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Seed-mediated growth of gold nanoparticles using self-assembled monolayer of polystyrene microspheres as nanotemplate arrays*

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Arrays of noble metal nanoparticles show potential applications in (bio-)sensing, optical storage, surface-enhanced spectroscopy, and waveguides. For all such potential devices, controlling the size, morphology, and interparticle spacing of the nanoparticles is very important. Here, we combine seed-mediated growth with nanosphere lithography to study the controllable growth of gold nanoparticles (Au NPs), in which the self-assembly monolayer of polystyrene (PS) on a silicon surface is used to guide the modification of alkanesilanes and the subsequent adsorption of gold seeds; seed-mediated growth is applied to controlling the morphology and size of Au NPs. The size of adsorption region (determining the number of adsorbed gold seeds) is controlled by etching PS microspheres with oxygen plasma or annealing PS microspheres at the glass transition temperature. The size and morphology of the Au NPs are controlled by changing growth conditions. In such a way, we have achieved the dual control of the obtained Au NPs. Preliminary results show that this strategy holds a great promise. This approach can also be extended to a wide range of materials and substrates.

Keywords: self-assembling, polystyrene microspheres, gold nanoparticles, seed-mediated growth
PACC: 6146, 8110D, 8160, 8270D

1. Introduction

Recently, there has been aroused an intense interest in the surface plasmonic properties of noble metal nanostructures, as they exhibit selective photon absorption and scattering. These plasmonic properties are used in a variety of applications including optical devices,[1,2] optical energy transport,[3−6] chemical and biological sensors,[7−10] surface-enhanced spectroscopy,[11,12] and near-field microscopy.[13] Characteristically, surface plasmons are excited when a specific wavelength of light impinges on a noble metal particle and causes the plasma of conduction electrons to oscillate collectively.[14] And the frequency of collective oscillation is highly dependent on the composition, size, shape, and interparticle spacing of particles.[15,16] Therefore, it is very important for device applications to pattern the particles and control the shape and size of the particles at the anchoring positions.

There are currently two cheap, simple, and convenient strategies for the patterning of noble metal nanostructures on surfaces. One involves stamp preparation, microcontact printing functional molecules on surfaces, selective adsorption of nanoparticles or seeds, then growth of the seeds in solution.[17−19] This method is advantageous to controlling the size, shape of particles through suitable adjustment of the synthesis conditions, etc. However, the feature size of the pattern is restricted by diffraction-limited resolution as the stamps are prepared through traditional photolithographic tech-

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nique. And submicrometre size patterns are expensive and inconvenient.[20] The other is nanosphere lithography (NSL) that uses self-assembled arrays of colloidal particles as sacrificial masks, and the metals are deposited through the interstitial pores between the particles. The size and shape of the deposited particles can be manipulated by annealing the colloidal particles,[21,22] angle-resolved deposition,[23] and the multiple layering of colloidal particles.[24] But the size and spacing of the mask holes are coupled, and thus these properties cannot be separately controlled.

Herein we develop a method to combine the two strategies to achieve noble metal nanostructure arrays with flexible feature size and spacing in a submicrometre size range, and adjustable shape by growth conditions in solution. We use a polystyrene (PS) colloidal particle self-assembly monolayer (SAM) to determine the pattern and spacing, and control the size and shape by changing growth conditions in solution. Our strategy is shown in Fig.1. First, the close-packed PS SAM is covered on the hydroxyl-terminated silicon substrates. Second, oxygen plasma is used to burn PS SAM into a nonclose-packed pattern, and annealing is used to make the PS particles partly softened and stick to the substrate. Third, the regions unoccupied by PS particles are modified with octadecyltrichlorosilane (OTS) molecules. Fourth, the PS particles are removed by ultrasonic cleaning, and the regions formerly occupied by PS particles are modified with 3-aminopropytrieththoxysilane molecules (APTES). Fifth, seeds of gold nanoparticles (Au NPs) are selectively adsorbed in the APTES modified regions. Sixth, seed-mediated growth of metal nanostructures takes effect in a growth solution. The spacing can be controlled by PS SAM with different particle diameters, and the size of seed-adsorbed regions can be controlled by the duration of annealing or oxygen plasma etching. Although we have shown only the controllable growth of Au NPs in the seed-adsorbed regions, the growth of triangle- and hexagon-shaped gold nanorods is feasible in our system as it has been reported that these shapes can directly grow up from surface-attached seeds.[18,19] Additionally, our investigation is significant for extending the applications of nanosphere lithography.

