



Assembly of Gold Nano Particles on a Modified Glass Silicone Surface

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Recent development in the field of technologies has pushed towards miniaturization of materials on the nanometer levels which are critical and encouraging to design of new nanoscale materials systems which is having a novel and/or enhanced properties without resorting to new synthetic chemistry with the associated environmental and cost issues. In order to discuss these issues an effort was made to describe a facile method for stabilizing gold nano-particles over a modified cover glass surface layers of dimension 18 mm × 18 mm samples. In this study, the different sized gold nano-particles were synthesized by standard methods. The modified glass surfaces containing assembled gold nano-particles were analyzed by scanning electron microscopy, transmission electron microscopy, atomic force microscopy and other spectral studies. With this method, uniformly shaped rods with high aspect ratio can be prepared and assembled.

Key Words: Gold nano-particles (GNPs), Assembly, Nanostructure, Nano-composite, Nanoscopic textures.

INTRODUCTION

One of the major themes of nanotechnology has been the search to produce techniques for self-assembling nanoparticles to construct architectures on a solid-state surface for different applications. Currently, many advanced techniques are available to produce low dimensional assemblies of colloidal nanoparticles for the fabrication of nanostructures which are essential for developing and capitalizing upon the emerging field of nanoscience¹⁻⁴. Novel patterning approaches of gold nanoparticles (GNPs) have been made to achieve a sub 100 nm resolution using electron-beam lithography^{5,6}, dip-pen nanolithography (DPN)⁷, micro contact printing (mCP)⁸ and scanning probe lithography (SPL)⁹⁻¹¹. For foregoing and burgeoning lithography applications of nanoscience, selectively positioning chemical component molecules into a desired region on a solid silicon dioxide surface is a crucial technique. Among the advanced lithography methods, scanning probe lithography has been demonstrated to be a powerful tool in nanofabrication¹¹⁻¹⁵. Scanning probe lithography is a high-resolution patterning technique that uses a conductive tip to pattern a thin layer of an electron sensitive material or conductive surface. On the other hand, self-assembled monolayer (SAM) technology^{16,17} also provides an easy route for surface functionalization with organic molecules containing functional groups, such as -SH, -COOH, -NH₂ and silanes, on selected metallic materials as well as

semiconductor surfaces. Many studies have been shown that trimethylsilyl chemical monolayer on a thin silicon dioxide surface can be locally removed by scanning probe lithography¹⁸⁻²¹. In these studies, the patterning region where the monolayer had been removed was then selectively modified with a second self-assembled monolayer of organosilane molecules.

Hoepfener *et al.*²² combined the surface self-assembly method with nanoelectrochemical patterning using a conductive atomic force microscopy (AFM) tip. A second highly ordered long-tail nonadecenyltrichlorosilane (NTS) monolayer is then allowed to selectively self-assemble on top of the AFM patterned octadecyltrichlorosilane (OTS) monolayer; then, the terminal ethylenic function groups of NTS are subsequently photo reacted with H₂S. Ling *et al.*¹⁰ and Sugimura and Nakagiri¹⁸, reported similar results with a two-step surface modification, *i.e.*, the electrical-field-induced local oxidation removal of an OTS self-assembled monolayer through scanning probe lithography, followed by the selective chemisorption of a second monolayer of (3-aminopropyl)-triethoxysilane (APS) molecules, resulting in the formation of a self-assembled monolayer confined to the scanning probe lithography-defined pattern. The selective deposition of APS on an OTS assembled monolayer, resulted in the assembly of latex gold nanoparticles outside of the oxide domains. Using scanning probe lithography, the control and selective binding of the component chemical organic molecules can be achieved on a desired functionalized-

surface pattern that can be linked to two different chemical molecules. Moreover, it is already known that tunneling electrons can be used to break molecular bonds on conductive metal surfaces using scanning tunneling microscopy (STM)^{23,24}. This is straightforward patterning technique which demonstrates the deposition method for the assembly of a few gold nanoparticles (GNPs) onto a modified glass surface.

