

## Negative-Type Photolithography of Functionalized Gold Nanoparticles

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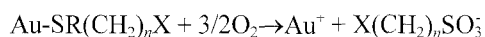
### Introduction

Gold nanostructures have been studied extensively for their potential applications in areas, such as catalysis, optics, electronics and biological devices.<sup>1-5</sup> In particular, the ability to generate patterns of various metals on a solid surface is important for optoelectronic technology and biotechnology. Patterning of nanoparticle assemblies can be achieved using a variety of methods. These include microcontact printing, micromolded hydrogel stamping and scanning probe dip-pen nanolithography.<sup>6-8</sup>

Recently, Kaltenpoth *et al.* reported that gold coated polystyrene beads could be adsorbed selectively onto areas functionalized with carboxyl groups via microcontact printing to form continuous patterns.<sup>9</sup> However, these methods involve time-consuming fabrication steps at high cost. Of them, the application of photolithographic technology to the generation of patterned functional images has attracted considerable attention in fundamental and applied research. For example, optical or electron beam lithography can be used to generate a mask through which a surface can be functionalized with molecules to which the nanoparticles can bind selectively.<sup>6,10</sup>

The process underlying photopatterning of self assembly monolayers (SAMs) on gold and silver is known at the phenomenological level.<sup>11,12</sup>

Alkanethiolates formed by the adsorption of alkanethiols are oxidized to alkylsulfonates upon exposure to UV light in the presence of air:



The mechanism of this reaction has been the subject of

some debate. Several studies have suggested that ozone is the active agent, and that irradiation by light with a wavelength < 200 nm is necessary to cause SAM photooxidation.<sup>13,14</sup> Recently, it was reported that oxidation can occur in the absence of ozone using a UV source emitting at 254 nm, where the reaction involved specific photochemical oxidation of the sulfur headgroup to a sulfonate species.<sup>15</sup>

In this study, thiol-stabilized gold nanoparticles were synthesized using a two-phase process. When the gold nanoparticles were exposed to UV light, photooxidation occurred and the alkylthiolates were converted to weakly bound alkylsulfonates, which were subsequently removed to leave gold patterns on the substrate. Overall, this method is a simple process for producing the gold nanoparticles patterns on a glass surface by UV irradiation.

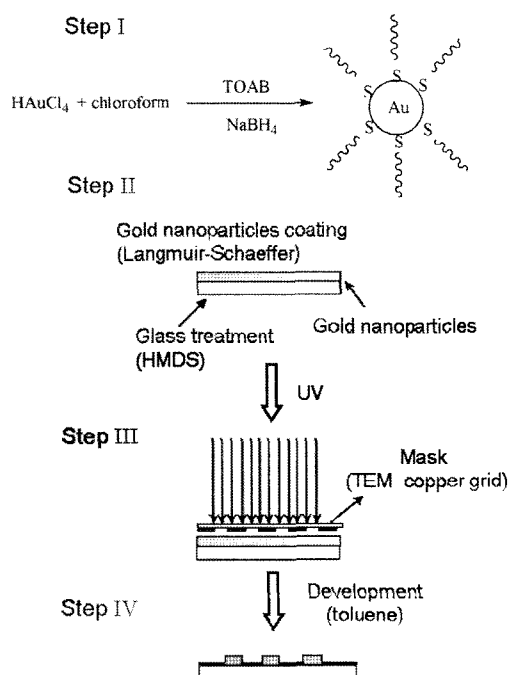
### Experimental

**Materials.** Hydrogen tetrachloroaurate(III) trihydrate ( $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ ), tetraoctylammonium bromide (TOAB), 1-dodecanethiol, chloroform, sodium borohydride ( $\text{NaBH}_4$ ), hexamethyldisilazane (HMDS) and absolute ethanol were obtained from Aldrich and used as received. Water was purified ( $18 \text{ M}\Omega \text{ cm}^2$ ) using a Millipore Milli-Q water-purification system and used in all experiments.

