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Fabrication of Designed Architectures of Au Nanoparticles on Solid Substrate with Printed Self-Assembled Monolayers as Templates

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This paper provides a convenient method for fabricating architectures of Au nanoparticles on solid substrate, with precise position and density control. Our strategy is to modify Au substrate with self-assembled monolayers (SAMs) terminated with different functional groups. They were chosen to be −CH$_3$/−NH$_2$ or −CH$_3$/−SH according to their affinities to Au nanoparticle. Au nanoparticles assemble selectively on −NH$_2$ or −SH terminated locations, the −NH$_2$ functional group binding electrostatically to the nanoparticles whereas the −SH groups bonding chemically. The SAMs, acting as guiding templates for Au nanoparticles, were fabricated by the microcontact printing (μCP) technique. A patterned or unpatterned SAM was prepared by using patterned or unpatterned poly(dimethyl)siloxane (PDMS) stamp, respectively. The coverage of −CH$_3$ terminated SAM in the contact region is controlled by changing the concentration of "ink" solution for the stamp. After immersing the printed SAM into −SH or −NH$_2$ thiol solutions for 2 h, a mixed SAM with a predetermined coverage of −SH or −NH$_2$ was formed in the contact regions, and a pure −SH or −NH$_2$ SAM was formed in the intervening area. The position and density of nanoparticles on the surface were determined by the distribution of the underlying functional groups.

Introduction

Driven by the increasing need for miniaturized, faster, and more powerful electronics, strong research interests have been activated to fabricate new generation electronic or optical devices, which are based on a quantum mechanism. Nanoparticles readily exhibit quantum phenomena[1−3] and are hopefully the ideal candidates as building blocks for the new generation devices. To harness their quantum property within a novel device, however, requires attaching them onto solid surface, precisely controlling their size and position, and electrically connecting them to the macroscopic world as well. To fabricate a nanoparticle-based quantum electronic device, Samuelson et al. drove a 50 nm individual Au particle into the gap of metal leads using atomic force microscopy (AFM).[4] Despite the capability to manipulate an individual nanoparticle on a precision of angstrom level, this technique is still far from industrial applications due to the slow rate of AFM. Natan et al.[5,6] first exploited the approach to spontaneously assemble colloidal Au and Ag particles onto chemically functionalized substrates. This method, simple and fast, generally offers limited control over the coverage and the spatial distribution of the particles on the surface.[7] Sato et al. combined this method with conventional electron beam lithography techniques and prepared patterned Au nanoparicle structures for a single electron device.[8] Well, it is still a practical challenge to control simultaneously the density and pattern of nanoparticles.

We have made continuous efforts at fabricating Au, CdS, and PbS nanoparticle assemblies on Au and Si using a similar strategy for the purpose of SERS, electrochemistry, and room-temperature single electron tunneling studies.[9−14] To create an appropriate interaction between the self-assembled monolayer (SAM) linker and colloidal nanoparticles, AFM-based direct force measurements have been carried out for understanding the nature and strength of various interactions.[15−18]

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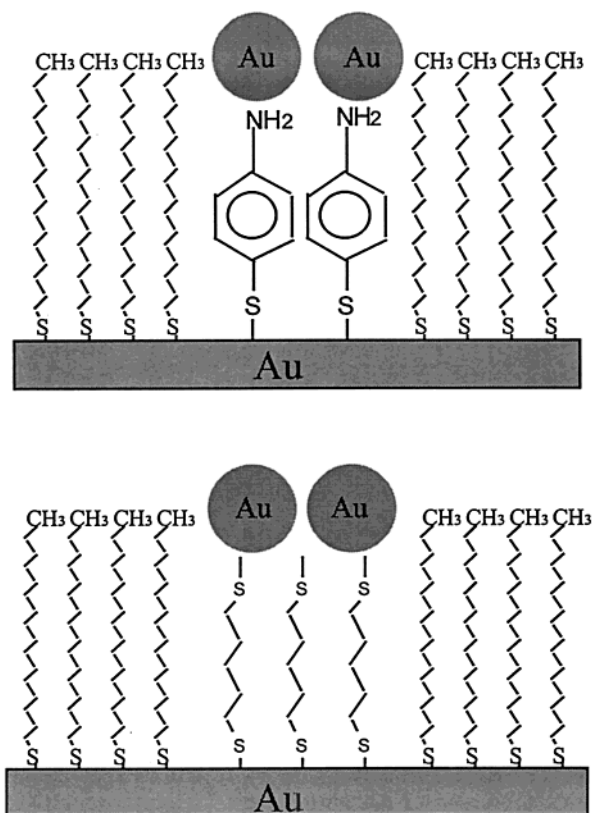
Figure 1. Strategy for fabricating designed Au nanoparticle structures on solid surface directed by printed self-assembled monolayer: (a) Au colloidal in water; (b) Au nanoparticles in hexane.

