functional groups in the monolayers. The $^1\text{H-NMR}$ spectroscopy was used to determine the extent of the ligand exchange.

Synthesis of Citrate-Stabilized Nanoparticles (CT NPs)

The citrate-stabilized nanoparticle synthesis began with the boiling of 1 mM HAuCl_4 solution with constant stirring in the presence of 38.8 mM sodium citrate to form water-soluble gold colloids (~ 10 nm).²⁴ The color of the solution changed from light yellow to dark burgundy. After an additional 10 minutes of boiling, the solution was allowed to cool to room temperature and then vacuum filtered. The resulting filtrate was then used immediately for the layer growth.

Synthesis of Thioctic Acid-Stabilized Nanoparticles (TA NPs)

To prevent aggregation in solution, the CT-NPs were immediately treated with thioctic acid.²⁵ The pH of the solution was adjusted to 11 by addition of 0.5 M NaOH solution. Then an equal molar amount of thioctic acid to HAuCl_4 was added to the reaction mixture. This solution was left overnight to stir and stored in the dark before using for the layer growth.

Functionalization of Glass Slides

The silanization procedure started with glass microscope slides that were cleaned in a "piranha" solution (3/1 $\text{H}_2\text{SO}_4/\text{H}_2\text{O}_2$), sonicated in nanopure water for 10 min, rinsed thoroughly with nanopure water and methanol, and placed in a 50 mL methanol solution containing 2 mL of triethyl 3-mercaptopropyl trimethoxysilane and 1 mL of nanopure water for 24 h.²⁶ (Caution: Piranha solution reacts violently with organic materials and should be handled with extreme care.) The glass slides were rinsed with methanol and ethanol and blown dry with N_2 . The prepared glass slides were stored in a dry cabinet for future use.

Preparation of Gold Nanoparticle Multilayer Films

For multilayers containing polymer linkers, 10 mg of PAH (M.W. 70,000 or M.W. 15,000) was dissolved in 10 mL of nanopure water yielding *ca.* 14 μM or 65 μM solution concentrations, respectively. The *ca.* 30 μM MUA-NP solutions used in the buildup of multilayers were made by dissolving 10 mg of MUA NPs in 10 mL of ethanol. To build the gold nanoparticle multilayers onto glass slides, the MPTS-functionalized glass slides were placed in the ethanol solution containing MUA NPs ($\sim 2.2 \pm 0.8$ nm in diameter) for 24 hours.²⁷ Then, the slides were alternately placed in the aqueous solution containing PAH and in the nanoparticle solution for five minutes each to build the second layer of the gold

nanoparticle films. This last procedure was repeated three more times to build five layers of the gold nanoparticle multilayer films.²⁷ CT NP and TA NP multilayer films were prepared using the same procedure. UV-vis spectroscopy was used to monitor the multilayer film formations.

Heat Treatments of Nanoparticle Multilayer Films

Nanoparticle multilayer films were heated in a Barnstead Thermolyne 1300 furnace under air for one hour and characterized by monitoring the changes in the absorbance of nanoparticle films by UV-vis Spectrophotometer. The controlled temperature was set at 500 °C, 525 °C, 550 °C, 575 °C, 600 °C, or 625 °C each within ± 5 °C. The heated slides were left to cool in air to room temperature and stored immediately in a dry cabinet.

Preparation of Biotin-Functionalized Gold Nanoisland Arrays and Streptavidin Binding Studies

The nanoisland slides were first placed overnight in 1.0 mM MUA solution in ethanol. The MUA-functionalized slides were placed briefly in a 10 mM DCC solution in ethanol before placing in an ethanolic solution containing 0.1 M ethylene diamine for 3 hours. The amine-terminated slides were treated with an ethanolic solution containing 1.0 mM biotin and 2.0 mM DCC for 3 hours. Each slide was placed tightly in a home-made cell with PBS solution before measuring the absorbance. The PBS solution was removed carefully with a syringe and the streptavidin (100 μ g/ml in PBS) solution was added to the cell. The UV spectra of the slide in streptavidin solution were measured every 2 minutes until no change was observed. The sensitivity of 2 - 3 slides for each films prepared at different temperature was studied.