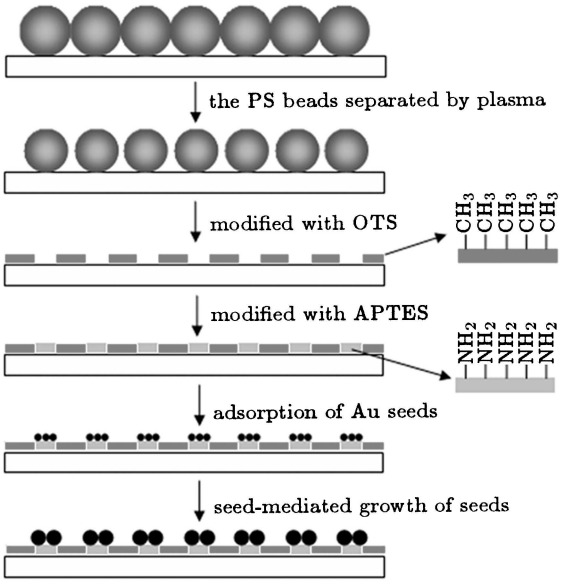


Fig.1. Strategy for patterning gold nanoparticle arrays on silicon surface directly by PS self-assembled monolayers. First, the non-closely packed PS monolayer is obtained by oxygen plasma, and it is used to guide the modification with OTS; then the PS beads are removed by sonication, the amino-terminated APTES layers are formed in the bare regions, i.e. at the previous positions of PS beads; third, the Au seeds are adsorbed in the amino-functionalized regions; finally, the seed-mediated growth method is used to control the size and morphology of the Au NPs.

2. Experiment

2.1. Materials

3-Aminopropyltriethoxysilane (Acros), octadecyltrichlorosilane (Avocado), trisodium citrate (Alfa), sodium borohydride (Alfa), chlorauric acid ($HAuCl_4{\cdot}3H_2O$) (Alfa), cetyltrimethylammonium bromide (Alfa), L-ascorbic acid (Alfa), anhydrous hexane (Alfa) and polystyrene microspheres (Microparticles GmBH, Germany) are all used as received. Milli-Q water (18MΩ·cm, resistivity) is used for all solution preparations.

2.2. Seed synthesis

Au seeds are synthesized by adding 0.6-mL sodium borohydride aqueous solution (0.1 mol/L) to 19.4-mL aqueous solution of chlorauric acid (0.25 mmol/L) and trisodium citrate (0.25 mmol/L) while stirring magnetically.[25] The diameters of the seeds are 5–10 nm.

2.3. Substrate preparation

Silicon substrates are pretreated through the following procedure in order to remove various impurities: (1) immersing them in a piranha solu-

tion (H_2SO_4/30%H_2O_2=7:3 v/v) and boiling them for 30 min; (2) immersing in a $NH_3{\cdot}H_2O/H_2O_2/H_2O$ (1:1:5 v/v) solution at 80° for 30 min; (3) immersing in a $HCl/H_2O_2/H_2O$ (1:1:5 v/v) solution at 80° for 30 min. After that, the wafers are thoroughly rinsed with de-ionized water, and dried under N_2. Then a short-time (30s) oxygen plasma treatment is applied just before depositing the beads. This pretreatment makes the silicon surface rich in hydroxyl groups, which are used to link the OTS and APTES molecules.