The present work is built on the above studies by developing a facile procedure to create preordained Au nanoparticle architectures following thermodynamic predictions, rather than a rate-determining and/or concentration-controlling mechanism. Our strategy, schematically shown in Figure 1, is to modify the substrate by chemically patterned SAMs for Au nanoparticles to spontaneously assemble onto the desired locations. Considering the nature and strength of the anchoring force, the patterned SAMs are designed to be terminated with $-CH_3/-NH_2$ or $-CH_3/-SH$ groups, and two different kinds of Au colloidal suspensions are used. The key point here is to fully use microcontact printing (μCP), to fabricate not only patterned SAM but also mixed SAM with controlled density of reactive functional groups in a predeterministic way.[19–21] Integrating these two capabilities of μCP, a patterned SAM with controlled coverage of reactive functional groups in each region was fabricated using a patterned PDMS stamp in the printing process. Using these SAMs as templates, we can make precisely position controlled, density controlled, or even simultaneously position and density controlled Au nanoparticle architectures on the substrates.

Experimental Section

Materials. 1,6-Hexanedithiol ($HS(CH_2)_6SH$) was synthesized and purified in our laboratory. 4-Aminothiophenol (4-$H_2NC_6H_4$-SH) and hexadecylmercaptan ($HS(CH_2)_{15}CH_3$) were purchased

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from T.C.I. Tokyo KASEI. Chlorauric acid ($HAuCl_4 \cdot 3H_2O$), trisodium citrate dehydrate, sodium oleate, and magnesium chloride were purchased from Aldrich. Ultrapure water with a resistance of 17 M$\Omega\cdot$cm was used throughout the experiments. Two different Au colloidal suspensions, one in aqueous medium and the other in organic medium, were prepared as described below.

Au Colloid Preparation. Monodispersed Au colloid in water was prepared following the recipe described in ref 22. $HAuCl_4$ was boiled with trisodium citrate in an aqueous solution for 10–15 min to form a colloidal suspension. By changing the molar ratio of trisodium citrate to $HAuCl_4$ in the solution, monodispersed Au colloids with different average sizes can be obtained. In this work, the molar ratio was set to 1.56. The formation of the Au colloidal particles was examined using a UV–vis spectrum, which yielded a strong surface plasma resonance at 519 nm, characteristic of monodispersed colloidal Au. The particle size was 12 $\pm$ 4 nm, as confirmed by transmission electron microscopy (TEM).

An Au colloidal suspension in organic solvent was prepared by phase transfer method.[23] Hexane and sodium oleate was added to the Au colloidal suspension in water. The mixture was emulsified by vigorous stirring at room temperature for 1 h. Magnesium chloride in water (0.08 g/mL) was added to the mixture while stirring. On standing for 4 h, the mixture was transformed from an emulsion into two liquid layers: the bottom layer was a transparent and colorless aqueous solution, and the top layer was dark red Au colloidal suspension in hexane, which was isolated using a separatory funnel.

Fabrication of Patterned and Mixed SAMs by μCP. Au substrates were prepared by sputtering high-purity Au onto cleaned Si(100) wafers with a Ti adhesion layer (250 nm Au and 10 nm Ti). The resulted Au substrates were cleaned in a piranha solution (98% H_2SO_4:30% H_2O_2, 3:1 v/v, 90 °C, 3 min) prior to derivatization.