Measurements

Transmission UV-vis spectra of nanoparticle multilayer films and nanoisland films were acquired on a Shimadzu UV-2450 UV-vis spectrophotometer with a film (slide) holder. A baseline correction procedure (the spectrum of a standard glass slide was taken as baseline) was executed prior to each measurement session.

Atomic force microscopy (AFM) images were acquired in an ambient condition with Nanoscope IIIa Multimode scanning probe microscope (Digital Instruments, Santa Barbara, CA) using tapping mode. A silicon probe with the EV scanning head was employed. The nanoisland films were imaged with no further sample preparations. Most of the images were obtained using Tap 150Al-G tips from BudgetSensors. Scanning parameters varied with individual tips and samples, but typical ranges were as follows: tapping frequency of 150 kHz and scan rate of 1 – 3 Hz. The grain size distribution was obtained from the AFM images using watershed segmentation in ImageJ.

RESULTS AND DISCUSSION

UV-vis Spectroscopy of Gold Nanoisland Films Prepared at Different Temperature

For the formation of gold nanoisland films in our approach, nanoparticle-polymer multilayer films were heated at high temperature (500 - 625 °C) to thermally evaporate polymer (PAH) linkers. Heating at the temperature lower than 500 °C fails to remove PAH linkers completely and heating at the temperature higher than 625 °C causes the deterioration (notable shape change) of the glass slides. The LbL films of gold nanoparticles-PAH (MW 70,000) linkers (MUA NPs-PAH_{70K}) were grown on the surface of reactive glass substrates as described in Experimental Section. The SP band of gold appears with the formation of nanoparticle-PAH multilayer films and it becomes more evident as successive layers are added.^{27,28} We have shown that the gold nanoisland arrays

with various grain density and different average sizes could be obtained by controlling the overall thickness (number of layers) of nanoparticle multilayer films.²⁹ Gold nanoisland films obtained from the nanoparticle 2-layer films were quite polydisperse. Nanoisland films generated from the nanoparticle 8-layer films contained grains with higher density compared to the island films generated from the nanoparticle 5-layer films. Since the gold nanoisland arrays prepared from the nanoparticle 5-layer films display good spacing between island domains (*vide infra*), all island films in the present study were prepared from the assembled films with five nanoparticle layers. Figure 1 shows the SP band at ~550 nm of the five layered nanoparticle multilayer films undergoes a large evolution after heat treatments at 500 °C. This spectral evolution agrees that the gold nanoparticles undergo nucleation and coalescence on the glass surface resulting in the formation of larger gold nanoparticle-like structures.^{29,30}

The MUA NPs-PAH_{70K} films with five nanoparticle layers were each heated at 525 °C, 550 °C, 575 °C, 600 °C, and 625 °C to investigate the effects of heating temperature. UV-vis spectra of the series of annealed films are shown in Figure 2 (a). The baselines (absorbance at 700-900 nm) in UV-vis spectra for the gold nanoisland films are slightly different due to the disparity in the thickness, roughness, etc. of glass slides. The average SP band intensities at λ_{max} for six sets of gold nanoisland films are plotted against the heating temperature in Figure 2 (b). The overall trend clearly showed the increased SP band intensity for the nanoisland films generated at higher temperature. Hypothetically, the higher intensity of SP bands can be resulted from either the islands with larger average domain size or the islands with higher density.³⁰⁻³² Since the concentration of gold nanoparticles on solid surface in a specified area is approximately same for the films prepared from the same nanoparticle solution, the UV results along with the AFM data (*vide infra*) indicate that the island films prepared at higher temperature have the higher density of smaller islands on glass surfaces. The maximum wavelength (λ_{max}) data in Figure 2(c) shows a small increase for the nanoislands prepared at or above 575 °C. This change might indicate a slightly decreased average island-island distance after heat treatments at higher temperature resulted from the increased density of islands.³⁰ The reduction in average separation is expected to cause a red shift in the plasmon peak.³³ The results also confirmed that the continuous gold metallic films, which should exhibit a damped SP optical feature, were not produced.^{26,34}