**Synthesis of Gold Nanoparticles.** The synthesis of thiol-stabilized gold nanoparticles involved the phase transfer of an anionic Au(III) complex from an aqueous to organic solution in a two-phase liquid system, followed by reduction with sodium borohydride in the presence of a thiol stabilizing ligand.<sup>16</sup>  $\text{HAuCl}_4$  (0.5 g) was dissolved in 50 mL deionized water, and phase transfer TOAB (0.1 g) was dissolved in 50 mL  $\text{CHCl}_3$ . Both solutions were combined to form a two-phase mixture, and stirred vigorously for 30 min at room temperature. The mixture was added to a separation funnel, and the organic layer ( $\text{CHCl}_3$ ) was separated. Dodecanethiol (1 mL) was then added to the solution and stirred continuously for 30 min. After 30 min, complete transfer of the  $\text{AuCl}_4^-$  anion to the organic phase was confirmed by the color changes in the two phases: the initially yellow water solution became completely colorless, while chloroform turned to orange. A solution of  $\text{NaBH}_4$  (1 M) was added dropwise to the organic solution with constant stirring, and the mixture was stirred for a further 3 h. Upon the addition of  $\text{NaBH}_4$ , the organic phase changed color from orange to deep brown within a few seconds. Finally, the organic phase was separated, washed repeatedly with deionized water and ethanol.

**Sample Preparation.** Figure 1 shows a schematic diagram of the process steps involved in the photolithography on the glass substrate. Immediately before use, the glass substrates were cleaned with acetone for 2 h. Hexamethyldisilazane (HMDS) was spin-coated onto a substrate surface

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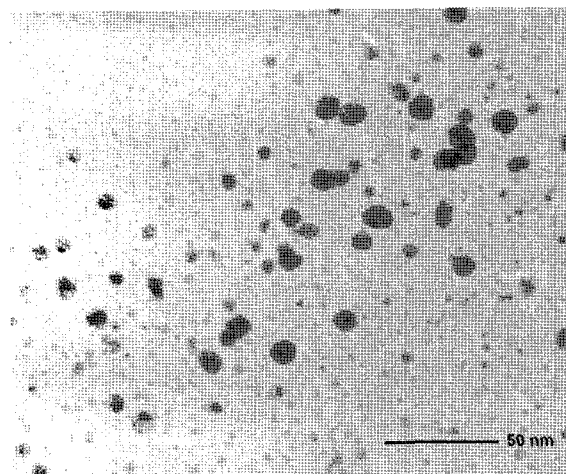
**Figure 1.** Schematic diagram of the procedure used to fabricate the gold nanoparticle patterns. The stabilized gold nanoparticles were synthesized using a two-phase reduction method (step I). A stabilized gold nanoparticle solution was deposited onto a hydrophobic substrate using the Langmuir-Schaeffer method (step II). The micro-patterns were fabricated by exposure to UV light (step III). After irradiation, the patterns were developed (step IV).

at a rotational speed at 1,200 rpm for 2 min. The substrate was then heated for 2 min at 120 °C on a hot plate. Silanization with HMDS made the substrates more hydrophobic and greatly improved the adhesion of gold nanoparticles monolayer to the substrate. The stabilized gold nanoparticle solution was deposited onto the hydrophobic substrate using the Langmuir-Schaeffer method.<sup>17</sup> For patterning of the samples, 200 mesh copper electron microscopy grids (square dimensions 90  $\mu\text{m} \times 90 \mu\text{m}$ , pitch dimensions: 35  $\mu\text{m} \times 35 \mu\text{m}$ ) placed directly onto the gold coated substrate. Micro-patterns were fabricated by exposure to UV light (1 W/cm<sup>2</sup>, Oriel Instrument NEWPORT 66923). After irradiation, the patterns were developed in toluene during the 30 s, and rinsed repeatedly with deionized water.

**Characterization.** The size, size distribution, elemental composition and structure of the gold nanoparticles were investigated by high-resolution transmission electron microscopy (HR-TEM, JEOL, 300KV). The patterns formed were examined by optical microscopy (Model: I Camscope G, Plus win, Korea). The surface profiler (KLA Tencor Alphastep IQ) was used for the thickness of gold patterns.

## Results and Discussion

TEM imaging of the thiol-stabilized gold nanoparticles



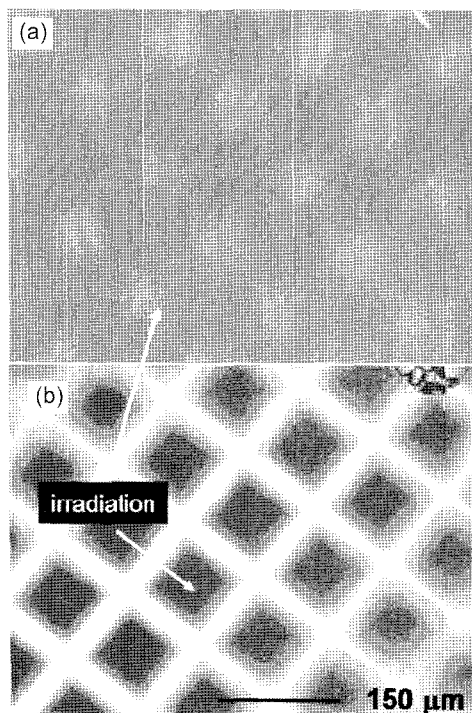
**Figure 2.** TEM image of the thiol-stabilized gold nanoparticles.