Patterned SAM and unpatterned mixed SAMs on Au substrates were fabricated using patterned and unpatterned PDMS stamps, respectively. These stamps were prepared from Sylgard 184 (Dow Corning, Midland, MI) using the method described by Whitesides et al. and Delamarche et al.[19–21] Before use, the stamps were sonicated for 30 s in ethanol and rinsed successively with heptane and ethanol. After drying with a flowing stream of nitrogen, the stamp was "inked" with ethanol solution of hexadecanethiol. After the bulk of the ink liquid was evaporated, the stamp was brought into contact with a clean Au substrate for 10 s. The resulting substrate was either patterned with SAM or completely covered with SAM depending on the stamp used. The formed $-CH_3$ terminated SAM was either closely packed or loosely packed depending on the concentration of the "ink". The substrate was then immersed in another thiol (1 mM $HS(CH_2)_6$-SH or 4-$H_2NC_6H_4SH$ in ethanol) for 2 h, a compromise time chosen to form a closely packed SAM in the uncontacted regions and reduce the replacement of $HS(CH_2)_{15}CH_3$ by $HS(CH_2)_6SH$ or 4-H_2-NC_6H_4SH thiol in the contact regions. Consequently, any area left uncoated with $-CH_3$ SAM after stamping was now coated with SAM of this thiol. Thereafter, the substrate was sonicated in ethanol (30 s) and water (30 s) successively and dried in a stream of nitrogen. Finally, Au nanoparticle architectures were formed by immersing the modified Au substrate into an Au colloidal suspension for a period of time.

All the resulting SAM and Au nanoparticle architectures were characterized using scanning probe microscopy (SPM). Atomic force microscope (AFM), friction force microscope (FFM), and tapping mode atomic force microscope (TM AFM) imaging were performed with a multimode Nanoscope IIIA system (Digital Instruments).

Results and Discussion

1. Position Au Nanoparticles onto Given Areas by Self-Assembly from Au Colloidal Aqueous Solution. Previous work demonstrated that exposing a $-NH_2$ functional group modified surface to aqueous Au colloidal suspensions could spontaneously form well-defined uni-

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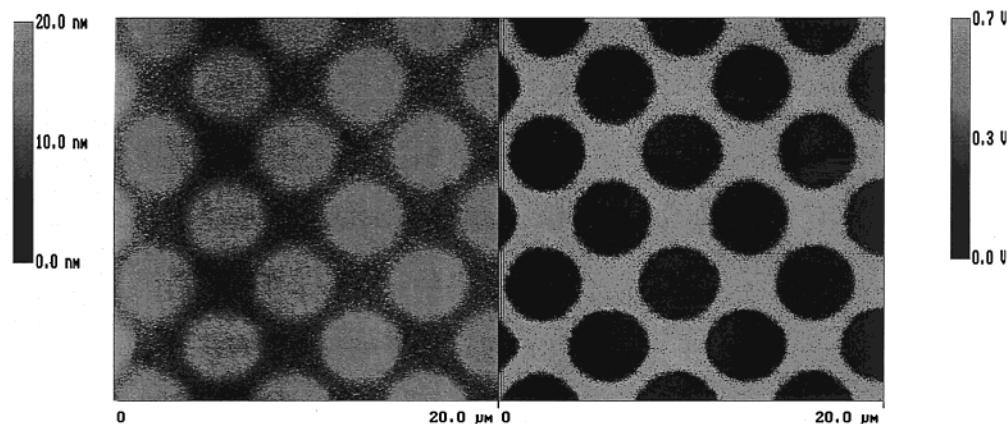(23) Hirai, H.; Aizawa, H. *J. Colloid Interface Sci.* **1993**, *161*, 471.

Figure 2. AFM topographic (left) and friction force images (right) of patterned SAM terminated with $-CH_3$ and $-NH_2$ groups acquired with a Si_3N_4 tip. The images were collected concurrently, and the scan direction was from left to right.