Surface Characterization of Gold Nanoisland Films Prepared at Different Temperature

Atomic force microscopy (AFM) has been used for the shape and size analysis of the nanostructured films such as nanoislands.¹¹ AFM images have been found to correspond reasonably well with high resolution scanning electron microscopy (HRSEM) results. Although AFM slightly overestimates the size of nanoislands due to the AFM tip convolution effect, it can still provide an opportunity to directly compare the relative size and distributions of nanostructured films. Therefore, AFM images were analyzed without the tip deconvolution and the values of the grain areas and heights are mostly used to obtain the qualitative understanding of the surface morphology changes. The AFM images of different nanoisland films obtained at various temperatures should provide some insights on the effect of heating temperature.

After the heat treatment of nanoparticle multilayer films for one hour, all films showed rounded, nanoparticle-like morphologies with some separations among the island domains in AFM images. These results confirmed that the heating of MUA NPs-PAH_{70K} multilayer films caused the nucleation and coalescence of gold nanoparticles and the formation of nanoisland structures on the glass surfaces (Figure 3). The collected images clearly suggested a general decrease in grain area and size with increasing temperature up to 600 °C. There was less clumping of the grains at temperatures higher than 575 °C and the grains are distributed more uniformly. These AFM results corresponded well with UV-vis spectra

which showed relatively higher absorbance and longer maximum wavelength (λ_{max}) for the SP bands of nanoisland films obtained at the temperature of 575 °C and 600 °C. Although the size of nanoislands was relatively smaller, large number of island grains after higher temperature heat treatments at 575 °C and 600 °C increased the overall density of nanoisland grains and made SP bands of gold more intense. The AFM image of the nanoislands obtained at 625°C was more polydisperse and less uniform than the islands prepared at 600°C. The reason was a slight melting of the glass microscope slides and embedding of gold nanoislands. Higher temperature annealing is known to cause a slight embedding of nanoisland arrays on the glass surface at the high temperature due to partial melting of glass substrates.²¹ When the part of gold nanoislands sunk down into the glass, it resulted in different average size and height of islands in the AFM image. The morphology of glass surfaces after the complete dissolution of the gold nanoisland in aqua regia showed that the detectible embedding started to take place for nanoisland films prepared at 600 °C. This was evidenced by many pits appeared as dark spots in the AFM images for the slides heated at 600 °C. The pits got slightly larger and deeper for the slides heated at 625°C (Figure S1 in Supporting Information).

After modification of the AFM images to remove the scanning artifacts, the watershed algorithm in ImageJ was used to measure and analyze island grains. The grains in the edge of the scanned area were not included for the analysis to reduce the error. Figure 4 (a) is a histogram showing the number of island grains against the area (derived from the radii) for nanoisland films generated at different heating temperatures. The nanoisland films obtained at the lower temperature are much more polydisperse than the ones generated at the higher temperature (above 575 °C). The average grain areas of the nanoisland films obtained from three different samples are shown in Figure 4 (b). The areas of the grains, or gold nanoislands, did not change significantly for temperatures from 500 to 575 °C. The average areas of the images fluctuated from about 300 to 500 nm² for nanoislands generated at the lower temperature. Marked decreases in area were noted for samples heated at 600 and 625 °C, where grain sizes typically ranged from 200 to 300 nm². The number (density) of islands also clearly increased with the increased heating temperature as shown in Figure 4 (a). The analysis of the AFM images using the autocorrelation function provided the autocorrelation length which is related to the island size and the island-island distance in the sample. The autocorrelation length of the nanoisland films prepared at and below 575 °C ranged in 14 ~ 19 nm while the same length for the films prepared at 600 °C ranged in 9.8 ~ 11 nm. This abrupt drop in the autocorrelation length confirms visibly smaller island size in the nanoisland films prepared at 600°C. Since the islands are closely packed in these films, the reduced island size could be translated to the reduced island-island distance. Figure 4 (c) shows the average heights of nanoisland films, which decreased with the increased heating temperature. This decrease in height is likely caused by both the formation of smaller island domains at higher temperatures (575 °C - 625 °C) and the slight embedding of islands due to melting of the glass slides at the temperature at and above 600 °C.