(Figure 2) shows that they have a spherical shape with diameter ranging from 2 to 13 nm.

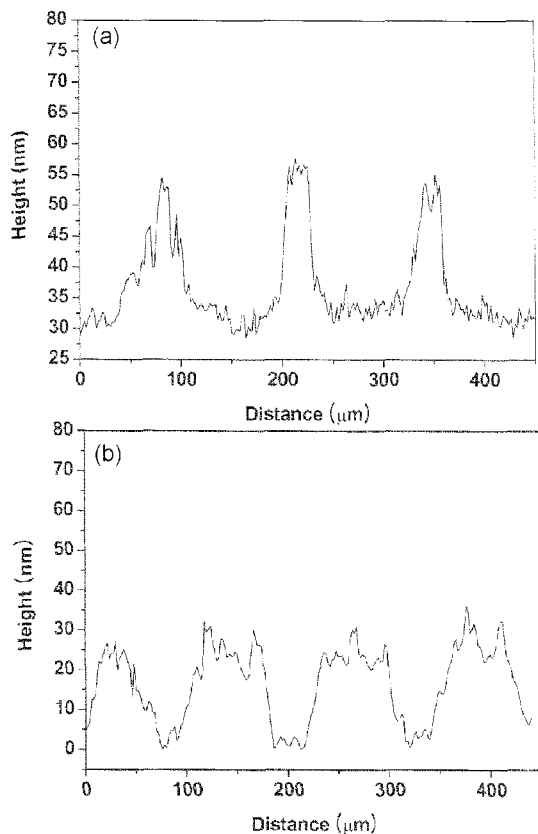
Figures 3(a) and 3(b) compare the optical micrographs of the sample of before and after rinsing with toluene. The stabilized gold nanoparticles behave as a negative resist. When the stabilized gold nanoparticles are exposed to UV light, photooxidation occurs and the alkylthiolates are converted to alkylsulfonates. Although, the square pattern could not be clearly observed (Figure 3(a)), it can be seen that unoxidized gold nanoparticles are completely removed after rinsing with toluene (Figure 3(b)). The irradiated areas (squares) show a dark contrast (Figure 3(b)). After exposure and rinsing, it was found that the micropatterns with width of approximately 76  $\mu\text{m} \times 76 \mu\text{m}$  formed on the glass substrate were a little smaller than on the TEM grid. In addition, the edges of the square micropatterns show different colors according to the irradiated and non-irradiated regions.

Figures 4(a) and 4(b) show the surface profiler of Langmuir-Schaeffer films of gold nanoparticles before (a) and after rinsing to remove unoxidized gold nanoparticles. The thickness of gold nanoparticles layer which was prepared on the glass by Langmuir-Schaeffer method was approximately 57 nm.

As can be seen in Figure 4(a), the thickness of oxidized regions decreased from ca. 57 nm to ca. 32 nm after irradiation. When the sequential rinsing process, the unoxidized gold nanoparticles were removed while oxidized gold nanoparticles were maintained on the glass substrate. This indicated that the thickness of metal layer is reduced by UV light, and final well-defined micropatterns (ca. 28 nm) were observed. These results are in good agreement with the optical micrographs in Figure 3. Consequently, it was speculated that the exposed gold nanoparticles should lead to depassivation of the nanoparticles followed by coagulation or aggregation, while the unexposed nanoparticles remain



**Figure 3.** Optical micrograph of the gold nanoparticles patterns formed on the glass substrate (a) before and (b) after rinsing to remove unoxidized gold nanoparticles.



**Figure 4.** The surface profiler results: (a) before and (b) after rinsing to remove unoxidized gold nanoparticles.

stabilized. Subsequently, the width and thickness of the oxidized area suggests that coagulation or aggregation proceeds through collapse of the structure from its edges, leading to dense continuous structures and smaller square pattern sizes and thicknesses. Further study should be performed to identify the morphology of gold nanoparticles and structural development of gold patterns during the UV irradiation and washing processes.

## Conclusions

Thiol-stabilized gold nanoparticles ranging in size from 2 to 13 nm were synthesized using a two-phase reduction method. The thiol-stabilized gold nanoparticles formed micropatterns on a glass substrate through UV irradiation and chemical oxidation. Overall, the micro-pattern obtained through this simple procedure has great potential in the electronics industry.

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