In this study we describe a single-step surface modification process where we have synthesized different sized GNPs by standard methods and allowed to self-assemble over modified glass surface in a solution state by a simple of stirring the solution containing GNPs in the presence modified glass surfaces. The modified glass surfaces containing assembled GNPs were analyzed by UV-VIS spectra, AFM and TEM. With this method, uniformly shaped rods with high aspect ratio can be prepared and assembled.

EXPERIMENTAL

The thin plate glasses for the surface modification that is cover glasses were purchased from Marienfeld, Germany. All the chemical are of AR grade chemicals used in this study were purchased from Sigma-Aldrich and were used without any purification. Known concentration (M) of chemicals namely, 2-isopropanol, hydrogen tetrachloroaurate (HAuCl₄), ascorbic acid, vinyltriethoxysilane (VTES) tri-sodium citrate, sodium borohydride (NaBH₄) and cetyltrimethylammonium bromide (CTAB) were obtained as stock solutions in deionized water using standard methods. Required amount of concentration of each solution was obtained by appropriate dilution of stock solutions. A three-step seeding method was used for the nanorod preparation, the procedure for preparing different sized GNPs are taken from the method of Murphy *et al.*²⁵. Three test tubes as labeled A, B and C, each containing 9 mL growth solution, consisting of 2.5×10^{-4} M HAuCl₄ and 0.1 M CTAB, were mixed with 0.05 mL of 0.1 M ascorbic acid. Next, 1.0 mL of the 3.5 nm seed solution was mixed with sample A. The colour of A turned red within 2-3 min. After 4-5 h, 1.0 mL was drawn from solution A and added to solution B, followed by thorough mixing. The colour of solution B turned red within 4-5 min. After 4-5 h, 1 mL of B was mixed with C. Solution C turned red in colour within 10 min. All of the solutions were stable for more than a month. The aspect ratio of the solutions A, B and C are considered to be around 3.5 ± 1 , 4.6 ± 1 and 13 ± 1 , respectively²⁵.

Cleaned cover glasses of dimension 18 mm × 18 mm were sonicated for 15 min in 2-isopropanol to remove any trace organic residue and to ensure a uniform oxide coat. The pre-cleaned silicone wafers were immersed into 0.1 N KOH for 2 min and 0.1 N HNO₃ for 10 min, respectively and the wafers are washed with an excess of water. The silicon wafers were further dried under flowing nitrogen gas. To generate functional groups on the surface of the cover glasses, the dried cover glasses were immersed into anhydrous toluene containing 5 vol % vinyltriethoxysilane (VTES). The reaction was performed in a plate-bottom flask connected to a reflux condenser for 24 h. The cover glasses were washed with dichloromethane and sonicated in 2-isopropanol to quench any residual organosilane remaining after the reaction. The cover glasses

were dried under a stream of dry nitrogen gas overnight at room temperature to allow interstitially trapped solvent to evaporate. The surface modified cover glasses were placed in a stand were immersed in A, B and C seed solution containing GNPs for a period of 1hrs and to obtain control the density adsorbed particles. Meanwhile the solution was stirred to provide a uniform media which facilitated the adsorption of GNPs over the modified cover glass. After then the cover glasses were washed carefully by sonication in distilled water and finally dried with a N₂ stream. Fig. 1 shows the surface modification of cover glass and the process of self-assembly of GNPs gold nano-particles on the modified cover glass.