The overall results shown in Figure 4 suggested that the nanoisland films generated at the higher temperature have more grains with smaller average sizes and lower average heights. The peak of the distribution (histogram) also moved to a lower value (smaller average core size) suggesting a better monodispersity in the size of islands. These results showed that the gold nanoisland films generated at higher temperature have a slightly higher island density along with a high concentration of smaller grains. The high concentration of smaller island domains for nanoisland films was also indicated in UV-vis spectra (Figure 2) as highly intense SP bands of gold. The results clearly suggested that the heating temperature alters the morphology of nanoisland films by affecting the coalescence process of nanoparticles on solid surface.

Stability Evaluation of Gold Nanoisland Films Prepared at Different Temperature

Gold nanoisland films prepared at the lower heating temperature (500 °C) exhibited noticeable morphology changes upon exposure to alkanethiols, acidic solutions, and even organic solvents.^{9,29} To examine the stability of the produced nanoisland films at different temperatures, the nanoisland arrays were placed in 1.0 mM 11-mercaptoundecanoic acid solution in ethanol for at least 24 hours and then characterized with the UV-vis spectrophotometer (Figure 5). Thiol treatment is a simple and fast way to prove the stability of nanostructured films. Since the SP band of gold in UV-vis spectra is very sensitive to the change in the structure of the nanostructured films, any morphological variation will result in the change in the intensity, peak width, and/or the wavelength of the SP band.^{9,21,29} It is also known that the reflective index changes caused by MUA assembly could result in the shift and/or increase in plasmon band. Therefore, to confirm the changes caused by MUA assembly was due to the morphological changes of the island films, we have examined the response of island films generated at different temperature using the streptavidin/biotin model system (Figure S2 in Supporting Information). The results clearly suggested that the less stable films prepared at temperature 500 – 550 °C was less responsive to the model system after the surface functionalization (*vide infra*). This confirmed that the changes we observe in Figure 5 for the island films obtained at temperature 500 – 550 °C is likely due to the morphology changes instead of the reflective index changes.

The results showed that the nanoisland gold films prepared at the heating temperature of 500 °C exhibit large red-shift of the SP band of gold ($\Delta\lambda_{\text{max}} = \sim 40$ nm) after MUA treatment, indicating large morphological changes of nanoisland films.^{29,30} The nanoisland films prepared at 525 °C showed similar changes but with less extent ($\Delta\lambda_{\text{max}} = \sim 25$ nm). The change was quite small but still clearly visible for the films generated at 550 °C ($\Delta\lambda_{\text{max}} = \sim 10$ nm). However, for the films generated at 575 °C or above, the SP band of Au didn't undergo any shift after the immersion in MUA solution for an extended period. Figure 5 clearly indicated that the films prepared at the higher temperature were much more stable than those prepared at the lower temperature. The small increase in the intensity of SP bands of nanoislands prepared in UV-vis spectra is due to the alteration in localized surface plasmon resonance of gold resulted from the difference in surrounding dielectric environments after the MUA assembly.²¹

Other Effects on Gold Nanoisland Film Formation: Nanoparticle Size, Stabilizing Ligands and Polymer Linkers