form nanometer-scale architecture.[5−7,9−12] To position the Au nanoparticles to the desired locations on solid surfaces using essentially the same strategy of self-assembly as described,[5−7,9−12] a patterned SAM terminated with different functional groups is needed, which is designed to have different affinities to Au nanoparticles. We used μCP to prepare a patterned SAM. This method has been used to pattern thiol monolayers on Au to form deterministic chemical patterns that can control the interfacial properties of the substrate such as its wetting or chemical reactivity.[24] In this work, before patterning, a $-CH_3$ functionalized surface prepared by self-assembling in hexadecanethiol ethanol solution for 24 h was tested for its adsorptive characteristics to Au nanoparticle. It was characterized by TM AFM before and after being immersed into Au colloidal solution for the same period of time as $-NH_2$ surface (for 6 h). No nanoparticles were found on the $-CH_3$ surface after exposing the substrate in Au particle solutions for 6 h, indicating that Au nanoparticles cannot anchor onto a closely packed $-CH_3$ surface. Accordingly, a patterned SAM was designed with regions terminating with a $-NH_2$ group onto which the nanoparticles are to be positioned and the remaining area terminating with a $-CH_3$ group. A patterned PDMS stamp with protruding features (3 μm diameter circles) was inked with 1 mM ethanol solution of hexadecanethiol and then brought into contact with Au substrate for 10 s. In the regions contacted with the stamp, a $-CH_3$ terminated SAM was formed by transferring the hexadecanethiol from PDMS stamp to Au. Upon putting this derived substrate into 1 mM 4-aminothiophenol solution in ethanol for 2 h, the uncontacted regions were filled with a SAM terminated with $-NH_2$. Figure 2 shows the AFM topographic and friction force image of the patterned SAM, which were recorded simultaneously. The scan direction is left to right (trace) at a rate of 2 Hz using a commercial Si_3N_4 AFM tip. In the AFM topographic image, the bright and the dark portions correspond to the higher and the lower regions of the monolayer surface, respectively. As expected, the higher regions in the topographic image arise from $-CH_3$ terminated SAMs which have a long carbon chain of 16. The lower regions correspond to $-NH_2$ terminated SAMs formed from 4-aminothiophenol. In the friction force image, the contrast reversed; the $-NH_2$ terminated regions exhibit higher frictional force than $-CH_3$ regions due to its higher surface free energy and the hydrophilic Si_3N_4 tip being used. This patterned SAM was immersed into Au colloidal aqueous solution for 6 h for Au nanoparticles
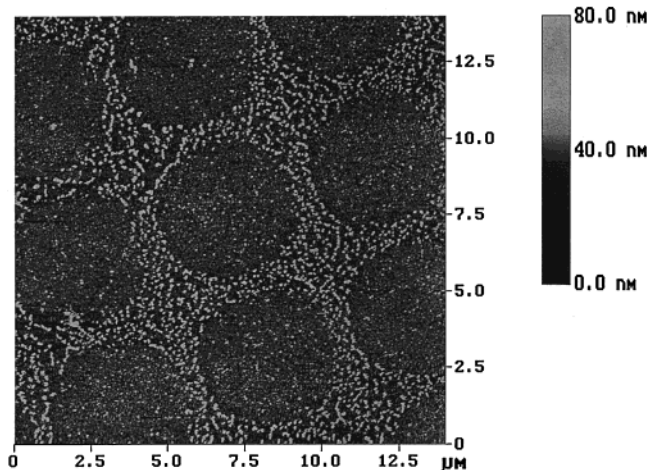

Figure 3. TM AFM image of patterned Au nanoparticles structure constructed by selectively anchoring Au colloidal on $-NH_2$ regions using a patterned SAM as a template.

assembling. From the TM AFM image (Figure 3) of the resulting Au nanoparticle structure, it can be clearly seen that the Au particles were following the geometry of the underlying active regions, selectively adsorbed on $-NH_2$ regions with submonolayer coverage. The size of Au nanoparticles is 35−40 nm measured from the TM AFM image, larger than determined from TEM and SEM (12 ± 4 nm). This magnification effect is attributed to the convolution of true particles with the AFM tip, which is often observed in AFM imaging.[25] In fact, if a section analysis is performed on the AFM image, it is found that the height of the particles is identical with that from TEM and SEM.

The surface of Au nanoparticle in water, formed by reduction of $AuCl_4^-$ with trisodium citrate, is negatively charged due to the adsorption of anions (e.g., citrate, chloride, Au chloride ($AuCl_4^-$), and hydroxide).[26,27] The driving force for the negatively charged Au nanoparticles to immobilize on $-NH_2$ terminated surface is electrostatic attractive force.[28] In our previous work, it has been demonstrated that the coverage of the Au nanoparticles on $-NH_2$ surface was closely related to the pH value of