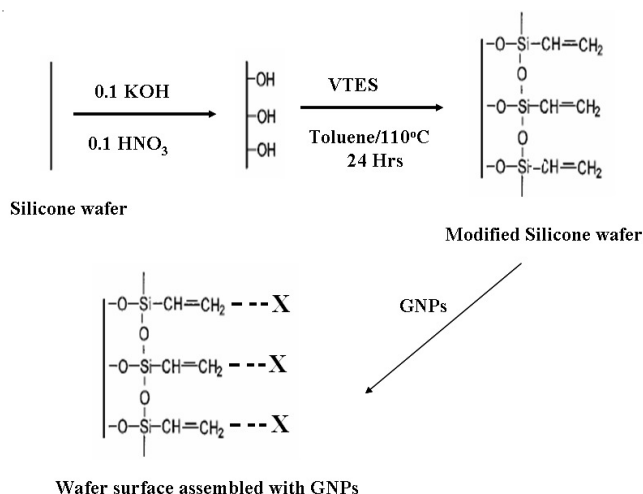


Fig. 1. Surface modification of cover glass and the assembly process for the GNPs on the modified cover wafer, X stands for GNPs and the dotted lines indicates a weak link between GNP and VTES

Extinction spectra at normal incidence were measured in air using a Varian Cary 50 UV/VIS spectrophotometer. The wavelength scan range was 350-1000 nm and the scan speed was 300 nm/min. The samples were placed in a special holder enabling transmission measurements of the same spot on the slide during all experimental stages. Atomic force microscopy (AFM) images were recorded in air using a Pico SPM instrument (Molecular Imaging, USA) operated in the acoustic AC (AAC) mode. The cantilevers used were NSC12 series of ultrasharp silicon (Mikro Masch, Estonia), with a resonant frequency of 100-200 kHz and an average tip radius of ≤ 10 nm. The morphological aspects of the wafer surfaces were analyzed by using the transmission electron microscopy (TEM, JEM-2010, JEOL, Japan) at accelerating voltage of 200 kV.

RESULTS AND DISCUSSION

Fig. 2 presents a typical AFM image of seed density linked to a modified glass surface. Although there was no direct evidence that the negatively charged seed particles were linked to VTES, it should be noted that without the VTES treatment of the substrates no seeds were observed in the AFM images (these images were studied but not shown here). The AFM images of the assembled GNPs of different sizes on the modified glass surface using the solution A, B and C (c) are shown in the Fig. 2(a-c), respectively. The images are obtained at 500 nm and these images show distribution of the GNPs