To obtain more insights into the mechanism of island grain formation, the composition of nanoparticle multilayer films was altered by using nanoparticles with different sizes (~2 nm vs. ~10 nm), nanoparticles with different stabilizing ligands (CT NPs vs. TA NPs), and using different polymer linkers (PAH with M.W. 70,000 or 15,000). We used modified citrate reduction of gold salts to synthesize well-known larger citrate-stabilized gold nanoparticles (CT NPs) in water.²⁴ The same process to build nanoparticle multilayer films using small ~2 nm gold nanoparticles (MUA NPs) was used for the formation of nanoparticle multilayer films. Figure 6 shows the UV-vis-spectra of nanoisland films generated from 5-layered multilayer films containing CT NPs and PAH (CT NPs-PAH_{70K}) after heating at 600 °C for 1 h. Compared to the UV-vis spectra of nanoisland films generated from ~2 nm gold nanoparticles (MUA NPs-PAH_{70K}, Figure 2), the UV-vis spectra of nanoisland films obtained from larger CT NPs have much broader gold SP band and the band is red-shifted to ~549 nm. This result indicates the nanoislands are more polydispersed and even partially aggregated.

However, nanoparticle multilayer films containing CT NPs was known to undergo a fast aggregation on the surface resulting in coalescence even at room temperature.²⁵ This was

evidenced by the UV spectra of nanoparticle multilayer films generated from CT NPs, which showed very broad absorption bands even right after the film preparation. Instead of well-defined SP bands, it showed a feature resembling that of thin gold films.^{26,34} We prepared more stable TA NPs from CT NPs by ligand exchange and used these TA NPs to prepare nanoisland films.²⁵ This research was to observe the effects of ligand surrounding nanoparticles during the coalescence process. The UV-vis spectra of multilayer films containing TA NPs (TA NPs-PAH_{70K}) showed more defined SP bands of gold than that generated from CT NPs (CT NPs-PAH_{70K}). However, the produced nanoisland films from both CT NPs-PAH_{70K} and TA NPs-PAH_{70K} exhibited almost identical SP bands of gold. This result suggested that the ligand surrounding gold nanoparticles was not an important contributor in the coalescence process during the heating process. The evaporation of organic ligands likely takes place prior to the major coalescence process of nanoparticles during the formation of nanoisland structures.

AFM results also showed that, by changing the size of nanoparticles in multilayer films, the density and the average diameter of island grains changes dramatically. Gold nanoisland films obtained from larger nanoparticles at 600 °C turned out to be quite polydisperse (Figure 7). There were many large grains (~100 nm) all over the surface. In addition, many smaller original gold particles with the size of ~10 nm also could be seen in the obtained AFM images. This indicated the coalescence process of large particles is very difficult to control and unpredictable. There were no discernible differences for AFM images obtained from nanoisland films generated from CT NPs-PAH_{70K} and TA NPs-PAH_{70K} multilayer films.

Another component in the multilayer films that can alter the growth of nanoisland arrays might be the linkers with distinct sizes and linking sites. To briefly survey the importance of linkers between nanoparticles, two different poly(allylamine) hydrogen chloride (PAH), one with a molecular weight of 15,000 and the other with 70,000, were used to build nanoparticle (2 nm) multilayer films. Figure 8 shows UV-spectra of the 5 layered gold NP films with the M.W. 15,000 PAH (MUA NPs-PAH_{15K}) and the 5 layered gold NP films with the M.W. 70,000 PAH (MUA NPs-PAH_{70K}). After the heat treatments at 600 °C, the nanoisland films generated from both MUA NPs-PAH multilayer films exhibited SP bands of gold at ~540 nm with similar intensity and shape. This result suggests that the size of polymer linkers does not have a great impact on the mechanism of nanoisland grain formation. Evaporation of polymer seems to take place prior to the major coalescence of nanoparticles.