2.4. Assembly of nonclosely-packed PS monolayer

We adopt a spin-coating procedure in creating 2D colloidal crystal templates.[26] The typical PS spheres used here for the monolayer self-assembly are 500 nm in diameter and they are purchased from Microparticles GmbH (Germany) as a 10 wt% water solution. Before being used, the solution is diluted by mixing it with an equal amount of ethanol. About 5 μL of the prepared solution is applied to a 1.5cm×1.5 cm silicon substrate that is spun at 500 rpm for 3 s and followed by another 60 s at 3000 rpm. Before applied to the 500-nm PS spheres, the oxygen plasma is used to test its influence on the size of the 1.4-μm PS spheres on a gold substrate. The results are shown in Fig.2. Scanning electron microscope (SEM, Hitachi S-5200) images demonstrate the transformation of a 2D closely-packed PS monolayer to 2D nonclosely-packed ones and the reduction in PS sphere size, with the plasma etching performed. With etching time increasing, the diameter of the PS spheres gradually decreases. For example, by a 4-min etching, the size of PS spheres changes from 1.4μm to 1μm; and by an 8-min etching, it changes to 600 nm. The size decreases roughly in a linear manner with etching time.

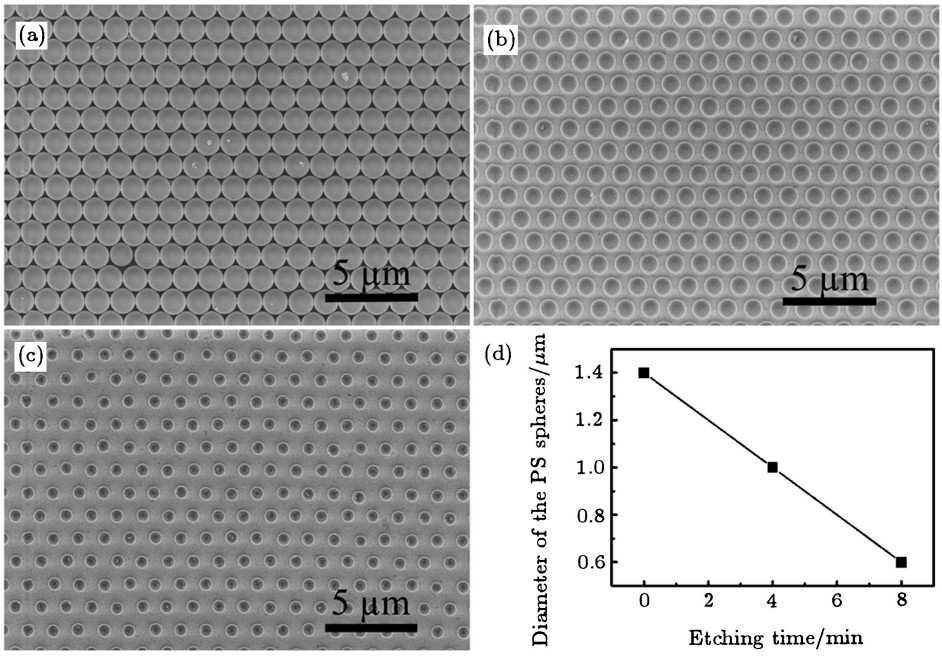


Fig.2. SEM images: (a) the closely packed PS SAM on gold wafer; (b) the nonclosely packed PS SAM after oxygen plasma etching for 4 min; (c) the nonclosely packed PS SAM after oxygen plasma etching for 8 min. The original diameter of the PS spheres is 1.4μm; (d) the linear relation between the diameter of the PS spheres and the etching time.

2.5. Fabrication of patterned Au seeds

First, the substrate covered with nonclosely packed PS spheres is held for 1 min on a heating plate at 100°C in order to make the PS spheres partly softened and stick to the substrates (glass transition temperature for the PS spheres being in the range of 95°C–105°C). Second, the substrate is immersed in a 10-mmol/L OTS solution of hexane for 3–5min in the open air to assemble OTS molecules in the regions uncovered by the PS spheres, and then it is subsequently rinsed in hexane and ethanol to remove polymeric residuals. Third, the spheres are removed by sonication in an ethanol bath. After these proce-

dures, the amino-terminated APTES layers are selectively formed in the formerly sphere-covered regions by boiling the substrate in a 1-mmol/L APTES solution of ethanol for 30mins, followed by its rinsing successively in ethanol and water. And then the substrate is kept in a hydrochloric acid solution at pH 2 for 12 hours to make the amino groups positively charged. Finally, the gold seeds are assembled on the chemically patterned surface by immersing the substrate in the good colloids suspension for 2–5 hours. The substrate is thoroughly rinsed with water immediately after it is taken out of the gold suspension.