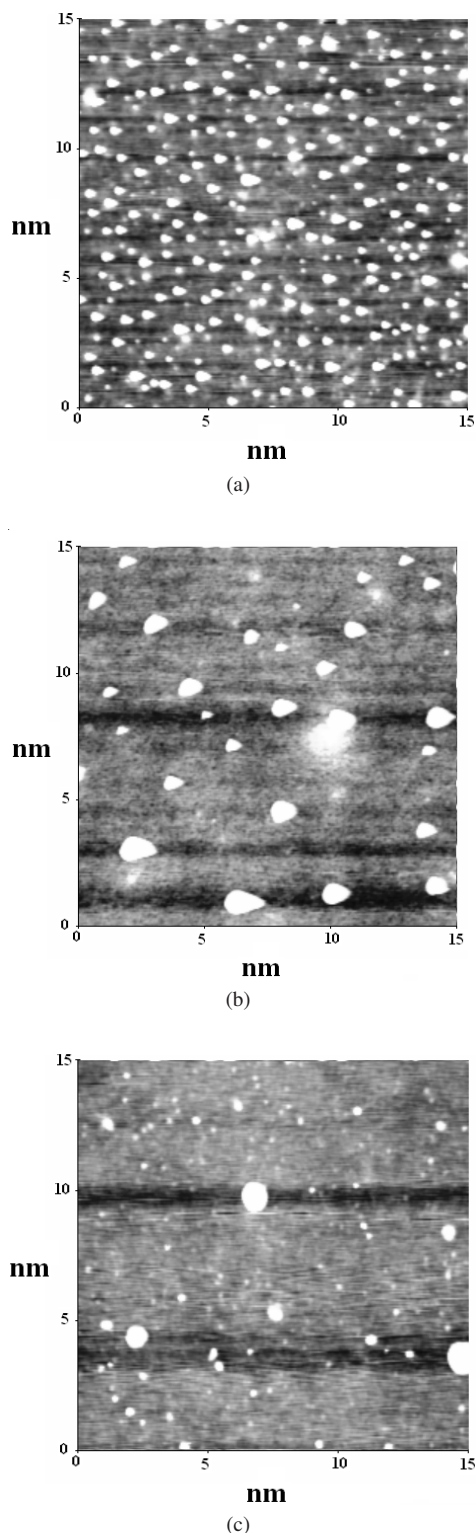


Fig. 2. AFM images of the self-assembled gold nanoparticles of different sizes on the modified glass surface using the solution A (a), B (b) and C (c)

assembled over the surface of the modified glass plate. Further the surface plots for the glass surfaces assembled by the GNPs of A, B and C are shown in the Fig. 3. These figures are the values of vertical surface. Each peak in Fig. 3 especially the larger ones represents large distribution of the GNPs. The noisy surface at the bottom of these peaks probably indicates the empty space which is occupied by the VTES.

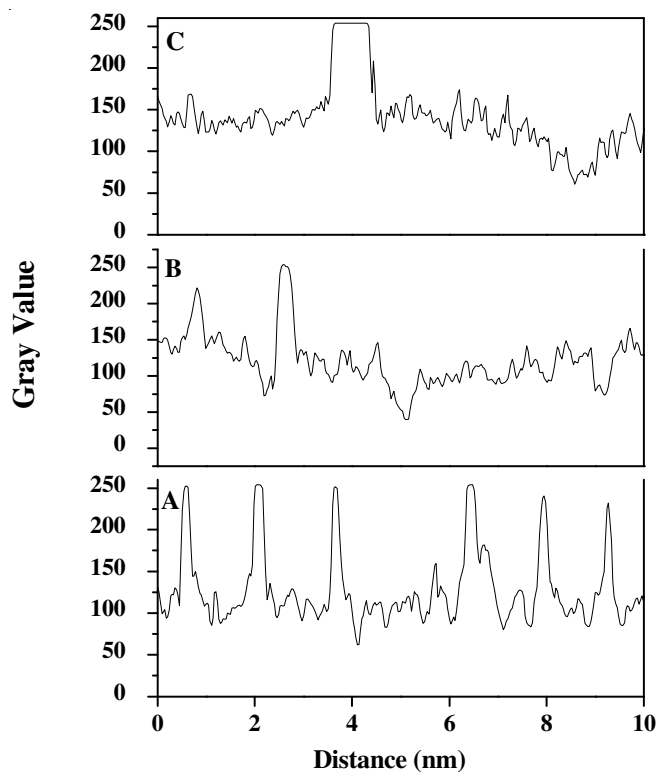


Fig. 3. Surface plot profile for the surface containing assembled GNPs different sizes on the modified glass surface using the solution A, B and C

The modified glass surfaces containing assembled GNPs were also studied by UV-VIS spectroscopy. Fig. 4 shows UV-VIS spectra of A, B and C. A change in the shape and intensity of the peak is seen after the assembly of different sized GNPs reflecting a decrease in the intensity of the spectra of the assembled surface of the modified silica plate. With an increase of the aspect ratio of the assembled GNPs increases the peaks become sharper and gradually shift towards lower region. Fig. 5 shows TEM images of the assembled GNPs of different sizes on the modified glass surface using the solution A(a), B (b) and C (c) at 50 nm. The images shows the surfaces are almost uniform containing different sized GNPs in the solution containing A, B and C. The size and shape appears nearly uniform. This may be due the synthetic condition of these GNPs. Because these GNPs are stable and distributed very well in water. The stable distribution may be due to the heavy capping with at least a bilayer of CTAB on the surface of the GNPs, which keeps them well separated over the surfaces of the modified glass plate.