T-LSPR Sensing of Gold Nanoisland Arrays

The surface property of gold nanoisland films was further controlled by the self-assembly of functionalized alkanethiols followed by the biotin immobilization.³⁵ Transmission localized surface plasmon (T-LSPR) sensitivity of gold nanoisland arrays prepared at different temperatures was also examined by studying biotin-streptavidin interactions.

The slides heated at different temperature (500 °C – 625 °C, 2-3 slides each) were used for the study. The gold island films were functionalized with 11-mercaptoundecanoic acid (MUA). The carboxylic acid groups were then subsequently treated with *N,N*-dicyclohexylcarbodiimide, ethylenediamine, and biotin, which resulted in the attachment of biotin on the surface of gold nanoisland films.³⁶ For the biosensing studies, first, the transmission-localized surface plasmon resonance (absorbance) of the biotin-functionalized nanoisland films in phosphate buffered saline (PBS) solution was taken using UV-vis spectroscopy. Second, the PBS was replaced by the streptavidin (100 µg/mL – 10 µg/mL) solution in PBS and UV-vis spectra were taken after 2 minutes. The T-LSPR results of this study showed that the intensity of SP bands of gold was increased for nanoisland films

prepared at 575 °C and 600 °C after the exposure to streptavidin solution in PBS. The prolonged immersion of the films in the streptavidin solution did not induce any further change in UV-vis spectra indicating that the response time for the nanoisland arrays to the immobilization of streptavidin is less than 2 min. The response of nanoislands towards streptavidin solution could be observed at the streptavidin concentration at 100 µg/mL (Figure 9). The change was always about 2–3% in the overall absorption intensity of gold SP bands for nanoisland films prepared at 575 °C and 600 °C. However, the same study using a lower concentration of streptavidin showed no such change in the intensity of SP bands of gold. In addition, non-specific binding studies using MUA-functionalized gold nanoisland films did not exhibit any change. The less stable films prepared at temperature 500 – 550 °C was much less responsive to the presence of streptavidin after the biotin/MUA functionalization. The sensitivity of the films was also affected by the embedding of gold islands when the films are formed at 625 °C. Exposing the biotin/MUA-functionalized gold nanoisland films generated at this temperature to the streptavidin solution showed no change in the SP band (Figure S2 in Supporting Information).

CONCLUSION

Gold nanoisland thin film arrays were prepared by thermal evaporation of organic matters from layer-by-layer assembled nanoparticle-polymer multilayer films. When the nanoparticle multilayer films were heat-treated at the temperature ranging from 500 °C to 625 °C, a nucleation and coalescence of nanoparticles on the solid surface resulted in the formation of gold nanoisland arrays. The collected data suggested that the nanoisland films prepared at different temperature exhibited a general decrease in grain area and heights with increasing heating temperature. In particular, large decreases in areas were observed for heating temperature of 600 °C. Overall, the coalescence process of nanoparticles in nanoparticle-polymer multilayer films could be altered by using different heating temperature and nanoparticles with different sizes. However, the organic ligands surrounding nanoparticles and the linkers between nanoparticles did not have any influence over the structure and morphology of nanoisland films. This result suggested that the major nucleation and coalescence process during the heat treatments seems to take place when most of organic moieties in the nanoparticle multilayer films are eliminated by evaporation.

The study also proved that the high temperature heating dramatically improve the overall stability of nanoisland films. The gold nanoislands heated at high temperatures at or above 575 °C were much more stable than that prepared at the lower temperature. For the films generated at 575 °C and 600 °C, the good sensitivity of biotin-immobilized nanoislands towards streptavidin was observed.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

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References

- 1). Whang D, Jin S, Wu Y, Lieber CM. Nano Lett. 2003; 3:1255–1259.
- 2). Röck F, Barsan N, Weimar U. Chem. Rev. 2008; 108:705–725. [PubMed: 18205411]
- 3). Stewart ME, Anderton CR, Thompson LB, Maria J, Gray SK, Rogers JA, Nuzzo RG. Chem. Rev. 2008; 108:494–521. [PubMed: 18229956]