2.6. Growth of the patterned Au NP arrays

To achieve the control of size and morphology of the patterned Au NPs, three types of growth solutions are chosen.[27] Before this experiment, we have firstly tested the three growth conditions by adding seeds directly into the solution. Growth solution A is typically used for the growth of Au nanorods, and consists of 10 mL of 0.1-mol/L CTAB, 500 μL of 0.01-mol/L $HAuCl_4$, 15μL of 0.04-mol/L $AgNO_3$, and 55 μL of 0.1-mol/L AA. Growth solution B is used for the growth of hexagon-shaped Au NPs. 1.6 mL of 0.1 mol/L-CTAB, 80 μL of 25-mmol/L $HAuCl_4$, and 0.3 mL of 0.1-mol/L AA are mixed together, and then the resulting solution is diluted to 10 mL. In growth solution C, 1.6 mL of 0.1-mol/L CTAB, 200 μL of 10-mmol/L $HAuCl_4$, and 32 μL of 0.1-mol/L AA are mixed together, and then the solution is also diluted to 10 mL. For growth solution C, Au nanorods and other triangle-shaped and square-shaped Au NPs are formed. The substrates patterned with gold seeds are immersed in the corresponding growth solutions for 12 hours at 25°. Then the substrates are removed from the growth solution and rinsed with water.

3. Results and discussion

Following the procedure explained above, we are able to fabricate arrays of Au NPs via the selective adsorption of seeds and restriction of seed-mediated reduction. Alkanesilanes with hydrophobic or hydrophilic end groups can be formed on the oxidized silicon surface because the surface contains hydroxyl groups. Due to the close sticking of the PS spheres to the substrate after being partly softened, the OTS film is formed only in the regions uncovered by the PS spheres. When the substrate partly modified by OTS is boiled in the APTES solution of ethanol, APTES modifies only the regions unoccupied by OTS, i.e. the previous positions of the PS spheres. The OTS SAM cannot be displaced by APTES molecules because it is more stable than APTES SAM thermodynamically. Thus the surface of the substrate is patterned in regions of $-CH_3$ terminated and $-NH_2$ terminated alkanesilanes. Before patterning gold seeds, we have tested the $-CH_3$ functionalized surface for its adsorptive characteristics to gold seeds. No seeds are found on the $-CH_3$ functionalized surface after exposing the substrate in an Au seed solution for 6 hours, indicating that Au seeds show negligible anchoring on a closely packed $-CH_3$ terminated surface. Previous work has demonstrated that there is a specific affinity when the amino-terminated surface is exposed to aqueous Au colloidal suspensions.[28] As the gold colloids are dominantly negatively-charged due to the citrate capping agent, the specific affinity here originates from strong electrostatic attractions between the negatively-charged gold nanocolloids and the positively-charged amino groups. Thus, the gold seeds are merely formed in the $-NH_2$ (NH_3^+) functionalized regions, the previous positions of PS spheres. Figure 3 shows the SEM image of the patterned Au seeds with a high density. It exhibits that no seeds are observed in the OTS-covered regions, while a monolayer of the seeds is clearly observed in the APTES-covered regions.

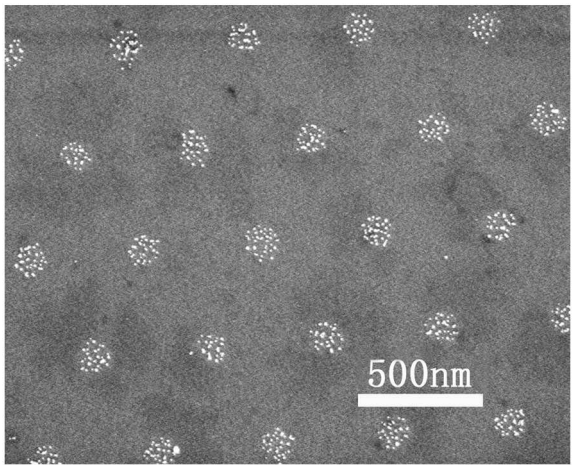


Fig.3. Adsorption of the gold seeds in APTES-modified regions. The nonclosely packed 500 nm PS beads are obtained after a 2-min oxygen plasma etching, and the size of the pattern is about 130 nm.