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the Au colloidal solution.[9] When the pH value of the colloidal solution is higher than the surface pK_a of 4-aminomercaptan formed SAM, the positive charge of the $-NH_2$ surface decreases, and as a result, few nanoparticles were anchored on the substrate. Whereas, when the pH value of colloidal solution is lower than the $-NH_2$ surface pK_a, protonation makes the amino group positively charged. Consequently, the adsorption of Au nanoparticles gets easier, and extensive coverage of Au nanoparticle assemblies can be obtained. Since no electrostatic attractive force exists between the negatively charged Au nanoparticles and $-CH_3$ surface, and the hydrophobic property of $-CH_3$ terminated surface does not facilitate to access for the hydrophilic Au nanoparticles, we did not found any Au nanoparticle attached to the closely packed $-CH_3$ surface as stated above. Different from the case of pure $-CH_3$ surface, however, we do find a few of nanoparticles on the $-CH_3$ regions of the patterned SAM surface. This possibly arises from $-CH_3/-NH_2$ mixed nature on the nominal $-CH_3$ regions. By microcontact printing hexadecanethiol, we created circular $-CH_3$ patterns on an Au surface. When this substrate was put into a 4-aminothiophenol solution, the 4-aminothiophenol molecules not only covered the bare Au regions but also entered into the loosely packed $-CH_3$ regions. As a result, the $-CH_3$ region is only nominal, and a mixed monolayer of hexadecanethiol and 4-aminothiophenol has been formed during the μCP process. This hypothesis was also supported by force volume image in our other paper.[16] In fact, the formation of a defect-free SAM is possible by inking the stamp with a higher concentration of hexadecanethiol solution.[19-21]

Fabrication of Chemically Bonded and Patterned Au Nanoparticle Structures on Solid Surface. Organic molecules containing an $-SH$ group can be spontaneously and chemically adsorbed onto the Au surface to form well-organized, closely packed, self-assembled monolayers (SAMs) via a Au$-$S bond.[29] It was not difficult to think of its reverse process, chemically bonding colloidal Au particles on the $-SH$ surface to form two-dimensional arrays of Au nanoparticles. Using direct force measurements with AFM, we studied the replacement adsorption of 4-mercaptopyridine onto citrate ions preadsorbed Au surface in aqueous solution. The result illustrated the possibility to immobilize Au colloids onto solid substrate via $-SH$ terminated SAM.[15] However, it was found that the Au nanoparticles in water were difficult to immobilize on the $-SH$ terminated surface, and the coverage was much lower than on the $-NH_2$ terminated surface. Although the Au nanoparticles can be covalently bound to the $-SH$ group, the hydrophobic property of the $-SH$ surface is not facile for negatively charged Au particles to access and adsorb. To make two-dimensional Au nanoparticle self-assembly arrays by chemically anchoring on a solid surface, we prepared Au colloidal solution in hexane by the phase transfer method.[23] Figure 4 presents a TM AFM image of Au nanoparticle arrays fabricated by immersing the $-SH$ terminated surface to this solution for 30 min. Obviously the Au nanoparticles were scattered over the surface with submonolayer coverage. Sonicating this sample in hexane does not influence the coverage of Au particles, suggesting the immobilization of the particles on the surface is via the strong covalent Au$-$S bond. On the contrary, some of the Au nanoparticles were removed from the $-NH_2$ surface after sonication in water. Patterned SAM terminated with $-CH_3$ and $-SH$ groups was prepared following a similar procedure for patterning
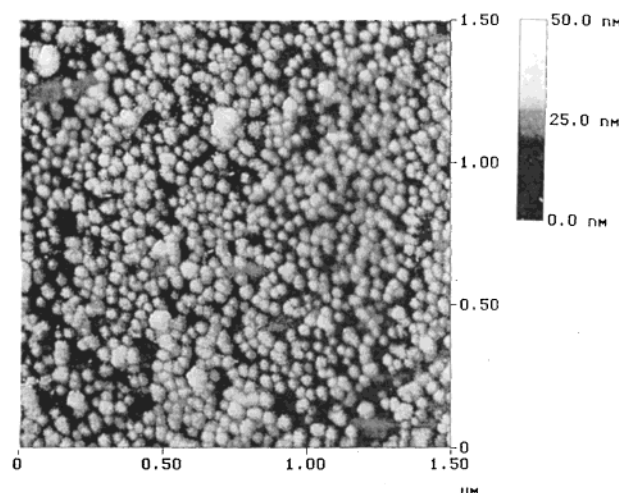

Figure 4. TM AFM image of Au nanoparticles assembled onto $-SH$ terminated SAM modified surface from colloidal Au in hexane.