- 4). Lin L, Harris JW, Thompson HGR, Brody JP. *Anal. Chem.* 2004; 76:6555–6559. [PubMed: 15538776]
- 5). Wark AW, Lee HJ, Corn RM. *Anal. Chem.* 2005; 77:3904–3907. [PubMed: 15987090]
- 6). Zhao J, Das A, Schatz GC, Sligar SG, Van Duyne RP. *J. Phys. Chem. C.* 2008; 112:13084–13088.
- 7). Sherry LJ, Jin R, Mirkin CA, Schatz GC, Van Duyne RP. *Nano Lett.* 2006; 6:2060–2065. [PubMed: 16968025]
- 8). Hicks EM, Lyandres O, Hall WP, Zou S, Glucksberg MR, Van Duyne RP. *J. Phys. Chem. C.* 2007; 111:4116–4124.
- 9). Doron-Mor I, Barkay Z, Filip-Granit N, Vaskevich A, Rubinstein I. *Chem. Mater.* 2004; 16:3476–3483.
- 10). Bendikov TA, Rabinkov A, Karakouz T, Vaskevich A, Rubinstein I. *Anal. Chem.* 2008; 80:7487–7498. [PubMed: 18754673]
- 11). Ruach-Nir I, Bendikov TA, Doron-Mor I, Barkay Z, Vaskevich A, Rubinstein I. *J. Am. Chem. Soc.* 2007; 129:84–92. [PubMed: 17199286]
- 12). Dahlin A, Zäch M, Rindzevicius T, Käll M, Sutherland DS, Höök F. *J. Am. Chem. Soc.* 2005; 127:5043–5048. [PubMed: 15810838]
- 13). Lassiter JB, Sobhani H, Fan JA, Kundu J, Capasso F, Nordlander P, Halas N. *J. Nano Lett.* 2008; 8:3184–3189.
- 14). Sannomiya T, Hafner C, Voros J. *Nano Lett.* 2008; 8:3450–3455. [PubMed: 18767880]
- 15). Mayer CM, Lee S, Liao H, Rostro BC, Fuentes A, Scully PT, Nehl CL, Hafner JH. *ACS Nano.* 2008; 2:687–692. [PubMed: 19206599]
- 16). Gao S, Koshizaki N, Koyama E, Tokuhisa H, Sasaki T, Kim J-K, Cho Y, Kim D-S, Shimizu Y. *Anal. Chem.* 2009; 81:7703–7712. [PubMed: 19697928]
- 17). Odom TW, Nehl CL. *ACS Nano.* 2008; 2:612–616. [PubMed: 19206589]
- 18). Hiep HM, Yoshikawa H, Saito M, Tamiya E. *ACS Nano.* 2009; 3:446–452. [PubMed: 19236084]
- 19). Chang W-S, Slaughter LS, Khanal BP, Manna P, Zubarev ER, Link S. *Nano Lett.* 2009; 9:1152–1157. [PubMed: 19193117]
- 20). Juluri BK, Lu M, Zheng YB, Huang TJ, Jensen L. *J. Phys. Chem. C.* 2009; 113:18499–18503.
- 21). Karakouz T, Tesler AB, Bendikov TA, Vaskevich A, Rubinstein I. *Adv. Mater.* 2008; 20:3893–3899.
- 22). Shon, Y-S. Metal Nanoparticles Protected with Monolayers: Synthetic Methods. In: Schwarz, JA., editor. *Dekker Encyclopedia of Nanoscience and Nanotechnology*. Marcel Dekker; New York: 2004. p. 1-11.
- 23). Daniel M-C, Astruc D. *Chem. Rev.* 2004; 104:293. [PubMed: 14719978]
- 24). Kimling J, Maier M, Okenve B, Kotaidis V, Ballot H, Plech A. *J. Phys. Chem. B.* 2006; 110:15700–15707. [PubMed: 16898714]
- 25). Russell LE, Galyean AA, Notte SM, Leopold MC. *Langmuir.* 2007; 23:7466–7471. [PubMed: 17559246]
- 26). Wuelfing WP, Zamborini FP, Templeton AC, Wen X, Yoon H, Murray RW. *Chem. Mater.* 2001; 13:87–95.
- 27). Isaacs SR, Choo H, Ko W-B, Shon Y-S. *Chem. Mater.* 2006; 18:107–114.
- 28). Wang L, Miller D, Fan Q, Luo J, Schadt M, Rendeng Q, Wang GR, Wang J, Kowach GR, Zhong C-J. *J. Phys. Chem. C.* 2008; 112:2448–2455.
- 29). Choi HY, Guerrero MS, Aquino M, Kwon C, Shon Y-S. *Bull. Korean Chem. Soc.* 2010; 31:291–297.
- 30). Sugden MW, Richardson TH, Leggett G. *Langmuir.* 2010; 26:4331–4338. [PubMed: 20163132]
- 31). Mulvaney P. *Langmuir.* 1996; 12:788–800.
- 32). Ung T, Liz-Marzan LM, Mulvaney P. *J. Phys. Chem. B.* 2001; 105:3441–3452.
- 33). Rechberger W, Hohenau A, Leitner A, Krenn JR, Lamprecht B, Aussengg FR. *Opt. Commun.* 2003; 220:137–141.
- 34). Khawaja EE, Durrani SMA, Al-Shukri AM. *Thin Solid Films.* 2000; 358:166–171.