Figure 4 shows the SEM images of seed-patterned substrate after immersing it in the above-mentioned three growth solutions for 12 hours. For comparison, the Au NPs also grow directly from the corresponding solutions A, B and C, and the seeds used for them were 12 μL for A, 0.5 μL for B and C each. The results are shown in Fig.5. Obviously from Fig.4, with growth solutions A and B, Au NPs are well restricted to the predefined seeds-terminated regions, forming two-dimensional arrays on the silicon surface. This indicates that one can chemically position the nanoparticles on the silicon surface in a well-controlled way. For growth solution A, we observe a large difference in morphology between the Au NPs growing from the surface (Fig.4(a)) and those growing from the solution (Fig.5(a)). For the Au NPs growing in the solution, we obtain a high percentage of Au nanorods, which agree with the results in Ref.[29]. For the Au NPs growing from the surface, mainly irregular nanoparticles with a typical size of approximate 30–50 nm are formed. We believe that the large difference in morphology is mainly due to the density of the gold seeds. Previous studies both in solution [30] and on solid substrate [18] indicated that by fixing other conditions, with the increase of seed concentration, the rod length decreased, and ultimately very short rods[30] or spherical particles[18] appeared. In our case, the density of the gold seeds in solution phase reaction is around $10^4/\mu m^3$ whereas it is $3\times10^3/\mu m^2$ on the silicon substrate. Obviously, the density on the substrate is much higher than that in the solution. This leads to the formation of mainly spherical Au NPs in the growth process conducted on the substrate. For the growth solution B, however, the morphology of the Au NPs growing from the surface (Fig.4(b)) is similar to that growing from the solution (Fig.5(b)). One thing we want to point out is that although we tried several times to grow the hexagon-shaped Au NPs using the growth solution B as reported in Ref.[27], our efforts failed. We obtained only Au NPs with branched structures as shown in Fig.5(b). The reason for this discrepancy is unclear at present. One interesting feature in Fig.4(b) is that the seeds in the centre have not grown so big as the outer ones. An immediate intuition is that the high density of seeds in the central region prevents the Au NPs from growing up. However in the case of Fig.4(a), this feature was not prominent. Zamborini's group has studied the seed-mediated growth of gold nanorods on both unpatterned and patterned surfaces.[18,19,31] In their cases, this feature was not observed either. This indicates that the spatial confinement induced by the high density is not the only factor that needs to be considered. In Fig.4(c), Au NPs with various shapes such as spheres, rods, triangles and hexagons are formed, which agree with the results reported in Ref.[27] and our own results (Fig.5(c)). A difference is that much longer rods and larger triangles are formed on the edges of the patterns and protrude from there. This indicates that the seeds on the edges have more chances to grow up. Although at present the shape control of the Au NPs on substrates has not been so well as in solution, our attempt leaves much room for the further control of the morphology.