$-CH_3/-NH_2$ SAM. During the μCP process, we changed the ink solution to 10 mM hexadecanethiol ethanol solution, concentrated enough for defect-free $-CH_3$ SAM in the contact regions. And 4-aminothiophenol solution was replaced with $HS(CH_2)_6SH$ solution to form a $-SH$ terminated SAM in the uncontacted regions. Figure 5 gives the AFM and FFM image of the patterned SAM. The higher parts in the topography image corresponding to $HS(CH_2)_{15}CH_3$ SAMs show low friction force in the FFM image, while the lower parts corresponding to $HS(CH_2)_6$-SH SAMs exhibit high friction force. The reason behind is that the $-SH$ surface has a higher free energy than $-CH_3$ terminated surface. Immersing this patterned substrate into the Au colloidal solution in hexane, we got a patterned Au nanoparticle assembly array (Figure 6). Obviously, it is the patterned distribution of substrates which determines where nanoparticles are allowed or not allowed to immobilize. The Au nanoparticles selectively deposited on the $-SH$ region. No particles were observed on the $-CH_3$ regions, indicating that a closely packed SAM indeed formed in the contact regions during printing using 10 mM hexadecanethiol as ink solution. There is a tendency for the particles to stick to the boundary between neighboring regions; the origin of this edge effect is not clear at present. Similar phenomena had been observed by Sato et al., who suggested that if the edge effect encourages the formation of a one-dimensional coagulation aggregate on the pattern edge, this kind of method may be used to realize multiple-tunnel junctions of an Au-particle string.[8]

Simultaneous Pattern Fabrication and Density Control of Au Nanoparticles on Solid Substrate by the μCP Method. Electrochemical studies have demonstrated that Au clusters protected by thiol monolayer (MPCs) behave like nanoelectrodes with respect to diffusion.[30,31] At room temperature, the solutions of MPCs with monodisperse cores display an electrochemical "ensemble Coulomb staircase",[32,33] analogous to Coulomb staircases revealed by STM.[34] However, this kind of

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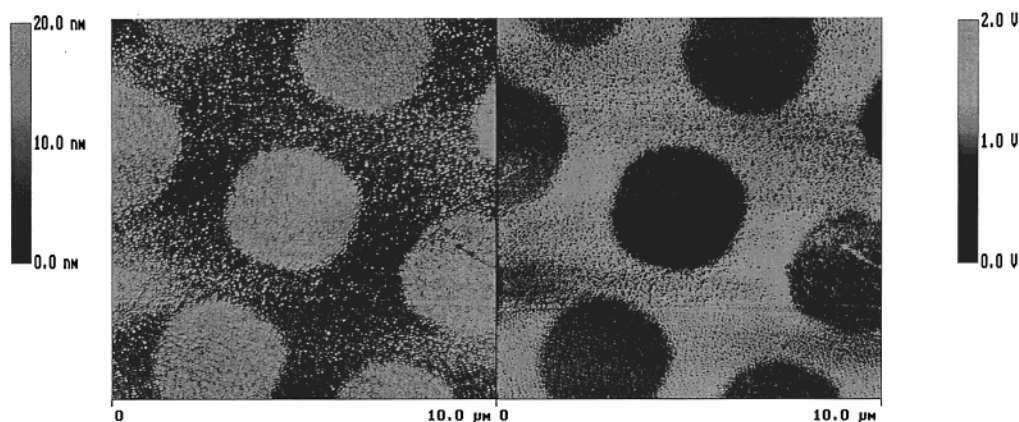
Figure 5. AFM topographic (left) and friction force images (right) of patterned SAM terminated with $-CH_3$ and $-SH$ groups measured with a Si_3N_4 tip. The images were collected concurrently, and the scan direction was from left to right.
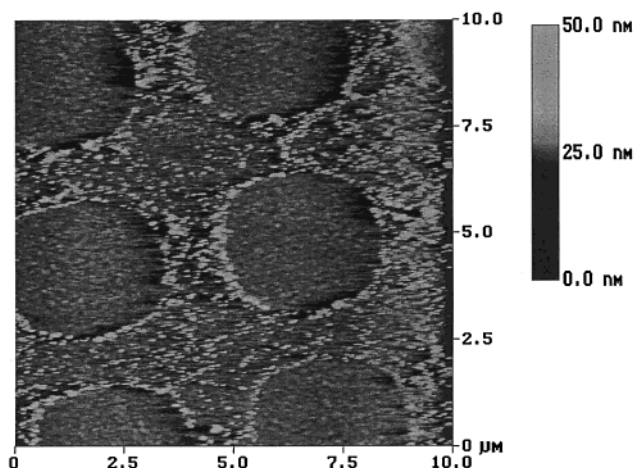