It is suggested that there was a formation of week interaction between the GNPs and the VTES present on the modified glass surface. However we do not have any experimental evidence to prove this type of interaction which is responsible for holding the GNPs on the modified glass surface. This interaction is considered to be weaker than any other bond, we have found out from this experiment that this interaction decreases as the particle size of the GNPs increases as it could be observable from the AFM and TEM images of A, B and C. The self-assembly of GNPs over modified glass plate is simple and can be achieved with common laboratory reagents. The assembly method prepares a desired aspect ratio of GNPs by

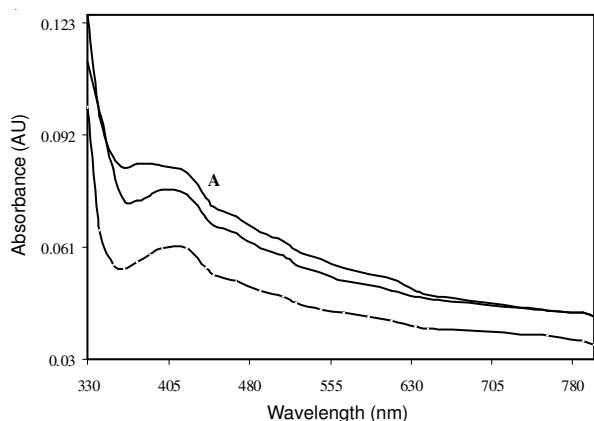


Fig. 4. UV-VIS spectra of self-assembled with GNPs of different sizes on the modified glass surface using the solution A (a), B (b) and C (c)

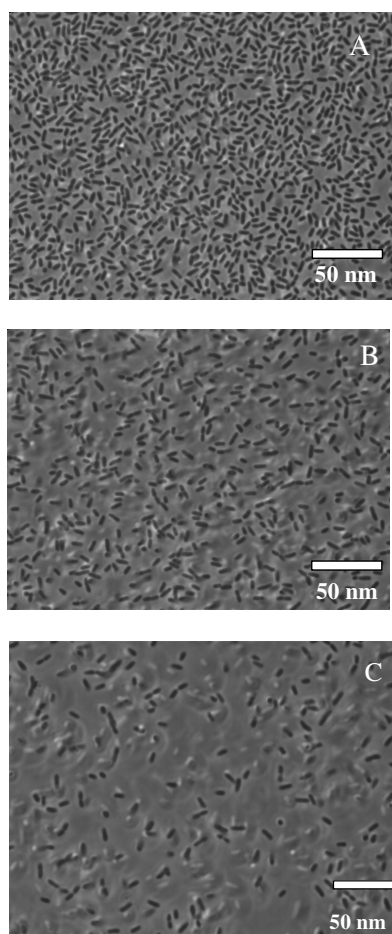


Fig. 5. TEM images of the self-assembled GNPs of different sizes on the modified glass surface using the solution A, B and C

a seeding growth method in an aqueous micellar template and can control the nano particle aspect ratio by properly adjusting the growth conditions. With this method, uniformly shaped with high aspect ratio of gold nanoparticles are also may be prepared. This method requires no nano porous template and therefore is more practical for large-scale synthesis.

Conclusion

In the present work, it is expected that the binding of the seed particle to a surface. We believe that this surface growth

procedure can be further improved to produce longer nanorods with better yields. Finding the optimal parameters for the surface growth process requires further search in parameters space. It is expected that the present studies on controllable connection of nanoscale building blocks into a desired shape might find application in future nanoelectronics and nano-devices. The technique presented here is a succeeding step along the path towards the fabrication of arrays of conducting nanowires in pure wet-chemical lithography-less process. Finding the optimal parameters for the surface growth process requires further search in parameters space. This surface growth procedure can be further improved to produce longer nanorods with better yields. Further development of the process described above should result in a technique to grow large aspect ratio gold and silver nanorods (*i.e.*, nano wires) with high yields. Later on, control over the position of the seed particles on the surface, possibly by some self-assembly technique and over growth orientation would lead to highly organized metal nanowire arrays on surfaces.

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