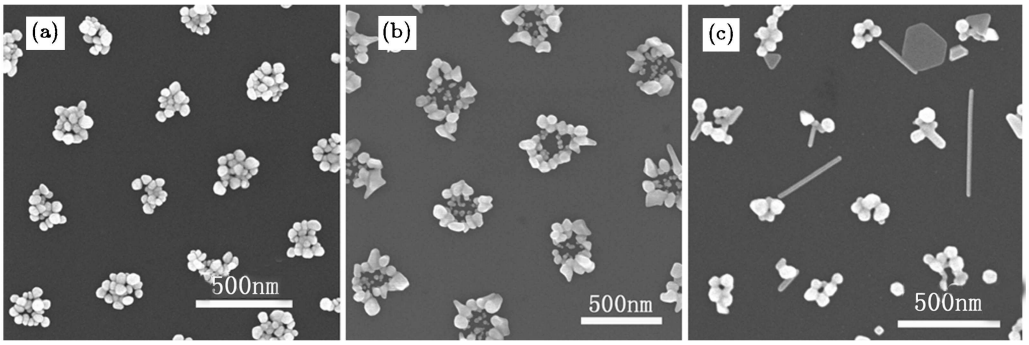


Fig.4. SEM images of the Au NPs on the silicon substrates after the seed-mediated growth in solutions A, B and C. In solution A, [CTAB]=0.1 mol/L, $[Au^{3+}]=5.0\times10^{-4}$ mol/L, $[AA]=5.5\times10^{-4}$ mol/L, $[AgNO_3]=6\times10^{-5}$ mol/L; In solution B, $[CTAB]=1.6\times10^{-2}$ mol/L, $[Au^{3+}]=2.0\times10^{-4}$ mol/L, $[AA]=3.0\times10^{-3}$ mol/L; In solution C, $[CTAB]=1.6\times10^{-2}$ mol/L, $[Au^{3+}]=2.0\times10^{-4}$ mol/L, $[AA]=3.2\times10^{-4}$ mol/L.

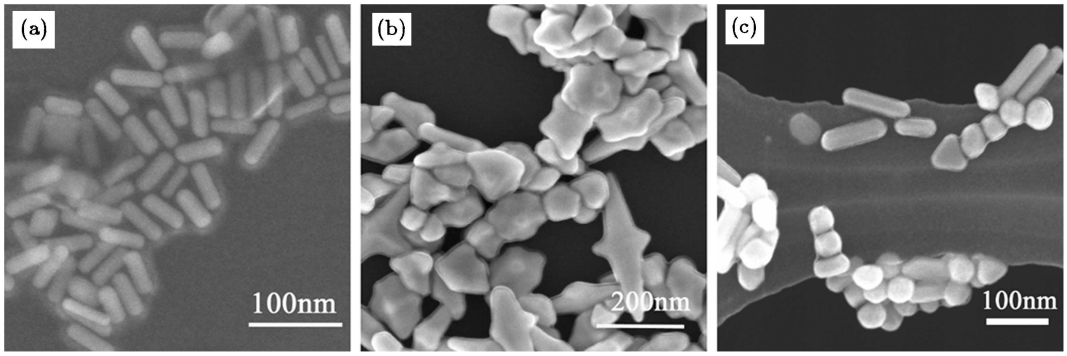


Fig.5. SEM images of the Au NPs directly grown from solutions A , B and C. In solution A, [CTAB]=0.1 mol/L, $[Au^{3+}]=5.0\times10^{-4}$ mol/L, [AA]=5.5×10^{-4} mol/L, $[AgNO_3]=6\times10^{-5}$ mol/L, $[Au]_{seed}=3\times10^{-7}$ mol/L; In solution B, [CTAB]=1.6×10^{-2} mol/L, $[Au^{3+}]=2.0\times10^{-4}$ mol/L, [AA]=3.0×10^{-3} mol/L, $[Au]_{seed}=1.25\times10^{-8}$ mol/L; In solution C, [CTAB]=1.6×10^{-2} mol/L, $[Au^{3+}]=2.0\times10^{-4}$ mol/L, [AA]=3.2×10^{-4} mol/L, $[Au]_{seed}=1.25\times10^{-8}$ mol/L.

To change the particle morphology, the annealing of the substrate in growth solution A is carried out at 1000°C for 30 min. The small nanoparticles melted and coagulated together into a big nanoparticle, and the crystals are tetradecahedron with a feature size of 150 nm (Fig.6).

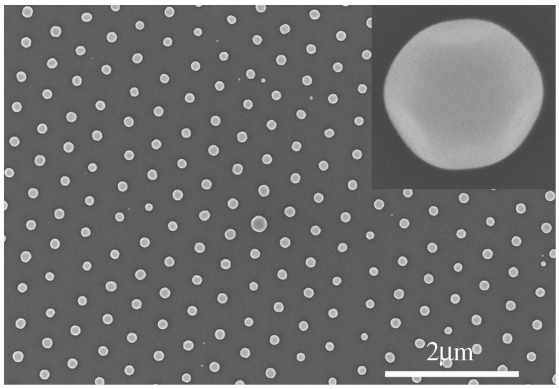


Fig.6. SEM image of gold nanoparticle arrays of substrate in Fig.4(a) after annealing at 1000° C for 30 min.

4. Conclusions

We have demonstrated the combination of nanosphere lithography with the seed-mediated growth directly on surface to fabricate well-controlled gold nanoparticle arrays. This study may provide a flexible and convenient approach to patterning metal nanostructures with controllable feature size, shape, and spacing.

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