Figure 6. TM AFM image of patterned Au nanoparticles structure constructed by selectively anchoring on $-SH$ regions using patterned SAM as a template from Au colloidal in hexane.

electrochemical "ensemble Coulomb staircase" behavior has not been observed so far on the mono- or multilayer nanoparticle structures on solid substrate, which stemmed from the nonuniformity of space arrangement of the Au nanoparticles.[35] In fact, it is difficult to measure the electrical property of an individual nanocrystal since it has to be isolated on the surface.[36] To pursue density-controlled nanoparticle architectures, Natan et al. reported a detailed study on the kinetics of colloidal Au particles binding to functionalized substrates.[7] However, the utility of nanoparticle-based devices, and particularly those based on self-assembly, will ultimately hinge on the reproducible nanostructures. Using mixed SAM with controlled coverage of reactive functional group as template should be an effective way to reproducibly fabricate relatively low-density nanostructures since it follows thermodynamic predictions. The conventional way to make a mixed SAM is putting an Au substrate into a mixed thiol solution consisting of two or more kinds of thiol molecules. The composition of the obtained mixed SAM depends on the concentration of thiols in solution and also depends strongly on the thiol molecular structure (carbon chain and functional groups).[37] It is not so easy to form a

preordained SAM structure with controlled coverage of reactive functional group for Au nanoparticles to selectively attach.

In our previous work, a patterned SAM fabricated by μCP was imaged by force volume imaging technique (FV).[38] Our results demonstrated that a mixed SAM could be formed on the nominal $-CH_3$ regions during μCP process.[16] In this work, as mentioned above, that some nanoparticles were observed on the nominal $-CH_3$ regions of $-CH_3/-NH_2$ patterned SAM gives additional strong evidence. All these observations remind us that the μCP technique is not only a simple method to make patterned SAM but also an effective way to form mixed SAM. The coverage of certain functional group in the mixed SAM is predetermined regardless of the thiol molecular structure. Recent research also demonstrated that the coverage in a SAM formed by μCP was determined by the amount of thiol present in the stamp, which was controlled by changing the concentration of the thiol "ink" solution.[19-21]

In this work, we tried to make an unpatterned mixed SAM with controlled coverage of reactive functional groups using μCP technique. Here, a flat PDMS stamp was used instead of a patterned one. The "ink" was chosen to be 0.5 mM hexadecanethiol solution in ethanol as to form a loosely packed $-CH_3$ SAM on Au, with the coverage being controlled by the concentration of the "ink" solution. Consequently, a mixed SAM with controlled coverage of $-SH$ group was obtained by putting this modified substrate into a $HS(CH_2)_6SH$ solution for 2 h. Since Au particles only selectively assemble on $-SH$ groups, the Au nanoparticle architecture on the substrate was predetermined by the mixed SAM functioned as a guiding template for Au nanoparticle assembling from Au colloidal solution. The TM AFM image (Figure 7) of thus prepared nanostructures shows clearly that the coverage of the Au nanoparticles is much lower than fabricated from a pure $-SH$ SAM template. In fact, using this method, a very scattered, even isolated Au nanoparticle structure can be formed, which is critical for observing the room-temperature single electron-tunneling phenomenon. Since this approach for controlling coverage of nanoparticles on solid surface follows thermodynamic predictions, high reproducibility of nanoparticle structure was achieved.

So far, it remains a practical challenge to control simultaneously the density and positions of nanoparticles using the self-organization process. Well, the μCP method provides us an artifice to prepare not only deterministic chemical patterns[24] but also mixed SAMs with controlled

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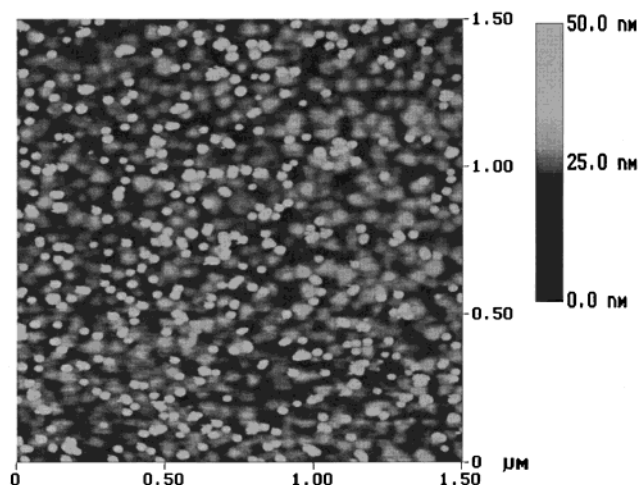
Figure 7. TM AFM image of Au nanoparticles structure with controlled Au nanoparticles density on the solid surface predetermined by using a mixed SAM with controlled −SH coverage as a directing assembly template.