- 35). Riboh JC, Haes AJ, McFarland AD, Yonzon CR, Van Duyne RP. *J. Phys. Chem. B.* 2003; 107:1772–1780.
- 36). Frederix F, Friedt J-M, Choi K-H, Laureyn W, Campitelli A, Mondelaers D, Maes G, Borghs G. *Anal. Chem.* 2003; 75:6894–6900. [PubMed: 14670050]

Figure 1. UV-vis spectra of 5-layered MUA NPs-PAH_{70K} multilayer films before and after heat treatments at 500 °C.

Figure 2.

(a) UV-vis spectra of gold nanoisland films prepared at the different temperatures ranging from 500 °C to 625 °C. (b) Average absorbance at ($\lambda_{\max}$) from UV-vis spectra of gold nanoisland films. (c) Average maximum wavelength ($\lambda_{\max}$) from UV-vis spectra of gold nanoisland films.

Figure 3.

AFM images of gold nanoisland films with a dimension of 350×350 nm were taken for 6 different temperatures: a. 500 °C, b. 525 °C, c. 550 °C, d. 575 °C, e. 600 °C, and f. 625 °C. Note the relatively smaller grain sizes for the 600 °C and 625 °C images, as well as their more uniform distribution.

(a)

(b)

(c)

Figure 4.

(a) Area distribution bars for each heating temperature. (b) Grain area vs. heating temperature chart. Each white point represents the average grain area of an individual slide, the triangle point represents the average grain area for three slides prepared at each temperature. (c) Grain height vs. heating temperature chart.

Figure 5. UV-vis spectra of nanoisland films prepared at different temperatures before and after the treatments with a 1.0 mM ethanolic solution of 11-mercaptoundecanoic acid.

Figure 6.
UV-Spectra of gold nanoisland films obtained from (a) citrate-stabilized gold nanoparticles (CT NPs) and (b) thiotic acid-capped gold nanoparticles (TA NPs)

Figure 7.
AFM image of island films prepared from citrate-stabilized gold nanoparticles (CT NPs).

Figure 8.

Nanoisland films generated from 2 nm gold nanoparticle multilayer films and (a) with M.W. 15,000 PAH linkers (b) with M.W. 70,000 PAH linkers

Figure 9. UV-vis spectra of biotin-functionalized gold nanoisland films prepared at 600 °C before and after exposure to streptavidin solution (100 $\mu\text{g/mL}$).