Figure 8. A demonstration of Au nanoparticle structrures with simultaneous pattern fabrication and density controlling by using a patterned SAM, which includes different regions with different coverage of −SH reactive functional groups as a directing assembly template.

coverage of functional groups.[19−21] By combining these two abilities of μCP, a patterned SAM with controlled coverage of functional groups within each region can be prepared. Using this patterned SAM as a template to direct nanoparticles assembling makes it possible, for the first time to our knowledge, to combine area-selective immobilization with density control of Au nanoparticles in each region. A patterned PDMS stamp was first inked with 1 mM hexadecanethiol ethanol solution and then put into contact with a clean Au surface for 10 s, resulting in a loosely packed −CH$_3$ terminated SAM in the contacted regions. By immersing this into 1 mM HS(CH$_2$)$_6$SH solution for 2 h, a patterned SAM consisting of two kinds of SAM regions was finally formed. One is a mixed SAM terminated with −SH and −CH$_3$ having predetermined coverage by μCP; the other was a pure −SH terminated SAM. Exposing this patterned SAM into Au colloidal solution in hexane for 30 min, we obtained a simultaneously density- and position-controlled Au nanoparticle structure, which includes regions with a different density of nanoparticles. On the −SH region, the coverage of nanoparticles is very similar to that on the pure −SH surface, while much higher than on the nominal −CH$_3$ regions (Figure 8). This is because the −SH fraction in the nominal −CH$_3$ regions was controlled much lower than the pure −SH regions. In the meantime, the number of nanoparticles (the density of nanoparticles) on the nominal −CH$_3$ regions was also less than that on the unpatterned mixed SAM stated above. This is because we chose 1 mM hexadecanethiol ethanol solution, while for the unpat-
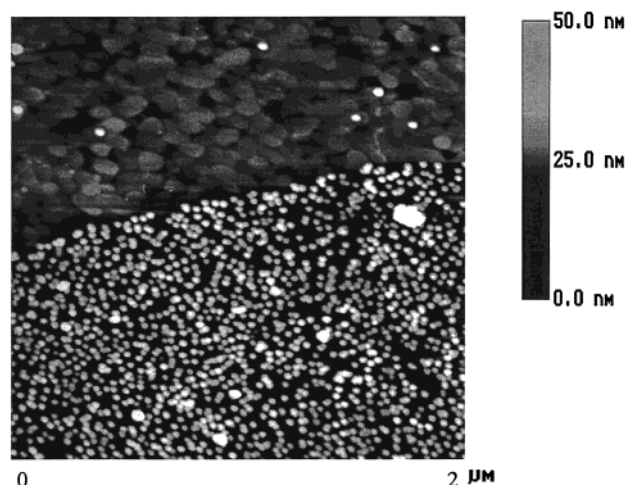
terned mixed SAM, 0.5 mM concentration was chosen as ink. Therefore, the coverage of −CH$_3$ groups was higher than the unpatterned mixed SAM, while the density of −SH groups was lower on this SAM.

Conclusions

The method we report here gives us the ability to fabricate Au nanoparticle architectures, with accuracy as to where nanoparticles are allowed or not allowed to immobilize. The μCP technique provides us a route to form a printed SAM, which serves as template to guide nanoparticle deposition. The positions of nanoparticles on the surface were determined by the patterned SAMs with −NH$_2$/−CH$_3$ or −SH/−CH$_3$ terminal groups. The regions where nanoparticles were designed to immobilize were terminated with −NH$_2$ and/or −SH; the other regions were terminated with −CH$_3$. By changing the distribution of reactive functional groups in a mixed SAM during μCP, we could control the density of nanoparticles on the surface. With a patterned SAM as template, within which the density of reactive functional groups in each region was controlled, a simultaneously position- and density-controlled Au nanoparticle structure was obtained by self-assembling following the thermodynamic prediction. We believed that our approach for successful and reproducible fabrication of nanostructures made a further step for manufacturing nanoparticle-based devices.